The effect of water storage and simulated cleansing on some properties of two newly developed denture base materials

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Certificate of approval

I confirm that, to the best of my knowledge, this thesis represents an original research carried out by **Ilham Hadi Abid Alabdulla** in fulfilment of the requirements for the degree of Doctor of Philosophy according to the regulations of Newcastle University.

Supervisor

Abstract

Heat-cured PMMA has been used to make denture bases about 80 years ago due to its having superior properties in comparison with other polymers. However, some properties need improvement, such as impact and fatigue strength and the long curing duration. Recently, new denture base materials have been developed and introduced to the market to overcome PMMA shortcomings. These new materials include the Eclipse resin system, a light-cured resin, and Weropress polymer, a pourable cold-cured resin, which can be polymerised in a relatively short time. No studies have been conducted measuring their properties for short and long term use. Therefore, these materials were tested and compared with heat- and cold-cured PMMA denture base materials, acting as positive and negative controls, respectively, to determine if they can be used as alternatives to conventional materials in long term use.

The comparison was performed in terms of flexural properties, water sorption and solubility, surface properties (roughness and hardness), and colour stability. The comparison was made in three stages, at the baseline, after water storage for different time intervals, and after simulated cleaning with a liquid-based cleanser (Dentural), and a tablet-based cleanser (Poligrip).

The findings showed that Eclipse was statistically superior to the positive control in all tested properties at baseline, after water storage, and after cleansing, except for roughness, although no statistically significant difference was found, while it was clinically superior in strength, hardness and colour stability. Weropress showed no statistically significant difference from that of the negative control, but did have very high colour stability, and it was not clinically lower than positive control except in strength.

To conclude, in terms of the tested properties, Eclipse can be used as an alternative denture base material, while Weropress is recommended as a denture base material for cases with high aesthetic demands and low mechanical needs, or as a denture base material on a temporary basis.

Dedication

To my great country, Iraq

To my precious parents

To the souls of my deceased brothers Haider, Ali, and Hussain in heaven and everyone sacrifices himself to spread peace on Earth

To my dearest brothers and sisters

To the future builders my nephews, nieces, and students

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List of abbreviations

PMMA	Polymethylmethacrylate
MMA	Methyl methacrylate
UDMA	Urethane dimethacrylate
BIS-GMA	Bisphenol A glycidyl methacrylate
PUDMA	Polyurethane dimethacrylate
DMPT	N-N’dimethyl-p-toluidine
CQ	Camphoroquinone
IPN	Inter-penetrating polymer network
min	Minute
h	Hour
ABC	Air Barrier Coating protective varnish
VLC	Visible Light Cure
SEM	Scanning electron microscopy
CV	Coefficient of Variation
ΔE	Colour change
DW	Distilled water
EXP	Experiment
WB	Water bath
DO	Dry oven
HC	Heat cured PMMA
CC	Cold cured PMMA
Ec	Eclipse
Ws	Weropress
µm	Micrometer
Temp	Temperature
NBS	National Bureau of Standard System

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Chapter 1 Introduction

Since the 1930s, polymethylmethacrylate (PMMA) has been the most commonly used material in the construction of denture bases (McCabe and Walls, 2009). Dentures made from PMMA are typically manufactured using thermal-activated polymerisation. That is, liquid methyl methacrylate (MMA) and pre-polymerised powdered PMMA are mixed together with a thermal initiator, such as benzoyl peroxide, to produce a dough. This dough is placed in a mould and heated to above 65°C, triggering polymerisation (Van Noort, 2013). While it is possible to produce PMMA-based dentures at room temperature using chemical activators such as N, N-Dimethyl-p-toluidine (DMPT), the polymerisation is not as efficient as when thermally-activated, resulting in dentures with inferior strength, and high levels of residual monomer. These chemically-activated materials tend to be used only for repairing broken dentures and relining (McCabe and Walls, 2009; Van Noort, 2013). Thus, heat polymerised PMMA has become the material of choice for the construction of dentures.

The popularity of PMMA in denture manufacture is based on a number of characteristics: low cost (Farina *et al.*, 2012), acceptable dimensional stability and low water sorption and solubility, and the ability to add pigments to the raw material (McCabe and Walls, 2009). However, it seems it is not the ultimate denture base material in certain aspects, since some PMMA properties are less than ideal for dentures. For example, the two main reasons for denture repair or replacement are due to failure caused by the low fatigue resistance and low impact resistance of PMMA (Narva *et al.*, 2005; Radzi *et al.*, 2007). The vast majority of denture fractures occur after being dropped on the floor, leading to instantaneous fracture or cracking. Therefore, the effect of impact are seen more frequently in the elderly, who may have neuro-muscular incoordination (Cilingir *et al*., 2013). Another cause of breakage is due to frequent bending (Vallittu *et al.*, 1993; Vallittu *et al.*, 1994; Van Noort, 2013). Additionally, the long curing procedure of PMMA-based dentures, and colour instability after exposure to disinfectant solutions, are further shortcomings (Neppelenbroek *et al.*, 2005; Hong *et al.*, 2009; Peracini *et al.*, 2010).

Consequently, considerable research has been conducted to develop materials with improved properties, such as the addition of fibres to PMMA, for instance glass or polymer fibres (John *et al.*, 2001; Kanie *et al.*, 2004b). However, this addition is often associated with an increase in production costs and some processing difficulties (Jagger *et al.*, 1999), and so these materials have not been widely adopted. Some materials have also been developed to overcome long curing time, such as pourable cold-curing PMMA and light cured materials, but poor mechanical properties restricted the use of these materials.

Recently, two newly improved denture base resins have been introduced to the market to provide easier and faster processing (Mumcu *et al.*, 2011). One is based around MMA and sold under the trade name Weropress (Weropress cold cure polymer, MerzDental, Germany). This material is designed to be used as a cold-curing material but the manufacturers claim that it has good transverse strength and high colour stability, and high polishability. They also claim that very little residual monomer is left after polymerisation (less than 2%). The second material is based on a different monomer, namely urethane dimethacrylate (UDMA), and the polymerisation process is activated using light accompanied with heat. This material was originally introduced in the 1980s under the trade name Triad (Dentsply International, USA) (Al-Mulla *et al.*, 1988). However, it was not widely adopted for use as a denture base because it was brittle and lacked sufficient impact strength. Following redevelopment, it was released under the trade name Eclipse (Eclipse Resin System, Eclipse Trubyte, Dentsply International, USA). The finished denture made of Eclipse Resin System is claimed to be free of residual monomer after polymerisation (Pfeiffer and Rosenbauer, 2004; Melilli *et al.*, 2009; Akin *et al.*, 2014b). In addition, previous studies have suggested that Eclipse exhibits superior mechanical properties over other types of denture base materials (Ali *et al.*, 2008; Diaz-Arnold *et al.*, 2008). Few data are available about the properties of new materials at the time of manufacture, as well as after long-term usage of the material, particularly after exposure to the oral environment or after cleaning in comparison with the conventional materials.

Chapter 2 Literature Review

2.1 History of denture base materials

Methacrylate polymers have been used in denture construction for more than 80 years (Cunningham, 2000) due to their distinctive characteristics for use in the oral cavity (Deb, 1998). Many materials had been used before methacrylate polymers but none approached the ideal requirements of denture bases. Ivory and wooden denture bases were used first (O'Brien, 2008), and then vulcanite was introduced as a denture base material in 1854. Vulcanite is natural rubber, highly cross-linked with sulphur (Rueggeberg, 2002). It is characterised by good material adaptation to underlying tissues and an insolubility in saliva. However, it is naturally dark brown in colour and it is difficult to acquire a pigment, resulting in poor aesthetics (O'Brien, 2008); it also has a high rate of saliva absorption, which influences the strength and fit of dentures later on (Rueggeberg, 2002; McCabe and Walls, 2009).

Celluloid products were first introduced to the market in 1869, which was characterised by its good pink colour. However, it was not used for a long time because of dimensional instability due to absorption of saliva resulting in green discolouration and producing a bad smell and leaching camphor which is harmful to the tongue and oral mucosa and causes staining. Camphor acts as a plasticiser which is a group of low molecular weight additives that increase the flexibility of the material and make it flow at low temperature to facilitate handling. Later many materials have been developed such as cellulose acetate which was produced in 1903. Cellulose suffered from dimensional instability (warpage), and Cellulose also loses its colour quickly (Rueggeberg, 2002; McCabe and Walls, 2009; Van Noort, 2013).

Since then, at the beginning of 20th century, many synthetic polymers have been investigated as possible denture base materials (Rueggeberg, 2002; McCabe and Walls, 2009; Van Noort, 2013). In 1930, phenol formaldehyde was the first synthetic polymer to compete with vulcanite, but suffered from strong discolouration. This was followed by vinyl acetate resins in 1932, but these were brittle and readily failed. When nylon and polyamides were used in 1934-1935, it was found that they absorb water excessively. Vulcanite was the most successful of all these materials (Van Noort, 2013) and thus the most commonly used before 1940. However, it was replaced with PMMA in

1936-1937 owing to the fact that PMMA has superior physical properties and can be easily mixed into a dough (Rueggeberg, 2002; Machado *et al.*, 2007; O’Brien, 2008). Nowadays, PMMA, popularly known as acrylic, is considered the most popular choice for denture base construction, mainly due to its simple processing, low cost of fabrication, and good aesthetics. The most common forms of acrylic used at the present time are: dough-type, gel-type, pour-type, high-impact strength type, and rapid heat-polymerised type. The next popular material is urethane dimethacrylate which is produced to the market in 1980s as Triad and developed at 2000s to release as Eclipse. (Dhuru, 2005; McCabe and Walls, 2009).

2.2 Denture base polymers

2.2.1 Introduction

Polymers are long chain molecules formed by a reaction between identical small molecules called monomers, in a method called polymerisation (Ferracane, 1995). There are two types of polymerisation either addition polymerisation also called free radical polymerisation when monomer molecules are added one after another to produce a polymer, such as PMMA and BIS-GMA (bisphenol A glycidyl methacrylate). The other method is condensation polymerisation, which is when a volatile by-product results from the reaction (Ferracane, 1995).

Polymer molecules are either primary and linear, or complex, with types being: branched, copolymer, cross-linked polymer or graft polymer. Denture base polymers are mainly based on a carbon backbone (O’Brien, 2008). The main bond in polymer chains is strong primary covalent, and bonds between chains are secondary weak van der Waals bonds, which maintain the shape and prevent permanent deformation or fracture (Dhuru, 2005). This kind of bonding is the key reason for poor strength and poor elastic moduli, high water absorption, and a high coefficient of thermal expansion of polymers. Exposure to heat causes chains to move farther apart to allow atoms to vibrate freely in the weak secondary bonds perpendicular to the chain direction, thus expanding the mass. Therefore, a cross-linking agent may be added to the material to bind chains with a strong primary covalent bond and improve polymer properties (O’Brien, 2008)

The properties of a polymer are influenced by the chemical composition, degree of polymerisation, number of branches and cross-linking. Generally, longer chains and subsequent higher molecular weight provides a polymer with many favourable properties, including high strength, hardness, stiffness, and low creep. High cross-linking increases the molecular weight, rigidity, and strength due to increasing the number of strong covalent bonds. Some polymer structures permit the coiling of chains, which in turn leads to uncoiling and recoiling, providing high flexibility. The structure can also be either crystalline or amorphous which is the regular or irregular arrangement of atoms in space respectively. Crystalline or amorphous structure influences the strength. This is because crystalline polymers are stronger, stiffer, and absorb less water than amorphous.

The presence of small plasticiser molecules surrounding chains facilitates their free movement, and reduces rigidity and the glass transition temperature (Tg), and in turn this makes the polymer more flexible at lower temperatures. Tg is the minimum temperature required to deform the material permanently (O’Brien, 2008). Temperature is another factor which influences the properties of material, so increasing the temperature reduces the strength properties. Volumetric shrinkage is a general property of all denture base polymers (about 6% for denture resins), which produces internal stress, while reheating produces warpage which results in shape deformation (O’Brien, 2008).

2.2.2 Classification

Polymers used for denture base construction can be classified according to International Standard Organisation (ISO) 20795-1:2013 into various types, with type 1 and 2 being the most widely used products (BSI, 2013; McCabe and Walls, 2009):

Type 1 Heat polymerisable material

- Class I Powder and liquid
- Class II Plastic cake

Type 2 Auto polymerisable material

- Class I Powder and liquid
- Class II Powder and liquid for pour type resins

Type 3 Thermoplastic blank or powder

Type 4 Light activated material

Type 5 Microwave-cured material

2.2.3 Chemical composition

Type 1 class I

Denture base polymers of type 1 class I are heat-activated PMMA-based, and are the most commonly used material for denture base fabrication; they are often referred to as conventional denture base materials (Anusavice *et al*., 2012; Ferracane, 1995; Craig *et al*., 2004). The raw material is in powder and liquid form. The powder consists mainly of pre-polymerised micro-sized beads (spheres) and/or granules of PMMA or its copolymer, with a range of particle sizes up to 100µm and high molecular weight. These beads and granules are produced in a suspension polymerisation process. Beads are larger than granules and take longer to dissolve in monomer (Van Noort, 2013). The powder also contains the initiator, usually benzoyl peroxide at approximately 0.5-1% by volume (McCabe and Walls, 2009; Craig *et al*., 2004). The initiator is responsible for releasing free radicals and initiating the reaction. The powder also contains pigments, such as organic dyes which are mercuric sulphide (red), cadmium sulphide (yellow), or ferric oxide (brown) and pink synthetic fibres to simulate veins made of nylon or acrylic, to improve aesthetics. In addition, powder contains plasticisers or softeners such as dibutyl phthalate or low molecular weight ester (Van Noort, 2013; Dhuru, 2005), and opacifiers such as titanium or zinc oxides to control translucency (McCabe and Walls, 2009). The powder is stable and has a very long shelf life (Van Noort, 2013; Anusavice *et al*., 2012, McCabe and Walls 2009; Ferracane, 1995; Dhuru, 2005, O'Brien, 2008).

The liquid consists of predominantly methyl methacrylate monomer (MMA), and an inhibitor such as methyl ether or hydroquinone at 0.003-0.1% by volume (Craig *et al*., 2004; Dhuru, 2005). The inhibitor prevents spontaneous premature polymerisation of monomer by stabilising free radicals (McCabe and Walls, 2009), and thereby it prolongs the shelf life of the monomer; however, in excess of 25% by volume influences the strength (Dhuru, 2005). The inhibitor also increases working time by inhibiting the curing process (Anusavice *et al*., 2012). Free radicals can be activated spontaneously by the effect of the surrounding radiation, such as visible light or ultra violet radiation, during storage, and so the monomer is stored in dark, amber coloured bottles (McCabe and Walls, 2009). Another factor that may cause premature polymerisation of the monomer is contamination with a few particles of powder, because these particles contain benzoyl peroxide that will initiate the polymerisation process even in small quantities (as will be discussed later) (Van Noort, 2013).

The liquid is clear and colourless with a low viscosity and density of about 0.95g/ml; it has a distinct sweetish odour exaggerated by high vapour pressure. It is very volatile and toxic if inhaled for a prolonged period, highly flammable, unstable, and can be readily polymerised by exposure to visible light or ultra-violet radiation or heat. Thus, it is always stored in a can or well-sealed dark glass container away from flames or heat to keep it safe and increase its shelf life. The molecular weight of monomer is about 100 g/mol and it has a low boiling point of 100-100.8 °C close to that of water (Anusavice *et al*., 2012, McCabe and Walls 2009; Ferracane, 1995; Dhuru, 2005).

The cross-linked type resin contains cross-linking agent in the liquid, which is typically diethylene, triethylene or tetraethylene glycol dimethacrylate or 1,4-butylene glycol dimethacrylate, at a concentration of 1-15% by volume (Ferracane, 1995; McCabe and Walls, 2009; Anusavice *et al*., 2012). The cross-linker improves the strength of the polymerised material (Arima *et al.*, 1995a; Arima *et al.*, 1995b), by virtue of glycol dimethacrylate being chemically and structurally similar to MMA. However, it possesses two double bond sites as difunctional organic molecules, which enable it to connect to several adjacent polymer chains (Van Noort, 2013). Therefore, it either makes a loop in the chain or connects two chains (O'Brien, 2008). It also increases denture base resistance to absorbing solvents such as ethanol by forming interconnections yielding in a netlike structure, and, eventually, reducing the occurrence of crazing. Crazing is tiny cracks spread over the surface of the material caused by organic solvent attack, such as acetone (Jagger and Huggett, 1990; McCabe and Walls, 2009). The cross-linker glycol dimethacrylate is of low vapour pressure, which means it can be processed at high temperature (100-150 ˚C) without the risk of porosity. Cross-linking the polymer influences its physical characteristics (Craig *et al*., 2004), improves elastic properties (Dhuru, 2005), and accelerates the increase in molecular weight during the polymerisation process. It must be noted, however, that excessive levels of cross-linking produce a brittle material (O'Brien, 2008).

Type 2 class I

Type 2 class I is also called cold-cured, auto-cured, chemical-cured, or self-cured PMMA-based denture base material. It contains the same constituents as type 1 class I with the addition of the presence of a chemical activator as a reducing agent in the liquid, such as a tertiary amine like n-n'dimethyl-p-toluidine and (DMPT) N,N-dihydroxy ethyl-para-toluidine, or sulfonic acids (Sugino, 1976), or barbituric acid derivatives (O'Brien, 2008). The chemical activator is approximately 1% by volume, and it activates the initiator to breakdown at room temperature, producing peroxyl free radicals (McCabe and Walls, 2009, O'Brien, 2008). In addition, the size of the powder particles is smaller, with a lower molecular weight than those in type 1 class I, to hasten and facilitate its dissolution in the liquid (Van Noort, 2013). The ratios of benzoyl peroxide and DMPT which is most likely to produce favourable denture base characteristics are 0.26% and 0.025% by volume, respectively (Jerolimov *et al*, 1989).

Type 2 class II

This is a pourable type cold-cured PMMA-based denture base material which has the same composition as type 2 class I (Ferracane, 1995), but the beads are smaller in size than in type 2 class I (Dhuru, 2005). Granules have a molecular weight as low as 190,000 g/mol and the cross-linker ratio is 0-9% by volume. A balance between the size of granules, their molecular weight, and plasticiser content should be achieved to produce a high penetration of monomer at low viscosity to allow pouring, but it is difficult to achieve this, resulting in high residual monomer and low cross-linker densities. Therefore, there are different ranges of molecular weights and cross-linker concentrations, which results in products with different physical and mechanical properties (O'Brien, 2008).

Type 4

This is also known as light-curable UDMA-based denture base materials or resin-based composite (Ferracane, 1995). It is supplied as premixed sheets in lightproof sachets (McCabe and Walls, 2009). These sheets consist of urethane dimethacrylate monomer (UDMA) as a matrix, as shown in Figure 2.1, micro fine silica particles as the inorganic fillers, PMMA beads or acrylic copolymer as the organic filler, and a light sensitive initiator such as camphoroquinone (CQ) and amines, as a source for free radicals (McCabe and Walls, 2009). UDMA has a higher molecular weight than MMA and higher viscosity, so it has less polymerisation shrinkage (Van Noort, 2013). The functions of the silica particles are to control the viscosity, reduce the polymerisation shrinkage, and improve the mechanical properties (strength, stiffness and abrasion resistance) (Al-Mulla *et al.*, 1988), reduce water uptake, and reduce the coefficient of thermal expansion, as it has low magnitude in contrast to the matrix (Nicholson, 2002). Fillers can also reduce the cost, provide radiopacity, and control colour and translucency (Van Noort, 2013).

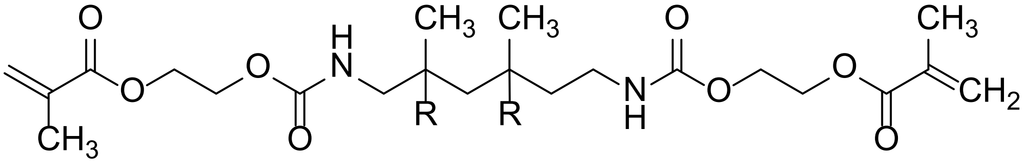


Figure 2.1 Urethane dimethacrylate monomer chemical structure (R=H or CH3)

2.2.4 Mixing and packing

Type 1 class I, type 2 class I, and type 2 class II

The appropriate powder/liquid ratio is of considerable importance in order to increase denture fit on the residual ridge by reducing dimensional instability, to improve physical characteristics (Anusavice *et al*., 2012), and control workability (McCabe and Walls, 2009). The powder/liquid ratio should be 2-2.5:1 by weight (McCabe and Walls, 2009; Van Noort, 2013) or 1.6-3:1 by volume (Van Noort, 2013; Anusavice *et al*., 2012; Craig *et al*., 2004), or 2:1 g/ml (Johnson *et al*., 2015) for type 1 and 2 class 1.

When mixing, the consistency passes through five gelation forms: sandy, sticky or stringy, doughy, rubbery, and hard (McCabe and Walls, 2009). In the sandy stage, the beads get wet with monomer and swell, and take on a grainy texture with no molecular interaction. In the sticky stage, the granules start to disperse in the liquid and uncoil, increasing the viscosity. Viscosity also increases because low molecular weight granules dissolve and thicken the interstitial monomer.

In the dough stage, the number of dispersed polymer chains in the solution increases exponentially with increasing the number of undissolved swollen beads, with no more tackiness or adherence to the container or fingers and loss of gloss from the surface. During this stage, the material can be moulded because it is a coherent mass, and can be kneaded due to being stiff enough to maintain its shape, while also being soft enough to be pushed into all details of the mould (Craig *et al*., 2004). Dough characteristics are governed by particle size distribution, molecular weight distribution, and plasticiser content in granules, where a higher molecular weight and lower plasticiser in particles are favoured to provide better physical and mechanical properties. If curing has performed at the dough stage before the deep penetration of monomer into the centre of the beads, it will result in reduced flexural strength and crack propagation at the border between the cross-linked interstitial phase and pliable beads (O’Brien, 2008).

During the rubbery stage, the monomer is dissipated by evaporation and further penetration into the beads; the mass loses its fluidity and has a tendency to spring back to a similar shape and size after the release of any applied force, much like a rubber. Curing at this stage results in homogenous distribution of stress and the formation of IPN (inter-penetrating polymer network), which is a tough three dimensional network within amorphous (O’Brien, 2008). In the last stage, it becomes hard, stiff and strong as more liquid evaporates (Anusavice *et al*., 2012). Cold-cured materials harden at this stage, but heat-cured materials remain rubber-like until exposed to heat (Ferracane, 1995).

These forms, which are physical forms, are composed by the dissolution of small beads in monomer and swelling of large beads, increasing the viscosity of the liquid, and forming a dough; however, for type 1, no chemical polymerisation takes place unless heat is applied, while for type 2, polymerisation starts with mixing and continues through all physical stages (Deb, 1998; McCabe and Walls, 2009).

Doughing or dough-forming time is the time required to reach the doughy stage from the onset of mixing, while working time is the duration of time at doughy consistency when the mass is mouldable. Both times can be controlled by the bead size, the molecular weight of the powder, and the ambient temperature. The smaller the beads and lower the molecular weight of powder, the faster the dissolution in the monomer (McCabe and Walls, 2009). In most cases, dough forming time is less than 10 min, while working time follows American National Standard Institute/ American Dental Association Specification No. 12, which should not be less than 5 min (Anusavice *et al*., 2012; Swaney *et al*., 1953).

Mixing is usually performed by slowly adding powder to liquid to guarantee complete wetting of the powder. The mixing vessel should be covered with a lid to prevent the volatilisation of the monomer, which may result in granular porosity in the set material and a blotchy appearance due to there being less monomer to bind the polymer beads. Granular porosity may also occur when using a high powder to liquid ratio (McCabe and Walls, 2009) (covered in detail in Section 2.2.7).

There are three packing ways to load the material into the mould: compression, pouring and injection. The compression method is the most frequently used (Craig *et al*., 2004), and consists of packing denture base mixture at the dough stage into the moulds under pressure. This pressure should be maintained during polymerisation because it reduces the potential for porosity caused by polymerisation shrinkage by reducing the effect of shrinkage (as will be mentioned later in Section 2.2.7). It also increases the adaptation and fit of the dough on the cast and prevents an increase in the vertical dimension of occlusion (Ferracane, 1995; McCabe and Walls, 2009).

The ratio for mixing powder to liquid for type 2 class II, pourable type, is very low, resulting in a slurry-like mixture with high fluidity rather than a dough (Dhuru, 2005). This resultant mixture can be poured into a specifically designed flask containing a reversible hydrocolloid investment mould via channels or sprue holes prepared for this purpose (Anusavice *et al*., 2012).

Type 4

Light-cured denture base polymers are produced as flexible pre-packaged sheets stored in lightproof sachets. They are moulded with fingers on an accurate cast and then coated with a passive layer of carboxymethyl cellulose to prevent the polymerisation process being inhibited by oxygen (Ali et al., 2008; McCabe and Walls, 2009; Nicholson, 2002).

2.2.5 Mechanism of polymerisation

Type 1, Type 2 class I and II

PMMA-based denture base polymers (type 1 and type 2) are produced by polymerisation. The MMA monomer contains carbon-carbon double bond (C=C) which is relatively unstable and has high energy, but a reaction needs to be stimulated under suitable conditions (Ferracane, 1995). This stimulation can be achieved by activating the material via different means, either by heat or chemicals predisposing the mixture to pass through four chemical stages of addition reaction: activation, initiation, propagation and termination (O'Brien, 2008).

The first stage is activation, during which the activator break downs the weak bonds in benzoyl peroxide initiator, producing free radicals from initiator decomposition. Free radicals are electrically neutral species with free unpaired electrons, as shown in Figure 2.2. In the second stage, initiation, these free radicals attack monomer molecules, splitting C=C to -C-C- and reacting with the monomer to start a chain. This reaction begins in many sites throughout the mixture. In the third, propagation stage, the reaction continues to elongate chains by breaking more C=C bonds and adding more monomer molecules. These chains keep growing and attach to pre-polymerised polymer, and also start new molecules, as in Figure 2.3. When the free radicals become less available and the viscosity of the mixture increases, impeding molecule movement, the termination stage starts. In this stage, the reaction stops, either because two growing chains react to each other, or hydrogen ion transfers from one chain to another to form stable molecules, meaning that the free radicals react to each other. The reaction may also stop when a free radical reacts with a molecule which is not a monomer, such as an impurity, or when the inhibitor (hydroquinone) reacts with free radicals. Termination stage is shown in Figure 2.4. Some of the monomers may be left unreacted and trapped within polymer chains, in addition to some oligomers, which are polymers with less than 100 repeated units (Van Noort, 2013; O'Brien, 2008). Two effects accompany this reaction: the release of heat as an exothermic reaction, and volumetric shrinkage of the mass (Van Noort, 2013).

MMA addition reaction is characterised by gradual depletion of monomer. Molecular weight increases rapidly at the beginning and stays steady of formed molecules while the reaction continues to form more new molecules (Dhuru, 2005).

The molecular weight is of a substantial importance to explain the variation in polymer properties (Van Noort, 2013). Polymers with molecular weights less than 10,000 g/mol are termed low polymers, and those whose molecular weight is higher than 20,000 g/mol are called high polymers. Typical dental processing of PMMA produces polymers with a molecular weight of 50,000 g/mol, most commonly with a range of 10,000-50,000 g/mol. (Craig *et al*., 2004; Dhuru, 2005)

Some parameters are used to measure the length of chains or molecular weight. These are average molecular weight or degree of polymerisation, and degree of conversion or degree of curing. Molecular weight or molar mass is the weight of one polymer molecule and is equal to the sum of the molecular weight of units forming that polymer. Degree of polymerisation is the average number of monomers which react to form a chain of mers in each polymer molecule. Degree of conversion is the percentage of unsaturated C=C (double) bonds converted to C-C (single) bonds in the mass, measured using the infrared spectroscopic technique. The most frequently repeated molecular weight is termed distribution of molecular weight. Degree of polymerisation is generally about 30-80 % for PMMA (Craig *et al*., 2004; Dhuru, 2005; O'Brien, 2008). Some polymers with a molecular weight less than 5,000 g/mol are liquid and viscous. These polymers of pourable type, need to achieve minimum molecular weight 150,000 g/mol by cross-linking (O'Brien, 2008).

The main concern during polymerisation is about binding the fresh newly formed polymer or matrix with pre-polymerised polymer beads, which in turn affects the mechanical properties. The formation of IPN depends on certain factors such as the molecular weight of bead polymer, the mixing ratio, and the contact time between beads and monomer before polymerisation depletes the monomer. Molecular weight of the bead polymer is normally about 5×10^5. Bead cross-linking reduces monomer penetration. High monomer content increases wetting and penetration but also increases the polymerisation contraction. The duration of contact between beads and monomer, before the polymerisation process depletes the monomer, is important and gives an indication of the differences between heat- and cold-cured polymerisation (McCabe and Walls, 2009).

The resultant polymer chains interact with each other by secondary weak van der Waals bonds, and by ‘entanglement’. The latter increases alongside chain length, and this in turn increases the strength, stiffness, solubility resistance, and dimensional stability (Dhuru, 2005).

PMMA is a linear polymer with one functional group, whose internal structure looks amorphous or randomly oriented. However, if PMMA is cross-linked, it looks like a regular network, orderly or crystalline, and this increases its stability and resistance to solvents. PMMA is a rigid glass-like polymer as it is formed from a stiff monomer. If there is a large side group attached to PMMA, or small unattached molecules are added to the polymer, they will reduce entanglement and thus strength. These molecules are termed ‘plasticisers’, which have the advantage of making material capable of being moulded and fit, increasing fluidity, and reducing brittleness. The disadvantages of plasticisers are: reducing mechanical properties; decreasing Tg and decreasing the elastic modulus of the set mass by breaking or obstacle secondary bonds formation. Permanently attached plasticiser should be compatible with the polymer, with low vapour pressure and low diffusion rate. Unattached plasticisers or external plasticisers can diffuse out of the polymer during ageing, increased temperature, and immersion in liquid for a long time. Residual monomer is an example of an unattached plasticiser which evaporates in air, or dissolutes in water, thus increasing the hardness (Ferracane, 1995; Dhuru, 2005, Van Noort, 2013).

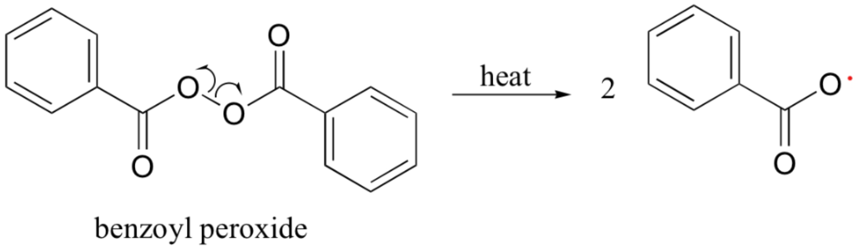


Figure 2.2 Decomposition of benzoyl peroxide during activation by heat

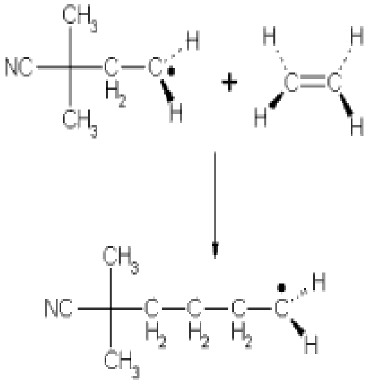


Figure 2.3 Reaction of monomer molecules to each other at propagation stage

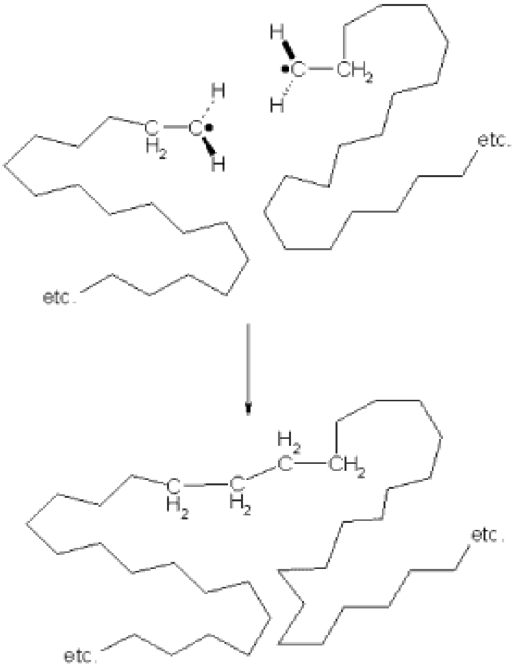


Figure 2.4 Reaction of two growing chains to each other during the termination stage

Type 4

Light-cured denture base polymers are polymerised in the four stages of activation, initiation, progression, and termination, except that activation occurs by light. Photo-dissociation starts when photo initiator CQ molecules absorb light and break one of the bonds, producing free radicals (O'Brien, 2008). The presence of photo sensitiser CQ and amine reducing agent as the hydrogen donor is essential for the release of intensified free radicals, and to make the degree of curing more efficient than photo-dissociation using CQ alone. The free radicals attack the bicarbonyl group of monomers and change C=C to C-C (Brantley and Eliades, 2001). The resultant material is a polymer PUDMA along with silica fillers and PMMA (O'Brien, 2008).

A little unpolymerised monomer may be left as the reaction stops when a thick consistency is achieved, as this impedes electron movement. Residual monomer acts as a permanent (pendant side chain), or temporary plasticiser which leaches into saliva. Increasing the degree of conversion may increase monomer shrinkage (Brantley and Eliades, 2001).

2.2.6 Methods of activation

Heat-activated polymerisation (type 1):

It is a process of applying temperature above 65°C to the mixture to start the polymerisation process. This is the necessary temperature to decompose the initiator, and release free radicals as mentioned in Section 2.2.5 (Van Noort, 2013). Heat can be applied by a water bath, or a dry heat oven, although there is controversy about the efficiency of each of these methods of curing dentures to produce good physical and mechanical properties (Anusavice *et al*., 2012; McCabe and Walls, 2009).

Nejatian *et al*. (2015) have found that the temperature rise inside the flask after using a dry oven is dependent on the number of flasks inside the oven chamber. Accordingly, the temperature may not reach a level high enough to cure samples if a large number of flasks are loaded; vice versa, it may exceed the monomer boiling point with too few flasks. The water bath exhibits the same pattern of temperature rise with differing numbers of flasks. This result is in agreement with previous studies, which found that few dental laboratories have been using dry ovens because of the poor control over temperature (Harrison and Huggett, 1992; Anusavice *et al*., 2012).

Various initiators decompose at different rates at different temperatures. These differences are termed as initiator half-life, or t1/2, which is the time required to decompose half the original value of a given concentration. The t1/2 for benzoyl peroxide is 7.3h at 70˚C, 1.4h at 85 ˚C, and 19.8 min at 100 ˚C (O'Brien, 2008).

Many curing cycles are available, but in general for any cycle the following should be considered: temperature for initiator decomposition is above 65˚C; the reaction is exothermic; the monomer boiling point is low (100.3˚C); and, the curing should produce both a high degree of conversion and high molecular weight. The most popular cycle is curing for 7 h at 70°C, and then 3 h at 100°C boiling. Seven hours dissociate bezoyl peroxide and converts most of the monomer and achieves a high molecular weight, as it is close to t1/2 for benzoyl peroxide. Boiling point is required to remove or convert almost all the residual monomer, and it finally sets with good mechanical properties and minimum residual monomer between 0.2-0.5% (Anusavice *et al*., 2012).

If boiling occurs in the first 1 h, by a rapid rise in temperature such as by immersing the flasks in boiling water, this will lead to the formation of a large number of free radicals all at once and a high rate of polymerisation, releasing a great deal of heat by exothermic reaction. These factors result in monomer boiling, make the set material porous (as will be mentioned in Section 2.2.7) (McCabe and Walls, 2009), and influencing strength and aesthetics. A high rate of polymerisation also produces many growing chains which collide and increase branching, resulting in a mass which is not as tough (McCabe and Walls, 2009; O'Brien, 2008). A slow rise in temperature produces a tougher mass, less branching, and a high molecular weight because fewer chains are grown all at once. It also results in less free monomer, because a steadier rise in polymer viscosity permits easier access of monomer to growing chains, and completely polymerised cross-linkers with lower creep properties due to the removal of the plasticising effect of unreacted cross-linkers (O'Brien, 2008). Whenever the main bulk of the monomer is partially polymerised into low molecular weight polymer (oligomers), the mixture can be heated to boiling temperature to achieve maximum polymerisation with less chance of porosity

(Dhuru, 2005). No final boiling (Canadas *et al*., 2010) or rapid curing produces a high residual monomer of about 1-4% (Dhuru, 2005).

Using a water bath to apply heat in a rapid cycle increases water temperature up to 100 ˚C within 60 min, and likewise the temperature of stone increases quickly; however, the temperature of resin lags in the early stages as it is located in the centre of the stone mould. Polymer temperature rise quickens when the machine's temperature arrives at about 75˚C due to the initiation of an exothermic reaction, which in turn increases the rate of polymerisation. In this reaction, the temperature moves in excess of 130˚C within approximately 30 min because of poor dissipation of temperature by poor thermal conductors, i.e. resin and stone. This temperature causes the unreacted monomer to boil, and porosity occurs (Anusavice *et al*., 2012).

Chemical-activated polymerisation (type 2):

With this type of polymer, a combination of physical and chemical changes take place by mixing powder and liquid at room temperature. During mixing, tertiary amine in the liquid, e.g. DMPT, which is a chemical activator, reacts with benzoyl peroxide to release free radicals (Van Noort, 2013). Activation in this type is termed a redox reaction, which is when an electron transfers from one species to another to form a free radical. (O'Brien, 2008). The small granules dissolve more readily in liquid and the larger ones swell, contributing to an increase in the viscosity. The polymerisation starts immediately alongside with physical changes. This process of synchronisation results in a rapid rate of polymerisation and increased temperature by exothermic reaction. Both processes deplete monomer quickly and increase the viscosity; the mixture thus reaches the termination stage quickly, meaning that the dough time and working time are short. Monomer depletion and the short contact time between powder beads and monomer leads to insufficient liquid penetrating the beads, and hence poor binding between pre-polymerised beads and monomer (McCabe and Walls, 2009). A rapid increase in viscosity restricts the movement of monomer molecules, resulting in high levels of free monomer. The presence of an inhibitor in the liquid is another factor responsible for retarding the polymerisation process (Dhuru, 2005). On the other hand, in type 1, there is enough time for the mixture many minutes until being packed (McCabe and Walls, 2009). Accordingly, chemical activation is less efficient than heat activation, resulting in a set mass with a low degree of polymerisation, low molecular weight, and a high degree of residual unreacted monomer (Van Noort, 2013).

The resultant residual monomer, which is around 1-5% (Anusavice *et al*., 2012; Dhuru, 2005), lowers the transverse strength because of its action as a plasticiser, and compromises biocompatibility because it irritates the vital tissue (Anusavice *et al*., 2012). One of the main differences between heat- and cold-cured PMMA dentures post-production is the presence of residual monomer; if this is allowed to leach into water, heat- and cold-cured dentures will be similar in some properties (Craig *et al*., 2004).

Working time in such case can be controlled by adding a high ratio of small size beads of low molecular weight polymers to powder. Beads of such size facilitate powder solubility and reaching the dough stage, before getting too thick and hard to adapt as a result of progression in reaction (Van Noort, 2013). Working time can also be controlled by lowering the monomer temperature via keeping the liquid or mixing vessel in the fridge before mixing. The composition of cold-cured materials, including the activator, inhibitor, rate and size of molecules, and the short working time and low temperature of polymerisation, eventually reflect on the degree of conversion (high residual monomer) (Bayraktar *et al.*, 2006), molecular weight and Tg of the set mass (Van Noort, 2013). The degree of polymerisation of cold-cured polymers is about 60-70% (Dhuru, 2005).

The set mass, if compared to heat-activated materials, shows colour instability, prone to yellowing, and poor mechanical properties (Ali *et al.*, 2008; Van Noort, 2013). The remnants of tertiary amines cause discolouration due to oxidation, so it is advised to add a stabilising agent (Anusavice *et al*., 2012).

Chemically activated polymerisation leads to a reduced Tg, typically between 75°C and 90°C. This temperature is close to the temperature of hot food and drinks entering the oral cavity, and results in distortion of the denture base by creep (McCabe and Walls, 2009; Van Noort, 2013). All the aforementioned criteria give rise to unfavourable mechanical and physical properties in the set material of self-cured polymer, such as high water sorption and solubility, low transverse bending strength, and colour instability (Arima *et al.*, 1995b). Thus, it is not used for making dentures and is usually used for repairing and relining dentures, and fabricating temporary devices such as record bases and special trays (McCabe and Walls, 2009).

Pourable type cold-cured resin is cured under pressure in a pressurised chamber for approximately 20-45 min at temperatures between 37-55°C (Sugino, 1976; Mutluay *et al*., 2013). A pressure of about 6.8 bar reduces the porosity by compressing air included during mixing, raising the density of polymer and improving tension by 20% (Keller and Lautenschlager, 1985), and increasing flexural strength to be greater than heat-cured polymers (O’Brien, 2008).

The main advantage of the pourable type is that less time and effort is required for production and finishing (Pattanaik and Pattanaik, 2013). The set mass of type 2 class II is characterised by reproducing an accurate detail of tissue surface due to high fluidity. It shows a lower dimensional change than heat-cured PMMA, which is about 0.2% (Ferracane, 1995). However, its properties are inferior to type 1 class I and type 2 class I, due to high creep (O’Brien, 2008), and high susceptibility to air entrapment within denture bases, so it is reduced in use as denture bases (Van Noort, 2013; Anusavice *et al*., 2012; Keller and Lautenschlager, 1985). Its reduced popularity is also related to incorrect processing (O’Brien, 2008). In addition, it has low mechanical properties and while the mould is typically made from hydrocolloid rather than stone there is the possibility of distortion during processing as hydrocolloid cannot grip artificial denture teeth properly (McCabe and Walls, 2009). Wax remnants on teeth may also prevent adequate wetting by the mixture, and subsequent tooth adhesion failure, which is less common with heat-cured resin at an elevated temperature. In addition, colour instability, reduced stiffness, and high residual monomer are other disadvantages (O’Brien, 2008). Residual monomer, which is about 1-4% (Ferracane, 1995), is associated with the formulation set by the manufacturer, which is the powder/liquid ratio, cross-linker content, and accelerator/catalyst ratio in addition to granules size and their molecular weight and plasticiser content (O’Brien, 2008).

Light-activated polymerisation (type 4)

Light-cured denture base polymers are cured without pressure and are exposed to radiation in a special oven at normal atmospheric pressure (McCabe and Walls, 2009).

They are polymerised by high intensity visible light at 400-500 nm wavelength for different time periods of approximately 5-15 min for 4-8 mm thickness, in the light chamber of a special oven which produces a temperature of approximately 75.5°C coming from halogen lamp (O'Brien, 2008; Al-Mulla *et al.*, 1988; Ali *et al.*, 2008; Dhuru, 2005). A halogen lamp is used in this kind of oven which emits heat (Craig *et al.*, 2004). Since no pressure is applied in the oven, this may lead to the formation of internal voids during polymerisation, which could be overcome using a dry cast with a rubber dam and vacuum assistance, as suggested by Tan *et al*. (1989). Large quantities of oxygen inhibit the reaction and the degree of polymerisation is about 65-80% (Dhuru, 2005).

2.2.7 Imperfections caused by the polymerisation process

Porosity:

Porosity is one of the inherent, undesirable characteristics which is most likely to occur with PMMA-based polymers during processing, causing persistent defects. Surface or subsurface voids can adversely affect the aesthetic, mechanical, physical, and hygienic properties of denture bases (Anusavice *et al*., 2012, Keller *et al* 1985). Porosity is a complex phenomenon of multi-factorial origin. These factors include the curing cycle, involving temperature, time and pressure (Keller *et al.*, 1974; Compagnoni *et al.*, 2004; Canadas *et al.*, 2010; Nejatian *et al.*, 2015; Yau *et al.*, 2004; Yannikakis *et al.*, 2002; Jerolimov *et al.*,1989), curing machine (Compagnoni *et al.*, 2004; Canadas *et al.*, 2010; Nejatian *et al.*, 2015; Abood, 2007; Pero *et al.*, 2008; Yannikakis *et al.*, 2002; Kasina *et al.*, 2014; Reitz *et al.*, 1985), number and position of flasks inside curing machine (Oliveira *et al.*, 2003; Nejatian *et al.*, 2015), mixing ratio (Keller *et al*., 1974; Nejatian et al., 2015), chemical formulation of the material (Singh *et al.*, 2013; Compagnoni *et al.*, 2004; Pero *et al.*, 2011; Nejatian *et al.*, 2015; Yannikakis *et al.*, 2002; Jerolimov *et al*,1989; Kasina *et al*, 2014), proportions of ingredients (Jerolimov *et al*,1989), quality of manipulation (McCabe and Walls, 2009), geometry and thickness of the specimen (Wolfaardt *et al.*, 1986, Singh *et al.*, 2013; Pero *et al.*, 2011; Abood, 2007; Pero *et al.*, 2008; Yannikakis *et al.*, 2002; Jerolimov *et al.*,1989), particle size (Keller *et al.*, 1974) and probably many others. Porosity has been reported to occur in 39.8-52.3% of all cured specimens and it is not possible to get below this ratio despite modifying several factors, so it is not easy to obtain a denture base free of porosities due to the interactions between these factors (Wolfaardt *et al.*, 1986). In general, the two most common causes of porosity are: polymerisation shrinkage, and boiling or volatilisation of the monomer during curing (Van Noort, 2013).

Porosities can be classified into four main types: contraction, gaseous, granular, and air porosities (Anusavice *et al.*, 2012). They can occur in different sizes, shapes and positions, and it is difficult to distinguish any single type due to the similarity of their characteristics and the interaction of various factors (Wolfaardt et al., 1986). However, each type has general characteristics, described below (Anusavice *et al.*, 2012).

Contraction porosity is caused by polymerisation shrinkage.This consists of monomer contraction which occurs as molecules bind together. The amount of contraction in monomer volume can be reduced from about 20-21% to about 0.2-0.5 % if a powder and liquid system is used rather than liquid alone. The monomer contraction starts along with the polymerisation process. For heat-cured materials, it starts by elevating the temperature of curing above 65˚C, emitting heat from the reaction and increasing the temperature to about 100˚C. For cold-cured materials, it starts when powder is mixed with liquid. During this time, the monomer starts shrinkage by starting the polymerisation. Moulding requires sufficient and continuous pressure application and a sufficient amount of dough material, as, if the mould is over packed, the mixture flows into the gaps or spaces created by monomer shrinkage, compensating for the contraction (O'Brien, 2009). If there is insufficient pressure and material, or if the material is moulded before the dough stage, there is a loss of pressure and contraction porosity occurs. Once the reaction temperature falls below Tg, by passing the main stage of the exothermic reaction, the resin hardens and thermal contraction takes effect (Van Noort, 2013; Johnson *et al.*, 2015). A high monomer content increases the percentage of the contraction (Van Noort, 2013). This type of porosity is relatively large and has an irregular shape; it appears abundant and renders the colour of the dentures lighter if it was closed (Anusavice *et al.*, 2012).

Gaseous porosity is mainly due to the boiling of monomer in the early stages of polymerisation; this occurs when it reaches boiling point quickly by the heat of activation and the heat of exothermic reaction with little ability to dissipate this heat (Van Noort, 2013; Johnson *et al.*, 2015). That produces a gaseous mass take on a gaseous porosity in the set material. These porosities are usually small, subsurface or internal, and regular in shape (Anusavice *et al.*, 2012).

Two main factors in the occurrence of this porosity are the amount of heat released and the ability to dissipate the temperature from the material. The amount of heat released and, in turn, the temperature rise during the exothermic reaction depends on the amount of material loaded into the mould, the powder/liquid mixing ratio, and the speed with which the applied heat for activation reaches the resin inside the flask (Van Noort, 2013; Johnson *et al.*, 2015; McCabe and Walls, 2009). Heat arrival depends on thermal diffusivity, which in turn depends on thermal conductivity, and specific heat. Thermal conductivity determines the speed of entrance and spread of heat through a given thickness of the material to change the temperature by 1˚C (O'Brien, 2009). Specific heat is the amount of heat required to increase the temperature of a unit volume by one centigrade (Van Noort, 2013). A low powder/liquid ratio increases the amount of heat released by the exothermic reaction due to the high ratio of monomer molecules needed for conversion to polymer. Accordingly, a low powder/liquid ratio can result in high monomer contraction, high thermal contraction, and thus a high possibility of contraction and gaseous porosities (Van Noort, 2013). Whether the monomer boils is also dependent on the boiling point of the monomer, the temperature of the curing machine, and the temperature at which maximum polymerisation happens (Dhuru, 2005).

The ability to dissipate heat depends on denture thickness, and therefore monomer boiling is more likely to occur in the thick areas (Yannikakis *et al.*, 2002; Wolfaardt *et al.*, 1986). It also depends on the position of the specimen inside the flask, which is why gaseous porosity can occur in areas close to the centre of the mould rather than the periphery. The material near the periphery dissipates the heat away by virtue of being close to the metallic flask, which is a good thermal conductor, at a speed which prevents the temperature from reaching boiling point. In contrast, material near the centre of the mould is surrounded by thick gypsum, which is a good insulator, and so heat is retained within the material, causing the monomer to boil (Anusavice *et al.*, 2012). For the same reason, the percentage of porosity near centre of the specimen is higher and of a different shape to that near the periphery. Porosity at the centre can be attributed to the volatilisation of the monomer (gaseous porosity), while that near the periphery may be due to the vigorous contraction of the monomer (contraction porosity) (Yannikakis *et al.*, 2002).

This type of porosity can be avoided by applying heat to ensure a slow rise in temperature to 70˚C for 5-7 h, until the main bulk of the mixture is polymerised and the temperature of the exothermic reaction is passed; this reduces the chance of the temperature reaching more than 100˚C during this time. Accordingly, gaseous porosity occurs with heat-cured resin only (Van Noort, 2013; Johnson *et al.*, 2015).

Granular porosity is caused first by improper mixing of powder and liquid, resulting in a non-homogenous mass and non-homogenous shrinkage manifested as voids. The second reason is too high a powder/ liquid ratio, which produces a dry and slow flowing mixture due to inadequate liquid to wet powder particles, eventually producing a weak porous material. The third reason is evaporation of the monomer in uncovered mixture during manipulation. This kind of porosity has a blotchy appearance with large irregular surface voids due to localised shrinkage (McCabe and Walls, 2009).

Air porosity occurs most commonly with the pourable type of polymer due to air incorporation during mixing and pouring, resulting in a relatively large air bubble. In order to avoid this, careful mixing, pouring, vibration, and venting are required (Anusavice *et al*., 2012). It also of high occurrence in light-curable UDMA-based polymer and can be reduced by using an evacuator (as mentioned in 2.2.6) (Tan *et al*., 1989).

Processing strains

Processing stress represents internal stress generated in the dough during processing by curing contraction, thermal contraction below Tg, and through the differential coefficient of thermal expansion between stone, artificial teeth and resin (McCabe and Walls, 2009). Strain occurs after the relief of stress by exposing the material to a temperature over Tg, such as when the denture is immersed in hot water or exposed to heat generated by polishing. This heat causes a release of the internal stress (Devlin and Kaushik, 2005), which in turn causes crazing or warpage. Crazes are minute defects or flaws or surface micro-cracks which give a foggy appearance, representing a localised area of plastic deformation. Crazing may predispose the denture bases to fracture. The high differential coefficient of thermal expansion between PMMA denture base acrylic resin and porcelain teeth, which is about 1:10, causes the teeth to loosen and be lost (McCabe and Walls, 2009). A similar differential coefficient between PMMA and gypsum product (1:10) increases the internal stress and leads to further crazing (Marra *et al.*, 2009). Rapid cooling increases internal stress as well (McCabe and Walls, 2009). Internal stress can be reduced by using acrylic teeth instead of porcelain teeth, the avoidance of overheating such as during polishing and allowing the flask to cool slowly after curing (Ferracane, 1995).

Crazing can also occur as a result of solvent attack, such as ethanol or MMA (as mentioned in Section 2.2.3). The occurrence of this type can be reduced by cross-linking the polymer chain (Van Noort, 2013; Johnson *et al*., 2015; Anusavice *et al*., 2012; Jagger and Huggett, 1990). It can also occur with repeated wetting and drying of the denture due to rapid water gain and loss to the surface, and so the denture should be kept moist at all times (McCabe and Walls, 2009).

The magnitude of stress and further crazing depends on the maximum temperature at which the mass arrives and the cooling rate (Ferracane, 1995). Accordingly, cold-cured resin creates less thermal contraction than heat-cured resin, because the maximum temperature at which it may arrive is 60˚C, but may be 100˚C for heat-cured resin (Anusavice *et al*., 2012).

2.2.8 Characteristics and limitations

Many merits of PMMA have enabled it to be used as a denture base material for a long time. However, although a combination of virtues rather than a single desirable property accounts for its popularity and usage (Jagger *et al.*, 1999), it does have some properties which are not ideal. PMMA-based material will be described in terms of the ideal criteria mentioned in Table 2.1, in comparison with UDMA denture base properties before the development of Eclipse.

PMMA dentures have an adequate stiffness for use as a denture base material. It satisfies the minimum requirements of modulus of elasticity for acrylic dentures (2.5 GPa, following ISO 20795-1:2013). Its modulus of elasticity is 2.5 -3.8 GPa (McCabe and Walls, 2009), and modulus of elasticity is an indication of stiffness or flexibility within the elastic range (O’Brien, 2008).

High flexural strength is crucial for the success of the denture, since alveolar bone foundations physiologically undergo a continuous natural remodelling process. This remodelling may leave irregular bone foundation under the denture, leading to the frequent denture bending over the midline suture during mastication; this can produce a fracture in the maxillary denture at the midline (John *et al.*, 2001).

PMMA-based dentures and UDMA-based dentures have flexural strength or transverse strength enough to resist high masticatory forces (Ferracane, 1995; O’Brien, 2008; Van Noort, 2013). The minimum requirement of transverse strength of types 1 and 4 is 65 MPa, and for type 2 is 60 MPa, following ISO 20795-1:2013. Some authors have reported that the flexural strength values of UDMA-based dentures are comparable to that of heat-cured PMMA or even higher (Sun *et al.*, 2003; Khan *et al.*, 1987; Qasim *et al.*, 2012; Dar-Odeh *et al.*, 1997). In contrast, some authors have found that UDMA-based light-cured polymers showed a lower flexural strength than other PMMA-based polymers both before and after water storage for different time intervals (2, 28, 30, 60, 90 days), which is less than the minimum requirement for flexural strength (Kanie *et al.,* 2004a; Machado *et al.*, 2007; Dixon *et al.*, 1991; Al-Mulla *et al.*, 1988; Al-Mulla *et al.*, 1989). This result can be explained by the fact that these authors cured the material for 5-10 min on the top only, or top and bottom, which was less exposure time than has been used in other studies (Alpoz *et al.*, 2008).

The flexural modulus of both PMMA and PUDMA is also high enough to comply with masticatory forces. It is 2000 MPa for types 1 and 4, and 1500 MPa for type 2 following ISO 20795-1:2013 (Kanie *et al.,* 2004a; Al-Mulla *et al.*, 1988; Sun *et al.*, 2003). The flexural modulus of PMMA dentures is usually between 2.2-2.5 GPa (McCabe and Walls, 2009). In some studies, UDMA-based dentures were lower than that of heat-cured PMMA due to the presence of residual monomer caused by the short polymerisation cycle, which is 5 min, as Kanie *et al.* have suggested (2004). This modulus increases after water immersion and becomes significantly higher than heat-cured PMMA, which due to the dissolution of free monomer into water (Al-Mulla *et al.*, 1988; Ogle *et al.*, 1986; Al-Mulla *et al.*, 1989).

Low impact and low fatigue fracture strength are the main problems of PMMA denture bases, and can incur costs and time for repair (McCabe and Walls, 2009). The first reason of PMMA denture fracture is fatigue, also termed a fracture *in situ.* This is caused by an intermittent stress over a long period in` conjunction with low bending. Intra-orally, it is caused when the denture has been subjected to repeated masticatory forces (Vallittu *et al.*, 1993; Vallittu *et al.*, 1994; Narva *et al.*, 2005; Deb, 1998; Jagger *et al.*, 1999; El-Sheikh and Al-Zahrani, 2006; Goguta *et al.*, 2006). A high fatigue resistance is necessary for any denture to be durable in the patient's mouth and less prone to clinical failure due to cyclic or repeated application of masticatory forces. Accordingly, a long fatigue life, which is the number of stress application cycles until fracture, and a high fatigue limit, which is stress magnitude to crack initiation, are required to avoid crack formation and propagation during mastication (Van Noort, 2013; McCabe and Walls, 2009). Fatigue failure can occur as a result of ill-fitting dentures, attributed to irregular bone resorption or a badly designed denture that impairs denture adaptation on the underlying bone. Other reasons for ill-fitting dentures may be the presence of a high spot area due to dimensional changes during laboratory steps (Vallittu *et al.*, 1993; El-Sheikh and Al-Zahrani, 2006; Vallittu *et al.*, 1994). Therefore, a mid-line fracture of a maxillary complete denture is the reason for 30% of denture repair (Vallittu *et al.*, 1994; McCabe and Walls, 2009), owing to the morphology of the palate accompanied by residual ridge resorption, which causes the denture to rock over the prominent bony mid palatine suture (Vallittu *et al.*, 1993). Fatigue resistance of acrylic dentures is usually about 17 MPa at 1,500,000 cycles (Craig *et al.*, 2004). However, there is little research on fatigue resistance for PUDMA dentures for comparison with PMMA.

PMMA dentures often fracture following extra-oral high impact forces, such as accidental dropping on a floor, or hitting or collision with a hard object, due to poor impact resistance (Radzi *et al.*, 2007). Impact resistance is a function of toughness, and is a measure of the energy required to initiate and propagate a crack. Initiation of a crack is facilitated by denture anatomy, such as deep notching at the labial fraenum because acrylic is a notch sensitive material (McCabe and Walls, 2009). PMMA dentures are considered brittle because the percentage of distortion is less than 5% at fracture (Craig *et al.*, 2004). Impact failure is the main reason for more than 60% of denture repairs (Vallittu *et al.*, 1993; El-Sheikh and Al-Zahrani, 2006). Brittleness and low impact resistance are also a disadvantage of UDMA-based materials (Qasim *et al*., 2012; Al-Mulla *et al.*, 1988; Al-Mulla *et al.*, 1989; Dar-Odeh *et al*., 1997; Sun *et al*., 2003). In these materials, the impact strength was lower than heat-cured PMMA before and after water storage, and after different durations of light exposure. The brittleness is a major disadvantage of cross-linking and micro-fine silica filler (Vaidyanathan and Vaidyanathan, 1995), but it may also be due to poor bonding of silica particles with the matrix, since silica has shown about a 14% dislodgment under SEM (Al-Mulla *et al.*, 1988, 1995). For this reason, UDMA-based light curable polymers were undesirable for making permanent dentures (Vaidyanathan and Vaidyanathan, 1995).

PMMA denture base polymers have sufficient surface hardness and abrasion resistance to resist masticatory forces, unless in contact with abrasive food, hard toothbrushes or abrasive dentifrices. In such cases, wear and abrasion will occur. Knoop hardness for heat-cured PMMA may be 20-21 kg/mm^2, and for cold-cured PMMA it is between 15-18 kg/mm^2 (Anusavice *et al*., 2012; Ferracane, 1995; Craig *et al*., 2004; Dhuru, 2005; McCabe and Walls, 2009). UDMA-based materials were significantly harder than heat- and cold-cured PMMA before and after immersion in water for different time intervals (Al-Mulla *et al*., 1988, Dar-Odeh *et al*., 1997; and Khan *et al*, 1987). They also showed a higher wear resistance after brushing with different dentifrices (Haselden *et al*, 1998).

PMMA denture base polymer is relatively stable in oral fluids as it has a low rate of water absorption (Harrison *et al.*, 2004). The maximum limit of water sorption for polymers is 32 µg/mm^3, according to ISO 20795-1:2013. The coefficient of diffusion for heat-cured PMMA is lower than that for cold-cured PMMA. In contrast, UDMA-based dentures show a more gradual pattern of water uptake for UDMA-based light cured polymers, compared to a steep pattern for PMMA polymers due to the different backbone polymer and subsequently different coefficient of diffusion being lower for light-cured PUDMA (Al-Mulla *et al*., 1989). Water uptake during long-term water storage of UDMA-based dentures was higher than that for PMMA-based denture base polymers, and can reach 3.6 times after 40 days of water storage (Khan *et al*., 1987). However, this high water sorption of Triad satisfies the maximum requirements for type 4 water sorption according to ISO 20795-1:2013.

Water solubility for PMMA-based denture base polymers is low. The maximum limit of water solubility, as determined by ISO 20795-1:2013, should be 1.6 μg/mm^3 for types 1 and 4 polymers, and 8 μg/mm^3 for type 2 after 7 days water immersion (McCabe and Walls, 2009; Asar *et al.*, 2013; Mutluay *et al.*, 2013). PMMA is insoluble in oral fluids unless it contains water-soluble constituents such as plasticisers, pigments and residual monomer (Van Noort, 2013); this is why the high water solubility of type 2 is related to high residual monomer content (McCabe and Walls, 2009). Cross-linked PMMA-based denture base resins are insoluble in oral fluids (Anusavice *et al.*, 2012, Craig *et al.*, 2004).

PMMA denture base polymers have an acceptable dimensional stability (McCabe and Walls, 2009) but are susceptible to distortion (Van Noort, 2013). Dimensional stability depends on the investing media, method of processing, and temperature increase. All polymers undergo polymerisation shrinkage, water absorption, and water solubility, and have a high coefficient of thermal expansion (Dhuru, 2005). Dimensional change may occur as a result of these properties, in addition to the relief of internal stress; moreover, the different coefficient of thermal expansion between teeth and denture base is another cause of dimensional changes (Van Noort, 2013; McCabe and Walls, 2009). Polymerisation shrinkage during processing, which is about 5-7% volumetric shrinkage and 0.5% linear shrinkage, consists of monomer contraction during polymerisation, followed by thermal shrinkage when the temperature drops under Tg (Craig *et al.*, 2004). Thermal contraction forms the major cause for most of the noticeable volumetric dimensional changes of the denture base, which are mainly linear, due to transference from the curing temperature to room temperature. For this reason, cold-cured polymers have a better primary fit on the denture bearing area due to negligible thermal changes. However, whilst initially well-fitting, it is more prone to distortion, because the weak mass of cold-cured PMMA and low Tg increase the likelihood of creep and distortion (Anusavice *et al.*, 2012; Craig *et al.*, 2004). Too low a powder/liquid ratio increases the polymerisation shrinkage due to high monomer content, causing loss of fit to the denture-bearing surface (Van Noort, 2013) (as mentioned before in Section 2.2.7). Absorbing water by about 1% by weight could offset 0.23% thermal shrinkage (Anusavice *et al.*, 2012); however, high water sorption causes a swelling of the material (Seo *et al.*, 2006). Another reason for dimensional instability is exposure to heat, which causes a release of internal stress and subsequent dimensional change and crazing (as mentioned before in 2.2.7). Thermal cycling may cause dimensional change due to successive expansion and contraction (Yeung *et al.*, 1995). Having a high enough Tg increases the dimensional stability, and in particular intraoral temperature may reach 70˚C. Generally, the thermal stability is sufficient for dentures, because the Tg of most denture base polymers is around 95-100˚C; this remains acceptable as long as the denture is not placed in very hot water or exposed to high temperature (Ferracane, 1995; Craig *et al*., 2004). Desorption or dryness also causes dimensional change and loss of fit, and so patients are advised to keep their dentures wet (Dhuru, 2005).

Regarding PUDMA dentures, these show good fit in the finished denture associated with a high dimensional stability. High dimensional stability is related to higher molecular weight of UDMA oligomers and high viscosity, which reduces the polymerisation shrinkage to 3% in comparison with 7% for heat-cured PMMA. Accordingly, UDMA-based light-cured polymers produce better initial fit of the denture on the denture bearing area than heat-cured polymers (O'Brien, 2008; Van Noort, 2013; Dhuru, 2005). In addition, this superiority in dimensional stability continues even after water immersion in short-term because the water absorbed was just enough to compensate for the contraction (Ogle *et al*., 1986).

The Tg of PMMA denture base polymers is about 105-125°C (Deb S, 1998; , McCabe and Walls, 2009) for type 1 and 60-90°C for type 2, and so type 2 can be distorted more readily in hot water. Tg depends on molecular weight and residual monomer (McCabe and Walls, 2009) and the presence of plasticiser, in addition to the inherent monomer structure. Therefore, the high residual monomer of cold-cured resin has reduced its Tg (Ferracane, 1995). UDMA based light curable materials have a higher Tg than type 1 (Deb, 1998; McCabe and Walls, 2009), which is why it is dimensionally stable after thermocycling (Vaidyanathan and Vaidyanathan, 1995).

PMMA denture base polymer has an excellent appearance as it accepts pigments, providing different colours, shades, and translucency to meet the needs of different ethnicities for good aesthetics (McCabe and Walls, 2009). In terms of light-curing polymers, these show good aesthetics since they are available in a range of colours and can match different gingival colours (Haeberle and Khan, 1997).

PMMA denture base polymers have clinically acceptable colour stability (McCabe and Walls, 2009; Fernandes *et al.*, 2013). However, bleaching or whitening of the denture base can occur with long term use of disinfectants (Moon *et al.*, 2014) such as sodium hypochlorite and alkaline peroxide. This whitening is caused by a combination of circumstances rather than disinfection alone, such as immersion in very hot water, exposure to solvents, or underdeveloped IPN of polymer. Whitening can affect pink as well as clear acrylic since it is associated with a mismatch in the refractive index between beads and the polymer matrix (McCabe and Walls, 2009).

UDMA-based light-cured polymers tend to have rougher surfaces than PMMA-based dentures (Ferracane, 1995; Ogle *et al*., 1986). These authors undertook scanning electron microscopy which showed a surface of Triad with micro-porosity. This latter observation was confirmed by Tan *et al*. (1989), who also reported a poorer rating of the surface quality of the underside of Triad due to air entrapment. This roughness in the VLC Triad surface could be due to the separation of silica particle fillers (Al-Mulla *et al*., 1988) and low packing pressure, or finger pressure. Pressure or the vacuum adaptation technique could help to overcome porosities in Triad light-cured material (Tan *et al*., 1989). In comparison with PMMA-based polymers, self-cured appears to have more micro-porosity, while heat-cured was the densest and smoothest, and was most free of micro-porosity (Ogle *et al*., 1986).

PMMA denture base polymer is light in weight as it consists of light atoms: carbon, oxygen, and hydrogen, and its specific gravity is 1.2 gcm^{-3}. This is beneficial to increase retention and reduce displacement of the maxillary denture by gravity (McCabe and Walls, 2009). UDMA-based light-cured polymers are durable and light in weight, and so were considered beneficial for obturator construction (McCabe and Walls, 2009; Fischman, 1989).

PMMA- and UDMA-based materials are reported to be biocompatible. Allergens may be induced by MMA in dental laboratory personnel, causing contact dermatitis (Geukens and Goossens, 2001) or irritation by inhalation of vapour (Borak *et al.*, 2011), and this must be kept to a minimum by good ventilation (McCabe and Walls, 2009). Residual monomer produces cytotoxicity to cells of oral mucosa (Goiato *et al*., 2015; Melilli *et al.*, 2009) and may cause irritation and further allergy to patients, although very minor

(Pfeiffer and Rosenbauer, 2004). Residual monomer will leak into the saliva intra-orally (Bural *et al.*, 2011), potentially causing a burning sensation, erythema, and erosion of the oral mucosa and tongue in those who are sensitive (Jorge *et al.*, 2003). A quantity of 0.3-0.4% of free monomer always remains even with the best curing cycle (Dhuru, 2005). To prevent this adverse effect, newly manufactured dentures should be immersed in water for 17-48 h before delivery to a patient (Melilli *et al.*, 2009), and by using a slow curing method which ends with boiling, rather than a fast one (Duymus and Yanikoglu, 2004). The manufacturer should recommend the curing cycle, to reduce the free monomer to less than 1%. Thus, the last 2-3 hours of the curing cycle in boiling water minimises the residual monomer to less than 1%. The maximum allowable limit for residual monomer is 2.2% by weight for types 1 and 4, and 4.5% for type 2 (McCabe and Walls, 2009).

Regarding UDMA-based dentures, these are more biocompatible than type 1 and 2 polymers, as they are not based on MMA, the known sensitiser in PMMA-based dentures. Hence, UDMA-based materials eliminate the potential for contact or respiratory allergy to MMA (Van Noort, 2013). The lack of MMA suggests that a light curable system can be used for patients with MMA sensitivity (O'Brien, 2008). Type 4 biocompatibility can also be attributed to a high degree of polymerisation (65-80%) and less residual UDMA monomer after polymerisation (Dhuru, 2005). For this reason, no tissue reaction was observed in clinical long-term performance after 18 months of using light-cured dentures (Gohlke-Wehrbe *et al*., 2012) and no sign of inflammation was observed in patients after their use for relining (Ogle *et al*., 1986).

UDMA-based light cured polymers are well accepted by the patient due to good denture fit on the denture bearing area, comfort, and satisfaction with the lack of tissue reaction and unobjectionable taste of the uncured material (Ogle *et al*., 1986), as well as good aesthetics (Haeberle and Khan, 1997). In addition, they have good retention in terms of having high dimensional stability, and being light weight and biocompatible (Sipahi *et al.*, 2001).

PMMA- and UDMA-based denture bases are radiolucent, and therefore they are undetectable on a standard radiograph when swallowed or aspirated by accident, as C, O, and H atoms are poor x-ray absorbers. (McCabe and Walls, 2009). To solve this problem, 10-15% bismuth or uranyl salts are added to increase radio-opacity; however, this reduces transverse strength and water sorption and makes it difficult to handle (Craig *et al.*, 2004).

Poor thermal conductivity is another limitation of PMMA and UDMA denture bases. Clinically, it deprives the patients of natural physiological feeling and the protective reflex response to heat when having hot food or drink, until it arrives at the throat, causing burning (Van Noort, 2013). In the lab, it causes a problem during processing with the poor dissipation of heat in heat-cured polymers, and this increases the possibility of porosity (Craig *et al.*, 2004).

PMMA dentures are relatively low cost to fabricate (McCabe and Walls, 2009), and are easily manipulated and repaired (Goguta *et al.*, 2006; McCabe and Walls, 2009). This relative ease is related to the concept of using a powder and liquid system rather than liquid alone, as the mixture is processed at the dough stage as a workable mass after mixing (Anusavice *et al.*, 2012). Another benefit of this system is minimal polymerisation shrinkage. Using this system also reduces the heat of the exothermic reaction released at about 80kJ/mol to convert each C=C to –C-C-. Therefore, the chance of overheating and subsequent thermal contraction is reduced (Van Noort, 2013). PMMA dentures are also easy to polish (Al-Mulla *et al.*, 1988; McCabe and Walls, 2009).

UDMA-based light-cured polymers are easily manipulated and time saving as they exclude or eliminate some of the steps in preparing heat-cured polymers, such as proportioning for mixing, the flask procedure, and wax elimination (Mumcu *et al.*, 2011). They are also polymerised with a short cycle of light curing at about 10-15 min (O'Brien, 2009), so this saves a significant amount of time for both technicians and patients. Accordingly, a complete denture can be finished in one day, which is advantageous for medically or physically compromised patients (Khan and Haeberle, 1992; Fellman, 1989; Haeberle and Khan, 1997; Assery and Al-Shamrani, 1995). In addition, their production is economic as it eliminates the need for flasks, wax, and the boil-out tank, packing press and heat-processing unit needed for conventional denture base material (O'Brien, 2009; Khan and Haeberle, 1992). The method of polymerisation is clean and safe as there is no need for an open flame (Grossmann and Savion, 2005). They can be partially cured in the mouth or on the cast with a hand-held light, which can provide an initial hardening of the material while maintaining shape and preventing flow during relining or a teeth arrangement procedure, or during transference between the clinic and the dental laboratory (Ogle et al., 1986; Fellman, 1989). Therefore, this safety, cleanliness and simplicity enable the clinicians to produce the appliance in their clinic (Haeberle and Khan, 1997).

PMMA and PUDMA dentures can bind to other resins during relining or repair. UDMA-based polymers have often been used to repair acrylic dentures as it bond to other resins with no exothermic reaction. Nevertheless, this bond is stronger between similar resins than dissimilar ones due to the high rate of cross-linking between similar resins, and poor adhesion and lack of interaction between dissimilar ones (Stipho and Talic, 2001; Dar-Odeh *et al*., 1997; Andreopoulos and Polizois, 1994). They found that repairing or relining light-cured resin (Triad) with Triad VLC, and repairing or relining heat-cured PMMA with heat- or auto-polymerised resin results in better bonding and better mechanical properties than repairing or relining PMMA-based with UDMA-based, and vice versa. In contrast, Kostoulas *et al*. (2008) reported that poor mechanical properties resulted from repairing Triad with microbase VLC, which may be due to poor wetting by high viscous repair material applied on the butt joint. This bond strength can be increased by the use of a suitable bonding agent, such as MMA (Craig *et al*., 2004; Yanikoglu *et al*., 2002).

Mechanical bonding is required between the light-cured denture base and denture teeth, according to the manufacturer. However, there is no need for this with PMMA heat-cured dentures due to high temperature and similar MMA monomer which favour a more effective diffusion of the monomer of the denture base material into the tooth surface molecules. The diffused monomer wets, and softens tooth surface polymer molecules by diffusion between chains and increases IPN at the interface between the tooth surface and the denture base material (McCabe and Walls, 2009). High cross-linking of denture teeth sometimes impairs bonding even with PMMA denture base because cross-linked denture teeth are more resistant to diffusion and dissolution by monomers (O’Brien, 2008).

The present bonds in the structure of UDMA and PMMA, shown in Figure 2.1 and 2.5 respectively, exhibit two active sites for bonding in UDMA (bicarbonyl difunctional group) and one active site in PMMA (as explained in 2.2.5). The chemical bonding between UDMA and PMMA denture teeth is poor, which due to poor wetting and poor diffusion of highly viscous UDMA denture base monomer into the tooth surface, in particular, with highly cross linked denture teeth (Yanikoglu *et al*., 2002), and also inclusion of porosities between the tooth surface and denture base may be another reason (Cilingir *et al.,* 2013). Therefore, some studies have been conducted to develop chemical bonding between UDMA-based dentures to PMMA denture teeth by the use of a suitable bonding agent. The bonding agent is important to provide wetting and dissolve the tooth surface at the interface as a solvent and allow subsequent polymer cross-linking with the UDMA denture base material and increasing IPN (Yanikoglu *et al*., 2002).

As a result of a mismatch between the denture tooth polymer (PMMA) and denture base monomer (UDMA), different types of bonding agents have been developed to produce tooth wetting by dissolving and cross linking tooth surface with denture base, such as Triad bonding agent, Vitacoll (MMA and butanone), and experimental bonding agent (a solvent, a mild acid, and a cross linker) (Cunningham, 2000). The magnitude of bond strength has increased until it became comparable to that of heat-cured resin, when the artificial tooth has been roughened and a bonding agent is used so that both chemical and mechanical bonding occur (Marra *et al.*, 2009).

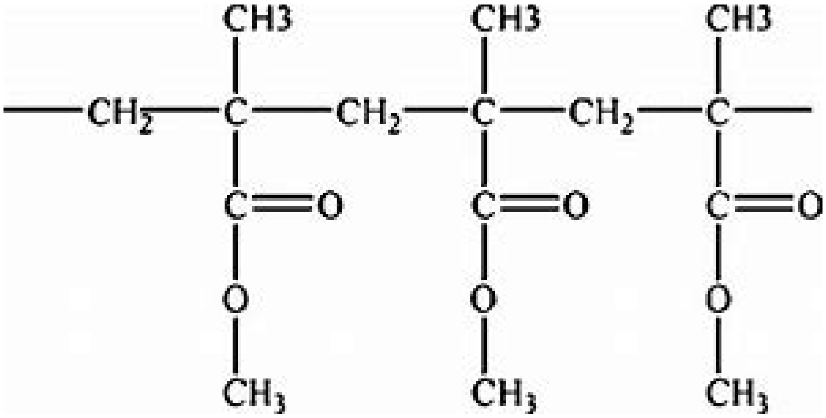


Figure 2.5 Chemical structure of PMMA

Ideal properties	PMMA-based materials	UDMA-based materials
Accept pigments to match the natural colour of the gingiva	yes with acceptable colour stability	yes with poor colour stability
Dimensionally stable in the oral environment	Acceptable stability	More stable than PMMA
Light in weight	yes	yes
Good thermal conductivity	Poor conductor	Poor conductor
Radiopacity	radiolucent	radiolucent
Enough rigidity	Adequate	No research
High flexural strength	Acceptable	Higher than PMMA
High fatigue resistance	poor	poor
High impact resistance	low	Less than PMMA
Sufficient abrasion resistance	acceptable	Higher than PMMA
Low water sorption and solubility	Low	Higher sorption than PMMA
Biocompatibility	Good	Better as no free MMA
Does not allow fungal or microbial growth	Smooth surface, less susceptible	Less smooth surface, more susceptible
Non-toxic or irritating during handling	Contact or inhalation to MMA cause sensitisation	No reported toxicity or irritation
Tasteless and odourless	Yes	Yes
Cheap	Yes	Yes
Easily manipulated and easily repaired	Yes	Yes and takes shorter time
Easily cleaned	Yes	Not reported
Accurate reproduction of surface details	Adequate accuracy	More accurate due to lower contraction
Retentive to other polymers and metals	yes	yes
Resistant to solvents	Acceptable resistance	Poor resistance

Table 2.1 Ideal properties for denture base materials (Van Noort, 2013; McCabe and Walls, 2009; O’Brien, 2008) and summary of PMMA and UDMA materials

2.3 New Denture Base Materials

2.3.1 Eclipse resin system

Introduction

The Eclipse prosthetic resin system is a recently released denture base material which uses the Triad system (Ali *et al.*, 2008; Van Noort, 2013; Fellman, 1989). However, there are some differences in the chemical composition from Triad, such as the absence of fillers and in turn difference in properties. Triad was available for more than 20 years and serves mainly for repair and relining (Diaz-Arnold *et al*., 2008; Stipho and Talic, 2001; Dar-Odeh et al., 1997; Andreopoulos and Polizois, 1994; Ogle et al., 1986).

According to Dentsply International, the Eclipse resin system consists of three resins which are chemically a little different, and can be handled as wax. These resins are: base plate, set up, and contour resin. Base plate resin is used to make the record base that will later form the permanent denture base. Set up resin is used to arrange teeth on a polymerised denture base, but there is no chemical bonding between denture teeth and resin base and so mechanical retention is required. This problem can be a particular disadvantage when there is a limited inter-arch space, so Eclipse bonding agent should be used in such cases to increase the bonding (Akin *et al*., 2014b). Contour resin is overlaid over the base plate and on the necks of the teeth and carved, as wax, to simulate the gingival form. The resin system is also available in four shades for each resin: original, light pink, reddish pink, and dark pink, in addition to clear. It comes as two forms: horse shoe-shaped for the maxillary and bar-shaped for the mandibular arch (International Dentsply).

Two Eclipse light-curing systems are available. The first Eclipse processing unit (Eclipse® EPU 2) consists of six halogen bulbs and 1200W, and can reach a maximum temperature of 129°C (Grossmann and Savion, 2005). It can cure all kinds of appliances, according to the manufacturer. This oven is accompanied by a conditioning oven which is used to warm the cast before the application of the material. The second system (Enterra® VLC Unit) consists of three bulbs and a rotating platform to provide a rich zone of light at 400W. It is used to cure baseplates and night guards, in addition to provisional and diagnostic appliances and Triad materials. This oven is accompanied by a hot plate to heat models. A hot air fan comes with both systems and replaces the Bunsen burner in conventional dentures. Both systems deliver light of 400-500 nm wavelength for 10-15 minutes.

Generally, the published research conducted on Eclipse has concentrated on looking at either the mechanical properties (Machado *et al.*, 2007; Ali *et al.*, 2008; Diaz-Arnold *et al.*, 2008; Machado *et al.*, 2012b; Mutluay *et al.*, 2013; Al-Kheraif, 2014) or the biological properties of the material (Melilli *et al.*, 2009; Koch *et al.*, 2013; Akin *et al.*, 2014b). Most often, the mechanical properties have been compared to other denture base materials, such as PMMA.

Eclipse can be used to make all kinds of appliances according to the manufacturer. However, it cannot be used to repair or reline other polymers as the high temperature needed for polymerisation may distort these polymers. Thus, Eclipse can only be used to repair or reline Eclipse resins.

Chemical composition

According to the manufacturer, the Eclipse base plate resin consists mainly of acrylated urethane oligomers, which are aliphatic urethane dimethacrylate, octadecyl acrylate (stearyl acrylate), and hexandiol dimethacrylate as a cross linker. Using multiple monomers avoids the negative properties of using UDMA alone, such as high water sorption (Gajewski *et al*., 2012). The cross linker resists oxygen inhibition (O'Brien, 2008).The initiator is aromatic phosphine oxide/ camphoroquinone/ acrylated amine, which absorbs light and releases abundant free radicals to initiate the polymerisation process (Jakubiak *et al*., 2003). The light initiator is dissimilar from that used in the Triad system according to the manufacturer. The inhibitor is butylated hydroxytoluene to prevent premature polymerisation, and in addition it contains pigments and fibres such as titanium dioxide, yellow iron oxide, red azo pigment, and red acetate fibres. There are no fillers in the composition.

Manipulation

Each dental appliance needs different procedures for their construction but in general they follow general principles. The procedures for making baseplates are described in detail by the manufacturer. Initially the master stone cast should first be checked for being of an appropriate height for the inside of the curing unit, so that it can be located within the maximum lighting zone to maximise the curing of the material. This height is marked by a line or other symbol on the back wall of the oven. If necessary, the stone model base height should be adjusted accordingly.

