

The viscoelastic properties of some dental soft lining materials.

Saber-Sheikh, Kambiz

The copyright of this thesis rests with the author and no quotation from it or information derived from it may be published without the prior written consent of the author

For additional information about this publication click this link.

<http://qmro.qmul.ac.uk/jspui/handle/123456789/1709>

Information about this research object was correct at the time of download; we occasionally make corrections to records, please therefore check the published record when citing. For more information contact scholarlycommunications@qmul.ac.uk

**THE VISCOELASTIC
PROPERTIES
OF SOME
DENTAL
SOFT LINING MATERIALS**

Kambiz Saber-Sheikh

**Thesis Submitted to the University of London
for the
Degree of Doctor of Philosophy**

December 1997

IRC in Biomaterials, Queen Mary and Westfield College
Department of Biomaterials in Relation to Dentistry.
St Bartholomew's and the Royal London School of Medicine and Dentistry.

Abstract

The viscoelastic properties of soft lining materials are of enormous interest and importance as they clearly govern the biomechanical function of these materials.

Forced vibration (Non-resonant) dynamic mechanical analysis was used to characterise the viscoelastic properties of a wide range of commercial (8 brands) as well as experimental soft liners (7 formulations). Forced vibration DMA is the ideal way of studying these materials as it can closely and accurately mimic physiological temperatures and frequencies under which they operate.

The materials were studied as processed, and subsequently after simulated ageing for time periods up to twelve months. The water absorption and the subsequent changes in the viscoelastic behaviour of these materials are important as they spend a large part of their working lifetime immersed in solution.

The results, where possible, were compared with the work of other researchers, and any sources of discrepancy examined. It was noted that the materials whose glass to rubber transition (T_g) was near their operating temperature (i.e. the acrylics) were particularly prone to any changes in the time and temperature domain of the experiment.

A large variation was observed in the properties of the commercial materials available. At 37°C and 1 Hz a seven fold range was seen in the real part of the modulus (2.79-19.7 MPa), and a fifty fold range was observed in the loss tangent (0.029-1.52). Given this wide disparity it is surprising that a universally recommended range of properties does not exist, although there is some speculation in the literature.

The study of the ageing behaviour of these materials in water showed that the traditional hardening of the acrylics has been overcome. A heat cured silicone material was seen to be virtually unaffected by time, while for a cold cured competitor the opposite was true. New and experimental materials showed a wide range of behaviour after immersion in water.

Acknowledgements

I would firstly like to thank my supervisor Dr Richard. L. Clarke. for his guidance, patience, friendship and support over the last three years. His many interjections have been like breaths of fresh air! Prof. M. Braden also deserves thanks and gratitude for his help and advice on numerable occasions.

I would like to thank all the members of the Department of Biomaterials, too many to mention by name, for their help and support.

Last but not least I would like to acknowledge and thank my parents, for their support, care and struggle over the last 25 years.

For their financial support I am indebted to the EPSRC and Bonar Polymers Ltd.

Contents

Title Page	i
Abstract	ii
Acknowledgements	iii
Contents	iv
List of Figures	vii
List of Tables	xii
CHAPTER ONE INTRODUCTION	1
1.1 Soft Lining Materials: Basic Definitions	2
1.1.1 A Brief History of Soft Lining Materials	2
1.1.2. Uses and Function of Soft Lining Materials	4
1.1.3. Ideal Properties of Soft Lining Materials	9
1.1.4. Aims and Objectives	13
1.2 Viscoelastic Properties of Polymers	14
1.2.1. The Origins of Viscoelasticity	14
1.2.2. The Mechanical States of Polymers	15
1.2.2a. Creep Testing	16
1.2.2b. Stress Relaxation	19
1.2.3. Dynamic Mechanical Analysis (DMA)	21
1.2.3a. Complex Notation	23
1.3 Molecular Interpretation of Viscoelasticity in Polymers	25
1.3.1. Temperature Dependence	26
1.3.2. Time and Frequency Dependence	27
1.3.3. Glass Transition Temperature	28
1.3.4. Measurement of the Glass Transition	29
1.3.5. Theories of the Glass Transition	32
1.3.5a. Thermodynamic Theory	32
1.3.5b. Free Volume Theories	33
1.3.6. The Effect of Chemical Structure	38
1.4. Materials Under Investigation	44
1.4.1 Acrylic Based Soft Lining Materials	44
1.4.2. Silicone Soft Lining Materials	48

1.4.3.	Polyphosphazine Soft Lining Materials	50
1.4.4.	Light Curing Material	51
1.4.5.	Experimental Soft Lining Materials	52
1.4.5.a.	Elastomer / Methacrylate Hybrids	52
1.4.5.b	Polymerisable Plasticiser Acrylic Materials	53
1.5	Soft Lining Materials, Mastication and the Oral Environment	55
1.5.1.	Cushioning Effect of Oral Mucosa and Soft Liners	55
1.5.2.	Biomechanics of the Masticatory Cycle, and the Effect of Soft Liners	61
1.5.3.	Alveolar Bone Loss and it's Relationship to Soft Liners	64
CHAPTER TWO THEORY		68
2.	Linear Viscoelastic Theory	69
2.1.	Viscoelastic Models	70
2.1.1.	Maxwell and Voigt Models Under Static Conditions	70
2.1.2.	Maxwell and Voigt Models Under Dynamic Conditions	74
2.1.3.	The Four Element Model in Creep	77
2.1.4.	The Four Element Model Under Dynamic Excitation	78
2.1.5.	Spectral Models	80
CHAPTER THREE LITERATURE SURVEY		84
3.1	Methods of Measuring Viscoelasticity	85
3.1.1	Transient	85
3.1.2.	Low Frequency Free Vibration	86
3.1.3.	Forced vibration	87
3.1.4.	High Frequency Resonance Methods	87
3.1.5.	Wave Propagation	87
3.2.	Determination of the Viscoelasticity of Soft Liners	88
CHAPTER FOUR INSTRUMENTATION: DYNAMIC MECHANICAL ANALYSIS		109
4.1.	Introduction to the Apparatus	110
4.1.1.a	The Hardware	110

4.1.1.b	The Measuring Systems	113
4.1.2.	The Software: Modes of Operation	114
4.1.3.	Fundamentals of DMA: Displacement, Force, Frequency and Temperature	115
4.2.	Experimental Methodology	120
CHAPTER FIVE RESULTS AND DISCUSSION		124
5.	Introduction	125
5.1	Initial Viscoelastic Characteristics	125
5.1.1.	Acrylic Based Materials	125
5.1.2.	Silicone Based Materials	132
5.1.3.	Miscellaneous Commercial Materials	138
5.1.4.	Experimental Materials	144
5.2	Ageing Characteristics	155
5.2.1.	Acrylic Based Materials	158
5.2.2.	Silicone Based Materials	166
5.2.3.	Miscellaneous Commercial Materials	173
5.2.4.	Experimental Materials	178
5.3.	General Discussion and Clinical Implications	183
5.4.	Sources of Errors, Reproducibility and Limitations	189
CHAPTER SIX CONCLUSIONS AND FUTURE WORK		192
6.1.	Conclusions	193
6.2.	Future Work	195
REFERENCES		197
APPENDIX A	DERIVATIONS	
APPENDIX B	THE VISCOELASTIC FREQUENCY RESPONSE OF SOFT PROSTHETIC MATERIALS	
APPENDIX C	LETTER TO THE MEDICAL DEVICES AGENCY	

List of Figures.

Number	Title	Page
1.1.1.	Representation of the role of soft liners.	5
1.1.2.	Improved retention with soft lining materials.	8
1.2.1.	Idealised creep curves for the four states of a polymer.	17
1.2.2.	Idealised stress relaxation for the four states of a polymer.	20
1.2.3.	The dynamic stress-strain behaviour of a viscoelastic material.	21
1.2.4.	Complex notation in dynamic mechanical analysis.	23
1.3.1.	The temperature dependence of a typical amorphous polymer.	25
1.3.2.	Expansion versus temperature for a typical polymer at its transition.	29
1.3.3.	Heat capacity of amorphous polypropylene (Gee, 1970).	30
1.3.4.	Diagrammatic representation of the change in volume and temperature for a polymer sample (Young & Lovell, 1995)	34
1.3.5.	Glass transition of styrene-butadiene random copolymer (Wood, 1958).	42
1.4.1.	A diagrammatical representation for the procedure used to make the samples investigated in this report.	47
1.4.2.	Infra-red spectrum of Triad (TR).	51
1.5.1.	Typical behaviour of mucosa under a constant load (Kydd & Daly, 1982).	56

1.5.2.	Co-factors affecting alveolar bone loss (Atwood, 1971).	64
2.1.1.	The Maxwell and Voigt elements.	71
2.1.2.	The time dependence of creep compliance of the Maxwell and Voigt elements.	72
2.1.3.	The Maxwell and Voigt elements in stress relaxation.	72
2.1.4.	Dynamic modulus of a Maxwell element.	75
2.1.5.	Dynamic compliance of a Voigt element.	75
2.1.6.	The four element model.	77
2.1.7.	Creep behaviour of 4 element model. (from data of Kawano et al, 1993)	78
2.1.8.	Generalised Voigt and Maxwell models.	81
4.1.1.	Schematic cross-section of the apparatus.	111
4.1.2.	The instrumental set up consisting of DMA 7 connected via the TAC 7/DX Thermal Analysis Instrument Controller to Computer.	112
4.1.3.	Close up of the 10 mm diameter Parallel Plate measuring system.	112
4.1.4.	The effect of amplitude on the quality of the results.	117
4.1.5.	Total force on the sample.	118
4.2.1.	Print out of a typical DMA method screen.	122
5.1.1.	Storage modulus of Futurasoft (FS).	126

5.1.2.	Loss Tangent of Futurasoft (FS).	126
5.1.3.	Storage modulus of Supersoft (NS).	128
5.1.4.	Loss Tangent of Supersoft (NS).	128
5.1.5.	Storage modulus of Supersoft (OS).	129
5.1.6.	Loss Tangent of Supersoft (OS).	129
5.1.7.	Storage modulus of Molloplast B (MP).	133
5.1.8.	Loss tangent of Molloplast B (MP).	133
5.1.9.	Storage modulus of Flexibase (FB).	136
5.1.10.	Loss tangent of Flexibase (FB).	136
5.1.11.	Storage modulus of Novus (NN).	138
5.1.12.	Loss Tangent of Novus (NN).	139
5.1.13.	Storage modulus of Novus (ON).	139
5.1.14.	Loss tangent of Novus (ON).	140
5.1.15.	Storage modulus of Triad (TR).	142
5.1.16.	Loss tangent of Triad (TR).	142
5.1.17.	Storage modulus of experimental BS material.	144
5.1.18.	Loss tangent of experimental BS material.	145
5.1.19.	Storage modulus of experimental SI material.	145
5.1.20.	Loss tangent of experimental SI material.	146

5.1.21.	Storage modulus of experimental PB material.	146
5.1.22.	Loss tangent of experimental PB material.	147
5.1.23.	Storage modulus of experimental PP material.	149
5.1.24.	Loss tangent of experimental PP material.	149
5.1.25.	Storage modulus of experimental C1 material.	150
5.1.26.	Loss tangent of experimental C1 material.	150
5.1.27.	Storage modulus of experimental PE material.	151
5.1.28.	Loss tangent of experimental PE material.	151
5.1.29.	Storage modulus of experimental PH material.	152
5.1.30.	Loss tangent of experimental PH material.	152
5.2.1.	Variations in the storage modulus (at 37°C, 1Hz) of FS against time together with variations of sample weight.	158
5.2.2.	Variation of $\tan \delta$ with respect to time for FS.	158
5.2.3.	Variations in the storage modulus (at 37°C, 1Hz) for NS, plotted against time. Together with variation of sample weight %.	161
5.2.4.	Variations in the loss tangent (at 37°C, 1Hz) for NS after storage.	161
5.2.5.	Variations in the storage modulus (at 37°C, 1Hz) for OS, plotted against time. Together with variation of sample weight %.	163
5.2.6.	Variations in the loss tangent (at 37°C, 1Hz) for OS, plotted against time.	163

5.2.7.	Variations in the storage modulus (at 37°C, 1Hz) for MP, plotted against time. Together with variation of sample weight %.	166
5.2.8.	Variations in the loss modulus (at 37°C, 1Hz) for MP, plotted against time.	167
5.2.9.	Variations in the storage modulus (at 37°C, 1Hz) for FB, plotted against time. Together with variation of sample weight %.	169
5.2.10.	Variations in the loss tangent (at 37°C, 1Hz) for FB, plotted against time.	170
5.2.11.	Variations in the storage modulus (at 37°C, 1Hz) for NN, plotted against time. Together with sample weight %.	173
5.2.12.	Variations in the loss tangent (at 37°C, 1Hz) for NN.	173
5.2.13.	Variations in the storage modulus (at 37°C, 1Hz) for TR, plotted against time. Together with sample weight %.	176
5.2.14.	Variations in the loss tangent (at 37°C, 1Hz) for TR.	176
5.2.15.	Variations in the storage modulus (at 37°C, 1Hz) for BS, plotted against time. Together with sample weight %.	178
5.2.16.	Variations in the loss tangent (at 37°C, 1Hz) for BS.	179
5.2.17.	Variations in the storage modulus (at 37°C, 1Hz) for PP, plotted against time. Together with sample weight %.	181
5.2.18.	Variations in the loss tangent (at 37°C, 1Hz) for PP.	181

List of Tables

Number	Title	Page
1.3.1	The dependence of the Tg of poly (3.3-bischloromethyloxacyclobutane) on the time scale of the experiment. (Sandiford, 1958).	31
1.3.2.	The effect on Tg from constituents of the polymer backbone (Young & Lovell, 1995).	39
1.3.3.	Relationship between Tg and side groups in the methacrylate family (Ferry, 1980; Braden et al 1997)	39
1.3.4.	The effect of polar or bulky side group on the Tg of vinyl polymers of the type: (CH ₂ -CHX) where X is the side group in question (Young & Lovell, 1995).	40
1.4.1.	Commercial materials under investigation.	44
1.4.2.	Typical plasticised acrylic soft lining materials. E : Ethyl, M : Methyl, B : n-Butyl, MA : methacrylate (Wright, 1981)	45
1.4.3.	Summary of composition for acrylic soft lining materials tested.	46
1.4.4.	Composition of Molloplast B (Braden et al, 1997).	49
1.4.5.	Composition of Novus (ON) (Braden et al, 1997).	50
1.4.6.	Elastomeric content of the Elastomer/Methacrylate soft lining materials.	53
1.4.7.	Liquid components and proportions (parts by volume) of the various polymerisable plasticiser systems, (Parker & Braden, 1989; IRC Annual Report, 1996/97).	54

1.5.1.	Effect of age on the deformation of the mucosa (Kydd & Daly, 1982).	57
1.5.2.	Material properties (Aydinlik et al, 1980)	59
1.5.3.	Material properties used in FEA. (Kawano et al, 1993).	60
1.5.4.	Mean Maximum bite force and masticatory effectiveness for various denture configurations (Wright, 1984).	63
1.5.5.	Average ridge reduction of the mandible and the maxilla after 6 months for various denture types (ElCharkawi & ElMahdy, 1988).	66
2.1.1.	Maxwell and Voigt static behaviour.	71
2.1.2.	The Dynamic behaviour of the Maxwell and Voigt models.	74
2.1.3.	The generalised Maxwell and Voigt models.	81
3.2.1.	The Work surveyed in this review.	88
3.2.2.	Viscoelastic parameters for of selected materials at 37°C (Braden & Clarke 1972).	92
3.2.3.	Young's Modulus (GPa) of various soft lining materials at room temperature (Clarke & Braden, 1982).	96
3.2.4.	Creep Modulus (MPa) carried out at room temperature (Robinson & McCabe, 1982)	97
3.2.5.	Effect of powder to liquid ratio on a natural rubber/2-ethoxyhexyl methacrylate system (Parker & Braden 1990).	99
3.2.6.	Effect of cross linking on viscoelastic properties of a butadiene acrylonitrile/2-ethoxyhexyl methacrylate system (Parker & Braden 1990).	100