According to the manufacturer, International Dentsply, two thin layers of Al-Cote separating medium, which is specific to the Eclipse material and contains potassium alginate, should be applied to a dry stone model with a brush and each layer allowed to dry completely. Then, the stone model should be preheated to a temperature of 55˚C in the conditioning oven (Fletcher-Stark *et al.*, 2011; Akin *et al.*, 2013; Akin *et al.*, 2014a; Ahmad *et al.*, 2009) or on a hot plate set to approximately this temperature, and the temperature indicator should be attached to the cast. When the indicator turns black, the cast should be removed. This preheating facilitates the handling and adaptation of the material on the cast. Refrigerated Eclipse baseplate material is then removed from the lightproof sheet and placed on the warm cast for a few seconds to absorb temperature. It should then be carefully adapted on the cast using fingers to avoid air entrapment. The entire material is then coated with Air Barrier Coating protective varnish (ABC), to prevent the inhibition of the polymerisation process by oxygen.

The stone model and its adapted base plate material should then be inserted into the centre of the rotating platform in the light curing oven, and exposed to light at 400-500nm wavelength for the recommended time, following the manufacturer instructions, of between 10-15 min. The generated heat depends on the number of lamps in the unit, as Eclipse needs both heat and light for polymerisation, according to the manufacturer. After finishing the cycle, the model is removed from the unit, and either allowed to cool on a bench or immersed in tap water for 5-15 min to facilitate baseplate separation.

After cooling, when using an Enterra® VLC Unit (Dentsply International), the tissue surface of the baseplate should be checked for the presence of any orange colour, which is a sign of not being well-cured. If this is the case, the baseplate should be turned upside down, coated with a layer of ABC, and returned to the processing unit following the manufacturer's recommended time. The baseplate is then washed to remove ABC to be ready for finishing and polishing (Grossmann and Savion, 2005; Machado *et al.*, 2007; Ali *et al.*, 2008; Ahmad *et al.*, 2009; Ariff *et al.*, 2011; Baig *et al.*, 2011; Qasim *et al.*, 2012; Al-Kheraif, 2014).

Method of polymerisation

Addition polymerisation is initiated by visible light. The photoinitiator system, aromatic phosphine oxide/ camphoroquinone/ acrylated amine produces intensive free radicals (Brantley and Eliades, 2001). In the uncured phase, the material contains a mixture of different dimethacrylate monomers with a higher molecular weight than MMA, in addition to oligomers. The free radicals react to the urethane dimethacrylate difunctional monomer and oligomers, which provide a more reactive group for free radical polymerisation, forming copolymers of UDMA. This reaction results in a high degree of conversion and high cross linking, in particular during exposure to both light and heat from halogen lamps (Ali *et al.*, 2008). Light triggers the reaction and heat accelerates it by increasing the speed of electron mobility to convert as much monomer as possible, while keeping the temperature above Tg before the material becomes viscous and the electrons become less mobile (O’Brien, 2008; Mutluay *et al*, 2013). The high degree of conversion produces no free monomer (Mellili *et al.*, 2009), creates long chains, and is highly cross-linked (Kerby *et al.*, 2009); this is facilitated by the presence of oligomers, which are semi-crystalline in nature and result in a higher Tg and molecular weight in the resultant polymer or copolymer than PMMA (Sun *et al.*, 2003).

Previous studies on Eclipse

Eclipse has the best reported fracture resistance in comparison with PMMA-based resin (Machado *et al.*, 2007). Machado *et al.* (2007) found that Eclipse had the highest transverse strength and flexural modulus in comparison with heat-cured PMMA (Luciton) and light-cured polymer (Triad) after two days of water immersion. Similar findings have been stated by Mumcu *et al.* (2011), after comparing Eclipse with five denture base materials, including cold-cured PMMA, heat-cured PMMA, and high impact resin heat-cured PMMA, within 15 days of water storage. Even after storing reinforced samples in artificial saliva for 30 days, Eclipse has the greatest fracture strength among other types of light-cured resin (Qasim *et al.*, 2012).

Fatigue resistance is another property of Eclipse, which was evaluated by Diaz-Arnold *et al.* (2008), who stated that although Eclipse has a greater flexural strength than many types of heat-cured PMMA after submission to static flexure, it still shows a brittle type behaviour when subjected to dynamic flexure where the cyclic loading was 5 HZ for 10^4 cycles after 30 days of water immersion. Accordingly, Diaz-Arnold and colleagues concluded that the use of the Eclipse resin system should be confined to low stress situations.

Eclipse has been tested for impact strength in comparison with heat-cured PMMA, self-cured PMMA, and experimental polyurethane material. Eclipse showed the highest impact strength (Radzi *et al.*, 2007), even after application of some effects such as thermo-cycling (Machado *et al.*, 2012b), and after the addition of single-walled carbon nanotubes (Qasim *et al.*, 2012). The latter two studies revealed a higher impact strength for Eclipse samples compared to the other types, including PMMA-based denture base polymers (Luciton) in the first study, and other visible light curing materials (Triad and light plast) in the second, despite its reduced impact strength after thermo-cycling. Good mechanical properties can be attributed to the crystalline nature and high Tg of Eclipse resin (Ali *et al.*, 2008), in addition to a high degree of monomer conversion, and less air incorporation during polymerisation than with Triad sheets (Pfeiffer and Rosenbauer, 2004; Radzi *et al.*, 2007; Qasim *et al.*, 2012).

Eclipse was also the hardest after 30 days of water immersion when compared to heat-cured and auto-cured PMMA-based denture base systems (Meliodent and Probase Cold, respectively) (Ali *et al.,* 2008). There are no other studies in the literature testing hardness.

Only one study has examined the roughness of the Eclipse system by comparing the effect of mechanical and chemical polishing on the roughness of heat cured PMMA and Eclipse (Al-Kheraif, 2014). The author found that mechanical polishing was more effective than chemical for smoothing, regardless the type of material, with Eclipse being smoother than heat cured PMMA.

Two studies have been conducted recently regarding water sorption, and showed a lower tendency of the Eclipse material to absorb water in the long term for 3-6 months than PMMA-based dentures (Akin *et al.*, 2014b), even after fibre reinforcement (Mutluay *et al.*, 2013). However, Eclipse resin reinforcement was not as successful as PMMA denture bases because storing samples in water for 76 days reduced flexural strength and stiffness due to poor impregnation of stick glass fibers with Eclipse.

The cytotoxicity of Eclipse was shown to be lower than that of heat-cured and self-cured PMMA due to the fact that Eclipse contains no unreacted monomer, as demonstrated when analysed for three subsequent days after polymerisation using spectrophotometry (Melilli *et al.*, 2009). The highest cytotoxic reaction for light-, heat-, and cold-cured materials occurred over 24-48 hr, and so the authors suggested keeping the dentures in water for 24-48 h after construction in order to avoid the tissue reaction.

Akin's study observed that Eclipse has a high affinity for the adherence and proliferation of *candida albicans* in comparison with other different denture base materials. The results of this comparison may be explained by the fact that the level of free monomer in heat-cured PMMA affects *Candida albicans*'s viability, which continues for up to seven days of water storage (Koch *et al.*, 2013).

Regarding relining studies, Ahmad *et al.* (2009) studied the shear bond strength for both the Eclipse system and heat-cured PMMA after relining with laboratory relining material and intraoral relining material. They discovered that each material had the highest bond strength when it was relined with the chemically similar corresponding relining material. Nevertheless, Eclipse showed adhesive failure even after the application of dichloromethane bonding agent, while heat-cured PMMA showed cohesive or adhesive failure or both. This was due to, as Ahmad claims, the poor penetration of monomer into highly cross-linked UDMA, or an inadequate adaptation of relining material, or air entrapment under Eclipse relining material (Ahmad *et al.*, 2009). The function of the bonding agent is to dissolve and roughen the surface, and to increase the surface area of contact. To overcome the problem of the adhesive failure with the Eclipse resin system, and to increase its bonding ability, two further studies were carried out in 2011. The first studied the effect of mechanical surface preparation by grinding with both a standard carbide and fine tungsten carbide bur (Baig *et al.*, 2011); the second investigated the effect of mechanical and chemical surface treatments (Ariff *et al.*, 2011). Both studies concluded that a decline in bonding strength will occur, even with mechanical preparation to the surface, unless it is treated with the Eclipse bonding agent. On the other hand, Akin *et al.* (2013) explored the bonding effect of silicone-based soft liner with Eclipse using surface treatments, a laser or Eclipse bonding agent, in comparison with that of PMMA-based dentures without treatment. It showed that there was no difference in tensile bond strength between two denture base materials without surface treatment. Eclipse resin treatment with laser irradiation significantly increased the bonding strength and showed 100% mixed failure compared to treating Eclipse with a bonding agent as a surface treatment, which reduced the adhesion and showed 100% adhesive failure. Thus, the bonding strength with Eclipse differs according to the type of surface treatment.

Eclipse dentures have no chemical bond with acrylic denture teeth according to the manufacturer; hence, many studies have been conducted aiming to improve this bond strength. Palitsch's study compared the tensile bonding strength of acrylic teeth and PMMA-based denture material with that of Eclipse after the application of different conditioning liquids and after thermo-cycling. It was found that Eclipse needs an appropriate conditioning liquid application with good compatibility to obtain an acceptable bonding strength to teeth. On the other hand, PMMA-based materials have optimal tensile bond strength with acrylic teeth with the application of MMA conditioning liquid (Palitsch *et al.*, 2012). The bonding strength of Eclipse to highly cross-linked denture teeth was better than that of PMMA after the application of acrylate bonding agent (Eclipse bonding agent), thermo-cycling and cyclic loading (Fletcher-Stark *et al.*, 2011). Akin *et al.* (2014a) concurred with these findings. Akin and colleagues concluded that Eclipse bonding agent should be used as the principal material in denture construction processes using the Eclipse resin system. These studies advocate using Eclipse bonding agent to improve the bonding strength of Eclipse to denture teeth.

The research on repair has also followed the same principles as research on bonding teeth. One study compared the flexural properties of heat-cured PMMA-based material and seven hypoallergenic denture base materials, including Eclipse, after repairing them with Eclipse or a corresponding repair material. The Eclipse system passed the requirements of flexural strength and modulus both before and after repair. The flexural strength of repaired Eclipse was higher than that of repaired PMMA (Pfeiffer *et al.*, 2008). In contrast, Cilingir *et al.* (2013) focused on repairing Eclipse resin system material only, first using the same material and then by auto-curing acrylic material. They established that the flexural strength does not depend on the type of resin used for repair rather than depending on the denture material itself. For this reason, they have suggested that self-curing resin can be used as an economic alternative repair material for the Eclipse resin system.

2.3.2 Weropress polymer resin.

Introduction

Weropress is a cold-cured PMMA-based pour type acrylic resin denture base material (type 2 class II). According to the manufacturer, it is characterised by high colour stability, high polishability, and extremely accurate fit. It can be used for the construction of all appliances and relining.

Chemical composition

This consists of powder and liquid. The powder consists of PMMA (polymer and copolymer), a barbituric acid catalyst system, organic colourants, and inorganic pigments. The liquid contains MMA, dimethacrylate as a cross-linker, and a barbituric acid catalyst system (MerzDental GmbH, Germany). The powder is available in a range of colours in addition to clear. This is the only chemical composition disclosed by the manufacturer. Barbituric acid compounds are thermodynamically stable, and crystalline (Lewis *et al*., 2004).

Manipulation

The material can be prepared using one of three methods: injection, press, or casting (details in Appendix C). Manipulation follows similar procedures as already mentioned for PMMA in 2.2.4 and 2.2.6.

Studies on Weropress

Only one study has been found which compared the flexural properties of Weropress and Eclipse, and four other types of conventional heat-cured denture base materials.

They were tested for flexural strength and modulus using a 3-point bend test after 15 days of water immersion at room temperature. The study revealed that Weropress had the lowest flexural strength, which was significantly different from Eclipse but not significantly different from other conventional materials. Weropress showed a lower modulus than other materials; however, there was no significant difference between all the compared materials. In conclusion, Weropress exhibited a simple preparation technique but it is poor mechanically, while Eclipse offers good mechanical properties as well as a simple technique (Mumcu *et al.*, 2011).

2.4 Denture Storage:

Normally, patients wear dentures during the day and immerse them in water or disinfectant at night (Machado *et al.*, 2011); as patients are advised not to let their dentures dry to avoid dimensional changes (Craig *et al*., 2004). Thus, *in vitro* studies, dentures or specimens are stored in distilled water at 37°C, as shown in Table 2.2, to simulate the effect of saliva on denture bases, because water forms the main constituent of saliva (Cucci *et al.*, 1998; Salim *et al.*, 2012).

Water is a complex solvent which interferes with polymer molecules that form hydrogen bonds, causing weakened interaction between molecules, swelling, plasticising of the mass, and eventual degradation of the material (Van Noort, 2013). This fact may influence its mechanical properties, such as hardness (Hamouda and Ahmed, 2010), wear resistance (Van Noort, 2013) and flexural strength (Kanie *et al.,* 2004a; Campanha *et al.*, 2005; Mutluay *et al.*, 2013).

Exposure of the denture to a changeable oral environment, such as variations in pH; temperature; saliva; masticatory forces; as well as immersion of the denture in water at night, accelerates the occurrence of ageing signs on the denture (Yeung *et al.*, 1995), which in turn influences its material properties. Temperature changes in the oral cavity can be simulated by thermal cycling, which can range from 0-68°C (Gale and Darvell, 1999; Van Noort, 2013). Most often *in vitro* dentures are exposed to 5000 cycles and 5-55°C as a temperature compatible with the oral cavity (Seo *et al.*, 2006). This thermal alteration may induce internal tension by the frequent expansion and shrinkage of material. This consecutive expansion and shrinkage influences the serviceability and durability of the denture base as it affects the bonding with relining material (Seo *et al.*, 2006), and bonding with teeth due to the difference in the coefficient of thermal expansion (Palitsch *et al*., 2012). It seems that temperature increases the water absorption rate, allowing water to diffuse more easily into the material and moving the polymer chain over each other under load, leading to softening of the surface and a reduction of the Tg (Devlin and Kaushik, 2005).

Proposed protocol of storage	Reference	Storage media
50 h, 1 month, 2 months, 6 months	Cucci *et al*. (1998)	Distilled water (DW)
1 day, 1 week, 1 month, 3 months, 6 months	Mese *et al*. (2008), Akin et al. (2014b)	DW
15 days, 1 month, 2 months, 3 months	Sharma *et al*. (2014)	DW
1 h, 1 day, 1 week, 2 weeks, 3 weeks, 4 weeks	Rahal *et al*. (2004)	DW
1, 2, 6, 12, 19, 26, 33, 40, 47, 54, 62, 69, 76 days	Mutluay *et al*. (2013)	DW
1 week, 3 months, 6 months	Finoti *et al*. (2012)	DW
15 days, 1 month, 2 months, 3 months, 4 months after disinfection	Neppelenbroek *et al*. (2005)	DW
1 day, 1 week, 1 month, and 2 months	Moradians *et al*. 1982	DW
15 days, 1 month, 2 months	Assunção *et al*. (2010)	Artificial saliva
16 h in saliva then 8 h in DW after exposure to UV light	Garcia *et al*. (2010)	DW and Artificial saliva
30 days	Qasim *et al*. (2012)	Artificial saliva

Table 2.2 Different regimes of denture or specimens storage *in vitro* studies

2.5 Denture cleaning

Denture cleaning should be carried out on a daily basis to reduce the incidence of plaque accumulation, staining, halitosis, calculus formation, and bacterial and fungal infection of the oral mucosa and gingivae (Mähönen *et al.*, 1998). This is particularly important for elderly and immuno-compromised patients. Cleaning dentures reduces the risk of a potentially fatal systemic respiratory tract infection in these patients, such as aspiration pneumonia and endocarditis, since unclean dentures are a reservoir for these bacteria (Sumi *et al.*, 2002).

Denture cleaning can be accomplished by mechanical or chemical methods. Mechanical methods include the use of a brush, microwave, or ultrasonic cleaner, while chemical methods include the use of disinfectants, and denture cleansing agents (Moon *et al.*, 2014), in addition to dentifrices, household cleaners, bleaching solutions, soap and mild detergents (Anusavice *et al*., 2012). Usually, mechanical cleaning is insufficient and should be accompanied by chemical cleaning (Mähönen *et al.*, 1998; Lima *et al.*, 2006), especially for elderly and disabled patients who have limited manual dexterity and low motor capacity (Kulak-Ozkan *et al.*, 2002). Nonetheless, mechanical cleaning is indispensable in the removal of biofilm and plaque (Da Silva *et al.*, 2008).

A number of potential adverse effects may result from inappropriate denture cleaning. For instance, mechanical cleaning with a hard brush is detrimental to the surface texture as it can increase the roughness of the denture base (Žilinskas *et al*., 2013). Improper use of a toothbrush may also impair denture teeth and the denture base due to surface abrasion, which in turn may lead to loss of surface detail and poor resultant fit of the denture base on the denture bearing area (Harrison *et al.*, 2004). Accordingly, patients are advised to brush the tissue side of dentures carefully using a soft brush (Žilinskas *et al*., 2013), and to avoid an abrasive dentifrice (Craig *et al*., 2004). Using brushes alone, without soap or dentifrice, and the use of abrasive household cleansers, will deteriorate the appliance aesthetically and functionally due to abrasion and wear (Anusavice *et al.*, 2012). The frequency of brushing is also an influencing factor (Mähönen *et al.*, 1998). Cleaning dentures in water at temperatures above 65˚C is not recommended because of the likelihood of distortion when the temperature is close to Tg, as released processing stresses cause warpage and dimensional changes (McCabe and Walls, 2009, Craig *et* *al*., 2004). Some chemicals may alter the colour of the denture base and artificial teeth over long term use such as bleaching agents (Hong *et al*., 2009). Consequently, a denture may need rebasing or repair to regain or recover its aesthetics, resulting in additional expenses (Moon *et al*., 2014). For these reasons, denture cleansers should have ideal properties, as defined in Table 2.3, to be used safely. These properties depend on certain factors such as suitable time of immersion, and type and concentration of disinfecting solution (Silva *et al*., 2008). Many studies have been undertaken to compare several types of disinfectants with each other, and accordingly several regimes of disinfection have been suggested to discover the most efficient in removing debris, killing microbes and safest way for disinfection, as in Table 2.4.

Chemical type denture cleansers are either paste or immersion, and the most commonly used are those based on immersion, such as powder or tablet (Anusavice *et al*., 2012). The potential for cleaning by paste comes from the size and hardness of abrasive particles, and the speed and force of its application on the denture base material (Freitas-Pontes *et al*., 2009). Typical abrasive agents are calcium carbonate, dicalcium phosphate, and aluminium oxide, which are the most commonly used, although silica, zirconium and PMMA may also be included. For immersion cleaning, the most common ingredients are alkaline compounds, sodium perborate, detergent, and flavouring agents. The chemical cleaning agent is typically an effervescent peroxide or sodium hypochlorite (Harrison *et al*., 2004; Anusavice *et al*., 2012).

Sodium hypochlorite (NaOCl) is the most effective agent for removing plaque (Kulak *et al*., 1997). When it is applied at a concentration 0.02% for 8 h it is fungicidal (Webb *et al*., 1998). When it is used daily at a concentration of 0.5% for 10 minutes for four days, good disinfection is reported, with no change in the roughness of the denture base (Lima *et al*., 2006). It has also been reported that it is effective against spores (Pavarina *et al*., 2003) and removal of the remnants of dead organisms. Household bleaches are used after dilution mostly to remove stains but, sadly, they cause discolouration and whitening of the denture base (Anusavice *et al*., 2012). Care must be taken when using sodium hypochlorite in proximity to metals as it leads to corrosion of the metal (Webb *et al*., 1998). In addition, disinfection with sodium hypochlorite is time consuming and may cause bleaching of the acrylic denture base by the chlorine group (Baysan *et al.*, 1998), whose odour and taste is also objectionable (Pavarina *et al.*, 2003).

Alkaline peroxide-based disinfectants are the most widely used disinfecting agents for denture bases (Peracini *et al.*, 2010; Moon *et al.*, 2014). By dissolving the tablet in water, sodium perborate will release alkaline peroxide, which produces the peroxide group (H_2O_2) and kills microorganisms (broad spectrum) (Pavarina *et al.*, 2003). This, in turn, releases oxygen, which decomposes oral plaque (Anusavice *et al.*, 2012). Therefore, alkaline peroxide cleans and removes stains, and does not have a distinct odour (Pavarina *et al.*, 2003). However, it has been reported to reduce the flexural strength, but within the allowable range (65 MPa), and increase the roughness of heat-cured PMMA denture base materials (Peracini *et al.*, 2010). It has also been shown to alter the colour of denture bases but within a clinically acceptable range (Moon *et al.* 2014). In addition, it might contribute to the degradative change of acrylic denture base material (Nakahara *et al.*, 2013).

Ideal Property	Reference
Easy to use	Baysan *et al.* (1998)
Compatible with denture base material and has a minimal effect on mechanical properties	Machado *et al.* (2009); Peracini *et al.* (2010)
Effective in removing debris and plaque	Webb *et al.* (1998); Lima *et al.* (2006)
Effective in removing stain and deposits	Alam *et al.* (2011)
Has no adverse effect on colour	Hashiguchi *et al.* (2009)
Kills bacteria (bactericidal)	Paranhos *et al.* (2007)
Prevents growth and attachment of *Candida albicans*	Nalbant *et al.* (2008)
Minimises the potential for cross-contamination	Da Silva *et al.* (2008)
Acceptable taste and odour	Pavarina *et al.* (2003)
Safe to use with metals	Webb *et al.* (1998)

Table 2.3 Ideal denture cleansers' properties

Cleaning and disinfection of the denture base material	Reference	Key results
Using alkaline peroxide (BonyPlus tablet In 200ml water) for 5 min, and brushing with dentifrice for 20 s using a new brush with each specimen	Oliveira Paranhos *et al.* (2009)	Different denture hygiene method affects different microbial biofilm
Using 1-4.5 glycine amphoteric surfactant, or enzymatic denture cleaner (Polident) for 60 times immersion	Hashiguchi *et al.* (2009)	Glycine amphoteric surfactant solution is an effective denture cleanser with ultrasonic cleaning device
Using microwave for wet and dry disinfection at 720 watt for 5 or 15 min	Hamouda and Ahmed (2010)	Microwave cleaning method reduces mechanical properties of dentures
Using Antifungal nystatin, or fluconazole, and water as control	Al-Dwairi *et al.* (2012)	Nystatin influences roughness and wettability while fluconazole influences surface free energy
Using 7 days regime of 4% chlorhexidine gluconate or 1% sodium hypochlorite plus 7 cycles daily microwave sterilisation for teeth hardness testing	Campanha *et al.* (2012)	Disinfection reduced hardness of resin denture teeth
Using either an Efferdent tablet at 37°C for 15 min, or 4% chlorhexidine, or 1% hypochlorite, for 3 min, 3 times a week for 60 day, each day rinsing and storage at 37°C distilled water	Goiato *et al.* (2013a)	Thermal cycling and disinfection discoloured denture but clinically acceptable
Using H_2O_2 with photolysis for 1 week	Nakahara *et al.* (2013)	Cleaning by this way has a minimal degradation effect on the acrylic denture bases

Using a microwave power 450, or 630, or 900 w for 3 min for 6 or 36 cycle with dentures immersed in water at the interval	Senna *et al.* (2011)	Microwave disinfection for the first two powers is safe on PMMA
Using 1% NaOCl, or 2% Peracetic acid for 30 or 60 min	Fernandes *et al.* (2013)	Disinfection altered roughness and colour of acrylic dentures
Wiping with 4% chlorhexidine then 10 min immersion in one of the following disinfectants: 4% chlorhexidine, 1%NaOCl, iodophore, or Amosan (alkaline peroxide), for infection control	Pavarina *et al.* (2003)	This is a viable method to reduce cross contamination between dental personnel and patients
Using 50% sodium perborate for 10 min or microwave for 6 min, and then water storage for 7 days	Machado *et al.* (2009)	Disinfection did not reduce hardness but influenced roughness variably
Using one of the following denture cleansers, Corega, Protefix, or Valclean, daily for 15 min at 50°C for 20 days and immersion of specimens in distilled water at the intervals	Durkan *et al.* (2013)	Denture cleansers changed roughness, hardness and colour of some resins
Using one of the following disinfectants: 1% NaOCl, 2% chlorhexidine, 2% glutaraldehyde, 100% vinegar, 3.8% sodium perborate, and sodium perborate tablets for 10 days with immersion for 10 min/day and storage at room temperature at the intervals. Roughness was measured before and after 10 days	Da Silva *et al.* (2008)	These methods are valid alternatives to disinfect acrylic dentures
Using one of the following regimes: toothpaste, toothpaste with stain remover, denture-cleaning paste, immersion type cleaner at 50°C, Water was a control group. Brushing daily for 365 days 10 min/day with electric toothbrush. Measuring roughness pre and post-cleaning	Harrison *et al.* (2004)	Immersion type cleanser is the most suitable cleaner due to effective removal of organic debris and low abrasivity

Using 4 cycles for one of the following disinfectants: 1% sodium hypochlorite, 2% alkaline glutaraldehyde, 4% chlorhexidine. Each cycle for 10 min with 30 min interval between cycles, then immersion in water for 90 days, testing hardness at 15, 30, 60, and 90 days	Sharma *et al.* (2014)	Immersion cleansers reduced hardness of acrylic dentures. This effect is reversed after 15 days water immersion
Using 4% chlorhexidine for 1 min for scrubbing then immersion in one of the following disinfectants: 4% chlorhexidine, 1% NaOCl, 3.78 sodium perborate, immersion for 10 min then water immersion for 3 min. The cycle was repeated 4 times then dryness followed by water immersion for 120 days. Hardness was measured at 15, 30, 60, 90 and 120 days	Neppelenbroek *et al.* (2005)	Immersion cleansers reduced hardness of acrylic dentures. This effect is reversed after 15 days water immersion.
Using 5.25% sodium hypochlorite immersion for 7 days to test colour	Salloum AM (2014)	Disclouration increase with increasing immersion time in acrylic dentures and in liners
Using nystatin, fluconazole, propolis materials separately in deionized water for 14 days, changing water daily plus brushing 3 times daily with a toothbrush by hand for 5s, and toothpaste. Samples were soaked in water at 37°C for 1 week before disinfection. Hardness and roughness were measured before and after the regime	Silva *et al.* (2008)	Propolis have changed the hardness and roughness of acrylic dentures due to microbial adhesion. Other cleansers' effect was similar to water
Using an alkaline peroxide tablet (Efferdent) at 40°C soaking for 30 days and changing daily. Water sorption, roughness and hardness were measured before and after the regime	Devlin and Kaushik (2005)	Hot water reduced hardness and caused whitening of acrylic denture bases
Immersion for 5 min in Corega tablet (alkaline peroxide), or 3 min in BonyPlus (alkaline peroxide) for 30 times/6 days to simulate disinfection for 180 days. It was kept at intervals in distilled water 23°C. Physical properties were tested	Peracini *et al.* (2010)	Denture cleansers caused clinically insignificant discolouration and increased roughness and reduced flexural strength

Immersion in 1% sodium hypochlorite, or 2% chlorhexidine, or Corega tablet (sodium perborate) (200ml water at 40°C) for 5 min, 30 time /6 days to simulate 180 days, and distilled water soaking at time intervals. Teeth bonding was measured before and after disinfection	Carolina Pero *et al.* (2013)	All cleansers were detrimental to acrylic denture base than to cross linked teeth following breakage except Corega
Immersion in 3.8% sodium perborate at 50°C for 8 h and then in distilled water for 16h at 37°C (similar to daily use) for 4 weeks and changing water daily. Roughness was measured at 1, 3, and 28 days	Machado *et al.* (2011)	Roughness of hard reliner was influenced by all disinfection procedure
Storing samples for 24 h in water then disinfecting them with Clorox bleach, Polident 3 minute, Efferdent, or Kleenite for 10 h daily (overnight) and storage for 14 h in distilled water. The regime continued for 48 weeks. Colour was measured at baseline, 4, 12, 24, 36, and 48 weeks	Moon *et al.* (2014)	All cleansers produced clinically acceptable colour change
Using Lavaruck, Steradent, Polident, Pika, Correct, Quick Denture Cleaner, Dr.OhHa, ZTC Denture Cleaner. Immersion 12 h at room temperature, and 12 h water soak at 37°C each day, for 365 times in total. Colour was measured at 90, 180, 365 days	Hong *et al.* (2009)	Colour stability of PMMA is influenced by degree of polymerisation and type of the cleanser

Table 2.4 Different regimes of denture cleaning and disinfection

2.6 Testing materials for some properties

2.6.1 Porosity testing

There are a number of methods to assess porosity and each one has its indications and limitations. Therefore, no general method can be used in all cases where it differs with different material, pore type, shape, and size. Some researchers have used an arithmetic method to calculate the percentage volume of porosities in each specimen using water sorption by calculating the weight of the specimen before and after its immersion in water, after repeated weighing of the samples until obtaining equilibrium in air and in water (Compagnoni *et al*., 2004; Pero *et al*., 2008).

According to Compagnoni *et al.* (2004), the following equations were used to gain the porosity percentage volume:

$$W_a = g\ (\rho_r - \rho_a)(V_{sp} - V_{ip})$$

$$W_w = g\ (\rho_r - \rho_w)\ (V_{sp} - V_{ip}) + (\rho_a - \rho_w)\ Vip$$

$$\%\ \text{Porosity} = V_{ip}/V_{sp}*100$$

Where W_a is a specimen weight in air; W_w is a specimen weight in water; g is gravitational acceleration constant; ρ_r is a density of PMMA; ρ_a is a density of the air; ρ_w is a density of the water; V_{sp} is volume of the specimen, and V_{ip} is a volume of the internal porosities. Similarly, Kartika *et al.* (2015), Abood (2007), and Kasina *et al.* (2014) used the same equations, while Pero *et al.* (2008) used the equations below to calculate the volume of the specimen in and out of water:

$$V_d = (m_d - m'_d)/\rho_w$$

$$V_s = (m_s - m'_s)/\rho_w$$

$$\%\ \text{Porosity} = ((V_s - V_d)*100)/\ V_d$$

Where V_d is dried specimen volume, V_s is water saturated specimen volume, m_d is dried specimen mass in air, m'_d is dried specimen mass in water, ρ_w is water density, m_s is saturated specimen mass in air, m'_s is saturated specimen mass in water.

Another group of researchers used a different method to evaluate porosity by magnification using different devices. They counted the number of pores in each specimen using different microscopes and at different magnification powers, or investigated pore shape and concentration after immersion in dye for half an hour (Canadas *et al.*, 2010). For example, a light microscope was employed at a range of magnification X8-X60 (Wolfaardt *et al.*, 1986; Reitz *et al.*, 1985; Oliveira *et al.*, 2003; Canadas *et al.*, 2010; Yannikakis et al., 2002).

A third group of researchers took photographs using a microscope with x100 magnification, and some accompanying devices, to calculate surface area (Yannikakis *et al.*, 2002). They compared results when using a spectrophotometer (Jerolimov *et al.*, 1989) and a scanning electron microscopy (Keller *et al.,* 1985; Novais *et al.*, 2009).

A limited number of researchers have evaluated porosity by visual inspection based on the specifications of the Revised American Dental Association No. 12 (Materials and Devices, 1975) and on the fact that, unless porosities can be recognised with the naked eye, they will be clinically negligible and not affect the aesthetic (Wolfaardt *et al.,* 1986; Yau *et al.*, 2004).

2.6.2 Water sorption and solubility testing

Water sorption means water absorption to the interior of the material and adsorption to the surface of the material (Ferracane, 1995; O'Brien, 2008). The presence of weak secondary bonds in polymers allows water molecules to penetrate between chains, which breaks down bonds and forces chains apart during water absorption, thus causing expansion or swelling of the polymerised mass. This absorption has a positive effect in that it compensates for processing shrinkage relieving the stress and causing an insignificant change in shape, as well as a negative effect since it interferes with the entanglement of polymer chains acting as plasticisers and it also causes hydrolytic degradation (O'Brien, 2008). Polymers can be degraded by the physico-chemical process after absorbing a high amount of water, starting with swelling which causes dimensional distortion (Polat *et al.*, 2003). This is then followed by dissolution as water ions weaken the polymer, acting as a plasticiser, and reducing strength, such as flexural strength (Seo *et al.*, 2006; Mutluay *et al.*, 2013). It also increases its flexibility and potential to fracture (Machado *et al.*, 2012b), and reduces hardness (Dhuru, 2005).

Thus, water sorption is one of the causative factors which compromise mechanical properties and reduce Tg. Therefore, water absorption property is important for the durability of the denture in clinical use (McCabe and Walls, 2009). It also increases the likelihood of discolouration or staining, malodour, and leaching of unreacted components (Van Noort, 2013; O'Brien, 2009).

Absorbed water, as a solvent, may dissolve water-soluble ingredients (Van Noort, 2013). The amount of water sorption is related to soluble fraction, which includes water-soluble components such as a plasticiser, residual monomer, initiator, and activator (McCabe and Walls, 2009). Soluble ingredients leach into the oral cavity (saliva), reducing the volume of the material (Van Noort, 2013) and leave spaces in the denture which are later occupied by water or colonised by microorganisms such as *Candida albicans*. Fungal infections, can however, be minimised by cleaning the denture. (Van Noort, 2013).

In light-cured materials, water sorption is related to the presence of air voids and hydrolytic breakdown of the bond between filler and matrix, which accelerates material deterioration and increases its wear (Van Noort, 2013). Leached ingredients may have an adverse effect on biocompatibility (Melilli *et al.*, 2009). Therefore, these two properties, water sorption and solubility, should be minimised as much as possible to maintain material properties. Water solubility can be managed by controlling the amount of water-soluble components (Van Noort, 2013). Solubility is hastened by dissolution in absorbed water (Van Noort, 2013). The solubility of the denture base intraorally includes solubility in water and acids or alkaline entering the oral cavity with the aid of mechanical forces, which cause erosion. Testing solubility with water only is not ideal because it does not represent the reality of the oral cavity, but it does provide preliminary data about the effect of the major part in saliva (McCabe and Walls, 2009).

Water sorption and solubility tests are a measure of a material's liability to absorb and dissolve in fluids such as water or saliva (McCabe and Walls, 2009). It is the amount of increase or decrease in mass per unit volume (µg/mm^3). The standard method of measuring water sorption or solubility according to ISO 20795-1:2013 is by storing samples immediately after manufacture in a desiccator containing silica gel to remove moisture gained from everywhere. Samples are repeatedly weighed until a fixed weight

(W_0) is obtained, and then the volume (V) is calculated. Then, the samples are immersed in water for different lengths of time. After removal from water, the samples are weighed immediately to obtain (W_1). Then the samples are placed back in the desiccator and weighed in the same way as before immersion until a fixed weight (W_2) is obtained. Water sorption and solubility can be calculated according to the following equations:

Water sorption $=W_1-W_2/V$

Water solubility $=W_0-W_2/V$

Water sorption and desorption curves should be similar but in reverse order, except for a small reduction in the original weight, which is the soluble part (Dhuru, 2005).

Water sorption is a multifactorial phenomenon. These factors may influence water sorption either directly or indirectly. Water sorption is a temperature dependant process (Seo *et al.*, 2006; Machado *et al.*, 2012b). A high temperature expands the material and facilitates the diffusion of water between polymer chains, although very high temperatures greater than Tg can break molecules, degrade the interstitial matrix, and form voids. The absorbed water then softens the material, and distorts the material and reduces its strength (Devlin and Kaushik, 2005).

The water sorption process is also dependent on the time of saturation, which is governed by the diffusion coefficient and rate of water uptake. Water absorption starts with diffusion and progresses by polarity (Jagger and Huggett, 1990; Melilli *et al.*, 2009; Mutluay *et al.*, 2013; Van Noort, 2013; McCabe and Walls, 2009). Water sorption in polymers requires a considerable time to reach saturation, several days or weeks, due to the low diffusion rate, and reaches an equilibrium at the range 1- 2% by weight. Typical time for polymers saturation is 17 days, according to Mutluay *et al.* (2013) but depends on the thickness of a denture (McCabe and Walls, 2009; Asar *et al.*, 2013; Van Noort, 2013). In addition, water sorption is also influenced by material formulation (Pfeiffer and Rosenbauer, 2004), and the homogeneity of the polymer matrix (Polat *et al.*, 2003). Therefore, cross-linking for more than 5% reduces water sorption (Rahal *et al.*, 2004; Polat *et al.*, 2003; Goiato *et al.,* 2013b; Arima *et al.*, 1995b). Additionally, this process also depends on the polishing technique of the material, and therefore the rough surface is more hydrophilic (Rahal *et al.*, 2004). Finally, the curing temperature is another factor influencing sorption (Dogan *et al.*, 1994; Duymus *et al.*, 2004).

Previous studies have reported a lower water sorption for Eclipse than heat-cured PMMA; this was not statistically significant in the short term up to one month, but became so in the long-term, 3-6 months, and both reached saturation at 3 months (Akin *et al.*, 2014b). Sorption and solubility occur at the same time in heat-cured PMMA as it contains free MMA in addition to other soluble ingredients. Those may slow down the process of absorption until most soluble ingredients have leached. On the other hand, Eclipse's semi-crystalline cross-linked structure and the low coefficient of diffusion have reduced and slowed down the absorption (Al-Mulla *et al*. (1989). Eclipse also had a lower water sorption than pourable PMMA (Palapress) within 76 days of water immersion at 37˚C (Mutluay *et al.*, 2013). This study revealed no significant difference of water uptake at the equilibrium; however, Eclipse reached equilibrium on the 70th day, while Palapress did so during the 50-60th days. This finding was attributed to a gradual and slower rate of water absorption by UDMA-based polymers and a rather steeper and faster absorption by both heat-cured and pourable PMMA (Al-Mulla *et al.*, 1989). At equilibrium, Eclipse did not absorb significantly less water than pourable PMMA because Eclipse was prepared (in a way which did not follow the manufacturer's instructions) using light for 30 min with no heat, which might have influenced the quality of the cured material (O'Brien, 2008; Mutluay *et al.*, 2013; Alpoz *et al.*, 2008). No previous study has investigated the difference between cold-cured PMMA and Eclipse. In light of the above mentioned studies, Eclipse demonstrated less absorption than PMMA-based polymers, even after saturation, and this is mainly due to the composition of the copolymer of UDMA, which shows hydrophobic properties. In addition, Eclipse has a high degree of conversion with no residual monomer (Melilli *et al.*, 2009), a semi-crystalline cross-linked structure (O'Brien, 2008), and less soluble content (Van Noort, 2013; Mutluay *et al.*, 2013).

Unlike Eclipse, Triad demonstrated a higher water uptake than PMMA-based polymers, due to the difference in the ingredients of Eclipse and Triad's uncured material, which includes silica fillers. Hydrolytic breakdown of the bond between the filler and matrix (Van Noort, 2013), and the high potential of Triad to develop air bubbles under the sheets of viscous monomer (Tan *et al*., 1989) provided spaces for absorbed water. In addition, it have mainly been caused by the high water sorption of PUDMA (Gajewski *et al*., 2012).

Previous studies have demonstrated a lower water uptake by cold-cured, and injectable cold-cured PMMA than heat-cured PMMA stored for 7-90 days in water at 37˚C, despite that the diffusivity in cold-cured PMMA is higher, which probably due to higher roughness (Al-Mulla *et al*., 1988; Cucci *et al*. 1998; Polat *et al*., 2003). These findings are similar despite the different duration, temperature and pressure for polymerisation, and different mixing ratios, possibly due to the relationship between free monomer with water sorption. One of differences between heat- and cold-cured PMMA is the amount of free monomer, which is higher with cold-cured PMMA than heat-cured PMMA. The amount of free monomer may impede water absorption before complete leaching into water (Braun *et al.*, 2003). This is because water absorption and solubility take place at the same time, and weight lost through solubility can be regained by water absorption (McCabe and Walls, 2009). In regard to heat-cured PMMA, there is a positive relationship between sorption and free monomer (Dogan *et al*., 1994), but no positive correlation regarding PMMA-based materials in general (Pfeiffer and Rosenbauer, 2004). This is because most of the free monomer can leach within a highly variable period of time, ranging from seven days at 37˚C water (Lamb *et al.*, 1982) up to five years (Sadamori *et al*., 1992). For this reason, water sorption is the worst predictor for degree of conversion and free monomer (Rueggerberg and Craig, 1988). Therefore, other water soluble ingredients such as plasticiser and initiator can be used to explain the sorption ranking of PMMA materials. These ingredients may be high in heat-cured PMMA when it has caused higher sorption. Also, other factors influence sorption, as mentioned above, and should be taken into consideration.

Water solubility depends on the amount of soluble ingredients (Van Noort, 2013) and feasibility of dissolving them within the polymer structure. The feasibility in turn depends on the diffusion rate and on solubility of ingredients themselves in water (Arima *et al*., 1995a). Residual monomer is one soluble ingredient where water solubility increases as residual monomer increases (Cucci *et al*., 1998). Similarly, hot monomer used for chemical polishing of heat-cured PMMA can significantly increase the solubility in water because monomer works as a solvent before immersion in water (Rahal *et al*., 2004; Machado *et al.*, 2004). However, a low monomer level does not mean low solubility. This finding was supported by Pfeiffer and Rosenbauer (2004), who compared some hypoallergenic materials in regard to the level of residual MMA and water solubility. This finding was previously revealed by Polat *et al*. (2003), who reported a significantly higher solubility of heat-cured PMMA than injectable cold-cured PMMA, which was even higher than the minimum requirement of ISO 20795-1:2013 for denture bases after seven days of water immersion at 37˚C. These results could be attributed to the presence of other soluble ingredients. In addition, other parameters may influence the release of residual monomer, such as polymerisation duration and temperature, which in turn influence homogeneity and the degree of conversion of the material. Fragile bonding with no cross-linking of molecules facilitates the breaking of the union and entry of water to release water-soluble substances. However, cross-linker up to 40% by weight causes a very small decrease in solubility with more than this ratio increases the solubility (Arima *et al*., 1995a). Short term water immersion is usually related to the leaching of soluble ingredients, while long term is related to the elution of degradation products (Ferracane, 2006).

In regard to the dimensions of the specimen used to test water sorption and solubility, Table 2.5 shows that researchers have used variable specimen dimensions. Some researchers have used a 3-point bend test to test solubility (Mutluay *et al*., 2013).

Length (mm) or diameter	Width (mm)	Thickness (mm)	Specimen shape	Study (year)	Standard numbers
65	10	3	Rectangular	Vuorinen *et al.* (2008)	-------
1	1	1	Cubic	Akin *et al.* (2014b)	ISO 1567:1997
40	--------	0.5	Disk	Salim *et al.* (2012)	-------
50	--------	0.5	Disk	Cucci *et al.* (1998), Rahal *et al.* (2004), Asar *et al.* (2013)	ISO 20795-1:2013 and ADA specification no. 12

Table 2.5 Dimensions of water sorption and solubility specimen

2.6.3 The testing of flexural properties

Terminology:

Flexural load is a combination of tensile and compression forces (McCabe and Walls, 2009). A material’s behaviour under stress can be represented in a curve called a stress strain curve shown in Figure 2.6. Stress is the magnitude of any force applied per unit of area. Strain is the magnitude of change in length per primary length, with no units. Stiffness is the material of a definite dimensions' resistance to dimensional change under a given load. Rigidity is same as stiffness without taking material dimensions into consideration. Stiffness and flexibility are used as indications of the modulus of elasticity. Stiff means there is a high modulus of elasticity, while flexible means a low modulus (O’Brien, 2009). Modulus of elasticity (also called Young’s modulus) represents the linear part of the curve, which ends with the elastic limit. Elastic limit is also called proportional limit, although this is a little higher experimentally (Dhuru, 2005). Elastic limit is the maximum stress applied on the material which allows it to recover completely to its original dimensions after releasing the load without onset of failure, that is, within its elastic or recoverable region or springiness. After this stress, the load causes a permanent, a plastic or an irrecoverable deformation. The extent of the recovery is a function of the elastic properties. Flexible material has higher strain than stiff, and therefore high flexural deflection (within elastic limit) also refers to high flexibility (Dhuru, 2005). Flexibility is the ability of the material to deform elastically under a specific load. Maximum elastic strain at proportional limit is called maximum flexibility. Yield stress or proof stress refers to the stress at which a 0.1-0.2% permanent deformation can occur, and its strain is referred to as “offset”. Plastic deformation caused by tension is referred to as elongation. Ductility is the ability of the material to bend or stretch a considerable amount without fracture, while malleability is the ability of the material to compress a considerable amount without fracture. The maximum stress before breakage is called ultimate strength or stress, and these can be classified as: tensile, compressive, shear, torsion, or flexural strength. Stress causes a catastrophic fracture called a breaking or fracture stress. Brittle materials are those materials which have low ductility. Resilience is energy absorbed by deforming the material elastically (springiness) while toughness is the energy absorbed by breaking the material. Tough is opposite to brittle, while rigid or stiff is opposite to flexible (Ferracane, 1995; Dhuru, 2005; Van Noort, 2013, O'Brien, 2009).

Ultimate flexural strength, also called bending strength or transverse strength, is the maximum resistance of the material to deformation under flexural load. Transverse strength is the most important clinical criteria, as bending load is the most relevant load type for denture bases (Dhuru, 2005). Fractures occurring on the tension side are facilitated by the presence of surface defects, voids, or any imperfections, particularly with brittle materials. These defects cause stress concentration. Accordingly, transverse strength is influenced by the surface imperfections (McCabe and Walls, 2009).

The most common test used to measure transverse strength is called a three-point bending test or transverse strength test. Its principle is similar to the load applied on the maxillary denture *in situ* (Machado *et al.*, 2012b). An external force is applied to the mid-point of a test beam until failure, as in Figure 2.7. Flexural strength can be calculated according to the following equation (McCabe and Walls, 2009)

$S = 3FL/2bd^2$

Where, L is the distance between the supporting points, b is the width of the specimen, and d is the height of the specimen.

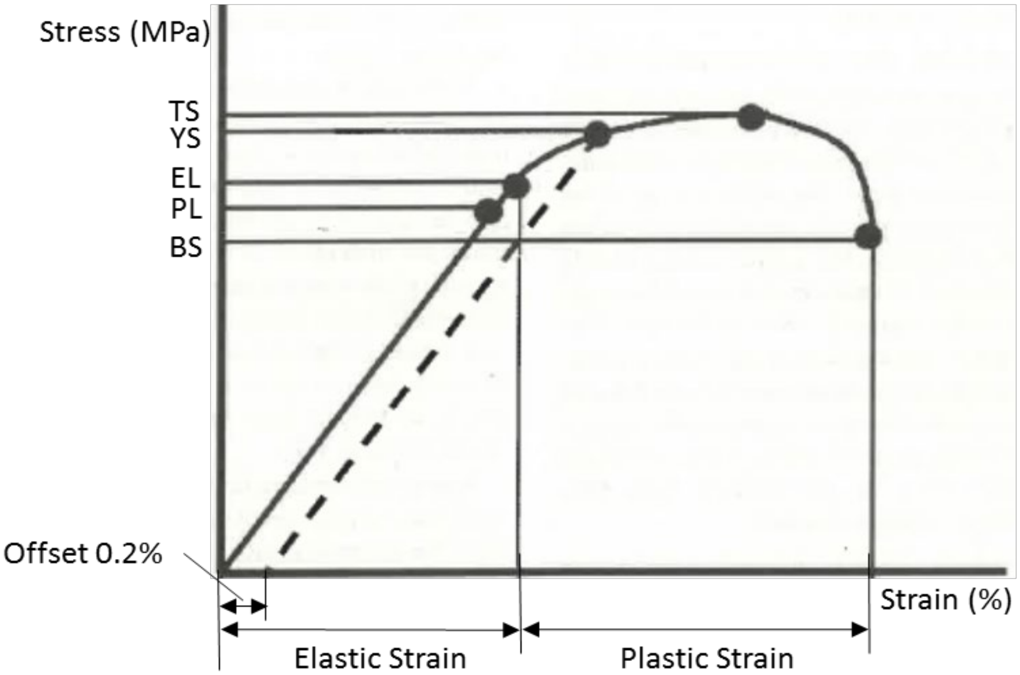


Figure 2.6 Stress-strain curve (TS- Ultimate tensile strength, YS-Yield strength, EL-Elastic limit, PL-Proportional limit, BS- Breaking strength) (Dhuru, 2005)

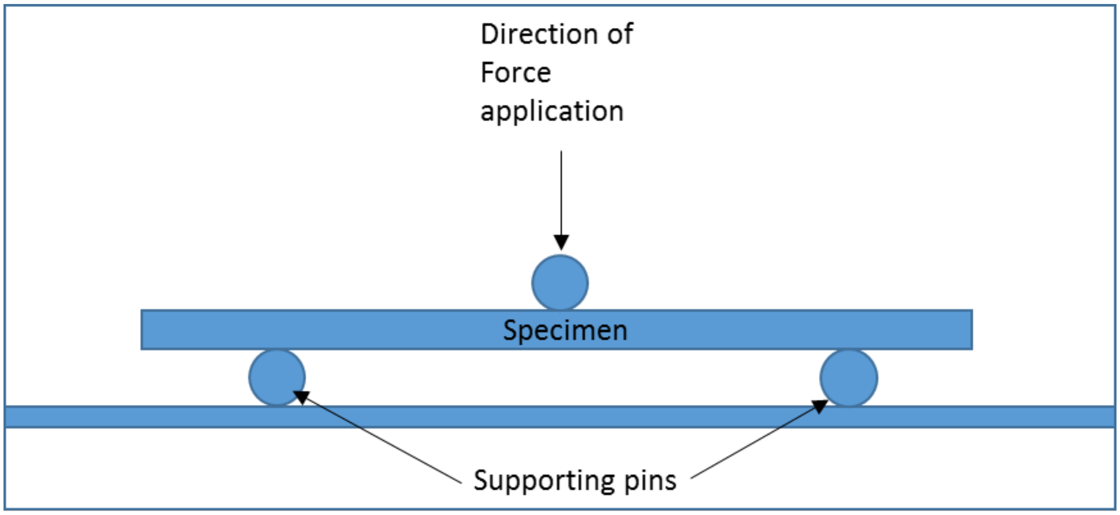


Figure 2.7 Diagram of a 3-point bend test

Previous studies

Eclipse visible light-cured material showed superior flexural properties over other visible light-cured materials (Sun *et al*., 2003; Qasim *et al*., 2012). Triad exhibited lower flexural strength values than Eclipse in a fresh condition and after different water immersion periods, as shown in Table 2.6 (Machado *et al*., 2007; Qasim *et al*., 2012). The strength variation of Triad in different studies may be due to different durations of light exposure (Alpoz *et al*., 2008). Many reasons have been proposed for this improvement in the flexural strength of Eclipse, such as different forms of material, monomers, and initiator systems (as suggested by the manufacturer) (Sun *et al.,* 2003), and the absence of fillers, according to the composition previously mentioned 2.3.1, 2.2.3. Regarding the form, Triad comes in sheets, while Eclipse comes in paste form, and this might have resulted in a reduction of bubble formation caused by air entrapment between the sheet baseplate and stone cast during adaptation, producing no crack under loading (Pfeiffer *et al.*, 2005). The presence of silica filler in the Triad composition may interfere with polymerisation as it reflects or scatters light as an opacifier, reducing the intensity of light (Shortall *et al*., 2008). Silica fillers might also have weakened the material under flexural load, due to either poor bonding with the matrix or the absence of a coupling agent. This concept was confirmed by scanning electron microscopy for Triad specimens on the fracture side after the application of a three-point bending test. This microscopy revealed spherical pits where silica particles had withdrawn, indicating poor bonding with the matrix (Al-Mulla *et al*., 1988). In terms of different monomer and initiator systems, these reflect on the low homogeneity of the Triad material (Al-Mulla *et al.*, 1988) in comparison with semi-crystalline highly cross-linked Eclipse (Sun *et al*., 2003). In addition, Triad consist of PUDMA, while Eclipse may consist of copolymer UDMA. The low strength of Triad continues even after being cured on both sides. Hence, different light exposure cycles and machines, and in turn different light intensities because of different exposure time and number of lamps, in addition to different temperature inside the curing machine, may be the reasons for the strength difference between Triad and Eclipse (Al-Mulla *et al.*, 1988). A Triad processing unit contains one halogen lamp and a maximum temperature of 75˚C, while the Eclipse processing unit is 3-6 halogen lamps and a temperature of 108-129˚C (Kurtzman and Melton, 2004; Ali *et al*., 2008). All previously mentioned findings refer to the fact that the superiority of Eclipse's flexural strength is multifactorial.

Eclipse also showed a stronger behaviour and higher flexural modulus than PMMA-based denture base polymers, including conventional heat-, self-cured and pourable cold-cured polymers before and after storage in water at different time points (2, 15, 30, 76 days) (Sun *et al*., 2003; Machado *et al*., 2007; Ali *et al*., 2008; Diaz-Arnold *et al*., 2008; Mumcu *et al*., 2011, Machado *et al*., 2012b; Mutluay *et al.,* 2013; Hashem *et al*., 2014). This superiority regarding flexural properties occurs even after repair (Pfeiffer *et al*., 2008) despite using a different curing machine in each study (Enterra VLC Curing Unit, Ivoclar, Triad curing machine, Eclipse processing unit), different mould material (stone, Teflon, metal), exposure on one side or two, different time of light exposure, with and without heat, storage at room temperature or at 37˚C, and different testing conditions (inside or outside water). These results are due to differences in the chemical composition of uncured Eclipse, in comparison with PMMA-based materials, in that it contains UDMA instead of MMA monomer, and is a light sensitive initiator system, rather than thermal initiator (as mentioned before in Section 2.3.1). The resultant higher degree of conversion (Dhuru, 2005), high cross-linking, and semi-crystalline nature with subsequent greater molecular weight of Eclipse, in addition to the lack of residual monomer after polymerisation (which acts as a plasticiser) (Pfeiffer *et al*., 2005; Melilli *et al*., 2009), are all an indication of high strength and flexural modulus (O'Brien, 2008; Van Noort, 2013). Although the plasticising effect of water reduces the mechanical properties, the low water sorption properties of Eclipse helps to maintain its higher flexural properties (Akin *et al*., 2014b; Mutluay *et al*., 2013).

Eclipse's flexural strength showed a noticeable variation ranging from 2-20% for a storage time of 0-76 days in different studies, as shown in Table 2.7. The data in the table indicate no clear relation between time of storage and coefficient of variation (CV, standard deviation/ mean*100) even after the exclusion of small sample sizes of less than 10. This is due to different conditions and variations in preparation between different studies. This variation might most often relate to the method of manipulation and polymerisation. Using hand pressure to adapt a highly viscous material on a preheated mould, using no pressure during polymerisation, and no flasking, might have caused variations in specimen fabrication and producing materials of variable density (Keller and Lautenschlager, 1985). Highly viscous material is susceptible to air incorporation during handling and this can cause voids (Qasim *et al.,* 2012). These voids fill with air, which inhibits the polymerisation of the surrounding layer and results in different polymerisation degrees in different layers of each specimen. Different number and size of voids in each specimen may also have produced a different ratio of water uptake, and this difference may be another reason for high variation in strength (Akin *et al*., 2014b). In addition, these voids may form a nucleus for stress concentration, and trigger premature fracture as brittle materials (McCabe and Walls, 2009).

Storage Time (days)	Flexural strength (MPa)		Reference
	Triad	Eclipse	
0	84	119	Sun *et al*. (2003)
2	58	116	Machado *et al*. (2007)
30	95	115	Qasim *et al*. (2012)

Table 2.6 Some studies on flexural strength of Triad and Eclipse

Storage time (days)	Sample size (respectively)	Flexural strength (MPa)	CV % of flexural strength	Flexural modulus (GPa)	Reference (respective)
0	6	101, 119	19	2.8	Mutlucy *et al*. (2013), Sun *et al*. (2003)
2	20, 10, 10, 5	122, 116, 136, 106	10,14, 5, 2	-, -, -, 2.3	Hashem *et al*. (2014), Machado *et al*. (2007), Machado *et al*. (2012), Pfeiffer *et al*. (2008)
15	8, 10	114, 88	8, 20	2.4, 1.7	Mumcu *et al.* (2011), Cilingir *et al*. (2013)
30	10, 10, 10	115, 103, 127	4, 3, 11,	-, 2.4	Qasim *et al*. (2012), Ali *et al*. (2008), Diaz-Arnold *et al*. (2008)
76	6	92	16	1.9	Mutlucy *et al*. (2013)

Table 2.7 Summary of flexural strength studies on Eclipse

In the light of studies in the literature, heat-cured PMMA is usually stronger and of higher flexural modulus than cold-cured PMMA and pourable cold-cured PMMA, although, after water immersion, modulus is not significantly different at some time points (Ali *et al*., 2008; Sun *et al*., 2003; Mumcu *et al*., 2011; Al-Mulla *et al*., 1988; Johnston *et al*, 1981). The flexural properties of denture bases, as one of the important mechanical properties, vary according to the method of activation, and chemical composition. Both are reflected in the degree of conversion, type of bonding, length of chains, number of branches, and degree of cross-linking (O'Brien, 2008; Anusavice *et al*., 2012; Van Noort, 2013). The main differences between heat- and cold-cured PMMA are in the method of polymerisation and chemical composition (as mentioned before in Section 2.2.3); these result in low molecular weight and a high quantity of free monomer of cold-cured PMMA (Van Noort, 2013). Free monomer is water soluble, and some authors have claimed that if residual monomer is allowed to leach into water, heat- and cold-cured PMMA may show some comparable properties (Craig *et al*., 2004). Sugino (1976) compared commercial and experimental pourable, self-curing and heat-cured PMMA, and found that mechanical properties and Tg is a function of polymerisation temperature rather than mixing ratio. The ranking order begins with type 2 class 1 PMMA as the weakest and with the lowest curing temperature, rising to heat-cured PMMA as the strongest with the highest curing temperature, and the pouring type in between. Free monomer concentration follows the opposite order, with type 2 class 1 being highest, and type 1 class 1 lowest, with the pouring type in the middle. Accordingly, both the level of residual monomer and the physical and mechanical properties are affected by the temperature of polymerisation, the powder/liquid ratio, and the pressure applied. In addition, they are also influenced by the formulation of the resin, which may be of different molecular weight and particle size, different activator/inhibitor ratios, and varying cross-linker concentrations (Bayraktar *et al*., 2006; O'Brien, 2008; Keller *et al*., 1985; Sugino, 1976). In brief, the strength of PMMA depends on the formulation of the material and conditions of polymerisation, but, in general, heat-cured PMMA is the strongest compared to type 2 denture base polymers.

In regard to specimen dimensions, the literature reveals that various dimensions have been used as flexural test specimens, as in Table 2.8. However, that used by most researchers is nearly the same as for that of ISO 20795-1:2013: 64*10*3.3 mm.

Specimen dimensions (mm)	References
64*10*3.3 64*10*3.5 64*10*2.5 65*10*3 65*10*2.5	Pfeiffer *et al.* (2005), Senna *et al.* (2011), Lee *et al.* (2012), Machado *et al.* (2012), Diaz-Arnold *et al.* (2008), Pfeiffer *et al.* (2008), Mumcu *et al.* (2011), Cilingir *et al.* (2013), Vuorinen *et al.* (2008), Al-Mulla *et al.* (1988), Cucci *et al.* (1998), Ali *et al.* (2008), Regis *et al.* (2009), Arıkan *et al.* (2010), Hamouda and Ahmed (2010), Ladha and Shah (2011), Mutluay *et al.* (2013), ISO 1567:1999, and ISO 20795-1:2013
70*11*3	Mansour *et al.* (2013) and ISO 178
80*10*4	Venkat *et al.* (2013)
50*25*3.5	Machado *et al.* (2007)
50*6*4	Qasim *et al.* (2012)
30*3*3	Murakami *et al.* (2013)

Table 2.8 Dimensions of transverse strength specimen (specimen’s dimensions were written as length, width and thickness respectively)

2.6.4 Hardness testing

Hardness is the resistance of a material to a permanent surface penetration by a hard indenter. Scratching or abrasion resistance is a function of material hardness. Hardness and wear are associated with the presence of filler, although with a high quantity of filler, wear resistance reduces but hardness does not (Van Noort, 2013). Denture wear can occur in response to toothpaste, solvents, denture cleanser and tooth brushing (Ferracane, 1995; Harrison *et al.*, 2004; McCabe and Walls, 2009; Van Noort, 2013). Thus, hardness indirectly predicts how easily the material will respond to abrasive and indenting forces, and provides an indication of mechanical properties (Dhuru, 2005). Hardness is also a measure of polishability, and a high level of hardness makes polishing difficult (McCabe and Walls, 2009). Hardness values are inversely proportional to the size of the indentation, and the larger the indent, the softer the material (McCabe and Walls, 2009; O'Brien, 2009).

There are five popular methods for testing the surface hardness of dental materials, which are: Vickers, Knoop, Brinell, Rockwell, and Shore. Both the Vickers and Knoop hardness tests are based on an indentation of a diamond square or rhomboidal pyramid, respectively. The Brinell test employs a steel ball indenter, which leaves a circular-shaped cross-section indentation. Hardness value is a function of the mean distance across the diagonal axis of the indent for both Vickers and Knoop, and the diameter of the circle for Brinell test. These tests are termed micro-hardness due to the size of the indent, are evaluated under a microscope, and are most commonly used in dental materials. The Brinell hardness number can be multiplied by 1.05 to obtain the Vickers hardness number. The Rockwell test applies a conical diamond indenter or hardened steel ball under different loads. Each combination forms a specific scale which is used for a certain material of a definite hardness. The hardness value here is related to the direct measurement of the indentation's depth. The type of test selected depends on the nature of the material (McCabe and Walls, 2009; O'Brien, 2009). In the Shore test, a durometer is used to test the hardness of rubber and soft plastic. Its scales range between 0-100, and the number increases with decreasing penetration depth (O'Brien, 2009). Most researchers use the Vickers test, but some use the Knoop test for denture bases.

The method of polymerisation influences the hardness of the denture base material. Heat-cured PMMA is harder than cold-cured PMMA at the time of manufacture. This superiority continues after storage in water for different durations of up to six months. This finding belongs to the fact that heat-cured PMMA contains a lower level of free monomer, which acts as a plasticiser (Braun *et al.*, 2003; Mese and Guzel, 2008; Azevedo *et al*., 2005; Lee *et al*., 2002). Light-cured Eclipse specimens have also been compared to heat- and cold-cured PMMA specimens; the Eclipse specimens were found to be the hardest (Ali *et al.*, 2008) due to their high degree of conversion, inherent highly cross-linked hard semi-crystalline structure based on the copolymer of UDMA. In this respect, and as noted earlier, the hardness values of denture base material can be ranked in descending order from light- to heat- and then auto-cured polymerisation.

The polymerisation cycle mainly influences hardness due to the relation between the processing cycle and degree of conversion, namely residual monomer (Kedjarune *et al*., 1999), and in turn hardness. Neppelenbroek *et al*. (2005) tested two heat-cured PMMA of a different curing cycle. The materials showed a superior hardness for the material cured at 73°C followed by boiling, rather than that cured at boiling temperature only. Lee *et al.* (2002) tested auto-polymerising PMMA cured under variable conditions regarding pressure, temperature and curing media for the amount of monomer elution and hardness. They found that a harder surface was related to material with less MMA elusion.

In general, absorbing water has an adverse effect on the hardness of PMMA-based material due to being a plasticiser. Kanie *et al*. (2004b) investigated the effect of storing PMMA in water and air at 37˚C concerning Knoop hardness. They found that specimens stored in water showed lower hardness values than those stored in air, because increasing water content causes a softening of the surface. However, this effect depends on additional accompanying effects, such as polishing technique. Braun *et al.* (2003) conducted a study to show the effects of polishing and method of polymerisation on hardness. In this study, heat- and cold-cured PMMA specimens chemically polished with hot MMA at 75°C, and stored in water for up to 32 days, exhibited a continuous increase in hardness. On the other hand, the mechanically polished specimens exhibited a continuous decrease in hardness of the heat-cured PMMA samples, and an increase in the cold-cured PMMA hardness after storage. This can be explained by the high levels of remaining monomer which chemical polishing or curing can create, thus increasing hardness after leaching of monomer in water; conversely, the low levels of free monomer in heat-cured PMMA due to mechanical polishing results in a reduction in hardness after water storage due to the plasticising effect of the water. From all previous studies, it was clear that two processes happen simultaneously: water absorption, and the leaching of free monomer or other plasticisers. The amount of monomer or plasticiser governs the effect of the water. If there were small amounts of plasticiser and free monomer, the softening effect of water may well be profound and vice versa. In addition the effect of monomer for plasticization was higher than that for water.

The temperature of water correlates adversely with hardness (Devlin and Kaushik (2005). In this study, the authors investigated the effect of thermal cycling using alkaline peroxide at 100°C for 30 cycles on Vickers hardness, and they found a reduction in hardness. Therefore, the softening effect could be related to other factors, such as the effect of water temperature (100°C) or the chemical effect of alkaline peroxide used in this study. High temperature could act as a modifying agent by maximising water sorption, causing a weakening of the intermolecular bonds, leading to a reduction in hardness. Therefore, softening occurred as a result of the indirect effect of heat by increasing water sorption (Assuncao *et al*., 2010).

Chemical cleansers have variable effects on the surface hardness, depending on the type of cleanser and the temperature used for the cleanser. In some research, hardness reduces at a temperature of 50°C (Durkan *et al*., 2013), or even at room temperature regardless of the type of cleanser (Neppelenbroek *et al.,* 2005). In other research, there was no change in hardness (Machado *et al*., 2009; Nakahara *et al.* 2013), in comparison with non-exposed samples (Silva *et al*., 2008; Al-Dwairi *et al*., 2012), except for one disinfectant (propolis), which was found to accumulate on the surface and increase hardness (Silva *et al*., 2008). These studies reveal that there is no rule for the effect of chemical cleanser on surface hardness, unless there is an individual comparison between each denture base material in terms of chemistry, cleanser chemistry, degree of temperature, concentration of cleanser, number of cycles, time interval, water immersion period, and other accompanying effects.

With light-cured polymers, the hardness of the top after polymerisation is different from that of the bottom because of the way in which different light intensity reaches the bottom and is absorbed across the thickness of the specimen (Pilo *et al*., 1999). This finding is in agreement with Ali *et al.* (2008), who tested the hardness of the top and bottom of Eclipse resin polymerised at different curing times using a six halogen lamp curing machine, at a temperature of 129˚C. They found that samples polymerised for less than 10 min revealed a significant difference between top and bottom hardness, while no significant difference was found between them at more than 10 min polymerisation (Alpoz *et al*., 2008; Leprince *et al*., 2013).

From the published literature, it was found that the specimens used for testing hardness do not depend on a definite system for dimensions. ISO 20795-1:2013 gives standard specimen dimensions for polishability as 65*40*5 mm. However, polishability does not mean hardness, even though the two are related. The specimens used in the literature are of variable dimensions, and shape, as shown in Table 2.9. Sometimes the same specimens are used for other tests such as for colour and roughness (Durkan *et al*., 2013; Regis *et al*., 2009; Senna *et al*., 2011). In addition, most research has used the remnants of flexural test samples, after applying a 3-point bend test, to test hardness (Vuorinen *et al*., 2008; Kanie *et al*., 2004b).

Specimen dimensions (mm)	Specimen shape	References
65*40*5	Rectangular	Polishability test in ISO 20795-1:2013
65*10*2.5	Rectangular	Ali et al. (2008), Farina *et al*. (2012)
12*12*3	Square	Machado *et al*. (2009)
20*20*2.5	Square	Al-Dwairi *et al*. (2012)
38*38*1.32	Square	Al-Mulla *et al*. (1988)
20*3	Disc (same for colour	Durkan *et al*. (2013)
14*4	Disc (same for colour)	Regis *et al*. (2009)
30*5	Disc (same for roughness)	Senna *et al*. (2011)
13*8	Disc	Neppelenbroek et al. (2005), Sharma *et al*. (2014)
50*30*20	Rectangular	Fujii *et al*. (2002)

Table 2.9 Dimensions of hardness test specimen (specimen's dimensions refer to length, width and thickness or diameter and thickness respectively)

2.6.5 Roughness testing

The property of roughness is the degree of surface discrepancy of a material. It is most often measured using a contact stylus profilometer, which consists of a sharp tip attached to the end of a long arm. This tip traces along a definite distance of the surface of the material and records the vertical movements (Van Noort, 2013). Profilometry is a technique which yields numerical data or a quantitative evaluation of the surface. Many parameters used to measure roughness, and by far the only reported roughness parameter for denture bases is Ra. Ra represents the difference between the peaks and valleys compared with the midline of the surface of the material (Fernandes *et al.*, 2013). The Ra value can be defined as the arithmetic average of the surface profile deviation (Van Noort, 2013), and a small deviation indicates a smooth surface. The limitation of this parameter is that it measures average and gives no information about real deviation; however, it is simple and quick (Field *et al.*, 2012).

The main purpose of polishing the denture base is to produce a significantly smooth surface (Gungor *et al.*, 2014, Rao *et al.*, 2015). Any roughness greater than 0.2µm is problematic as it causes plaque accumulation and the adhesion of *Candida albicans* and other microbes; this potentially leads to periodontal disease and stomatitis (Bollenl *et al.*, 1997). A rough surface can also provide a shelter to protect microorganisms from shear forces and cleaning measures, allowing them to reinvade the surface and form colonies, and again this can result in denture stomatitis (Al-Dwairi *et al.*, 2012). For this reason, roughness as 0.2µm is called the roughness threshold (Bollenl *et al.*, 1997), and it has been reported that all denture base materials had a roughness higher than the threshold before polishing (Zissis *et al.*, 2000). It is worth pointing out that this effect of roughness on the adhesion of plaque and microbes is greater when measured *in vitro* than *in vivo* due to the washing effect of saliva (Radford *et al.*, 1998; Nevzatoğlu *et al.*, 2007).

Denture polishing is of two types, either mechanical or chemical, and its effect depends on the type (Bollenl *et al.*, 1997, Gungor *et al.*, 2014). Mechanical polishing is the more conventional polishing which uses the lathe technique (Gungor *et al.*, 2014), and increases smoothness by about 20 times (Abuzar *et al*., 2010). Chemical polishing uses hot MMA at 75˚C for polishing by immersion for 10 s (Rahal et al., 2004; Al-Kheraif, 2014; Al-Rifaiy MQ, 2010). According to Al-Kheraif, mechanical polishing of both heat-cured PMMA and UDMA-based light-cured denture bases with fine size abrasive particles produced a smooth surface. However, chemical polishing produced a rough surface (>0.2µm), regardless of the type of polymer used. This result could be due to the fact that the hot MMA molecules used during chemical polishing, roughened the surface, or may has dissolved some of the surface ingredients to leave an irregular surface texture. In addition, hot monomer dissolves tiny scratches and leaves large ones, while the fine abrasive particles of the mechanical method smooth large scratches leaving tiny ones (Al-Kheraif, 2014). This concept was previously confirmed qualitatively by scanning electronic microscopy (SEM) of the surface of heat- and cold- cured specimens polished using the chemical method. The SEM showed a smooth and wavy surface of specimens which had been chemically polished (Braun *et al.*, 2003).

The findings on mechanical polishing are variable according to different modalities, because polishing with abrasives depends on material composition, abrasive particle size and structure, and application technique (O'Brien, 2002). Mechanical polishing using pumice is more effective than a chairside silicone polishing kit (Gungor *et al*., 2014), but less effective than polishing with paste containing aluminium oxide. Nevertheless, pumice polishing was well within the threshold (0.2µm) (Rao *et al*., 2015).

Several factors which may influence initial roughness values before denture use include material composition and method of polymerisation, homogeneity, processing porosity, moulding procedure, and polishing programme. First, roughness is material dependent (Bollenl *et al*., 1997). It has been stated that Eclipse has better surface characteristics than heat-cured PMMA dentures after polishing with various types of mechanical and chemical polishing (Al-Kheraif, 2014). Gungor *et al*. (2014) also found no significant difference between different regimes before and after the polishing of heat- and cold-cured PMMA. Heat-cured PMMA dentures exhibited a smooth and dense surface via SEM (Ogle *et al*., 1986). Second, the method of moulding also has an impact on the roughness, so that material moulded against a glass slab has a lower roughness than material moulded against plaster (Nevzatoğlu *et al*., 2007; Zissis *et al*., 2000).

Other factors which might influence denture base roughness after use are cleaning, exposure to acid; alkaline; abrasive food; cigarettes…etc. These factors can affect surface roughness by, for instance, the deposit of cigarette smoke (Mahross *et al*., 2015). Another factor is degradation by solvents, such as exposure to an acidic dietary product which damages the material's surface integrity (Constantinescu *et al*., 2007). Pure alcohol and some alcohol products represent other solvents. PMMA denture bases have shown an irregular surface caused by the protrusion of PMMA molecules, shown on a SEM image, after immersion in the aforementioned products for 30 months (Vlissidis and Prombonas, 1997). Mechanical cleaning using a hard brush may increase roughness by scratching the surface (Harrison *et al.*, 2004), while chemical cleaning may dissolve some ingredients and degrade the surface, thus disturbing its texture (Peracini *et al.*, 2010). Regarding water, little research has been found regarding the effect of water storage on the roughness of denture bases.

Disinfection and denture cleaning is an important step in keeping dentures clean and reducing cross-contamination. Irrespective of whether mechanical or chemical procedures were followed, cleaning and disinfection influence the roughness of the material. An example of mechanical means is microwave and ultrasonic cleaners, which increases the roughness of mechanically polished samples and decreased it for chemically polished samples (Sartori *et al.,* 2006; Bollenl *et al*., 1997). This greater roughness increases as the number of microwave cycles increases (Senna *et al*., 2011). However, it is not significant (Hashiguchi *et al.*, 2009), and roughness was still below the roughness threshold (Braun *et al.,* 2003). Chemical disinfection and cleaning has a variable effect on roughness, either increasing it, decreasing it, or having no effect, such as using sodium hypochlorite, glutaraldehyde, or chlorhexidine gluconate (Lima *et al*., 2006; Da Silva *et al*., 2008; De Rezende Pinto *et al*., 2010; Peracini *et al*., 2010; Durkan *et al*., 2013; Fernandes *et al*., 2013). For instance, chlorine solution and sodium perborate did not change the roughness of specimens with either polishing method (Sartori *et al.*, 2006; Machado *et al.*, 2009). Briefly, previous studies have reported that both mechanical and chemical disinfecting and cleaning procedures influence the roughness of the material.

The effect of the chemical cleansers and disinfectants on denture base roughness has been determined with respect to initial roughness values, material chemical composition (Machado *et al.*, 2011). It is also determined by the type of active agent in the cleanser and its concentration, and length of immersion, and temperature (Lima *et al.*, 2006; Da Silva *et al.*, 2008; De Rezende Pinto *et al.*, 2010; Peracini *et al.*, 2010; Durkan *et al.*, 2013; Fernandes *et al.*, 2013; Porwal *et al.*, 2017). Roughness may be increased, which is the most common effect due to the dissolution of the surface, such as by sodium perborate, sodium hypochlorite, or alkaline peroxide, or decreased due to the wearing of peaks, such as by chlorhexidine (Da Silva *et al.*, 2008). Alternatively, it may be unaffected, for instance, by the photolysis of H_2O_2 (Nakahara *et al.*, 2013). Interestingly, these cleansers, in some research, changed the roughness so that it considerably exceeded the threshold (Al-Dwairi *et al.*, 2012), while in other research only a minimal effect was produced with no clinical significance (Da Silva *et al.*, 2008) because of the interactions between factors. Therefore, the effect of cleansers on roughness is multifactorial and chaotic.

Roughness also affects the colour of the material (Sepúlveda-Navarro *et al.*, 2011) due to its adverse effects in terms of retaining stain and interfering with stain removal, since surface irregularities obstacle the action of the chemical cleanser or mechanical brushing (Harrison *et al.*, 2004). Another reason is because of the effect of surface topography on the lightness parameter of the colour (*L* values), since surface irregularities scatter light in different directions, that is, the rougher the surface, the darker the colour, and the smoother the surface, the lighter the colour (Briones *et al.*, 2006).

In regard to specimen dimensions used for roughness testing, many different specimen dimensions and shapes have been used when testing various materials, as shown in Table 2.10. However, all studies employed the same device (a profilometer). Therefore, any specimen size suitable for use with this device can be used.

Specimen dimensions (mm)	Specimen shape	References
12*12*2	Square	Machado *et al.* (2011)
12*12*3	Square (same for hardness)	Machado *et al.* (2009)
20*20*2.5	Square (same for hardness)	Al-Dwairi *et al.* (2012)
30*5	Disc (same for hardness)	Senna *et al.* (2011)
15*4	Disc (same for colour)	Baig *et al.* (2011), Fernandes *et al.* (2013)
20*2	Disc	Harrison *et al.* (2004)
20*3	Disc (same for hardness and colour)	Durkan *et al.* (2013)
75*22*4	Rectangular	Abuzar *et al.* (2010)
30*15*3	Rectangular	Al-Kheraif (2014)
65*10*3.3	Rectangular (used later in a flexural strength test)	Regis *et al.* (2009)

Table 2.10 Dimensions of roughness test specimens (specimen's dimensions refer to length, width and thickness or diameter and thickness respectively)

2.6.6 Colour stability testing

Colour matching of the denture base with that of oral soft tissues is an important aesthetic requirement (Ferracane, 1995). The aesthetic appearance of dental restoration is related to colour, translucency, gloss, and fluorescence. These factors are influenced by a light source (illuminant), inherent optical parameters in the object (modifier) which interact with the light source, and lastly, an observer's capacity to receive the modified light. The characteristics of the lighting source are important in the evaluation of colour since intensity distribution, or spectra in regard to wavelength, recognises the light spectrum available and its interaction with the object. Daylight is usually preferred for colour matching because it is white and close to natural light. The object interacts with light either by transmission or reflection, and absorption accompanies both. The object presents a colour from a reflected spectrum and absorbs all others (O'Brien, 2009). The observer could be a human eye or a device, such as colorimeter and spectrophotometer (O'Brien, 2009). Translucent material gains the colour of the spectra transmitted through it, and translucency decreases and opacity increases as scattering increases. An opacifier, such as titanium dioxide or fillers in composite, act as scattering centres. The amount of light scattering depends on the size, shape and number of scattering centres, and the refractive index between them and the matrix. Gloss results from the equality of an angle formed by incident light with that formed by reflected light. A lustrous appearance is related to smooth surfaces, which in turn increase the intensity of reflected light and reduce the effect of colour differences (O'Brien, 2009).

Generally, there are two main methods of colour evaluation. The first method is visual, which is subjective called Munsell colour system). Human perception is complex, and may not be reliable. It differs with ambient lighting or illumination and from time to time as it is associated with inherent inconsistency in colour perception (Johnston and Kao, 1989). The human eye may be fatigued by constantly looking at the same stimulus colour (O'Brien, 2009). The second method involves using analytical instruments, such as colorimetry, spectrophotometry, or computer analysis of a digital image (Hersek *et al.*, 1999; Joiner, 2004; Hong *et al.*, 2009; Sepúlveda-Navarro *et al.*, 2011; Fernandes *et al.*, 2013; Salloum, 2014). The second type of method is more objective, particularly colorimetry, and so it is more accurate and reproducible as it gives quantitative measures uninfluenced by variations between inspectors (Johnston and Kao, 1989; Horn *et al.*, 1998). Therefore, it standardises two determinants of colour, the illuminant and observer, and avoids bias in colour assessment (Ferracane, 1995). In addition, there are other means of colour matching, such as the projection of photographic slides and shade guide matching as other evaluation methods. Each method has its different merits and limitations (Joiner, 2004). However, in either method, colour measurement is affected by modifier surface roughness (Sepúlveda-Navarro *et al.*, 2011), in addition to modifier composition and thickness (McCabe and Walls, 2009).

Two systems are used to assess colour and colour difference: the Munsell colour system or visual system, and the standard Commission Internationale de L'Eclairage (CIE L*A*B*) colour system or spectrophotometric system (Hersek *et al.*, 1999). The Munsell colour system is described in terms of hue (wavelength), value (brightness or lightness) and Chroma (intensity). Hue enables the colour family (red, blue, green, yellow) to be distinguished, while value indicates the lightness of the colour from 1 to 10 black to white for reflective objects, and black to clear for translucent object, and Chroma describes the degree of colour saturation from 1 to 10, where 10 is saturated (Joiner, 2004). The value of colour relies on the surface finish (roughness) which is related to luminous reflectance, and the nature of the incident light and background (Dhuru, 2005; Van Noort, 2013; McCabe and Walls, 2009). Hue and Chroma are inherent in the material and can be changed by a molecular transformation reaction between components, or by the absorption of extrinsic or intrinsic stains (McCabe and Walls, 2009).

For the CIE L*A*B* colour system, colour is demonstrated in terms of three coordinate values: L, A, and B. "L" represents lightness or luminosity (Goiato *et al.*, 2013a) ranging from 0-100. "A" represents redness to greenness value, and "B" represents yellowness to blueness value. A positive value of "A" or "B" means red or yellow, while a negative means green or blue, respectively. Overall, colour and numerical colour variation can be given using the following expressions (Nakahara *et al.*, 2013):

$\Delta E = ((\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2)^{1/2}$

ΔL, Δa, Δb are the differences obtained in the respective coordinate after application of an effect. The American Dental Association (ADA) recommend the use of this assessment system for colour evaluation (Hong *et al.*, 2009; Purnaveja *et al.*, 1982) as it can be expressed in units and related to visual perception and clinical significance, according to NBS (see Table 2.11) (Joiner, 2004), in addition to testing under standard conditions. NBS value can be found according to the following formula (Standards, 1968):

$\text{NBS unit} = \Delta E * 0.92$

The colour stability of the denture is an important property associated with keeping the same colour of a material under different conditions, such as water storage, thermal cycling, cleaning and exposure to stains (Singh and Aggarwal, 2012; Goiato *et al.*, 2013b; Moon *et al.*, 2014). It is also considered one of the most important clinical characteristics for all dental materials, as this property is a sign of material ageing or damage (Devlin and Kaushik, 2005; Salloum, 2014) and may refer to the degree of serviceability (longevity) and durability of the material (Hong *et al.*, 2009). Some studies have revealed that a colour shift (ΔE) of 1 unit can be perceived by 50% of human assessors (Douglas *et al.*, 2007), but generally they regarded a shift in ΔE of less than 1 is not visually perceptible, ΔE between 1 and 3.3-3.7 is visually perceptible but clinically acceptable, and ΔE of more than 3.3 has a clinically significant difference and is unacceptable (Salloum, 2014; Rosentritt *et al.*, 1998; Hong *et al*. 2009; Johnston and Kao, 1989). Moreover, denture base colour stability is equally as important in aesthetics as that of the artificial teeth shade for most if not all patients (Hersek *et al.*, 1999).