3.2.7.	DMA properties of commercial soft liners (Kalachandra et al, 1995).	105
3.2.8.	Viscoelastic properties of Supersoft (Wagner et al, 1995a).	106
3.2.9.	Viscoelastic properties of Novus (Wagner et al, 1995a).	106
3.2.10.	Viscoelastic properties of Molloplast (Wagner et al, 1995a)	106
3.2.11.	DMA properties of 3 commercial soft liners after accelerated ageing (Wagner et al, 1995b).	107
3.2.12.	DMA and water absorption of BS material (Kalachandra et al, 1996).	108
3.2.13.	Shear storage modulus and the loss tangent of selected soft liners (Waters et al, 1996).	108
4.1.1.	DMA Measuring systems.	114
4.1.2.	The dependence of data quality on the measured parameters.	116
4.2.1.	Summary of experimental parameters	123
5.1.1.	The viscoelastic properties of FS at mouth and room temperature.	125
5.1.2.	The viscoelastic properties of NS and OS at room and mouth temperature.	130
5.1.3.	The viscoelastic properties of MP at room and mouth temperature.	134
5.1.4.	The viscoelastic properties of FB at room and mouth temperature.	137

5.1.5.	The viscoelastic properties of NN and ON at room and mouth temperature.	140
5.1.6.	The viscoelastic properties of TR at room and mouth temperature.	143
5.1.7.	The viscoelastic properties of BS, SI and PB at room and mouth temperature.	147
5.1.8.	The viscoelastic properties of PP, C1, PE and PH at room and mouth temperature.	153
5.2.1.	Ageing data for FS including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation.	159
5.2.2.	Ageing data for NS including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation.	162
5.2.3.	Ageing data for OS including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation.	164
5.2.4.	Ageing data for MP including storage modulus, loss tangent and weight change together with the associated standard deviation.	167
5.2.5.	Ageing data for FB including storage modulus, loss tangent and weight change together with the associated standard deviation.	170
5.2.6.	Ageing data for NN including storage modulus, loss tangent and weight change together with the associated standard deviation.	174

5.2.7.	Ageing data for TR including storage modulus, loss tangent and weight change together with the associated standard deviation.	177
5.2.8.	Ageing data for BS including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation.	179
5.2.9.	Ageing data for PP including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation.	182
5.3.1.	Summary of results at physiological conditions.	183
5.3.2.	The viscoelastic properties of some soft lining materials after a years storage in water (values at 37°C, 1Hz).	187

CHAPTER ONE

INTRODUCTION

1.1. Soft Lining Materials: Basic Definitions

Soft lining materials were defined by Wright (1980a) as: '*Soft, elastic and resilient materials forming all or part of the fit or impression surface of a denture.*' Their main aim being to protect or increase comfort for patients who can not tolerate a hard denture base.

Softness can be defined by the elastic modulus (E) or compliance (D) where one is the reciprocal of the other ($E = 1 / D$). Modulus for a given material is in turn defined by the amount of stress needed to achieve a certain strain ($E = \text{stress} / \text{strain}$). Elasticity implies that a material will return to its original shape after a given deformation.

Resilience being related to the rate of recovery, a resilient material recovering quickly. The label 'Resilient' lining material is also in common usage (Storer, 1962a,b; Bascom, 1966). Resilient is not a good name for these materials as it does not imply softness, steel for example being a very resilient material.

1.1.1. A Brief History of Soft Lining Materials.

The first mention of soft lining materials was in 1869 by Twitchell. These early materials were made from natural rubber products. The exclusive use of natural rubber continued until the middle of this century when the first synthetic soft lining materials were developed. The move away from natural rubber was partially due to its high water absorption which led to dimensional instability and fouling over time. Another reason was the change over from vulcanite (a hard rubber based material) to polymethylmethacrylate (PMMA) as the main denture base material. Although recently new improved experimental natural rubber materials have been investigated (Wright 1981), they were again found to be unsatisfactory, due to high water absorption and toxicity. By far the biggest share of the research in this field is therefore directed towards synthetic materials.

Plasticised polyvinylchloride (PVC) was one of the first synthetic materials to be used towards the end of second World War (Matthews, 1945). The main problem with this material was that the plasticiser leached out, hence hardening the material. Problems with adhesion to the denture base were also found. PVC's use in one form or another was continued until the 1960's, but the problems associated with this material were never solved and its use has been discontinued.

Other early contenders were the plasticised acrylic materials (Bates and Smith, 1965). This class of material shared the problem of hardening due to the loss of plasticiser with the PVC materials, but had the advantage of good adhesion to the PMMA denture base, being of a similar chemical family. Several routes have been taken to relieve this hardening problem. One is by using a base material with a lower T_g such as a higher methacrylate (e.g. swapping ethyl for methyl). This relieves the need for large quantities of plasticiser. Two other philosophies include the use of an unleachable polymerisable plasticiser. The other, the use of elastomers mixed in with the methacrylate monomers. Both methods have achieved some success (Parker, 1982). Acrylic materials are still widely used today forming part of the work carried out in this thesis and so will be dealt with in detail in a following section.

Silicone soft lining materials based on dimethylsiloxane appeared at about the same time and like the acrylics have passed the test of time and are still used today. The early silicones suffered from requiring high processing temperatures and containing toxic lead catalysts (Lammie and Storer, 1958). This problem has been solved and, as will become apparent, materials today can be either heat or cold cured. The problems traditionally associated with the silicones have been poor adhesion with PMMA and poor tear strength.

Of the materials that have come and gone through the years the hydrophilic acrylic materials are one of the more interesting ones and deserve a mention. These were acrylic

polymer with hydrophilic groups. They were supplied in gel form and become hard and brittle after polymerisation. On immersion in water, water readily migrates into these materials and softened them by acting as a plasticiser. Materials of this type suffer because of the volume change associated with their water absorption. One way around this would be to manufacture them in a solvent, which would later leach out and be replaced with water, volume for volume. In practice this has not been successful (Wright, 1976).

Other developments in the field include a polyphosphazine based elastomer (Gettleman & Gerbert, 1987), a fluoroelastomer (Braden et al, 1997) and light cured soft lining materials for chair-side convenience (See section 1.4). The polyphosphazine, and a light cured material will be discussed in more detail as they are two of the materials being investigated in this report.

Liquid supported dentures have also been suggested as an alternative to soft lining materials (Davidson and Boere, 1990a,b). The basic concept is to make a denture whose base is covered with a pre-shaped flexible foil containing a high viscosity liquid. The idea being that the fit surface of the denture would continuously respond and adapt to the mucosa. While a good conceptual idea, clinical trials were not successful as the majority of the dentures were found to leak.

1.1.2. Uses and Function of Soft Lining Materials.

The uses of soft lining materials in medicine and dentistry (Wright, 1980a; Lammie & Storer, 1958) can be summarised as follows:

- In lower and upper dentures when the patients masticatory mucosa is found deficient.
- For developing retention by engaging undercut areas.

- The manufacture of obturators for the aid of patients with clefts or defects of the palate.
- Other uses: maxillofacial prosthesis, mouth guards, hearing aids.

This first application of soft lining materials is the most widely spread as pointed out by Storer (1962a) '*...the greatest number of cases in which resilient linings are helpful are those showing senile or presenile atrophy of tissue.*' In old age the human body suffers from degradation and the oral tissues share in this phenomena. The mucosa shows a reduction in the number of cell layers, thickness, resilience and the effective area of the load bearing surface of dentures is reduced* (Lammie and Storer, 1958). The result of this increase in the effective stress is often bruising and pain as the nerve endings in the mucosa are compressed between the hard denture base and the underlying bone.

Lammie and Storer state : "*Even in severe cases, comfort may be obtained by making a complete lower denture with a soft lining.*"

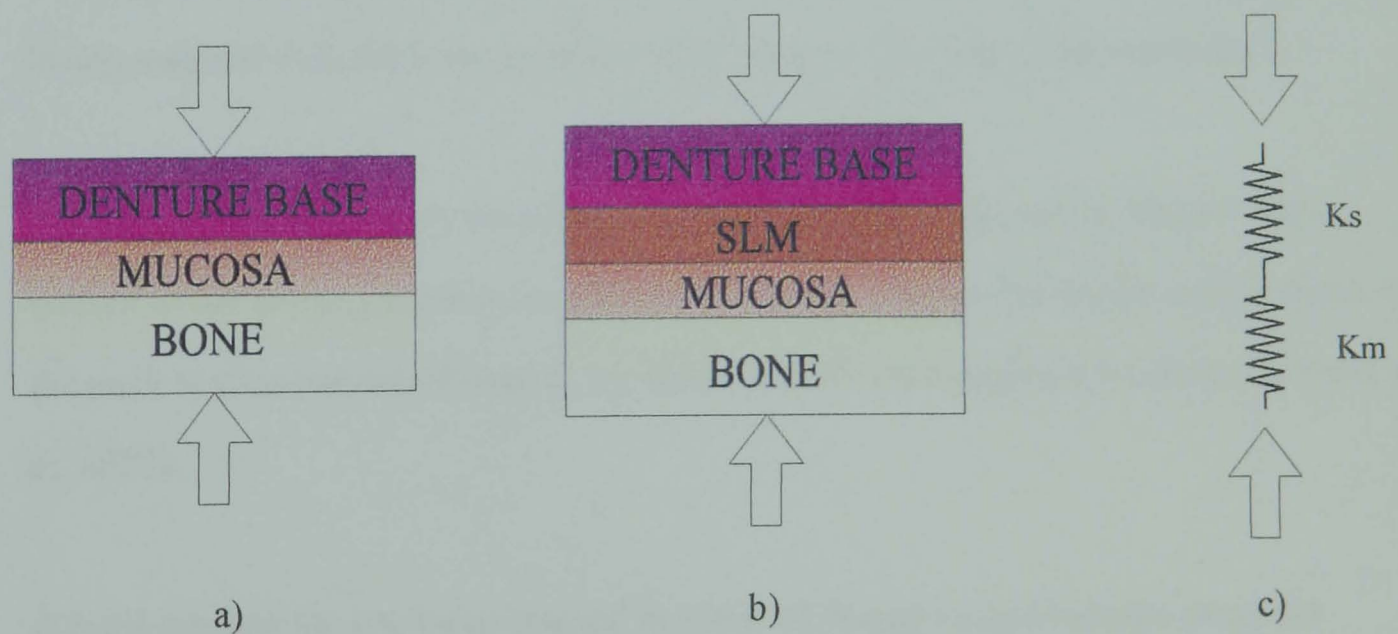


Figure 1.1.1. Representation of the role of soft liners. a) shows the case where a soft liners is not used, the mucosa is compressed between the denture base and bone. b) shows the case where a soft lining material is available and c) is a simple physical model representing the mucosa and the soft lining material.

* The deficiency of the oral mucosa may, in addition to atrophy be due to injury, oral surgery or trauma from ill fitting dentures.

Figure 1.1.1b is a diagrammatic representation of the application of soft lining materials (SLM) in the denture mucosa interface as opposed to using a hard denture base (1.1.1a). Although this is by no means the universal application. There have also been reports of using soft liners in the interface between the artificial teeth and the denture base (Bernhausen, 1971). In either case although the clinical success of soft lining materials has been demonstrated over the years (Storer, 1962b; Bates & Smith, 1965; Schmidt & Smith, 1983a,b) the exact mechanical function of soft lining materials is still open to debate (Braden et al, 1995). Theoretically however three possible mechanisms can be found in the literature:

One is by distributing the given biting load evenly, thus relieving the patient of 'sore spots' of high mechanical stress. A common misconception (Qudah et al, 1990; McCabe 1990) is that soft linings somehow reduce the total masticatory forces transmitted by the denture to the underlying tissues, this is not true (Braden et al, 1995) by virtue of Newton's third law of motion. For example, lining a bathroom scale with a layer of soft lining material will not have an affect on the weight (i.e. force) registered by it.

The second mechanism by which soft liners work is by reducing the impact stress carried to the underlying mucosa. That is to say they reduce the height and intensity of the peak at the moment of impact, by virtue of their time dependent nature (Kawano et al, 1993).

A third mechanism can be envisaged in terms of energy considerations using the following mechanical model. Consider the soft lining material and the mucosa as two simple springs in series, with stiffnesses K_s and K_m respectively (figure 1.1.c). The deformation of each spring (X) as a result of a masticatory force F is obtained from Hooke's law. Thus:

$$F = X_s \times K_s \quad \text{and} \quad F = X_m \times K_m \quad 1.1.1.$$

The formula linking the Force across a spring to its energy content (W) is

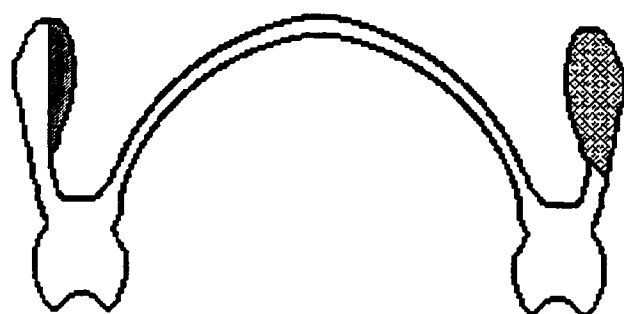
$$W = \frac{F^2}{2K} \quad 1.1.2.$$

This applied to our two springs in series yields

$$W = \frac{F^2}{2} \left(\frac{1}{K_m} + \frac{1}{K_s} \right) \quad 1.1.3.$$

It can be seen from equation 1.1.3. that the layer of soft lining material stores some of the masticatory energy, and indeed if softer than the mucosa most of the energy (Braden et al, 1995). This is of course a simplification, as the effect of the viscoelasticity of the soft lining material or the mucosa is not taken into account. The biomechanics and clinical implications of soft lining materials are discussed in greater detail in section 1.5.

The second use of soft liners mentioned by Lammie and Storer (1958) was to increase retention of the denture where parts of the fit surface of the mouth are undercut. Fig 1.1.2. aims to explain the problem. If a soft liner is unavailable then the usual procedure is to remove some of the hard acrylic from the fit surface of the denture. As can be seen on the left hand side of the diagram below, the dark grey area is removed. The problem being that an air pocket is left which reduces the retention of the denture. On the right hand side of the diagram, the procedure with soft lining materials is shown. The light grey area represents the soft liner. As this is inserted into the mouth the compliant flanges are displaced and if elastic will spring back as the denture is inserted into position. Thus the increase in the retentive force is two fold, that due to the elimination of the air pocket, and the elastic grip of the soft lining material.



The dark grey area represents the area cut away when soft lining materials are not available, leaving an air pocket.

The light grey area, on the right represents the case where soft lining materials are used.