Colour change can occur due to intrinsic or extrinsic changes (Goiato *et al.*, 2013b), attributed to a reaction between ingredients and the subsequent forming of new molecules or their transformation, or the absorption of staining (Van Noort, 2013). Intrinsic changes may occur as a result of exposure to chemicals such as solvents (Ferracane, 2006; Regis *et al.*, 2009), bleaching disinfectant (Peracini *et al.*, 2010; Salloum, 2014), or physical effects, such as by thermal alteration, or thermal cycling, which may degrade material due to repeated shrinkage and expansion (May *et al.*, 1996; Goiato *et al.*, 2013a; Goiato *et al.*, 2013b). Extrinsic changes include the effect of absorbing water (Devlin and Kaushik, 2005) and staining agents (Hersek *et al.*, 1999; Imirzalioglu *et al.*, 2010; Sepúlveda-Navarro *et al.*, 2011). Staining is usually influenced by roughness (Sepúlveda-Navarro *et al.*, 2011). As an example of intrinsic changes, Goiato *et al.* (2013b) added nanoparticle pigments to different denture base materials and applied thermo-cycling by ultraviolet (UV) light. They observed variation in colour stability between different materials, which was associated with the chemical compatibility of pigment constituents and material ingredients.

The majority of materials used in denture prostheses are subjected to water sorption following exposure to oral fluids. Water absorption can influence colour (Van Noort, 2013; Devlin and Kaushik, 2005), as can certain drinks containing colour, such as tea, coffee, and soft drinks. These colours or stains accelerate discolouration and augment ageing and exert the strongest effect on colour stability (Hollis *et al.*, 2015; Singh and Aggarwal, 2012; Imirzalioglu *et al.*, 2010). Staining from these drinks is greatly determined by water uptake, roughness, and porosities (Ferracane, 2006). This was an example of extrinsic stain.

There are different discolouration tendencies between different polymerisation materials. In regard to light-cured resins, earlier versions showed a different affinity for staining in comparison with PMMA, depending on their composition and type of stain (Rutkunas *et al.*, 2010). Triad demonstrated a high susceptibility to tea staining at different temperatures in comparison with no staining in PMMA-based materials (Khan *et al.*, 1987). Triad showed a slight to noticeable discolouration according to NBS after ageing under UV or visible light in humidity at 43˚C. This discolouration was greater than that for heat-cured PMMA, but less than cold-cured PMMA (May *et al.*, 1992). These characteristics are related to Triad being porous, rough (containing large size filler), and experiencing the chemical breakdown of components (Van Noort, 2013) and high water absorption (Al-Mulla *et al*., 1988; Al-Mulla *et al*., 1989).

Another material that is similar chemically to composite is Versyo, which is a light-cured material with no silica filler; it had a stable colour during a 1.5 year observation in an *in vivo* study which was identical to pourable cold-cured PMMA (Gohlke-Wehrbe *et al*., 2012). The newly released Eclipse showed less staining with colourant solutions (strawberry, coffee, tea) with no significant difference between immersion times after 10 days than heat-cured PMMA (Asal *et al*., 2015). In another study, Eclipse showed a quite variable response to staining according to the kind of colourant solution (cola, coffee, grape juice), but no significant difference was found between heat- and cold cured PMMA, although heat-cured PMMA was less stained with the different colourants used (Hollis *et al*., 2015). Also in this study, cola was the most staining colourant of Eclipse compared to coffee and grape juice, and water was the worst cleaner of staining in relation to Polident and Efferdent. Therefore, type of stain alongside type of polymer and polymerisation method determines the tendency to staining or discolouration. Overall, cold-cured resin was the lowest rated regarding discolouration by ageing and staining due to the rough surface, porosity, and high residual monomer indicated for high absorption, in addition to its inherent tendency to discolouration caused by oxidation of remnants of tertiary amines by exposure to light (Dulik, 1979). However, the pourable type showed identical colour changes to light-cured composite in the abovementioned study because it contains a stabiliser or antioxidant (Anusavice *et al*., 2012), and was cured under a higher temperature and pressure, which reduced the possibility of porosity (Keller and Lautenschalger, 1985). Therefore, the relation between heat-cured PMMA and light-cured UDMA-based materials concerning discolouration depends on the composition of each individual material and colourant composition.

Denture cleansers are another cause of the colour change of denture bases, depending on the active agent in the cleanser (Hong *et al*., 2009), concentration, length of immersion time (Fernandes *et al*., 2013; Goiato *et al*., 2013a; Salloum, 2014), chemical composition of denture base (Sepúlveda-Navarro *et al*., 2011), and the method of polymerisation (Fernandes *et al.*, 2013). In addition, colour change may be associated with the texture of the denture base, which affects the light reflectance (Keyf and Güngör, 2003). By comparing Triad disinfection to heat- and cold-cured PMMA for 72 h, Triad had the highest discolouration in response to four disinfectants due to high water sorption (McNeme *et al.*, 1991). Different brands of denture cleansers (Chlorox bleach, Polident, Efferdent, and Kleenite) have variable whitening effects, even if they have the same active cleaning agent (Haghi *et al.*, 2015). This difference might have occurred as a result of different ingredients being present in each cleanser product, which have a different effect on roughness, in addition to the cleaning agent itself (Moon *et al.*, 2014). The Moon study stated that a difference in colour shift may occur with different denture base materials. Similarly, Goiato *et al.* (2013a) found that a difference in polymerisation method, denture base product, disinfectant product, and disinfection time, with no interference or conflict between these factors, can influence the colour change. The study also observed that colour change increases with time, regardless of the brand of acrylic denture base or disinfection procedure, suggesting that colour change caused by cleansers is multifactorial.

Regarding dimensions of specimen used for testing colour, previous studies showed quite variable specimen dimensions in size and shape, as shown in Table 2.12. Accordingly, any specimen size reproducible and fit with the device can be used for testing colour stability.

Critical remarks on colour difference	ΔE NBS units
Trace	0.0-0.5
Slight	0.5-1.5
Noticeable	1.5-3.0
Appreciable	3.0-6.0
Much	6.0-12.0
Very much	+12.0

Table 2.11 The National Bureau of Standards' system to express colour difference (Standards, 1968)

Specimen dimensions (mm)	Specimen shape	References
50*0.5	Disc	BSI (2013)
20*20*2	Square	Salloum (2014)
20*20*3	Square	Singh and Aggarwal (2012)
10*10*2	Square	Hong *et al.* (2009)
20*10*1.5	Rectangular	Hersek *et al.* (1999)
14*4	Disc	Regis *et al.* (2009)
15*4	Disc	Fernandes *et al.* (2013)
20*3	Disc	Sepúlveda-Navarro *et al.* (2011)
22*3	Disc	May *et al.* (1996)
30*3	Disc	Goiato *et al.* (2013a), Goiato *et al.* (2013b)
35*3	Disc	Moon *et al.* (2014)
2.5*2	Disc	Imirzalioglu *et al.* (2010)

Table 2.12 Dimensions of colour test specimen

Chapter 3 Aims and Objectives

3.1 Aims

This study was conducted to establish whether the two new materials, Eclipse (Ec) and Weropress (Ws), are appropriate for use as denture base materials in relation to long lasting performance following characterising them, and what their order is in relation to conventional denture base materials, and whether they can be used as efficient replacements to conventional denture base materials.

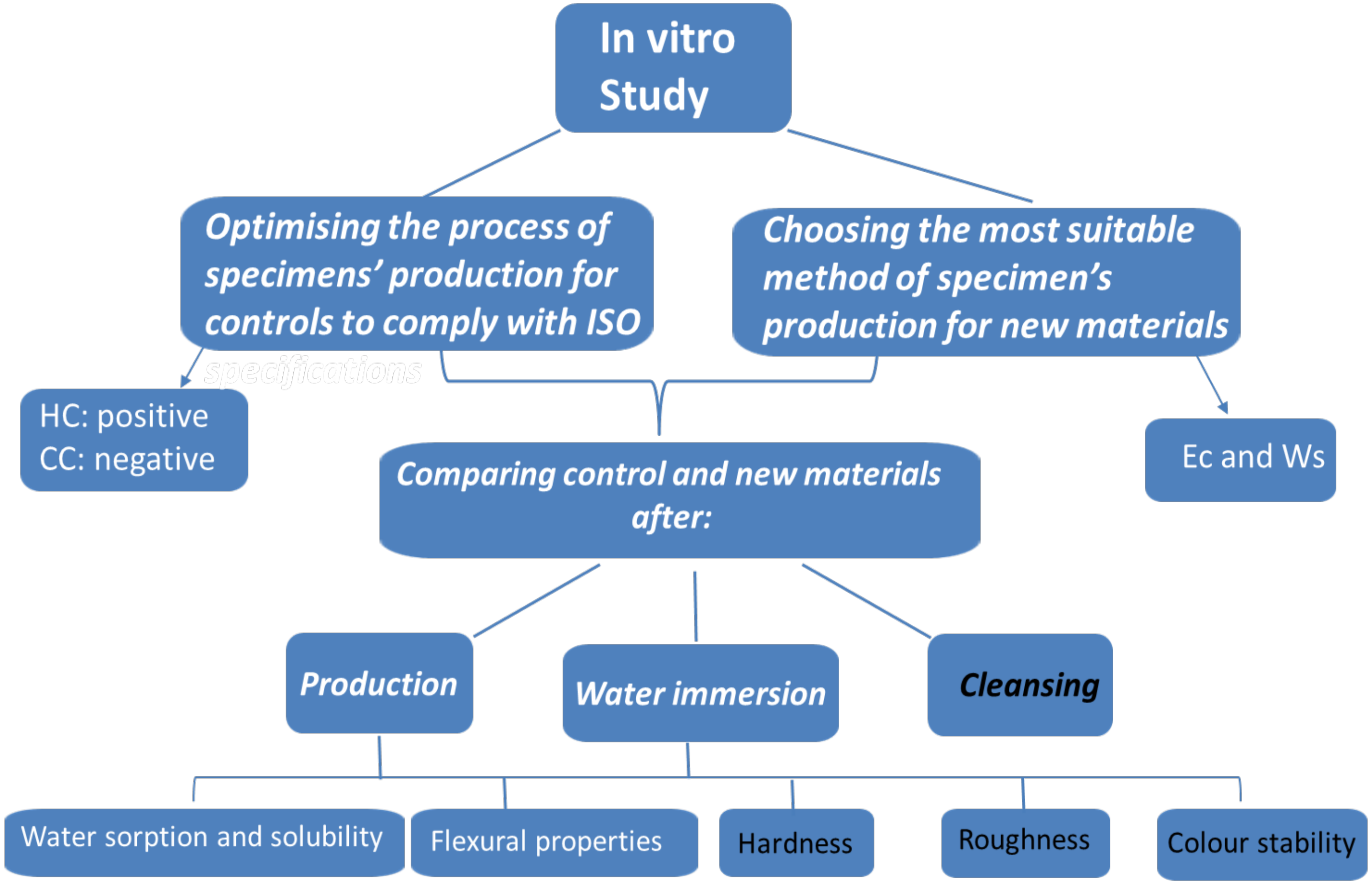
Heat- cured PMMA (HC) (Wintercryl, pink with fibre, John Winter & Co Ltd, UK) and cold-cured PMMA (CC) (Wintercryl, pink with fibre, John Winter & Co Ltd, UK) were used as positive and negative controls for the study, respectively. As heat-cured PMMA was the most commonly used denture base material so it represented a good comparator, while cold-cured PMMA represented a bad comparator as it showed the worst criteria as a denture base material, in addition to its chemical similarity to Ws.

After reviwing the literature, a group of properties were decided to be tested in this project which are: water sorption and solubility, flexural strength and modulus, colour stability, roughness, and hardness. These properties are the most commonly prioritised tests in other research to characterise materials. They link together and suitable for the time available in this project. In addition, sorption and solubility have been prioritised as they have an impact on other properties, such as mechanical properties, hardness and flexural modulus, so they influence the durability of dentures in clinical use. They also influence the likelihood of discolouration, staining, and dimentional stability. They cause leaching of free monomer and other soluble ingredients, and may be related to malodour. Flexural properties are the most relevant intraoral load type (Dhuru, 2005), and most important mechanical property, thery also give an information about denture flexibility. Colour stability is the most important clinical property as it influences aesthetics and is considered as a sign of aging. It was tested also to address the claim of the manufacturers as both materials show high colour stability. Material roughness is associated with colour and aesthetics, and important for oral hygiene and denture stomatitis. Material hardness is important mechanical property which is associated with roughness. It was tested to deal with the claim of the manufacturers as Ws of high polishability. These properties were discussed in detail in the literature review (2.6.2 - 2.6.6).

3.2 Objectives

1. Measuring and comparing the above mentioned properties of the new materials to that of the control materials at the time of manufacture
2. Measuring the effect of exposure to an aqueous environment on these properties after two days, one week, and one, three, and six months' time intervals, and comparing this effect to that of the control materials.
3. Measuring the effect common cleaning procedures have on hardness, roughness and colour stability and comparing this effect to that of the control materials. This was because cleansing was most commonly tested following these three properties according to the literature.

3.3 Design of the study



Chapter 4 Optimising the controls and the new materials

4.1 Introduction

Optimisation or careful development of sample preparation procedures when characterising the properties of new materials against the current clinically approved material is important preliminary step before starting the experiment. The main reason for optimisation was specimens were used for different mechanical and physical lab testing rather than dentures with consequent difference in the thickness and geometry. Using specimens can be considered as a limitation as for any *in vitro* study, but it is a strong point due to following standard dimensions and procedure.

The other reason for optimisation was the difference in consistency and route of production, so the aim and procedure of optimisation were different between different materials, whether control or new materials, whether heat cured, cold cured or light cured, and whether compression or pourable material.

Control materials are representative of a certain group of materials and should provide consistent results for that group. Accordingly, the control materials in this study, shown in Table 4.1, needed to be optimised to produce the best possible specimens which meet the international standard organisation requirements regarding denture base polymers' properties (BSI, 2013). This optimisation was necessary to produce a valid comparison with the investigated new materials.

The specimens were optimised in terms of appearance and aesthetics. Optimising the specimens in terms of appearance included inspecting specimens visually by naked eye for being free from porosity, as the occurrence of porosities is associated with improper polymerisation of the material and influences aesthetics (Van Noort, 2013; Johnson *et al*., 2015). According to the tests undertaken in this project, the flexural test was the only test which evaluates strength, and its specimen dimensions were the biggest (65*10*3.3 mm) according to ISO 20795-1:2013 for denture bases (BSI, 2013). Therefore, these specimens were used to optimise materials in terms of strength. Flexural strength of the specimens was improved to comply with the minimal requirements of ISO 20795-1:2013 for type 1, class I, and type 2, class I, denture bases, respectively. These specimens were also used to evaluate porosities.

Prior to testing the new materials, if the manufacturer's instructions involved more than one method for handling, the most suitable and easiest method of production has been selected in terms of time required, feasibility, and the capability to produce sound specimens as much as possible. It was possible to optimise the Ws method of production but not the Ec, because there was only one handling option for Ec.

4.2 Aims and objectives

The aim of the studies undertaken in this chapter was to optimise the specimens for the control materials and the method of production for new materials. In terms of control materials, optimisation was undertaken to obtain the best possible specimens and which meet ISO requirements (BSI, 2013). This optimisation was achieved through the following steps:

1. Achieve the best aesthetics by reducing porosities. This can be achieved by changing the determinant parameters and inspecting specimens visually.
2. Achieve optimal flexural strength by changing same parameters.

In terms of new tested materials, the process was performed to find the most applicable, reproducible, and time saving method of producing sound specimens, according to the manufacturer's instructions.

Product	Activation mode	Manufacturer
Heat-cured resin (control)(HC)	Heat	Wintercryl, John Winter & Co Ltd, UK
Cold-cured resin (control)(CC)	Chemical	Wintercryl, John Winter & Co Ltd, UK
Eclipse resin (Ec)	Visible Light	Trubyte, Dentsply International, USA
Weropress (Ws)	Chemical	MerzDental, Germany

Table 4.1 Materials used in this study

4.3 Optimisation of the positive control

4.3.1 Materials and methods

Mould production for flexural test specimens

Moulds were made from silicone. Four metal bars with dimensions 70*10*5-5.5 mm were prepared a little bigger than the dimensions required of ISO 20795-1:2013 for denture bases to provide excess material for polishing (BSI, 2013). Putty silicone impression material (C & J. Chaperlin & Jacobs Ltd, Surrey) was mixed following the manufacturer's instructions and were used to fill one half of a metal denture flask whose dimensions 120 mm width, 85 mm length, 60 mm height. These bars were arranged horizontally, about 10 mm apart, and pressed on the silicone impression surface up to 5 mm depth. The silicone surface was flattened to the level of the flask using a flat glass slab, making the specimens level with the top of the flask. After the silicone had set about 5-7 min, the metal bars were removed, leaving the silicone mould, as in Figure 4.1A.

Then, a wax replica was made by melting pink modelling wax sheets (PremEco Line, MerzDental, Germany) on a heater (Stuart, UK) inside a beaker. The melted wax was poured into the silicone mould to produce, after hardening, wax bars, as in Figure 4.1B. Wax bars were softened and adjusted to dimensions 67*10*5-5.5 mm using a hot plate, as in Figure 4.1C.

After this, a stone mould was produced using the wax bars. Stone moulds were required because stone is more resistant to high temperature and the pressure which would be applied later during the packing and curing stages. The inside of the denture processing flask was coated with a thin layer of Vaseline (petroleum jelly, Unilever, India) to facilitate the separation of stone from the flask. The dental stone (Formula Saint-Gobain, UK) was mixed with tap water following the manufacturer's instructions at a ratio of 300 g/90 ml, and a fresh mixture was used to fill the lower half of the metal denture flask. Four wax bars were then embedded horizontally into the surface of the stone mixture to half their depth, and aligned in parallel in the same way as the metal bars in the silicone mould. The excess stone was then trimmed using a wax knife. The stone was contoured and smoothed under running water before setting completely. Complete set took 45 min from the start of mixing, after which the surface of the stone was coated with a thin layer of Vaseline to facilitate the separation of the two flask halves. The upper half of a denture flask was positioned on top of the lower half and then another mixture of stone was made and poured into the upper half of flask under mechanical vibration (Bios.Ges. H. Bitter, Osnabruck), until it was full and the lid of the flask was gently seated; the stone was then permitted to harden for 45 min. After that, a boiling-out machine (Wax dispenser, Electrothermal, UK), was heated for 1 h, and the flasks were placed inside it and left there for 9 min under a flush of hot water. The flasks were then removed from the tank, opened by loosening the join gently with a plaster knife, and replaced into the boiling-out machine again. The flask halves were flushed with hot water to clean the moulds from any wax remnants. An example of a stone mould is shown in Figure 4.2. The procedure for stone mould production was almost the same as for the mould preparation during denture processing, with some modifications to suit the number and geometry of specimens; for example, no levelling is performed with dentures (Anusavice *et al*., 2012; Johnson *et al*., 2015; Ferracane, 1995; Craig *et al*., 2004; Dhuru, 2005).

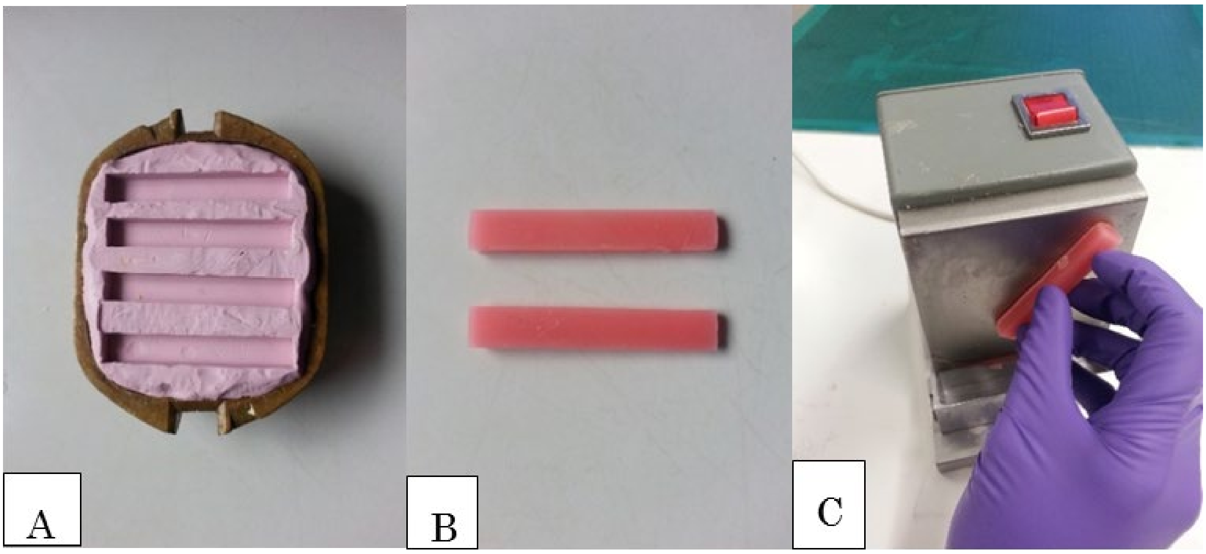


Figure 4.1 Flexural specimen mould production (A) silicone mould, (B) wax bars, (C) adjusting the wax bar on the hot plate

Figure 4.2 Stone mould for HC and CC specimens

Specimens’ optimisation in terms of appearance

The process of sample fabrication was similar to the packing of dentures, with some modifications (Johnson *et al.*, 2015; Dhuru, 2005) to accommodate the specimen.

A series of experiments were undertaken until good specimens were obtained, starting with a batch of four flasks of HC specimens, four specimens in each flask to be 16 specimens in total. Stone moulds which had been previously produced were coated with a thin layer of Vaseline as a separating medium to prevent the adherence of acrylic to stone. Then, HC powder and liquid were mixed manually in a clean ceramic crucible with a lid at a ratio of 2:1 g /ml, 32/16 g/ml for each of the two flasks, following the mixing ratio used by technicians in a prosthetic laboratory at the Dental Hospital of Newcastle NHS Hospitals Trust and Dental School at Newcastle University. Mixing was performed by adding liquid to powder gradually and mixing slowly and thoroughly with a clean wax knife, until all the powder particles were fully wet. The crucibles were then covered with a plastic lid to prevent evaporation of the monomer. Dough time was about 5 min (at 23˚C room temperature) following the manufacturer’s instructions.

The dough was then kneaded by hand, manipulated to form a disc, and applied to the top of one half of the stone mould; the flasks were closed and pressurised to 4 kg/cm^2 one by one, to permit uniform flow of the material using a hydraulic denture flask press (Silfradent, UK). The pressure allows the excess material to be extruded as a flash, which means that the mixture quantity is enough to fill the flask, according to the manufacturer. After 5 min at this pressure, the flask was removed and left on the bench while the same procedure was followed with the other flask. Then, both flasks were transferred to a two-flask spring clamp, which was immediately tightened firmly by hand so that the pressure of flask assembly was maintained. The same procedure was repeated with the other two flasks. Curing was done using a dry heat oven (DO) (Ditton Curer, UK) to polymerise the specimens, as shown in Figure 4.3A. The oven timer was set at 70°C for 7 h, followed by boiling at 95°C for 2 h of overnight curing, according to the text book recommended cycle (Johnson *et al.*, 2015); this same cycle is used by technicians in the dental laboratories of Newcastle

University. At the end of the polymerisation cycle, the flasks were left for bench cooling at room temperature before deflasking, rather than being cooled with tap water, to avoid warpage (Anusavice *et al*., 2012). Lastly, the clamps were released, the flasks were opened, and the samples were removed and inspected visually for porosities. Where porosity was not visible, the specimens were finished and polished with a simple conventional method using a tungsten carbide bur (Dentorium, USA) and low speed hand piece (NSK Kakanishi Inc., Japan), followed by sand paper of 320-grit (3M, USA) (Gungor *et al*., 2014), to trim the excess material and clear the surface for inspection. The specimens were then checked again for porosity by visual inspection.

As the specimens were all porous, this required changes to parameters and adopting further experiments. A summary of these experiments can be seen in Table 4.2 (set 1), and they followed the same steps as above, except for the parameters determined in the table. The same number of flasks was used for all the above experiments, as it has been proposed that curing quality depends on the number of flasks in a DO (Nejatian *et al*, 2015).

Regarding experiment 3, set 1, new stone moulds were required. Therefore, wax bars were reduced to 3-3.5 mm thickness using hot plate. These new wax bars were used for the fabrication of a stone cast, with four specimens for each flask, similar to the procedure mentioned above.

According to experiment 4, set 1, the trial closure polythene sheet was applied to the material before initial closure and 3 kg/cm^2 pressure was applied to the flasks initially. Then, following the extrusion of flash material, the flasks were re-opened, and the polythene sheet and flash were removed with a wax knife. After this, the mould sections were reassembled, and finally brought incrementally to approximately 4 kg/cm^2.

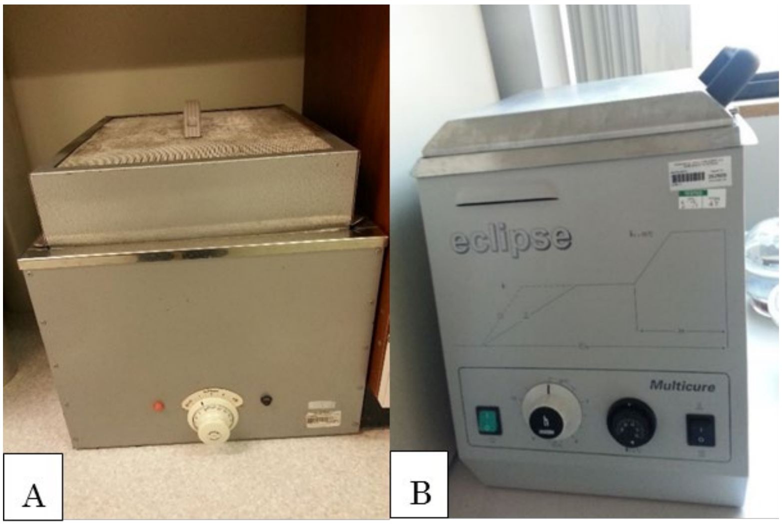


Figure 4.3 Curing devices (A) Dry heat oven, (B) Water bath

Exp. No. / **Parameters**	**Baseline** **Exp No. 1**	**Pressure application mode and mixing ratio** **Exp No. 2**	**Different Thickness** **Exp No. 3**	**Trial closure** **Exp No. 4**	**Material volume in each clamp** **Exp No. 5**
Mixing ratio	2:1	2.3:1 (manufacturer ratio)	2.3:1	2.3:1	2:1 to reduce possibility of granular porosity
Dough time	5 min (manufacturer)	5 min (manufacturer)	5 min (manufacturer)	7 min (manufacturer)	7 min (manufacturer)
Pressure application	Flasks were pressurised one by one	2 flasks were pressurised one by one and 2 flasks were pressurised together	Each set of 2 flasks of different specimen thickness was pressurised together	Each set of 2 flasks was pressurised together; 2 of them with trial closure and the other 2	Each set of 2 flasks with the same specimen thickness was pressurised together with trial closure

				with no trial closure	
Sample thickness	5-5.5 mm	5-5.5 mm	2 flasks with 3-3.5 mm thickness and 2 flasks with 5-5.5 mm thickness because specimen thickness influence porosity (Wolfaardt *et al.*, 1986, Singh *et al.*, 2013; Pero *et al.*, 2011; Abood LN, 2007; Pero *et al.*, 2008; Yannikakis *et al.*, 2002; Jerolimov *et al.*,1989)	5-5.5 mm	2 flasks with 3-3.5 mm thickness and 2 flasks 5-5.5 mm thickness
Result	All specimens were porous	The result has improved but the same number of	The result has improved. There was no difference	The result was highly improved. For	The result was highly improved. The clamp with low volume

		porous specimens was obtained in two methods, although fewer than in the baseline experiment results	in appearance between two thicknesses, but each individual specimen was less porous in general than the previous experiments	trial flasks, all specimens had little granular porosity. For non-trial flasks, specimens were highly porous (granular and contraction or gaseous porosities)	material has produced 7/8 sound specimens, while the other clamp produced 2/8 sound specimens but still have granular porosity
Conclusion	Further experiments were needed with further changes to conditions	Method of applying pressure did not cause a clear difference in results. However, pressurising flasks together and transferring them immediately to the clamp, and	As there was no effect of thickness on porosity in this experiment, thin specimens were used for subsequent experiments, following the	Trial closure is a necessary step and was used following this point	A clamp with low volume of material (thin specimens) was used for the following experiments

		using the manufacturer's mixing ratio of 2.3:1 reduced porosities, and was also used for the next experiment	standard dimensions of ISO		

Table 4.2 Optimisation experiments for HC specimens, set 1

In the light of the results and conclusions of previous experiments, another set of experiments was tried with a large number of specimens. The criteria followed were: thin specimens 3-3.5 mm thickness, following the ISO 20795-1:2013 (BSI, 2013); 2.3:1 mixing ratio; 7 min dough time; trial closure following the manufacturer's instructions; and, each set of two flasks were pressurised together, and clamped together. The second set of experiments (set 2) were performed to obtain sound HC specimens, and are summarised in Table 4.3.

Before starting experiment 5, set 2, a simple mixture of powder and liquid was made as in experiment 4 of set 2, and dough time was measured from the beginning of mixing until the dough stage. The mixture was monitored by frequently checking the consistency, until getting a good workable material appeared with no sticky appearance, which could break cleanly with a snap when jerked apart (Craig *et al.*, 2004). The dough time was 14 min.

Despite the method of making specimens being developed step by step, starting with the manufacturer's instruction, all the samples obtained from the DO up to experiment 5, set 2, were extensively porous after inspection with the naked eye. This observation led to the thinking that the manufacturer's instructions were sub-optimal, and further optimisation was required to produce sound specimens, free of, or with minimum, porosities. At this stage, a small experiment was undertaken to measure the temperature inside the DO using an alcohol thermometer (Brannan, UK) during different cycles. This experiment showed that the temperature was rising continuously over time, and did not follow the oven thermometer. It also showed that the temperature was not homogenous inside different parts of the DO. According to the results of these experiments, and as supported by the results of the latter experiment, the curing machine was substituted with a water bath as an alternative conventional curing machine (McCabe and Walls, 2009).

Exp. No.	**No. of specimens**	**Standard criteria**	**Modified criteria**	**Results**	**Conclusion**
1	40 (10 flasks)	3-3.5 mm thickness, 2.3:1 mixing ratio,7 min dough time, trial closure	Polythene sheets were used and left inside the flask during curing	5 samples failed in addition to having generalised granular porosities	Future experiments should be performed accordingly: no polythene sheet to be left in the flask while curing; powder to be added to the liquid when mixing and not vice versa; pressure to be applied slowly
2	32 (8 flasks) were divided into two groups	3-3.5 mm thickness,7 min dough time, trial closure with polythene sheets	One group used 2.3:1 mixing ratio and the other group used 2:1 ratio; removing polythene sheet while curing,	There were fewer failed specimens in the second group (3/16)	2:1 mixing ratio, adding powder to liquid, and removing polythene sheets while curing should be used in future experiments. In addition, it is

	of 16 specimens		adding powder to liquid during mixing	than in the first group (7/16)	recommended to close the gap between the two halves of some flasks, and increase dough time
3	16 were divided equally into two groups	3-3.5 mm thickness, mixing ratio 2.3:1, trial closure with polythene, no polythene sheets during curing, adding powder to liquid during mixing	Dough time was 12 min. Mixing was by gradual addition of powder and stirring in one group, while in the other group powder was added in one step and stirring started immediately. The gap was closed between the two halves of the flasks	6/16 specimens failed, 3/8 specimens from each group had failed with some granular porosity	The mixing method had no effect on the quality of the specimens, although increasing dough time reduced porosities in general. The next step was changing the separating medium and the specimen dimensions, and reducing the mixing ratio to reduce granular porosities and facilitate mixing

4	16 were divided into two groups	trial closure with polythene, no polythene sheets while curing, adding powder to liquid during mixing, and 12 min dough time	Mould dimensions were 5 mm width*5 mm thickness*50 mm length. One group had Vaseline as the separating medium and another had a cold mould seal. 2:1 mixing ratio	There were fewer failed samples with the cold seal (3/8) than with Vaseline (4/8); granular porosities have reduced	The specimen dimensions had no effect on the occurence of porosities. Increasing dough time, lowering mixing ratio, and using a cold mold seal as a separating medium reduced porosities in general and granular porosities in particular. A cold mould seal will be used for future experiments
5	8 (2 flasks)	3-3.5 mm thickness, trial closure with polythene sheets	A different technician carried out the experiment using a 2.3:1 ratio, dough time 14 min,	The result was specimens full of contraction and granular type porosities	Increasing dough time did not solve the problem of contraction porosities, and increasing the mixing ratio increased granular porosities.

			cold mould seal separating medium		From all previous experiments, it was difficult to find any consistent results or any clear reasons for porosities. Accordingly, the DO was substituted a with a water bath (WB) for the next experiments
6	8 (2 flasks)	3-3.5 mm thickness, trial closure with polythene sheets, mixing ratio of 2:1	Curing in a water bath (Eclipse dental manufacture Ltd, Multicure, UK), shown in Figure 4.3B, overnight at 70°C for 7 h and 95°C for 2 h (same cycle used previously with DO)	Specimens were free of any sign of porosities	The water bath was used for curing in all of the next experiments

7	Two batches, each of 16 specimens	3-3.5 mm thickness, cold mould seal, 14-15 min dough time, WB curing machine shown in 4.3B	One batch mixing ratio was 2:1 and other one was 2.3:1	2/16 porous specimens were obtained from each batch	No difference was found between the two mixing ratios regarding appearance

Table 4.3 Optimisation experiments for HC specimens, set 2

For the two sets of experiments, sound specimens were obtained after using the WB with 3-3.5 mm thick specimens, a cold mould seal as the separating medium, and 14 min dough time. However, the effect of the mixing ratio, which was changed more than once, was unclear. Therefore, the last experiment in set 2 was added later to compare two mixing ratios, which had no difference. Although there were still some porous specimens, they had the least ratio of all the previous experiments. Accordingly, these specimens were considered as having optimal appearance and were used for optimising strength.

Specimen optimisation in terms of strength

Following the optimising of the specimens in terms of appearance, the specimens of last experiment of set 2 were subjected to a flexural test. For the purpose of comparing these specimens with the specimens produced by the DO, two groups were selected from previous experiments which used the two different mixing ratios, and submitted to flexural testing as well. These two groups were experiment 4, set 1 (the trial closure group), and experiment 5, set 1 (the thick specimen group). These two experiments were selected as all the procedures were the same except for the mixing ratio.

The testing procedure started by measuring the thickness and width of each specimen three times using a digital Vernier calliper (Mitutoyo, Japan) and their means were calculated. All groups were subjected to a 3-point bending test using a universal testing machine (Instron 5567, Berks, UK) to assess flexural strengths and flexural moduli.

The testing procedure and calculations followed ISO 20795-1:2013 (BSI, 2013). Each specimen was placed on the supporting heads, which were adjusted to be 50 mm apart. The loading plunger was calibrated to move at a cross head speed of 5 mm/min toward the centre of a specimen, and to stop at 20 mm extension. The specimens were loaded until failure, distortion or breakage. Flexural strength was calculated using the following equation:

$S= 3FL/2bh^2$

Where S is the flexural stress at the mid span, expressed in MPa; F: Maximum load, expressed in N; L: Support span length, expressed in mm; b: Width of the specimen, expressed in mm; h: Thickness of the specimen, expressed in mm.

The following equation was used to calculate flexural modulus:

$M=F_1L^3/4bh^3d$

F_1: a load at a point on the straight line with the maximum slope of load/displacement curve, expressed in N; d: the deflection at point $F_{1,}$ expressed in mm.

The mean and standard deviation were calculated for flexural strength and modulus of each group using Microsoft Excel 2016. The data were analysed using two-way analysis of variance because they were found to be normally distributed, with the Holm-Sidak method used to determine the significant difference between groups (Sigma Plot version 13.0) at a confidence level of 95%.

4.3.2 Results

A comparison regarding specimen appearance revealed highly porous specimens, very easily distinguished with the naked eye, in a group polymerised in the DO, in comparison with sound ones in a group polymerised in the WB, as in Figure 4.4. The ratio of porous specimens for the DO and WB is shown in Table 4.4. Porosities were both granular and gaseous, with granular type mainly occurring at a ratio of 2.3:1.

In terms of flexural properties, Figure 4.5 and Figure 4.6 show typical graphs representing the specimens whose flexural strength and modulus values were the closest to the means. All the graphs consist of a primary distance of the curve which represents the distance of plunger as it moved until it touched the specimen. The curve then rose until it reached maximum force, at which point breakage occurred and the curve dropped.

Force and extension cannot be compared because the specimens were of a different thickness. Typical graphs of the WB were very similar, except that those with a 2.3:1 ratio were a little of higher force, while those for the DO look quite different regarding force and extension. However, in general, all the graphs share similar characteristics.

A comparison between groups of flexural strength and modulus means is shown in Figure 4.7. Bar graphs show very clearly that specimens polymerised by the WB were stronger and of a higher modulus than those by the DO for both ratios. Mann-Whitney and t-test revealed a significant difference between the two machines for both strength and modulus ($P \leq 0.05$). No significant difference was found between the two WB ratios ($P > 0.05$), while there was a significant difference between the two DO ratios in strength only ($P \leq 0.05$).

Experiment group	Frequency of porosity
Curing with WB and mixing at 2.3:1 ratio	2 /16 (gaseous porosities)
Curing with WB and mixing at 2:1 ratio	2 /16 (gaseous porosities)
Curing with DO and mixing at 2.3:1 ratio	8/8 (mainly granular type)
Curing with DO and mixing at 2:1 ratio	8/8 (granular and gaseous porosities)

Table 4.4 Frequency and type of porosity in each group

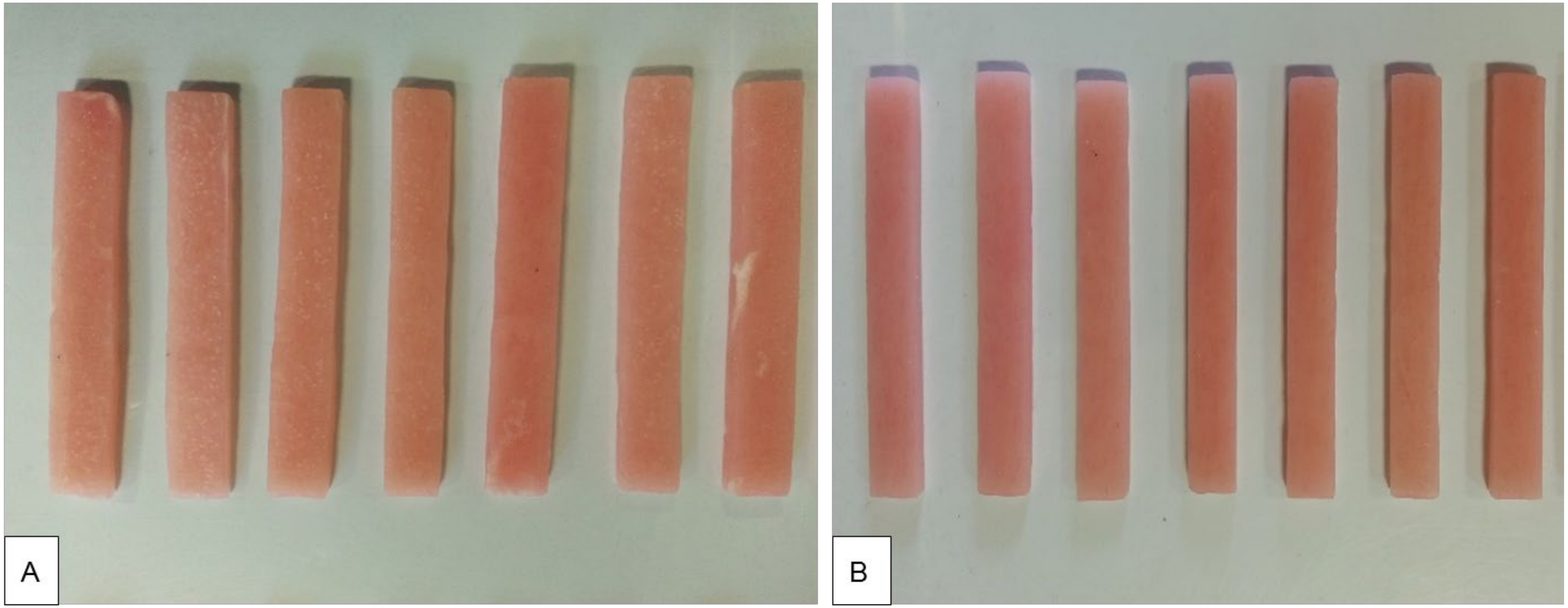


Figure 4.4 Specimens polymerised by different machines: (A) DO-cured, showing porous specimens, (B) WB cured, showing sound specimens

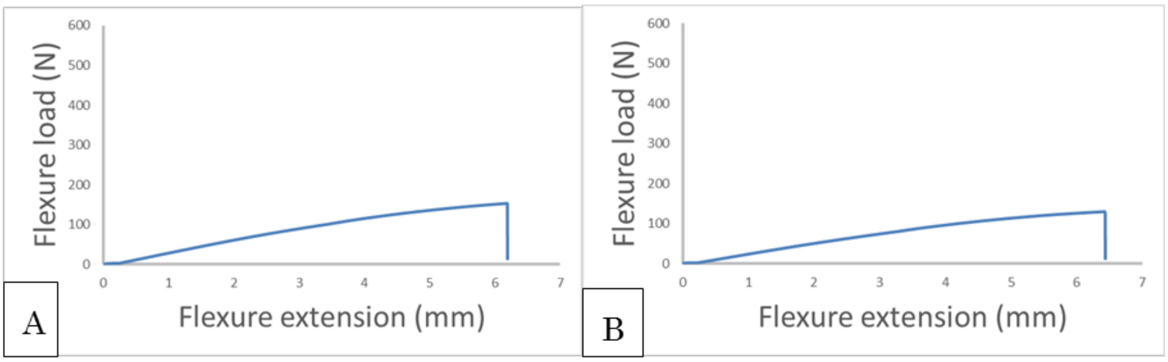


Figure 4.5 Typical bending curve of HC specimens polymerised by WB with a mixing ratio of: (A) 2.3:1 g/ml, (B) 2:1 g/ml

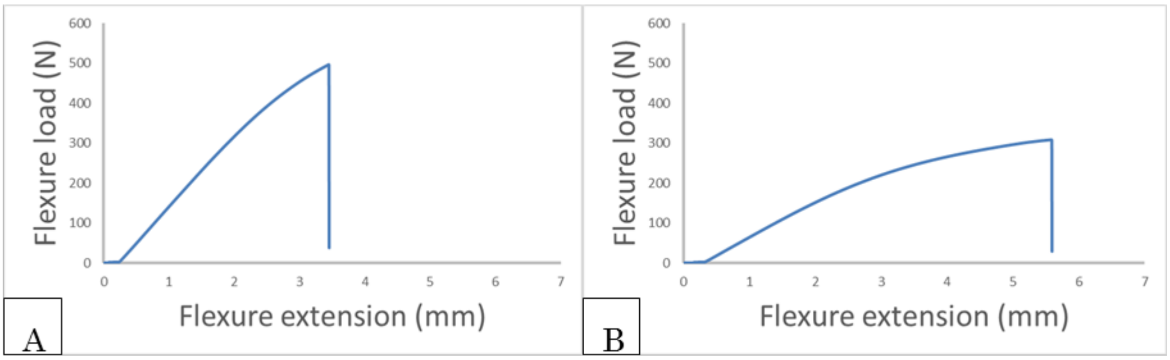


Figure 4.6 Typical bending curve of HC specimens polymerised by DO with a mixing ratio of: (A) 2.3:1 g/ml, (B) 2:1 g/ml

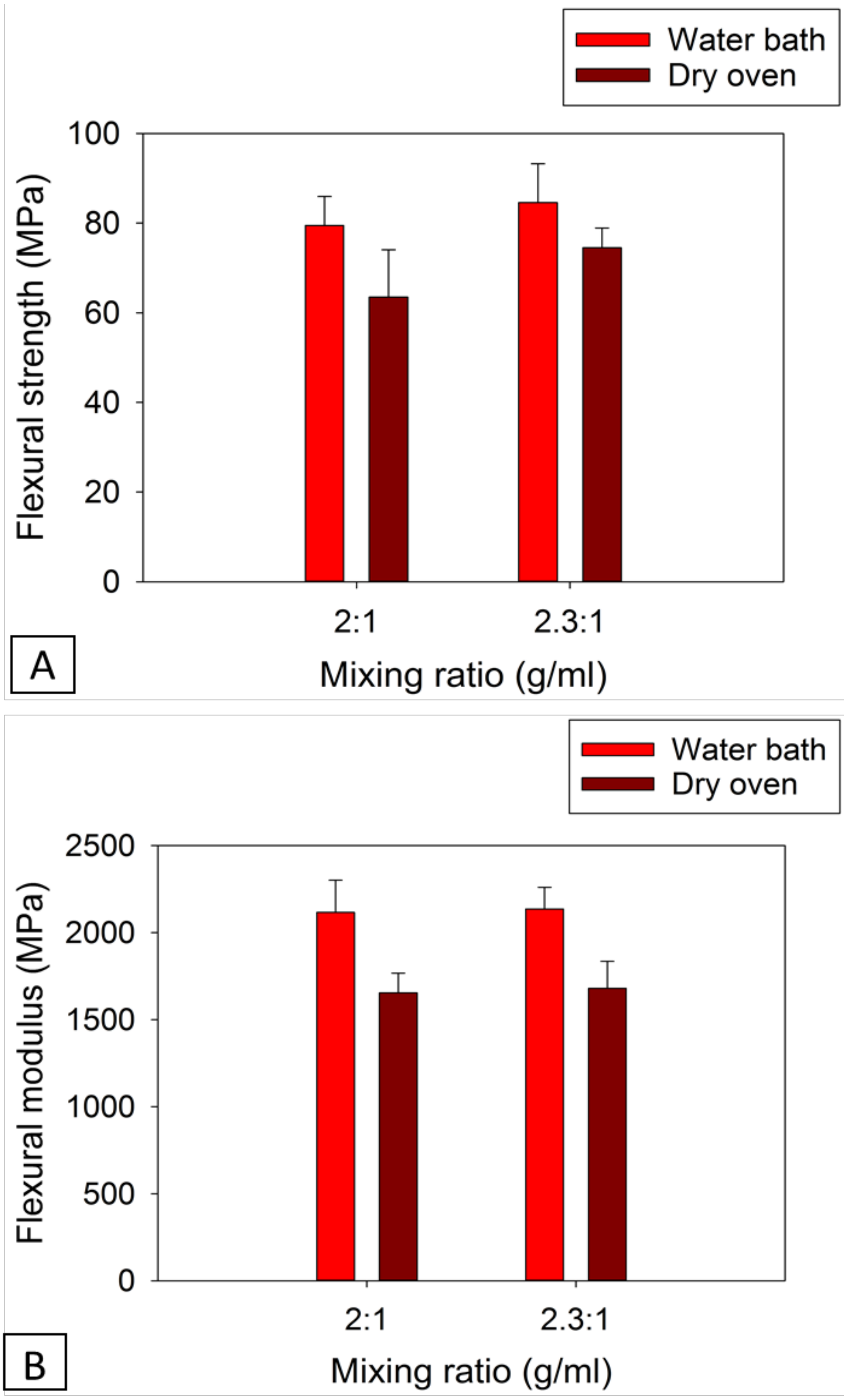


Figure 4.7 A comparison of HC specimens according to: (A) Flexural strength means, (B) Flexural modulus means. Error bars represent standard deviation

4.3.3 Discussion

The positive and negative controls of the study were very important because the properties of the new materials were evaluated according to the control properties. Therefore, the method of manipulating the control materials was optimised to ensure the specimens had properties which satisfied ISO requirements for denture base polymers in terms of aesthetics and strength (BSI, 2013). The aesthetic optimisation includes checking for porosities as an essential requirement for dentures, in addition to the negative influence of porosities on mechanical properties. Flexural properties were also optimised, as they are one of the main properties of conventional materials as bending load is the most relevant load type for denture bases (Dhuru, 2005), and, crucially, are the main mechanical property tested in this study. The optimisation steps necessitated changing all the factors influencing material properties.

The inspection of porosities with the naked eye may be uncommon because of subjectivity and inaccurate results which do not take account of subsurface voids. However, the main purpose of investigating porosity in this study was to obtain specimens free of porosities, rather than to test the type, frequency, and concentration of this porosity. Visual inspection guarantees the production of specimens which are acceptable aesthetically, showing no gross pores or bubbles, as recommended by the Revised American Dental Association Specification no. 12, 1975 (Anusavice *et al*., 2012; Materials and Devices, 1975) and in International Standard Organisation requirements (BSI, 2013). In particular, after using thin specimens with big surface area (bar specimens), which increases the chance of recognising subsurface porosity from both sides and over a wide area. Visual inspection is also an attempt to simulate the prosthetic technician’s inspection of dentures after finishing an appliance (Johnson *et al*., 2015). Even if this method is not efficient, all causative factors were modified following inspection to obtain specimens which were as sound as possible. Despite this, there is still a possibility of producing specimens with porosity, whichever approach is used for evaluation, because of the interaction between multiple causative factors (Wolfaardt *et al*., 1986; Yau *et al*., 2004). However, flexural strength was also tested to comply with standard requirements which confirm there was no significant effect of porosity on physical and mechanical properties.

HC specimens were cured for 7 h at 70ºC and 2 h at 95ºC. The curing cycles proposed by the manufacturer were four options, with three cycles for a WB and one for a DO. This last option was unclear, which is why it was not tried for the two sets of experiments. All cycles recommended for the WB by the manufacturer were deleterious, according to Van Noort (2013), because they were brought to boiling within the first hour before complete polymerisation takes place. Therefore, the aforementioned cycle was followed to produce maximum degree of conversion (McCabe and Walls, 2009; Harrison and Huggett, 1992; Nejatian *et al*, 2015) and reduce the chance for porosity occurrence (Anusavice *et al*., 2012, Van Noort, 2013).

According to the findings of this research, the specimens polymerised by the DO were both very porous, and more frequently porous, than specimens cured by the WB, despite changing many parameters. This observation does not appear to have been previously reported in the literature. The curing means delivering heat is another factor to which porosity can be attributed, as it controls the curing cycle parameters, time and temperature, and the homogeneity of heat spread inside and outside the flask (Canadas *et al*., 2010; Nejatian *et al*., 2015; Harrison and Huggett, 1992). Poor control of the temperature rise inside the flasks within the DO was the reason for porosity. This poor control on temperature rise is perhaps the main reason why this method is scarcely used in dental laboratories (Harrison and Huggett, 1992) and not widely adopted as a means of curing (Anusavice *et al*., 2012). The temperature inside the flask is also extremely influenced by the number of flasks loaded into the DO, according to Nejatian *et al*. (2015). Nejatian found that loading the DO with up to two flasks, after setting the cycle up, allowed the temperature to reach 100ºC within approximately 2.5 h. In contrast, loading five flasks allowed a gradual increase in temperature to 100℃ after more than 4.5 h, while loading ten flasks allowed the temperature to reach a maximum of 80ºC after 4.5 h. On the other hand, the pattern of temperature rise related to the WB specimens showed an identical curve when loading either five or ten flasks, which may be due to the homogenous spread of temperature by water rather than air. For this reason, specimens cured in a WB are free from, or have minimum, porosity (Pero *et al.,* 2008; Singh *et al*., 2013). This concept was supported by Yannikakis *et al.* (2002), who photographed specimens of 3-6 mm thickness under microscope at 100x magnification. In the current study, four flasks were loaded in the set 1 experiments, meaning that the temperature may have arrived at 100 ℃ rapidly, instead of completing a phase of 7 h at 70ºC in the aforementioned cycle. A different number of flasks was used in set 2, but porosity remained, which might be due to the presence of more than one kind of porosity, and more than one reason for it. In contrast, some authors state that the boiling point of monomer inside clamped flasks is elevated to 228ºC, as a function of the pressure rise to 22 atm inside the flasks. Thereby, it reduces the likelihood of reaching the boiling point of the monomer, and subsequently porosity is caused by vaporisation (Yau *et al.*, 2004). However, the flasks in this research were only pressurised to 4 kg/cm^2, and this is not sufficient enough to elevate the boiling point to a level which is far higher; that is, such a temperature cannot be reached by the DO. Canadas *et al.* (2010) contradicted the notion that DO specimens are more likely to be more porous than WB specimens However, this result can be attributed to the differences in curing cycles used. Therefore, the specimens in Canadas's study cured by both machines were equally likely to be porous.

From the results in the current study, the flexural properties of DO specimens are significantly inferior to those of WB specimens, and even lower than the minimal value specified by ISO 20795-1:2013 (BSI, 2013). The abundance of porosity in specimens produced by the DO is an indication of poor flexural properties (Jerolimov *et al.*, 1989). In addition, the low degree of conversion was caused by early maximisation of temperature, leading to the boiling of the monomer, forming porosity, and leading to the release of a high concentration of free radicals. At the same time, this increases the rate of polymerisation and formation of many short polymer chains, producing low molecular weight and high residual monomer. Porosity, residual monomer, and low molecular weight all result in inferior flexural properties (Beech, 1974).

In regard to the results of the two sets of experiments in this study, two mixing ratios were tried. The 2.3:1 ratio was the manufacturer’s ratio, which may have been the reason for granular porosity (McCabe and Walls, 2009); for this reason, a lower mixing ratio of 2: 1 g/ml was chosen. This ratio is mainly used by technicians in the Dental School of Newcastle University, as noted in a personal communication with them (Appendix D), and is also used in the literature (Johnson *et al.*, 2015). However, the specimens showed no gross changes in the frequency of porosity for both curing machines. This result of porosity was probably not caused by the high powder to liquid ratio (McCabe and Walls, 2009; Van Noort, 2013; Johnson *et al*., 2015; Anusavice *et al*., 2012), as there may be another causative factor, or probably the change was very small and could not be recognised by the naked eye (Wolfaardt *et al.,* 1986).

The 2:1 mixing ratio caused a significant reduction in transverse strength for the DO specimens from that of the 2.3:1, while no significant effect was found with the WB. This is an expected result according to the aforementioned supposition, in that increasing the temperature in the DO to an unexpected level within an uncertain time will have a deleterious effect. Reducing the mixing ratio means supplying more monomer for boiling, thereby exaggerating the adverse effects of the monomer on porosity occurrence by both evaporation (Harrison and Huggett, 1992) and contraction (Van Noort, 2013). Accordingly, increasing the concentration of porosity, although not noticeable to the naked eye, detrimentally influenced the transverse strength (Jerolimov *et al*., 1989). In addition, lowering the ratio may have increased the possibility of creating excess monomer. However, Harrison and Huggett (1992) noted that the DO is one method which produces the least residual monomer, but the mixing ratio implied in that study (3.7g: 1ml) was higher than in this (2g: 1ml). The high residual monomer in turn reduced the flexural strength (Beech *et al.*, 1974), while reducing the mixing ratio had a negligible effect on the flexural strength of the WB specimens. This result is supported by the findings of Nejatian *et al.* (2015), who found that changing the ratio within the range 1.77:1- 2.95:1 g/ml and using a WB had no significant effect on flexural strength.

The different thicknesses of the specimen comparison groups had no effect on results because, according to Jerolimov *et al.* (1989), the HC specimen cured at 3-9 mm thicknesses does not increase porosity. Although an increase in thickness causes an increase in the amount of heat released by the exothermic reaction, it seems that the amount of this increase was not high enough to elevate the temperature to a level which causes vaporisation of monomer. This notion is supported by Abood (2007) and Pero *et al.* (2008). Conversely, Wolfaardt *et al.* (1986) observed that the liability of generating porosity increases with thick sections; however, the threshold of thickness in which this effect starts was not mentioned in this reference. Moreover, the difference in thickness has no effect on flexural strength and flexural modulus values, because all specimen dimensions are taken into consideration during calculating the equation. As a point of reference, appropriately processed HC produces minimum porosity even with a thickness of 20 mm (Ferracane, 1995).

4.3.4 Conclusion

In the light of previous optimising experiments, the procedure for making specimens in experiment 7, set 2, was followed in all next experiments, as shown in Table 4.3. Stone moulds produced previously in 4.3.1 with 3-3.5 mm thickness wax bars, were coated with a thin layer of alginate-based solution (cold mould seal PCS plaster coating solution, Metrodent, England) as a separating medium. This is a sodium alginate viscous solution which converts to calcium alginate in contact with gypsum

(McCabe and Walls, 2009). It was spread with a fine brush and permitted to dry to prevent the adherence of acrylic to stone. Then, the HC powder and liquid were mixed manually in a clean ceramic crucible with a lid at a ratio of 2.3:1 g /ml, 37/16 g/ml for each of the two flasks. Mixing was performed by adding the powder to the liquid gradually and mixing slowly and thoroughly with a clean wax knife until all the powder particles were fully wet. The crucibles were then covered with a plastic lid to prevent evaporation of the monomer. Dough time was about 14-15 min (at 23˚C room temperature), and the mixture was monitored by frequently checking the consistency until a good workable material with no sticky appearance was achieved; this can be easily identified as it breaks cleanly with a snap when pulled apart rapidly.

At the end of the dough time, the dough was kneaded by hand, manipulated to form a disc, and applied to the top of one half of the stone mould cavity and covered by a polythene sheet; then the flasks were closed and pressed slowly together to permit uniform flow of the material, using a hydraulic denture flask press, up to 3 kg/cm^2 initially. This pressure allowed the excess material to be extruded as a flash. Following this, the flasks were re-opened, and the flash and polythene sheet were removed. The mould sections were re-assembled and the pressure was brought incrementally to approximately 4 kg/cm^2 in the press. After 5 min at this pressure, the flasks were removed and transferred to a two-flask spring clamp, which was immediately tightened firmly by hand to maintain the pressure on the flasks.

Curing was achieved using a WB to polymerise the specimens. It was set up at 70°C for 7 h, then boiled at 95°C for 2 h. The flasks were then bench cooled and all samples were recovered by deflasking.

4.4 Optimisation of the negative control in the study

4.4.1 Materials and methods

CC specimens were made following the manufacturer's instructions (Appendix B), as follows. The stone moulds made previously in Section 4.3.1, for HC specimens with dimensions of 67*10*3.5 mm wax bars, as shown in Figure 4.2, were used to produce CC specimens. The moulds were coated with a thin layer of cold mould seal separating medium, which was then left to dry. The CC powder and liquid were mixed thoroughly and manually with a clean wax knife in a clean ceramic crucible for 20-30 s at a ratio of 1.3/1 g /ml. The mixture in each crucible 20.8:16 g/ml, was enough for two flasks. The crucible was left covered with a lid for 8-12 min. This dough time was not provided in the manufacturer's instructions, and depends on the laboratory temperature (Van Noort, 2013). Therefore, the dough time was determined by regularly assessing the mixture's consistency via a visual inspection for the disappearance of the stringy consistency, at which time it was ready for packing. The dough was manipulated by hand to form a disc and packed into the top of the lower half of each mould, and then the upper half of the flask was reassembled and pressurised. Each set of two flasks was closed together and subjected to pressure with a hydraulic denture flask press up to 3 kg/cm^2. After the extrusion of the flash, the pressure was increased to 3.5 kg/cm^2. The working time was not more than 2 min. Next, the pressure was released and the flasks were left on the bench to set for 15 min and then opened; the samples were retrieved from the flask, polished in a similar way to the HC specimens in Section 4.3.1, and inspected for porosities. The specimens showed many large and small scattered porosities, as in Figure 4.8. According to this result, the optimisation process followed two steps to optimise the appearance and the strength.

A. Optimising the setting method

Specimens were made in three groups following the manufacturer's setting method.

The method of producing specimens followed the same steps as described above, again following the manufacturer’s instructions, except for the setting method. Three mixtures were made, and each was enough for eight specimens (two flasks), following a different setting method. The setting methods used are summarised in Table 4.5. After pressurising the group 1 flasks, the flasks were removed from the press, placed in a pressure pot (Polipress Leone, USA) containing warm water at 40˚C, enclosed, and pressurised to 2 kg/cm^2 for 10 min. According to the manufacturer, the pressure should be 3.5 kg/cm^2 but the pressure pot could not be used over 2 kg/cm^2 for safety purposes. For group 2, the flasks were left in the press at 3.5 kg/cm^2 for 15 min at room temperature, as in Figure 4.9. For group 3, the flasks were removed from the press and left on the bench for 15 min. At the end of the polymerisation time, the pressure was released and the flasks opened. The specimens were finished and polished the same way as the HC specimens in Section 4.3.1, and checked for porosity. They were then tested for flexural strength following a similar procedure to that described for HC specimens in Section 4.3.1.

Groups	Method of setting N=8	Polymerisation conditions
Group 1	Pressure pot	2 kg/cm^2, 40˚C, 10 min
Group 2	Press	3.5 kg/cm^2, room temperature, 15 min
Group 3	Bench	0 kg/cm^2, room temperature, 15 min

Table 4.5 CC setting method optimisation by group

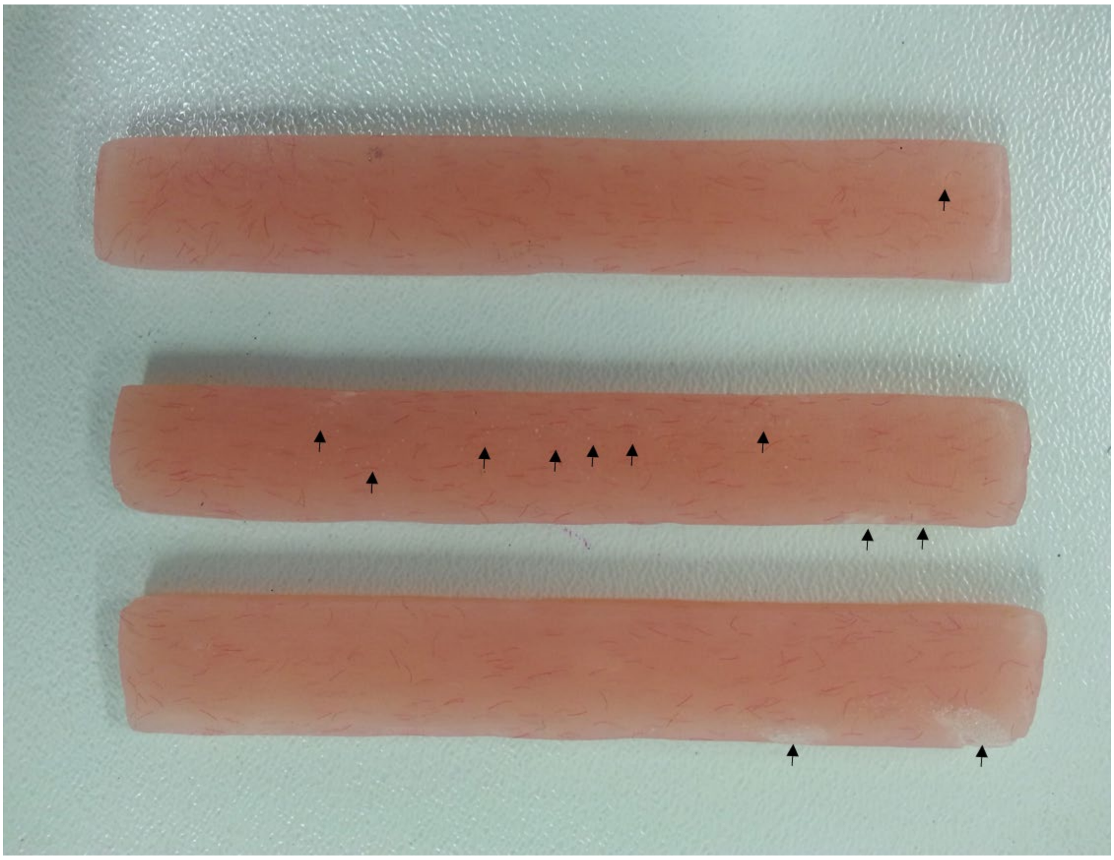


Figure 4.8 CC specimens showing porosities (arrows) before optimisation

Figure 4.9 Pressurising two flasks

B. Optimising the mixing powder to liquid ratio

Following the results of the setting method optimisation, which will be discussed in Section 4.4.2, group 2 was selected to continue optimisation. The same steps for making specimens as mentioned above were followed to fabricate three more groups, but at different mixing ratios. The mixing ratios were selected for this optimisation following the literature (McCabe and Walls, 2009; Van Noort, 2013; Johnson *et al*., 2015; Anusavice *et al*., 2012; Craig *et al*., 2004). Mixing ratios, dough time, and sample size are summarised in Table 4.6.

Groups	Mixing ratio (g/ml)	Sample size	Dough time (min)
Group 2	1.3:1 (manufacturer's instruction)	8	9
Group 2a	2:1	8	5
Group 2b	2.5:1	12	4
Group 2c	2.8:1	16	3

Table 4.6 CC mixing ratio optimisation by group

All samples were polished and tested for flexural strength following a similar procedure to HC in Section 4.3.1.

The median and interquartile ranges were calculated for the flexural strength and modulus of each group because they were not normally distributed, and the data were analysed using Kruskal-Wallis one way Analysis of Variance on ranks. A Tukey test was used for the setting groups and Dunn's method was employed for the mixing ratio groups, to determine the significant difference at a confidence level of 95% (Sigma Plot 13.0).

4.4.2 Results

A. Optimising the setting method

In regard to appearance, all groups displayed porous specimens, as in Figure 4.10. In terms of specimen behaviour during testing, a typical graph for each group can be seen in Figure 4.11. Typical graphs represent graphs of the specimens whose flexural strength and modulus values were the closest to the medians. In general, the typical graphs follow the same description mentioned in Section 4.3.2. A comparison between the typical graphs reveals that a high force was required to distort the specimens of group 2, as these had less extension and were stiffer than the other two groups.

A group comparison graph in regard to flexural strength and modulus can be seen in Figure 4.12. It can be seen that group 1 specimens demonstrated the highest flexural strength, and group 2 showed the highest modulus. However, statistical analysis revealed non-normally distributed data, which is why medians were used to represent typical graphs. Kruskal-Wallis and Tukey tests showed no significant difference among all the tested groups for both strength and modulus ($P>0.05$), except for group 2 and group 3 moduli ($P=0.04$).

The optimisation process continued, although the flexural strength and modulus were within normal range of ISO 20795-1:2013 for type 2 class I denture base requirements, because the occurrence of porosities still adversely influences the aesthetics (BSI, 2013). The mixing ratio, 1.3:1 g/ml, was less than any reported ratio in the literature (McCabe and Walls, 2009; Van Noort, 2013; Johnson *et al.*, 2015; Anusavice *et al.*, 2012; Craig *et al.*, 2004) for type 2 class I polymers and even less than the ratio for type 2 class II (pourable). It produced a very thin mixture because of the high amount of monomer, which might have been responsible for the occurrence of contraction porosity. It also showed that only 50% of specimens were broken during the bending test. The latter observation may be because of the presence of high residual monomer that causes greater plasticisation. Hence, it was necessary to modify the mixing ratio of the manufacturer.

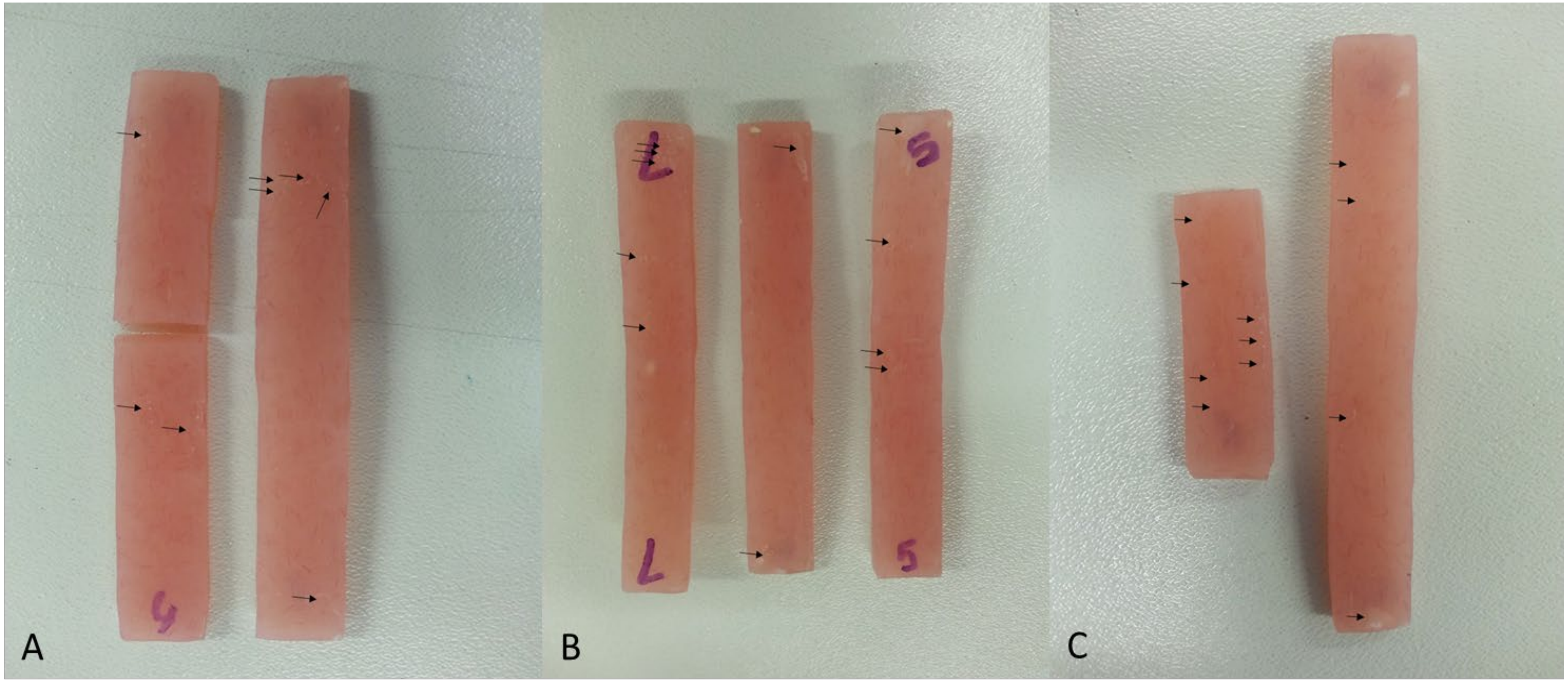


Figure 4.10 Specimens from the optimisation of the setting method, showing porosities (arrows): (A) Group 1, (B) Group 2, (C) Group 3

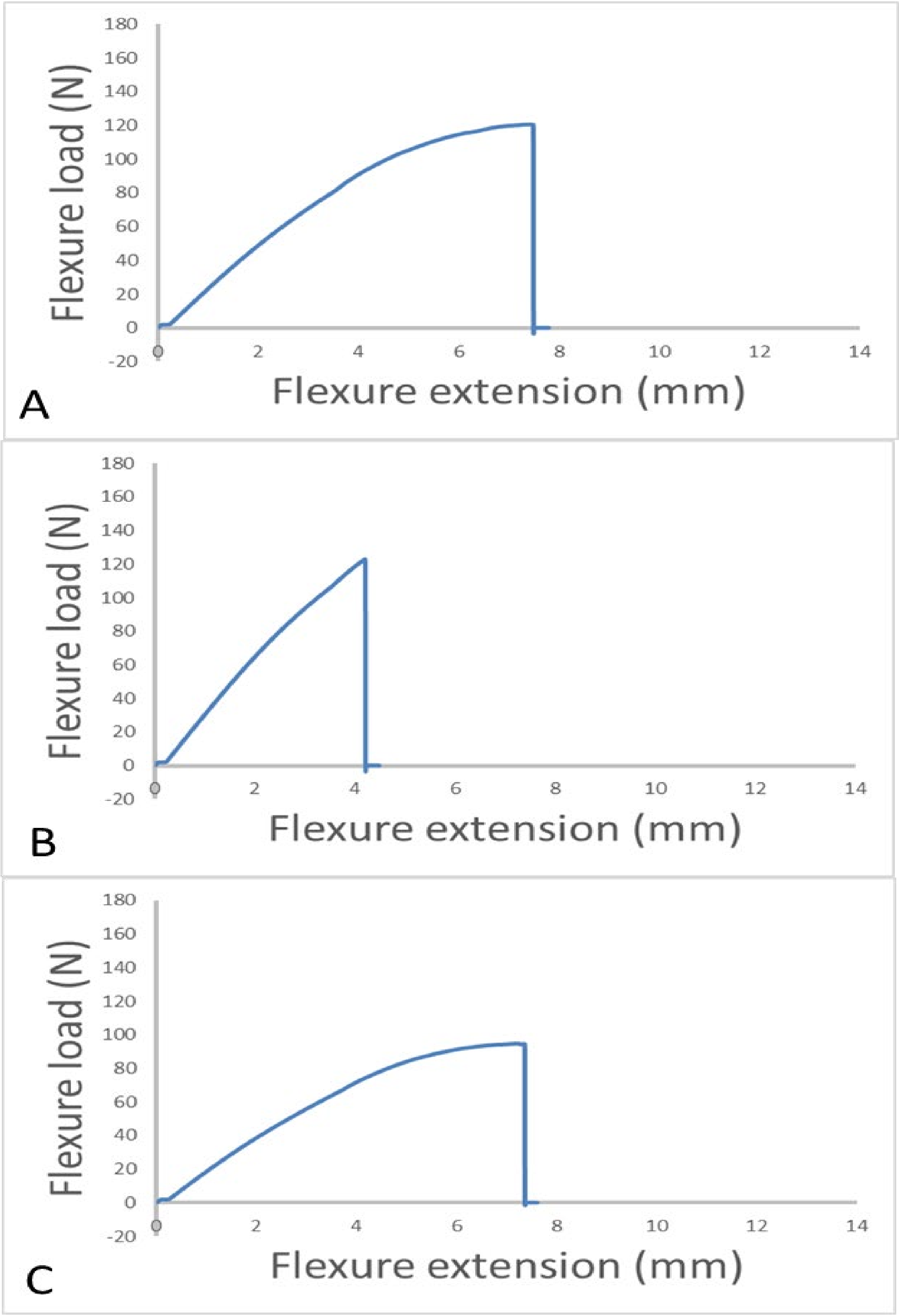


Figure 4.11 Typical graphs for CC optimisation groups of setting method: (A) Group 1, (B) Group 2, and (C) Group 3

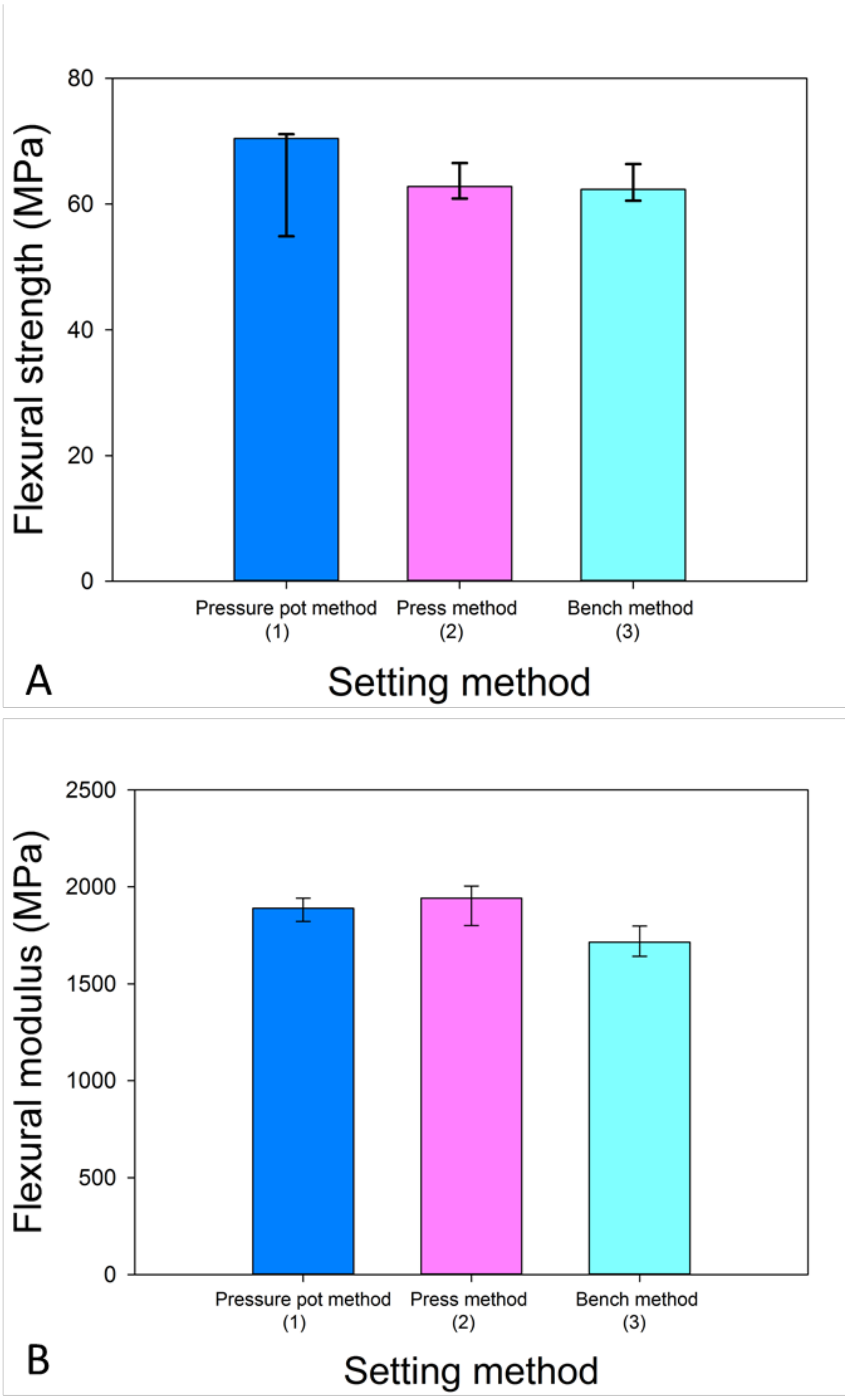


Figure 4.12 Comparison graphs for three setting methods of CC: (A) Flexural strength medians, (B) Flexural modulus medians. Error bars represent the interquartile range

B. Optimising the mixing ratio

The comparison based on appearance showed no sign of visible porosities with Group 2a, and granular porosities with Group 2b, and Group 2c, as in Figure 4.13. In terms of flexure properties, Figure 4.14 demonstrates typical graphs for each group. Typical graphs for the different mixing ratio show the different properties of each ratio. They are about the same force, except for Group 2c, which had the highest force to fail specimens due to thick consistency, due to the high powder/liquid ratio. For extension, this was greatest with Group 2b. All typical graphs were tough except for Group 2.

A comparison of the groups summarised in Figure 4.15 shows that Group 2c was the strongest and of highest modulus, while Group 2 had the least strength. Black dots in the graph refer to values which were much higher or much lower than median value. Kruskal-Wallis and Dunns *post hoc* tests on ranks of strength showed a highly significant difference among the tested groups ($P \leq 0.001$), except for between Group 2a and Group 2b, with Group 2c being the highest and Group 2 the lowest. When the same tests were applied on the ranks of modulus, they revealed no significant difference between groups ($P=0.19$).