Figure 1.1.2. Improved retention with soft lining materials

Soft lining materials can also be used as obturators. The defects of the palate and their treatment is dealt in some detail by Watt (1957). The aims of the treatment being to eliminate feeding difficulties and restoring normal speech, this being achieved either by surgery or the obturation of the defect. The main problem with the prostheses of the cleft palate is one of retention, where the principles used in full dentures are implemented. Watts lists pre-vulcanised latex as his material of choice, although admits that it deteriorates after a few months. More recently Polyzois (1992), has used a light curing material as an obturator, and states the ease and rapidity of the technique as its main advantages.

Soft lining materials are also used in the fabrication of maxillofacial prostheses. Murray (1979) showed the applicability of a soft liner to the treatment of various patients using maxillofacial prostheses. Protective mouth guards utilise a similar family of materials although different physical properties are looked for (Going et al, 1974). Soft lining materials also have possible application as ear mould materials (Okpojo and Braden, 1993).

Tissue conditioners are a class of materials similar to, but distinct from soft lining materials, both in terms of physical and chemical properties. They are briefly discussed here for completeness. The literature abounds with cases where the two classes have

been confused (Duran et al, 1979; Ellis et al, 1980; Graham et al, 1990). Tissue conditioners are designed for temporary usage only (Braden, 1971). This fact is sometimes not taken into account and the two classes of material are, unfairly, judged against each other. The tissue conditioners are then found to have weaker properties and subsequently dismissed as inferior materials.

Tissue conditioners are supplied as powder/liquid system (usually: poly-ethylmethacrylate powder and liquid comprising a phthalate plasticiser and ethanol). When mixed the ethanol swells the polymer beads and allows penetration by the plasticiser. A gel is formed by the entanglement of the polymer chains, it contains no permanent cross-links. This gel is viscoelastic in that it will flow under constant loads as a fluid, but will respond elastically to dynamic loading, as in mastication (Braden, 1971). They are used primarily after tissue trauma, either from surgery or ill fitting dentures.

1.1.3. Ideal Properties of Soft Lining Materials

The fact that so many types of soft lining materials exist is proof that none of them have the ideal properties which the clinician and the patient look for. More than 40 proprietary soft liners had been reported in the literature in 1980(a) by Wright, this number has certainly increased with time. The search for the perfect soft lining material requires an understanding of the ideal properties which are required. A short discussion of the ideal properties is therefore given below.

Soft lining materials and their components need to be compatible with body tissues with which they come into contact. They have to be tasteless and odourless and most importantly non-toxic. Several liners have had to be withdrawn for fear of toxicity in one of their components, e.g. those containing 2-ethoxyethylmethacrylate (Aiken, 1988).

They should not stain or otherwise be affected by food, tobacco, alcohol and denture cleaners. It was found in particular that the denture cleaner used can have a dramatic effect on the mechanical properties of soft liners (Bates and Smith 1965).

The soft lining material must not support the growth of bacteria and micro-organisms, notably *Candida Albicans* (Wright, 1980b). In wearing hard dentures, the surface is smooth and good oral hygiene is sufficient to keep the oral environment in a healthy state. Conversely most soft lining materials show surface irregularities after a few months wear. This makes adequate hygiene difficult and so it is important that the material itself inhibits the growth of *Candida Albicans*.

The material should be easily processed by conventional dental technology (Storer, 1962a). Traditionally this has involved heat curing, under pressures available using a hand screw press and at temperatures not exceeding 100°C. Two types of curing systems exist for chair-side use. 'Cold curing' materials have been developed which do not require heat, but use an *activator* to achieve polymerisation. Light curing materials are also available where light instead of heat initiates the reaction. Generally speaking light and cold curing materials are easier, quicker and more convenient to use, whereas the heat cured materials are often found to be more reliable. Microwaves have also been used as an alternative to heat curing (McKinstry, 1991).

Ideally the material should be easy to work with (and if necessary repair) and inexpensive. Soft lining materials maybe used relatively infrequently in dental work shops and therefore need a good shelf life to be acceptable (Wright 1980a).

A useful property for a soft liner, looked for by the clinician, is whether the material can be polished. Some materials whilst compliant at mouth temperatures become hard enough at lower temperatures to be conveniently trimmed and polished using standard

dental techniques. A smooth polished surface makes it harder for bacteria to live on the soft liner and therefore improves oral hygiene.

They must be dimensionally stable during processing and use (Wright, 1981). This often implies low water absorption, as uptake invariably leads to swelling. There are two advantages of dimensional stability. Firstly the fit between the soft lining material and the mucosa does not deteriorate leading to loss of comfort or retention. Secondly any dimensional change would put a strain on the denture base/soft lining material interface thus increasing the likelihood of a crack.

The material must adhere well to the rigid denture base (Storer, 1962a). This increases the life of the denture, provides better stability and reduces the likelihood of *Candida Albicans* growing at the soft lining/denture base interface.

Good Viscoelastic properties are needed. The material should be soft and have a low modulus, although the degree of compliance is at present uncertain and a range of materials with different stiffnesses have been reported as successful (Bates & Smith, 1965; Braden & Clarke, 1972; Braden et al, 1997). The material should be reasonably elastic (not lose its shape), although problems with a 'rubber ball' or bounce effect have been mentioned (Bascom, 1966). The effective softness of the lining material can in part be altered by its thickness, a thick layer of material feeling softer (Wright, 1976).

Although this is true the thicker the soft lining layer, the thinner the denture base has to be as there is only a limited amount of space in the mouth. A thin denture base means a flexible one which is prone to fracture. So in effect the thinner the layer of soft liner, the better. Soft lining materials should also retain their shape, as loss of shape has a detrimental effect on the fit of the denture which will lead to loss of comfort and retention.

The soft lining material should have a reasonable life span and in particular have permanency of compliance. Lammie and Storer (1958) noted that the function for which the material is being used for is an important consideration. In cases of tissue trauma a liner which hardens gradually was suggested as possibly being the best solution. Five years is normally considered to be an average age for a denture and PMMA has sufficient mechanical properties for this. (Wright 1980a). Gonzales & Laney (1966) suggest 2 years to be an adequate life for a soft liner. There have been reports of soft lining materials lasting up to 8 years and even outlasting the acrylic teeth used in the denture (Wright, 1994).

The frictional properties of soft lining materials have also been the subject of debate (Suchatlampong et al, 1986). In general the coefficient of friction of soft lining materials is higher than that of poly(methylmethacrylate) denture base materials, which can lead to loss of comfort for some patients. Related to the frictional properties of a soft lining material are its wettability characteristics. Wettability is important for the comfort and retention of the denture (Wright, 1981), this is particularly important in a dry mouth. Poor wettability can lead to increased irritation.

High abrasion resistance is another important property (Storer, 1962a). If abrasion resistance is low the surface quickly loses its original shape, which can lead to a loss of comfort as far as the patient is concerned. On a microscopic level it will also have detrimental effects on oral hygiene as noted above.

Lastly the soft liners should be aesthetically pleasing, matching the colour of the denture base.

1.1.4. Aims and Objectives.

Although all the above properties are important for a successful soft lining material; this contribution will focus specifically on their viscoelastic properties. This is important, as noted by Watts in 1994: '*An understanding of both moduli and viscoelasticity is valuable in the appraisal of clinical performance of biomaterials*'. It is thought that an investigation of this kind would be particularly useful with respect to soft liners. This is because their biomechanical function is clearly dependent on their viscoelastic characteristics.

The aim of this work, therefore is to study the viscoelasticity of soft lining materials at frequencies and temperatures encountered in the oral environment. The manner in which such viscoelastic properties change in the wet oral cavity, throughout the life of the material are also very relevant and thus the effect of ageing will also be investigated.

1.2. Viscoelastic Properties of Polymers.

This section introduces the concept of viscoelasticity in polymers, together with some of the experimental techniques used to gauge it.