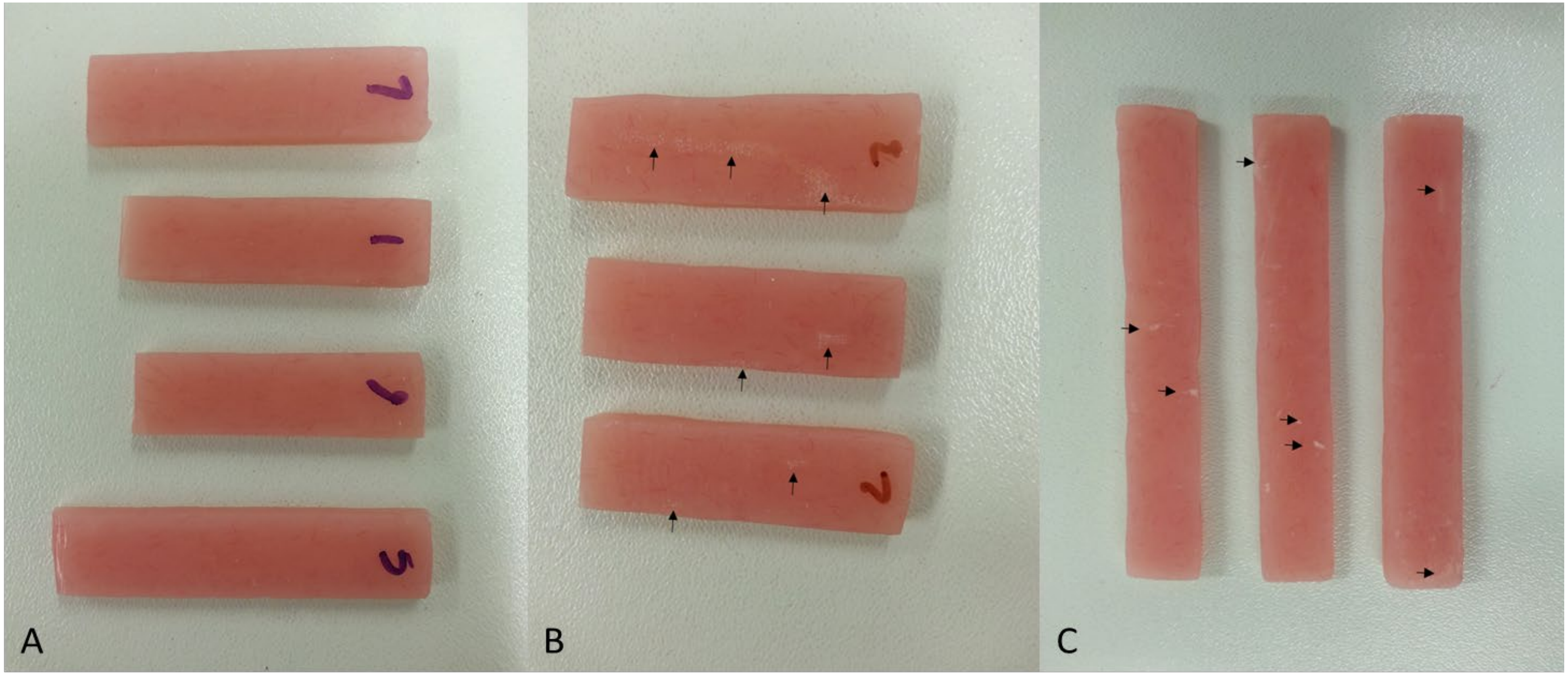


Figure 4.13 CC specimens of mixing ratio optimisation, showing porosities (arrows): (A) Group 2a, (B) Group 2b, (C) Group 2c

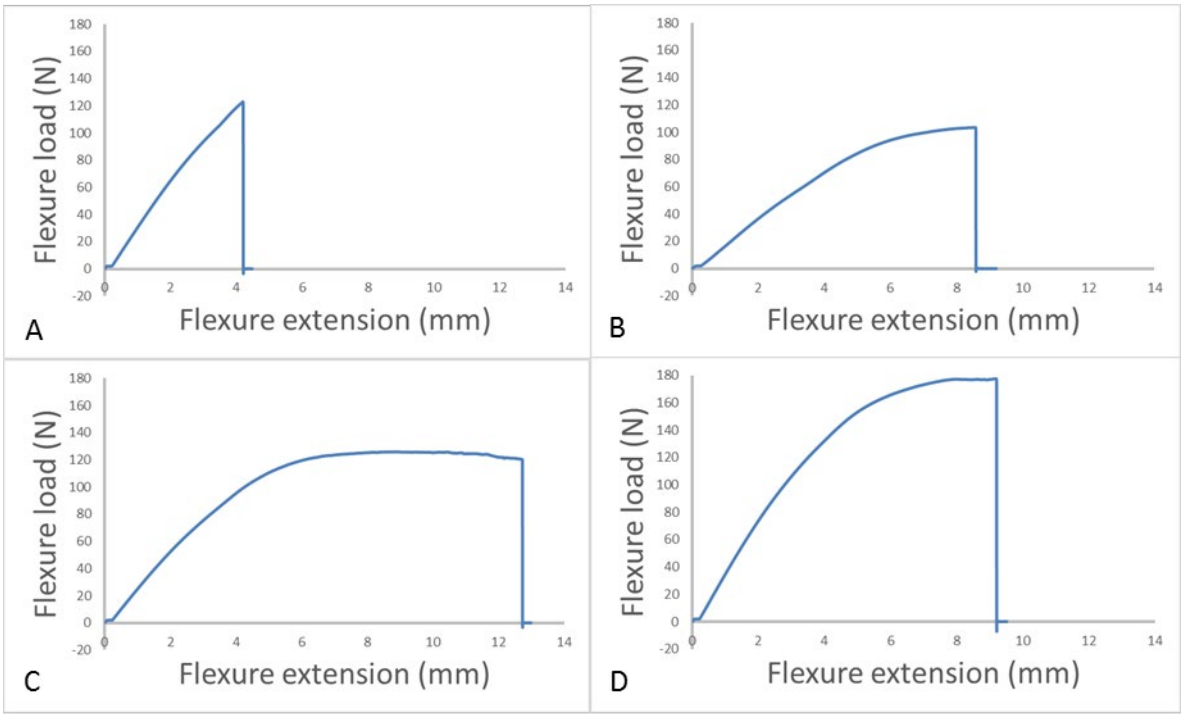


Figure 4.14 Typical graphs for CC optimisation groups of mixing ratio (g/ml): (A) Group 2, (B) Group 2a, (C) Group 2b, (D) Group 2c

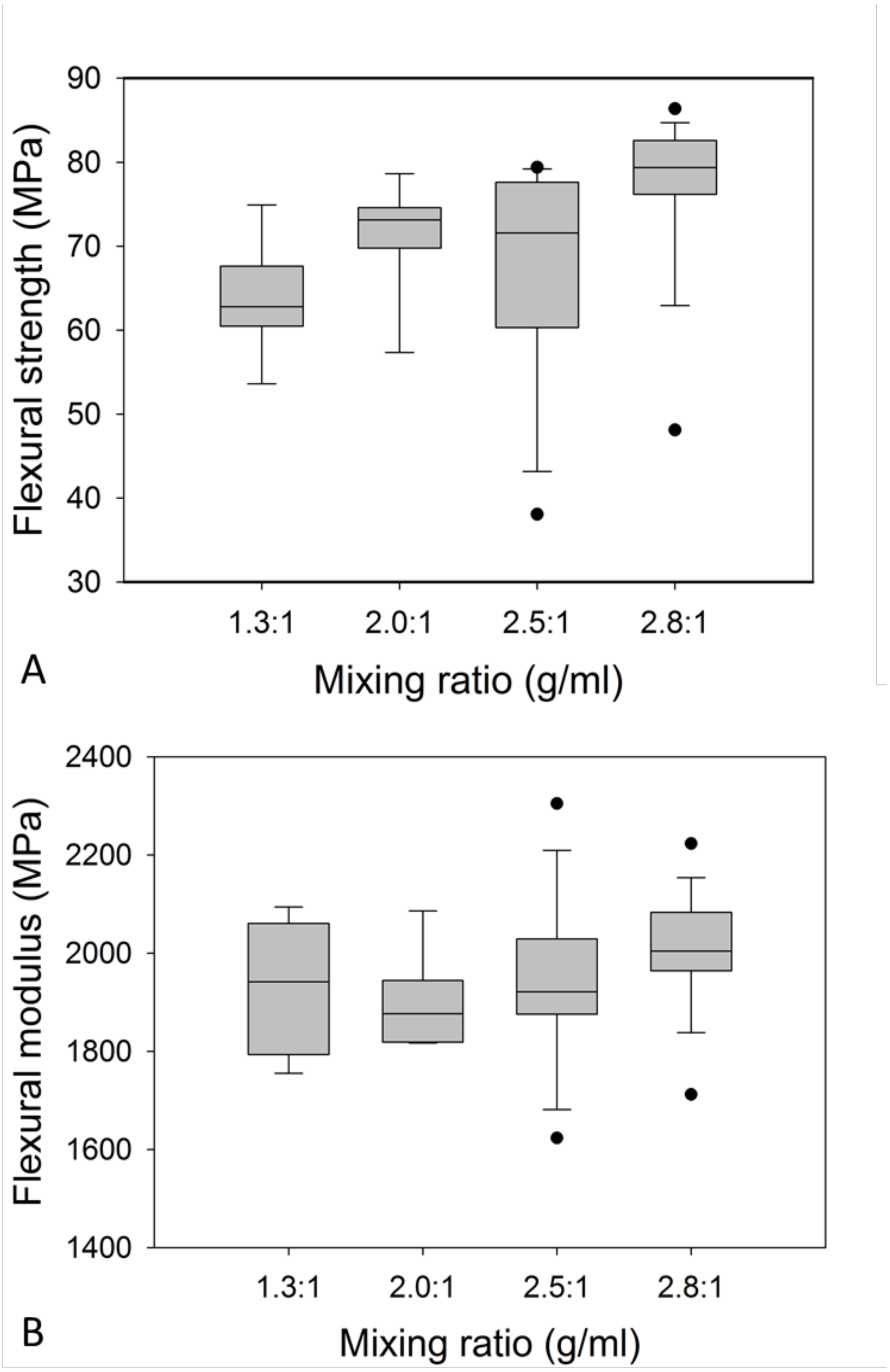


Figure 4.15 Box plots of different CC mixing ratios for: (A) Flexural strength values, (B) Flexural modulus values

4.4.3 Discussion

Optimisation of CC was undertaken because the specimens produced following the manufacturer’s instructions were porous. Therefore, it was optimised in terms of appearance and strength in the same way as the HC specimens, to avoid bias, and comply with the minimum requirements of ISO 20795-1:2013 for type 2 class I denture bases (BSI, 2013).

All groups of setting method showed porosity according to the results obtained in Section 4.4.2A. The kinds of porosity that occur in CC are contraction, granular, and air porosity. Gaseous porosity does not occur because there is less chance of the monomer boiling in the absence of heating, as explained in Section 2.2.7. Nevertheless, the porosities which occurred in this experiment cannot be differentiated into definite types in each case, due to the interaction between various causative factors (Wolfaardt *et al.*, 1986). However, generally speaking, the mixing ratio of 1.3:1 g/ml has a high monomer content which increases the likelihood of contraction, and contraction porosity, which is why all groups showed porosity (Van Noort, 2013). Another reason for the presence of porosity is the application of low pressure during polymerisation (Keller *et al.*, 1985).

Group 2 was selected from all the setting method groups to complete the optimisation process. In this group, the specimens were left in the press during polymerisation. Although no significant difference between flexural strength and modulus was found, Group 1 was excluded because specimen strength had the highest variation. Group 3 was excluded as the specimens had the lowest modulus. Group 2 was chosen as it had both the highest modulus and lowest variation. According to Keller *et al.* (1985), porosity is a function of density and pressure and there is a negative correlation between the pressure, and in turn the density, with porosity. According to Keller’s study, the maximum density was obtained when 40 bar pressure was applied, showing zero porosity. The pressure applied in the current study was 2, 3.5, and 0 bar, respectively, which can explain the presence of porosity.

Despite all the groups being porous, this notion explains that the specimens in Group 2 were denser and less porous than the other two groups, although this decline in porosity could not be recognised with the naked eye.

Group 2a was selected following a comparison of mixing ratios. According to the findings obtained in Section 4.4.2A, although the flexural strength and modulus of all groups were within the normal range of ISO20795-1:2013 for type 2 class I denture bases requirements, most groups were porous. By increasing the mixing ratio, the porosity gradually started to disappear at the ratio 2:1, and then reoccurred at 2.5:1 and 2.8:1. It seems that, at these ratios, contraction porosity probably caused by high monomer started to disappear, and granular porosity caused by increasing powder content started to appear, as explained in Section 2.2.7. Group 2c was the strongest and had the highest modulus; however, it was excluded from selection because it produced a very thick consistency during mixing that led to the appearance of granular porosities. This mixing ratio was also very sensitive to a small rise in room temperature which shortened the dough and working times substantially (Van Noort, 2013). Dough time, according to the American National Standard Institute/ American Dental Association Specification No. 12, should not be less than 5 min (Anusavice *et al*., 2012; Swaney *et al*., 1953).

Group 2 was also removed from selection due to the occurrence of porosities and high variation in modulus. The mixtures in Groups 2a and Group 2b produced a moderate consistency, and were less sensitive to an increase in room temperature; however, Group 2b was excluded because of porosity and a very high variation in flexural properties. Thus, Group 2a, with a 2:1 g/ml mixing ratio and minimal porosity, was used as an optimal ratio to undertake the next experiments.

4.4.4 Conclusion

In the light of these optimising experiments, the procedure for making specimens for all of the remaining experiments followed the manufacturer's instructions, as mentioned in Section 4.4.1, and used the Group 2 setting method and 2:1 g/ml mixing ratio.

4.5 Weropress optimisation

4.5.1 Materials and methods

The manufacturer supplied three options for moulding or processing Ws (Appendix C): injection, tamping/pressing, and casting pouring. The casting process has used plaster, and silicone or hydrocolloid. Therefore, several attempts were made to obtain a mould capable of producing and reproducing sound specimens.

Casting or pouring moulding technique

A. Mould production

I. <u>Hydrocolloid mould</u>

Agar agar hydrocolloid impression material (PremEcoLine, MerzDental GmbH, Germany), shown in Figure 4.16A, was used to construct a mould. 360g of Agar agar was chopped into small pieces and placed in a duplicating machine, as in Figure 4.16B, following the manufacturer's instructions (Appendix E). It took about 1 h to reach the melting point (95˚C). Then, the temperature was allowed to descend and settle at the processing temperature of 47-49 ˚C, following the machine set up.

A specifically designed flask was used for moulding (PremEcoLine casting flask, MerzDental GmbH, Germany), shown with its assembly in Figure 4.16C, D, and E. Four wax bars were arranged horizontally about 5 mm apart, and stuck with sticky wax to the internal surface of base of the flask. The flask was then reassembled and the screws were tightened. The molten Agar agar was poured from the tap of the duplicating machine into the upper opening of the flask at processing temperature until it was full. The flask was then immersed inside a container containing tap water for 45 min in an upright position for cooling. After this, the flask was inverted, unscrewed and opened carefully. The wax bars were removed from the mould, as in Figure 4.17. A sharp tube supplied with the flask, called a "cutter", was used to make a hole in the Agar agar to form a passage connecting the upper opening to the base of the flask, through which the material was poured onto the replica of wax bars. This pathway was connected in all specimens. In addition, accessary passages were made to enable the exit of air. This pathway was made in many different designs to try to produce sound samples from a re-usable mould. These designs are shown in Figure 4.17, 4.18 and 4.19 and described in detail in the following:

a. Four bars arranged horizontally beside each other on the base and connected to each other in the middle by accessory pieces of wax. Two vertical holes were made for the passage of material connecting the upper opening to the accessory wax replica between the wax bars. The mixture was poured in a downward direction, as in Figure 4.18A.
b. Four bars arranged horizontally beside each other on the base and connected to each other via accessory pieces of wax connected close to the end of each bar, forming a W shape. One vertical hole was made for pouring connecting the upper opening to one of the specimen replicas, with a side hole connecting side opening to other specimen replica. The side openings acted as a passage for air exit. Side opening are plugged after pouring. The mixture was poured in a downward direction, as in Figure 4.18B.
c. Four bars arranged horizontally beside each other on the base and connected to each other in the middle by accessory pieces of wax. One vertical hole was made connecting the upper opening to one of the specimens, and a side hole was made, for pouring into the side opening, connected to the end of the closest specimen. The mixture was poured from the side opening and the exit of air was in an upward direction, as in Figure 4.18C.
d. This was the same as Design C, with the addition of another side hole connecting one end of the closest specimen to the other side opening. Side opening are plugged after pouring. Pouring was in a downward direction and side holes were used as air exits, as in Figure 4.18D.

e. This was the same as Design D, with the same number of holes and direction of pouring and expulsion of air, except that the connection between the wax bars was a W-shape, as in Figure 4.18E.
f. The design was the same as Design E, with the same number and position of holes, except that the direction of pouring was from both side holes and air exit was upwards, as in Figure 4.18F.
g. Four bars arranged horizontally beside each other on the internal surface of base. The flask was inverted, the base removed, and the mixture poured directly onto the top of the mould without connecting any passages. Then, the base was repositioned and tightened, as in Figure 4.17.
h. A parallel rectangular stone base with dimensions 69*50*15 mm was made and fixed to the base of flask with a magnet supplied with the flask. Four wax bars were arranged horizontally on the top of the stone base, as in Figure 4.19A. The flask was reassembled and Agar agar was poured from the upper opening. After Agar agar mould setting, as mentioned above, the flask was opened and appeared as shown in Figure 4.19B. One vertical hole was made connecting the upper opening to one of the specimens for air expulsion, and two side holes were made connecting side openings to the specimens for pouring. In addition, a track was made between specimens for the passage of mixture.

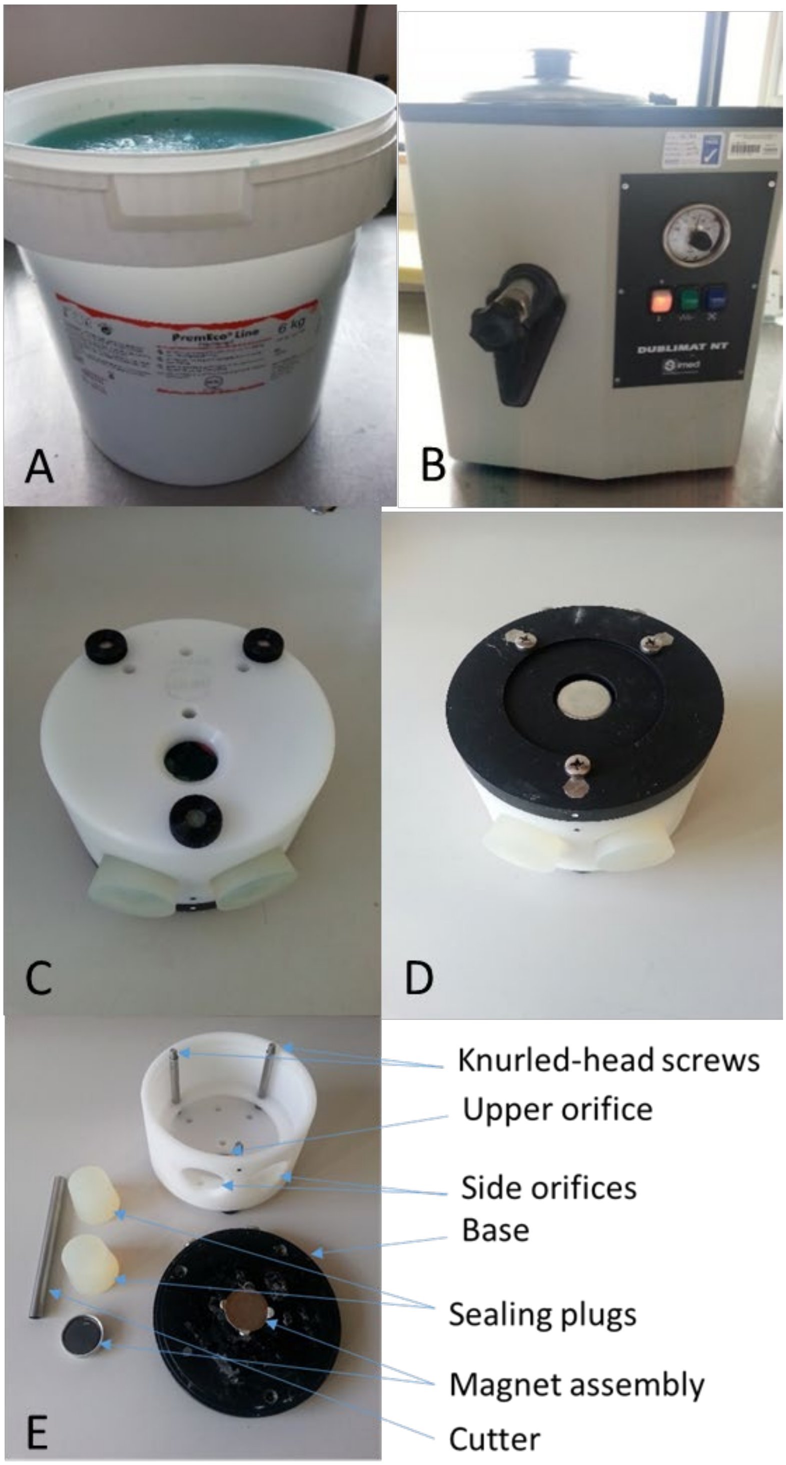


Figure 4.16 (A) Agar agar, (B) Duplicating machine, (C) Ws flask –upper view, (D) Ws flask –lower view, (E) Flask assembly

Figure 4.17 Hydrocolloid (agar agar) mould

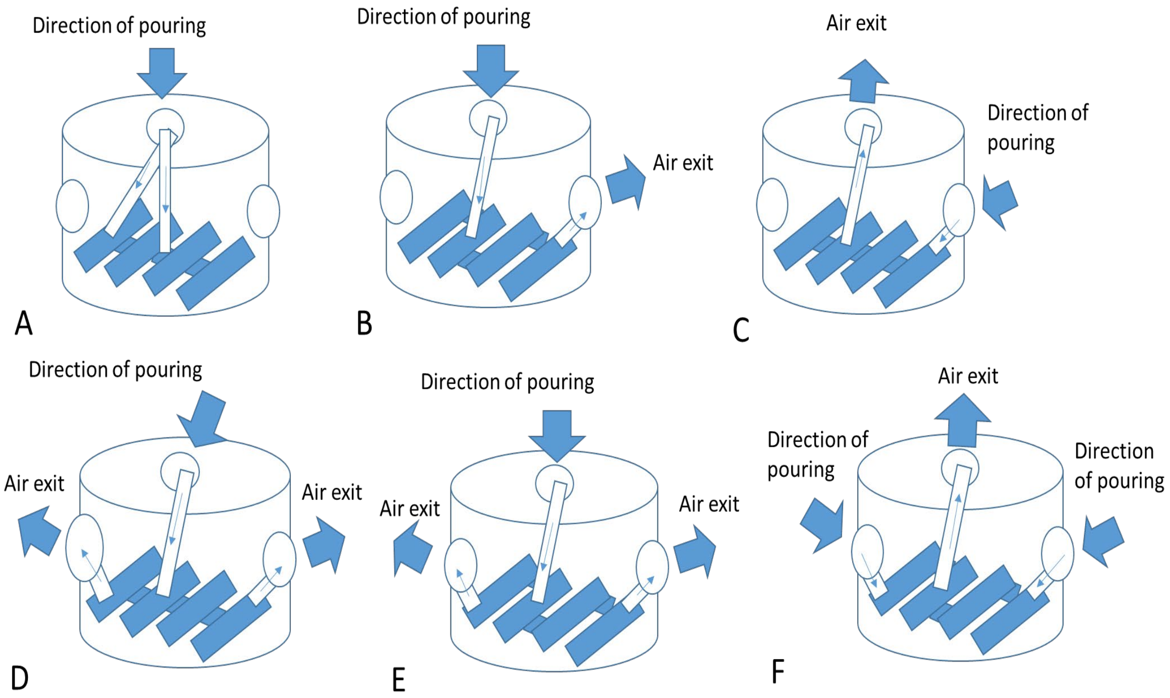


Figure 4.18 Pathway designs for pouring Ws in hydrocolloid (agar agar) mould

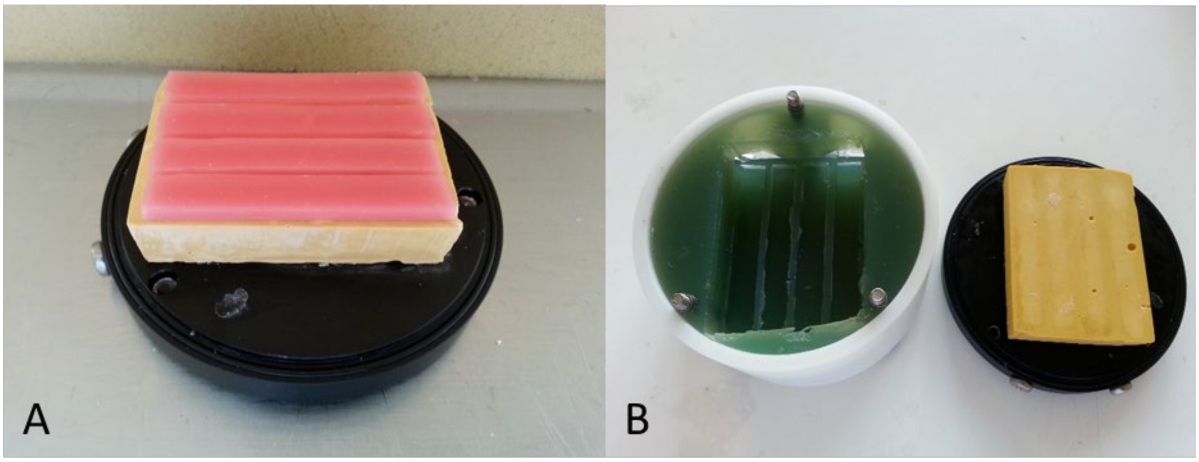


Figure 4.19 Agar agar mould for bars: (A) before pouring, (B) after pouring

II. **Stone mould**

A metal denture processing flask with dimensions 95 mm width, 85 mm length, and 50 mm height was used to make a stone mould. This size was checked and it was found that it is convenient for use with a pressure pot curing unit (Polipress Leone, USA). The inner surface of the lower half of the flask was lubricated with Vaseline to facilitate stone mould separation. Flask assemblies were checked for fit without excessive force application. Stone was mixed as recommended by the manufacturer (Formula Saint-Gobain, UK), which was 3/1 powder/water ratio, and used to fill the lower half of the flask. Three wax bars were completely and horizontally inserted alongside each other, 10 mm apart, leaving the surface exposed. Wax bars were positioned so that the upper surfaces of the bars were levelled with the edge of the flask. Two small pieces of wax at dimensions approximately 10 mm length 5 mm width and 3 mm thickness were added to each bar in a different position, according to the space available in the flask. These extras were used as a reservoir for Ws mixture during setting to restore some of the high dimensional shrinkage of the pourable type material, as in Figure 4.20.

All excess stone was removed from the edges to ensure close and intimate contact between the two halves of the flask. After complete stone setting, the surface of the stone mould was coated with a thin layer of Vaseline and the two halves of the flask were re-assembled, making sure that the lugs were engaged and two halves were pushed firmly. The pouring of the upper half of the flask, setting, and wax elimination procedures were followed exactly as for HC and CC moulds. A typical stone mould after being cleaned of wax is shown in Figure 4.21

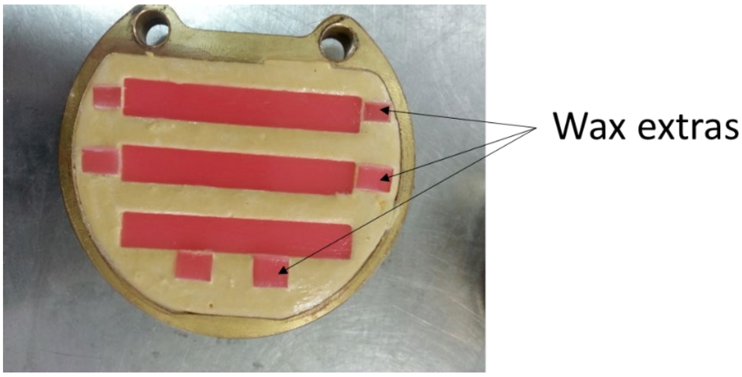


Figure 4.20 Wax bars of Weropress, showing the wax extras

Figure 4.21 Stone mould for Weropress

B. Specimen production with casting method

I. __The hydrocolloid mould__:

Following the manufacturer’s instructions, the Weropress powder and liquid were mixed manually with a wax knife in a ceramic crucible at a ratio of 1.4/1 g/ml. The mixture was stirred for 30 s and left covered for another 30 s (dwell time). Then the mixture was poured slowly into a hole made for this purpose, according to the design of the pathway mentioned above, until the material was no longer pourable due to increasing material viscosity. After this, the plugs in the side openings were closed.

II. __The stone mould__:

Stone moulds constructed beforehand were released from the metal flask and immersed in a bucket filled with warm tap water for 15 min to remove air trapped inside the stone mould (following the manufacturer’s instructions). After the moulds were removed from the water, they were repositioned in the metal flask. Then, the surface of the mould was dried with absorbent paper to apply a thin layer of separating medium. Some moulds were coated with alginate separating medium (alginate insulation, PremEcoLine, MerzDental, Germany), which comes with the product, following the manufacturer’s guidance, while other moulds were coated with a cold mould seal as used for HC and CC to find the best option. Next, Ws mixing was performed as described above and poured slowly into the top of the lower half of the stone mould. Some moulds were poured with no vibration, following the manufacturer’s guidance, whilst others were poured over a vibrator to dispel air entrapped in the mixture. The vibrator was set at 5˚ as a medium vibration. Vigorous vibration may move the mixture too much and push it out of the flask, while light vibration may have little effect. The vibration continued for 30 s after pouring stopped. The mixture ratio of 30: 21g/ml was enough for two flasks of bar samples. Pouring time was 1-5.5 min until the mould was overfilled and the material was no longer pourable as it had become thicker. These timings are based on a room temperature of 21˚C. By the end of the working time, the upper half of the flask was repositioned onto the lower half and pressed firmly against each other to produce close contact along the border.

For both types of moulds, polymerisation was conducted using a pressure pot filled with water at 45˚C, pressurised to 2 kg/cm^2); it was left for 15 min for the stone mould and 30 min for the hydrocolloid mould, (manufacturer's guidance). The pressure pot's size was enough for one flask with a hydrocolloid mould or four flasks of stone mould. The flasks were placed upright inside the pot, as in Figure 4.22. At the end of the polymerisation cycle, water temperature was usually approximately 35-37˚C. The flasks were opened and the specimens removed, finished and polished in same way as the HC and CC specimens in Section 4.3.1; they were then checked for porosities.

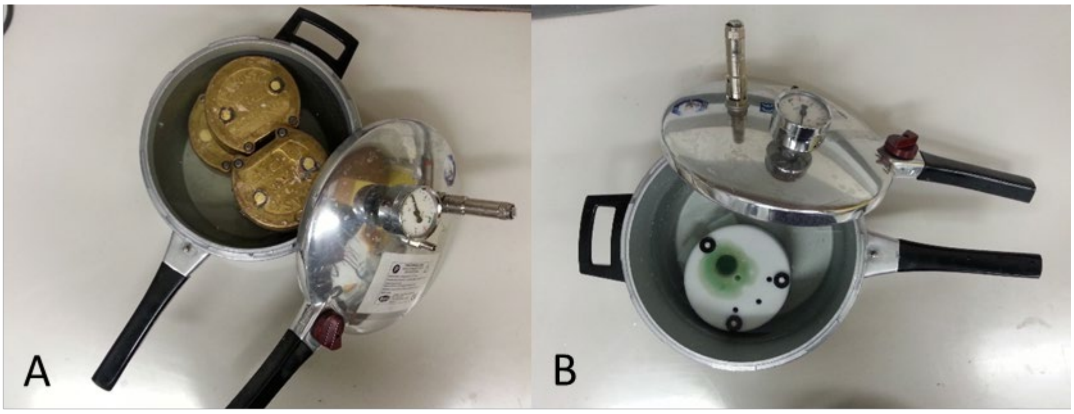


Figure 4.22 Pressure pot curing machine with flasks inside: (A) Stone moulds, (B) Hydrocolloid mould

Pressing/ tamping or compression moulding technique

Stone mould production for the press method followed the same procedure for making a stone mould as with the casting process described in Section 4.5.1, except with no wax extras because the monomer contraction was less as the mixing ratio of 2:1 g/ml was higher than in the casting method. No hydrocolloid mould was allowed in the manufacturer's instructions.

To produce specimens, the powder and liquid were mixed in a crucible at a ratio 2:1 g/ml for 30 s, following the manufacturer. The crucible was left covered for 8 min at 21˚C room temperature. Dough was then kneaded, applied, polymerised, finished, and polished in a way similar to that of CC in Section 4.4.1.

4.5.2 Results

Results of the casting method

All attempts made to produce specimens using Agar agar mould failed despite using different designs for material passage. This failure was mainly due to the entrapment of air and insufficient working time to fill the mould and may be improper design. Therefore, the specimens showed large porosities and irregular or short specimen, as shown in Figure 4.23.

Producing specimens using the stone mould and following the manufacturer's instructions was successful, but these specimens were porous, as shown in Figure 4.24. The irregularity of the specimens was again related to air entrapment in the mixture and the use of the alginate separating medium, which had formed a thick layer after its gelation on setting, which in turn affected the specimens' shape. This was because the pourable material is very sensitive to even tiny irregularities in the mould, due to its thin consistency and high fluidity, and which is why it is able to produce a perfect reproduction (Woelfel *et al.*, 1960; Anusavice *et al.*, 2012).

Substituting the separating medium with cold mould seal removed the distortion signs from the specimens caused by the alginate layer; however, the specimens still had many voids of entrapped air, various in size and position, both deep and superficial, as in Figure 4.25. Thus, a vibrator was suggested to expel air.

The specimens produced using the stone mould coated with cold mould seal separating medium and poured under vibration were better, with less entrapped air and thus fewer scattered pores, but they were still not ideal, as in Figure 4.26.

Results of the press method

Specimens produced using the press method were sound; these can be considered ideal in terms of being free from porosity, feasibility, reproducibility, applicability, and time saving, as shown in Figure 4.27.

4.5.3 Discussion

Regarding casting or pouring method, the poor quality of the specimens produced using Agar agar mould was due to: the lack of, or too few, air exit pathways; the mixture becoming thick very quickly within the working time; and, narrow sprues. These reasons lead to the occurrence of air bubbles, short specimens, and contraction porosities, despite using material in channels as a reservoir. Also, even though the venting and number of passages were increased, or the height of the pathway was reduced to control the time factor, it was still not possible to produce a sound specimen using Agar agar mould.

A stone mould was the second choice, following the manufacturer’s guidelines, this was somewhat successful and was used as a substitute for the hydrocolloid mould because it was able to produce specimens, and was time saving and productive. The mould was durable and four flasks can be polymerised together in 15 min, while the Agar agar mould distorted after each use and needed to be re-made, and only one flask could be polymerised at a time of 30 min. In addition, making the stone mould was more feasible than making a hydrocolloid mould as it does not need careful handling like Agar agar; also, working with stone had become familiar at this stage, as the HC and CC moulds were made of stone.

Although the press method produced the best samples, it could not be followed as a standard method for Weropress specimen production because the procedure was similar to the CC procedure and there was no point in making specimens for a pourable material with no pourable method (pressing method). The injection method was not tried as the mixing ratio was similar to the pressing method in terms of producing a thick mixture. The casting method, in which the material was mixed at a lower ratio, faced a problem of short working time, and therefore it was axiomatic that the injection method would face the same problem.

It was noticed that the most commonly occurring porosity types with pourable polymers are air and contraction porosity. Air porosity appears as a result of the incorporation of air with the mixture when mixing and pouring, due to its thin consistency and high fluidity (as mentioned before in Section 2.2.7). This porosity appears large in size and regular in shape, similar to air bubbles. In regard to the hydrocolloid mould, extra passages were used to expel air, but they were unsuccessful with the rectangular specimen geometry. In regard to the stone mould, a vibrator was used to expel air from the Ws mixture. Although vibration was not efficient enough to remove the incorporated air 100%, it at least removed most of the large and deep air bubbles after visual evaluation.

Contraction porosity is related to high monomer content compared to powder, which results in high monomer contraction during polymerisation. This contraction can be compensated for by the flow of enough dough under sufficient pressure (Van Noort, 2013), but the material was not moulded as a dough and reservoir material was not enough to compensate contraction. Sometimes, vibration forces the mixture to skid out of the flask or move to one side more than the other, resulting in there being not enough mixture to compensate for contraction, and subsequently in contraction porosity. In the hydrocolloid mould, under-estimation of the number of sprues (material passages), which were used as reservoirs, caused contraction porosity near the connection between the passage and the specimen.

Some attempts were made to find the reason for the, mainly, contraction porosities and air bubbles. The gap between the two flask halves due to improper closure was one possible technical error. No excess material extruding from the flask is another reason, as the excess material was used to compensate for the high polymerisation shrinkage, as sprues did with the hydrocolloid method. Both can be seen in Figure 4.28.

4.5.4 Conclusion

In the light of these experiments, the standard method followed for making all the remaining batches was the casting method with a stone mould, using a cold mould seal separating medium, and pouring material under vibration and taking into account the even distribution of the material at the top of the mould. Even distribution should be achieved by putting a vibrator on a balanced horizontal surface so that excess material was extruded all around the flask. In addition, it was necessary to reposition the stone mould properly in the flask to allow perfect closure of the flask. These criteria represent the best concluded method of obtaining specimens, although there were still an unpredictable number of porous specimens for unknown reason. Therefore, the specimens with large or deep surface porosities were excluded while specimens with tiny or shallow porosities were accepted.

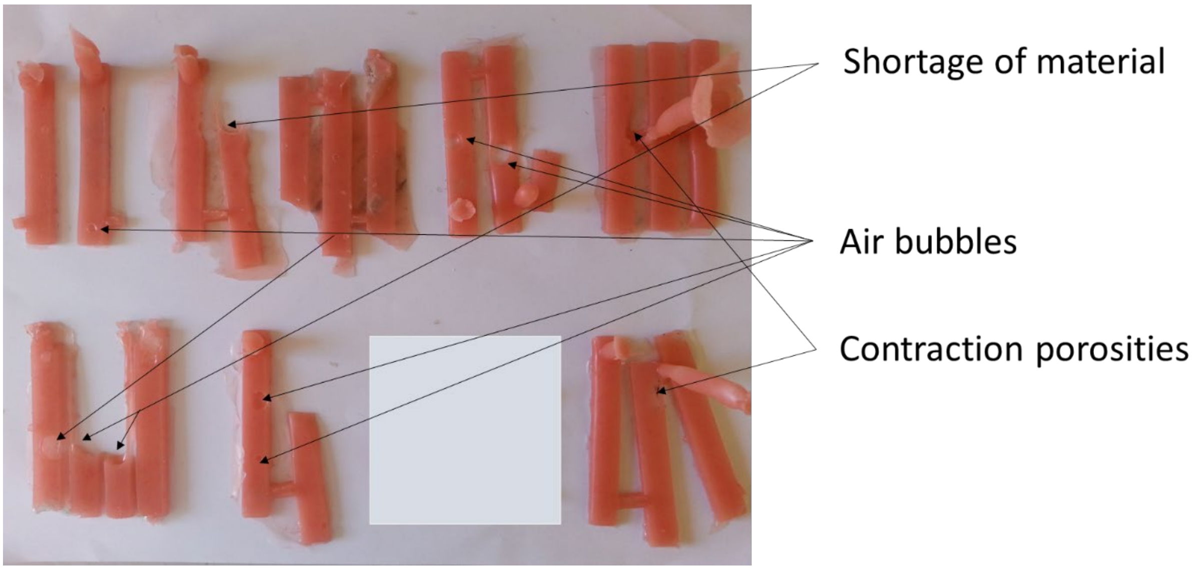


Figure 4.23 Weropress samples produced by Agar Agar mould

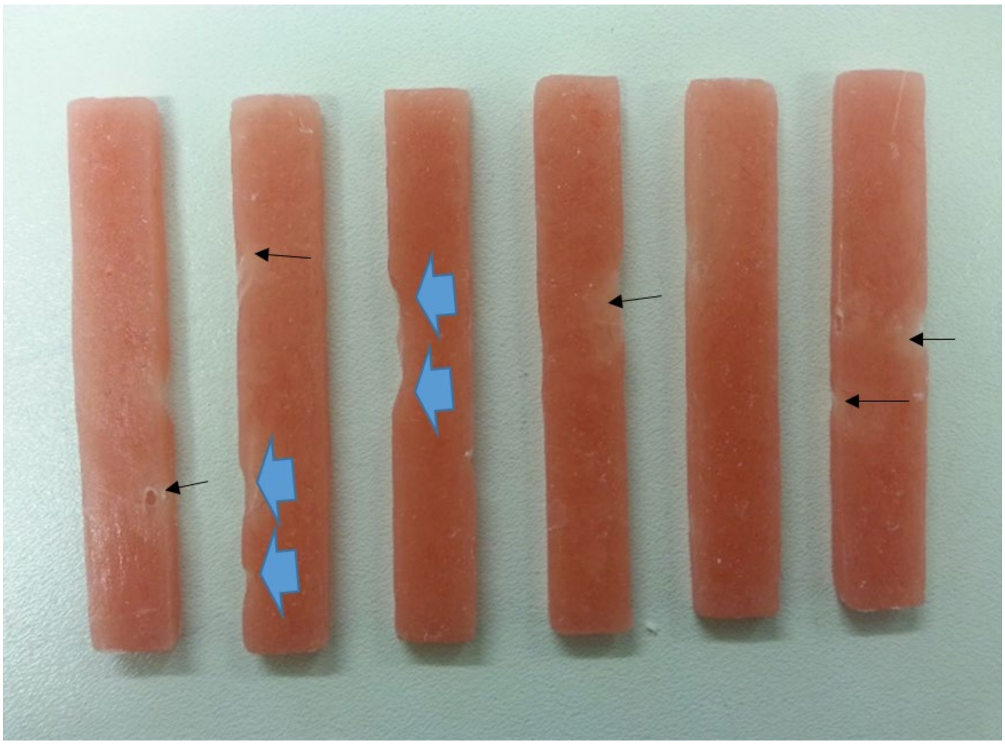


Figure 4.24 Ws specimens made with stone mould (blue arrows refer to distortion caused by alginate insulation, black arrows refer to air entrapment)

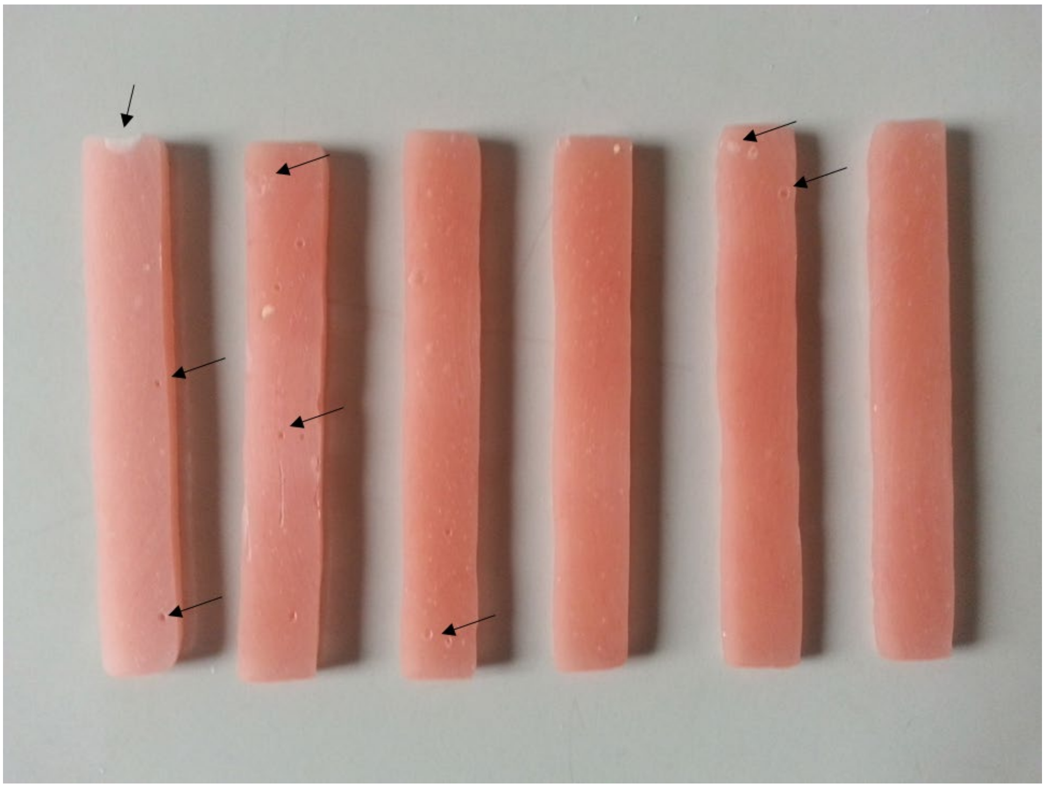


Figure 4.25 Ws specimens made with stone mould using cold mould seal separating medium and no vibration (arrows refer to air bubbles)

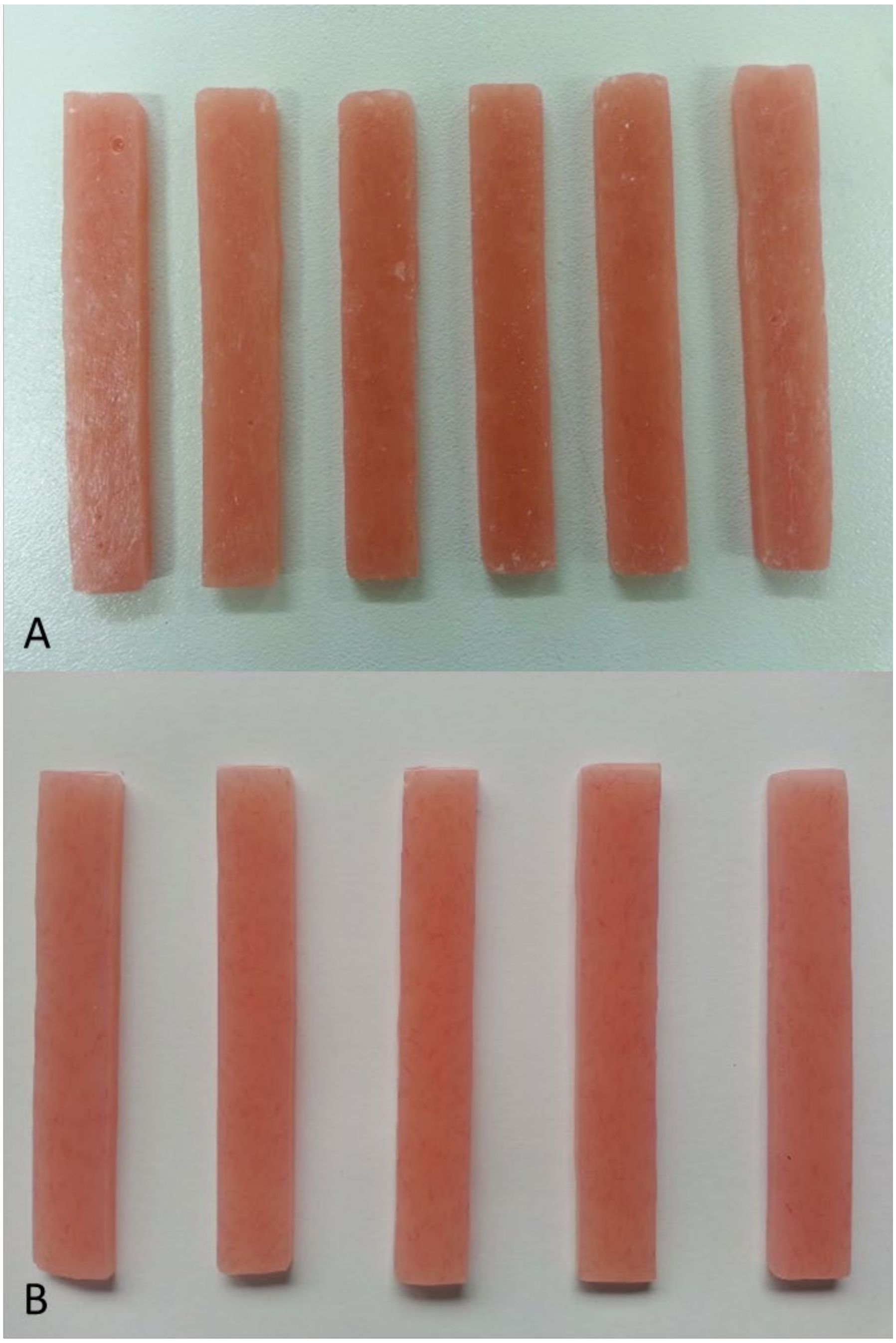


Figure 4.26 Weropress samples made using stone mould coated with cold mould seal separating medium and pouring with vibration: (A) before polishing, (B) after polishing

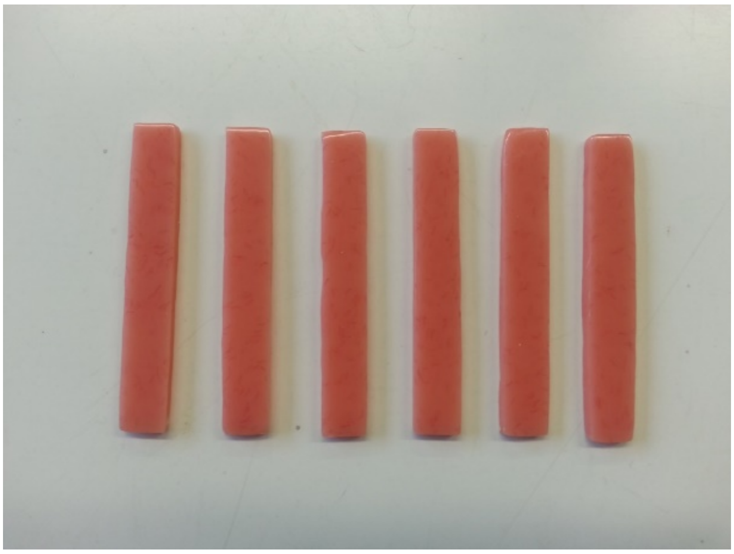


Figure 4.27 Weropress specimens produced by the pressing process

Figure 4.28 Some causes of Weropress porosities, marked with arrows: (A) Improper closure of flask and its consequences, (B) No excess material and its negative effect

Chapter 5 General Methodology

5.1 Mould production

According to the tests undertaken in this thesis, two moulds were produced for the requirements of this study.

5.1.1 Flexural test specimens' mould

The production of this mould was performed in three steps: silicone mould, wax bar, and stone mould. The first two steps were as performed in Section 4.3.1. The three steps were similar for all the tested materials except the stone mould, which was different for different denture base material.

HC and CC stone mould

The HC and CC stone mould was made previously, as described in Section 4.3.

Weropress stone mould

The stone mould was made previously, as described in Section 4.5, after optimisation.

Eclipse stone mould

The metal denture processing flask used to fabricate a stone mould for Ws was also used for Ec, as it fitted the space inside the Eclipse curing machine (Enterra VLC Curing Unit; Eclipse Junior, Dentsply, UK). The inner surface of the upper half of the flask was lubricated with Vaseline to facilitate the separation of the stone mould. Stone was mixed with water at a ratio of 3/1 following the manufacturer's instructions in a rubber bowl and manipulated with a spatula. Then, the mixture was poured into the lubricated part of the flask. Three wax bars were horizontally inserted into the stone mixture about 10mm apart, until it was the same height as the flask, leaving the bars' surface exposed. The wax melting machine was heated to 90˚C for 1 hr. After the stone had set for about 45 min, wax elimination procedures were followed by inserting the one half of the flask into the melting tank and leaving it for 9 min under running hot water. In this case, only one half of the flask was used because the specimens need to be uncovered when exposed to light inside the curing machine; in contrast, the HC, CC and Ws moulds required two flask halves to confine the denture base material, whilst applying pressure and curing in the water bath or pressure pot. Lastly, after the complete cleaning of the wax, and cooling, the stone moulds were released from the metal flask, as it does not need any more support when curing. However, HC and CC were not removed from flask because the pressure is applied on metal flasks when curing in the water bath. A typical stone mould is shown in Figure 5.1A. The stone moulds of Eclipse were then checked for being of an appropriate height inside the curing unit. This height was judged via a row of holes in the back wall of the chamber; the top of the mould should be located below this line to maximise the curing of the specimens, as in Figure 5.1B. The height of the stone mould could be adjusted accordingly.

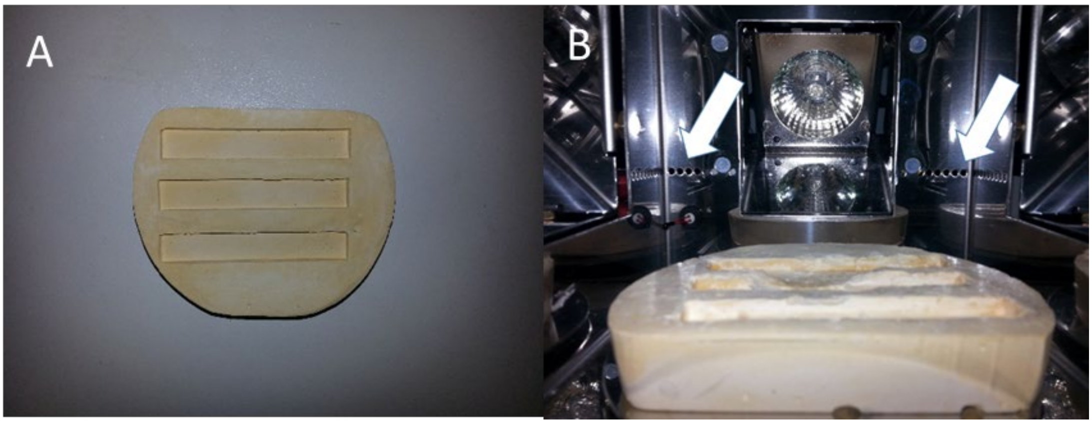


Figure 5.1 (A) Typical stone mould for Eclipse, (B) The interior of the curing unit, showing the reference line (arrows) for the height of the mould

5.1.2 Hardness, roughness, and colour stability tests' specimens' mould

Disc specimens 20 mm diameter and 5 mm thick were used for the hardness, roughness, and colour tests. This size was selected in the light of research published in the literature, shown in Tables 2.8, 2.9, and 2.11, and American Dental Association number 17 (Shahdad *et al*., 2007; Durkan *et al.*, 2013; Harrison *et al.*, 2004; Sepúlveda-Navarro *et al.*, 2011), as it fits with the spectrophotometer aperture, profilometer and hardness tester. As the sizes of the disc specimens were different from the preceding bar ones, different numbers could be produced at any one time from each flask, as follows: HC and CC specimens - nine specimens per flask, Eclipse - five specimens per flask and Weropress - six specimens per flask.

The steps which were followed to make the silicone moulds; bar wax; and stone moulds for the bar specimens in Sections 4.3.1 and 4.5 were also followed for making disc moulds. This was with the exception that metal discs 20mm diameter by 5mm thick in dimensions were used instead of metal bars. Silicone mould and disc wax is shown in Figure 5.2A and B. For the Ws mould, a small rectangular wax piece, approximately 20 mm long, 10 mm wide, and 3 mm thick was added to each disc of wax in the form of a spoon handle to enable the extra wax material to act as a reservoir and compensate for monomer shrinkage during setting, as in Figure 5.2C. Figure 5.3 shows the stone moulds of the tested materials.

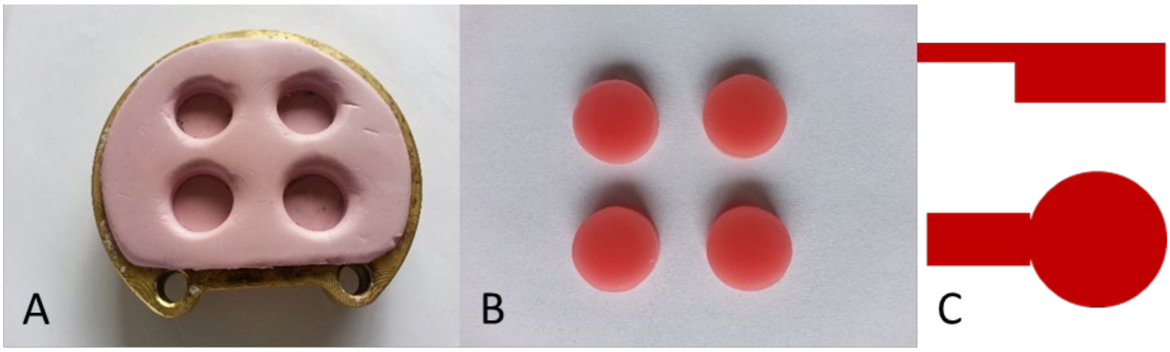


Figure 5.2 Specimen moulds for the hardness, colour, and roughness tests. (A) Silicone mould, (B) Disc wax model, (C) Lateral and top views of spoon-shaped wax for Weropress

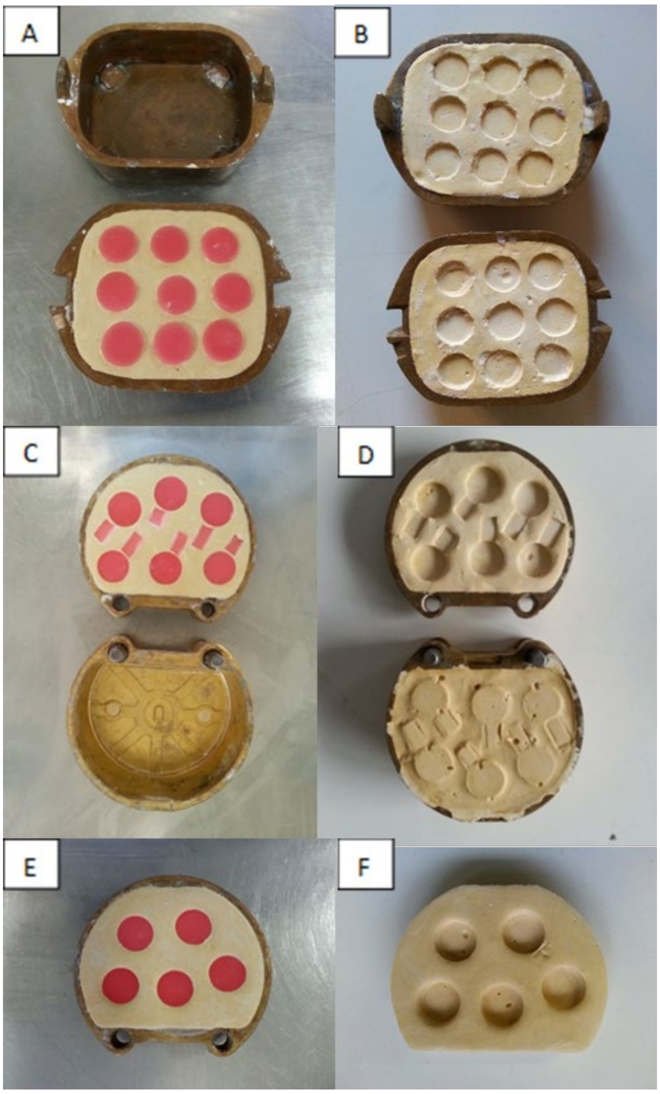


Figure 5.3 Stone moulds during the preparation stage, and after wax elimination. (A) and (B) HC and CC stone moulds, (C) and (D) Weropress stone moulds, (E) and (F) Eclipse stone mould

5.2 Specimen production

5.2.1 HC specimen production

Bar specimens were produced following optimisation, as described in Section 4.3.4. The disc specimens were produced following the same steps as the bars, except that the material mixed for each pair of flasks was 46:20 g/ml. Ten flasks, clamped in five clamps, were usually polymerised in one batch.

5.2.2 Cold-cured PMMA specimens' production

Bar specimens were made following the optimisation, according to Section 4.4.4. The disc specimens were produced with the same procedure as the bars, except that the mixture quantity was 40:20 g/ml for each pair of flasks.

5.2.3 Weropress specimen production

Specimen production for the flexural test followed the previously concluded method described in Section 4.5.4. Disc specimens were fabricated following the same procedure as the bar specimens, except that the mixing quantity was 40/28 g/ml for each pair of flasks

5.2.4 Eclipse specimen production

Eclipse resin was produced following the manufacturer's instructions. Two thin layers of Al-Cote separating medium (potassium alginate, Dentsply Trubyte, USA) were applied to a dry stone mould with a brush, and each layer was dried with hot air. After this, the stone mould was preheated inside the curing unit to a temperature of 55˚C for 4 min and 15 s, using the pre-heat cycle pre-programmed on the curing unit. This preheating was done to facilitate the softening and adaptation of the material on the cast. The Eclipse baseplate material (original-pink) was removed from the fridge and package was opened, then placed on the warm mould for 1 min to absorb temperature and become easily manipulated.

Then, the baseplate material was applied to the mould using finger pressure, trying as much as possible to apply the material gradually from one side to the other, beginning with deep areas, to avoid air incorporation. The excess was cut with a wax knife and the surface was smoothed with the fingers. Each sealed packet of upper baseplate was enough to make three bar specimens or four disc specimens.

The material was then coated with Air Barrier Coating protective varnish (ABC) (Eclipse ABC, Dentsply International Inc., USA), to prevent the polymerisation process being inhibited by oxygen. Then, the filled stone mould was immediately placed in the centre of a turntable inside the curing unit, and the door was closed tightly. The curing unit was set on the pre-programmed “Flipper/ Base” cycle, which lasts for 14 min, during which the temperature reaches between 108-112˚C. There are three halogen lamps in the curing unit, shown in Figure 5.4.

At the end of the curing cycle, the fan works automatically for 3 min to cool the chamber. Afterwards, the mould was removed and immersed in a bowl filled with tap water for 10-15 min, while ensuring that the water did not touch the specimens, so as to avoid contaminating the inferior and incompletely cured surface, thus interfering with its curing later.

After cooling, the specimens were turned upside down and covered with a layer of ABC, and then the mould was returned to the curing unit in the same way as before. The specimens were exposed to the light for 6 min at a temperature between 40-44˚C, using the pre-programmed “BP tissue side” cycle on the curing unit. This step polymerised the inferior surface of the specimen. At the end of the cycle, the automatic fan cooled the specimen again, for 3 min. The specimens were then removed from the moulds, and checked to ensure they were free of porosities.

5.2.5 Porosities

As noted earlier, the occurrence of porosities was a general problem with all materials. The number of porous specimens, types of porosity, and the conditions of their occurrence, were different, as explained in Table 5.1. An example of a porous specimen can be seen in Figure 5.5, Figure 5.6, and Figure 5.7. Following optimisation of HC, no specimen were discarded because optimisation has reduced porosity to a not significant level by testing both its effect on aesthetics and strength. All CC specimens were used following optimisation providing that they should be produced in a standard conditions of room temperature (19-24C). Ec and Ws produced so many porous specimens. In order to reduce the significant effect of porosity on their properties, some strategies were followed.

1. Being selective in choosing specimens and discarding the highly porous specimens and specimens which have big porosity by distinguishing them via visualisation.
2. Polishing specimens to remove superficial porosity.
3. Trying to avoid grossly porous areas during roughness and hardness testing.
4. During testing colour, same specimens were used before and after cleaning so that effect of porosity was ignored on colour change.
5. Fracture sides of 3 point bend test were visualised
6. Specimens of water sorption and water solubility were selected to be very small size and thin, that facilitate choosing specimens free of visible porosity.

Figure 5.4 Eclipse@ junior VLC Curing Unit

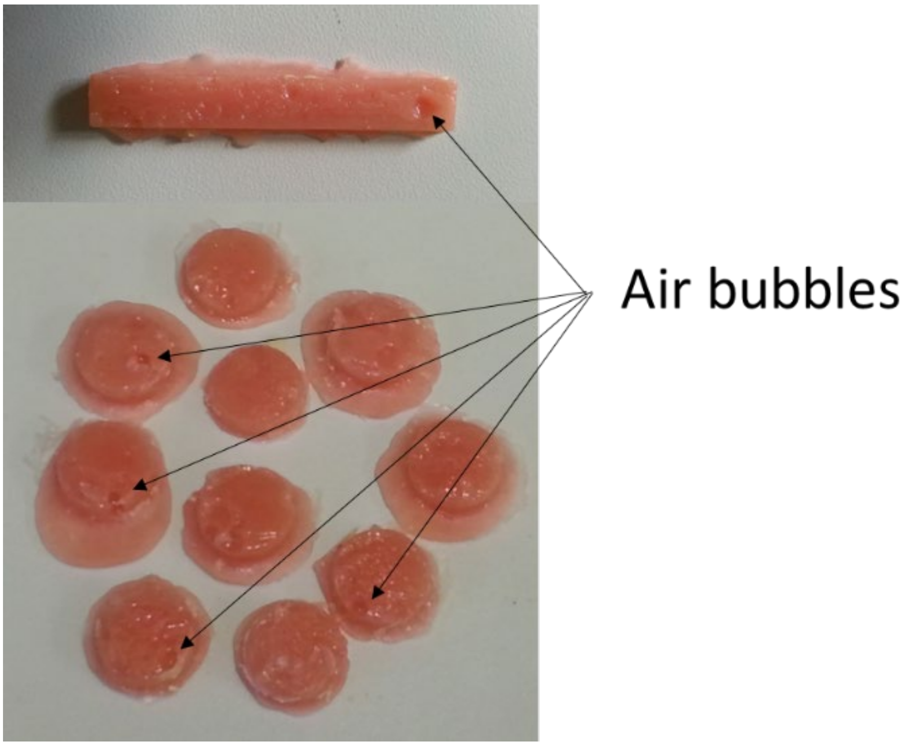


Figure 5.5 Porous Eclipse specimens

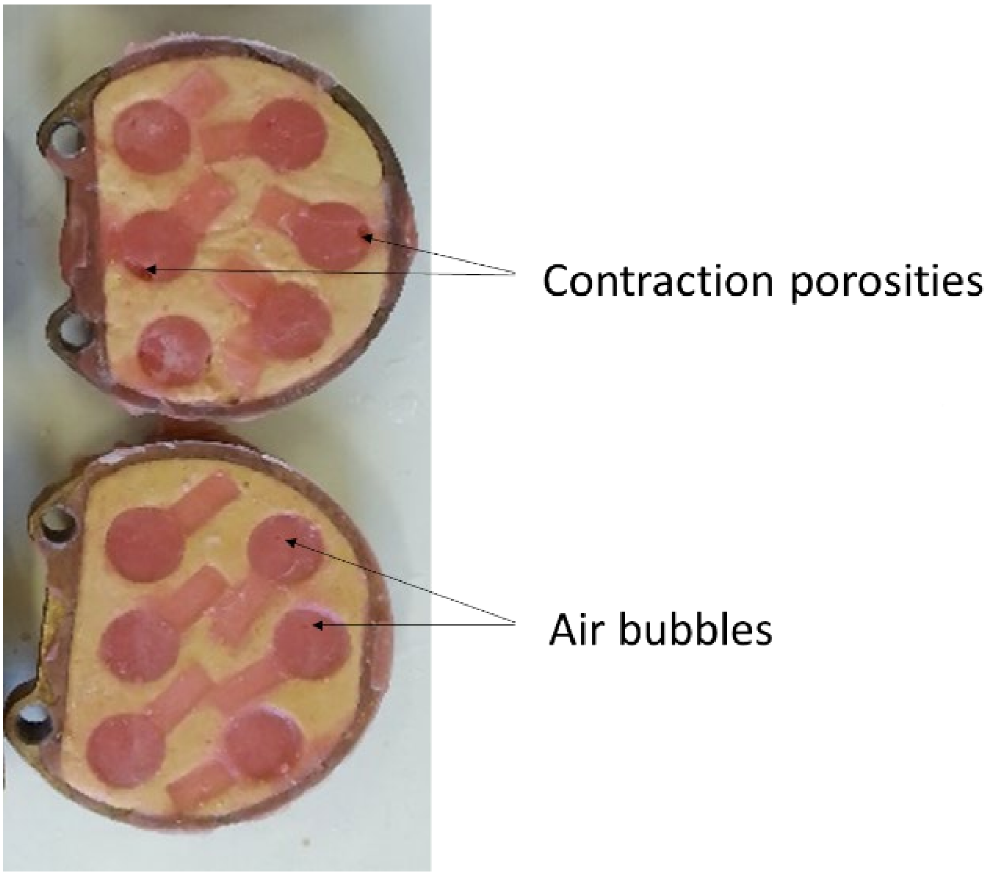


Figure 5.6 Porous Weropress specimens

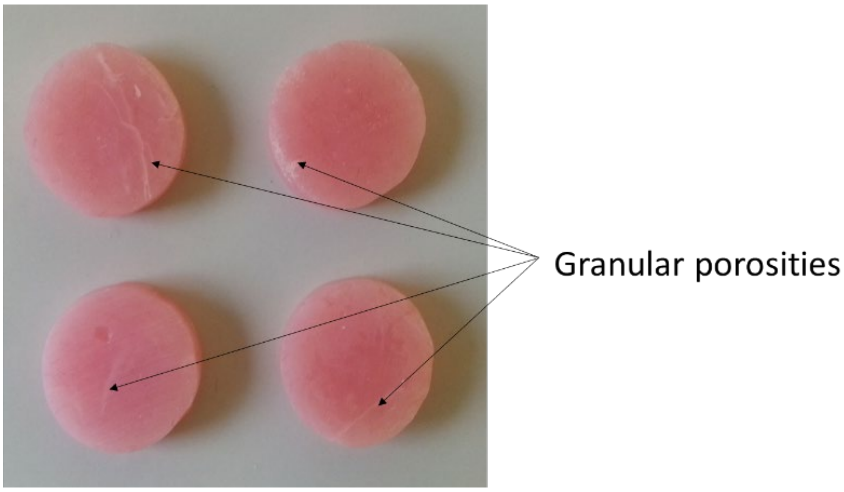


Figure 5.7 Porous CC specimens

Material	Specimen's shape	No. of porous specimens	Total no. in the batch	Type of porosity
HC	Bar	4	40	Gaseous
	Bar	1	40	
	Bar	0	40	
	Bar	0	40	
	Disc	3	90	
CC	Bar	0	40	Granular (at room temperature above 24 ˚C)
	Disc	0	90	
	Bar	40	40	
	Disc	90	90	
Ws	Bar	2	12	Contraction porosities and air bubbles
	Bar	9	24	
	Bar	2	12	
	Bar	6	12	
	Bar	6	12	
	Bar	1	6	
	Disc	12	24	
	Disc	12	24	
	Disc	6	18	
	Disc	6	12	
	Disc	1	12	
Ec	Disc	All specimens	All batches	Air porosity
	Bar	All specimens	All batches	

Table 5.1 Number of porous specimens in the tested materials

5.3 Polishing samples

The specimens of all the materials, after production, were trimmed to remove excess material, nodules and gross irregularities using a tungsten carbide bur (Dentorium, USA), mounted on a low speed hand piece (NSK Kakanishi. Inc., Japan). The specimens were then polished under tap water cooling, using P320 and P400-grit wet carbide sand paper (3M, USA) with a polishing machine (Metaserv 250, Buehler, UK), at a speed of 200 rpm, until they had flat upper and lower surfaces. These were checked by visual inspection.

The specimens were polished with a brush wheel and slurry of wet pumice (fine grain size) (Steribim, Metrodent, UK) to obtain the initial highly polished surface. The specimens were polished using a traditional technique for polishing by wetting a pumice with water until a mud-like material was produced. The wet pumice was then scooped by hand and placed randomly on the specimen, which was subsequently pressed against a rotating brush (Stoddard, Skillbond, UK) mounted on a lathe (Degussa, Germany), to gradually eliminate fine scratches. This procedure was repeated numerous times until the specimen surface was rendered smooth. The wet mass of sand contained in the holding pan was reused for all the specimens, and the brush was changed after being used with 20 specimens. The final high shine was achieved using a soft cloth wheel as polishing mop (Canning-lippert, Skillbond, UK) mounted on a lathe rotating at 2000 rpm with polishing compound (Canning-lippert Vanax, Skillbond, UK).

The specimens were checked with the naked eye for a smooth, scratch-free and glossy surface, which is the method followed by prosthodontic technicians when making dentures in Newcastle University Dental School. All the specimens were also evaluated for porosity by visual inspection. Highly porous specimens or specimens with large or deep porosities were discarded. Lightly porous specimens were also avoided as much as possible, unless it was impossible to make sound ones, or if their production was extremely time consuming. Small or shallow porosity can be removed or reduced by polishing. All the specimens were finished and polished by the same operator, who also judged the end polishing process to ensure the specimens had a highly polished surface.

The protocol of polishing was designed and developed according to the conventional and most commonly used polishing methods in prosthetic laboratories. Mechanical finishing using rotary instruments with a tungsten carbide bur and sand paper was followed by polishing with the pumice and polishing compound proved to be more effective than chemical polishing at producing a smooth surface (Al-Kheraif, 2014; Al-Rifaiy, 2010), and worked well within the roughness threshold (Rao et al., 2015). The grit size of the sand paper employed (P320 and P400) was the most common found in the literature (Mese and Guzel, 2008; Machado *et al*., 2012a; Peracini *et al*., 2010; Lima *et al*., 2006; Lira *et al*., 2012; Koroglu *et al*., 2016; Ural *et al*., 2011; Sharma *et al*., 2017; Regis *et al*., 2009). Regarding the quality of polishing, this grit size was also used following counseling from three dental technicians working in the Dental Hospital of Newcastle University.

Chapter 6 Comparing the physical and mechanical properties pre- and post-water immersion

6.1 Introduction

Normally, after production the dentures are worn in the mouth during daytime and immersed in water or disinfectant at night (Machado *et al.*, 2011). Therefore, they spend all their time immersed either in saliva, which mainly consists of water, at body temperature, or in water at room temperature (Cucci *et al.*, 1998; Salim *et al.*, 2012).

Water is a solvent and can be absorbed by polymers, thus interfering with polymer structure (Devlin and Kaushik, 2005), and it requires a considerable time to reach an equilibrium in polymers (McCabe and Walls, 2009; Asar *et al.*, 2013; Van Noort, 2013). In addition, polymers usually have some water soluble ingredients such as a plasticiser, residual monomer, initiator and activator, which dissolve in water (McCabe and Walls, 2009; Van Noort, 2013).

Previous studies have shown that these two properties, water sorption and solubility, influence material properties (Van Noort, 2013). They influence mechanical properties such as hardness (Kanie *et al*., 2004b; Neppelenbroek *et al.*, 2005; Sharma *et al.*, 2014), flexural strength (Sun *et al*., 2003; Machado *et al*., 2007; Qasim *et al*., 2012), and flexural modulus (Al-Mulla *et al.*, 1988; Ogle *et al*., 1986; Al-Mulla *et al*., 1989).

Denture base polymers show differences in their properties because of different polymerisation methods and the chemical composition of the resin. These reasons reflect on the molecular weight, amount of free monomer and degree of cross linking (O'Brien, 2008). Denture base polymers also show different responses following immersion in water. Therefore, any new material produced for the market is worthy of being tested for characterisation in fresh conditions and after exposure to aqueous solution at body and room temperature for different intervals of time. It is also important to arrange this material correctly in regard to other conventional materials.

6.2 Aims and Objectives

The aim of this chapter was to characterise Ec and Ws materials and find out their ranking in comparison with HC as a positive control and CC as negative control. This characterisation and comparison was achieved as follows:

1. Testing materials for flexural strength and modulus, hardness, and roughness after production for characterisation and ranking.
2. Testing specimens for water sorption and solubility, flexural strength and modulus, hardness, roughness, and colour stability after immersing them in water for different lengths of time, including: 2 days at RT, 1 week, 1 month, 3 months, and 6 months at 37ºC, then, characterising and ranking materials.

6.3 Water sorption and solubility

6.3.1 Materials and methods

Bar specimens were prepared and polished as previously described for each material (Sections 5.2.1, 5.2.2, 5.2.3, 5.2.4 and 5.3). These specimens were sectioned under water cooling using disc bur (Skillbond, UK) to produce square-shaped specimens (10 x 10 mm, 3.5 mm thick, n=50), as in Figure 6.1A. The specimens were divided into 5 groups (n=10) as described in Table 6.1 (but no BL group as this group represents pre-water immersion). The specimens were then stored in individual cylinder plastic containers (25 mm diameter x 38 mm height, polystyrene, Fisher Scientific). The steps for performing the water sorption and solubility test were based on ISO 20795-1:2013 (BSI, 2013), except for the size of the specimen.

The specimens of each group were placed separately inside marked unsealed containers, and then inside a desiccator containing fresh silica gel, and kept in an oven for 24 h, as in Figure 6.1B. All groups were stored at 37˚C, except group 2D which was stored at room temperature. The desiccator was then removed from the oven and left for two hours at room temperature. Next, the samples were weighed using an analytical electronic balance with an accuracy of 0.01 mg (Mettler AE 240, Switzerland), and returned to the sealed desiccator. This cycle was repeated and samples were weighed daily until an equilibrium was established, defined as when there was no more than 0.2 mg reduction in mean weight between each 24 h interval. This weight was called the conditioned weight and was designated as m_1. After conditioning and prior to storing samples in water, volume was calculated for each specimen (V), using the means of three lengths, three widths, and three thicknesses measurements. Then, the specimens were stored in their individual containers filled with distilled water. Storage followed the storage groups shown in Table 6.1.

At the end of each time point, the specimens were removed from distilled water, wiped with a clean towel until they became free of visible surface moisture, waved in air for 15 s whilst being held with tweezers, and weighed within 1 min of removal from the water. This weight was designated as m_2.

Specimens were then reconditioned to a dry constant mass following identical procedures of conditioning samples. This constant mass was designated as m_3. The temperature of conditioning and reconditioning was similar to the temperature of storage. Water sorption (Wsp) and solubility (Wsl) then were calculated, in µg/mm^3, using the following equations:

Water sorption $= m_2 - m_3 / V$

Water solubility $= m_1 - m_3 / V$

The results were rounded up to the closest 0.1 µg/mm^3. All data were tested for normality using the Shapiro-Wilk test. Where data were found to be non-normally distributed, the median and interquartile ranges were calculated as measures of average value and variability. The data were analysed using the Kruskal-Wallis test, and the Tukey-post hoc method was used to determine the significant differences between groups (Sigma Plot version 13.0) at a confidence level of 95%.

Period of Storage in Distilled Water (days)	**Temperature of Water**	**Group Symbol**
0	-----------	BL
2	Room temperature	2D
7	37˚C±1	1W
30	37˚C±1	1M
90	37˚C±1	3M
180	37˚C±1	6M

Table 6.1 Storage test groups

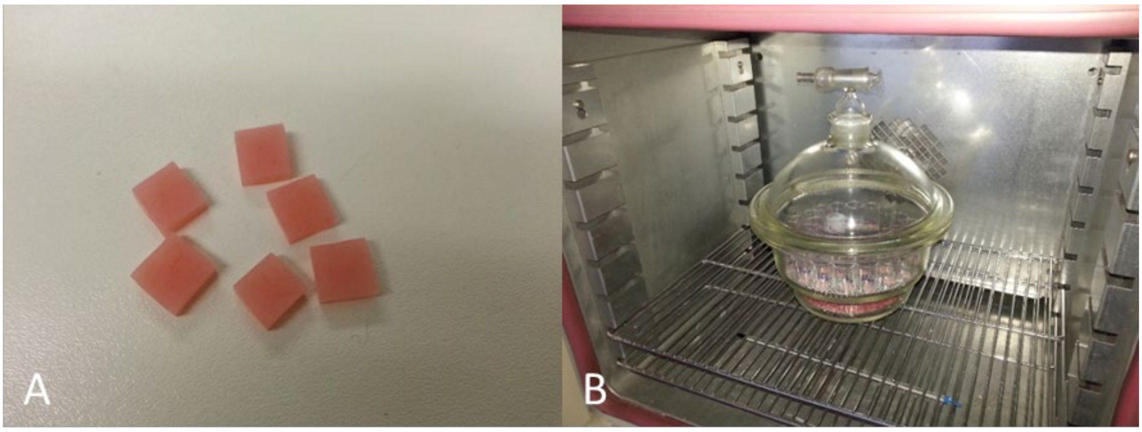


Figure 6.1 (A) Water sorption specimens, (B) Water sorption specimens inside an incubator in a desiccator

6.3.2 Results

The results of the water sorption test were not normally distributed data (Shapiro-Wilk test, $P<0.001$). Details of median values can be seen in Table 6.2. Typical graphs, representing specimen's weight behaviour for each individual group during the whole period of conditioning; water immersion; and reconditioning, are presented in Figure 6.2. Each graph for each material consists of three parts: the first part, which starts from the beginning and ends with the lowest point before ascending, represents the dehydration (conditioning) of specimens in silica gel until weight became constant; the second part is the ascending part of graph, which represents immersing samples in water; the third part is the descending part, which represents the re-dehydration (reconditioning) in silica gel after removal from water. The third part shows that losing moisture during re-dehydration was much faster than absorbing water in the second part. The shape of the first part for each material depends on how much moisture the specimens contain. The general shape of the curves was similar for HC, CC, and Ws, but different for Ec. The difference was mainly in the second and third parts, where the Ec curve did not rise to the same level as the other PMMA-based materials during a certain period, and descended more gradually and slowly than other materials. The standard deviation was high for all materials at all time-points, so no error bars are shown on the graphs for clarity.

Median water sorption values were summarised in a graph (Figure 6.3). The graph very clearly shows that the shape of the curve for all PMMA materials was similar, and different from the Ec curve. However, the results of Kruskal-Wallis of different materials were significantly different from each other ($P\leq0.001$), as shown in Table 6.2 and Table 6.3. For each individual material, Kruskal-Wallis also showed significant difference between storage groups. Tukey test showed no significant difference between 2D and 1W ($P>0.05$), which the former was significantly different from 1M, 3M and 6M ($P\leq0.05$); there was no significant difference between 1M, 3M, and 6M time points ($P>0.05$). HC showed the highest water sorption value, while Ec was the lowest ($P\leq0.05$). Ec was not significantly different from CC ($P>0.05$), but was significantly different from HC and Ws ($P\leq0.05$). Ws showed higher water sorption than CC, although there was no significant difference between them ($P>0.05$).

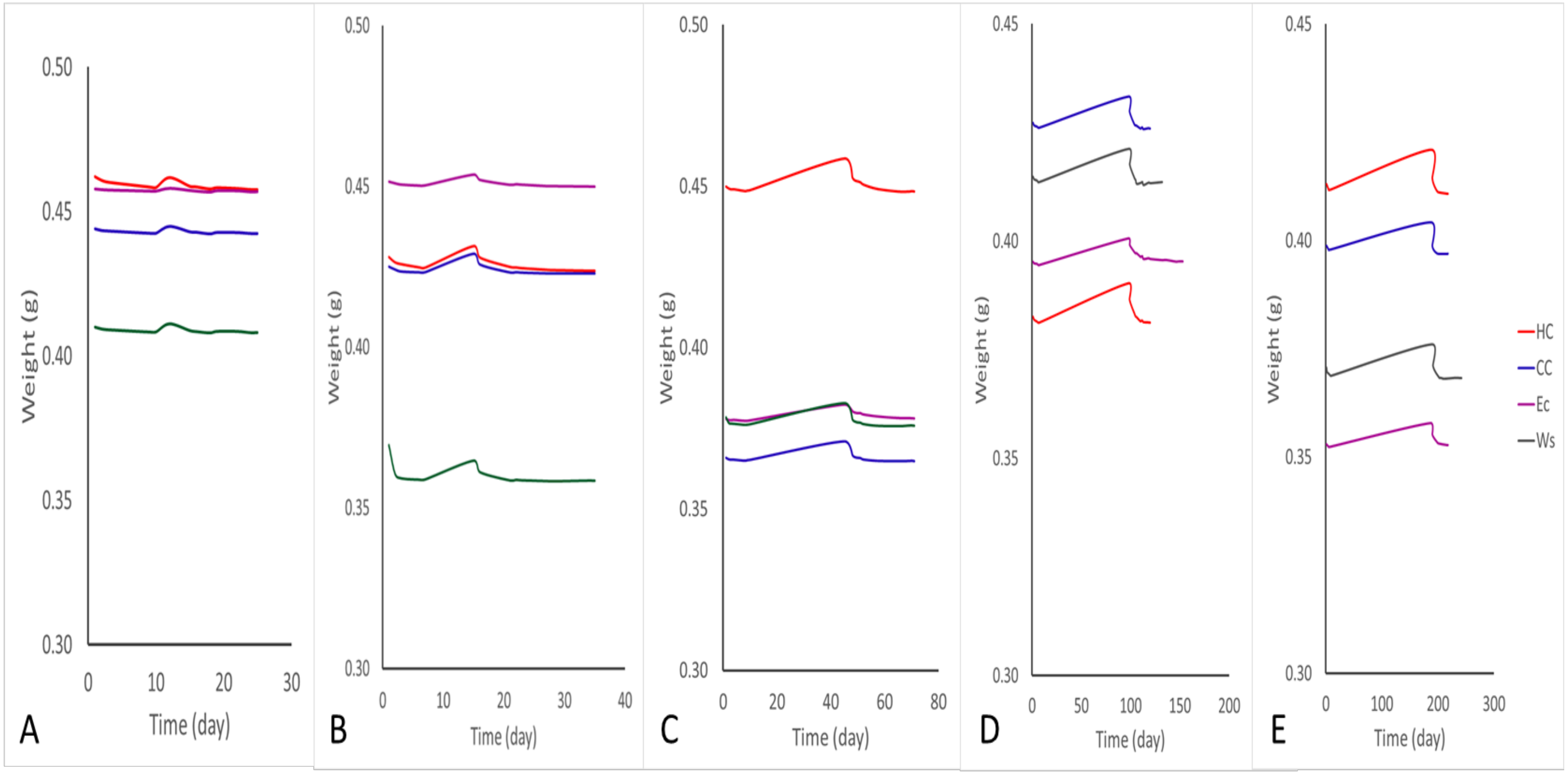


Figure 6.2 Typical behaviour of each of the four compared materials during the water sorption test: (A) 2D group, (B) 1W group, (C) 1M group, (D) 3M group, (E) 6M group

Material	**Storage Group**	**Water sorption [µg/mm^3] median (IQR)**
HC	2D	10.8 (0.9)^{aA}
	1W	21.5 (1.5)^{bC}
	1M	26.4 (0.4)^{aE}
	3M	27.3 (0.7)^{abG}
	6M	28.6 (0.7)^{abI}
CC	2D	6.7 (0.3)^{cA}
	1W	16.2 (0.3)^{dC}
	1M	19.2 (0.3)^{cE}
	3M	19.9 (0.4)^{cdG}
	6M	20.8 (0.3)^{cdI}
Ec	2D	3.3 (0.2)^{eAB}
	1W	8.8 (0.4)^{fCD}
	1M	12.8 (0.3)^{eEF}
	3M	15.2 (0.6)^{efGH}
	6M	15.6 (1.2)^{efIJ}
Ws	2D	8.3 (0.4)^{gB}
	1W	18.4 (3.5)^{hD}
	1M	21.3 (0.2)^{gF}
	3M	21.6 (0.7)^{gH}
	6M	25.0 (0.5)^{ghJ}

Table 6.2 Summary of water sorption values for compared materials and their significant differences (similar superscript letters refer to significant differences, uppercase letters for materials and lowercase letters for storage groups)

Storage group of water sorption	Materials	Kruskal-Wallis result (P-value)
2D	HC	≤0.001
	CC	
	Ec	
	Ws	
1W	HC	≤0.001
	CC	
	Ec	
	Ws	
1M	HC	≤0.001
	CC	
	Ec	
	Ws	
3M	HC	≤0.001
	CC	
	Ec	
	Ws	
6M	HC	≤0.001
	CC	
	Ec	
	Ws	

Table 6.3 Details of the group comparison of the water sorption test for different materials

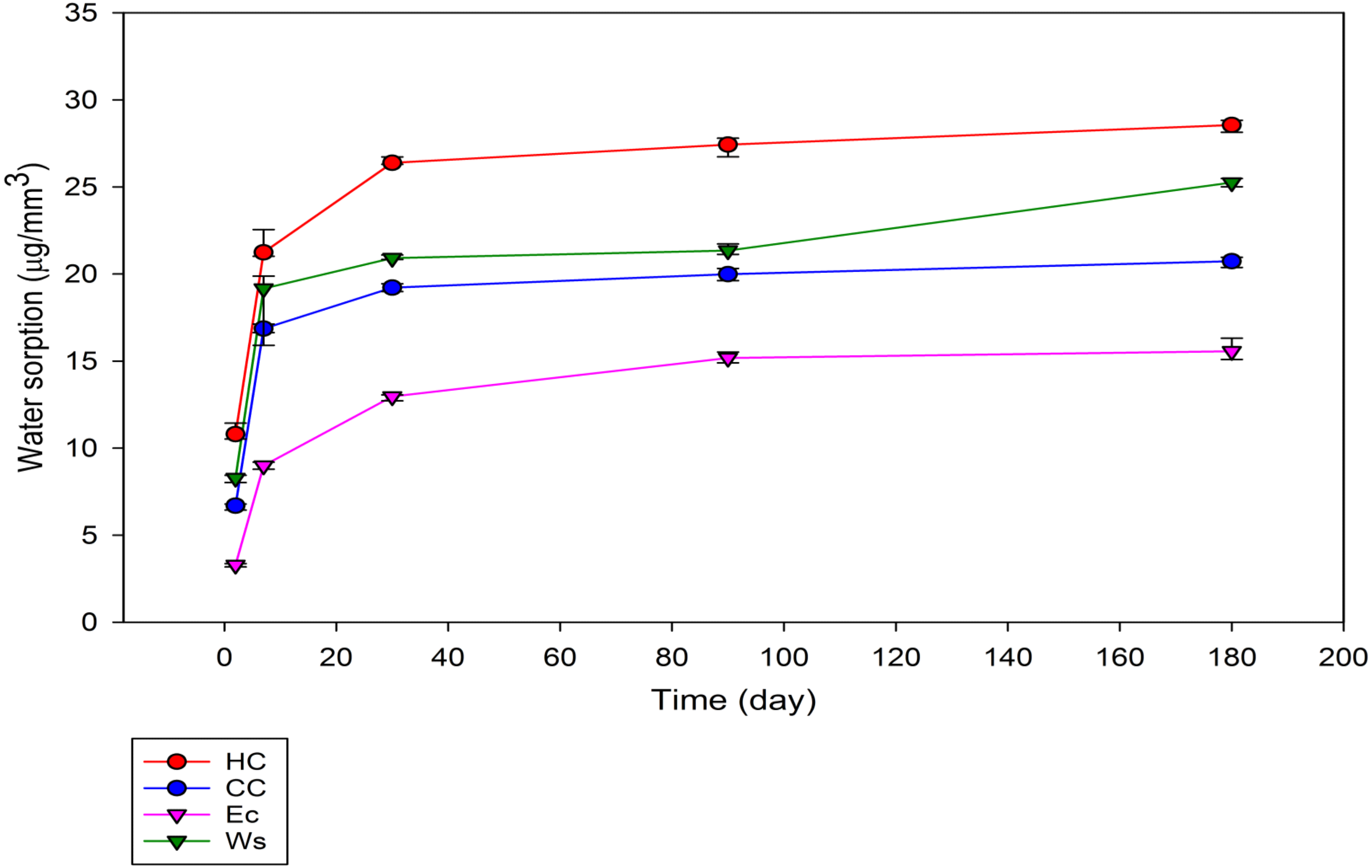


Figure 6.3 Summary of the median water sorption value changes over time for the four compared materials. Error bars represent upper and lower quartiles

The results of the water solubility test were not normally distributed data (Shapiro-Wilk test, P<0.001). Details of median values can be seen in Table 6.4. There is a highly significant difference between materials at each time point and, a highly significant difference between storage groups, for each individual material (Kruskal-Wallis, P≤0.001), as shown in Table 6.4 and Table 6.5.

Median values are represented in a graph (Figure 6.4). The most prominent result was that Ec showed the lowest value after 1W, which is located in minus area, while HC had the highest before 1M, and was significantly different from other materials (P≤0.05). Ec was significantly different from other materials (P≤0.05). Overall, Ec and HC showed a similar pattern, and Ws and CC showed a similar pattern. The highest solubility for HC and Ec was at 1W, while that for Ws was at 1M, and for CC was at 6M. Overall, the minimum solubility for all materials was reached at 3M, and after this it rose again. Ws was fluctuating but there was no significant difference from CC (P>0.05), except at 6M. The graph also demonstrates that all materials' solubility was in the positive area except for Ec after 1W and HC at 3M.

Material	**Storage Group**	**Water solubility [µg/mm^3] median (IQR)**
HC	2D	1.9 (0.1)^{aA}
	1W	2.8 (0.5)^{bB}
	1M	1.2 (0.2)^{cC}
	3M	-0.3 (0.3)^{abd}
	6M	2.5 (0.2)^{bcdH}
CC	2D	0.3 (0.2)^{aA}
	1W	0.4 (0.1)^{bB}
	1M	1.3 (0.3)^{acD}
	3M	0.3 (0.2)^{cdF}
	6M	2.6 (0.4)^{abdI}
Ec	2D	0.6 (0.1)^{aA}
	1W	0.6 (0.2)^{bB}
	1M	-2.0 (0.2)^{abCDE}
	3M	-2.4 (0.3)^{abFG}
	6M	-0.8 (0.9)^{bHI}
Ws	2D	0.5 (0.1)^{aA}
	1W	0.4 (0.3)^{bB}
	1M	1.6 (0.7)^{abcCE}
	3M	0.1 (0.6)^{cdG}
	6M	1.5 (0.3)^{abdI}

Table 6.4 Summary of water solubility values for the compared materials and their significant differences (superscript similar letters refer to significant differences, uppercase letters among materials and lowercase letters within same material)

Storage group of water solubility	Materials	Kruskal-Wallis result (P-value)
2D	HC	≤0.001
	CC	
	Ec	
	Ws	
1W	HC	≤0.001
	CC	
	Ec	
	Ws	
1M	HC	≤0.001
	CC	
	Ec	
	Ws	
3M	HC	≤0.001
	CC	
	Ec	
	Ws	
6M	HC	≤0.001
	CC	
	Ec	
	Ws	

Table 6.5 Details of group comparisons of water solubility between materials

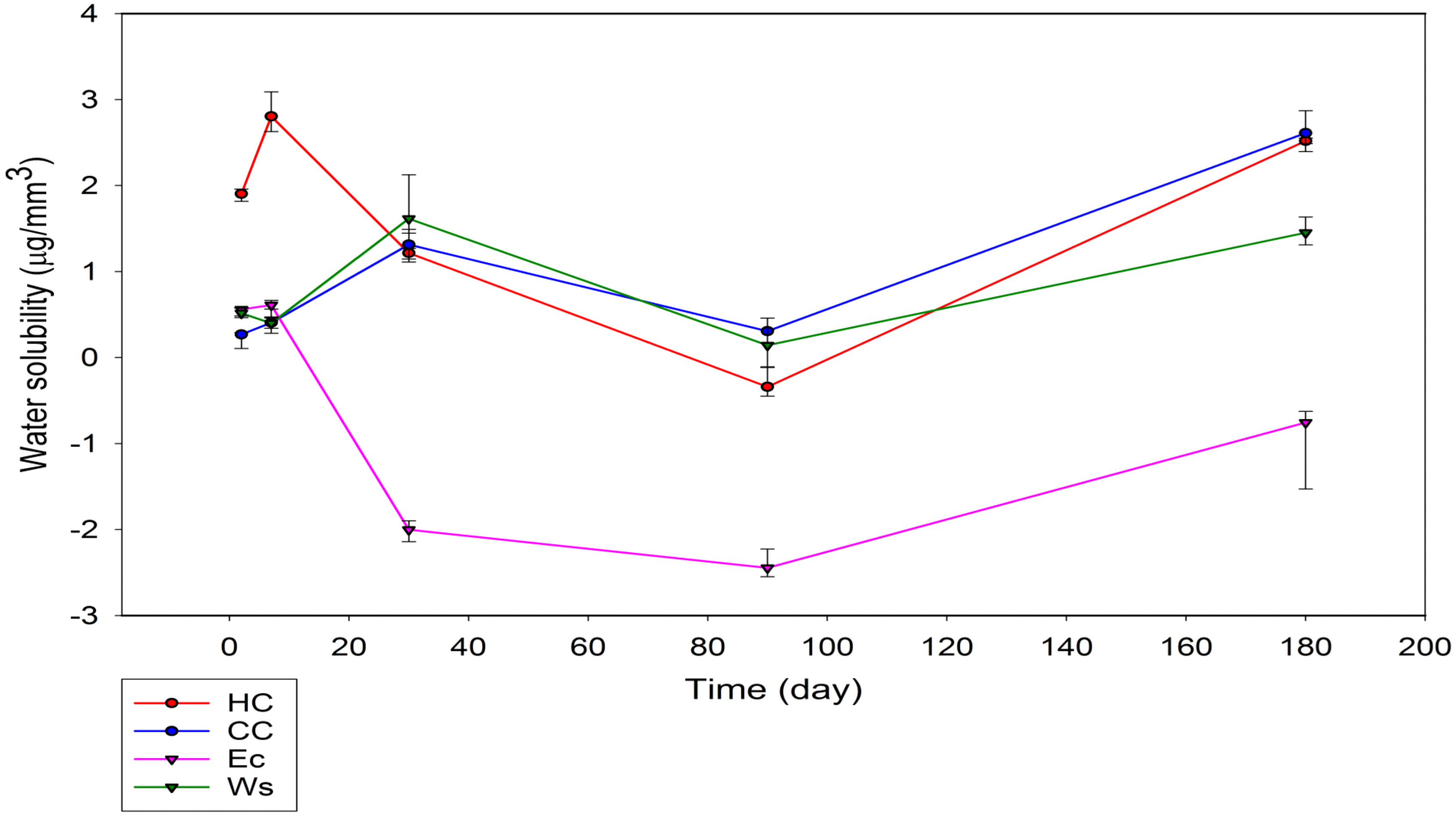


Figure 6.4 Summary of the median water solubility value changes over time for the four comparable materials. Error bars represent upper and lower quartiles

6.3.3 Discussion

In the current study, samples were stored in water at room temperature at 2D time-point to simulate the storage of dentures in water after fabrication and before insertion into a patient’s mouth. This is usually done to remove the major part of residual monomer (Vallittu *et al*., 1995; Melilli *et al*., 2009; Bayraktar *et al*., 2006; Jorge *et al*., 2003), and restore some of the volume lost by polymerisation contraction (McCabe and Walls, 2009; Van Noort, 2013). All other groups were stored at 37 ±1˚C to simulate body temperature (Cucci *et al.,* 1998; Mese *et al.* 2008; Akin *et al.,* 2014b; Sharma *et al.,* 2014; Rahal *et al.,* 2004; Mutluay *et al*. 2013; Finoti *et al.,* 2012; Neppelenbroek *et al.,* 2005). These time points were selected following the most commonly used regime in the literature (Table 2.2), to represent long term period (Hersek *et al*., 1999; Neppelenbroek *et al*., 2005), and to pass saturation time.

The most interesting findings revealed that Ec showed the lowest water sorption in comparison to other materials and at all-time points, which was significantly different from HC and Ws, but not from CC (Figure 6.3). This finding was supported by previous studies (Mutluay *et al*., 2013; Akin *et al*., 2014b), in which Ec was compared with heat-cured PMMA up to 6 months and with pourable type cold-cured PMMA up to 76 days, and showed a lower water sorption. There is no study in the literature which has compared Ec with either cold-cured PMMA or Ws, and so we have no other data to support or reject our findings regarding these materials. The finding that Ec absorbed less water than other PMMA materials can be attributed to the inherent structure of Ec, which most likely consists of a copolymer of UDMA rather than a polymer. UDMA monomer has a high water sorption and solubility with a high rate of polymerisation, 60% degree of conversion, and high molecular weight. Therefore, UDMA was mixed with hydrophobic monomers in the Ec ingredients to produce a copolymer showing favourable properties regarding sorption, solubility and the degree of conversion (Gajewski *et al*., 2012). Ec also has less soluble content and no free monomer (Melilli *et al*., 2009) as these ingredients may dissolve, leaving spaces for more water occupancy (Van Noort, 2013). In addition, the semi-crystalline cross-linked structure of Ec reduces the diffusivity (Sun *et al*., 2003).

Ec reached water saturation at 3M while HC, CC, and Ws have arrived at water saturation at 1M. This result needs to be interpreted with caution. Ec saturation occurred at this time point, although there was no significant difference between 3M and 1M and between 1M and 1W groups, due to a gradual and continuous increase in water sorption. However, 3M group was significantly different from 2D and 1W groups, and there was not significant increase in sorption values in 6M group. This finding is in line with the findings of Mutluay *et al*. (2013) and Akin *et al*. (2014b), in which the authors found that Ec reached saturation between 70-90 days. The saturation point of PMMA materials was at 1M because it was significantly different from the preceding time point (2D) and not significantly different from later time points which showed the least increase in sorption values. The difference in saturation time point between Ec and other PMMA-based materials is mainly due to the difference in the coefficient of diffusion between different backbone polymers (Al-Mulla *et al*., 1988; Al-Mulla *et al*., 1989). The coefficient of diffusion influenced the pattern of water absorption, which was gradual for Ec and steeper for Ws, HC, and CC, as approved in previous studies (Mutluay *et al*., 2013; Akin *et al*., 2014b).

HC absorbed the highest amount of water compared to other PMMA materials; however, it was within International Standard Organisation requirements. It was significantly different from CC but not significantly different from Ws, as found in previous study (Cucci *et al*. 1998; Polat *et al*., 2003). This high absorption may be due in part to high solubility, where soluble ingredients provided spaces for more water absorption (Figure 6.4). It may also be due to the curing method followed for Ws and CC, which used pressure, and which in turn increased the density and reduced the size of the air voids that could be included (Keller and Lautenschlager, 1985) and subsequently decreased water sorption to be less than HC.

Ws absorbed more water than CC but not statistically significant despite both being of the same type of polymer and method of polymerisation. Different formulation of materials including mixing ratios, the accelerator, and cross-linker might have increased the free monomer level in Ws and subsequently increased the absorption indirectly (Dogan *et al*., 1994; O'Brien, 2008). Free monomer raises the likelihood of getting porosity in addition to contraction porosity caused by low mixing ratio (shown in Table 5.1) (Keller *et al*, 1974; Keller and Lautenschlager, 1985; Nejatian *et al*, 2015). These porosities absorb more water until being full. Higher pressure was applied on CC than Ws when setting which might have caused a difference in the density, resulting in CC being denser than Ws and absorbing less water (Keller and Lautenschlager, 1985). For the latter reason, CC was also not statistically significantly different from Ec.

The water uptake at 1W was higher than at 2D but not significantly for all materials, possibly due in part to the increase in water temperature from room temperature to 37˚C. This increase in temperature helps the material expand, and increases the mobility of water molecules into the material (Machado *et al*., 2012b). It may also be due to increasing the time of immersion in water before reaching saturation (Compagnoni *et al.,* 2004). The process of sorption and solubility take place concomitantly (McCabe and Walls, 2009) so the presence of soluble ingredients, including free monomer, slowed sorption in the first 2 days (Melilli *et al*., 2009). After this, more spaces left by the dissolution of these ingredients were available for occupation by water.

The most interesting solubility result is related to Ec, as it had the lowest solubility in comparison with the other materials and reached the maximum at 1W. This may suggest there was no free monomer (Melilli *et al*., 2009) and very few water soluble ingredients. It may also be due to low sorption.

After the peak, the solubility curve was mainly located in the minus area of the curve, which means the specimens after re-dehydration or reconditioning were heavier than those before immersion in water. In other words, the specimens could not be dehydrated completely and some water molecules were trapped inside the polymer network, or reacted with them. The difficulty of dehydrating Ec specimens, as shown in Figure 6.2, may be attributed to the entrapment of water molecules in a semi-crystalline, highly cross-linked structure or reaction of water molecules with material. The solubility curve continued downward up to 3M, which means the amount of water trapped within the material was increasing with increased water absorption, until saturation at 3M. After this, the solubility increased again but not significantly. This increase in solubility might be attributed to the dissolution of the polymers after storage in water for more than 3 months (Van Noort, 2013).

HC showed the highest solubility of other PMMA comparator materials. This value exceeds the minimum requirement for water solubility according to ISO 20795-

1:2013 (BSI, 2013), and was also reported Polat *et al*. (2003). Although CC and Ws are chemically cured and have a strong tendency to have free monomer, the high solubility of HC might be associated with the amount of water soluble ingredients, such as the initiator and plasticiser, and their formulation, as the material's formulation and its cross linkage has not been disclosed by the company regarding these components (Pfeiffer *et al*., 2004; Jagger and Huggett, 1990). This high solubility might also lead to high water sorption.

HC solubility reached a peak at 1W, meaning that most of the soluble ingredients of HC were removed rapidly within this time. Dissimilar to HC, Ws and CC solubility reached a peak at 1M, which might be attributed to a difference in the solvolysis or feasibility to dissolve the soluble constituents predominant in Ws and CC (Arima *et al*., 1995a). After 1W, HC solubility had reduced to the minimum. This reduction is attributed to the increasing tendency of the PMMA to trap water molecules, or to react with them (Ferracane, 2006). After the peak of HC solubility, there was no significant difference between HC, CC, and Ws, similar to what reported by Craig *et al*. (2004). This result was also supported by previous results from Al-Mulla *et al*. (1988), Cucci *et al*. (1998), and Polat *et al*. (2003).

All materials in this study showed an increase in solubility at 6M, which might be attributed to dissolution. Therefore, it can be hypothesised that increasing the solubility at 6M for all compared materials means initiation of dissolution after the dentures are used for more than three months in aqueous solution. This increase in solubility did not cause an opposing increase in sorption, as dissolution might have caused a reduction in the volume, so that no more water could be absorbed by the fully saturated specimens.

Ws solubility behaviour was similar to CC with a little higher solubility but there was no statistically significant difference between them, up to 90 days, because they have the same type of polymer (type 2) and thus same chemical reaction. However, different formulations of mixing ratio, cross-linker, and accelerator may account for the slight difference, as it increases the free monomer and subsequent solubility (O'Brien, 2008). At 6M, Ws solubility was statistically significantly lower than CC, as Ws has less potential to dissociate. This potential may be attributed to the presence of crystalline barbituric acid compounds (Lewis *et al.*, 2004). The dissociation of CC and Ws at 6M may be accompanied by the leaching of plasticizers which have not leached yet.

Water solubility in PMMA-based materials is highly variable because it is related to free monomer as one of the main soluble ingredients, in addition to other soluble ingredients. In addition to the type of reaction, the amount of free monomer might be related to mixing ratio (O'Brien, 2008), and the way of dealing with specimens such leaving specimens in air for different lengths of time before starting the test may cause evaporation some of free monomer (Ferracane, 1995; Dhuru, 2005; Van Noort, 2013). Sample size, minute variations in manipulation, and using a different batch for different test groups, may also be responsible for these variations.

6.3.4 Conclusion

Ec showed the least water sorption value up to 180 days in comparison to the PMMA materials. Ws sorption was not significantly higher than CC, but less than HC. The descending order was: HC, Ws, CC, and Ec respectively.

Ec has the least solubility up to 180 days compared to the tested PMMA materials. Ws showed no significant difference in solubility from CC up to three months, but was variable in comparison with HC.

6.4 Flexural properties

6.4.1 Materials and methods

102 bar specimens for each of the four materials were made and polished with dimensions of 65*10*3.5 mm, following a similar procedure as described in Sections 5.2.1, 5.2.2, 5.2.3, 5.2.4 and 5.3. These specimens were divided into six groups (n=17 per group). Five groups were stored in distilled water following the storage regime illustrated in Table 6.1.

At the end of each storage period, the specimens were removed from water and dried with absorbent paper. Next, they were numbered, and the thickness and width of each specimen were measured three times using a Vernier calliper (Mitutoyo, Japan), and the means were calculated for both dimensions.

All groups were tested with a 3-point bending test, as shown in Figure 6.5, and the flexural strength and flexural modulus were calculated following similar procedures to those explained previously (Section 4.3.1). The median and interquartile range was calculated for the flexural strength and modulus for each group. Statistical analysis on data was carried out using non-parametric group comparison using a Kruskal-Wallis test to show if there were significant differences between groups. Dunn’s method was used to test the power of significance between multiple groups using Sigma Plot statistical software version 13.0 at a confidence level of 95%.

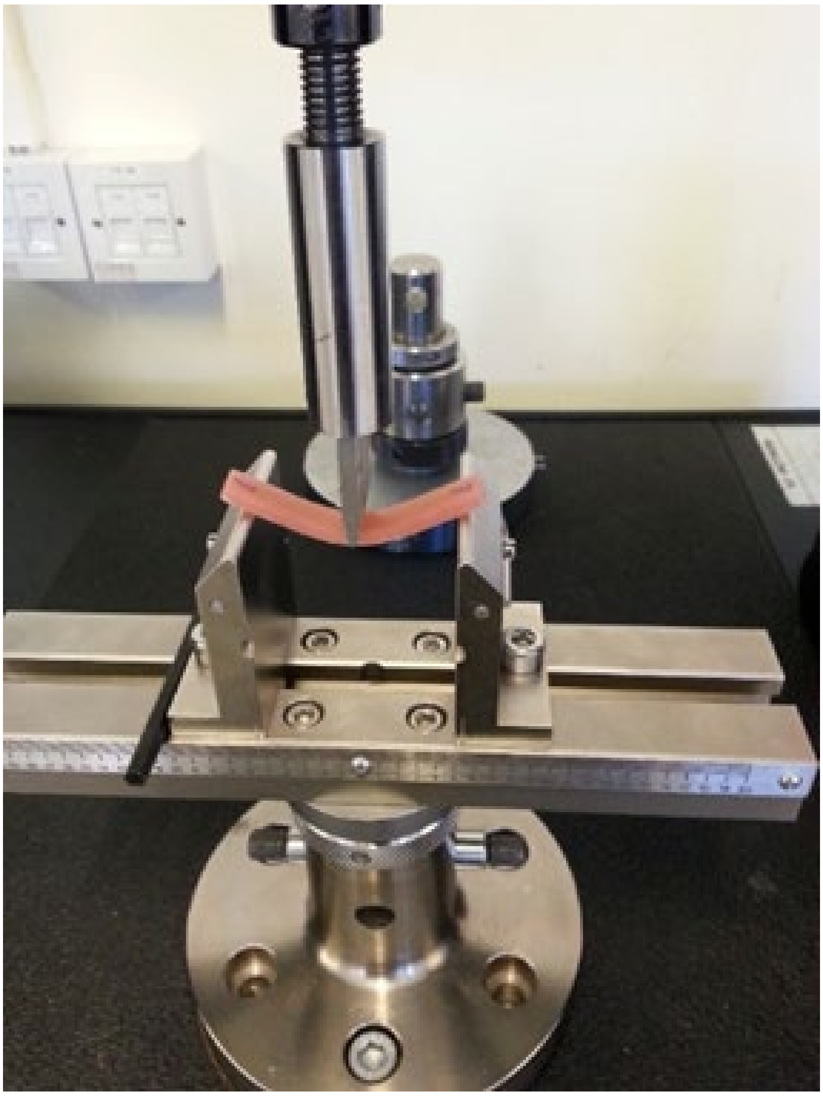


Figure 6.5 The three point bend test set-up showing a typical specimen during testing

6.4.2 Results

During the 3-point bending test, most specimens broke but some remained unbroken. The number of broken and unbroken specimens can be seen in Table 6.6. For the broken specimens, the breakage line was approximately in the middle, close to the point of load application, except for Eclipse, which fractured into many small pieces (see Figure 6.6).

Typical graphs for each material at each storage group are shown in Figure 6.7, Figure 6.8, Figure 6.9, and Figure 6.10 for HC, CC, Ec and Ws, respectively. These graphs show behaviour of selected specimens whose strength and modulus values were the closest to the median values for each parameter. All graphs show a primary area where there was no increase in the load applied, which represents the gap between the specimen and plunger before starting the test. Next, a straight ascending line represents the increase in load in the elastic region. Finally, the line continues non-linearly, according to plastic deformation, until the end of the curve at the fracture load. HC graphs showed no plastic deformation. The fracture load was the same as the maximum load, and is located at the end of the straight line. The displacement was approximately 6-9 mm at failure. The shape of the curves was consistent for all storage times. CC and Ws had similar graphs. Both indicated elastic and plastic deformation at BL and 2D, while all other testing time points showed no plastic deformation. In regard to CC, the displacement at failure was about 15 mm at BL, which reduced after 2D to a range of 4-7 mm. No further change in the overall shape of the curve was found at 3M and 6M groups. In regard to Ws, the displacement was 13 mm at BL, and after 2D was 4 mm. The graphs at 1M, 3M, and 6M showed the same overall shape. The Ec graphs had elastic and plastic deformation at BL, 2D, 1W, and 1M groups, while at 3M and 6M only elastic deformation was observed. The displacement was 11-14 mm until 1M and then decreased noticeably to 6.5-7.5 mm at 3M and 6M.

Group\Material	HC	CC	Ec	Ws
BL	All broken	All broken	All broken	1 unbroken
2D	All broken	4 unbroken	2 unbroken	3 unbroken
1W	All broken	All broken	All broken	All broken
1M	All broken	All broken	All broken	All broken
3M	All broken	All broken	All broken	All broken
6M	All broken	All broken	All broken	All broken

Table 6.6 Number of broken and unbroken specimens for each test group

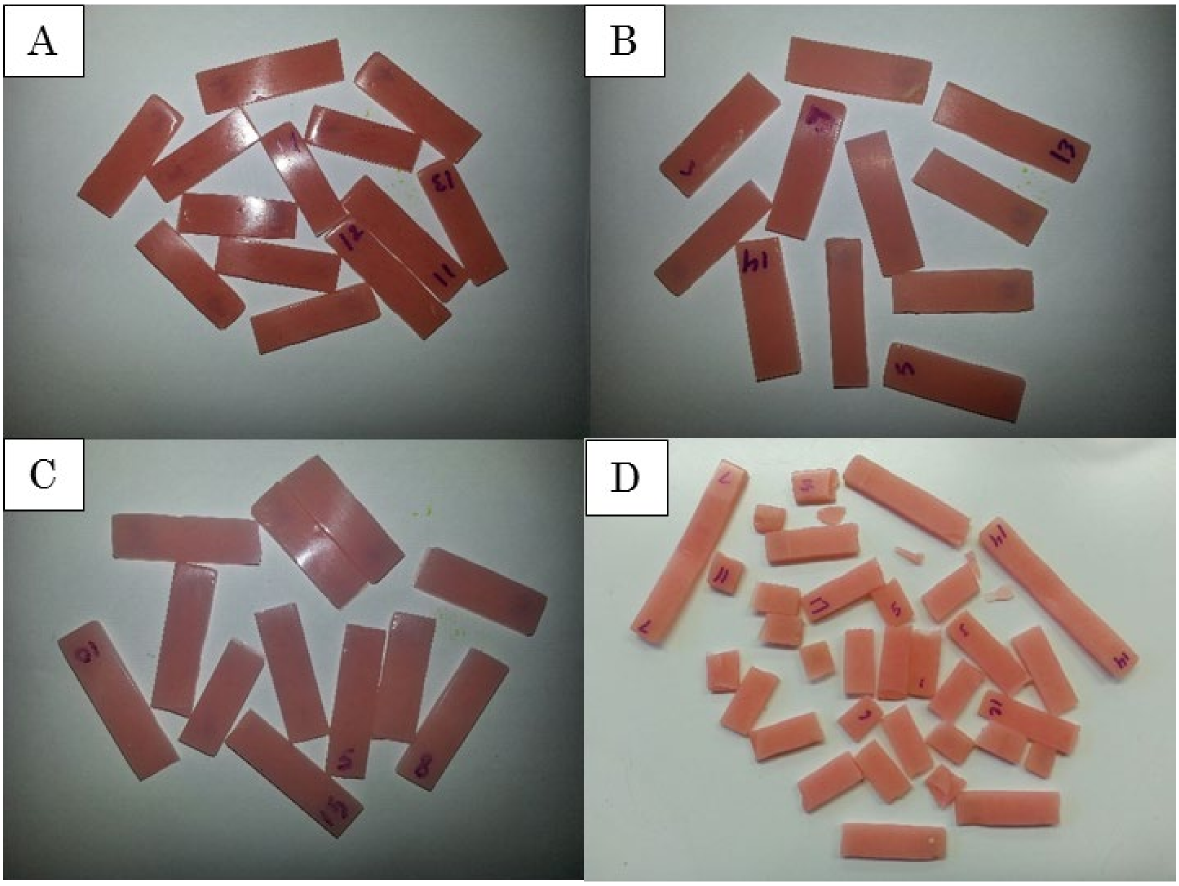


Figure 6.6 Specimens after the 3-point bend test application: (A) Ws, (B) CC, (C) HC, and (D) Ec

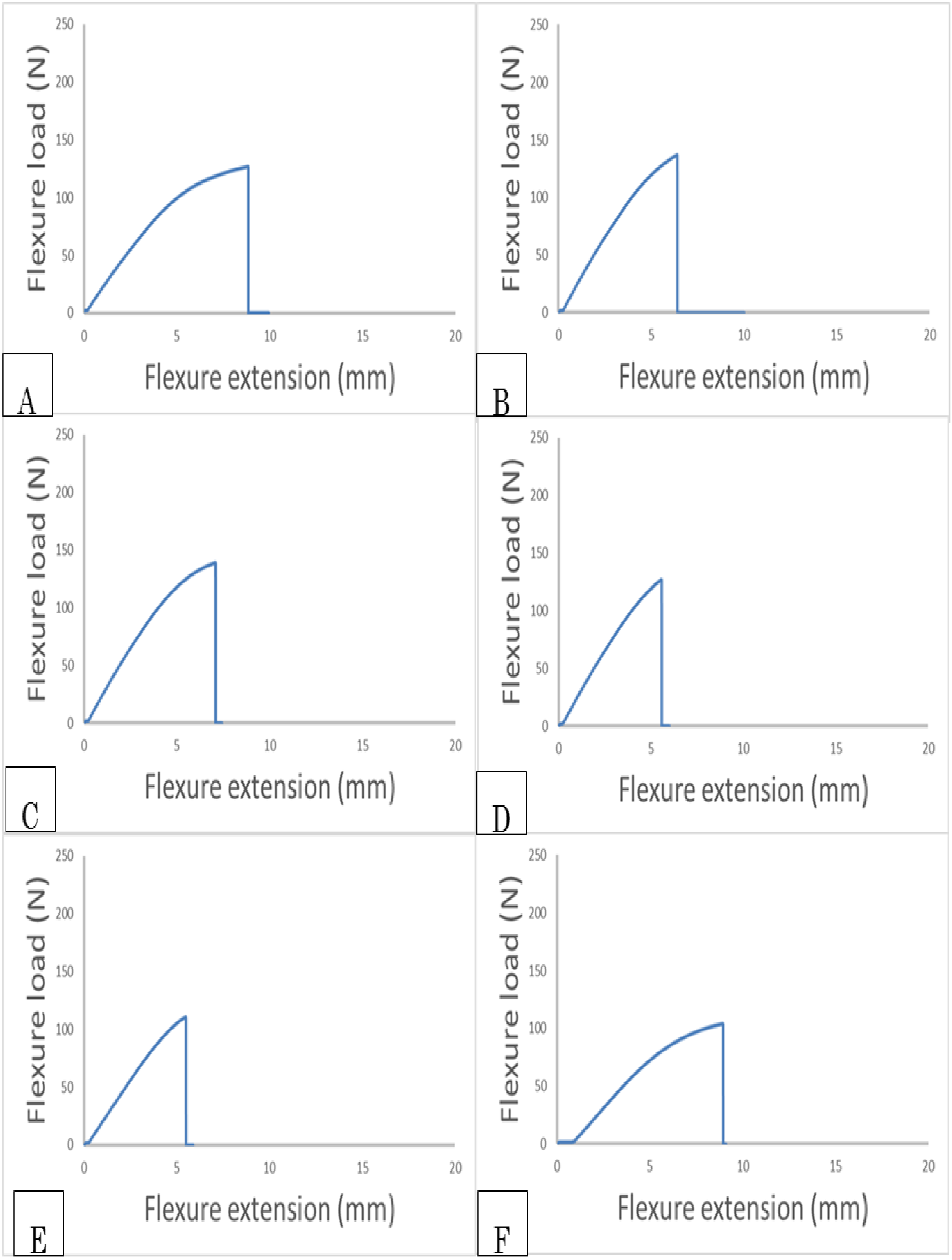


Figure 6.7 Typical curve for the flexural test of HC at different storage groups: (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

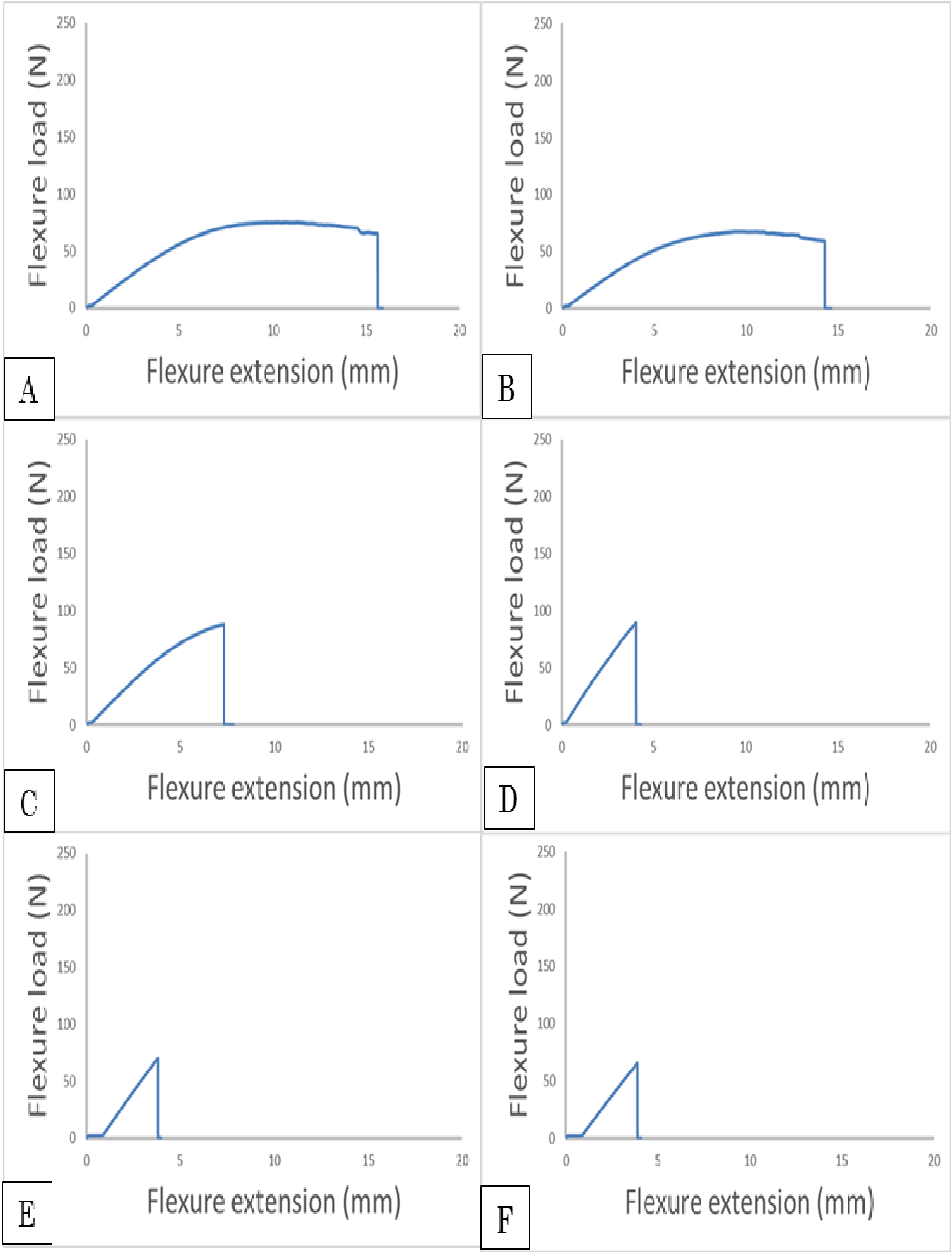


Figure 6.8 Typical curve for the flexural test of CC at different storage groups: (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

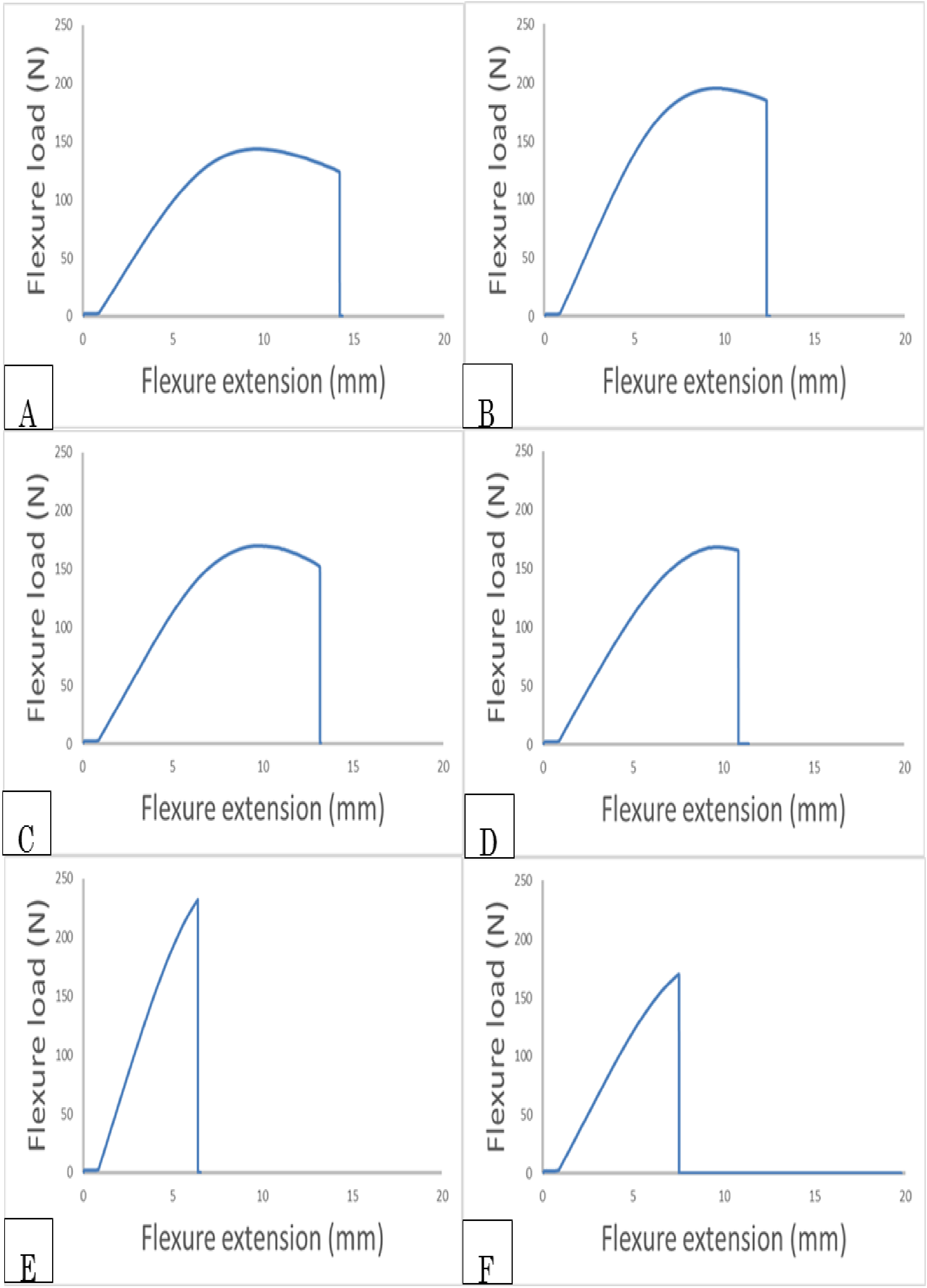


Figure 6.9 Typical curve for the flexural test of Ec at different storage groups: (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

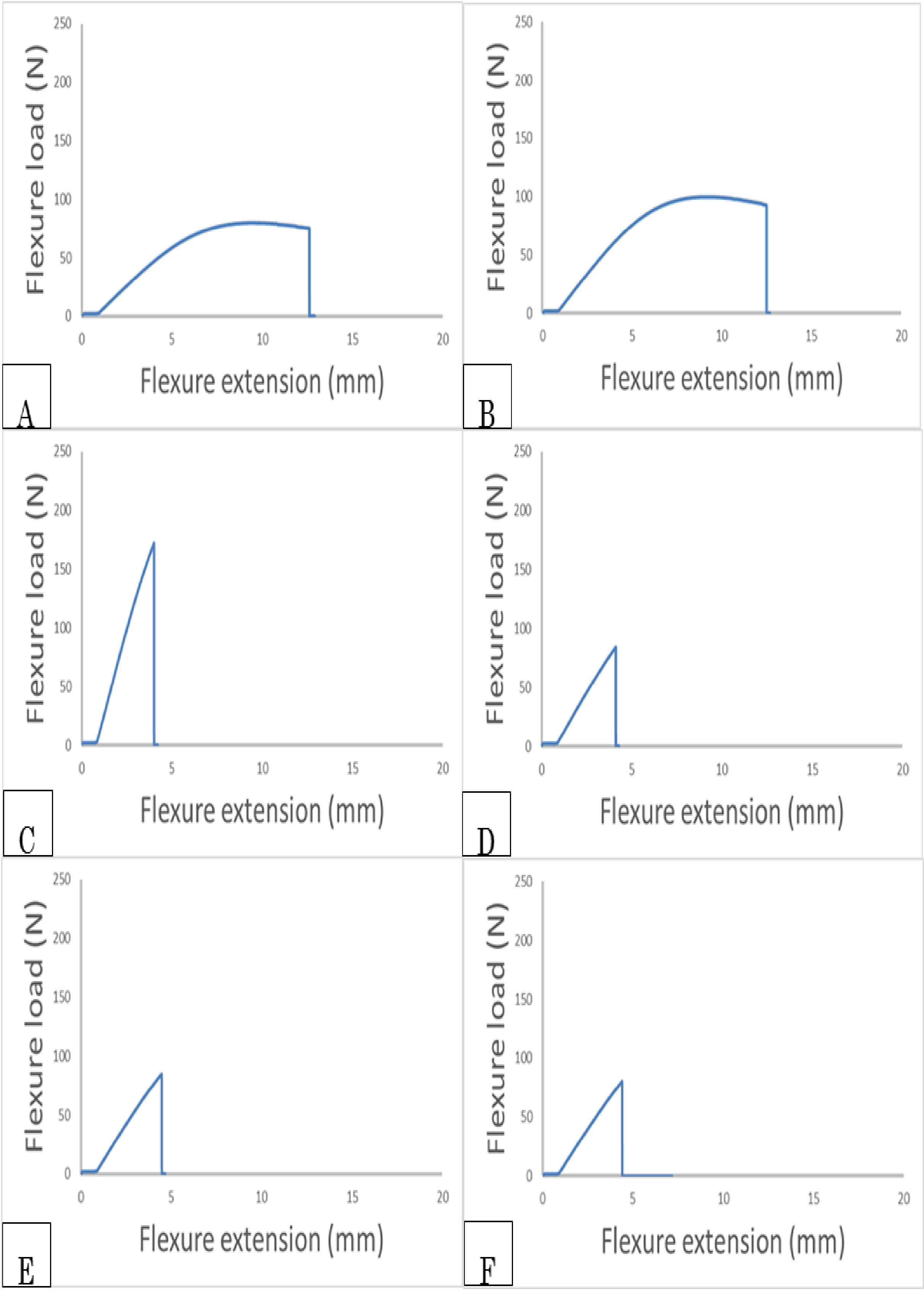


Figure 6.10 Typical curve for the flexural test of Ws at different storage groups: (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

The results of flexural strength and flexural modulus were non-normally distributed data (Shapiro-Wilk test, $P<0.001$). Descriptive statistical analysis of flexural strength and modulus including median, interquartile range (IQR) can be seen in Table 6.7 and Table 6.8, respectively. Figure 6.11 and Figure 6.12 summarise the flexural strength and flexural modulus medians of the different materials in relation to the different storage periods in water.

Regarding flexural strength, as can be very clearly seen in Figure 6.7, Ec was the strongest material at each time point. Before and after storage up to one week, the Ec specimens were significantly stronger than all other materials (Kruskal Wallis test and Dunn’s method indicated $P\leq0.05$), after which there was no significant difference to HC specimens ($P>0.05$) but was statistically different to CC and Ws. HC specimens were stronger than CC and Ws specimens but not significantly at BL or 2D; however, they were significantly stronger from 1W up to 6M time periods ($P\leq0.05$). No significant differences were found between CC and Ws at all-time points. Water storage did not reduce the strength of Ec significantly ($P>0.05$). For HC, CC and Ws specimens, the strength greatly dropped after water storage ($P\leq0.05$). The lowest strength of Ec occurred at 1W, for Ws at 1M.

Material	Storage Group	Flexural strength [MPa] median (IQR)
HC	BL	89 (8) ^{Aa}
	2D	82 (8) ^{D}
	1W	85 (6) ^{G}
	1M	83 (10) ^{J}
	3M	75 (12) ^{Ma}
	6M	81 (6) ^{Pa}
CC	BL	83 (9) ^{Bb}
	2D	77 (5) ^{Ec}
	1W	77 (10) ^{Hd}
	1M	62 (7) ^{JKb}
	3M	48 (5) ^{MNbcd}
	6M	48 (6) ^{PQbcd}
Ec	BL	113 (5) ^{ABC}
	2D	111 (15) ^{DEF}
	1W	106 (14)^{GHI}
	1M	111 (24)^{KL}
	3M	113 (41)^{NO}
	6M	106 (16)^{QR}
Ws	BL	80 (8) ^{Ce}
	2D	75 (5) ^{Ff}
	1W	66 (19) ^{Gleg}
	1M	55 (15) ^{JLef}
	3M	56 (9) ^{MOef}
	6M	54 (10) ^{PRefg}

Table 6.7 Summary of the flexural strength values for each material at different storage periods (similar superscript letters represent significant differences, uppercase letters among materials while lowercase letters within materials

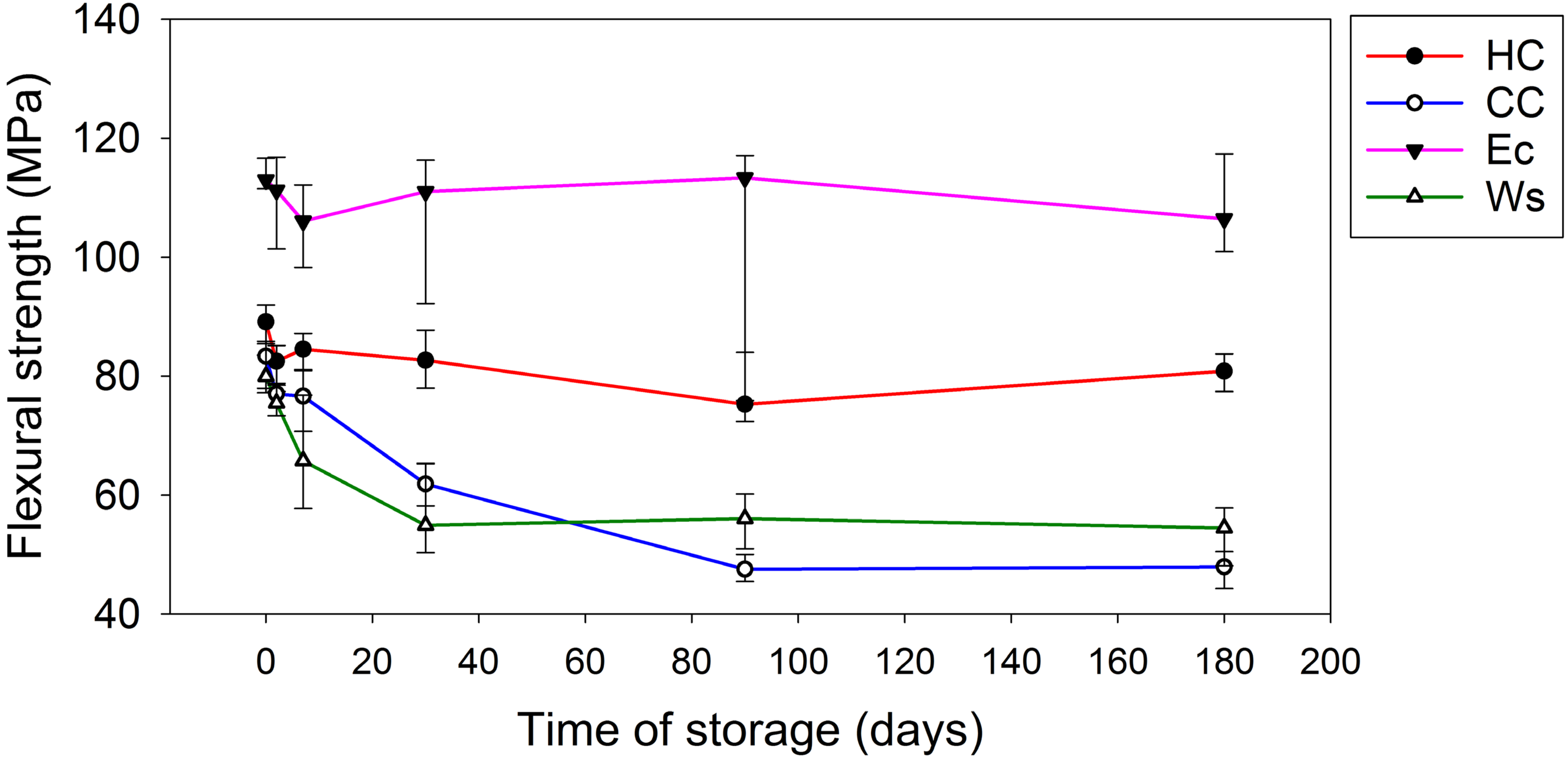


Figure 6.11 Flexural strength median values for the four materials, with respect to different intervals of water storage. Error bars represent upper and lower quartiles

Concerning flexural modulus, Kruskal-Wallis was used to analyse the results, as seen in Table 6.8. Water storage negatively influenced the modulus of all materials except for CC, which was not influenced significantly ($P>0.05$). Eclipse specimens had the highest modulus at all time-points ($P\leq0.05$), except at one week, where the lowest modulus for Eclipse specimens was measured. At this time point, it was not significantly different from HC and CC specimens ($P>0.05$). HC, CC, and Ws were not significantly different at BL. The modulus values fluctuated due to water storage, and by 3M and 6M there was no significant difference in modulus of three materials ($P>0.05$), with Ws being the highest. Ec at 6M was not significantly different from Ws and CC ($P>0.05$), but was statistically significantly different to HC ($P\leq0.05$). The lowest value for Ec was at 1W.

Material	Storage Group	Flexural modulus [GPa] median (IQR)
HC	BL	2.3 (0.2) ^{Aa}
	2D	2.2 (0.1) ^{Db}
	1W	2.2 (0.2) ^{Fc}
	1M	2.3 (0.2) ^{Hd}
	3M	2.1 (0.2) ^{Kabcd}
	6M	2.1 (0.3) ^{Nad}
CC	BL	2.3 (0.3) ^{B}
	2D	2.1 (0.2) ^{D}
	1W	2.1 (0.3)
	1M	2.1 (0.2) ^{I}
	3M	2 (0.3) ^{L}
	6M	2.1 (0.2)
Ec	BL	2.7 (0.1) ^{ABCe}
	2D	2.3 (0.4) ^{Eef}
	1W	2.1 (0.3) ^{Geg}
	1M	2.4 (0.2) ^{IJ}
	3M	2.5 (0.2) ^{KLMfg}
	6M	2.3 (0.4) ^{Ne}
Ws	BL	2.2 (0.2) ^{Ch}
	2D	2 (0.1) ^{DEh}
	1W	2 (0.2) ^{FGhi}
	1M	2 (0.2) ^{HJhj}
	3M	2.1 (0.2) ^{M}
	6M	2.1 (0.2) ^{ij}

Table 6.8 Flexural modulus median values and their significance (similar superscript letters represent significant differences, uppercase letters among materials while lowercase letters within materials)

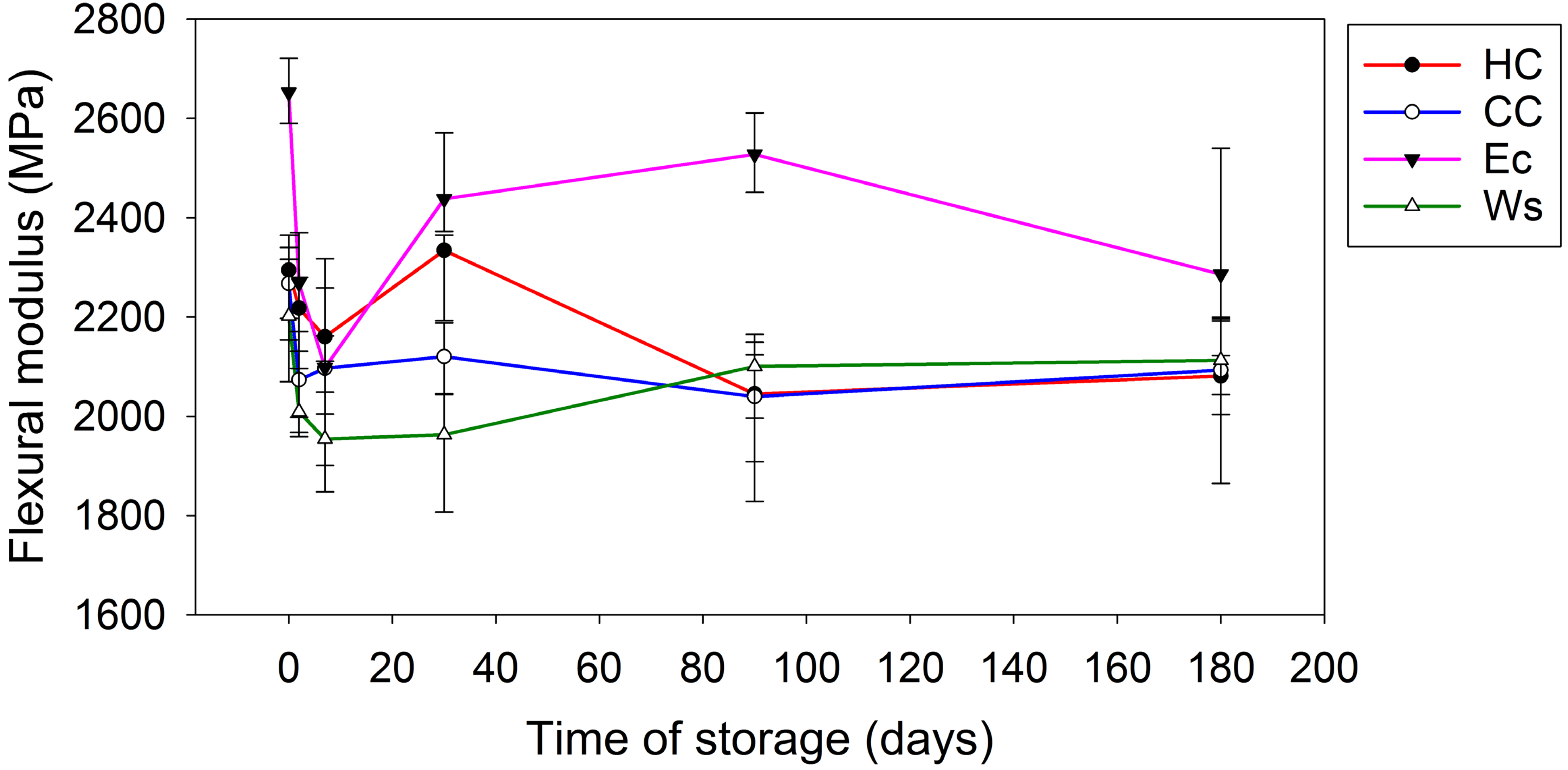


Figure 6.12 Summary of the median values of flexural modulus for comparable materials during water storage. Error bars represent upper and lower quartiles

6.4.3 Discussion

The results obtained from the current study showed clearly that Ec was the strongest and of highest modulus regarding flexural properties of all the compared materials at BL, and after water immersion of up to six months. Ec was followed by HC, although they were not significantly different at some time points, then CC and Ws. These findings are supported by the results obtained from previous studies (Sun *et al*., 2003; Machado *et al*., 2007; Ali *et al*., 2008; Diaz-Arnold *et al*., 2008; Pfeiffer *et al*., 2008; Mumcu *et al*., 2011; Machado *et al*., 2012b; Mutluay *et al.,* 2013; Cillingir *et al*., 2013; Hashem *et al*., 2014). This result is most likely associated with the inherent structure of Ec, which consists mainly of UDMA, characterised by high flexural strength and modulus and a higher molecular weight than MMA, with a high rate of polymerisation (Gajewski *et al*., 2012). It is also due to its low sorption and solubility, as shown in Section 6.3 (as mentioned in Section 2.3.1). Low water sorption and solubility is another reason for maintaining higher flexural properties than PMMA-based materials (Mutluay *et al*., 2013; Akin *et al*., 2014b). The high degree of conversion of Ec and lack of free monomer (Pfeiffer *et al.*, 2005), and high cross-linking, produced a semi-crystalline structure also contributed to the strong flexural properties (Kerby *et al*., 2009; Sun *et al*., 2003; O'Brien, 2008; Van Noort, 2013).

Ws was the weakest and lowest modulus material before and after immersion in water up to 1M, but this was always not statistically significantly different from CC. This result was supported by previous findings in the literature regarding Ws (Mumcu *et al*., 2011) or any class II type 2 (Johnston *et al*., 1981; Mutluay *et al*., 2013; Sun *et al*., 2003). These findings are mainly due to the similarity between CC and Ws based on chemical composition and method of polymerisation, which results in lower molecular weight and higher free monomer than HC and Ec (O'Brien, 2008; Ferracane, 1995). Free monomer works as a plasticiser and lowers the modulus (McCabe and Walls, 2009). The lower mixing ratio of the pourable type compared to CC, and the resultant unavoidable air porosity, also the higher water sorption of Ws compared to CC (Lamb *et al*., 1983); additionally, denser CC was produced by higher pressure, are all factors that might have caused the small differences between them (Anusavice *et al*., 2012; Van Noort, 2013; Keller *et al*, 1974; Keller and Lautenschlager, 1985).

In regard to the effect of water storage on Ec flexural properties, flexural strength was not influenced significantly by water storage for up to 6 months, while the modulus reduced significantly, similar to HC. The lowest value of Ec strength and modulus occurred at 1W and it would seem that this was probably due the highest rate of water absorption that occurred at this time interval (2D<1W>1M), as shown in Section 6.3 and in previous studies (Mutluay *et al*., 2013; Akin *et al.*, 2014), and maximum solubility as shows in Section 6.3, in addition to the effect of plasticisers. However, low water sorption caused no significant reduction in strength, but high deflection of the Ec specimen during the bending test. Similar deflection after a similar period of water storage has been noticed in previous studies (Cilingir *et al*., 2013; Mumcu *et al*., 2011). The Ec modulus reduced to become not significantly different from that of Ws at 6M. Similar results have been found on Eclipse and pourable PMMA, although with different storage times (Mutluay *et al*., 2013).

Water immersion significantly influenced the strength and modulus of Ws, as with other PMMA-based materials except for CC modulus. Water is a plasticiser which reduces the mechanical properties and allows leaching of water-soluble ingredients. The strength and modulus of HC, CC and Ws were not significantly different at BL and they started to differ after immersion in water until time of water saturation. This seems to be associated with the quantity of water soluble ingredients each material contained, including any free monomer. This result was supported by Mutluay *et al*. (2013). Ws strength reached very low value at 1M, which might be related to water saturation at this time point, and continued steadily until 6M with no significant change. Ws was significantly different to HC at the interval 1W-6M. This result disagrees with Mumcu *et al*. (2011), who tested Ws after 15 days of water immersion and found that it was not significantly different from various products of heat-cured PMMA. The reason for this contradiction might be due to using a lower sample size (n=8) in Mumcu’s study which suggested a high difference from our results. Other reasons may be a different mould material (hydrocolloid), which needs a different technique from that used in this study that might influence the resultant specimens’ integrity. In addition, different formulation of HC in our study, which were not disclosed by the manufacturer could be another reason. The Ws modulus dropped by water storage and was fluctuating, and has become not statistically significantly different to HC, CC and Ec after 3M. This may mainly due to leaching of free monomer and other plasticisers into water. These results are supported by Mumcu *et al*. (2011), who found no significant difference between Eclipse, Ws, and heat-cured PMMA modulus after water immersion. This result was also supported by Mutluay *et* *al*. (2013), who compared Eclipse to pourable PMMA (Palapress) for 76 days of water immersion. They found that the modulus of both materials was not significantly different after the designated period. These two studies showed similar results but at a different length of time that could be due to the reasons mentioned above in addition to different formulation of various pourable type products, unavoidable porosity in this study in Ws specimens, and the different polymerisation technique of Eclipse.

There was a high IQR of Ec flexural strength, which increased with greater immersion time, until it reached the maximum 41 in 3M group, and then dropped again (Table 6.7). This finding is supported by the results of previous studies, which are summarised in Table 2.7. This result may be mainly due to the method of material manipulation and adaptation using fingers, and lack of standard pressure application during polymerisation. Finger pressure is unstandardised and therefore can produce specimens of a considerably different density, which in turn influences porosity production (Keller and Lautenschlager, 1985). In addition, to a lesser extent the possibility of the presence of subsurface voids described in Section 5.2.5 may exacerbate variation. Subsurface voids cannot be observed by visual inspection as the material is not translucent. They tend to occur in highly sticky and viscous materials. This porosity triggers catastrophic fracture by representing a point for stress concentration, in particular if it is at the site of force application (McCabe and Walls, 2009). The voids also inhibit the polymerisation of the surrounding layer by their air content. Different numbers and sizes of voids reflect the different water capacity, and subsequently the variation in water sorption increases to reach the maximum at water saturation point (3M). These factors, voids and methods of manipulation impact on the specimens, which then have very high or very low bending strength. This caused the data to be non-normally distributed and increased the variation between values. Accordingly, the variation cannot be expected and it is just a matter of coincidence because causative factors of variation, such as applied pressure or the inclusion of bubbles, are difficult to standardise.

The graphs for Ec (Figure 6.9) show that it is tough, stiff, ductile and strong up to 1M of water immersion. These results were supported by Mumcu *et al*. (2011), who tested maximum displacement and maximum force for a 15 day period of water immersion and they obtained similar results of 11mm at 165N. Due to ductility, some specimens could not be broken at all at 2D time point. This finding may be due to the effect of both plasticisers and water. At 3M, the point of water saturation, and after leaching plasticisers, Ec started to be brittle and displacement was noticeably reduced. The graphs of HC (Figure 6.7) indicated that the material was brittle and less stiff and strong than Ec, which is why all specimens were broken in all tests before plastic deformation occurred.

The specimens of Ec at all times of testing were broken into many small irregular fragments similar to glass, as shown in Figure 6.6D. These fragments may be dangerous and are probably impossible to repair. Since it is destroyed and shattered into many small fragments, they can be lost, swallowed or inhaled by a patient into the respiratory tract, causing a danger of suffocation. They are also hard to match with each other to restore the original denture form. This mode of fracture was different from that of all other PMMA-based materials, which split into a maximum of two or three pieces, and the fracture line in most was located at the site of load application. The way in which the Ec specimens have been broken could be attributed to that Ec is highly-cross linked, since brittleness is a disadvantage of high cross-linking and dissolving plasticisers in water (O'Brien, 2008; Vaidyanathan and Vaidyanathan, 1995).

In the Ws and CC graphs in Figure 6.8 and Figure 6.10 present similar behaviour. They were ductile, flexible and weak at BL and 2D. Ductility explains why some specimens only deformed and did not break at the two testing time points, particularly at 2D, due to the effect of both plasticiser and water. Then, Ws and CC became brittle at the later time points because the plasticisers and free monomer leached into the water.

6.4.4 Conclusion

Ec material showed the best flexural properties of the compared materials, followed by HC, CC and Ws respectively before storage and after storage up to six months in water. However, on breaking it may be harmful, dangerous, and difficult to repair. Water storage reduced modulus significantly but not the strength.

Ws showed inferior flexural properties to HC, and was comparable to CC. Water storage reduced strength and modulus significantly.

6.5 Indentation hardness

6.5.1 Materials and methods

60 disk-shaped specimens with dimensions 20mm diameter × 5mm thick were made for each of the four materials. These specimens were fabricated and polished following the same steps mentioned beforehand (Sections 5.2.1, 5.2.2, 5.2.3, 5.2.4 and 5.3). Then, the specimens were divided into six storage groups, ten specimens per group. The groups were stored in distilled water following the storage regime illustrated in Table 6.1.

On the day of testing, the specimens were removed from water, dried with absorbent paper and individually marked with a number by a pen. The hardness was evaluated using a hardness tester machine (Zwick Z 2.5, Zwick GmbH & Co., Ulm, Germany) with indentation load 200 g and dwelling time 20 s, as in Figure 6.13. Vickers hardness (HV) was measured three consecutive times for each specimen at three randomly selected points spread over the surface, and then an average was calculated for each specimen. The length of the diagonal was measured automatically during the unloading movement of the indenter using TestXpert software (Zwick GmbH & Co.). The hardness was expressed as Newton per square millimetre and calculated automatically using the following formula:

$HV=1.854F/d^2$,

F: is load applied (Kgf), d: is the indentation diagonal length (mm) (BSI, 2006)

The median and interquartile ranges were calculated for the Vickers hardness of each group. The data were analysed using Kruskal-Wallis with a Tukey post-hoc test to determine the significant difference between groups using Sigma Plot statistical software version 13.0 at a confidence level of 95%.

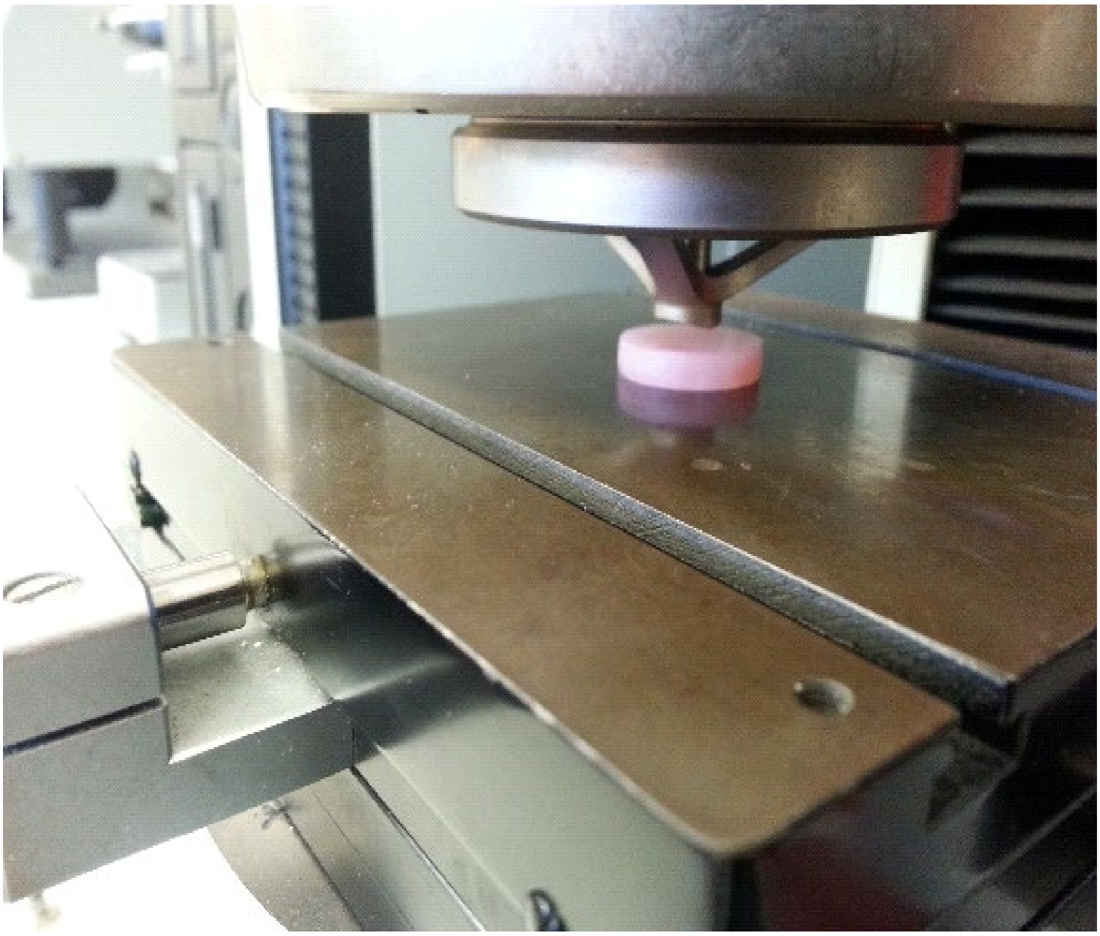


Figure 6.13 Hardness tester loaded with disk specimen

6.5.2 Results

Figure 6.14, Figure 6.15, Figure 6.16, and Figure 6.17 show typical force-indentation curves for each group, which represent the graph of a specimen whose hardness value was the closest to the median value for each group. The curves for all of the materials tested each time had the same general shape, showing a non-linear increase in force up to the maximum load, followed by a gradual increase in force during the dwell time, followed by a non-linear decrease in force during unloading. All materials exhibited a degree of plastic deformation on unloading with indentation depths of between 14 μm and 18 μm typically shown.

Data distribution of the results revealed non-normally distributed data (Shapiro-Wilk test, $P<0.001$), even after using multiple transformation. Descriptive statistical analysis with group comparison results of Vickers hardness for all tested materials were tabulated in Table 6.9.

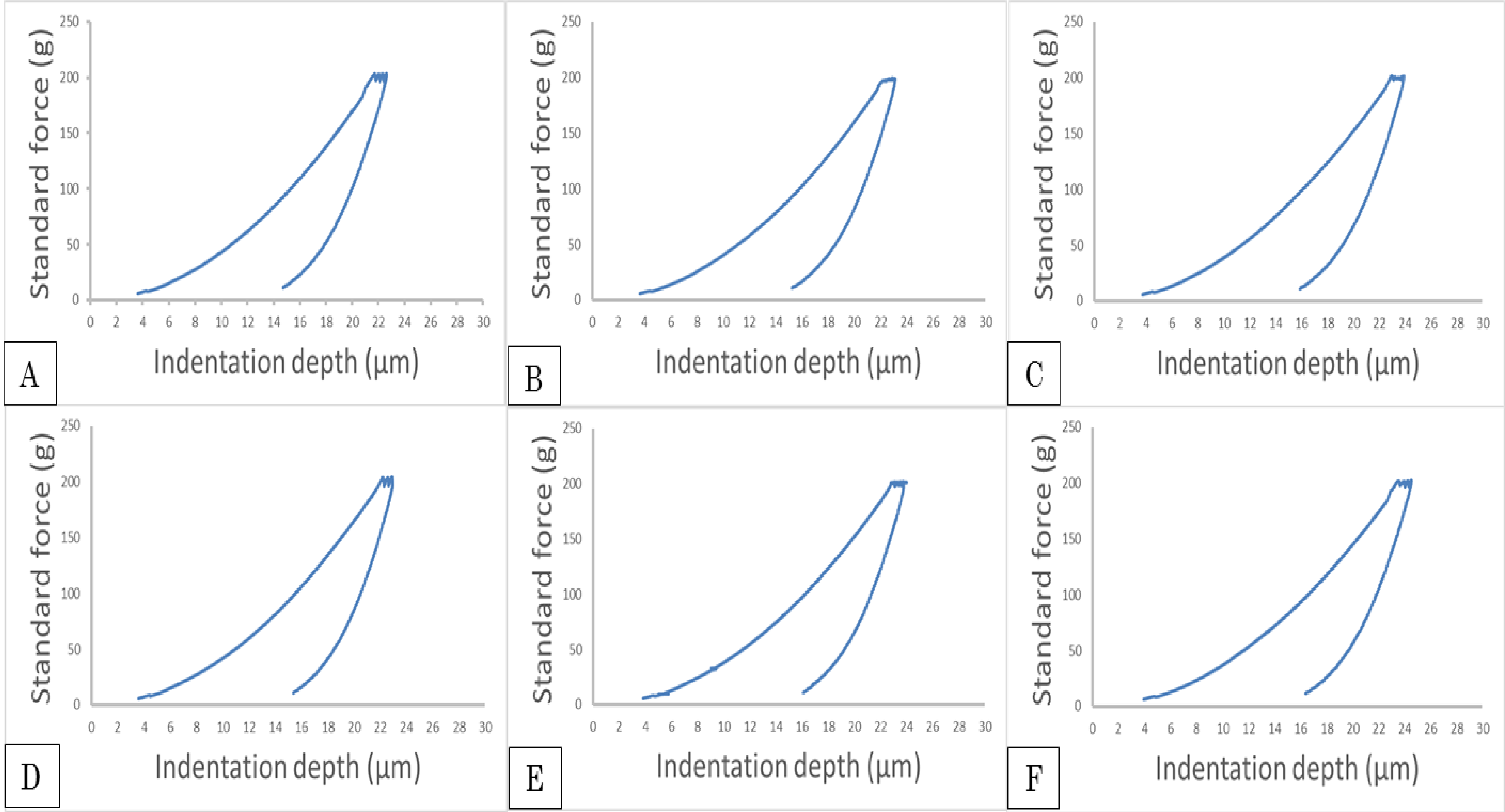


Figure 6.14 Typical Indentation curve of HC for the following groups: (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

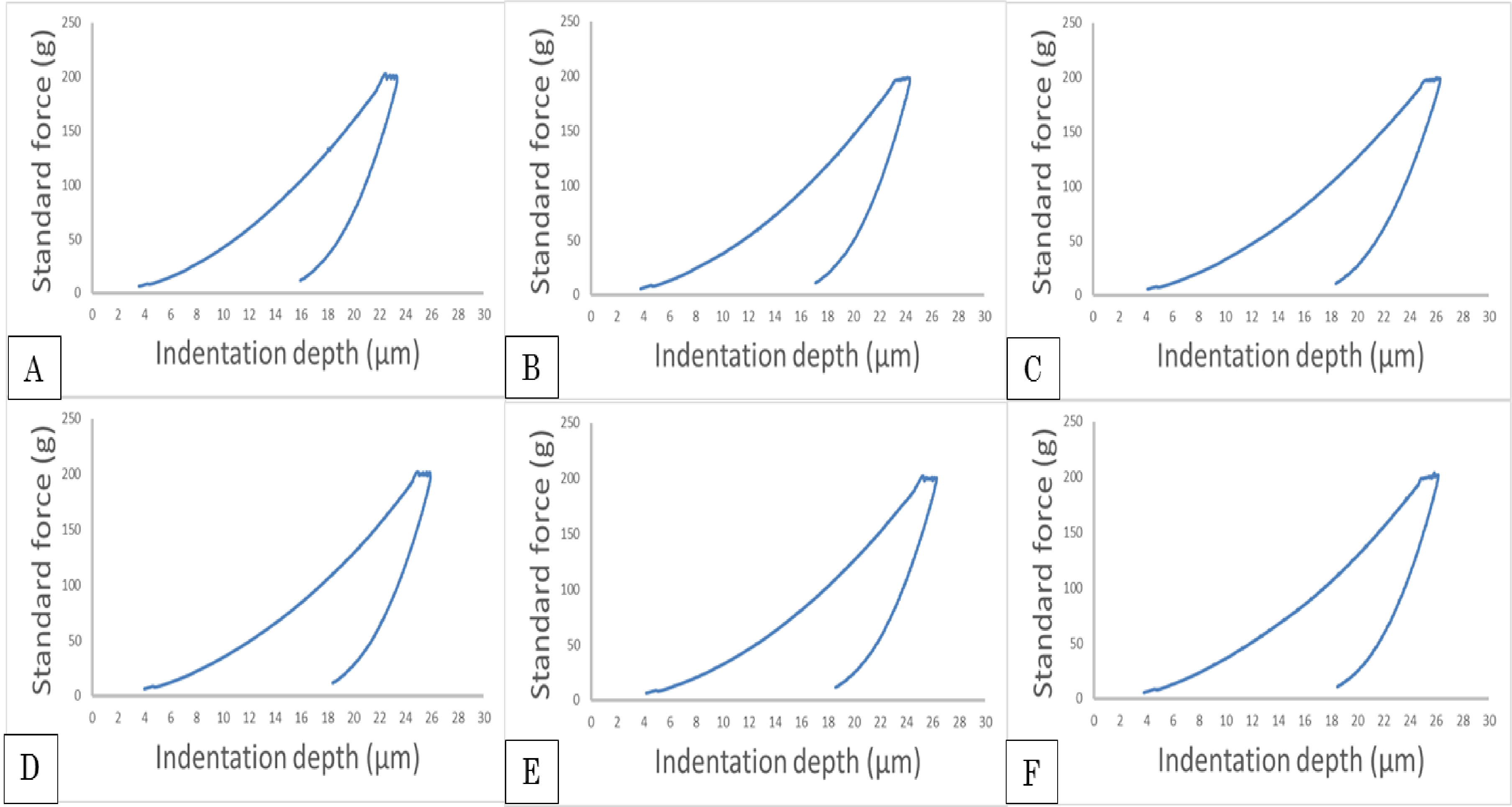


Figure 6.15 Typical Indentation curve of CC for the following groups A: BL, B: 2D, C: 1W, D: 1M, E: 3M, and F: 6M

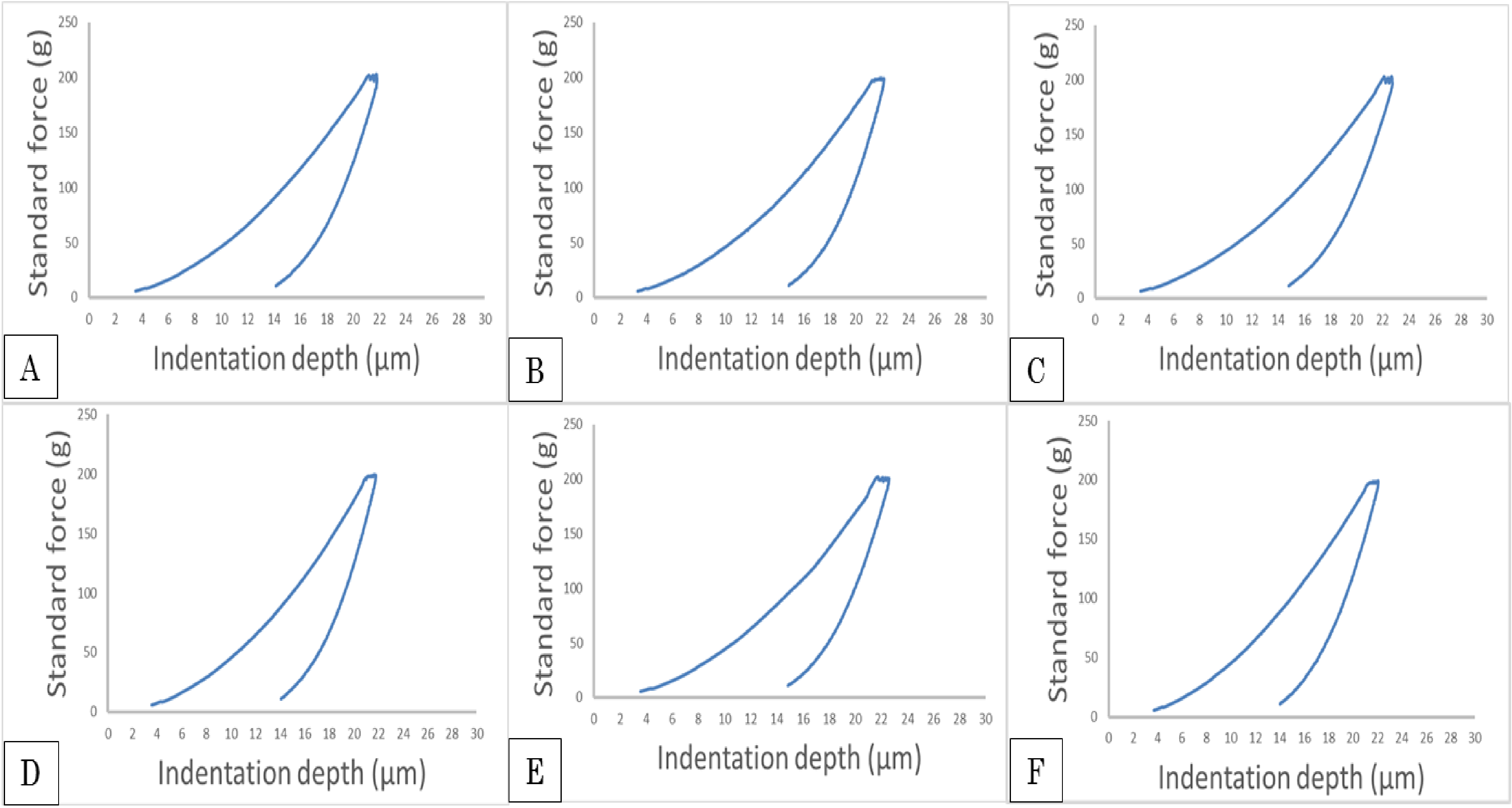


Figure 6.16 Typical Indentation curve of Ec for the following groups A: BL, B: 2D, C: 1W, D: 1M, E: 3M, and F: 6M

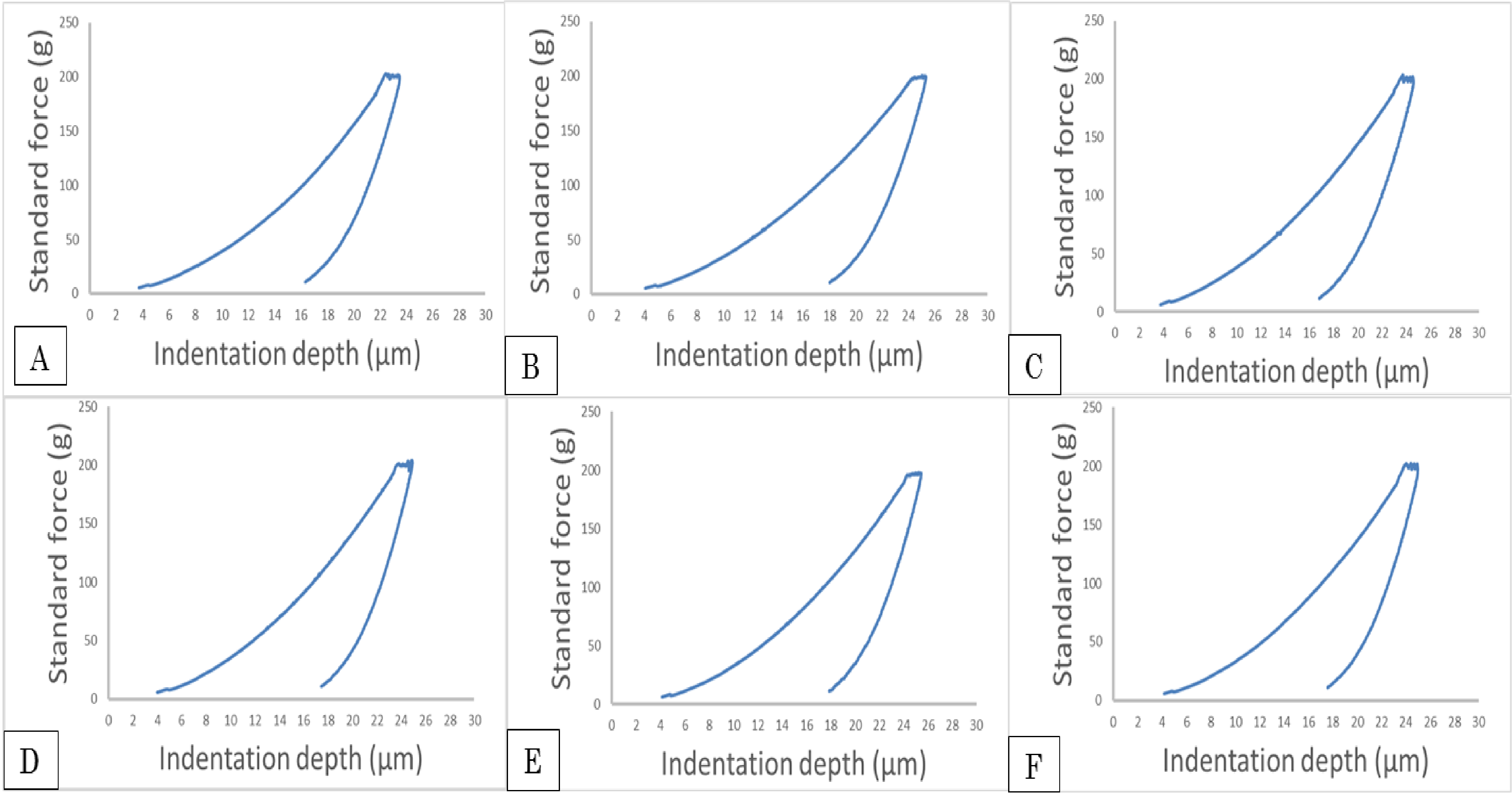


Figure 6.17 Typical Indentation curve of Ws for the following groups: (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

Graphic representation of the median and interquartile ranges for all groups can be seen in Figure 6.18. It clearly revealed that Ec was the hardest material at all time-points before and after storage ($P \leq 0.05$), although there was no significant difference with HC (Kruskal-Wallis, $P > 0.05$). HC was significantly harder than Ws at BL and 2D ($P \leq 0.05$); but thereafter, there was no significant difference ($P > 0.05$). Its difference from CC was exactly opposite to that of Ws. Ws was harder than CC from 1W up to 6M with no significant difference between them ($P > 0.05$). There was a statistically significant difference between the materials and a statistically significant difference for each material between different storage groups ($P \leq 0.05$).