1.2.1. The Origins of Viscoelasticity.

Mechanical properties of all common materials have traditionally been expressed by one of two physical laws, first formulated by two great scientists and rivals of the 17th and 18th centuries, Sir Isaac Newton¹ and Robert Hooke² (Tschoegl, 1989).

For solids, Hooke said that stress (σ) is always proportional to the strain (ϵ) and independent of the rate of strain. Any material obeying this law is referred to as a Hookian (linearly elastic) solid. Materials of this type store all their energy of deformation and will spring back if given the opportunity.

On the other hand Newton's law of liquids states that the stress is proportional to the rate of strain ($d\epsilon/dt$), but not to strain itself, and so any liquid exhibiting this phenomena is termed Newtonian. This class of material dissipates all the deformational energy put into it, as heat. These two ideas are often expressed in the following well known constitutive equations:

$$\sigma = E\epsilon \quad 1.2.1.$$

$$\sigma = \eta \frac{d\epsilon}{dt} \quad 1.2.2.$$

Where E and η are the constants of proportionality for the given material, in other words the material properties, elastic modulus and coefficient of viscosity respectively.

¹ Sir Isaac Newton, (1642-1727) English physical scientist and mathematician, one of the greatest figures in all of science.

² Robert Hooke (1635-1703) English experimental physicist, generally regarded as the founder of the theory of elasticity.

These two laws assume infinitely small strain and rate of strain respectively. As soon as the perturbations become large, springs will no longer be linear and will not spring back to their original shapes, and similarly liquids will not behave perfectly due to turbulence.

Furthermore Newton's and Hooke's laws are idealisations of the real world. No material is perfectly elastic or viscous. Take as an example the creep of steel pipes; or in relation to dentistry, the flow of amalgam under constant stress. These physical properties are in practice time and temperature dependent. For example, all metals go from the extreme of being a liquid at above their melting point to being a solid. In short no material obeys either of the above laws exactly and in reality all materials display some viscoelastic behaviour.

Although all materials are affected by temperature, polymers are unusual in that their material properties change rapidly from being a near perfect solid to a liquid over a relatively small temperature range (a few 100°C). The next section looks at the characteristics of polymers in their various physical states. Only amorphous materials are considered, as polymers used in dentistry are predominantly of this type.

1.2.2. The Mechanical States of Polymers

The classification of the thermo-mechanical properties of polymers based upon their stress-strain response was formally carried out by Meares in 1965 and reinforced in relation to dentistry by Clarke (1978). Four states of existence were distinguished, the first being at the low temperature (high frequency) end of the spectrum and the last being at the high temperature (low frequency) end:

- The Glassy state, or in other words low elastic region.
- The Leathery state, or retarded elastic region.
- The Rubbery state, or high elastic phase.
- The Viscous state, or the liquid phase.

Although these divisions are idealised they provide a good insight into the way the mechanical properties of polymers change with increasing temperature. More will be said of the molecular interpretation of the stress/strain response in the following section. In the present discussion the mechanical response of the different polymer phases is described by two transient methods of testing, retardation and relaxation testing, commonly called creep and stress relaxation, respectively.

1.2.2a. Creep Testing

What is meant by a creep test is that an instantaneous stress is applied to the sample and then held constant for a set time and then instantaneously released. This can also be termed a stress pulse (Figure 1.2.1). Meanwhile the strain behaviour caused by this perturbation is investigated:

In the glassy state, that is to say the low temperature or high frequency end of the spectrum*, the application of the stress produces an instantaneous strain AB whose magnitude is maintained until the load is removed at G. The strain then drops to zero along DG. There is no need to complicate the situation by differentiating between cross-linked and uncross-linked polymers as cross-links between polymer chains play no role in the glassy region, Figure 1.2.1a. represents the behaviour of any Hookian solid and glassy polymers can be considered as such for low strains.

* The relationship between temperature and frequency will be dealt with in a later section.

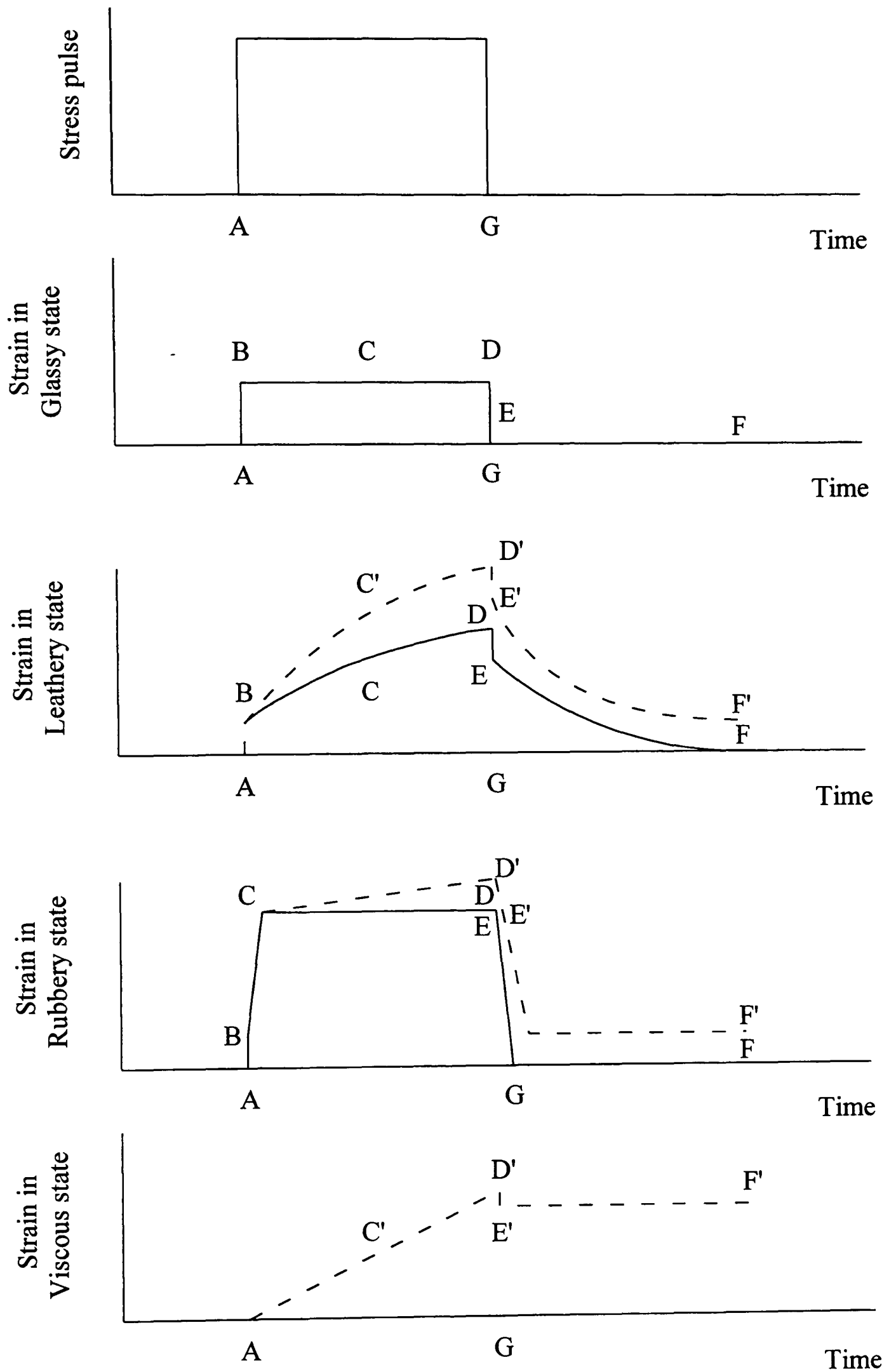


Figure 1.2.1. Idealised creep curves for the four (Glassy, leathery, rubbery and viscous) states of a polymer. The dashed lines indicate an uncross-linked polymer.