Water storage caused a significant reduction in hardness of PMMA materials ($P \leq 0.05$). Ec hardness fluctuated along the storage time but no significant difference was found between storage groups up to six months ($P > 0.05$). HC and Ws continued to reduce significantly ($P \leq 0.05$); CC significantly reduced during the early stages of storage ($P \leq 0.05$) and then continued at a steady level ($P > 0.05$).

Material	Storage Group	Vickers Hardness [Kgf/mm^2] median (IQR)
HC	BL	19.4 (1)^{aA}
	2D	18.6 (0.6)^{bD}
	1W	17.9 (0.5)^{aG}
	1M	18.5 (0.8)^{cJ}
	3M	17.4 (0.4) ^{abcM}
	6M	16.8 (0.5) ^{abcP}
CC	BL	17.9 (1.5) ^{dB}
	2D	16.4 (1.4) ^{eE}
	1W	14.3 (0.7) ^{deGH}
	1M	14.2 (1.4) ^{dJK}
	3M	14.1 (0.8) ^{deMN}
	6M	14.3 (0.4) ^{dPQ}
Ec	BL	21.5 (1.6)^{BC}
	2D	20.6 (0.6)^{EF}
	1W	19.9 (0.8)^{HI}
	1M	21.9 (1.4)^{KL}
	3M	20.3 (1.4)^{NO}
	6M	21.6 (1.3)^{QR}
Ws	BL	17.7 (0.9) ^{fAC}
	2D	15 (1.6) ^{fDF}
	1W	16.3 (0.6) ^{gI}
	1M	15.6 (1.6) ^{fL}
	3M	14.8 (1.5) ^{fgO}
	6M	15.3 (0.8) ^{fR}

Table 6.9 Summary of hardness values for compared materials and their group comparison results (superscript similar letters refer to significant differences, uppercase letters among materials and lowercase letters within the same material)

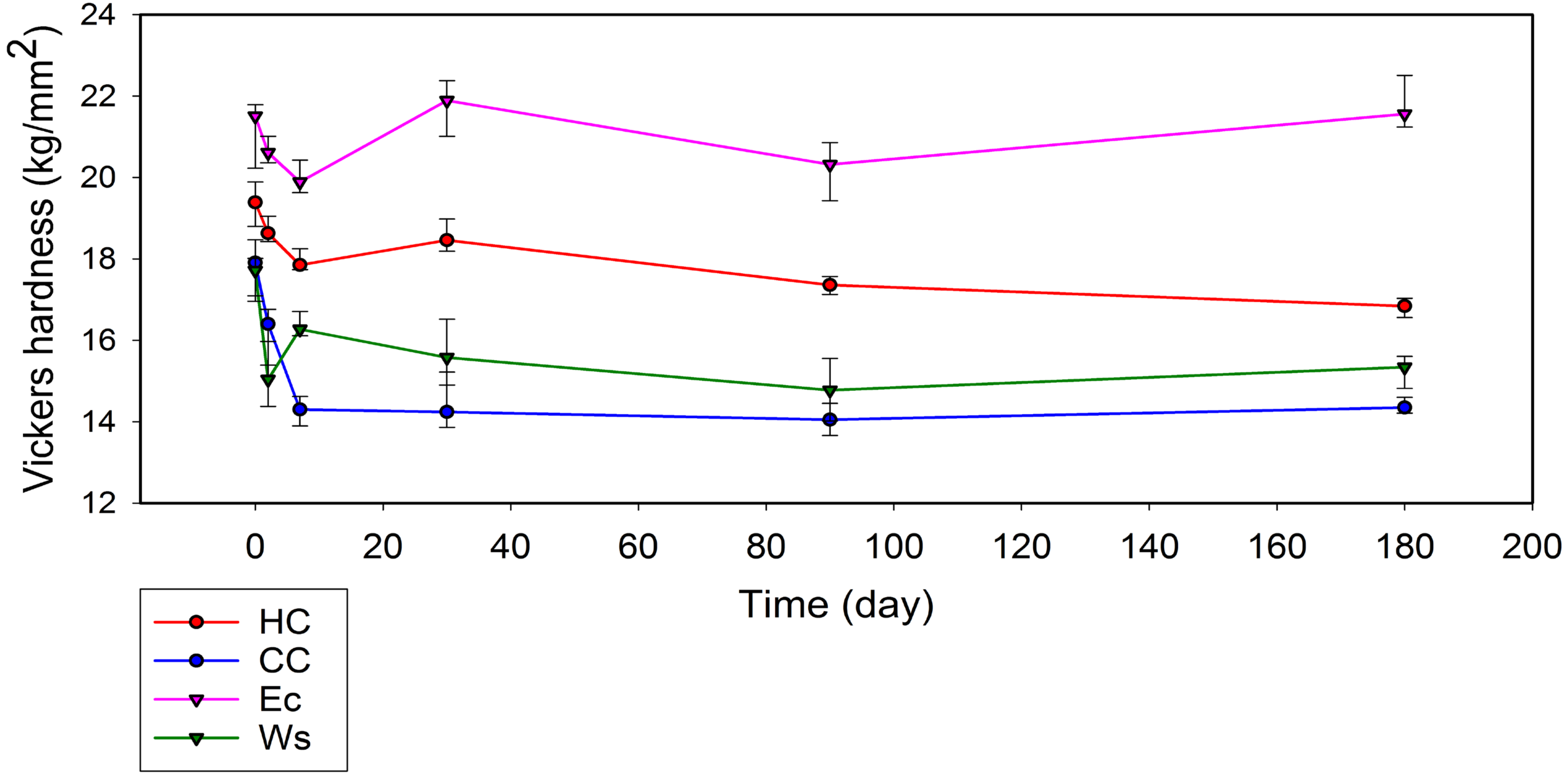


Figure 6.18 A summary of the Vickers hardness median values and their changes over time for the four materials during water storage. Error bars represent upper and lower quartiles

6.5.3 Discussion

In this study, Vickers hardness was used as it is the most common test regime used for measuring the hardness of denture base materials (Dar-Odeh *et al.*, 1997; Al-Mulla *et al.*, 1988; Azevedo *et al.*, 2005; Ali *et al.*, 2008, Sharma *et al.*, 2014; Farina *et al.*, 2012; Neppelenbroek *et al.*, 2005; Regis *et al.*, 2009; Machado *et al.*, 2009; Durkan *et al.*, 2013). The protocol followed for testing was a 200 g load applied to the surface and left for 20 s. The most common protocols used for testing heat- and cold-cured PMMA denture base materials employ 25-100g and remain for 30 s (Sharma *et al.*, 2014; Farina *et al.*, 2012; Neppelenbroek *et al.*, 2005; Regis *et al.*, 2009; Machado *et al.*, 2009; Durkan *et al.*, 2013). For testing light-cured denture base material, the previous protocols have used 300 g and 15 s (Dar-Odeh *et al.*, 1997; Al-Mulla *et al.*, 1988; Azevedo *et al.*, 2005; Ali *et al.*, 2008). The load in this protocol was chosen to be similar to that used for light-cured material, but a little less to avoid breakage of Ec, and because it has no silica filler which is responsible for hardness (Van Noort, 2013). The dwell time was thus selected as any length of time between 15 and 30 s.

The hardness tester used in this study is sensitive to surface roughness. Therefore, the samples were polished until flat, which necessitated a reduction in their thickness. Hardness values for Ec can be influenced by polishing specimens to different depths (Pilo *et al.*, 1999). However, light exposure of more than 10 min polymerises all layers of specimen equally and in turn there is no difference in hardness between different depths of specimen (Ali *et al.*, 2008).

The number of specimens used in this study was ten, and each specimen was tested three times to provide 30 readings, which are of a good power (0.95) and provide valid and reliable results, as shown by Ali *et al.* (2008). Ten specimens were also used to test hardness in other studies (Mese and Guzel, 2008; Pinto *et al.*, 2010).

In the current *in vitro* study, Ec was harder than the PMMA-based materials at all time-points before and after water immersion up to six months; however, it is not significantly different from HC. This result is in agreement with a previous study (Ali *et al.*, 2008), in which the author compared Ec to heat- and cold- cured PMMA after 30 days water immersion. This high degree of hardness may mainly be due to high degree of conversion of light-cured polymers (Al-Mulla *et al.*, 1988, Dar-Odeh *et al.*, 1997; Khan *et al*., 1987), as hardness is an indication of the degree of conversion of light-cured polymer (Rueggeberg and Craig, 1988). Thus, Ec is free of residual monomer, which lowers the hardness (Mellili *et al*., 2009). This result was supported by Campanha *et al*. (2012), who found significantly higher hardness values of composite teeth than acrylic teeth before and after water storage for 7 days at 37ºC. The difference in the structure is also due to the same reasons as for the superior flexural properties mentioned before in Section 6.4.3, which are mainly being inherently highly polymerised, and having a highly cross-linked Ec structure. The highly cross-linked structure of Ec produces a network structure which is stable in solvents such as water (Ferracane, 1995), and this may have also caused a low rate of water absorption.

It has been shown that exposure to moisture induced some fluctuation in Ec hardness but no significant differences were found between storage groups within the six month period. For this reason, it showed the least indentation depth change after storage in water, as shown in Figure 6.16. At 2D and 1W, there was a non-significant softening of the surface, in response to the plasticising effect of water. At 1M, it returned to approximately the same value as at BL. This result agrees with Khan *et al.* (1987), whose study tested Triad hardness after 40 days of water soaking. The water had overall no significant softening effect on Ec, which is most probably due to the low water absorption of copolymer and low rate of water uptake, as mentioned in Section 6.3.2 (Devlin and Kaushik, 2005).

Ws showed a lower hardness than CC at BL, and a higher one after absorbing water for 1W upward, but no significant differences were found between them. At BL, Ws was less hard than CC, which might be due to the higher ratio of residual monomer, as a result of a lower mixing powder to liquid ratio. At 2D, the hardness of Ws reduced due to absorbing water, and then increased again at 1W to be higher than that of CC, and not significantly lower than HC up to 6M. This increase might be due to the effect of changing the water temperature from room temperature to 37˚C, because this change causes an expansion of the material and increase in the amount of absorbed water. This in turn facilitates dissociation and the faster leaching of the residual monomer (Vallittu *et al*., 1995), as well as the occurrence of the inherent cross-linked Ws structural properties after dissolution of most free monomer (Lee *et al*., 2002). In contrast, CC did not benefit much from the change in temperature due to its denser material. For this reason, most studies test mechanical properties after immersion in water for a few days to exclude the effect of residual monomer on these properties (Lamb *et al*., 1982; Bayraktar *et al*., 2006; Jorge *et al*., 2003). Ws was harder than CC from 1W-6M, although this was not statistically significant. This order might be in some way due to the inherent crystalline structure of barbituric acid derivatives within Ws (Lewis *et al*, 2004). The fact that Ws was harder than CC is in agreement with Lee *et al*. (2002), who found that auto-polymerised PMMA cured under similar conditions to Ws was harder than the same material cured under similar conditions to CC, and a little softer than heat-cured PMMA after 7 d water storage at 37˚C. In the period 1M-6M, there was no significant change for both Ws and CC due to water saturation.

The results presented in this study reveal that water storage softened all PMMA-based materials significantly. This result was also previously found by Neppelenbroek *et al*. (2015), who noted that the initially high amount of water sorption was responsible for plasticising and softening the surface, and reducing the hardness. Further water absorption to the interior bulk of the material does not influence surface hardness significantly. The increase in hardness after the initial reduction occurred in some materials might be due to leaching of the plasticisers mainly free monomer, which acts as a plasticiser; however this increase is insignificant. This finding is in agreement with Neppelenbroek *et al.* (2005), and Sharma *et al.* (2014). Differences in material behaviour occurred across the period of water immersion may be related to differences in composition (Azevedo *et al*., 2005) and method of polymerisation, which influences the level of free monomer (Kedjarune *et al*., 1999). This behaviour of Ws, CC and HC might also due to the different intervals of time that these specimens remained in the air before storage, causing a further increase in hardness (Azevedo *et al*., 2005; Kanie *et al*., 2004b).

6.5.4 Conclusion

- All materials were softened significantly by water storage except Ec.
- Eclipse was harder than HC, CC and Ws at BL, and after water storage up to six months.
- Ws was the least hard material at BL, and became harder than CC after water storage but was still less hard than HC and Ec.

6.6 Roughness

6.6.1 Materials and methods

The same specimens that were used to test hardness were also used to test roughness, using the opposite side of the specimen. The stylus profilometer (Mitutoyo, Surftest SV-2000) and its associated software (Mitutoyo, SURFPAK-SV Version 1.600) were used to record surface profile and measure roughness (Ra), as shown in Figure 6.19A. The specimens were mounted on a piece of wax (PremEco Line, Merz Dental, Germany) over the holder to avoid any unpredictable movement of the stylus tip tracing, providing that the upper surface is horizontal. The levelling of the superior surface was verified with a spirit level (Mitutoyo. Japan), as in Figure 6.19B. Then the test was performed following the manufacturer’s instructions. The stylus was moving at a speed 0.5 mm/sec across the surface to trace 4 mm length, with a cut off value of 0.8 mm. The value has been obtained automatically using the equation (DeGarmo *et al.*, 2003):

$$R_a = \frac{1}{n}\sum_{i=1}^{n}|y_i|$$

The measurements at three randomly selected locations were recorded for each specimen. These three tracing points were about 2 mm apart from each other and located on a flat area of a specimen; the arithmetic mean value was then calculated using Microsoft Excel 2016.

The mean and standard deviation were calculated for the roughness values (Ra) of each group. The data were analysed using a two way ANOVA with a Holm-Sidak post-hoc test, to determine the significant difference between groups (Sigma Plot version 13.0) at a confidence level of 95%.

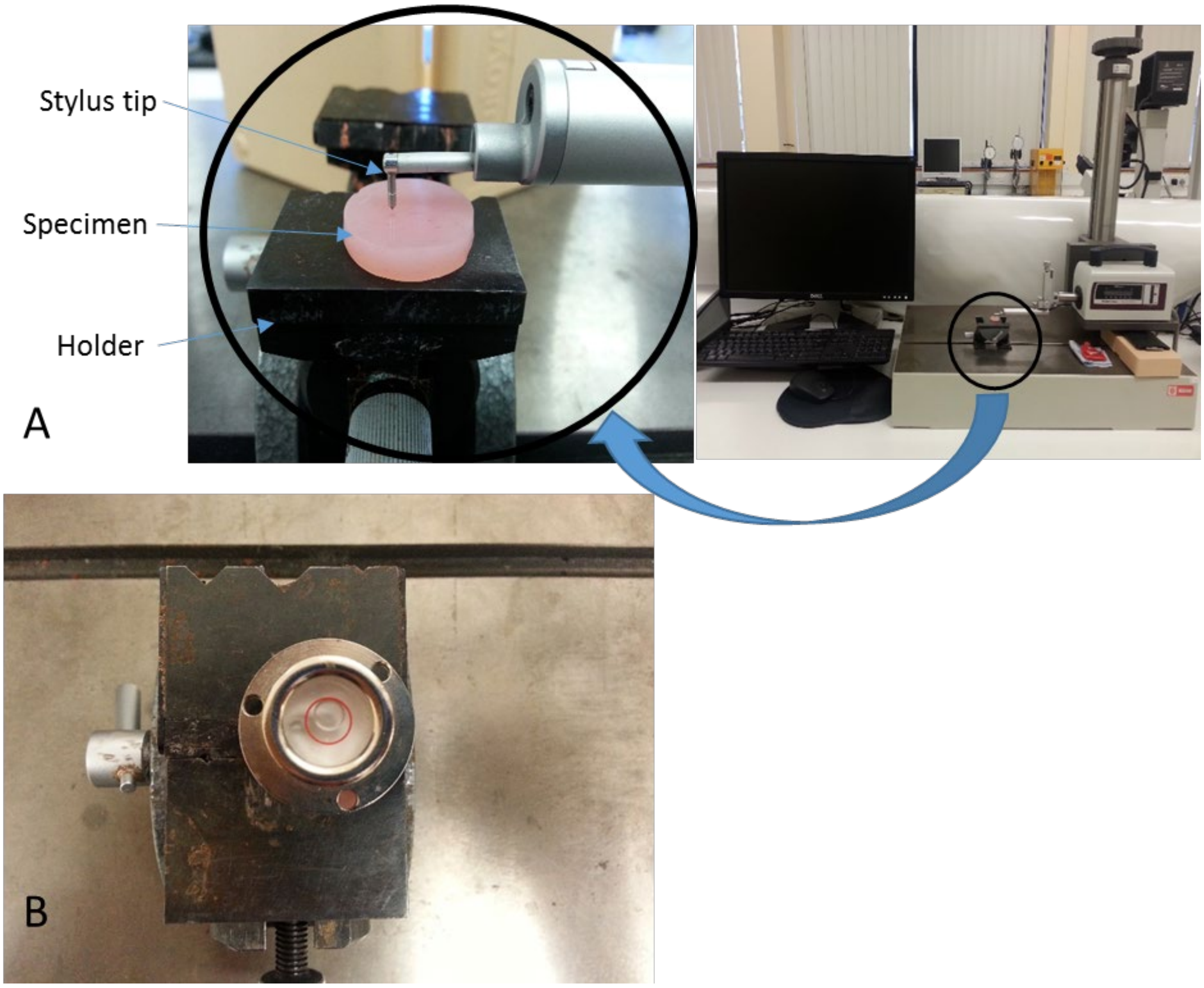


Figure 6.19 (A) Profilometer tracing a specimen surface, (B) Spirit level

6.6.2 Results

The data were normally distributed (Shapiro-Wilk test, P=0.778). Accordingly, a typical graph for each group was chosen for the specimen tracing whose Ra the closest to the mean of that group, as shown in Figure 6.20, Figure 6.21, Figure 6.22 and Figure 6.23. All materials showed undulating surfaces with peaks and troughs within the range of 1.4 -1.6 µm. Also, the Ws traces look much rougher than all the others.

Mean values and standard deviation were plotted in a comparison graph for four materials at different storage intervals (Figure 6.24). All descriptive statistics related to the mean, SD and CV are listed in Table 6.10 (CV is equal to SD divided by mean and multiplied by 100). This table also shows the group comparison results of the two way ANOVA. At BL, the graph shows that HC had the smoothest surface of the four materials and was significantly different from the other materials' Ra ($P \leq 0.05$). No significant difference was found between the Ra of CC, Ec, and Ws ($P>0.05$). In general, group comparison indicated that water storage had influenced Ra of Ec and CC significantly ($P \leq 0.05$), but not HC and Ws ($P>0.05$). The most prominent result that can be noticed in the graph is that HC had the lowest Ra values before, and after water storage and this was significantly different from other materials at all time-points ($P \leq 0.05$), except Ec at 3M and 6M ($P=0.08$). No significant difference was found between Ws, CC, and Ec at all time-points before and after storage ($P>0.05$), except at 2D where Ws was significantly higher, and at 6M where CC was significantly higher than other materials ($P \leq 0.05$). A two way ANOVA test indicated that there was a statistically significant interaction between materials and time points of testing ($P \leq 0.001$).

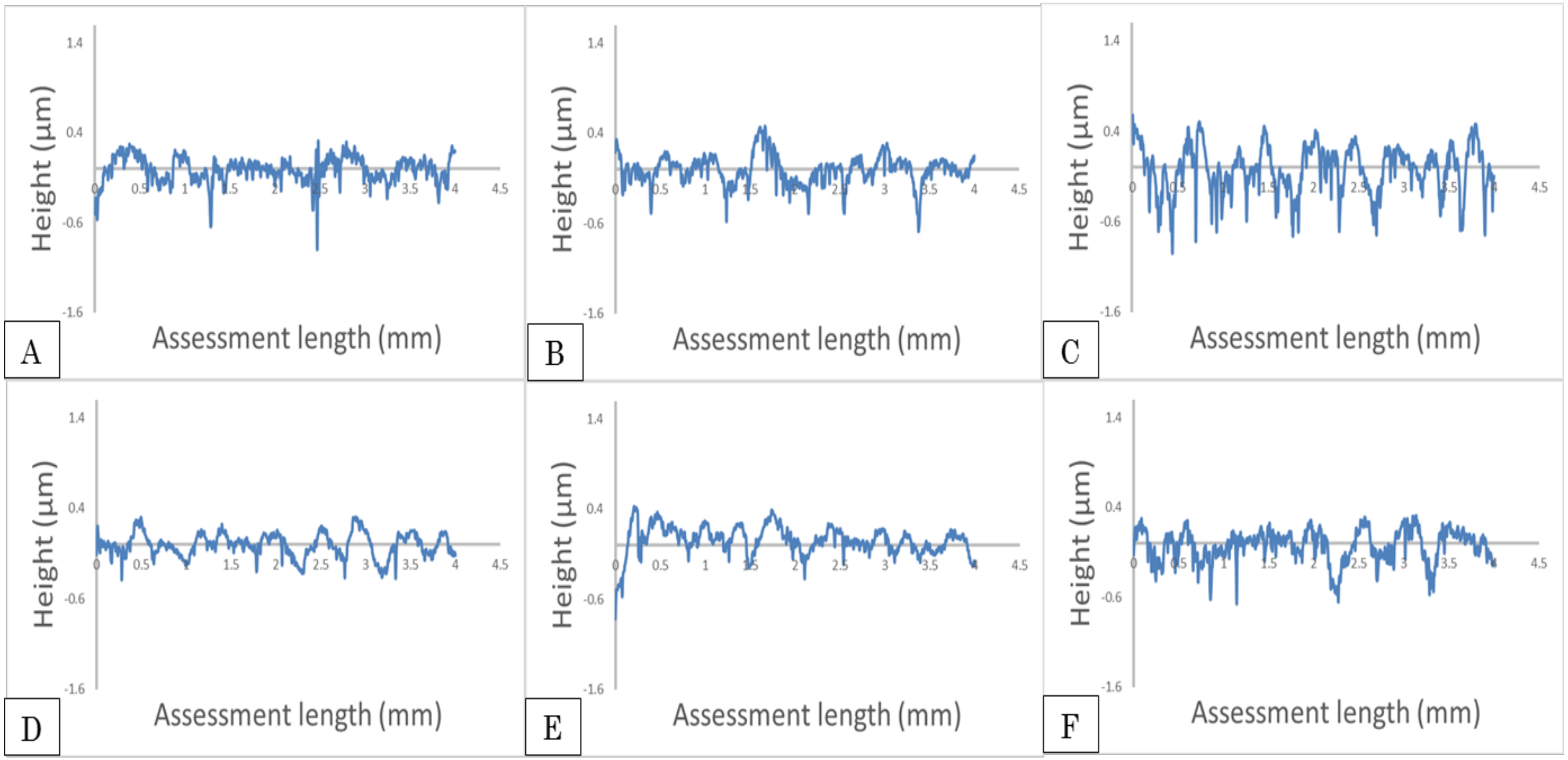


Figure 6.20 Typical stylus profilometry profile for HC at (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

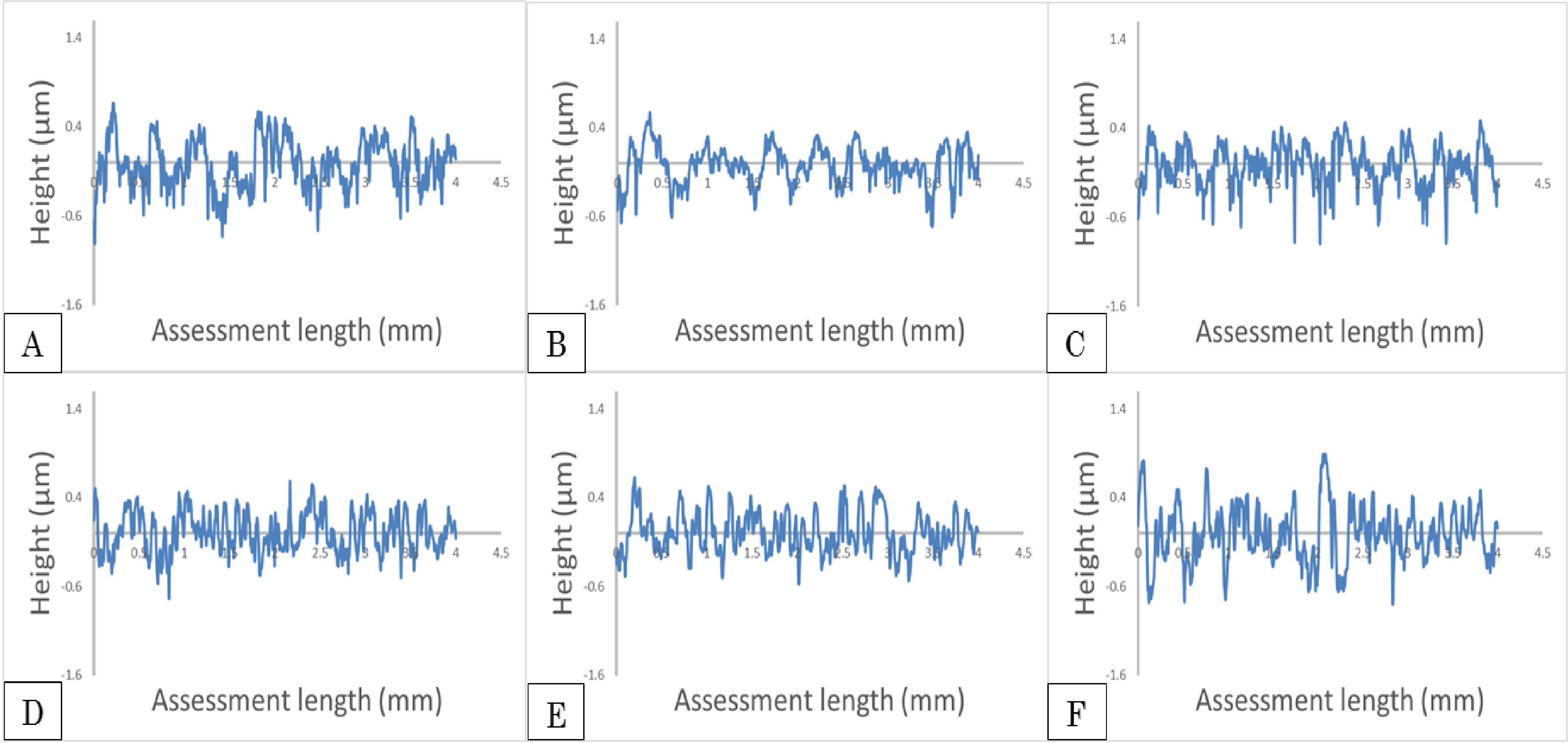


Figure 6.21 Typical stylus profilometry profile for CC at (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

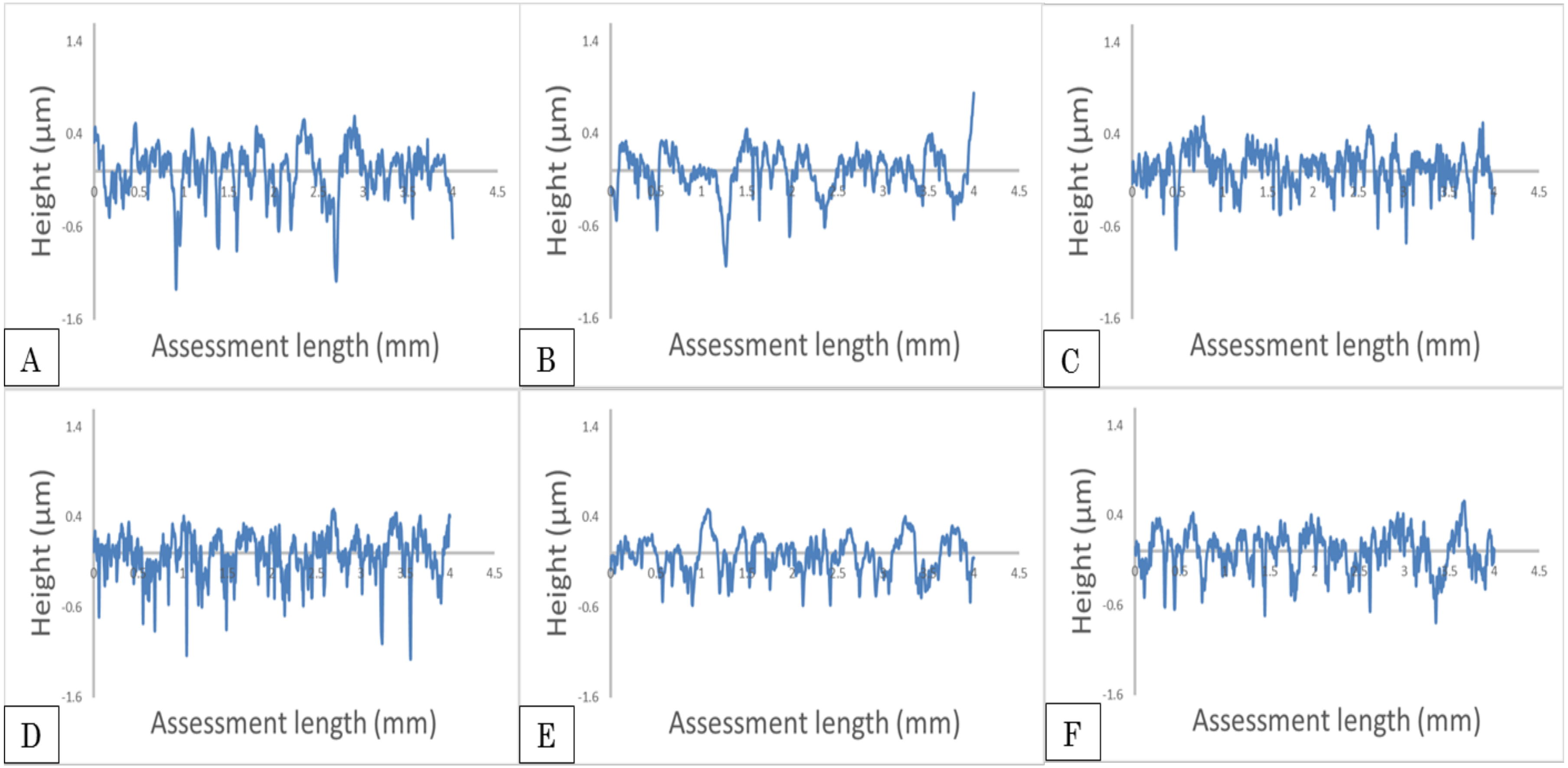


Figure 6.22 Typical stylus profilometry profile for Ec at (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

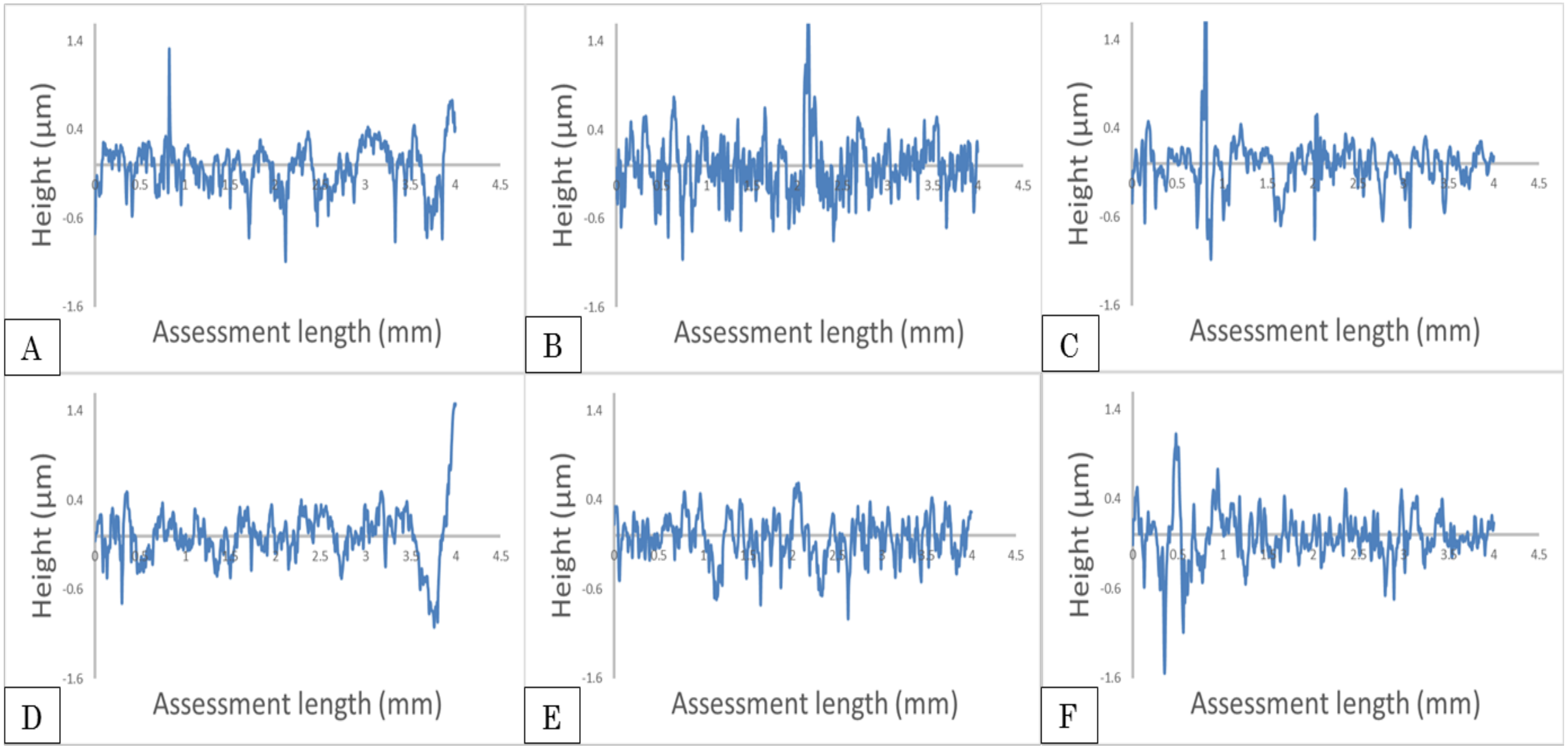


Figure 6.23 Typical stylus profilometry profile for Ws at (A) BL, (B) 2D, (C) 1W, (D) 1M, (E) 3M, and (F) 6M

Material	Storage Group	Roughness (Ra) mean (SD) (μm)	CV
HC	BL	0.11 (0.02)^{A}	18
	2D	0.12 (0.04)^{B}	33
	1W	0.12 (0.04)^{E}	33
	1M	0.10 (0.02)^{F}	20
	3M	0.13 (0.04)^{G}	30
	6M	0.14 (0.04)^{H}	28
CC	BL	0.22 (0.06) ^{Aa}	27
	2D	0.15 (0.05) ^{Cab}	33
	1W	0.19 (0.03) ^{Ec}	15
	1M	0.19 (0.02) ^{Fd}	10
	3M	0.19 (0.03) ^{Ge}	15
	6M	0.25 (0.05) ^{HIbcde}	20
Ec	BL	0.21 (0.06) ^{Af}	28
	2D	0.18 (0.03)^{BD}	16
	1W	0.16 (0.03) ^{Ef}	18
	1M	0.18 (0.03)^{F}	16
	3M	0.17 (0.02)	11
	6M	0.18 (0.02)^{I}	11
Ws	BL	0.21 (0.03)^{A}	14
	2D	0.23 (0.06)^{BCD}	26
	1W	0.19 (0.04)^{E}	21
	1M	0.21 (0.03)^{F}	14
	3M	0.19 (0.05)^{G}	26
	6M	0.20 (0.04)^{HI}	20

Table 6.10 Summary of Ra values for compared materials and their significant differences (superscript similar letters refer to significant differences, uppercase letters among materials and lowercase letters within same material)

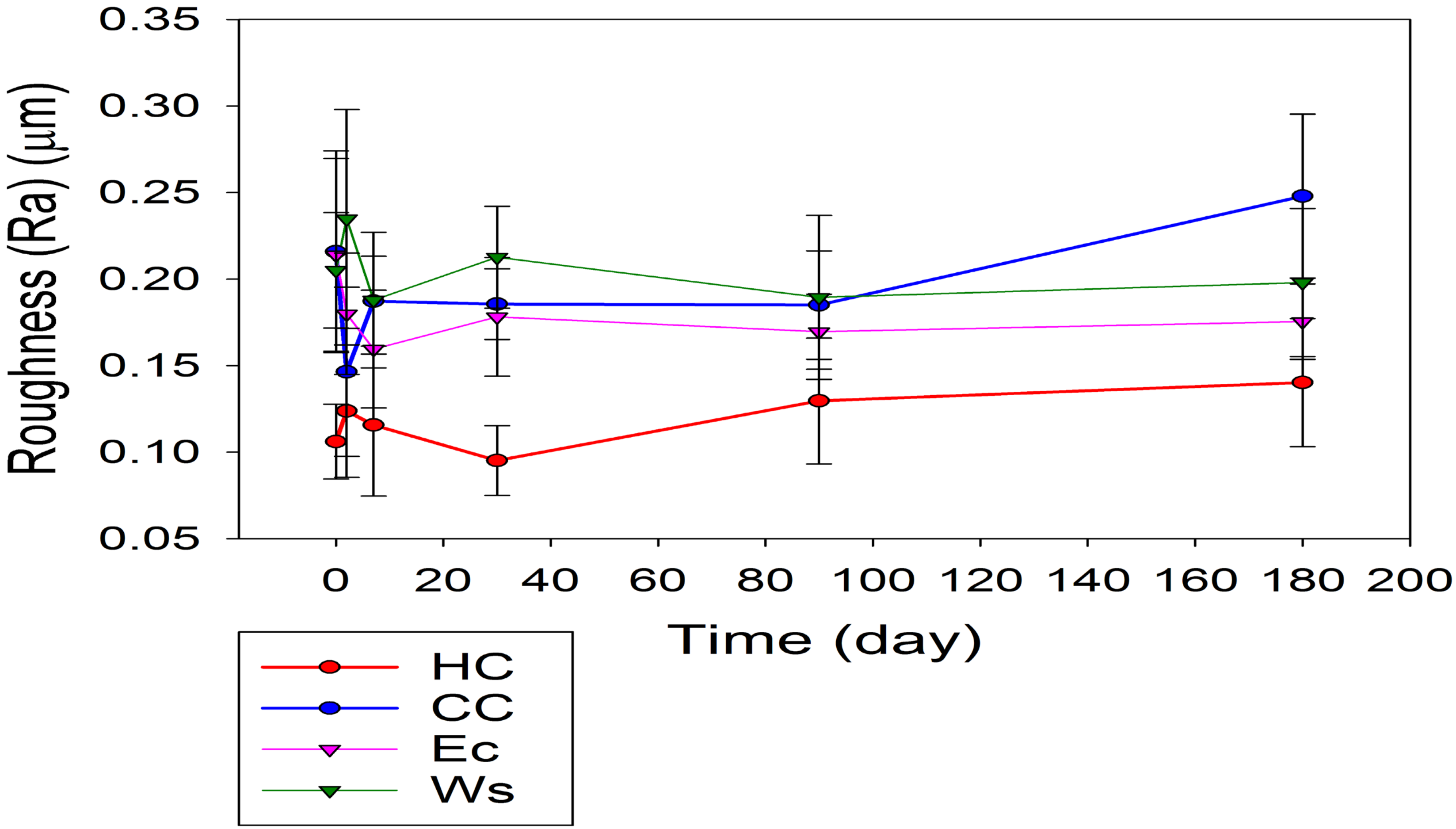


Figure 6.24 Summary of the mean roughness values of the four comparator materials during water storage. Error bars represent standard deviation

6.6.3 Discussion

Roughness was tested for the denture base materials in this study using a stylus profilometer. This machine is suitable for large specimens (20 mm diameter *4 mm thick). The Ra parameter was used to measure roughness, and has been the only parameter for testing denture base roughness, and the most common one as observed from the literature. This study considered ten specimens, like many other published studies. Each specimen was traced on three lines and the average was calculated, because average roughness values provide a more accurate value of the roughness of a specimen than one line only. However, three lines are still less than providing information on the whole surface using different devices, and so a sample size was calculated after running a pilot study. This sample size was 30 tracings as a minimum. From this, ten specimens, each with three measures, was enough to produce accurate values with high power. This sample size is also the most commonly used in the literature, which is why it was selected for running the test.

At BL and before water immersion, HC was significantly smoother than the three comparator materials. The Ra of HC was followed by Ws, Ec, and CC, respectively, which were not significantly different from each other. Previous research related to roughness before polishing has reported that the polymerisation method renders heat-cured PMMA smoother than other materials (Usta DF *et al*., 2016). This finding was confirmed with by SEM imaging, which showed a smooth and dense heat-cured PMMA surface, and rough and porous light- and cold-cured material surfaces (Ogle *et al*., 1986). The occurrence of porosity in Ec, CC, and Ws previously noticed in 5.2.5, and which is related to the handling and method of polymerisation, might be another reason for the rough surfaces of Ec, CC, and Ws, even after polishing. The Ra values of HC obtained in this study were comparable to results obtained following a similar finishing and polishing technique at BL (Rao *et al*., 2015). These findings, however, disagree with those of Mahross *et al*. (2015) and Al-Kheraif (2014), who found that Eclipse had a superior surface texture than heat-cured denture base PMMA after polishing, but this finding was not significant. Gungor *et al*. (2014) also demonstrated dissimilar findings to the current study regarding HC and CC. They found that heat- and cold-cured PMMA roughness was not significantly different neither before nor after polishing, regardless of the polishing regime. These two contradictory findings may be attributed either to a different heat-cured PMMA brand, which results in a different composition and behaviour (Rao *et al*., 2015), or to a high variation in Ra.

High variation is a well-known limitation of roughness, as observed in the results of many studies (Machado *et al*., 2012a; Peracini *et al*., 2010; Sartori *et al*., 2006; Lima *et al*., 2006; Koroglu *et al*., 2016; Moussa *et al*., 2016; Ural *et al*., 2011; Porwal *et al*., 2017; Sharma *et al*., 2017; Fergus *et al*., 2017). This was also noticed in the current study, despite the use of a high power (big sample size), as roughness is a highly variable property which is dependent on both the material and dexterity of the operator when polishing (Rao *et al*., 2015). Thus, a high variation is most probably due to the difficulty of polishing all specimens identically, for example, a lack of press-on force and time standardisation during polishing (Heintze *et al*., 2006). A subjective judgement about specimen smoothness is another cause of high variation, as a visual evaluation depends on being able to recognise a flat polished surface with no scratches using only the naked eye. Another probable reason is specimen size, as this can induce difficulty in controlling the specimen when polishing it with a lathe machine. All these points might have resulted in HC being significantly smoother than other materials.

After water storage, the Ra of HC and Ws showed no significant effect but those of CC and Ec were significantly influenced within a six month period. HC also showed the smoothest surface in comparison with other materials. Its Ra was significantly different from that of other materials at all-time points except from CC at 2D, and Ec at 3M and 6M. No previous research was found in the pertinent literature investigating the effect of water storage on roughness of the same or similar materials, or following the same polishing procedure to that used in this. However, water as a solvent causes leaching of the water soluble ingredients, which may disturb the integrity of the surface. With Ec, the Ra decreased significantly only at 1W, which is in favour of denture bases but no change at all other time points. Ec behaviour can be attributed to low water absorption and low solubility, so the solvent effect of water on the surface was minimal. The CC Ra reduced significantly at 2D, which might be due to its dense consistency and difficulty of water penetration deeply with low sorption. However, then Ra increased significantly at 6M to be higher than the threshold and significantly higher than all other materials corresponded with CC highest solubility, possibly because the molecules had started the process of dissolution and increased depth of valleys. Therefore, the ranking order changed at 6M, starting with HC as the smoothest surface followed by Ec, Ws, and CC, respectively. In spite of the fact that there were different values of water solubility, in general water solubility did not cause a significant increase in Ra values, except for CC at 6M. The latter results are in agreement with Mohammed *et al*. (2016), and Atroshi *et al*., (2015).

6.6.4 Conclusion

- Ws and HC were not significantly influenced by water, unlike Ec and CC
- The ranking of materials was HC, Ws, Ec and CC from smooth to rough at BL. The ranking order was changed after water storage to be HC, Ec, Ws, and CC respectively.

6.7 Colour stability

6.7.1 Materials and methods

10 Disk-specimens at dimensions 20 mm diameter and 5 mm thickness were made and polished for each material, as explained in Sections 5.2.1, 5.2.2, 5.2.3, 5.2.4 and 5.3. Each specimen was placed in a cylindrical plastic container (25 mm base diameter × 38 mm height, polystyrene, Fisher Scientific) labelled with a number, as in Figure 6.25. A spectrophotometer (Ci60 spectrophotometer, X-Rite, US) with an 8 mm aperture diameter, shown in Figure 6.26, was used to measure colour change.

The spectrophotometer rests on a base, whose top contains a circular dark orifice on one side and a circular white material on the other side for calibrating the device before testing begins, following the manufacturer instructions. This calibration expires daily. On the bottom of the base, there is a circular chamber for the specimen placement during testing. After calibration, this circular space was lined with white paper to act as the background, and was thus the set place for testing the specimens. Very close contact of the spectrophotometer aperture with the specimen was achieved during testing according to the manufacturer. This contact was checked by making the specimen height about 0.5-1 mm lower than the set place height, because the spectrophotometer cannot work if the specimen is a little higher as the device needs to be pressed together to close and provide a reading. The colour was then tested by setting the device on D65/10 spin standard illumination, and following the manufacturer’s instructions. The standard Commission International de L’Eclairage (CIE L*a*b) colour system was used to evaluate colour changes. The spectrophotometer was calibrated before each test, following the manufacturer’s instructions.

The specimens first were assessed for colour at BL, by testing both sides of each disk and then taking an average of the two readings as a BL score. The containers were then filled with fresh distilled water and the specimens were returned to the containers. They were kept in this manner for 2 d at room temperature. After two days, the specimens were removed from water one by one, dried with absorbent paper, and evaluated for colour following the same procedures as BL testing. The colour changes (ΔE) were calculated using the CIE L*a*b system, using the following equation:

$$\Delta E = ((\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2)^{1/2}$$

After this, the specimens were returned to the containers and filled with fresh distilled water, and stored in an incubator for 6M at 37°C. The colour was re-assessed at the end of 1W, 1M, 3M, and 6M, following the same procedures mentioned above. The distilled water was replenished with fresh water after each test.

The median and interquartile ranges were calculated for the colour change (ΔE) of each storage group. The data were analysed using Kruskal-Wallis one-way ANOVA test on ranks, and Tukey test method, to determine the significant difference between groups using Sigma Plot statistical software version 13.0 at a confidence level of 95% and power of 0.05.

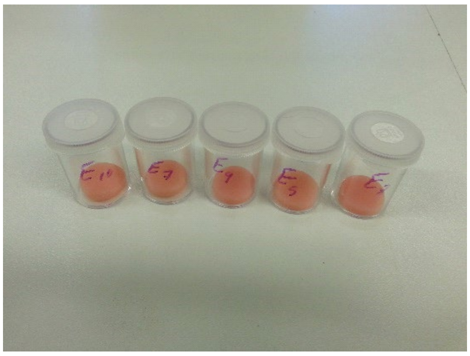


Figure 6.25 Disk specimens for colour test in labelled containers

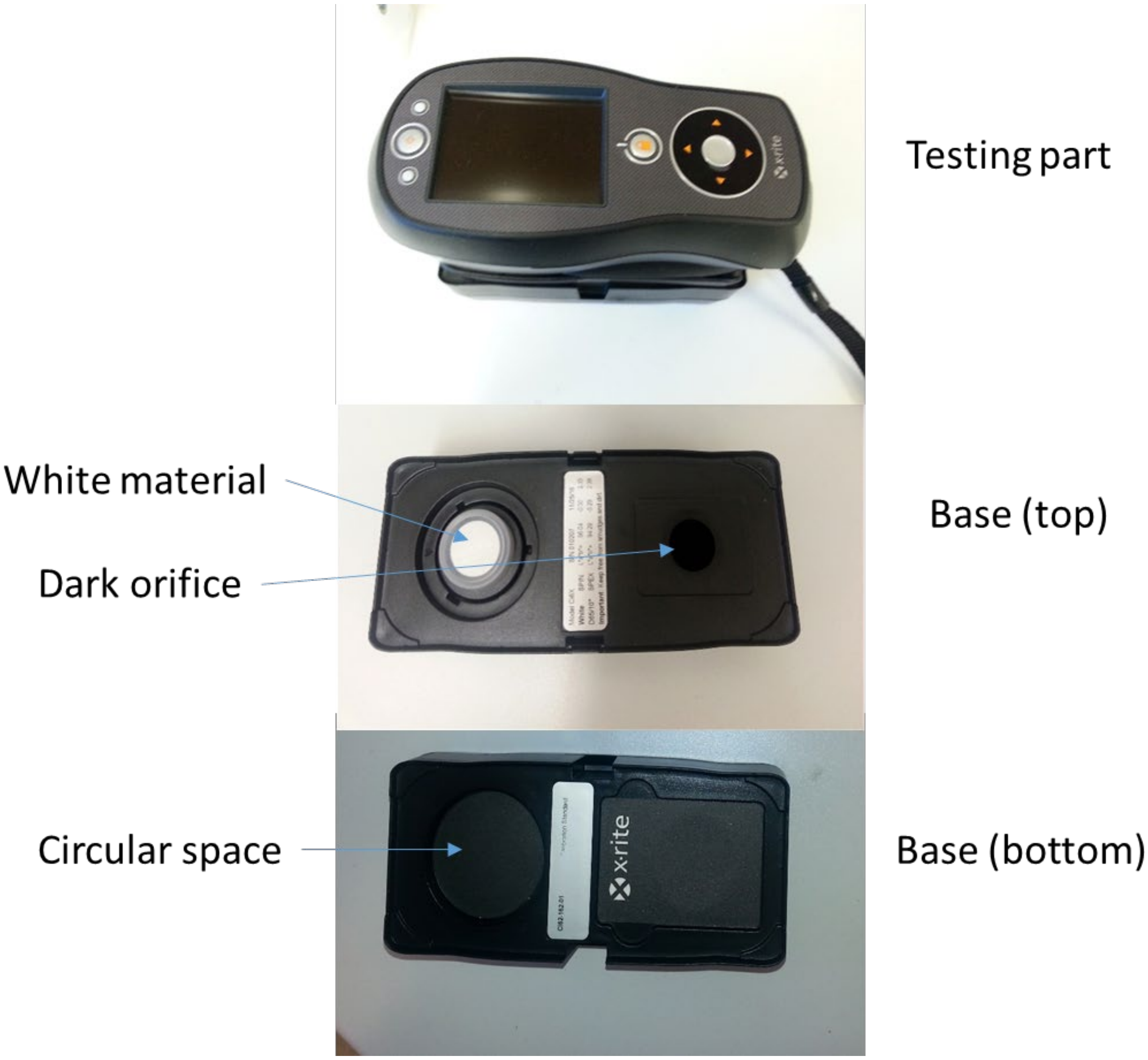


Figure 6.26 Spectrophotometer

6.7.2 Results

The data from testing colour change within 6M of water storage were non-normally distributed (Shapiro-Wilk test, $P<0.001$) even after using multiple transformations. Therefore, a multiple Kruskal-Wallis test was used to find significant differences between groups. Descriptive statistical analysis of the group comparison results for all tested materials is shown in Table 6.11. Graphic representation of median values and upper and lower quartiles of colour changes for all groups can be seen in Figure 6.27. It was found that water storage led to a significant change in colour in all materials and there was a significant difference between the tested materials ($P\leq0.05$). CC specimens exhibited a significant increase in colour changes throughout the whole period of water immersion, to reach 5.5 at 6M, at which it was significantly different from all other materials ($P\leq0.05$). The HC curve rose, showing a significant difference ($P\leq0.05$) during 6M period, reaching a maximum at 1M, which represents its maximum change (1.3). At this point it was significantly different from Ec ($P\leq0.05$). Ec and Ws showed significant but small changes in colour in comparison with other materials over 6M test period. The Ec curve rose gradually and continuously to reach 0.8 at 6M ($P\leq0.05$); Ws also grew gradually but at a lower rate, to reach a steady value with zero variation at 6M of 0.4 ($P\leq0.05$). Both these materials, as well as HC, showed no significant difference for 1M-6M storage groups.

Material	Storage Group	ΔE median (IQR) ANOVA on Ranks
HC	2D	0.5 (0.6) ^{aA}
	1W	0.8 (0.3)^{B}
	1M	1.3 (0.2) ^{aC}
	3M	1.2 (0.2)^{aE}
	6M	1.0 (0.2)^{G}
CC	2D	0.1 (0.2) ^{bA}
	1W	0.7 (0.1) ^{c}
	1M	1.3 (0.1) ^{bdD}
	3M	3.1 (0.2) ^{bcF}
	6M	5.5 (0.2) ^{bcdGH}
Ec	2D	0.2 (0.1) ^{e}
	1W	0.3 (0.6)^{f}
	1M	0.4 (0.2) ^{CD}
	3M	0.5 (0.2) ^{eF}
	6M	0.8 (0.2) ^{efH}
Ws	2D	0.2 (0.3) ^{g}
	1W	0.2 (0.1) ^{hB}
	1M	0.3 (0.1) ^{CD}
	3M	0.4 (0.1) ^{EF}
	6M	0.4 (0.0) ^{ghGH}

Table 6.11 Summary of colour changes for compared materials and the significant differences between them (superscript similar letters refer to significant differences, uppercase letters among materials and lowercase letters within same material)

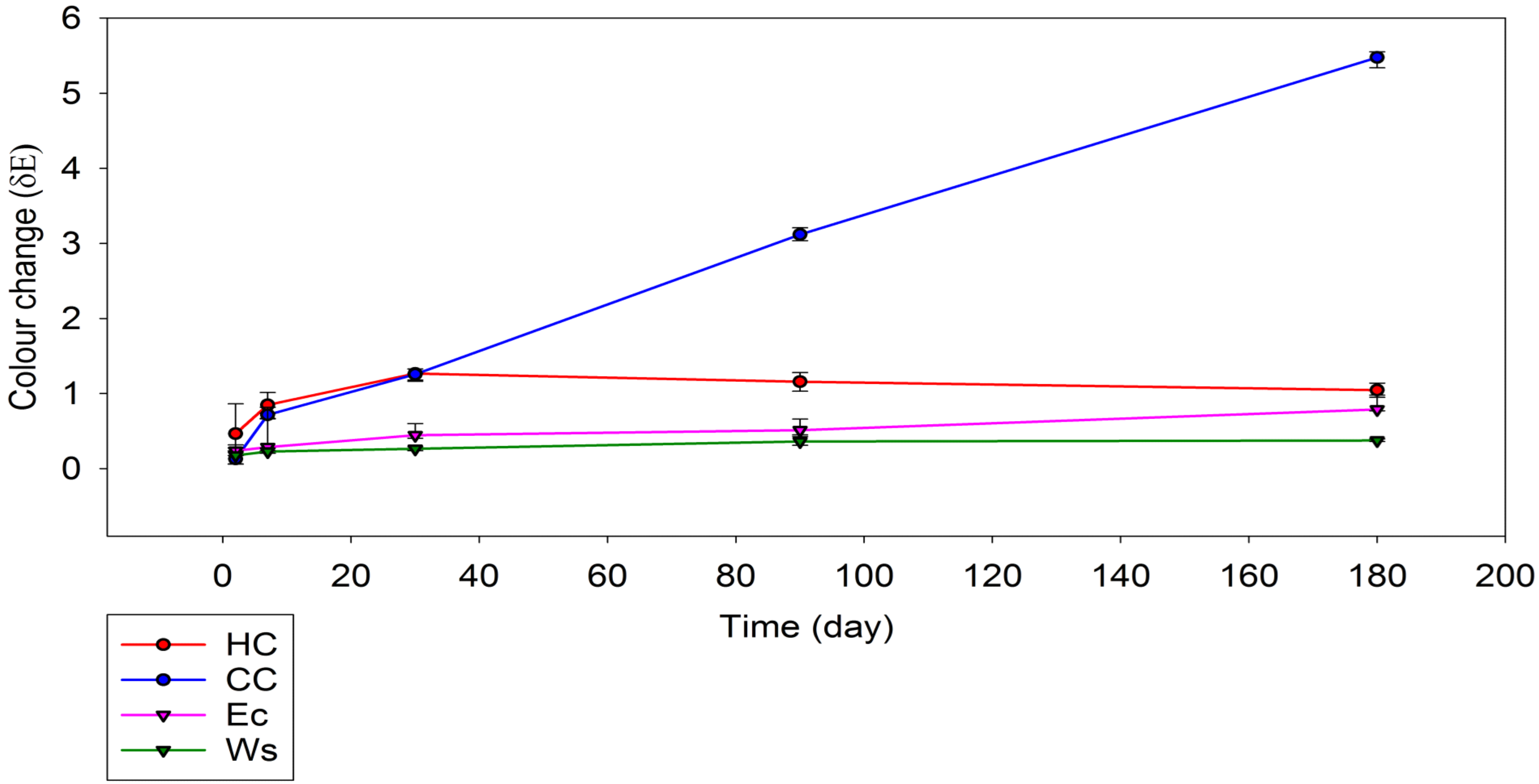


Figure 6.27 Summary of the colour change median values (ΔE) for the four comparator materials upon water storage. Error bars represent upper and lower quartiles

6.7.3 Discussion

The Tristimulus spectrophotometer is frequently used for this form of colour analysis. It provides an objective result as it does not depend on a human interpretation of colour change. In addition, the illuminant and observer were standardised, and so the inherent colour of the material was the only determinant factor in the changes.

The most prominent result which can be seen in Figure 6.27 is that HC, Ws and Ec changed little, and CC had more marked colour change, which is significantly different from the other three. The colour of CC changed greatly and continuously over time during storage in distilled water, and was significantly different from Ws and Ec at 1M and 3M, and from all materials at 6M time point. CC showed no obvious change in colour up to 1W, and then change became visually detectable but clinically acceptable up to 3M. After this, it became clinically unacceptable (Fernandes *et al.*, 2013; Hong *et al.*, 2009). Discolouration is inherent in chemically activated PMMAs since they contain an amine accelerator, such as tertiary amine. It has been reported that the amine remnants after polymerisation discolour readily upon oxidation after exposure to UV light from florescent light or any source from the surrounding environment, so it is advised to use an accelerator which is more colour stable (Dulik, 1979), or add a stabilising agent (Anusavice *et al.*, 2012). Therefore, increasing the immersion time increased the exposure to radiation from the surrounding environment and subsequently increasing ΔE. Another possible reason for colour change in CC is when water immersion was lengthy, which caused polymer hydrolytic degradation, linkage disconnection, and a gradual deterioration of its structure over time, resulting in subsequent discolouration (O'Brien, 2009). In addition, the severe roughness measured previously may also affect colour change, as mentioned in Sections 2.6.5 and 2.6.6 (Sepúlveda-Navarro *et al.*, 2011; Rutkunas *et al.*, 2010), in addition to the leaching of colourants from the materials (Anil *et al.*, 1998). In general, cold-cured PMMA continue to change colour during the lifetime of the denture (Purnaveja *et al.*, 1982). A similar outcome to that found in this study has also been reported by May *et al.* (1992), who observed a higher discolouration of cold-cured PMMA than both heat-cured PMMA and light-cured UDMA-based materials, after ageing under UV and visible light, in humidity, and at a temperature of 43˚C for 300 h.

The most important outcome obtained from the current experiment was that Ws showed the least change in colour (∆E 0.4) within 6M of water storage, followed by Ec. No significant difference was found between them within the previously defined storage periods. Colour change for HC was higher than Ec. HC was statistically significantly different from Ws from 1W up to 6M, but was not significantly different from Ec except at 1M. The level of change in ∆E for Ws and Ec cannot be detected visually, although for HC it was perceivable and within clinically acceptable parameters. HC reached its maximum change at 1M and then reduced, while the colour changes of Ws and Ec continuously but very slowly increased, with Ec being slightly faster than Ws. It seems that the ∆E of all three materials settled or optimised at 1M, and no significant difference was noticed after that. These changes may be partially attributed to the differences in the capability of water uptake and time point for water saturation in regard to HC and Ec, as noted earlier in Section 6.3 (Van Noort, 2013; Goiato *et al*., 2013b). HC had a comparable colour change after 1M of water storage to that in the study by Sepulveda-Navarro *et al*. (2011), and it has been noted that the colour change normally increases with time (Goiato *et al*., 2013a).

A relatively rough surface of Ec and the presence of porosity were not enough to discolour Ec noticeably upon water storage, due to its slow and minimal water sorption (discussed earlier in Section 6.3) (Akin *et al*., 2014b). Low Ec discolouration was supported by Asal *et al*. (2015), who observed a lower discolouration of Ec than for heat-cured PMMA in response to immersion in some colourant solutions.

With regard to Ws, despite the ingredients not being fully disclosed by the manufacturer, its chemical structure, namely the barbituric acid catalyst system, may have a role in colour stability. The role of this constituent is unclear, but it probably acts as a stabiliser antioxidant to prevent the oxidation of tertiary amine and discolouration of the specimens (Giziroglu *et al*., 2013). The barbituric acid catalyst system may also act as an activator instead of tertiary amine, which excludes the process of oxidation and discolouration at all (O’Brien, 2008). The result of this experiment was similar to that of a previous study (Gohlke-Wehrbe *et al*., 2012). In that study, light-cured UDMA-based material which was free of fillers was compared with pourable cold-cured PMMA containing a stabiliser, and both showed a stable colour within an 18 months observation period *in vivo*.

6.7.4 Conclusion

All materials changed their colour upon water storage; however, this change cannot be detected visually in Ws and Ec. Thus, Ws and Ec can be used to make denture bases with high aesthetic requirements, as they have good long-term colour stability upon water immersion. The ranking order was from low to high colour change: Ws, Ec, HC, and CC respectively.

Chapter 7 Comparing the mechanical and physical properties pre- and post-cleaning

7.1 Introduction

Proper hygienic care and denture cleansing is essential to maintain oral and general health for denture wearers (Sumi *et al.*, 2002). Immersion-type denture cleansers are the most commonly used, and typically contain either an effervescent peroxide or sodium hypochlorite as a cleaning agent (Anusavice *et al*., 2012).

Denture cleansers should perform cleaning (debris, dead microbes and stains) and sterilising effects (antimicrobial) (Pavarina *et al.*, 2003; Da Silva *et al*., 2008), without having an adverse effect on the physical and mechanical properties of the denture long term (Peracini *et al.*, 2010; Hashiguchi *et al.*, 2009). Therefore, any new denture base material should be tested for the influence of common cleansers on its properties before it is used by patients.

Previous studies have shown that the most commonly tested properties for the effect of cleansing are roughness, hardness, and colour, as these are mainly related to aesthetic and oral hygiene, either directly or indirectly (Pinto *et al*., 2009; Garcia *et al*., 2004; Machado *et al*., 2009; Mohammed *et al*., 2016; Fernandes *et al*., 2013; Moussa *et al*., 2016; Jeyapalan *et al*., 2015; Felipucci *et al*., 2011; Porwal *et al*., 2017; Sharma *et al*., 2017; Haghi *et al*., 2015; Lira *et al*., 2012). Cleansers can, either directly or by lowering hardness, increase the likelihood of scratching and roughness. Roughness is mainly responsible for holding stains (Mahross *et al*., 2015) and microbes (Koroglu *et al*., 2016; Harrison *et al*., 2004; Lima *et al*., 2006; Da Silva *et al*., 2008a; Radford *et al*., 1998; Bollenl *et al*., 1997). Stains disrupt the colour and aesthetics (Singh *et al*., 2012; Al-Huraishi *et al*., 2013; Alam *et al*., 2011; Hollis *et al*., 2015), while microbes contribute to oral stomatitis (Nalbant *et al*., 2008; Bollenl *et al.*, 1997; Al-Dwairi *et al.*, 2012). In addition, cleaners may have a bleaching effect causing discolouration (Joiner, 2004).

7.2 Aims and Objectives

The aim of this chapter is to evaluate two chemically different, commercially available immersion-type denture cleansers, containing the two main active cleaning agents, for their effect on the hardness, roughness and colour of the two newly developed materials (Ec and Ws), in comparison with HC and CC as a positive and negative control, upon simulated cleaning for six months. This was achieved by the following:

- Testing the effect of cleaning with sodium hypochlorite a ,bleaching liquid (Dentural, Martindale Pharmaceuticals, UK) and alkaline peroxide, an effervescent tablet (Poligrip 3 minutes, GSK, UK) denture cleansers on the hardness, roughness, and colour of Ec and Ws in regard to control materials via six months' simulated cleaning.
- Finding the order of materials regarding the influence of cleansers for each property and regarding the property itself.

7.3 Materials and methods

Twenty disc-shaped specimens were made at dimensions 20 mm diameter × 5 mm thickness, following the method described in Sections 5.2.1, 5.2.2, 5.2.3, 5.2.4; they were then polished as in Section 5.3. The specimens of each material were randomly subdivided into two groups for cleaning (n=10 per group). To aid subsequent identification, they were marked by carving a number on the lateral wall of the specimen to avoid interference with colour testing and to identify the superior surface from the inferior surface. The specimens were then evaluated for colour on the superior surface of each specimen, and for roughness on the inferior surface as BL tests. The roughness BL test was undertaken to reduce variation in this parameter (testing procedure will be mentioned in detail later in the roughness Section 7.4.1). The cleaning regime was then started, using two types of cleansers, either an effervescent tablet (Poligrip 3 minutes, GSK, UK) or a bleaching liquid (Dentural, Martindale Pharmaceuticals, UK). The ingredients of each product can be seen in Table 7.1.

The cleaning regime lasted three successive days to simulate the cumulative effect of cleaning dentures for six months (6M) or 26 weeks, with daily use of the Poligrip tablet or weekly use of Dentural, according to the manufacturer's instructions. Each day represented the effect of two months. This protocol was conducted in the shortest period possible to simulate the pure effect of cleaning on the materials as much as possible, with no other interfering or influencing factors, such as water immersion. The protocol of 6M was designed to accommodate the instructions of both cleansers. The 26W period were distributed on three days: the first and second days each represented 9W of cleaning (total 18W), and third day represented 8W of cleaning. Each group was cleaned with one of the cleansers, and as described in the next section.

Poligrip cleaning group

Ten specimens of each material were cleaned with an effervescent Poligrip tablet following the manufacturer’s instructions (Appendix F). Briefly, the ten specimen subgroup was immersed at the same time in 100 ml (Fergus *et al.*, 2017) of very warm distilled water in an individual plastic container (50 mm diameter × 70 mm height, polystyrene, Fisher Scientific) at a temperature of 45±3˚C. One tablet of Poligrip was added immediately, and the container was then stored in an incubator at 37±1 ˚C for 3 min according to the manufacturer. Each material was immersed in a separate container. This amount of water was the minimum volume to completely cover a medium sized maxillary complete denture in a vessel. The water was very warm according to the manufacturer’s instructions, and so the samples were stored in an incubator at 37˚C to keep warm. The temperature of the water 45±3˚C was selected to be midway between cold and hot, and above body temperature, as warmth is subjective. The range was ±3˚C because the time required for preparing water causes this range. After each use, the solution was discarded and the specimens were thoroughly washed with warm running tap water to remove the remnants of cleanser. This cycle was repeated 63 times on the first day, 63 times on the second day, and 56 times on the third day, to complete 182 cycles. This number of repetitions represents the number of days in 9W, 9W, and 8W respectively, corresponding to 182 days all together. The cumulative time of immersion was thus equal to 3.15, 3.15, and 2.8 h respectively, and the total cumulative time for immersion in Poligrip was 9.1 h.

Dentural cleaning group

Ten specimens of each material were cleaned with Dentural liquid following the manufacturer’s instructions (Appendix E). The ten specimen subgroup was immersed in 100 ml of warm distilled water at 45±3˚C, and 20 ml of Dentural was immediately added to the individual plastic container, which was then stored in an incubator at 37

±1˚C for 20 min, according to the manufacturer’s instructions. Each material was immersed in a separate container. After this, the specimens were washed thoroughly with warm running tap water and the water inside containers was replaced or discarded. According to the manufacturer, Dentural cleanser should be used once a week to clean specimens, which is why this cycle was repeated 9 times on the first day, 9 times on the second day, and 8 times on the third day, to total 26 cycles representing the number of weeks in 6M, and mimicking the normal cleaning procedure for denture wearers. The cumulative time of immersion was then equal to 3 h, 3 h, and 2.6 h respectively, and the cumulative total time of immersion in Dentural was 8.6 h.

At the end of each day’s cleaning regime, the specimens for each group were stored in a plastic container containing 100 ml distilled water in an incubator at 37±1 ˚C overnight to keep the specimens wet. On the fourth day, the samples were assessed for colour first, then roughness, and hardness (details of testing will be described in the next sections).

Cleaning product	Dentural	Poligrip
Ingredients	Sodium hypochlorite (1.5% w/v available chlorine), sodium hydroxide (1.7% w/v), purified water, Calgon S, sodium metasilicate, terpinolene, paraformaldehyde	Sodium bicarbonate, citric acid, potassium caroate (potassium monopersulfate), sodium carbonate, sodium carbonate peroxide, TAED, sodium benzoate, PEG-180, sodium lauryl sulfoacetate, PVP/VA copolymer, aroma, subtilisin, CI 42090, CI 73015, CI 19140

Table 7.1 Ingredients of Dentural and Poligrip

7.4 Roughness

7.4.1 Procedure for testing

Baseline roughness values (Ra) were recorded for each specimen of the previously produced specimens on one side three times before starting the cleaning regime mentioned above. This was done because roughness is a highly variable property to reduce its variability. The same procedures for evaluating roughness were followed as in Section 6.6.1. Then the cleaning regime was conducted.

After cleaning and on the day of testing, the specimens were removed from the distilled water, dried with absorbent paper, and evaluated for Ra. Roughness was re-assessed on the same surface of the same specimen as had been previously evaluated at the baseline. This surface was recognised by a sign carved on the lateral surface of each specimen, as mentioned before.

The means and standard deviation were calculated for Ra before and after cleaning, and the data were analysed using a two-way ANOVA repeated measurement, a two-way ANOVA to test factor interaction, and Holm-Sidak test method (Sigma Plot version 13.0) at a confidence level of 95%.

7.4.2 Results

For surface characterisation, one representative tracing from each group, whose Ra values were close to the mean value, was selected as a typical graph and is shown in Figure 7.1, Figure 7.2, Figure 7.3, Figure 7.4, Figure 7.5, Figure 7.6, Figure 7.7, and Figure 7.8. The HC graphs show a decrease in height of peaks and a depth of valleys in response to Dentural, while there is an increase in the depth of valleys in response to Poligrip. The CC graphs show an increase in the depth of valleys in response to Dentural, but show no clear change in response to Poligrip. The Ec graphs show a decrease in valley depth in response to Dentural, but an increase in valley depth in response to Poligrip. For the Ws graphs, there is an increase in the depth of valleys in response to Dentural, although there is no clear change in response to Poligrip.

The resultant data for each material and individual cleanser were normally distributed (Shapiro-Wilk test, P=0.6). Ra mean values before and after cleaning are tabulated in Table 7.2 and plotted in graphs, shown in Figure 7.9 and Figure 7.10.

Regarding Dentural cleanser, a two-way repeated measures ANOVA test revealed that Ra was significantly affected by cleaning (P=0.04), but no significant difference was found between the Ra of the materials (P=0.07). Therefore, there was no statistically significant interaction between the materials and different levels of Dentural use (Ra before cleaning and after cleaning) (P=0.55). According to Figure 7.11, the Ra of all materials have increased.

Regarding Poligrip cleanser, the two-way repeated measures ANOVA test revealed that no significant difference was found between the Ra of the materials (P>0.05), and, for each individual material, Poligrip had no significant effect on Ra (P>0.05), except for Ws (P=0.005). According to Figure 7.10, Ws became significantly rougher, whereas the three other materials were either unchanged or became smoother, but not significantly so, as shown in Figure 7.11. There was a significant interaction between the materials and levels of Poligrip (before and after) (P=0.01).

Comparing the two cleansers' effects on the Ra of all materials using the two-way ANOVA because they are normally distributed disclosed no significant difference between cleansers (P=0.18), while there was a statistically significant difference between materials (P=0.02). The Holm-Sidak method showed a statistically significant difference between HC and Ws (P=0.01). However, no statistically significant interaction occurred between materials and cleansers (P=0.4). Figure 7.11 represents the real change in Ra as box plot, plus highest and lowest value. All values located below zero level refer to a reduction in Ra, while those located above zero level refer to an increase in Ra. It can be seen that Dentural roughened all the materials, in particular Ws, whilst Poligrip softened HC and roughened all the other materials, in particular Ws. The figures also show the high variation in the effect between HC and Ws, and the significant difference between them.