In the leathery curve the given stress produces a small instantaneous strain AB followed more gradually by BCD, reaching an elastic limit at D. Removal of the stress is accompanied by an instantaneous drop in the strain DE followed more slowly by EF as the polymer slowly regains its original shape. The dashed lines represent the case for an uncross-linked polymer, the instantaneous response AB remains unchanged. The difference becomes apparent during BC'D' where no equilibrium is ever reached, the strain increasing indefinitely. The same type of behaviour is again seen on removal of the load, D'E' being instantaneous, followed by a slow recovery along E'F' which runs parallel to EF. This leaves a permanent deformation FF' in the material due to the plastic flow of the uncross-linked chains during AG. FF' is sometimes referred to as the permanent set of the material.

In the rubbery state the whole deformation is almost instantaneous, with BC being nearly vertical. The strain then remains constant during AG and upon release the material springs back to its original shape with no permanent deformation. This is not so for an uncross-linked specimen where the strain slowly increases during CD'. On removal of the stress the recovery is almost instantaneous, but not completely FF' again being equal to the plastic deformation during the experiment which is equivalent to DD'. Although the shape of the curves for the glassy and cross-linked rubber phase look very similar the scales are not. The rubbery phase being more extensible by a factor of many hundred percent.

The viscous phase occurs at the extremely high temperature end of the spectrum as the polymer melts into a viscous liquid. It can only exist for uncross-linked polymers and is briefly mentioned for completeness. Upon the application of the stress the material begins to freely flow, with no elastic response. Furthermore upon removal of the stress no appreciable recovery takes place.

1.2.2b. Stress Relaxation

The stress relaxation experiment involves imposing a constant strain on the sample for a set duration of time and investigating the change in stress which often ensues.

The behaviour of a glass is instantaneous as for an ideal Hookian solid. The relaxation behaviour for a cross linked polymer in the leathery region is shown in figure 1.2.2. For a cross-linked polymer the high stress initially produced relaxes to a small steady value D . Upon removal of the strain a similar, negative stress is produced which dies down to zero as can be seen. The uncross-linked specimen is characterised by the fact that the stress $BC'D'$ will decrease indefinitely and given the chance will eventually reach zero.

It can be seen that a cross-linked rubbery material shows no relaxation at all and as in the previous section differs from a glassy polymer only in magnitude rather than type of behaviour. The uncross-linked material behaves similarly to a leathery material in this test and eventually decays to zero stress on the application of the strain and its removal.

The viscous case shows a constant zero stress because a true liquid, no matter how viscous can not maintain a stress.

Strictly speaking the leathery region is the only one for which the term viscoelastic applies, but in reality all of the other phases can be modelled as viscoelastic providing that a suitable ratio of elastic to viscous components is chosen.

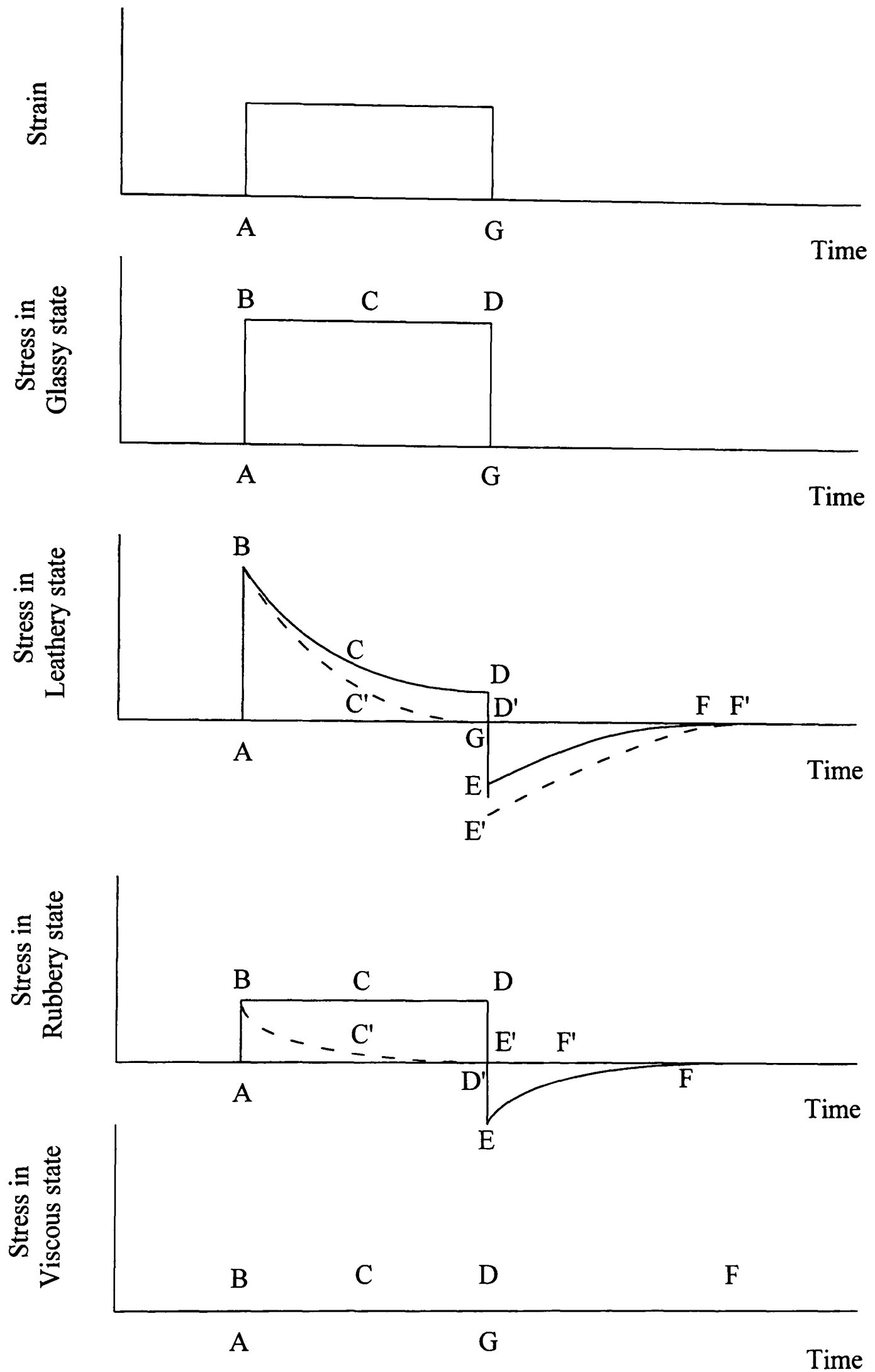


Figure 1.2.2. Idealised stress relaxation for the four (Glassy, leathery, rubbery and viscous) states of a polymer. The dashed lines indicate an uncross-linked polymer.

1.2.3. Dynamic Mechanical Analysis (DMA).

The two static experiments just described are ideal for investigating the viscoelastic behaviour of materials for significant time scales: minutes, hours, days or even longer periods. It is not however practical to carry out these transient experiments, for short time scales. One second is the shortest time limit for which stress relaxation and creep tests can be conveniently carried out. If shorter time spans than this are of interest then dynamic mechanical analysis (DMA) is used.