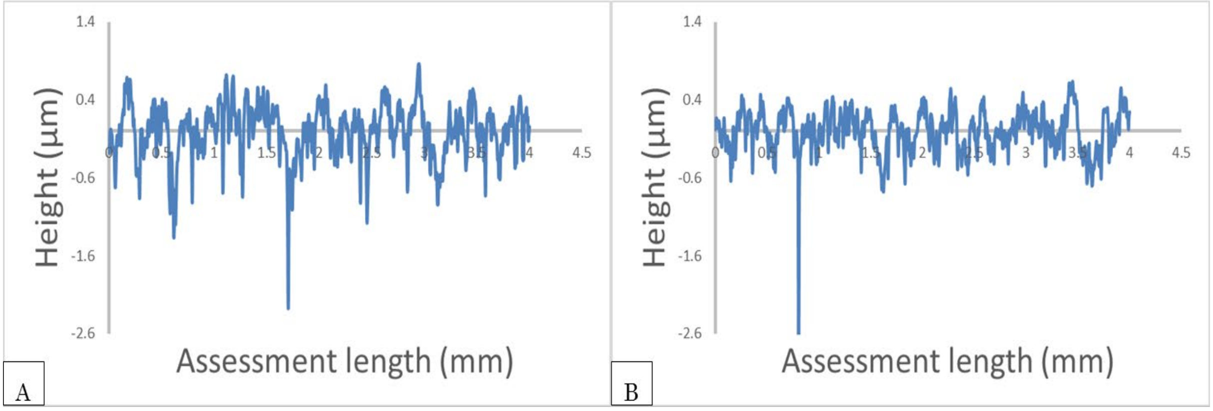


Figure 7.1 Typical stylus profilometry profile of HC specimens: (A) pre-cleaning, (B) post-cleaning with Dentural

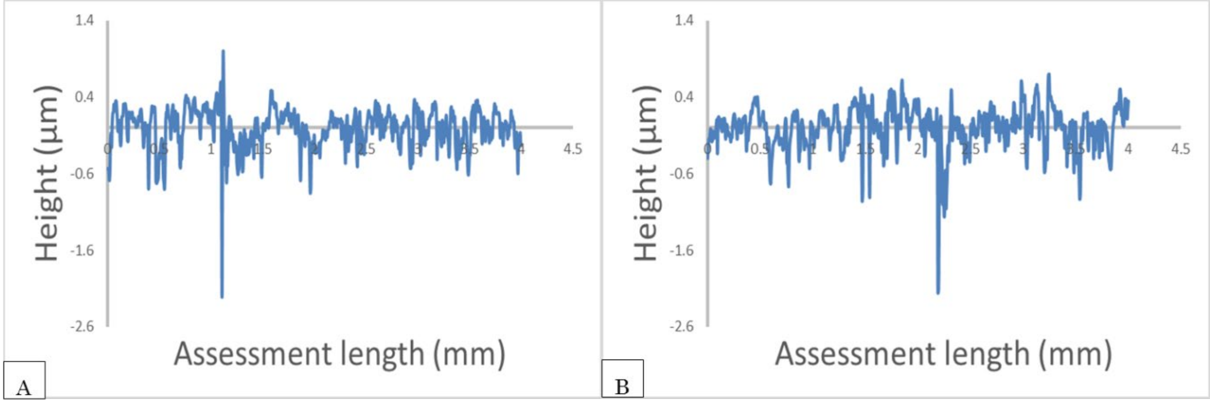


Figure 7.2 Typical stylus profilometry profile of HC specimens: (A) pre-cleaning, (B) post-cleaning with Poligrip tablet

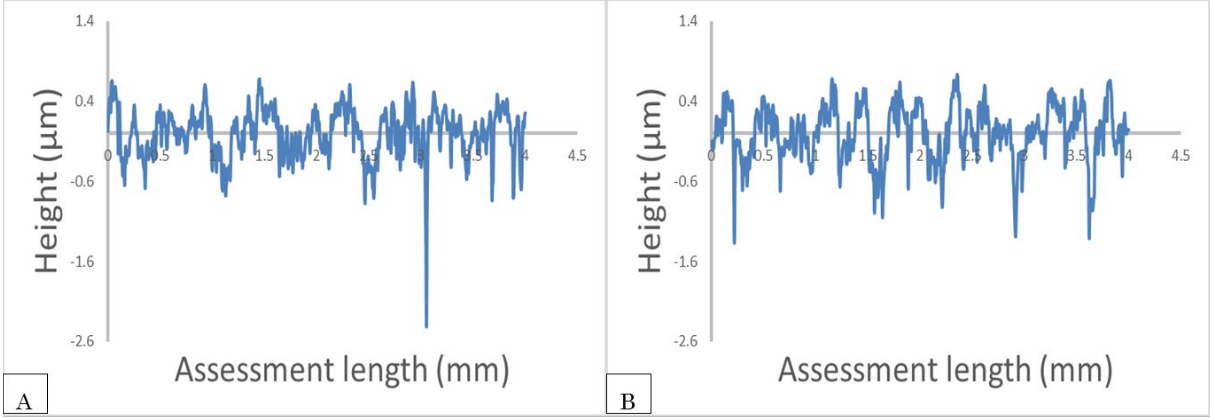


Figure 7.3 Typical stylus profilometry profile of CC specimens: (A) pre-cleaning, (B) post-cleaning with Dentural

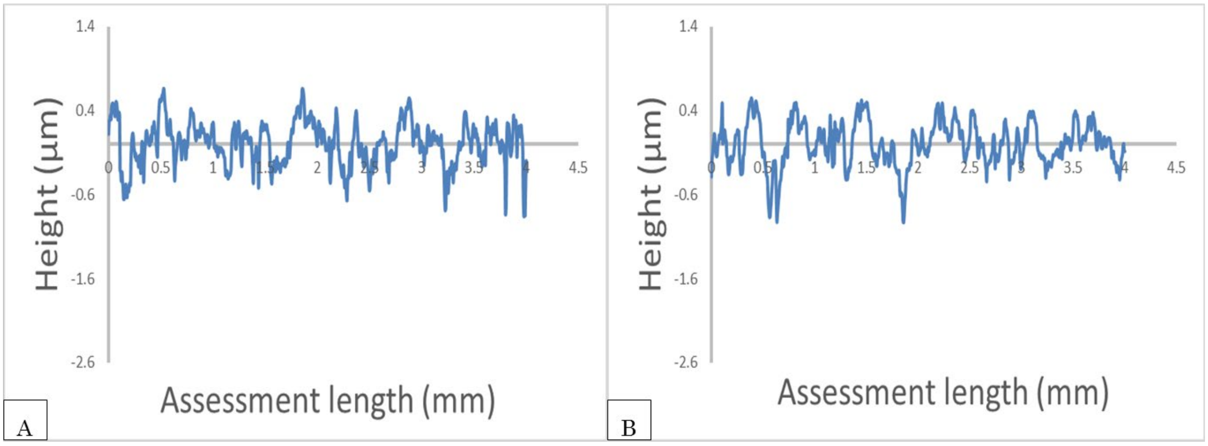


Figure 7.4 Typical stylus profilometry profile of CC specimens: (A) pre-cleaning, (B) post-cleaning with Poligrip tablet

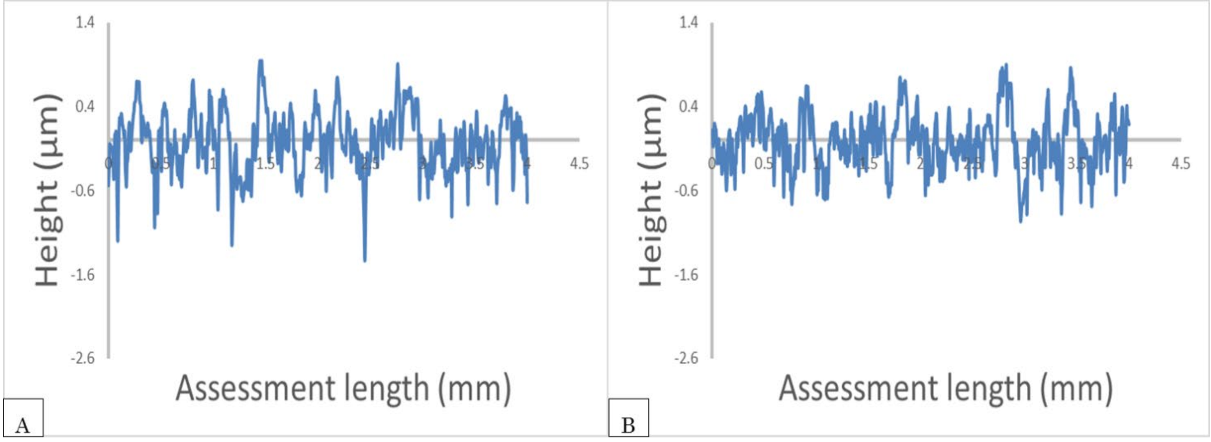


Figure 7.5 Typical stylus profilometry profile of Ec samples: (A) pre-cleaning, (B) post-cleaning with Dentural

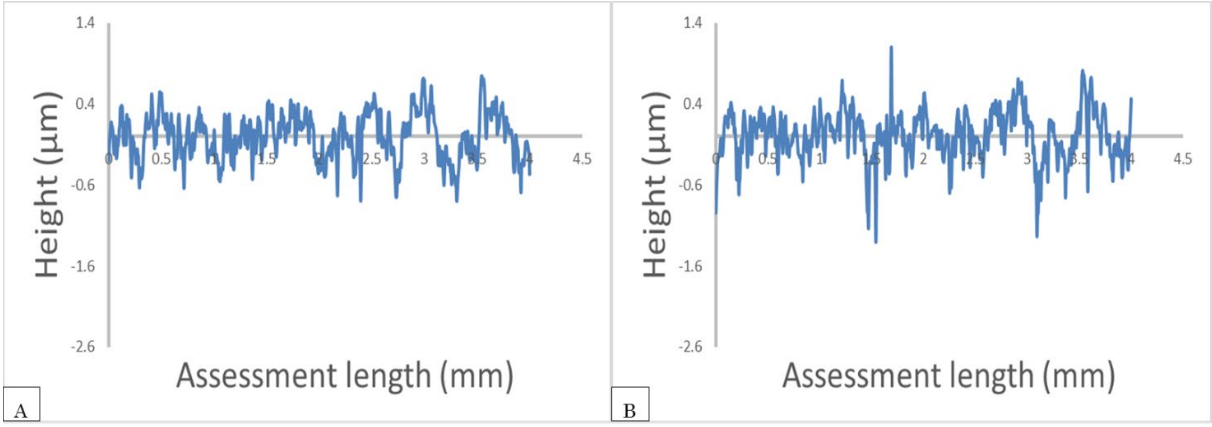


Figure 7.6 Typical stylus profilometry profile of Ec samples: (A) pre-cleaning, (B) post-cleaning with Poligrip tablet

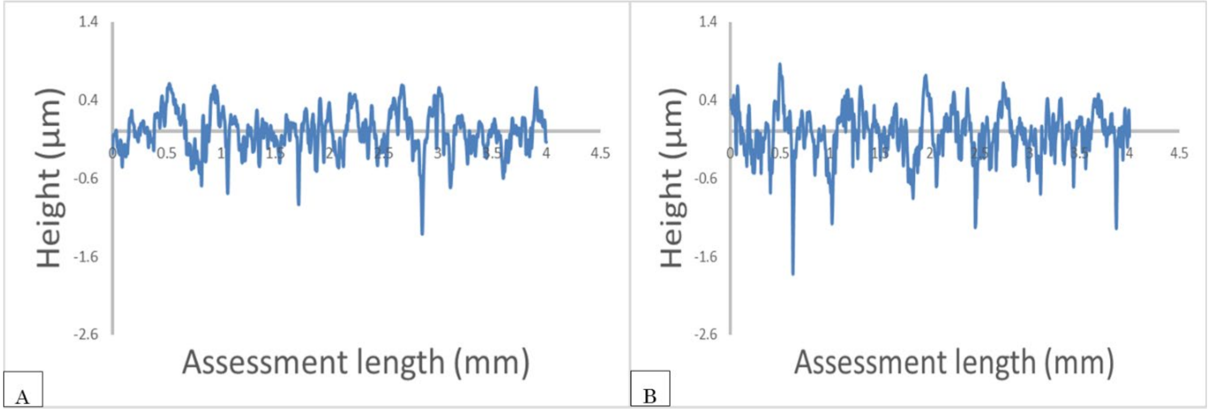


Figure 7.7 Typical stylus profilometry profile of Ws samples: (A) pre-cleaning, (B) post-cleaning with Dentural

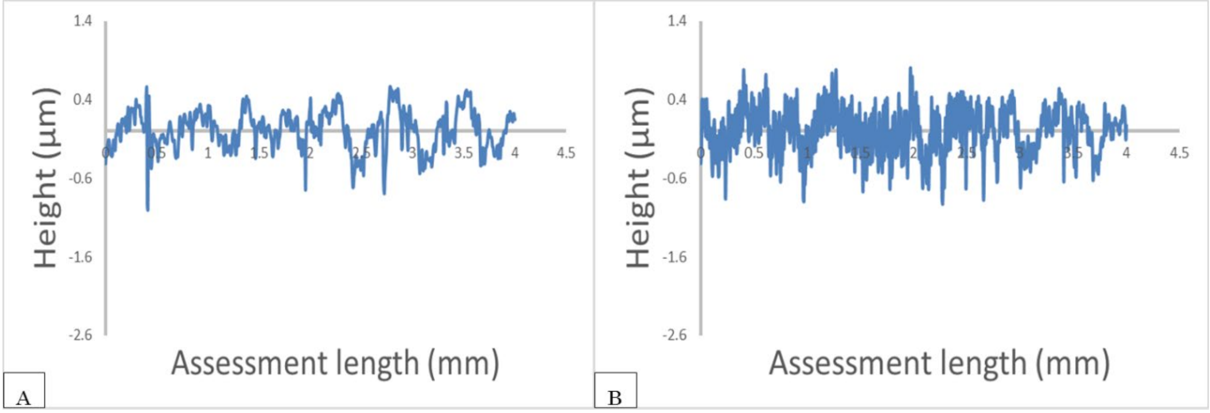


Figure 7.8 Typical stylus profilometry profile for Ws samples: (A) pre-cleaning, (B) post-cleaning with Poligrip tablet

Material	**Cleanser type**	**Roughness (Ra) mean (SD) (µm)**		
		Before	**After**	**Mean change in Ra (SD)**
HC	Dentural	0.21 (0.05)	0.21 (0.04)	0.00 (0.07)
	Poligrip	0.23 (0.02)	0.21 (0.04)	-0.02 (0.03)
CC	Dentural	0.24 (0.05)	0.26 (0.04)	0.03 (0.06)
	Poligrip	0.21 (0.06)	0.21 (0.04)	-0.01 (0.07)
Ec	Dentural	0.24 (0.04)	0.26 (0.06)	0.02 (0.05)
	Poligrip	0.23 (0.04)	0.23 (0.04)	0.00 (0.04)
Ws	Dentural	0.21 (0.05)	0.24 (0.04)	0.03 (0.03)
	Poligrip	0.20 (0.05)	0.24 (0.03)	0.04 (0.04)

Table 7.2 Summary of mean roughness values (Ra) before and after cleaning with the two cleansers

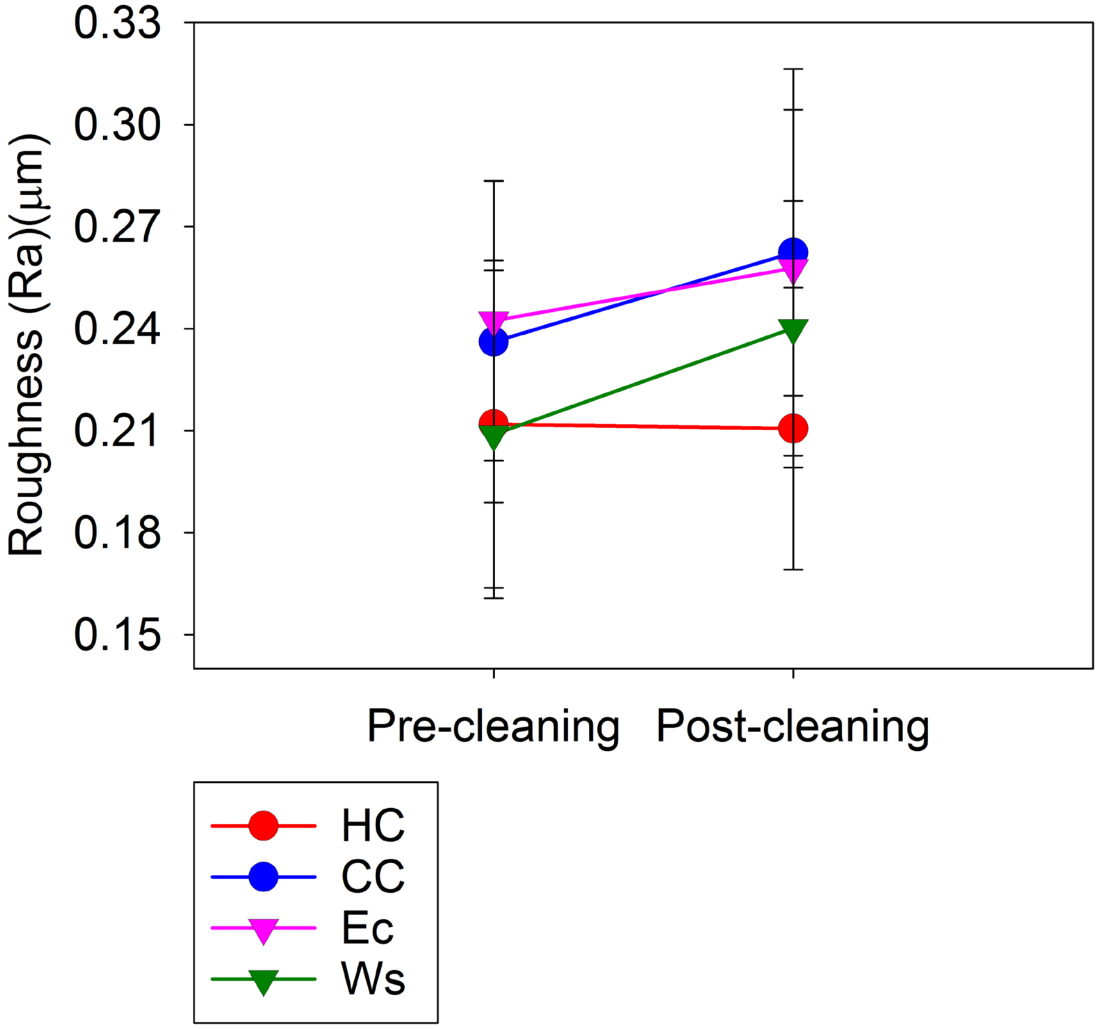


Figure 7.9 Summary of the mean roughness values of the four comparable materials before and after cleaning with Dentural cleanser. Error bars represent standard deviation

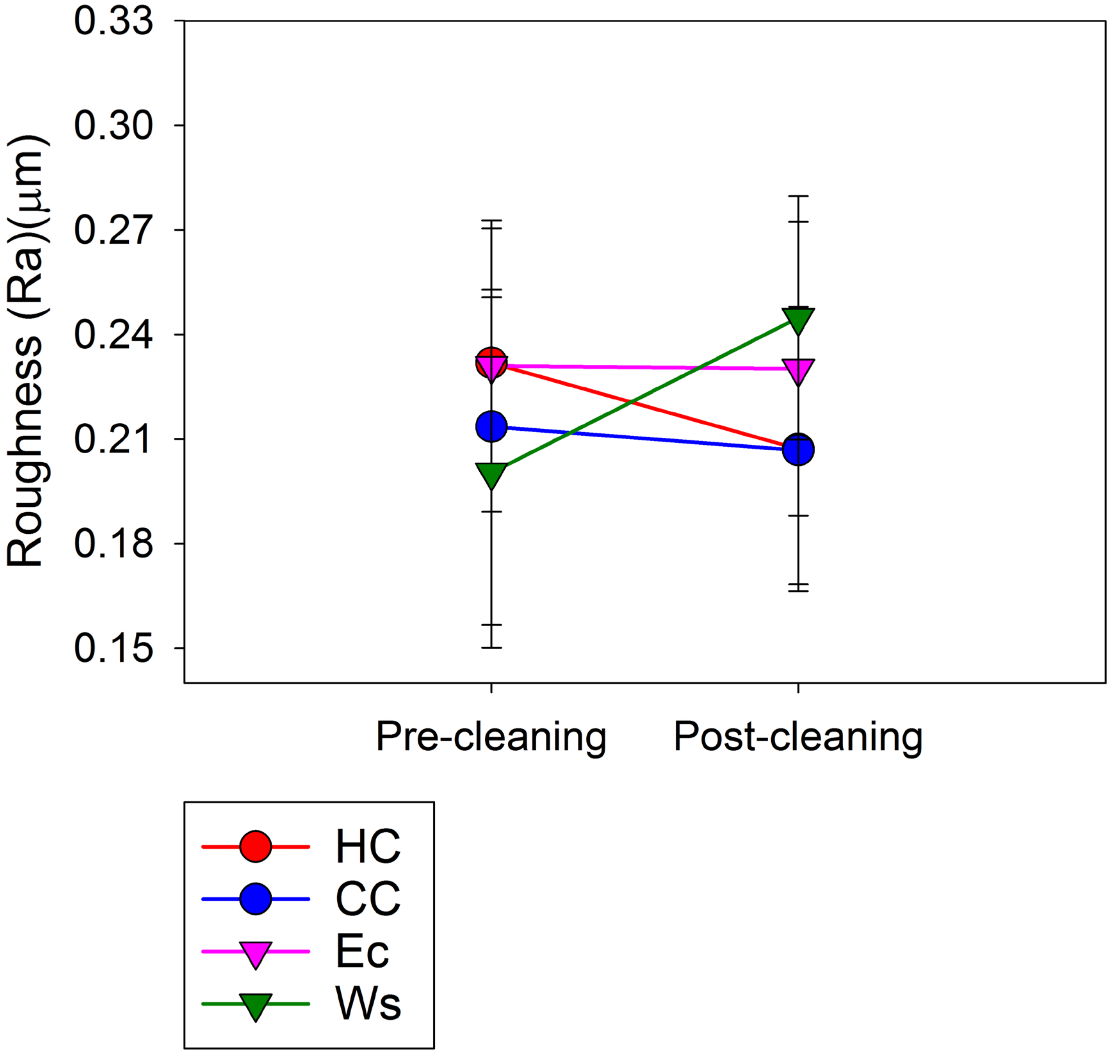
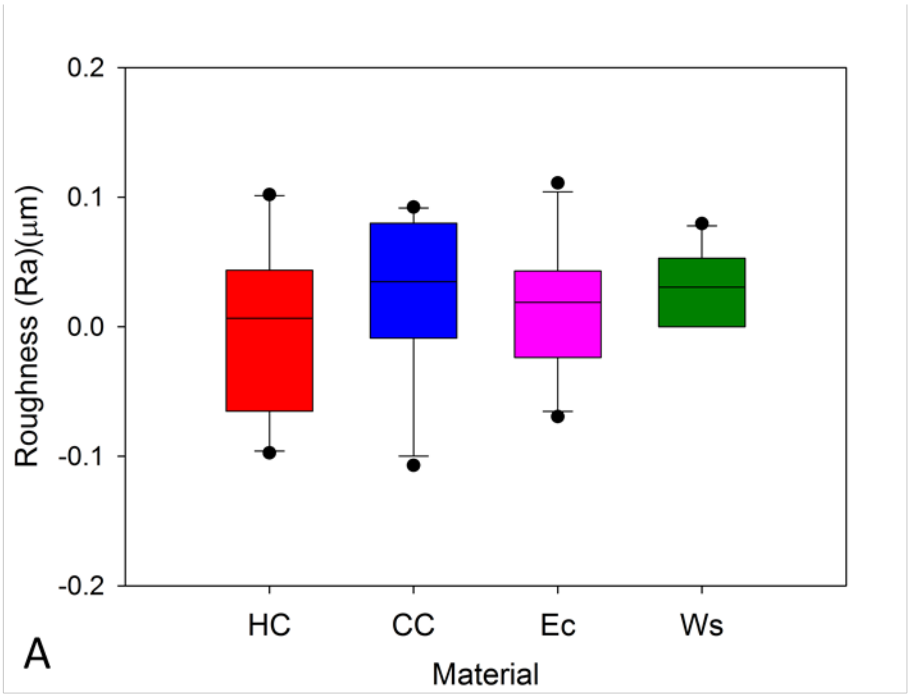


Figure 7.10 Summary of the mean roughness values of the four comparable materials before and after cleaning with Poligrip cleanser. Error bars represent standard deviation



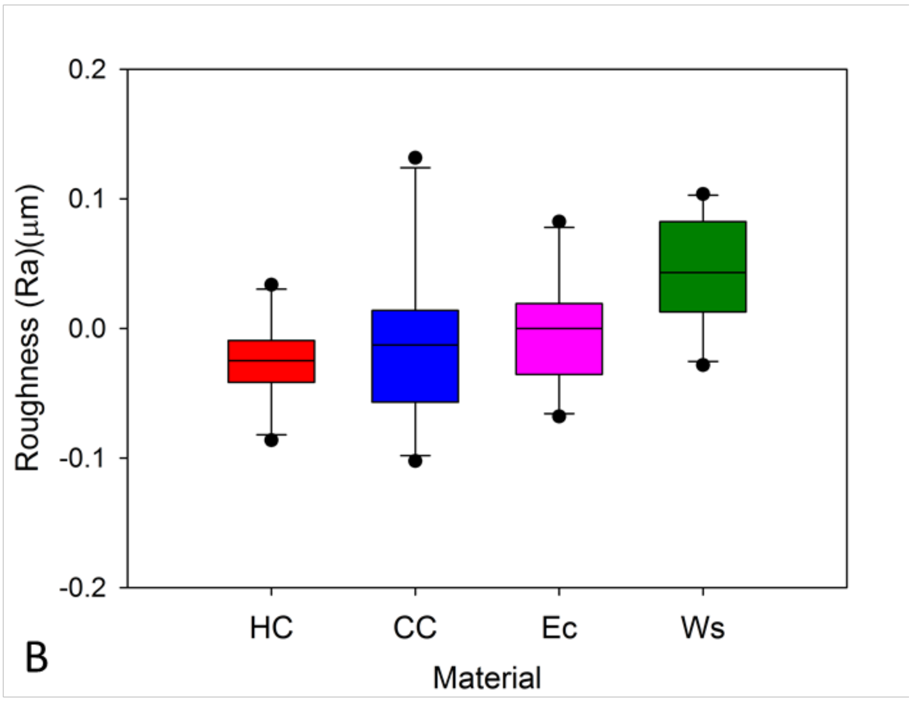


Figure 7.11 Box plots summarising changes in roughness values in response to cleansing: (A) Post-Dentural, (B) Post-Poligrip

7.4.3 Discussion

Brushing mechanical cleaning was not used in this regime, which is a limitation of the study due to no availability of machine or time to develop that machine. It needs a development of machine with definite pressure and time. There was also no dirt on denture to be removed by brushing. Brushing also has a detrimental effect on the surface roughness (Harrison *et al.*, 2004), which impairs testing hardness and colour. Dentures usually is made for elderlies, who in most cases suffer from muscle weakness and poor manual dexterity which necessitate the use of cleansers for efficiently cleaning their dentures more than brushing. Chemical cleaning was also selected as one component of cleaning regime to reduce the number of variables.

Dentural and Poligrip cleansers were chosen for the cleansing protocol in this study following a personal communication with Dr Ian Ellis and Professor John Mark Thomason at Newcastle NHS Hospitals Trust, regarding the oral instructions given to denture wearers (Appendix G). These cleansers were also chosen after checking the instruction sheets handed out to each denture wearer post-denture insertion at Newcastle NHS Hospitals Trust (Appendix H). They were also selected as two commercially available cleansers of different immersion forms (liquid and tablet), containing different main active agents (alkaline peroxide and sodium hypochlorite). Therefore, the behaviour of the materials in response to these cleansers can give an overview of their behaviour in response to immersion cleansing in general.

The cleaning protocol was designed to simulate the effect of long-term cleaning for 6M, but over three days. Hence, the specimens were exposed to cleaning and storage in water for three successive days, and each day represented an effect of two months. Following the manufacturer’s instructions, Poligrip should be used daily, and Dentural weekly. Accordingly, the protocol of six months was designed to accommodate the instructions of both cleansers, and therefore it was proposed to divide 6M period into 26 weeks, with the resultant number of weeks divided into three days. The first and second days simulated nine weeks, while the third day simulated eight weeks. The same 6M period was converted from weeks to days for the Poligrip effervescent tablet, which is why 63 tablets were used on the first day, 63 on the second day, and 56 on the third. 100 ml of water was used to store the specimens at intervals and to dilute both immersion cleaners (one tablet Poligrip or 20 ml Dentural per 100 ml water). The specimens immersed in cleanser were stored in an incubator at 37˚C to keep water warm during cleansing and reduce the effect of fluctuating room temperature. During intervals between cleaning days, the samples were stored in distilled water at 37±1˚C to simulate the presence of the denture inside a patient's mouth, and to keep the specimens wet, since patients are advised to do so (Dhuru, 2005). This protocol represents the cumulative effect of cleaning in a way somewhat similar to Pero *et al*. (2013), who disinfected specimens 30 times in six days to simulate 180 days' cleaning.

The testing protocol included using the same group of specimens to test the three properties to reduce the variations in making, polishing, and storing specimens between different specimen batches. Testing the same surface for the same property before and after applying the intervention reduced the variation in the property itself. This procedure was also followed in previous studies (Khan *et al*., 1987; Sepúlveda-Navarro *et al.*, 2011; Durkan *et al.*, 2013; Baig *et al.*, 2011; Fernandes *et al.*, 2013; Senna *et al.*, 2011; Al-Dwairi *et al.*, 2011; Machado *et al.*, 2009). Testing was done in the aforementioned order to avoid the harmful influence of testing machines on specimen properties. In other words, it was chosen to measure colour and roughness before hardness, because hardness testing can cause damage to the specimen.

All the results before and after cleaning showed roughness values higher than the roughness threshold for plaque accumulation (0.2 µm) (Braun *et al.,* 2003), as described in Section 2.6.5. This could be attributed to the mechanical polishing followed in this study, as sand paper and pumice are unable to produce ideal surface smoothness (Rao *et al*., 2015).

According to the findings of the current study, it has been shown that long-term simulated chemical disinfection with Dentural or Poligrip has a variable effect on the Ra level of materials. Dentural increased Ra significantly but Poligrip did not, with the exception of Ws; however, no significant difference was found between their effects. The effects of immersion cleansers on the tested denture base materials can mainly be attributed to their constituents. Water was the main constituent of the cleaning solutions because of each cleanser was mixed with 100 ml water, according to the manufacturer's instructions. The duration of cleaning was three days, through which the samples were immersed either in cleansers or in distilled water at 37ºC for overnight immersion. The results of roughness after water immersion (Section 6.6.2) at 2D were: for HC 0.12 (0.04), CC 0.15 (0.05), Ec 0.18 (0.03), and Ws 0.23 (0.06). Thus, by comparing the current result of cleaning with these results, it was found that the dissolving and absorbing effect of water on the materials had no significant effect on roughness, except for CC. Hence, in this study the main influence on Ra was the effect of the active ingredients in the cleansers on the surface integrity, rather than from water. Despite the immersion time for Poligrip and Dentural being different and different chemistry, there were no significant differences between their effects on the comparator materials. No study in the literature has tested the effect of cleansers on roughness using similar protocol to compare with.

Dentural generally increased roughness significantly. This effect occurred because Dentural contains sodium hypochlorite at a concentration 0.015% w/v after dilution with water, and is thus a strong oxidising agent. The oxidation process produces oxygen. There is no standardisation in the literature regarding the method of disinfection and testing, which is why our results cannot be compared directly with other research; however, an indirect comparison is possible. Many previous studies have used sodium hypochlorite (NaOCl) as a disinfectant. Silva *et al*. (2008), who tested the effect of using 1% NaOCl for 10 min a day for 10 sequential days on chemically cured materials, observed an increase in roughness, which is in line with the results of this study. Some studies demonstrated detrimental effects of NaOCl disinfection on heat-cured PMMA which is consistent with the results of this study. Fernandes *et al*. (2013) noticed increasing roughness after immersing specimens for 30 and 60 min in 1% NaOCl. Likewise, Sharma *et al*. (2017) used 1% NaOCl 10 min/day for three months, and Porwal *et al*. (2016) used 0.5% NaOCl daily 10 min/day immersion time for 180 days. Some other studies on heat-cured PMMA showed no effect on Ra. Sartori *et al*. (2006) tested the effect of immersion in chlorine solution for 24 h diluted with 500 ml water, twice at seven day interval and no significant changes were observed on roughness. Similarly, Jeyapalan *et al*. (2015) found that immersing heat-cured specimens in 1% NaOCl for 240 h resulted in no significant roughness change. The most probable reason for the inconsistent results between different studies is the different duration of immersion and different concentrations used in these studies.

Poligrip caused no significant change in roughness to all materials except Ws, which showed a significant increase in roughness. Poligrip is marketed as neutral peroxide with enzymes and contains a mixture of oxidising agents (sodium carbonate peroxide and potassium monopersulfate) and cleaning agents (sodium bicarbonate). These active ingredients contain peroxide, which releases oxygen after dissolution in water, thereby enabling mechanical cleaning by oxygen bubbles (Budtz-Jorgensen, 1979). Most previous studies disagree with the results of the current study, although their active ingredient was also alkaline peroxide, because there are many differences between these studies and the current study. Peracini *et al*. (2010) reported increasing roughness in heat-cured PMMA specimens after 30 immersions in the same oxidising cleanser (BonyPlus) in warm water (40˚C) for 5 min over six days, keeping samples in distilled water at room temperature at intervals to simulate 180 days' cleansing. Peracini *et al.* also observed no change in roughness by following the same protocol with the same active agent but a different product (Corega) for a 3 min immersion. Corega has similar constituents to Poligrip, with the exception of sodium perborate, and therefore that result can be said to be in line with the current study. Although BonyPlus and Corega both have alkaline peroxide as the active agent, they showed different behaviours because of the different cleanser constituents. This interpretation justifies the difference between the current findings and other studies. Koroglu *et al*. (2017) found a reduction in heat-cured PMMA specimen roughness after cleansing with Corega and simulating a three month nocturnal daily immersion for 8 h with one tablet in 200 ml distilled water. This means that even the same cleanser (Corega) can produce variable results over different cycles. Most of these results which are contrary to the current study can be explained due to the different chemistry of the resin used, such as containing a different amount of plasticiser (Cakan *et al*., 2015; Porwal *et al*., 2016). Other differences include: use of a different polymerisation machine and cycle (Gad *et al*., 2017), degree of cross-linking, surface treatment, finishing and polishing procedure, time of immersion, cleanser concentration, water temperature, the active agent in cleansers (Porwal *et al*., 2016) and different cleanser constituents (Peracini *et al*., 2010, Fergus *et al*., 2017). No standard result can be elicited from the literature to compare with.

In general, there was no significant difference between materials regarding the change in roughness following immersion cleaning, except for the significant difference between Ws and HC. Cleansing roughened the surface of Ws, while it smoothed that of HC. This difference in type of effect caused the significant difference between the effects on the two materials. However, no significant difference was found between the materials' Ra values after cleaning in regard to each individual cleanser. Accordingly, the ascending order of the materials' Ra after cleaning starts with HC, and is followed by Ec, CC and Ws, respectively. Ec Ra increased with these two cleansers to be higher than HC, despite it having a higher molecular weight. However, no significant difference was found between the cleansers' effects on HC and Ec Ra values. The notion that light-cured material is rougher than heat-cured after disinfection is supported by Mohammed (2011). Ws was significantly influenced by both cleansers, possibly due to its low molecular weight, i.e. short chains slightly inter-connected by cross-linkers, with high free monomer trapped in between. This structure might have allowed the cleanser to penetrate between the multi-chains, dissolving the monomer and oligomer. Porosity may be another causative factor, and was enlarged by the effect of the cleansers. In contrast, HC has no or low ratio porosity, a high molecular weight, meaning large molecules, and low levels of residual monomer. Ws has not influenced by water as mentioned in Section 6.6; hence, this may advocate the thinking that sodium hypochlorite and alkaline peroxide have a more profound solvent effect on barbituric acid derivatives. The concept of chemically-cured PMMA being more influenced than heat-cured PMMA was supported by Salama *et al*. (2017). No similar research in the literature was found for comparison.

7.4.4 Conclusion

Over 6M of simulated disinfection, sodium hypochlorite (Dentural) increased roughness significantly, while alkaline peroxide (Poligrip) did not influence the Ra significantly, except for Ws. However, no significant difference was found between their effects for each material.

Ws was the most detrimentally influenced material for both cleansers and surface was roughened by cleaning more than other materials. However, no significant difference was observed between the materials' Ra.

7.5 Colour stability

7.5.1 Procedure of testing

The 20 disc-shaped specimens were also used to evaluate the colour. Colour readings were measured first on dry specimens before cleaning as a BL value. Colour testing followed the same principles and steps as described previously in Section 6.7.1, except that colour was assessed only on the superior surface of each specimen in this section of the study. The surface to be tested was identified by a symbol engraved during the numbering process. ∆E was calculated using the same equation as in Section 6.7.1. The median and interquartile ranges were calculated for colour change (∆E) after cleaning. A two-way ANOVA with Holm-Sidak test method was used to determine the significant difference between groups (Sigma Plot version 13.0) at a confidence level of 95%.

7.5.2 Results

The results of colour change were non-normally distributed (Shapiro Wilk, $P<0.001$). Therefore, they were transformed to normal distribution using log 10 ($P=0.136$). Two-way analysis of variance on transformed data revealed no significant difference between the two cleansers ($P=0.07$) and no statistically significant interaction between a material and a cleanser ($P=0.15$). Materials ∆E were significantly different ($P\leq0.05$). Non-transformed data of colour changes (∆E) for both cleansers for all materials were tabulated in Table 7.3 and used to draw a box plot, as seen in Figure 7.12 and Figure 7.13. The box plot clearly demonstrate that CC had the greatest colour change, while Ws had the least. To find the significant differences between individual materials, a Kruskal-Wallis test was applied to the raw data. According to this test, no significant difference was found between HC ∆E and Ec ∆E for either cleanser; however, CC ∆E differed significantly from the other materials for Dentural, while for Poligrip, Ws ∆E differed significantly from HC ∆E and CC ∆E ($P\leq0.05$).

↓Material/Cleanser→	Colour change (∆E) median (IQR)	
	Dentural	Poligrip
HC	0.33 (0.23)^{A}	0.43 (0.14)^{C}
CC	0.60 (0.08)^{AB}	0.48 (0.14)^{D}
Ec	0.30 (0.1)^{B}	0.39 (0.17)
Ws	0.21 (0.14)^{B}	0.21 (0.16)^{CD}

Table 7.3 Summary of median colour change values (∆E) and variation after cleaning with each cleanser (superscript similar letters refer to significant differences within each cleanser)

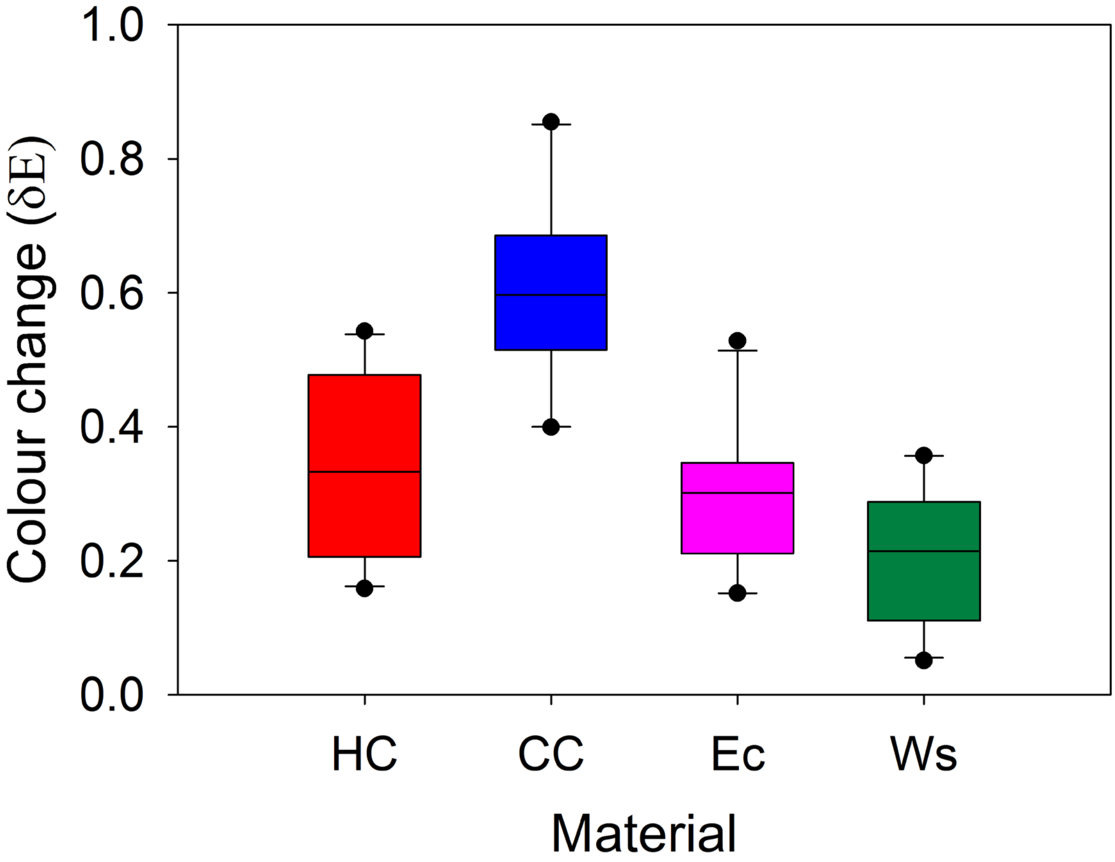


Figure 7.12 The effect of Dentural cleanser on colour change for the four comparable materials

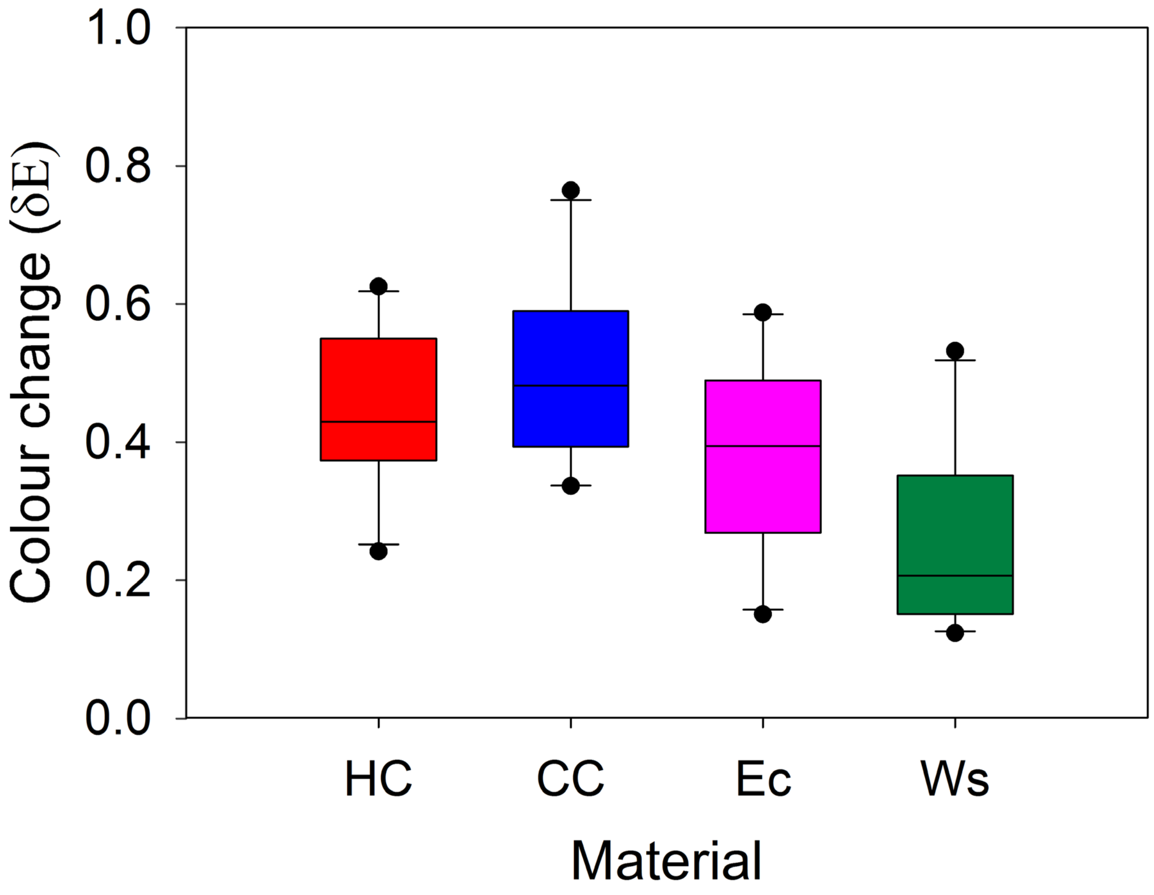


Figure 7.13 The effect of Poligrip cleanser on colour change for the four comparable materials

7.5.3 Discussion

The colour of the tested materials was variously influenced by cleansing. Minimal colour change occurred with Ws, while maximal change occurred with CC. Ec and HC were moderately affected by the cleansers and with no significant difference between their ∆E. This ranking is exactly the same as that in response to water storage (Section 6.7.2); therefore, differences in ∆E between the materials may be due to the same reasons given in 6.7.3. Hong *et al*. (2009) found a similar ranking of reliner materials after cleaning with nine different denture cleansers up to one year. In contrast, McNeme *et al*. (1991) found that a Triad light-cured denture base had a higher discolouration than cold- and heat-cured PMMA, and cold-cured was less colour stable than heat-cured PMMA. The reason for this was mainly due to different Triad ingredients, sorption and surface texture properties from that of Ec. There are few studies in the literature with which to compare.

Although Ws and CC are both chemically-cured PMMA, they exhibited a completely different response to cleansers. Ws showed the lowest ∆E value despite the high change in roughness, which may be mainly due to the presence of barbiturate derivatives which act either as a stabiliser or as an activator, instead of tertiary amine, as mentioned previously in detail in Section 6.7.3. CC showed a high ∆E in this study as a result of the leaching of colours and soluble components, oxidation of amines, increasing roughness, and tendency to absorb stains (Ma *et al*., 1997). High CC ∆E may also be due to material degradation, which can be triggered by exposure to cleansers, in particular cleansers containing many oxidising agents.

HC and Ec colour were moderately influenced by cleansing, with Ec ∆E lower than HC ∆E. This result may be related to the high molecular weight and highly cross-linked structure of Ec which impedes leaching of colours. Low water absorption causes a lower amount of the cleanser to be absorbed into the interior of the material, as the cleansers were diluted with water. The order of Ec ∆E might also result from the minimal influence of cleansers on roughness, as discussed in Section 7.4. The higher rate of water absorption and high solubility in HC also resulted in a slightly higher colour change than for Ec.

Different colour effects were produced by different cleansers on each material. However, no statistically significant difference was found between Dentural and Poligrip. The change in Ws was the same for both cleansers, while CC discoloured more with Dentural than Poligrip, possibly due to the effect of Dentural on increasing roughness, as discussed in Section 7.4. Regarding Ec and HC, the effect of Poligrip was higher than that of Dentural, but not statistically significantly. A similar grading of cleanser effect on light-, cold- and heat-cured polymers was found with cleansers which had chemically identical active ingredients (Hong *et al*., 2009).

The overall effect of cleaners on colour was minimal, visually undetectable, and not clinically significant (overall $\Delta E \leq 0.6$) upon 6 months' simulated cleansing. The major influence on colour can probably be attributed to water absorption rather than the chemical cleansing action, because the values of ΔE for all materials were similar to those obtained upon water immersion at the interval 2-7 days (Table 6.11). However, the readings of HC were a little lower and that of Ec a little higher than that measured at the 2-7 days interval. The difference in HC values was not significantly different from that of 2D group water storage ($P>0.05$). Differences in Ec might be due to the effect of cleansers on Ec roughness, which was increased rather than decreased. Another possible reason for differences associated with Ec is the presence of porosity. The findings of this study were similar to Ma *et al*. (1997), who reported ($\Delta E \leq 0.6$) clinically insignificant colour change after testing cold- and heat-cured PMMA and Triad light-cured material for continuous immersion up to seven days in three different cleansers with different active agents. Likewise, Moon *et al*. (2014) found visually perceptible but clinically insignificant colour shift after immersion of some denture base materials in five different denture cleansers for 10 h a day for one year. Similarly, McNeme *et al*. (1991) also recorded a similar result regarding sodium hypochlorite, which was used for 72 h immersion for heat- and cold-cured PMMA, and Triad light-cured material at 1% concentration, with no visual perceptible change in colour. By contrast, results obtained by Lohitha *et al*. (2016) showed a clinically significant and large degree of colour change according to NBS ($\Delta E \geq 12$) after 180 days of daily cleaning of heat-cured PMMA, with one of three cleansers and water immersion at intervals. The latter result might be due to the combined effect of water immersion and cleansing action for that length of time. The protocol followed for this study did not completely resemble the protocols used by other authors, as it was more realistic regarding cleaning dentures. It consisted of intermittent repeated exposure to cleansers rather than the continuous immersion for a long time (minutes, hours, days or months) followed in other studies, in addition to different concentrations. For these reasons, it produced visually imperceptible changes in colour, in contrast to the results obtained in other studies (Hong *et al*., 2009; McNeme *et al*., 1991; Durkan *et al*., 2013; Ma *et al*., 1997; Moon *et al*., 2014; Salloum, 2014; Jin *et al*., 2003; Fernandes *et al*., 2013).

7.5.4 Conclusion

Immersion in cleansers have no detrimental effect on the colour of Ec and Ws and other control materials during 6M of simulated cleansing. All colour changes produced were invisible and could not be perceived by the naked eye. Therefore, they are suitable denture cleansers for use with the tested denture base materials. The ranking of the materials, in descending order regarding colour changes, is CC followed by HC, then Ec, and lastly Ws.

7.6 Indentation hardness

7.6.1 Procedure for testing

The same surface used to evaluate the cleaning effect on colour change (∆E) was also used to evaluate the hardness caused by cleaning. The hardness was assessed following the same steps as explained in Section 6.5.1. The median and interquartile ranges for Vickers hardness were calculated for each group. The data were analysed using the Mann-Whitney and Kruskal-Wallis tests, with a Tukey test to determine the significant difference between groups (Sigma Plot version 13.0) at a confidence level of 95%.

7.6.2 Results

Typical hardness graphs for all materials before and after cleaning with cleansers can be seen in Figure 7.14. They represent the graphs of specimens which show the nearest values to the median of each group. The graphs show that HC and Ec are similar, as are CC and Ws. Both disinfectants caused an increase in the indentation depth. Regarding HC and Ec, the graphs for Dentural and Poligrip were similar, while for CC and Ws, Dentural demonstrated less indentation depth than Poligrip.

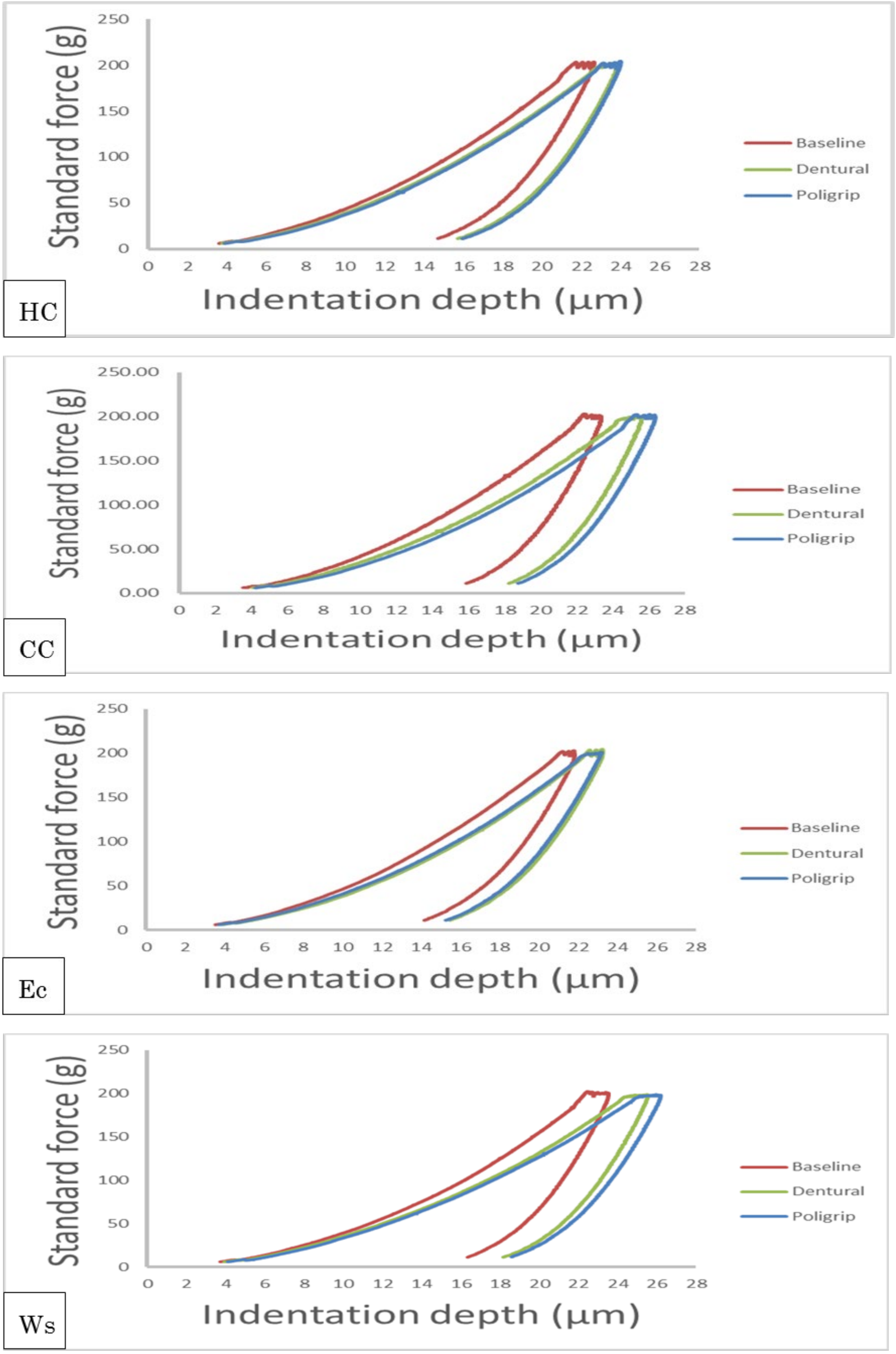


Figure 7.14 Typical Indentation curve before and after cleaning with Dentural and Poligrip

The descriptive statistical analysis is summarised in Table 7.4. The resultant data were non-normally distributed, and therefore the graphs showing the effect of the cleansers were drawn based on median values, shown in Figure 7.15 and Figure 7.16. These graphs show that hardness values reduced significantly with cleaning ($P \leq 0.05$), but no significant difference was found between the two cleansers for each material ($P > 0.05$). This was illustrated in the typical graphs shown in Figure 7.14, and in the results of the Mann-Whitney test between cleansers demonstrated in Table 7.4. The hardness at the baseline was compared previously in Section 6.5. There were significant differences between materials for both cleansers ($P \leq 0.05$). However, there was no significant difference between Ec and HC, or between Ws and CC ($P > 0.05$). The order of materials regarding hardness after cleaning remained the same as before cleaning, except for Ws after Poligrip cleaning, which was harder than CC, but not statistically significantly so. The relation between materials pre- and post-cleaning stayed the same as well, except for HC and CC, which became statistically significantly different post-cleaning ($P \leq 0.05$).

The line connecting pre- to post-cleaning hardness values indicates the different influence of the cleansers on the materials. The amount of hardness reduction in each material was calculated and compared for each cleanser using Kruskal-Wallis and Tukey tests, and these revealed a significant difference between HC and Ws for Dentural, and between HC and CC for Poligrip ($P \leq 0.05$). The Mann-Whitney test showed no significant differences between the two cleansers' effects on each material ($P > 0.05$). The maximum effect of Dentural was on Ws, but Poligrip's was on CC; both cleansers had the least effect on HC, as in Table 7.5. Ws was affected more than CC by Dentural, but less than CC by Poligrip; however, no significant difference was found between their effects. The different impact of cleaning on materials made HC and Ec HV closer to each other, and much farther from Ws and CC HV after cleaning, as in Figures 7.15 and 7.16.

Material	Cleanser Group	Vickers Hardness [Kgf/mm^2](median) (IQR)
HC	BL	19.4 (1.1) ^{aA}
	Dentural	17.9 (0.7) ^{aD}
	Poligrip	17.8 (1) ^{aI}
CC	BL	17.9 (1.5) ^{bB}
	Dentural	15.2 (1.3) ^{bDE}
	Poligrip	13.8 (1.5) ^{bIJ}
Ec	BL	21.5 (1.6) ^{cBC}
	Dentural	18.6 (1.7) ^{cEF}
	Poligrip	19.4 (1.4) ^{cJK}
Ws	BL	17.7 (0.9) ^{dAC}
	Dentural	14.0 (0.8) ^{dDF}
	Poligrip	14.3 (1) ^{dIK}

Table 7.4 Summary of hardness values before and after cleaning of four comparator materials with Dentural and Poligrip (similar superscript letters refer to significant differences, lowercase letters within the same material and uppercase letters between materials)

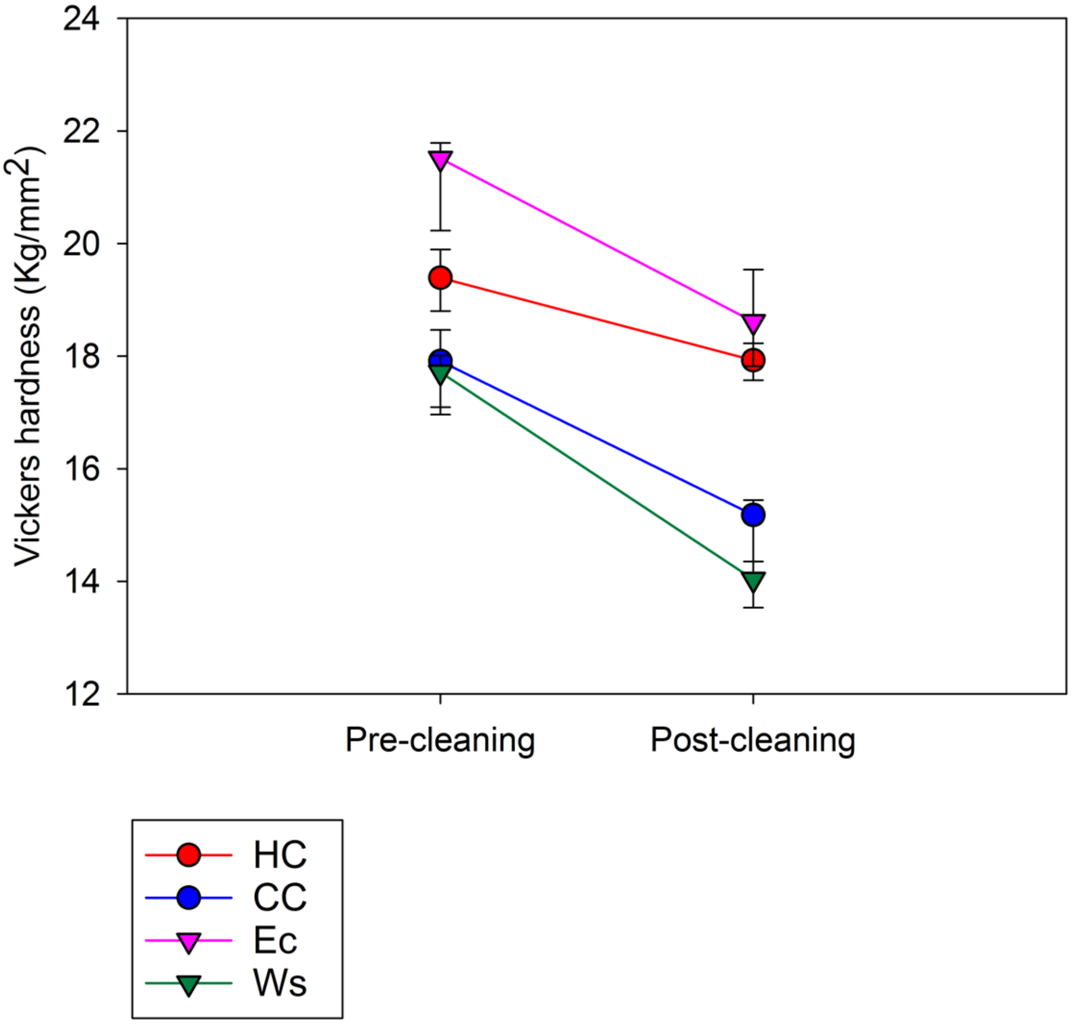


Figure 7.15 The effect of Dentural on the median Vickers hardness values of the four comparator materials. Error bars represent upper and lower quartiles

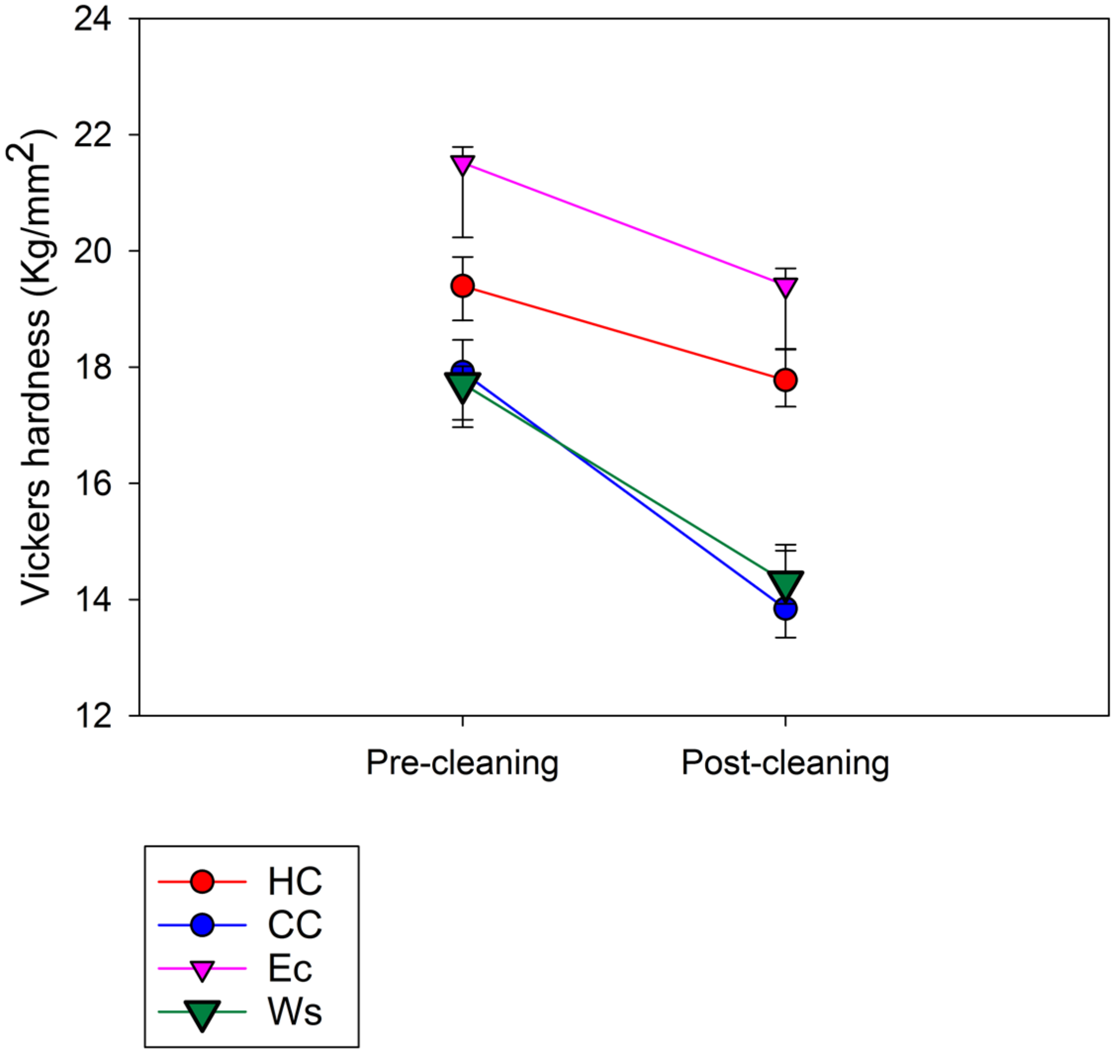


Figure 7.16 The effect of Poligrip on the median Vickers hardness values of the four comparator materials. Error bars represent upper and lower quartiles

Material	Cleanser Group	Median reduction in Vickers Hardness medians [Kgf/mm^2]
HC	Dentural	1.4^A
	Poligrip	1.5^B
CC	Dentural	3.2
	Poligrip	4^B
Ec	Dentural	2.2
	Poligrip	2.1
Ws	Dentural	3.6^A
	Poligrip	3.3

Table 7.5 Summary of reduction in hardness median values after cleaning with two cleansers for the four materials (similar superscript letters refer to significant differences, uppercase letters refer to differences between materials)

7.6.3 Discussion

The results revealed a significant softening of all materials after immersion cleaning, in line with many previous studies, although these used a different cleaning regime and different cleansers (Sartori *et al*., 2008; Pinto *et al*., 2009; Durkan *et al*., 2013). As the regime was three days, the results can be compared with that of water immersion at the interval of 2-7 days in Section 6.5.2. Compared with water, softening with cleansers was more progressive. The reason for this may have been the different water temperature used for the cleansers to that used to store the samples in water experiments, as the temperature increases the distance between chains, and subsequently increases the amount of water and chemicals absorbed by the materials (Devlin and Kaushik, 2005). The main cleaning ingredients of Dentural and Poligrip cleansers may also have contributed to reducing hardness. Dentural contains sodium hypochlorite, which bleaches and oxidises. Poligrip contains many oxidising agents such as sodium bicarbonate, potassium caroate, and sodium carbonate peroxide. Incorporating many oxidising agents in the product is important to produce a fast action in a short immersion time, rather than using overnight immersion (Lohitha *et al*., 2016). By dissolving an effervescent tablet in water, sodium bicarbonate decomposes to release peroxide, which, along with sodium carbonate peroxide, releases oxygen bubbles and loosens any dirt mechanically (Lohitha *et al*., 2016; McKillop and Sanderson, 1995). The chemical action of peroxide after its absorption may not be responsible for a softening, as reported by Nakahara *et al*. (2013). Other chemical ingredients attacking the materials as solvents, as well as the mechanical action of oxygen bubbles, may have reduced the hardness. Campanha *et al*. (2012) reported that 1% sodium hypochlorite reduced the hardness of light-cured composite teeth after seven days' immersion. The magnitude of reduction was higher than in this study because the immersion was longer and continuous, and the concentration higher (Porwal *et al*., 2016). However, this study disagrees with the results regarding the effect on PMMA-based material hardness, as there was no significant reduction in the Campanha study. It may be that the inconsistency in results lies in the fact that denture teeth are much more cross-linked than denture base materials. Similarly, Neppelenbroek *et al*. (2005) and Sharma *et al.* (2014) found a significant reduction in the hardness of heat-cured PMMA after four cycles of disinfection per 10 min for each cycle, with 1% sodium hypochlorite. The amount of reduction was the same as in this study, although the two cleaning regimes were different.

In the current study, the impact of cleansers varied across the materials, although both cleansers exerted not significantly different effects on hardness for each individual material. The softening was minimal on HC, but maximal on Ws and CC. Ec hardness was moderately influenced (Table 7.5). Despite the significant differences in the softening effects between different materials, the order of the hardness of the materials stayed the same after cleaning, with Ec being the hardest, followed by HC, and with no significant difference between them. This was then followed by CC and Ws, except that Ws and CC exchanged orders after being cleaned with Poligrip.

The ranking of the softening of the materials by cleansers follows the same order as softening by water absorption (Figure 6.18), except for HC, meaning Ec was influenced with cleansers more than HC. This means that softening is mainly due to water absorption, but also partly to the chemical dissolving action of cleansers. The high water absorption of HC, in particular at a warm temperature, accompanied by high water solubility at this point, might have provided a chance to remove the free monomer and subsequently increase in hardness faster than the other materials (Neppelenbroek *et al*., 2005; Sharma *et al.,* 2014). For HC, a concomitant increase in hardness due to the leaching of monomer and a decrease in hardness due to the cleansers might have caused it to be the least affected by softening. Another possible reason for this is that the influence of the cleansers on the materials was generally governed by the inherent structure of materials. For this reason, as strong, cross-linked, and high molecular weight materials, HC and Ec were less influenced than the weak and low molecular weight materials of CC and Ws. It was not possible to identify previous research that had investigated Ec or Ws before in terms of cleaning, and no study in the pertinent literature can be compared to this one directly or indirectly due to following different protocols.

7.6.4 Conclusion

Cleaning Ec and Ws with Dentural and Poligrip for six months' simulated cleaning reduced hardness significantly, similar to the results with the positive and negative controls of the study. The original ranking order of the materials regarding hardness before cleaning stayed the same after cleaning, although HC was the least influenced by the cleaning, and CC and Ws were the most influenced.

Chapter 8 General discussion

8.1 General discussion and conclusions

PMMA-based heat-cured denture base materials have long been used to make denture bases because of their low cost, good dimensional stability and good aesthetics (McCabe and Walls, 2009). Despite these advantages, however, they are brittle (Narva *et al.*, 2005; Radzi *et al.*, 2007) and have poor fatigue properties (Vallittu *et al.*, 1993; Vallittu *et al.*, 1994; Van Noort, 2013) in addition to long curing time. To address this, various newly developed materials have now become available, such as Eclipse, a UDMA-based light curable material, and Weropress, a PMMA-based cold curable material, which are characterised by their ease and speed of processing (Mumcu *et al.*, 2011). In addition, the manufacturers claim that they show good mechanical and aesthetic properties. While these materials have been tested at the manufacture, they have not been tested following long term use or after exposure to different effects (Ali *et al.*, 2008; Diaz-Arnold *et al.*, 2008; Mumcu *et al.*, 2011).

The aim of this project was to find out if these new materials had properties that would make them eligible to be used as denture base materials, and to establish if they are appropriate replacements for the currently used denture base materials. Eclipse and Weropress were compared with heat- and cold-cured PMMA as positive and negative controls for the study.

The comparison included testing materials at three stages: after production, after water immersion, and after simulated cleansing. The previously mentioned physical and mechanical properties were tested at first and second stages, while only hardness, roughness and colour stability were tested at the third stage.

This is an innovative study which tested the effect of water immersion on the colour stability, roughness, and hardness of Eclipse and Weropress (Ws) in both the short and long term, in comparison to other conventional materials. The water immersion regime started from two days at room temperature, and then at one week up to six months at 37±1 °C. Simulated cleansing was representative for six months' cleaning with one of two immersion cleansers: Dentural (liquid) and Poligrip (tablet). The study was also original as it aimed to chart the effect of water storage and simulated cleaning on these materials in comparison to conventional ones.

Regarding optimising the control materials, they were optimised to produce good specimens which comply with international standard organisation requirements for tests undertaken in this project for denture base polymers (BSI, 2013), with the ability to follow instructions other than the manufacturer's to provide correct comparison. These instructions were still in the acceptable range followed in the dental laboratories to make dentures. The new materials were optimised by choosing one of the production methods, which is most applicable, repeatable, easy, and time saving and producing as much sound specimens as possible. However, manufacturers' instructions must be followed exactly to provide correct characterisation.

Optimising the method of manipulation for Ws was undertaken to find out the correct method of manipulation to make bar specimens. The presence of more than one method of Ws manipulation allowed for optimisation, while only one method of Ec manipulation did not allow optimisation. Hydrocolloid is the most commonly used material for moulding Ws dentures, and so, all instructions accompanied Ws product were explaining Hydrocolloid's use. However, Hydrocolloid was not suitable to produce bar specimens owing to different thickness and geometry from that of dentures despite trying different designs. The main reasons were air confinement within the mould and short working time. Therefore, a stone mould was used and bar shape was modified to provide a reservoir for material. This was because no special design for stone flasks was provided in the instructions. In the case of Hydrocolloid, reservoir was represented by channels used for pouring and as air exit (sprues). This point might have created a limitation because the specially designed flask for producing dentures may produce dentures different in quality from specimens produced by a normal metal flask.

Overall, the study concluded that the manufacturer's instructions for the three optimised materials, while suitable for producing dentures, required optimisation to produce specimens for laboratory testing. In particular, optimisation was required to make specimens free of visible porosities. The limitation of this optimisation was that it has used bar specimens which are different in thickness and geometry from dentures. This may has led to the occurrence of porosity extensively. Bar specimens were selected for optimisation as they have the largest surface area specimens of all the other specimen dimensions used in this study and offer more opportunity to test for porosities. The advantage of optimisation was getting consistent results in aesthetics and strength for the control materials, but this may have had an influence on some properties (Anusavice *et al*., 2012).

Following optimisation, porosity was the main difficulty to get sound specimens and a persistent limitation for all materials. It occurred in relation to either consistency, route of production, chemistry, or using specimens' geometry. The reason of its occurrence was different with different material. Despite the optimisation procedure, some materials still showed porosities in different conditions. There were different reasons for the porosities in each material, as discussed in Section 2.2.6. CC specimens showed granular porosities which appeared when mixing took place at a room temperature exceeding 24˚C, because this temperature increases volatilisation of the monomer during mixing, causing less monomer to be available for the reaction. In addition, high room temperature accelerates the reaction and shortens the working time (Van Noort, 2013). The working time was therefore not enough to allow proper manipulation of the dough. Ws showed contraction porosities caused by high volumetric shrinkage of pourable material due to its high monomer content (O'Brien, 2008). Ec showed air porosity occurrence, which was unavoidable because the material was sticky and the shape of the mould was concave, rather than convex as is the edentulous arch; the former shape assists air inclusion between the mould and the material and it was difficult to expel it. HC showed gaseous porosity for an unknown reason, despite controlling all responsible factors, but this was at a low ratio. As mentioned in the literature, porosity has been reported to occur in 39.8%–52.3% of all cured specimens and it is not possible to lower this ratio, despite modifying several factors. Therefore, it is not easy to obtain a denture base free of porosities due to interactions between these factors (Wolfaardt *et al.*, 1986). Types, frequency and reasons for porosity can be seen in Table 5.1. Optimising Ec and Ws produced so many porous specimens. In such case, all specimens should be discarded and the materials are considered as not suitable to be denture base material following ISO rules. However, these materials were tested before in the literature and no previous research showed any clinical significance of porosity on the results. In addition, the occurrence of porosity in the current study may almost be related to using specimens not dentures. To address that, different strategies were followed to overcome the significant effect of porosity on the tested properties (mentioned in 5.2.5).

To address the statistical effects of aging on the properties, each property will be discussed before and after applying the effect. Regarding water sorption, Ec showed the least absorption, followed by CC, Ws and HC, respectively. Regarding water solubility, Ec showed the least solubility followed by Ws, CC and HC, respectively. Low sorption and solubility of Ec is attributed to the inherent structure of Ec, which most likely consists of a copolymer of UDMA with hydrophobic monomers (Gajewski *et al*., 2012), the semi-crystalline cross-linked structure of Ec reducing diffusivity (Sun *et al*., 2003), absence of free monomer (Melilli *et al*., 2009), and fewer soluble ingredients. The clinical implication of this current result was that water has shown a neglected effect on mechanical and physical properties and high dimentional stability. Ws is a cold-cured PMMA and as such has free monomer (Dogan *et al*., 1994; O'Brien, 2008), and porosity, as shown previously (Keller *et al.*, 1974; Keller and Lautenschlager, 1985; Nejatian *et al.*, 2015), caused its sorption and solubility order. HC contains highly water soluble ingredients, such as the initiator and plasticiser which increased its sorption and solubility, while dense structure of CC post optimisation reduced its sorption properties to be close to Ec.

The ranking of flexural strength and modulus at the baseline, starting with the highest to the lowest, was: Ec, HC, CC, Ws. The materials were arranged according to molecular weight and degree of conversion, because flexural properties depend on these, as discussed previously in Section 2.6.3.

Water storage significantly reduced the flexural strength of PMMA-based materials, but not significantly for Ec. Ec has a higher molecular weight than PMMA and semi-crystalline highly cross linked, and this reduced the influence of water on the strength of Ec in addition to low sorption and solubility properties. After water immersion, the ranking was similar to that at BL except that Ws exchanged its position with CC.

Water storage reduced flexural modulus for all materials as a result of the plasticising effect of water. The modulus order after absorbing water was similar to the water sorption order, which was: Ec, Ws, CC, and HC with exchanging CC and Ws their positions. Thus, the amount of absorbed water was the main determinant, although there was no statistical significant difference between the three PMMA materials. Changes in strength and modulus after water storage did not fall below standard values, except for the strength of Ws and CC. For that reason, they are unsuitable as denture base materials in terms of strength.

The hardness order of the materials was the same as flexural strength at BL and after storage in water for six months; this may be attributed to the same reasons. The effect of water storage on hardness was also the same as strength. Water as a solvent has little effect on Ec hardness because of the same above mentioned reasons relating to Ec structure in comparison with PMMA material structure. Three main reasons influence hardness: degree of conversion and amount of free monomer initially, water sorption after immersion, and inherent structure at late immersion. The effect of simulated cleansing reduced hardness significantly for all materials including Ec but the ranking order stayed same. This effect is due to the solving effect of cleansers with the aid of high temperature.

The order of the materials' roughness was different before water storage from that before cleaning because of the high variation in Ra but in general HC was the smoothest material. Water storage in general had either no significant change or a favourable effect on materials, except for significant roughening of CC at 6M. This effect might be related to the significant dissolution of the CC surface at 6M. Simulated cleansing showed variable effects. Ec surface was roughened with Dentural significantly but not with Poligrip, while Ws surface was roughened with both significantly; however, their Ra values after cleansing were not statistically significantly different from controls and from each other. A future SEM study may give a clearer picture of this effect. This finding might be due to the fact that sodium hypochlorite and alkaline peroxide have more powerful dissolving effects on barbituric acid derivatives and low molecular weight polymers (Salama *et al*., 2017), in addition to the possible effect of porosities.

Water storage and cleaning changed the colour of all the materials in the following descending order: CC, HC, Ec, Ws. Both effects were not visually perceived, except for HC and CC after water storage. The reasons for these changes were mentioned before in Section 6.7.3. Thus, water storage and cleaning with sodium hypochlorite and alkaline peroxide are safe on Ws and Ec in terms of colour.

During specimen production, some observations may have an impact on application in the clinical environment. In terms of the time required to produce dentures, the water bath used to polymerise HC was enough for five clamps of two flasks, while the Eclipse curing unit was enough for only one cast. Hence, ten dentures can be polymerised by water bath in one curing cycle, which is 9 hours, while one denture can be polymerised at once in an Eclipse curing unit, which takes about 45 min, taking into consideration the time required for cooling and polymerising the tissue side. By comparing these two materials' polymerisation, it can therefore be assumed that both consume an approximately similar time for the technician if they are cured in the dental laboratory as a batch, but Ec consumes less time for the prosthodontist if it is cured in the clinic as a single piece. In addition, there is no flasking, wax elimination, and packing procedure. Accordingly, Ec can be produced faster and is thus more feasible than HC in the clinic

To address the clinical relevance of aging on materials' properties, the difference between HC and CC in the standard values in ISO standard 20795-1:2013 (BSI, 2013) was considered as the threshold for clinical significance. This means the threshold was: flexural strength 5 MPa, flexural modulus 500 MPa, solubility 6.4 $\mu g/mm^3$, and hardness 5 Kg/mm^2. While, the roughness threshold was 0.2 μm, the threshold of plaque accumulation as mentioned in 2.6.5 (Bollenl *et al.*, 1997), and colour stability was any change more than 3.4 according to NBS as mentioned in section 2.6.6. Water sorption depended on subjective evaluation, where very high difference, which increases the denture weight noticeably, was considered clinically significant. This clinical guide cannot be considered as ideal because sometimes the change in the property is small and not statistically significant but it is clinically significant and vice versa. Also, the standard values were not based on clinical research but the difference in behaviour between HC and CC was clinically approved. This clinical guide was just an attempt to explain the expected clinical effects; however, the real clinical effects cannot be confirmed without performing a clinical trial.

By using the above mentioned guide, the effect of water storage on properties of each material were summarised. Accordingly, water storage has significantly reduced the flexural strength for all materials to a clinically significant level, while no clinically significant reduction has occurred for flexural modulus. Water has caused no clinical significant softening of all materials' surfaces. Water storage has no clinically significant influence on all materials' roughness. No clinically significant effect of water storage on all materials' colour except CC. All these results show that using distilled water alone has a little clinical influence on material's properties.

The accumulated effect of simulated cleansing on the properties showed no clinically significant effect on roughness, hardness and colour stability has occurred. Accordingly, using Dentural and Poligrip cleansers is safe regarding these three properties. This result impacts on the instructions given to patients following denture delivery.

Concerning Ec and in the light of the above mentioned results, accelerated aging by water and cleansers has produced no clinically significant effect, except on strength. Ec ranking in comparison with conventional materials showed that Ec was statistically superior to HC in all tested properties except roughness, which is a highly variable property, while clinically Ec is superior in strength, hardness post water storage and colour stability. These criteria have an impact on a clinical work. The patient will get a stronger, durable, more aesthetic, more resistant to abrasion measures and food, more dimensionally stable and time saving denture more than conventional dentures. For the technicians, it saves money, efforts and time as fewer machines and steps are required for its preparation, in addition to short curing time. For the dentists, it allows processing and repairing dentures at clinic because it is quick, clean and safe. However, there was a high possibility of porosities, which act as places for bacterial and plaque stagnation and fermentation, and increase staining liability and act as weak points to start fracture. In addition, the most important observation is that the shattering behaviour at fracture resulted in the fragmentation of specimens, which are dangerous and difficult to repair. To conclude, Ec can be used as a denture base material, and replace heat-cured PMMA in terms of the tested properties, but it needs further research regarding the above mentioned limitations.

Concerning Ws and in the light of the above mentioned results, accelerated aging by water and cleansers has produced no clinically significant effect, except on strength. Ws ranking in comparison with conventional materials, showed it was better than CC but there was no statistical significant difference between them in all properties except colour stability. In comparison to HC, Ws was statistically superior in some properties and inferior in others, while clinically it was inferior in strength and superior in colour stability. Due to this behaviour, Ws cannot be recommended to be used as a permanent denture base material; however, it can be used on temporary basis when high aesthetic requirements and low mechanical needs are required, such as immediate dentures.

One of the weaknesses experienced during the specimen production of Ec was the porosity, and this can negatively influence some of the physical properties. This porosity required polishing the specimens to a variable depth until the superficial visible porosities were removed or reduced and a flat surface was obtained. This required more time and exposed different layers in the specimen. Furthermore, the time for producing samples was another limitation. Each three bars or five disks needed approximately one hour for production because of the limited oven capacity. Accordingly, producing 17 bars or ten discs, sound or with minimum porosity, and finishing and polishing required a long time. Thus, the specimens produced for each group were fabricated at different time intervals and produced from different batches. As the specimens were produced from different batches and waited for different time intervals, this may have caused different degrees of polymerisation following the concept of the continuation of polymerisation after the cessation of light application mostly for 24 hours after the initial polymerisation (Pilo and Cardash, 1992). This necessitates testing specimens no less than 24 h after polymerisation. Configuration of the bar and disc specimens, in addition to their distribution in the stone cast during curing, may reflect differences in the amount of light absorbed on the rotating stage. It was difficult to deal with these limitations and they may have caused a high variation in strength. Also, only the Ec baseplate resin was used to test Ec in the experiments because it forms the main bulk of denture bases.

The limitation of Ws was the unavoidable and unexpected porosity, which may have weakened the structure and reduced the strength, forming a trigger point for a fracture and increasing the water uptake (Rutkunas *et al*., 2010). Each batch was 12 specimens; however, a high number of specimens exhibited porosity, and therefore many batches had to be produced to obtain the proposed sample size; obviously, this was accompanied by a great deal of waste of both material and time. Another limitation is making Ws specimens by pouring method only while there are other two methods.

A general limitations of this research is that the effects of water storage on properties were tested *in vitro*, while the real environment for using dentures is the oral cavity, *in vivo.* The oral cavity contains saliva, and fluctuations in temperature and pH, in addition to functional and para-functional masticatory forces. However, water forms the major component of saliva and is the main factor responsible for water sorption and solubility, so using water as a storage medium and applying one kind of force can be seen as a preliminary test. In particular, testing materials after storage in artificial saliva showed no significant difference to many denture properties from that of storage in water (Al-Mulla *et al*., 1989). This study's findings suggest that most of the effects on properties are related to water content. Additionally, specimens of different configuration is another limitation which are different from the actual denture. However, specimens provide data at standard specimen dimensions and conditions. As such, the effect of variable temperature or pH in the mouth or other masticatory forces can be investigated in a further separate study. The time of water storage as six months was another limitation of the study.

The cleaning regime used was another limitation when compared to cleaning dentures in real life. This model was designed in a way to both follow manufacturers' instructions as much as possible and to reduce the effect of other factors such as water storage. In such way, the pure effect of cleaning can occur on specimens. In reality the dentures are exposed to stain from food and drink and masticatory forces and immersed in saliva all day time in addition to cleaning. These factors influence the properties tested, for example stain influences colour, masticatory forces influence roughness and storage in saliva influences hardness (Neppelenbroek *et al*., 2005, Sharma *et al*., 2014). Therefore, all these factors were excluded to conduct a preliminary study on cleaning. Using three days regime in comparison with six months is also a limitation. However, no control group using water (only for three days) is a weakness of the design, but the results still can be interpreted to achieve the aim of the study. No brushing protocol in the study could be considered as a limitation but it was a strength for the reasons mentioned in section (7.4.3).

8.2 Suggestions for future work

1. The findings of this project provide information about the materials' behaviour *in vitro* using specimens; therefore, testing materials *in vivo* will be an important progression for future research. It will show the properties of real dentures under masticatory forces soaked in saliva, with the effect of thermal cycling and oral pH. In addition, it will show the real effect of daily cleaning procedure on dentures.
2. Despite the promising results shown by Ec regarding the tested properties until six months of storage, further work is required to establish its properties after storage in water for one year or more.
3. The materials were tested in air at room temperature after storage in distilled water not saliva, with no thermal cycling and no consideration to pH. Further studies which take these variables into account will need to be undertaken.
4. Specimens of Ec were tested using baseplate resin only, even though in the final denture the denture base consists of three resins. Further studies are required to test specimens made of three layers.
5. To develop a full picture of Ec and Ws properties, impact and dimensional stability should be investigated.
6. Cytotoxicity and biocompatibility were not tested in this research and need to be investigated in future studies.
7. Only three properties which are most common were tested after simulated cleaning. Further research can be undertaken to test other properties such as flexural strength and impact resistance.
8. Daily brushing was not addressed in this research, and therefore further research is recommended to test the effect of brushing on the properties.
9. Regarding fragmentation of Ec specimens after breakage, further study can be done to strengthen or modifying the structure such as by adding mesh to denture.
10. Investigating the cost difference between Ec and HC
11. Trying to make Ws specimens in different manipulation method and testing properties again.
12. Investigating Ec properties following using rubber dam and vacuum assistance during manipulation.

Appendices

Appendix A. Manufacturer's instructions of Heat-cured PMMA

JOHN WINTER & CO LTD

FOUNDRY & DENTAL SUPPLIES

PO BOX 21, WASHER LANE, HALIFAX

UK HX2 7DP

TEL: 00 44 1422 364213 FAX: 00 44 1422 330493

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WINTERCRYL HEAT CURE

Directions for Use

Wintercryl denture base material is a heat cured acrylic

based on methyl methacrylate and complies with

BS EN ISO 20795-1:2013 Type 1: Class 1.

INDICATIONS

A fast curing acrylic for aesthetic, full and partial dentures

for short term retention and use only. This Medical device

is for short term use in accordance with MDD 93/42/EEC

and has been classified as a Class I.

CONTRA-INDICATIONS

People with known allergies to methacrylates should only use

with suitable protection. Certain patients are unable to tolerate

the wearing of appliances made from methacrylates.

PHYSICAL DATA

Powder:liquid ratio 2.34g per ml

Dough time at 23°C 7±2 mins

Working time at 23 ± °C 20 mins

WAXING AND INVESTING

Invest in gypsum and follow procedure for gypsum models.

WAX REMOVAL

Immerse the flask in boiling water for five minutes. Remove and open the flask, lift out wax and flush thoroughly with boiling water to which detergent solution has been added, followed by clean boiling water. Allow to cool.

APPLY PLASTER SEALING SOLUTION (CMS)

Use a clean brush to apply plaster sealing solution to all plaster Surfaces. Absorb excess from around teeth while it remains fluid. Make quite sure there is none on the exposed surfaces of the teeth. Allow to dry before packing.

MIXING

Caution: Liquid flash point 9.5 °C – do not mix or store near naked flame.. Recommended ambient temperature for mixing and packing is 23 °C. Pour liquid into a mixing vessel and add appropriate powder in a slow stream (taking 30-40 seconds) until an excess appears on the surface. Hold the vessel in the hand, tap 3 or 4 times to bring the excess liquid to the surface and add sufficient powder to absorb this liquid.

Invert the vessel and discard any surplus powder. Thoroughly spatulate the mix for 1 minute. Cover the vessel and wait for the mix to reach the correct stage for packing and pressing (dough time). This stage is reached when the mix can be separated cleanly from the walls of the mixing vessel with a spatula.

PACKING

Care: Do not pack before the dough stage has been reached. The flask temperature should be 23 ºC.

Pack the material into the mould and cover with a thin polythene sheet. Assemble the flask and close slowly under a press. Open the flask, paint the model half of the flask with plaster sealing solution, remove separating sheet, and cut away the flash. Then reassemble the flask, close under press, and transfer to a security flask clamp. As an extra safeguard against porosity place a small additional amount of dough centrally in the flask. Do not pack after the end of the working time.

EXTENDED WORKING TIME

If storing the denture base for extended use, ensure that dough stage is reached prior to refrigeration.

RECOMMENDED CURES

Normal dentures

Immerse the clamped flask in cold, warm or boiling water.

Bring to the boil not less than 5 minutes and simmer for a further 25 minutes. Residual monomer content <0.6%.

Thick dentures

For thicker dentures place the clamped flask in boiling water and remove the heat source for 20 minutes. Bring to the boil in not less than 5 minutes and continue boiling for a further 10 minutes. Residual monomer content <0.6%.

Dentures with reduced residual monomer

Place the clamped flask in cold water and raise to 70 ºC. Hold this temperature for 90 minutes and then bring to the boil and continue boiling for 2 hours.

Residual monomer content < 0.6%.

ALTERNATIVE CURES

Other longer cure techniques can, if desired, be employed with the denture base material. When dry curing follow the instructions of the bath manufacturer.

Note: After all curing cycles bench cool the flask for 30 minutes prior to immersing in cold water before deflasking. Finish and polish in the usual manner. Store finished denture wrapped in damp tissue in a polythene bag.

INSTRUCTIONS FOR ADDITION AND REPAIRS

To obtain maximum repair strength, it is recommended that repairs or additions be made using the heat cure denture base. An autopolymerising resin such as repair acrylic may also be used for this purpose.

STORAGE

Store at room temperature (max 23 ºC) and avoid prolonged exposure to sunlight. Keep containers tightly closed when not in use.

Waste disposal

Do not empty monomer liquid into drains.

HEALTH AND SAFETY

Caution: Contains methyl methacrylate monomer. H225 Highly flammable liquid or vapour. H315 Causes skin irritation. H317 May cause an allergic skin reaction. H335 May cause a respiratory irritation. Avoid prolonged skin contact with unpolymerised material and excessive inhalation of monomer vapour especially with people with known allergies in particular to methacrylates.

Safety Advice Product should be used and container should be kept in a well-ventilated place. Product should be used in accordance with local regulations; use a suitable respirator and/or fume hood. P210 Keep away from heat/sparks/open flames/hot surfaces. No smoking. P261 Avoid breathing dust/fumes/gas/mist/vapours/spray. P280 Wear protective gloves/protective clothing/eye protection/face protection. P303+361+353 IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. P501 Dispose of contents/container in accordance with local regulations.

After use wash hands thoroughly with soap and water.

For further information request the material safety datasheet.

TECHNICAL ADVICE

John Winter & Co. Ltd. warrants that the material contained in this package shall conform to relevant internationally laid down standards and tested accordingly. When used in accordance with the given directions and employing good laboratory practices, the product will achieve optimum results. These instructions are valid only for the product as supplied and not for derivatives resulting from its use. The advice given here is in good faith but the product should always be tested as to the suitability for the intended processes and uses..

LOT NUMBERS

The Lot number and the expiry date are shown on all containers.

This product is specifically formulated for use in dentistry.

Issue date: 26.07.2017

Version: 4

Appendix B. Manufacturer's instructions of Cold-cured PMMA

JOHN WINTER & CO LTD
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TEL: 00 44 1422 364213 FAX: 00 44 1422 330493
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RAPID REPAIR POWDER

Directions for Use

Rapid Repair acrylic is formulated for the repair of denture bases based on methyl methacrylate and complies with BS EN ISO 20795-1:2013 Type 2:Class 1.

INDICATIONS

For the repair of acrylic denture bases, for short term retention and use only. This Medical device is for short term use in accordance with MDD 93/42/EEC and has been classified as a Class I.

CONTRA-INDICATIONS

Repair of high impact dentures where the high impact resistance is to be maintained. People with known allergies to methacrylates should only use with suitable protection. Certain patients are unable to tolerate wearing of appliances made from methacylates..

PREPARATION

Assemble the broken parts and cast the model. Cut back the broken area to leave a 1.5mm gap and bevel the edges to form a shallow V. Protect the fitting surfaces and nearby teeth with a thin film of petroleum jelly. Coat the model with plaster sealing solution and secure the denture to the model with sticky wax..

MIXING RATIO

13g powder : 10ml liquid

MIXING METHOD (A)

Moisten the contact surfaces of the repair with the Repair liquid. Add Repair powder and continue to moisten and add the powder until the repair has been built up in excess of the thickness required..

MIXING METHOD (B)

Pour 10 drops of liquid into a dry Dappen glass. Add powder evenly until all monomer is absorbed and there is a dry excess. Reverse the Dappen glass and tap in the palm of the hand to remove excess powder. Add four drops of monomer and stir gently for 20-30 seconds with a spatula. Avoid trapping air. The approximate working time is 2 minutes..

APPLICATION

The mix should be free flowing – if sluggish, discard and make a new mix. Apply using a thin bladed spatula and slightly overbuild. Once in position do not disturb. Excess of flow can be controlled with a dusting of dry powder..

CURING IN FLASK

Best results are obtained with flask curing. Immerse into water at 40ºC, bring the pressure to 50psi (3.4bar or 3.5kg/cm2). Hold for about 10 minutes. This may vary according to the type of flask used..

AIR CURING

It is also possible to obtain a porosity free repair by leaving undisturbed to cure in the air. In common with other acrylics, the setting time is sensitive to temperature and at 23ºC is approximately 15 minutes. Warm conditions will decrease this time and vice versa..

FINISHING

When completely set and hard, remove from model and trim and polish in the usual way.

Residual monomer content <0.6%.

STORAGE

Store in a dry place at room temperature (max 23ºC) and avoid prolonged exposure to sunlight. Keep containers closed when not in use..

HEALTH AND SAFETY

Caution: Contains methyl methacrylate monomer. H225 Highly flammable liquid or vapour. H315 Causes skin irritation. H317 May cause an allergic skin reaction. H335 May cause a respiratory irritation. Avoid prolonged skin contact with unpolymerised material and excessive inhalation of monomer vapour especially with people with known allergies in particular to methacrylates..

Safety Advice Product should be used and container should be kept in a well-ventilated place. Product should be used in accordance with local regulations; use a suitable respirator and/or fume hood. P210 Keep away from heat/sparks/open flames/hot surfaces.

No smoking. P261 Avoid breathing dust/fumes/gas/mist/vapours/spray. P280 Wear protective gloves/protective clothing/eye protection/face protection. P303+361+353 IF ON SKIN (or hair): Remove/Take off Immediately all contaminated clothing. Rinse skin with water/shower. P501 Dispose of contents/container in accordance with local regulations.

After use wash hands thoroughly with soap and water.

For further information request the material safety data sheet.

TECHNICAL ADVICE

John Winter & Co Ltd. warrants that the material contained in this package shall conform to relevant internationally laid down standards and tested accordingly. When used in accordance with the given directions and employing good laboratory practices, the product will achieve optimum results. These instructions are valid only for the product as supplied and not for derivatives resulting from its use. The advice given here is in good faith but the product should always be tested as to the suitability for the intended processes and uses.

LOT NUMBERS

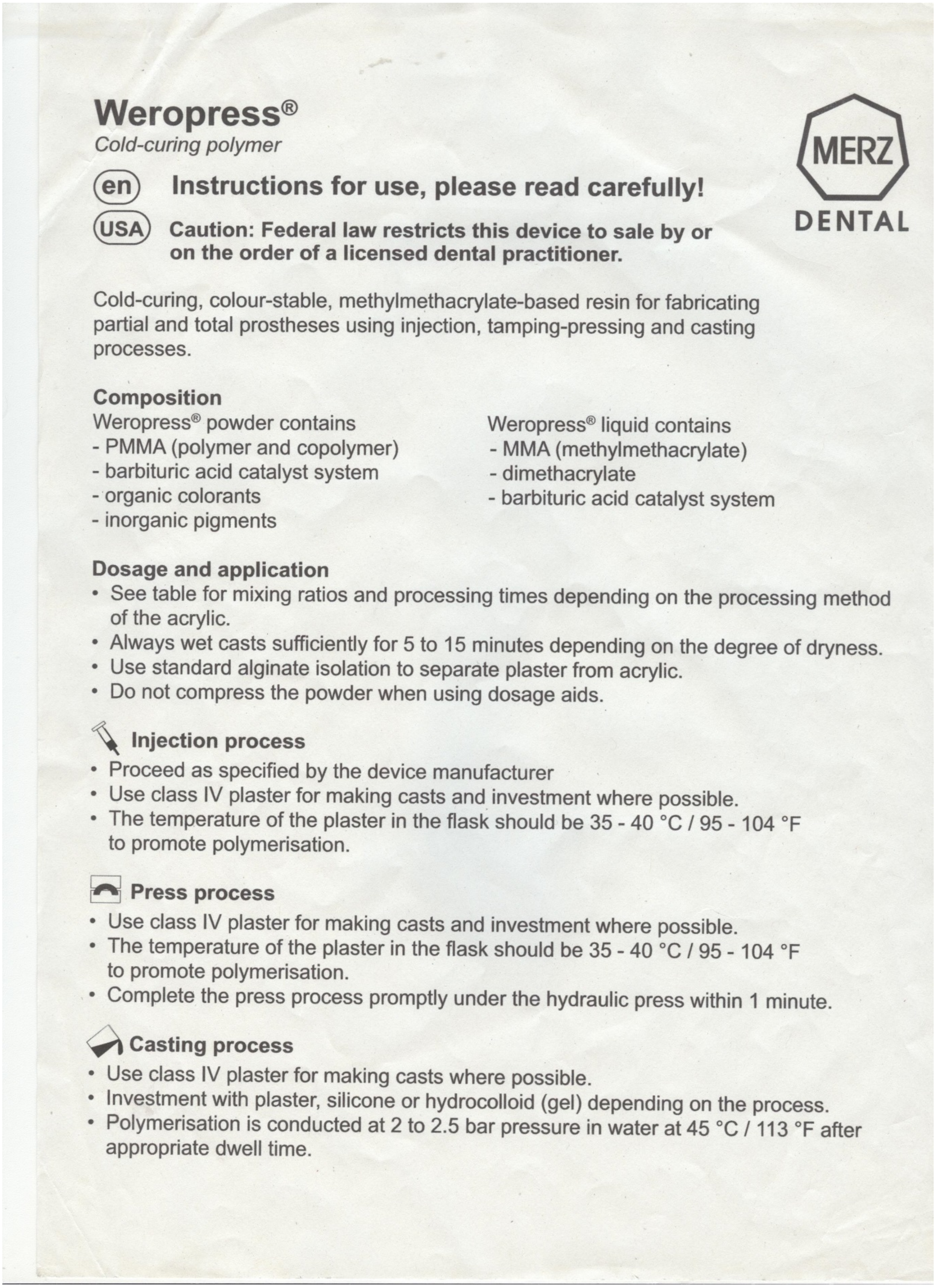
The Lot number and the expiry date are shown on all containers.

This product is specifically formulated for use in dentistry..

Issue date: 01.08.13

Version: 2

Appendix C. Manufacturer's instructions of Weropress



Weropress®

Cold-curing polymer

MERZ
DENTAL

(en) Instructions for use, please read carefully!

(USA) Caution: Federal law restricts this device to sale by or on the order of a licensed dental practitioner.

Cold-curing, colour-stable, methylmethacrylate-based resin for fabricating partial and total prostheses using injection, tamping-pressing and casting processes.

Composition

Weropress® powder contains	Weropress® liquid contains
- PMMA (polymer and copolymer)	- MMA (methylmethacrylate)
- barbituric acid catalyst system	- dimethacrylate
- organic colorants	- barbituric acid catalyst system
- inorganic pigments	

Dosage and application

- See table for mixing ratios and processing times depending on the processing method of the acrylic.
- Always wet casts sufficiently for 5 to 15 minutes depending on the degree of dryness.
- Use standard alginate isolation to separate plaster from acrylic.
- Do not compress the powder when using dosage aids.

Injection process

- Proceed as specified by the device manufacturer
- Use class IV plaster for making casts and investment where possible.
- The temperature of the plaster in the flask should be 35 - 40 °C / 95 - 104 °F to promote polymerisation.

Press process

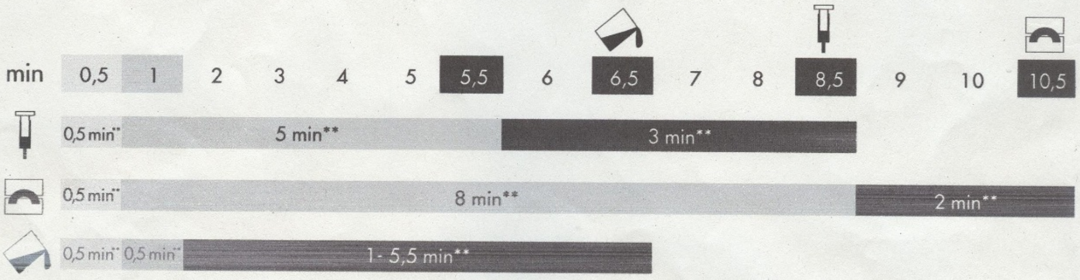
- Use class IV plaster for making casts and investment where possible.
- The temperature of the plaster in the flask should be 35 - 40 °C / 95 - 104 °F to promote polymerisation.
- Complete the press process promptly under the hydraulic press within 1 minute.

Casting process

- Use class IV plaster for making casts where possible.
- Investment with plaster, silicone or hydrocolloid (gel) depending on the process.
- Polymerisation is conducted at 2 to 2.5 bar pressure in water at 45 °C / 113 °F after appropriate dwell time.

Times and quantities

	Injection process	Tamping-pressing process	Casting process
Mixing ratio*	30 g : 15 ml	30 g : 15 ml	30 g : 21 ml
Polymerisation temperature	Residual heat in the flask	Residual heat in the flask	45 °C / 113 °F
Polymerisation time	15 min	15 min	15 min[1] / 30 min[2]
Pressure required during polymerisation	By device type	Pressure in the flask must be maintained during polymerisation	2 - 2,5 bar



▢ Mixing time

▨ Dwell time

■ Processing time (pourable consistency)
(Start and end of injection time/tamping time)

[1] in matrix technique, plaster, putty

[2] in flask duplication technique, duplication gel, duplication silicone

*see also dosage aid **REF 1090194**

**Based on a room temperature of 21 °C / 69,8 °F

Processing the acrylic

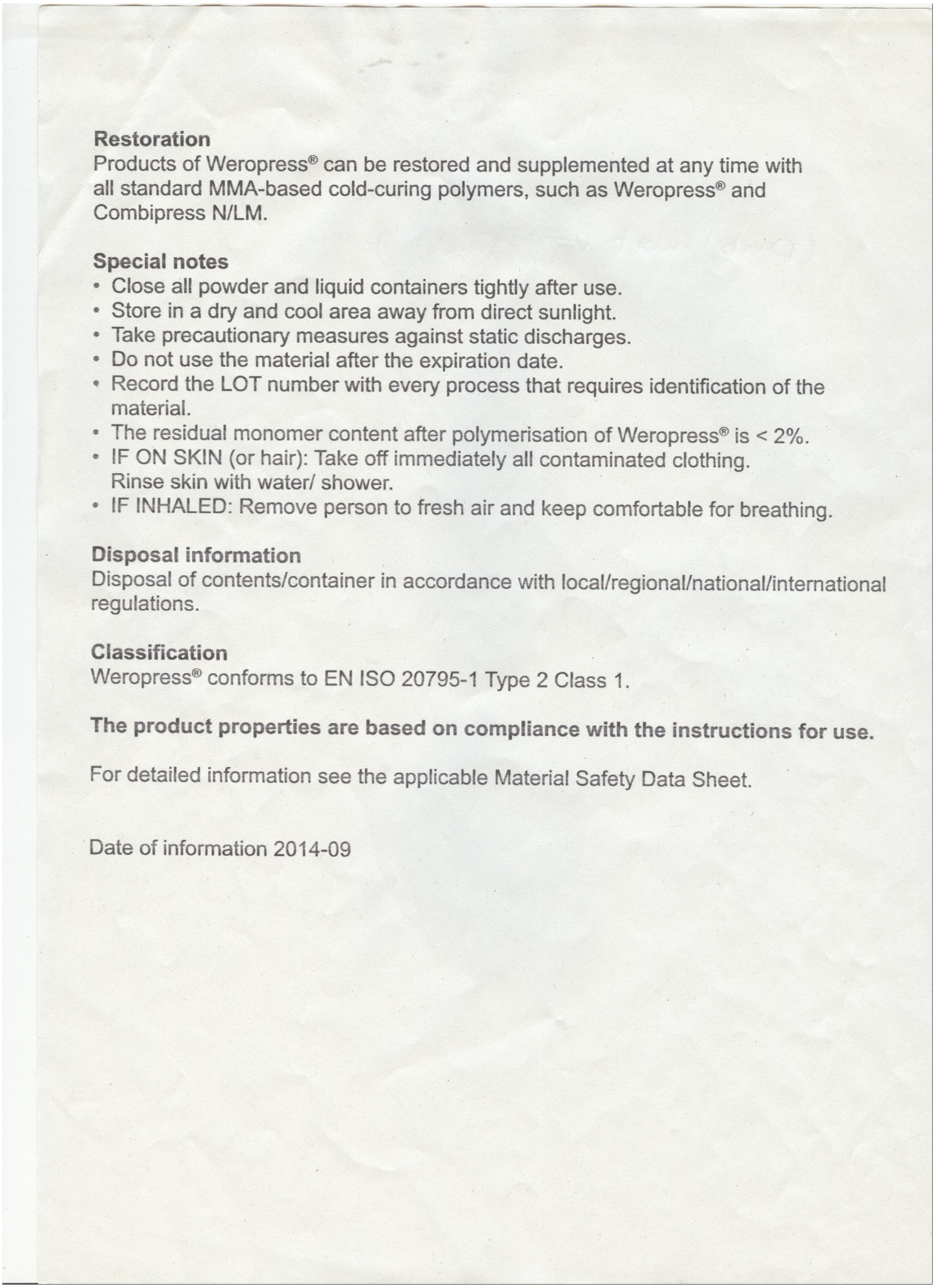
To reduce the residual monomer content, the finished (sanded) but not polished polymerised workpiece should be stored in water at room temperature for about 48 hours before delivery.

Trimming

To prevent inaccurate fitting after polymerisation, avoid excessive heat development during trimming and polishing.

Bond

- Roughen the basal surfaces of the acrylic teeth before bonding.
- Ensure that no impurities such as wax or isolating agent are present.
- Mechanical retention is recommended.
- Adequate mechanical retention is essential for ceramic teeth.



Restoration

Products of Weropress® can be restored and supplemented at any time with all standard MMA-based cold-curing polymers, such as Weropress® and Combipress N/LM.

Special notes

- Close all powder and liquid containers tightly after use.
- Store in a dry and cool area away from direct sunlight.
- Take precautionary measures against static discharges.
- Do not use the material after the expiration date.
- Record the LOT number with every process that requires identification of the material.
- The residual monomer content after polymerisation of Weropress® is < 2%.
- IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/ shower.
- IF INHALED: Remove person to fresh air and keep comfortable for breathing.

Disposal information

Disposal of contents/container in accordance with local/regional/national/international regulations.

Classification

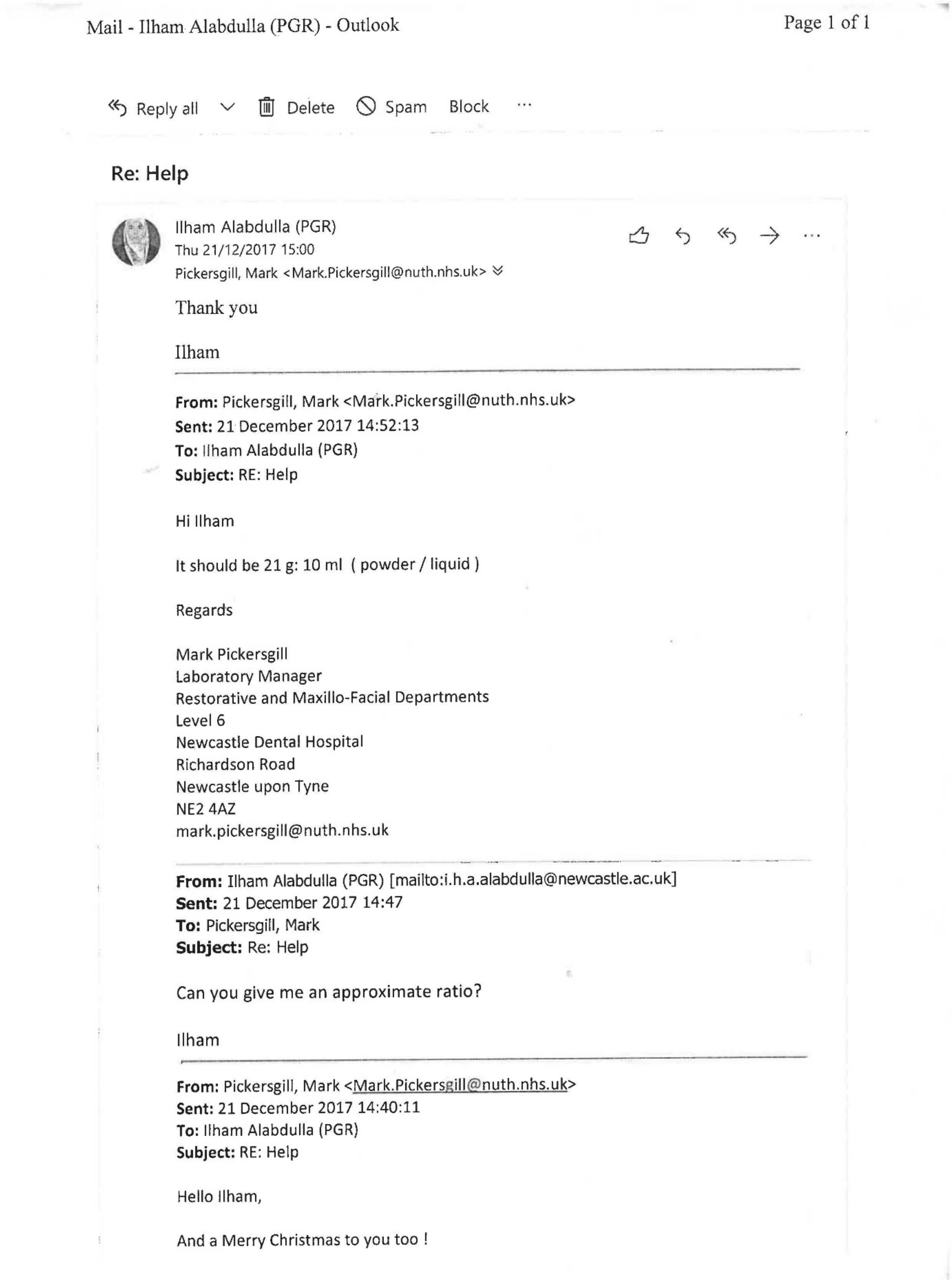
Weropress® conforms to EN ISO 20795-1 Type 2 Class 1.

The product properties are based on compliance with the instructions for use.

For detailed information see the applicable Material Safety Data Sheet.

Date of information 2014-09

Appendix D. Personal communication with dental technicians



Mail - Ilham Alabdulla (PGR) - Outlook

Page 1 of 1

Re: Help

Ilham Alabdulla (PGR)
Thu 21/12/2017 15:00
Pickersgill, Mark <Mark.Pickersgill@nuth.nhs.uk>

Thank you

Ilham

From: Pickersgill, Mark <Mark.Pickersgill@nuth.nhs.uk>
Sent: 21 December 2017 14:52:13
To: Ilham Alabdulla (PGR)
Subject: RE: Help

Hi Ilham

It should be 21 g: 10 ml (powder / liquid)

Regards

Mark Pickersgill
Laboratory Manager
Restorative and Maxillo-Facial Departments
Level 6
Newcastle Dental Hospital
Richardson Road
Newcastle upon Tyne
NE2 4AZ
mark.pickersgill@nuth.nhs.uk

From: Ilham Alabdulla (PGR) [mailto:i.h.a.alabdulla@newcastle.ac.uk]
Sent: 21 December 2017 14:47
To: Pickersgill, Mark
Subject: Re: Help

Can you give me an approximate ratio?

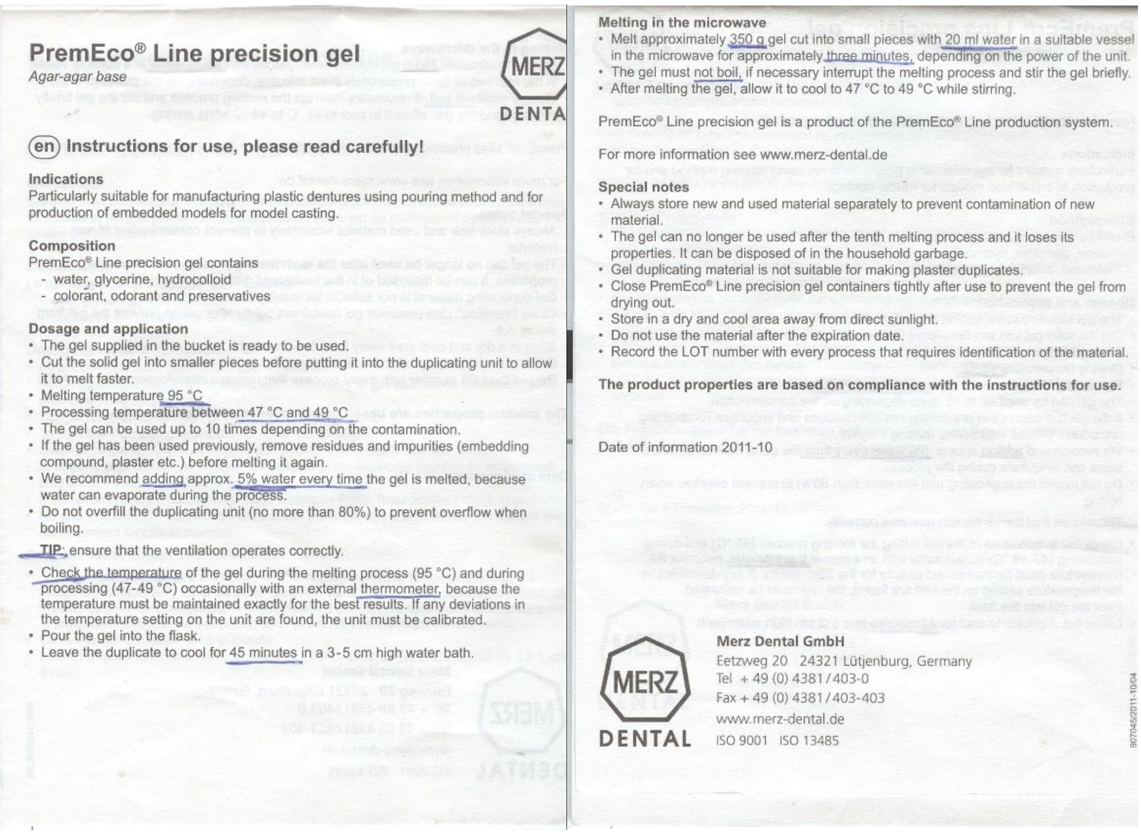
Ilham

From: Pickersgill, Mark <Mark.Pickersgill@nuth.nhs.uk>
Sent: 21 December 2017 14:40:11
To: Ilham Alabdulla (PGR)
Subject: RE: Help

Hello Ilham,

And a Merry Christmas to you too !

Appendix E. Manufacturer's instructions of Agar Agar



PremEco® Line precision gel

Agar-agar base

(en) Instructions for use, please read carefully!

Indications

Particularly suitable for manufacturing plastic dentures using pouring method and for production of embedded models for model casting.

Composition

PremEco® Line precision gel contains

- water, glycerine, hydrocolloid
- colorant, odorant and preservatives

Dosage and application

- The gel supplied in the bucket is ready to be used.
- Cut the solid gel into smaller pieces before putting it into the duplicating unit to allow it to melt faster.
- Melting temperature 95 °C
- Processing temperature between 47 °C and 49 °C
- The gel can be used up to 10 times depending on the contamination.
- If the gel has been used previously, remove residues and impurities (embedding compound, plaster etc.) before melting it again.
- We recommend adding approx. 5% water every time the gel is melted, because water can evaporate during the process.
- Do not overfill the duplicating unit (no more than 80%) to prevent overflow when boiling.

TIP: ensure that the ventilation operates correctly.

- Check the temperature of the gel during the melting process (95 °C) and during processing (47-49 °C) occasionally with an external thermometer, because the temperature must be maintained exactly for the best results. If any deviations in the temperature setting on the unit are found, the unit must be calibrated.
- Pour the gel into the flask.
- Leave the duplicate to cool for 45 minutes in a 3-5 cm high water bath.

Melting in the microwave

- Melt approximately 350 g gel cut into small pieces with 20 ml water in a suitable vessel in the microwave for approximately three minutes, depending on the power of the unit.
- The gel must not boil, if necessary interrupt the melting process and stir the gel briefly.
- After melting the gel, allow it to cool to 47 °C to 49 °C while stirring.

PremEco® Line precision gel is a product of the PremEco® Line production system.

For more information see www.merz-dental.de

Special notes

- Always store new and used material separately to prevent contamination of new material.
- The gel can no longer be used after the tenth melting process and it loses its properties. It can be disposed of in the household garbage.
- Gel duplicating material is not suitable for making plaster duplicates.
- Close PremEco® Line precision gel containers tightly after use to prevent the gel from drying out.
- Store in a dry and cool area away from direct sunlight.
- Do not use the material after the expiration date.
- Record the LOT number with every process that requires identification of the material.

The product properties are based on compliance with the instructions for use.

Date of information 2011-10

Merz Dental GmbH
Eetzweg 20 24321 Lütjenburg, Germany
Tel + 49 (0) 4381 / 403-0
Fax + 49 (0) 4381 / 403-403
www.merz-dental.de
ISO 9001 ISO 13485

907045/2011-10/04

Appendix F. Manufacturer’s instructions of Poligrip effervescent tablet and Dentural cleanser

Directions for use Dentural cleanser

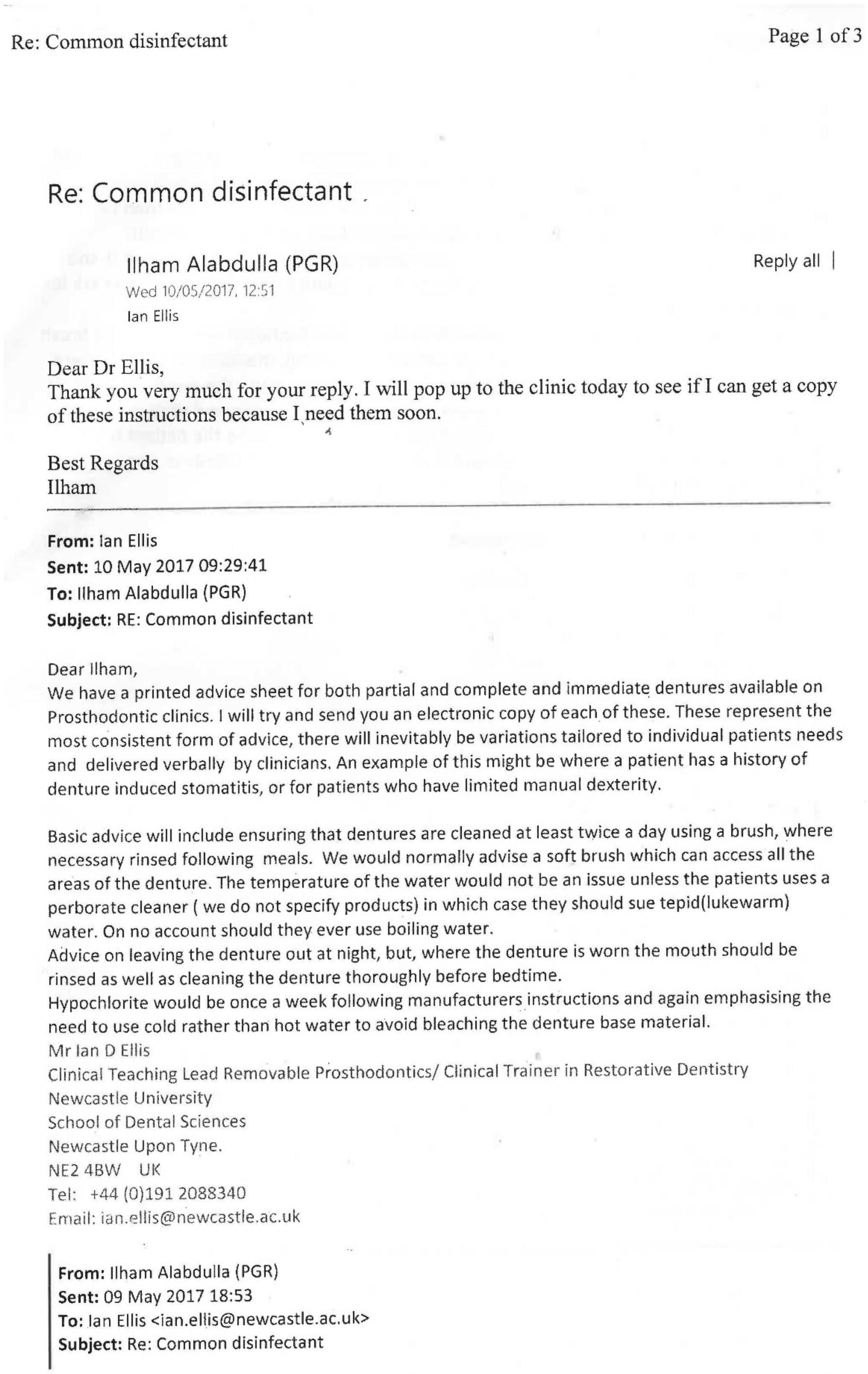
Quick method: cover the dentures in warm water and add 20 ml (four teaspoons) of Dentural. Leave for about 20 min. Rinse thoroughly in running water before replacing dentures in mouth.

Overnight method: Cover the dentures in cold water and add 10 ml (two teaspoons) of Dentural. Next morning, rinse thoroughly in running water before replacing the dentures in mouth.

Directions for use Poligrip tablet cleanser

Drop one Poligrip cleanser tablet into enough very warm (not hot) water to cover denture. After soaking for 3-5 min, brush denture with the solution using a soft brush. Rinse denture well with running water. Discard solution immediately after use.

Appendix G. Personal communication with dentists



Re: Common disinfectant Page 1 of 3

Re: Common disinfectant

Ilham Alabdulla (PGR)
Wed 10/05/2017, 12:51
Ian Ellis

Reply all |

Dear Dr Ellis,
Thank you very much for your reply. I will pop up to the clinic today to see if I can get a copy of these instructions because I need them soon.

Best Regards
Ilham

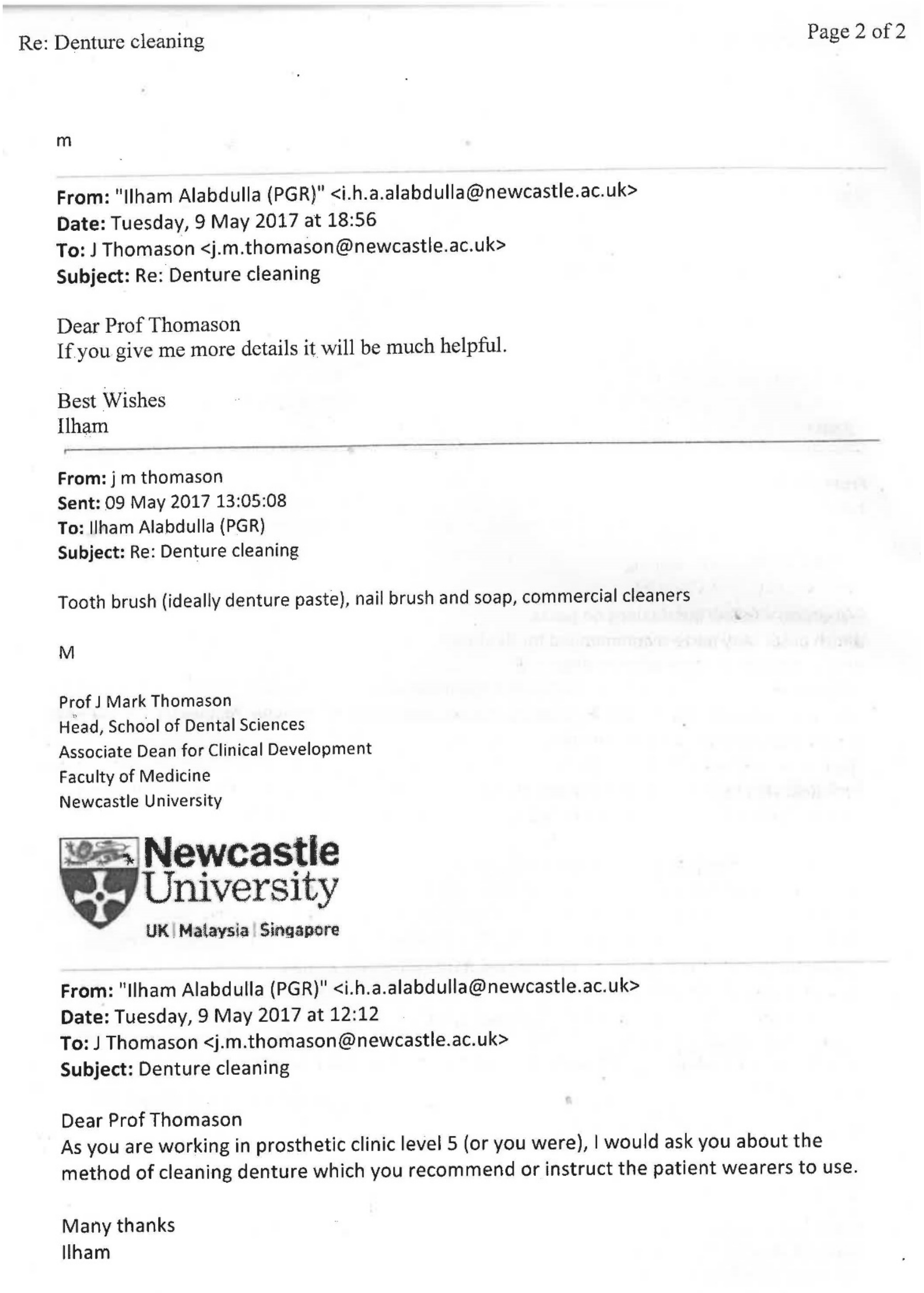
From: Ian Ellis
Sent: 10 May 2017 09:29:41
To: Ilham Alabdulla (PGR)
Subject: RE: Common disinfectant

Dear Ilham,
We have a printed advice sheet for both partial and complete and immediate dentures available on Prosthodontic clinics. I will try and send you an electronic copy of each of these. These represent the most consistent form of advice, there will inevitably be variations tailored to individual patients needs and delivered verbally by clinicians. An example of this might be where a patient has a history of denture induced stomatitis, or for patients who have limited manual dexterity.

Basic advice will include ensuring that dentures are cleaned at least twice a day using a brush, where necessary rinsed following meals. We would normally advise a soft brush which can access all the areas of the denture. The temperature of the water would not be an issue unless the patients uses a perborate cleaner (we do not specify products) in which case they should sue tepid(lukewarm) water. On no account should they ever use boiling water.
Advice on leaving the denture out at night, but, where the denture is worn the mouth should be rinsed as well as cleaning the denture thoroughly before bedtime.
Hypochlorite would be once a week following manufacturers instructions and again emphasising the need to use cold rather than hot water to avoid bleaching the denture base material.

Mr Ian D Ellis
Clinical Teaching Lead Removable Prosthodontics/ Clinical Trainer in Restorative Dentistry
Newcastle University
School of Dental Sciences
Newcastle Upon Tyne.
NE2 4BW UK
Tel: +44 (0)191 2088340
Email: ian.ellis@newcastle.ac.uk

> **From:** Ilham Alabdulla (PGR)
> **Sent:** 09 May 2017 18:53
> **To:** Ian Ellis <ian.ellis@newcastle.ac.uk>
> **Subject:** Re: Common disinfectant



m

From: "Ilham Alabdulla (PGR)" <i.h.a.alabdulla@newcastle.ac.uk>
Date: Tuesday, 9 May 2017 at 18:56
To: J Thomason <j.m.thomason@newcastle.ac.uk>
Subject: Re: Denture cleaning

Dear Prof Thomason
If you give me more details it will be much helpful.

Best Wishes
Ilham

From: j m thomason
Sent: 09 May 2017 13:05:08
To: Ilham Alabdulla (PGR)
Subject: Re: Denture cleaning

Tooth brush (ideally denture paste), nail brush and soap, commercial cleaners

M

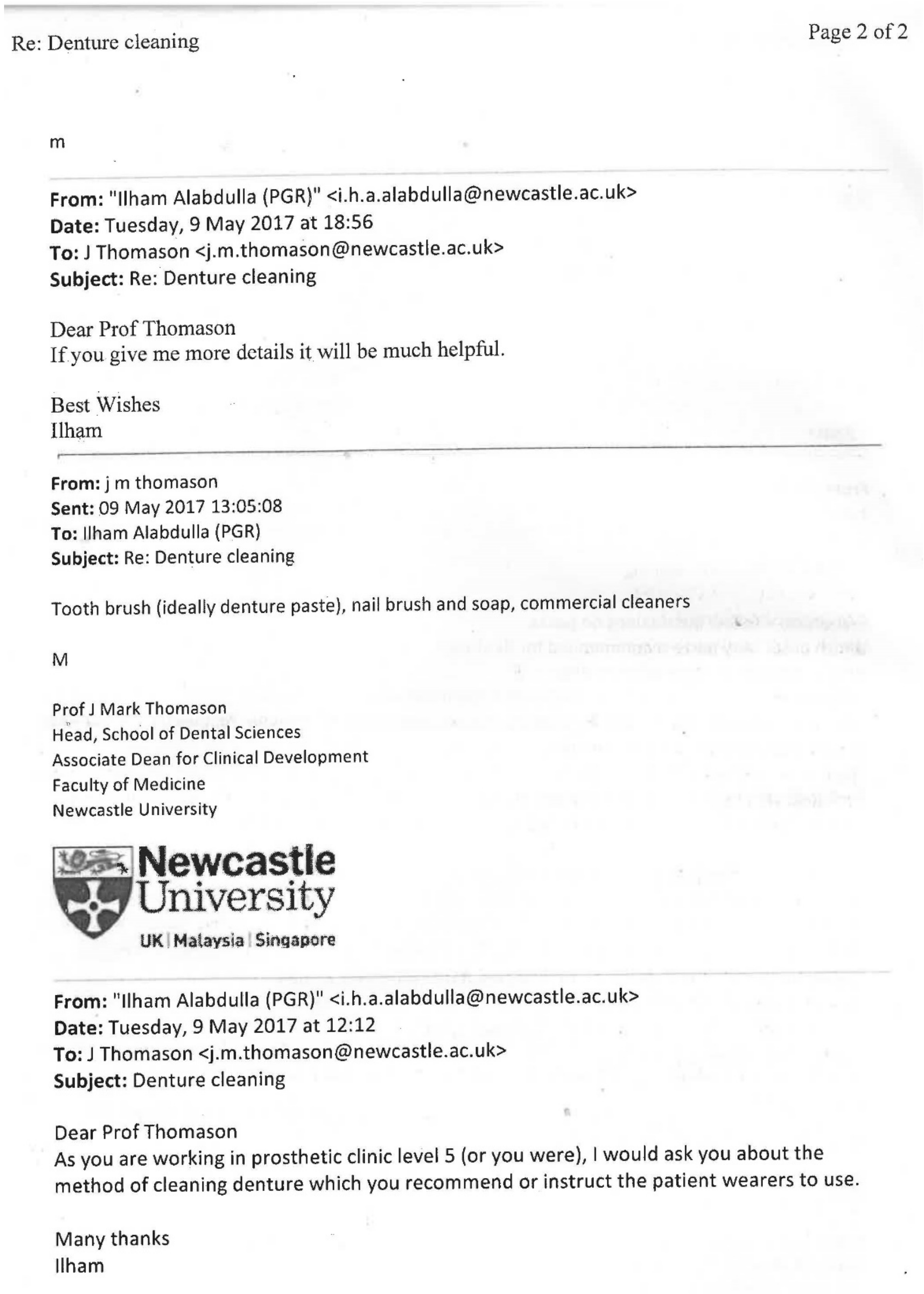
Prof J Mark Thomason
Head, School of Dental Sciences
Associate Dean for Clinical Development
Faculty of Medicine
Newcastle University

Newcastle University
UK | Malaysia | Singapore

From: "Ilham Alabdulla (PGR)" <i.h.a.alabdulla@newcastle.ac.uk>
Date: Tuesday, 9 May 2017 at 12:12
To: J Thomason <j.m.thomason@newcastle.ac.uk>
Subject: Denture cleaning

Dear Prof Thomason
As you are working in prosthetic clinic level 5 (or you were), I would ask you about the method of cleaning denture which you recommend or instruct the patient wearers to use.

Many thanks
Ilham



Re: Denture cleaning

Page 2 of 2

m

From: "Ilham Alabdulla (PGR)" <i.h.a.alabdulla@newcastle.ac.uk>
Date: Tuesday, 9 May 2017 at 18:56
To: J Thomason <j.m.thomason@newcastle.ac.uk>
Subject: Re: Denture cleaning

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Ilham

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Sent: 09 May 2017 13:05:08
To: Ilham Alabdulla (PGR)
Subject: Re: Denture cleaning

Tooth brush (ideally denture paste), nail brush and soap, commercial cleaners

M

Prof J Mark Thomason
Head, School of Dental Sciences
Associate Dean for Clinical Development
Faculty of Medicine
Newcastle University

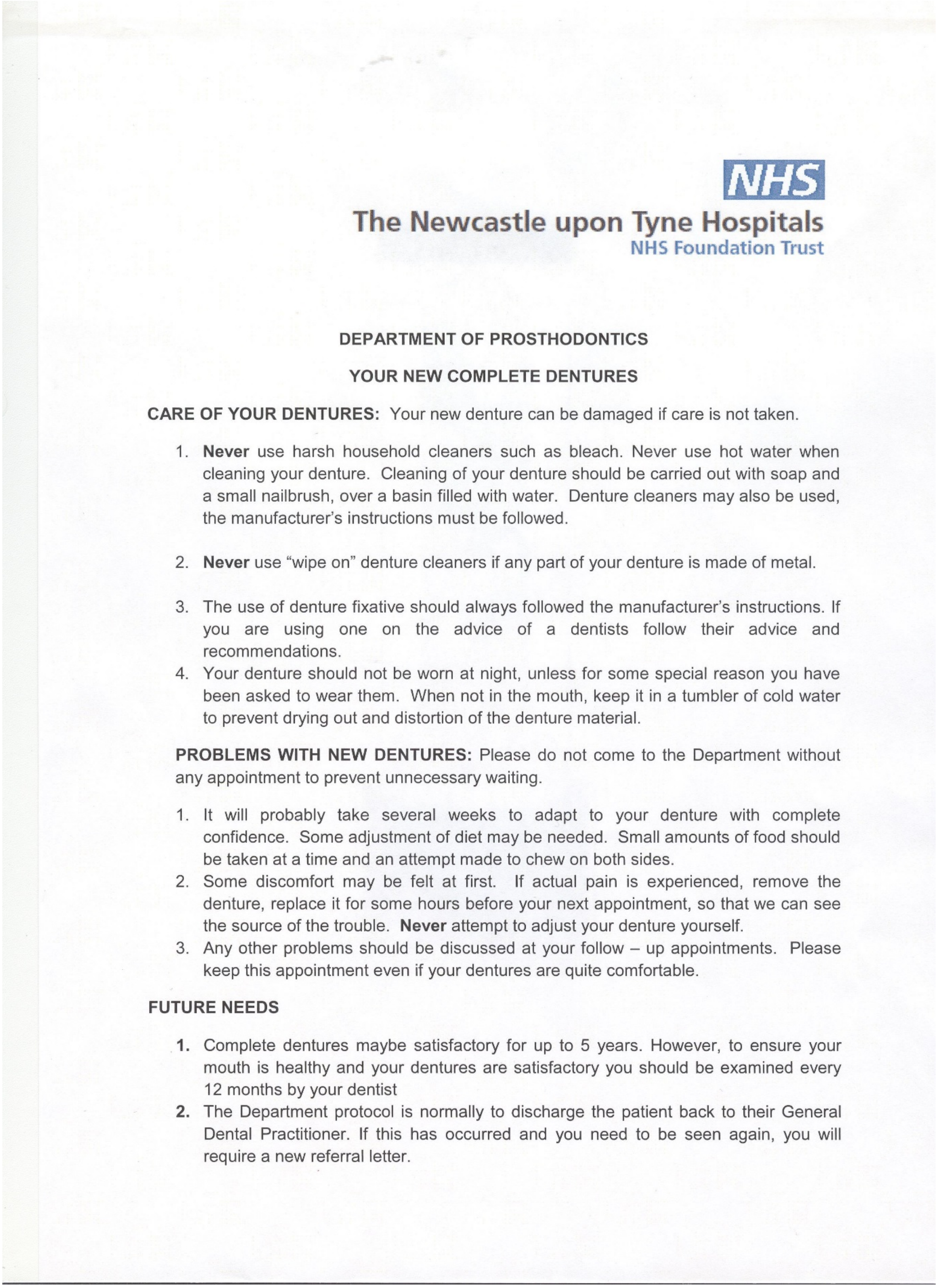
Newcastle
University
UK | Malaysia | Singapore

From: "Ilham Alabdulla (PGR)" <i.h.a.alabdulla@newcastle.ac.uk>
Date: Tuesday, 9 May 2017 at 12:12
To: J Thomason <j.m.thomason@newcastle.ac.uk>
Subject: Denture cleaning

Dear Prof Thomason
As you are working in prosthetic clinic level 5 (or you were), I would ask you about the method of cleaning denture which you recommend or instruct the patient wearers to use.

Many thanks
Ilham

Appendix H. Instructions hand out for denture wearers' patients



NHS

The Newcastle upon Tyne Hospitals
NHS Foundation Trust

DEPARTMENT OF PROSTHODONTICS

YOUR NEW COMPLETE DENTURES

CARE OF YOUR DENTURES: Your new denture can be damaged if care is not taken.

1. **Never** use harsh household cleaners such as bleach. Never use hot water when cleaning your denture. Cleaning of your denture should be carried out with soap and a small nailbrush, over a basin filled with water. Denture cleaners may also be used, the manufacturer's instructions must be followed.

2. **Never** use "wipe on" denture cleaners if any part of your denture is made of metal.

3. The use of denture fixative should always followed the manufacturer's instructions. If you are using one on the advice of a dentists follow their advice and recommendations.
4. Your denture should not be worn at night, unless for some special reason you have been asked to wear them. When not in the mouth, keep it in a tumbler of cold water to prevent drying out and distortion of the denture material.

PROBLEMS WITH NEW DENTURES: Please do not come to the Department without any appointment to prevent unnecessary waiting.

1. It will probably take several weeks to adapt to your denture with complete confidence. Some adjustment of diet may be needed. Small amounts of food should be taken at a time and an attempt made to chew on both sides.
2. Some discomfort may be felt at first. If actual pain is experienced, remove the denture, replace it for some hours before your next appointment, so that we can see the source of the trouble. **Never** attempt to adjust your denture yourself.
3. Any other problems should be discussed at your follow – up appointments. Please keep this appointment even if your dentures are quite comfortable.

FUTURE NEEDS

1. Complete dentures maybe satisfactory for up to 5 years. However, to ensure your mouth is healthy and your dentures are satisfactory you should be examined every 12 months by your dentist
2. The Department protocol is normally to discharge the patient back to their General Dental Practitioner. If this has occurred and you need to be seen again, you will require a new referral letter.

Appendix I. Conferences attendance and participation

- ❖ IADR in March 2017 in California/USA (poster presentation)

Newcastle University

UK | Malaysia | Singapore

#1362

Flexural Properties of New Denture Base Materials (Comparative Study)

Ilham H Alabdulla, M J German, J M Thomason
Centre for Oral Health Research, Newcastle University
Email: i.h.a.alabdulla@ncl.ac.uk

Introduction

The most commonly used denture base material, heat-cured polymethyl methacrylate (PMMA), shows non-ideal mechanical properties, with the majority of in service failures occurring due to either debonding of artificial teeth, fracture due to sudden impact or midline fracture due to flexure (1). Some new materials have been developed to facilitate denture production. Two of these new materials are a light curable UDMA-based materials (Eclipse) and a pourable PMMA-based materials (Weropress).

Aims

We compare the flexural properties of these two materials with those of conventional PMMA-based materials to establish whether the new materials can be used as alternatives for the conventional ones in terms of flexural strength and stiffness.

Methods

Four materials were selected (Table 1). 10 bar-shaped samples (70, 10, 3.5mm) were made for each material following each manufacturer's instructions. The heat-cured and the cold-cured materials were considered as the positive and negative controls respectively for the study. After curing, finishing and polishing, the samples' flexural strength and modulus were measured (3 point bend test, 5 mm/min, 50mm span, Instron 5567).

Group	Abbreviation	Manufacturer
Heat-Cured	HC	John Winter & Co LTD
Cold-Cured	CC	John Winter & Co LTD
Eclipse	E	Dentsply International
Weropress	W	MerzDental GmbH

Table 1: The four materials used in this study

Results

The results of the flexural strength values can be seen in figure 1 and those of flexural modulus in figure 2. No significant differences were found between the Eclipse specimens and the heat-cured and cold-cured specimens for both strength and modulus ($P>0.05$, Kruskal Wallis test). Weropress specimens exhibited low strength and modulus values that were significantly different from heat-cured and Eclipse materials ($P<0.05$).

Figure 1: Summary of the median flexural strength of the materials. Error bars represent upper and lower quartiles

Figure 2: Summary of the median flexural modulus of the materials. Error bars represent upper and lower quartiles

Discussion

In the current study:

- ❖ Eclipse showed a higher flexural strength than heat-cured PMMA, similar to that reported in previous studies (5, 6). Eclipse is based on UDMA, a bifunctional monomer that has a high rate of polymerisation (2,3), and high crosslinking (4) compared to PMMA. In addition, the manufacturer claims that the dual activation of polymerisation of Eclipse (both light and heat) increased the degree of polymerisation(5).

- ❖ Weropress exhibited a significantly lower flexural strength than Eclipse and heat-cured PMMA. This result is attributed to its method of polymerisation and chemical composition which is similar to cold-cured PMMA (negative control). In addition, pourable-type denture base materials have high monomer: polymer ratio, potentially resulting in the polymerised specimens having high residual monomer, which acts as a plasticiser resulting in low fracture strength and stiffness. This result of low flexural strength support a previous study (7).

Conclusion

Within the limitations of the current study:

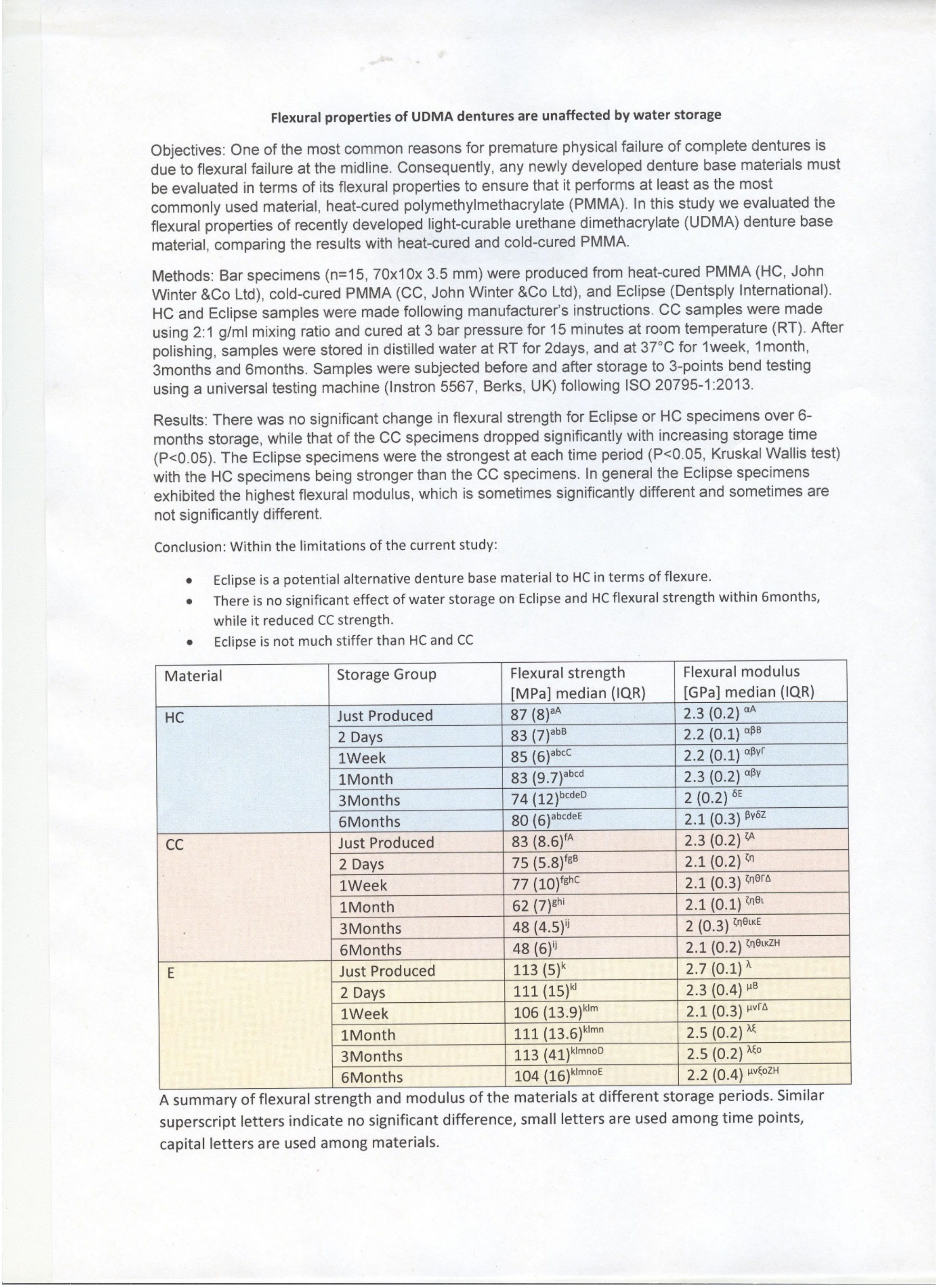
- ❖ Eclipse appeared to be a potential alternative for use as a denture-base material, as it was as strong and stiff as heat-cured specimens.
- ❖ Weropress specimens showed a significant difference to the currently used heat-cured materials.
- ❖ Further work is now required to see how these properties change over time, for instance after storage in an aqueous environment.

Acknowledgement: This project is funded by the Ministry of Higher Education and Scientific Research in Iraq.

References

1. Jagger DC, Harrison A, Jandt KD. J Oral Rehabil. 1999 Mar;26 (3):185-94.
2. Gajewski VE, *et al.* Braz Dent J.2012; 23(5):508-514.
3. Machado AL, *et al.* Gerodontology 2012; 29:e318:323.
4. Kerby RE, *et al.*. Dent Mats 2009; 25:302-313.
5. Ali IL, Yunus N, Abu-Hassan MI. J. Prosthodont. 2008; 17: 545-549.
6. Diaz-Arnold AM, *et al.* J Prosth Dent. 2008; 100 (1): 47-51.
7. Mumcu E, *et al.* J Adv Prosthodont. 2011; 3(3): 136-139.

- BSODR in September 2017 in Plymouth/UK (oral presentation as a part of Senior Colgate competition)



Flexural properties of UDMA dentures are unaffected by water storage

Objectives: One of the most common reasons for premature physical failure of complete dentures is due to flexural failure at the midline. Consequently, any newly developed denture base materials must be evaluated in terms of its flexural properties to ensure that it performs at least as the most commonly used material, heat-cured polymethylmethacrylate (PMMA). In this study we evaluated the flexural properties of recently developed light-curable urethane dimethacrylate (UDMA) denture base material, comparing the results with heat-cured and cold-cured PMMA.

Methods: Bar specimens (n=15, 70x10x 3.5 mm) were produced from heat-cured PMMA (HC, John Winter &Co Ltd), cold-cured PMMA (CC, John Winter &Co Ltd), and Eclipse (Dentsply International). HC and Eclipse samples were made following manufacturer's instructions. CC samples were made using 2:1 g/ml mixing ratio and cured at 3 bar pressure for 15 minutes at room temperature (RT). After polishing, samples were stored in distilled water at RT for 2days, and at 37°C for 1week, 1month, 3months and 6months. Samples were subjected before and after storage to 3-points bend testing using a universal testing machine (Instron 5567, Berks, UK) following ISO 20795-1:2013.

Results: There was no significant change in flexural strength for Eclipse or HC specimens over 6-months storage, while that of the CC specimens dropped significantly with increasing storage time ($P<0.05$). The Eclipse specimens were the strongest at each time period ($P<0.05$, Kruskal Wallis test) with the HC specimens being stronger than the CC specimens. In general the Eclipse specimens exhibited the highest flexural modulus, which is sometimes significantly different and sometimes are not significantly different.

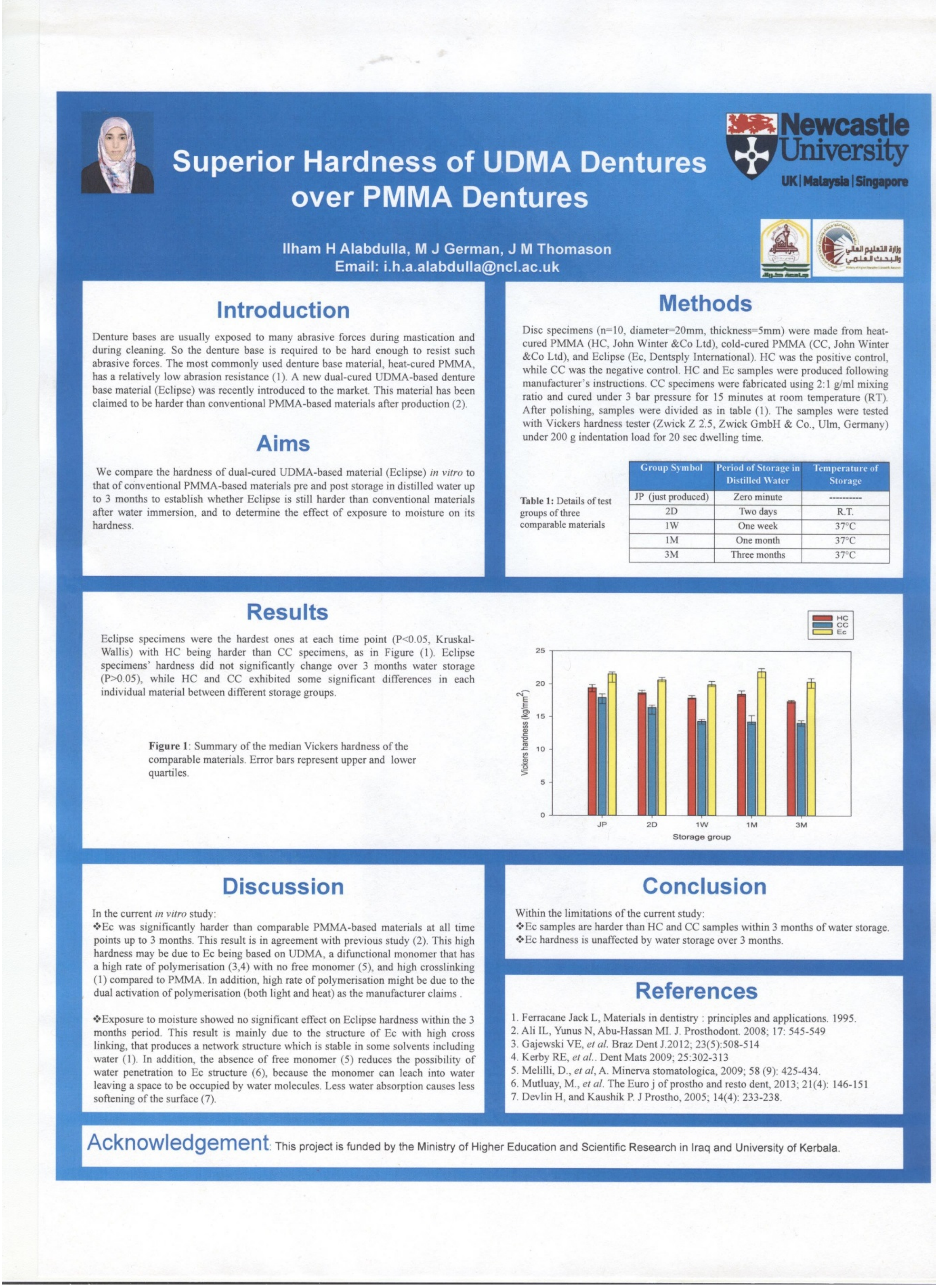
Conclusion: Within the limitations of the current study:

- Eclipse is a potential alternative denture base material to HC in terms of flexure.
- There is no significant effect of water storage on Eclipse and HC flexural strength within 6months, while it reduced CC strength.
- Eclipse is not much stiffer than HC and CC

Material	Storage Group	Flexural strength [MPa] median (IQR)	Flexural modulus [GPa] median (IQR)
HC	Just Produced	87 (8)^{aA}	2.3 (0.2) $^{\alpha A}$
	2 Days	83 (7)^{abB}	2.2 (0.1) $^{\alpha\beta B}$
	1Week	85 (6)^{abcC}	2.2 (0.1) $^{\alpha\beta\gamma\Gamma}$
	1Month	83 (9.7)^{abcd}	2.3 (0.2) $^{\alpha\beta\gamma}$
	3Months	74 (12)^{bcdeD}	2 (0.2) $^{\delta E}$
	6Months	80 (6)^{abcdeE}	2.1 (0.3) $^{\beta\gamma\delta Z}$
CC	Just Produced	83 (8.6)^{fA}	2.3 (0.2) $^{\zeta A}$
	2 Days	75 (5.8)^{fgB}	2.1 (0.2) $^{\zeta\eta}$
	1Week	77 (10)^{fghC}	2.1 (0.3) $^{\zeta\eta\theta\Gamma\Delta}$
	1Month	62 (7)^{ghi}	2.1 (0.1) $^{\zeta\eta\theta\iota}$
	3Months	48 (4.5)^{ij}	2 (0.3) $^{\zeta\eta\theta\iota\kappa E}$
	6Months	48 (6)^{ij}	2.1 (0.2) $^{\zeta\eta\theta\iota\kappa ZH}$
E	Just Produced	113 (5)^{k}	2.7 (0.1) $^{\lambda}$
	2 Days	111 (15)^{kl}	2.3 (0.4) $^{\mu B}$
	1Week	106 (13.9)^{klm}	2.1 (0.3) $^{\mu\nu\Gamma\Delta}$
	1Month	111 (13.6)^{klmn}	2.5 (0.2) $^{\lambda\xi}$
	3Months	113 (41)^{klmnoD}	2.5 (0.2) $^{\lambda\xi o}$
	6Months	104 (16)^{klmnoE}	2.2 (0.4) $^{\mu\nu\xi oZH}$

A summary of flexural strength and modulus of the materials at different storage periods. Similar superscript letters indicate no significant difference, small letters are used among time points, capital letters are used among materials.

- ADM in October 2017 in Nurnberg/Germany (Poster presentation as a part of Paffenbarger award)



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Superior Hardness of UDMA Dentures over PMMA Dentures

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Introduction

Denture bases are usually exposed to many abrasive forces during mastication and during cleaning. So the denture base is required to be hard enough to resist such abrasive forces. The most commonly used denture base material, heat-cured PMMA, has a relatively low abrasion resistance (1). A new dual-cured UDMA-based denture base material (Eclipse) was recently introduced to the market. This material has been claimed to be harder than conventional PMMA-based materials after production (2).

Aims

We compare the hardness of dual-cured UDMA-based material (Eclipse) *in vitro* to that of conventional PMMA-based materials pre and post storage in distilled water up to 3 months to establish whether Eclipse is still harder than conventional materials after water immersion, and to determine the effect of exposure to moisture on its hardness.

Methods

Disc specimens (n=10, diameter=20mm, thickness=5mm) were made from heat-cured PMMA (HC, John Winter &Co Ltd), cold-cured PMMA (CC, John Winter &Co Ltd), and Eclipse (Ec, Dentsply International). HC was the positive control, while CC was the negative control. HC and Ec samples were produced following manufacturer's instructions. CC specimens were fabricated using 2:1 g/ml mixing ratio and cured under 3 bar pressure for 15 minutes at room temperature (RT). After polishing, samples were divided as in table (1). The samples were tested with Vickers hardness tester (Zwick Z 2.5, Zwick GmbH & Co., Ulm, Germany) under 200 g indentation load for 20 sec dwelling time.

Table 1: Details of test groups of three comparable materials

Group Symbol	Period of Storage in Distilled Water	Temperature of Storage
JP (just produced)	Zero minute	----------
2D	Two days	R.T.
1W	One week	37°C
1M	One month	37°C
3M	Three months	37°C

Results

Eclipse specimens were the hardest ones at each time point ($P<0.05$, Kruskal-Wallis) with HC being harder than CC specimens, as in Figure (1). Eclipse specimens' hardness did not significantly change over 3 months water storage ($P>0.05$), while HC and CC exhibited some significant differences in each individual material between different storage groups.

Figure 1: Summary of the median Vickers hardness of the comparable materials. Error bars represent upper and lower quartiles.

Discussion

In the current *in vitro* study:

❖Ec was significantly harder than comparable PMMA-based materials at all time points up to 3 months. This result is in agreement with previous study (2). This high hardness may be due to Ec being based on UDMA, a difunctional monomer that has a high rate of polymerisation (3,4) with no free monomer (5), and high crosslinking (1) compared to PMMA. In addition, high rate of polymerisation might be due to the dual activation of polymerisation (both light and heat) as the manufacturer claims .

❖Exposure to moisture showed no significant effect on Eclipse hardness within the 3 months period. This result is mainly due to the structure of Ec with high cross linking, that produces a network structure which is stable in some solvents including water (1). In addition, the absence of free monomer (5) reduces the possibility of water penetration to Ec structure (6), because the monomer can leach into water leaving a space to be occupied by water molecules. Less water absorption causes less softening of the surface (7).

Conclusion

Within the limitations of the current study:
❖Ec samples are harder than HC and CC samples within 3 months of water storage.
❖Ec hardness is unaffected by water storage over 3 months.

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- ❖ IADR in July 2018 in London/UK (poster presentation)

#2020

Presenter:
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High colour stability of pourable and light-curable acrylic denture bases

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Introduction

Colour stability is an important aesthetic requirement for denture bases (Hersek *et al.*, 1999). It could be influenced by different conditions such as working in an aqueous environment (Devlin and Kaushik, 2005). Accordingly, any new denture base material should be evaluated for colour stability. Some new materials have recently been developed to shorten the time required for denture production. They are Eclipse, a light-curable UDMA-based polymer, and Weropress, a cold-cured PMMA pourable type.

Aims

Determining the ranking order of these new martials in comparison with conventional PMMA-based materials in regard to colour stability through 6 months of water storage and then to establish whether they are suitable to substitute for conventional denture-base materials in terms of aesthetics.

Methods

Ten disc specimens (diameter=20mm, thickness=4mm) were produced from materials Heat-cured PMMA (HC) (John Winter &Co Ltd); Cold-cured PMMA (CC) (John Winter &Co Ltd); Eclipse (Ec) (Dentsply International); and Weropress (Ws) (MerzDental GmbH) as tested materials. Ws and Ec samples were made following manufacturer's instructions. HC was made following manufacturer's instructions except dough time (14 min) and curing at 70°C for 7 h followed by boiling at 95°C for 2 h. CC samples were mixed at 2:1 g/mL and cured at 3 bar for 15 min at room temperature (RT). After polishing (P400 grit, fine grain pumice, polishing compound), the samples were stored in distilled water at RT for 2 days, then at 37°C for 180 days. Dry specimens were evaluated for colour before storage and at 2nd day, and then at 7th, 30th, 90th and 180th day of storage using a spectrophotometer (Ci6x, x-rite, US). Colour change was calculated following ISO 20795-1:2013.

Results

The colour changes can be seen in figure 1. Kruskal-Wallis and Tukey post-hoc test were used for testing. No significant change in Weropress colour has occurred over time ($P>0.05$), while for HC, CC, and Ec it was significantly increasing ($P<0.05$) with CC showing the highest discolouration, and Ws the lowest one ($P<0.001$). CC was significantly different from all materials at 90 day upward. HC was higher and significantly different from Weropress except at 2nd day group. HC was higher than Ec but they were not significantly different except at 30 day group.

Figure 1

A summary of the median colour change values (ΔE) of the four compared materials upon water storage. Error bars represent upper and lower quartiles

Discussion

Following the manufacturer's instructions for HC and CC caused porosity to occur in the cured specimens, which could have affect the colour measurements. Consequently, after a series of pilot studies, a modified production procedure was developed for these two materials.

Oxidation of tertiary amine in CC might has caused the high deviation of CC colour (Anusavice *et al.*, 2012). High colour stability of Ws may in high probability be due to barbituric acid catalyst system contents which act as antioxidants and colour stabilisers (Giziroglu *et al.*, 2013). Colour changes of HC and Ec perhaps due to absorbing water which might have changed the refractive index or degraded the material (Akin *et al.*, 2014b).

Conclusions

Within the limitations of this study:

- Ranking the materials from best to worst colour stability was: Ws, Ec, HC, and finally CC.
- Ws and Ec can be used as potential alternative denture base materials to HC in terms of colour stability.

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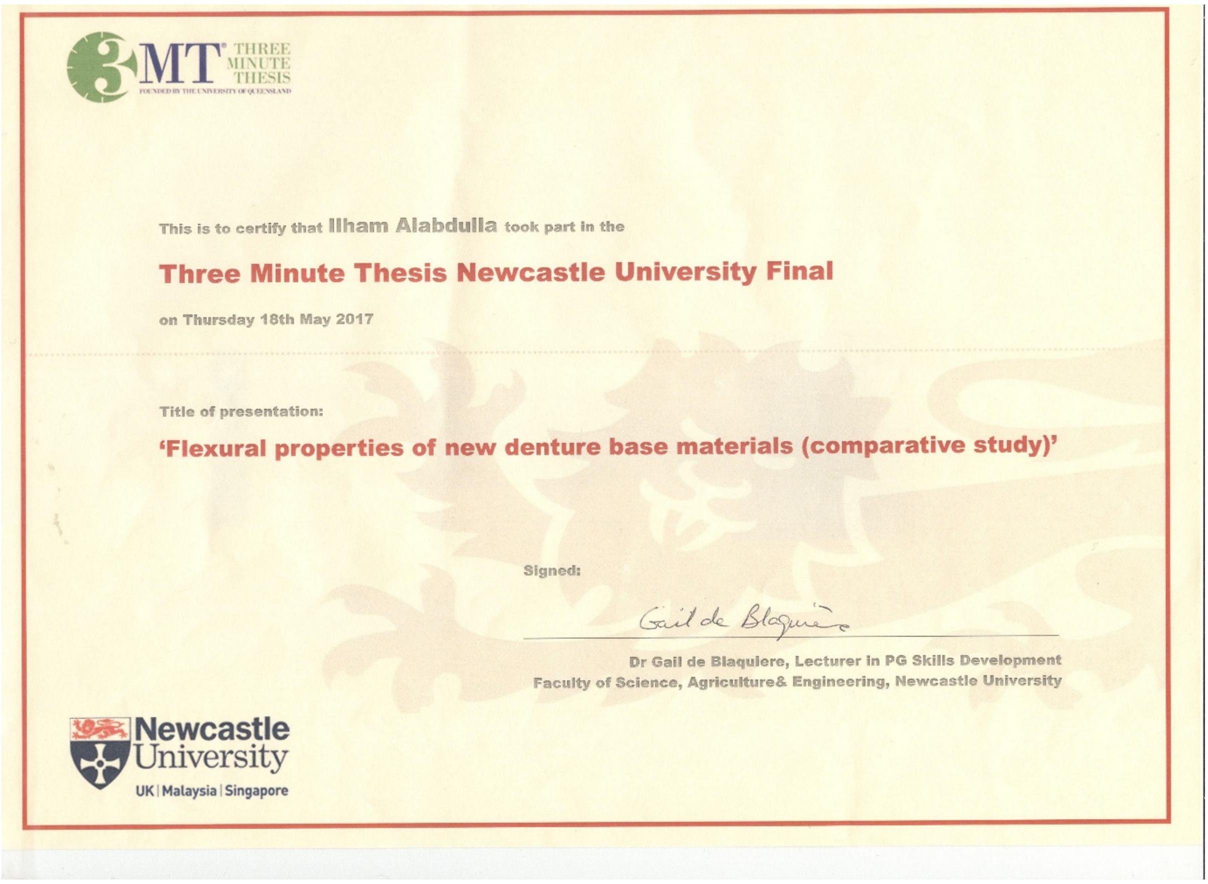
- Three minutes thesis in Newcastle University in May 2017 (oral presentation)



3MT THREE MINUTE THESIS
FOUNDED BY THE UNIVERSITY OF QUEENSLAND

This is to certify that **Ilham Alabdulla** took part in the

Three Minute Thesis Newcastle University Final

on Thursday 18th May 2017

Title of presentation:

‘Flexural properties of new denture base materials (comparative study)’

Signed:

Gail de Blaquiere

Dr Gail de Blaquiere, Lecturer in PG Skills Development
Faculty of Science, Agriculture& Engineering, Newcastle University

Newcastle University
UK | Malaysia | Singapore

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