In forced vibration dynamic testing, the sample is put under a dynamic load with frequency f (Hz)*. For a material subjected to a sinusoidally varying displacement the strain ϵ is given by

$$\epsilon = \epsilon_{\max} \sin \omega t \quad 1.2.3.$$

For a viscoelastic material the stress σ and the strain are found to be out of phase with each other by an angle δ , this is shown in figure 1.2.3. The stress is then given by

$$\sigma = \sigma_{\max} \sin(\omega t + \delta) \quad 1.2.4.$$

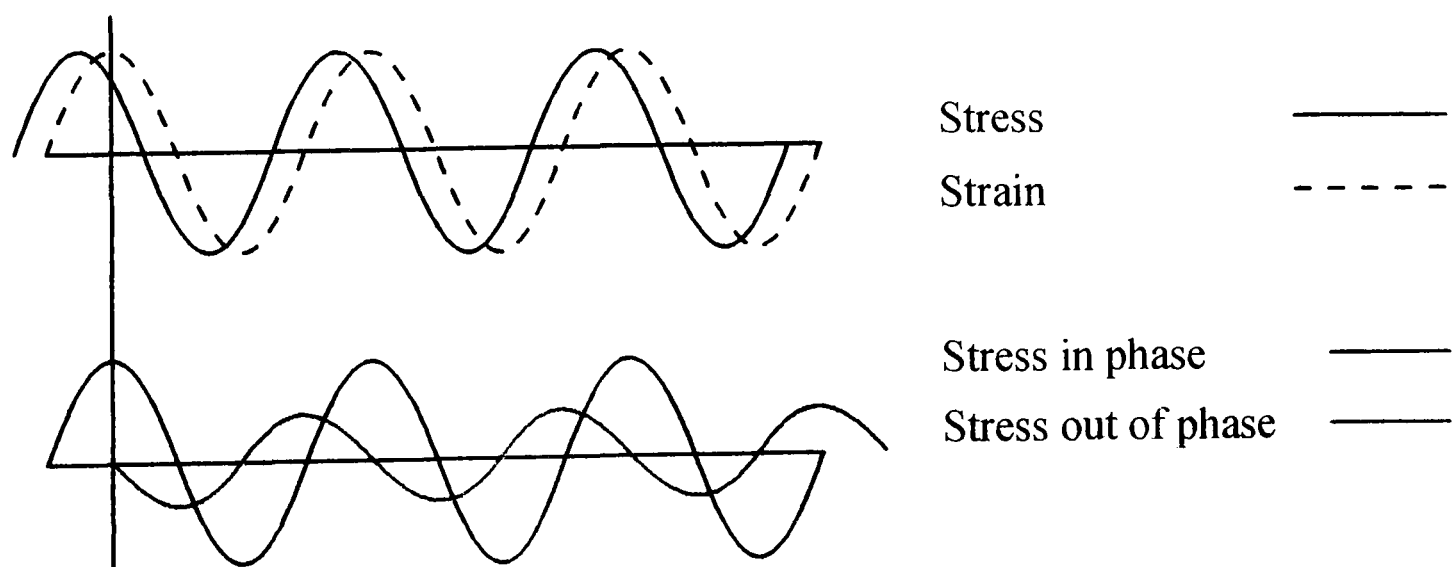


Figure 1.2.3. The dynamic stress-strain behaviour of a viscoelastic material.

* This is equivalent to an angular speed ω (rads/sec) and the two quantities are linked by the following equation $\omega = 2\pi f$. A dynamic test at ω , is qualitatively equivalent to a transient test of time $t = 1/\omega$

A more instructive way of expressing this equation is by splitting it up into two parts by trigonometric identities. One section containing the part of the stress in phase with the strain and the other part which is π radians (or 90°) out of phase with the strain thus:

$$\sigma = \sigma_{\max} (\cos \delta \sin \omega t + \sin \delta \cos \omega t) \quad 1.2.5.$$

This has a direct physical significance as the part in phase represents an ideal Hookian solid and the part out of phase represents an ideal Newtonian liquid, The mathematics is further clarified by writing

$$\sigma = \varepsilon_{\max} (E' \sin \omega t + E'' \cos \omega t) \quad 1.2.6.$$

where

$$E' = \left(\sigma_{\max} / \varepsilon_{\max} \right) \cos \delta \quad 1.2.7.$$

$$E'' = \left(\sigma_{\max} / \varepsilon_{\max} \right) \sin \delta \quad 1.2.8.$$

Where E' is known as the storage modulus and represents the elastic component of the modulus of the material, and E'' is known as the loss modulus and represents the viscous component of the modulus of the material.

$$E''/E' = \tan \delta \quad 1.2.9.$$

Tan δ is a useful ratio denoting the relative viscous and elastic behaviour of the material. E' , E'' and $\tan \delta$ are functions of temperature and frequency for a given polymer.

The above discussion is general in that no distinction arises between different modes of deformation and varying geometry's. Terminology relating to the dynamic mechanical method can be found in the literature (ASTM D 4092 - 90). In these standards E, G and K are used to denote tension/flexure, shear and compression respectively. This

nomenclature is not followed in this report, which is concerned mainly with compression, Here E is used to denote the modulus in compression.

1.2.3a. Complex Notation

An alternative way of expressing these ideas is to use complex notation. As will be shown in appendix A, complex notation can drastically simplify the mathematics of viscoelasticity. It has been seen that viscoelastic response is made up of two components out of phase with each other. This can be traced back to Hooke's and Newton's laws (equations 1.2.1. and 1.2.2.), which deal with strain and the rate of strain, respectively thereby introducing a 90° phase difference between the viscous and the elastic components.

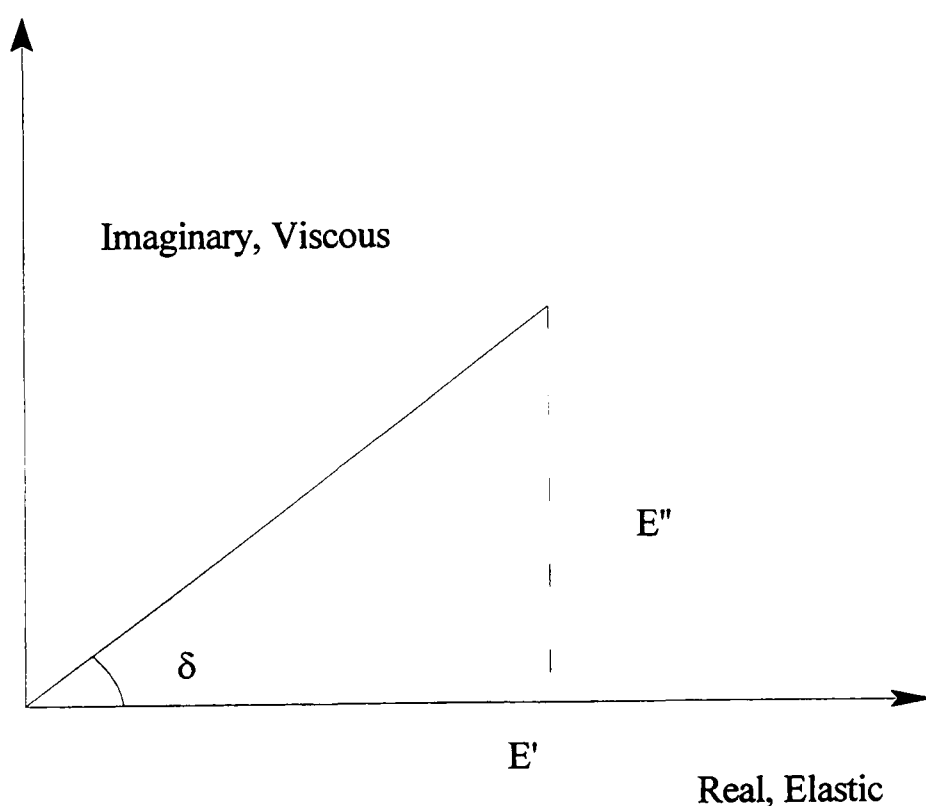


Figure 1.2.4. Complex notation in dynamic mechanical analysis.

In complex notation the strain and stress are :

$$\varepsilon = \varepsilon_{\max} \exp^{i\omega t} \quad 1.2.10$$

$$\sigma = \sigma_{\max} \exp^{i(\omega t + \delta)} \quad 1.2.11$$

Figure 1.2.4 shows the use of complex notation. As before E' is the storage modulus and E'' the loss modulus. The complex modulus E^* is defined such that

$$E^* = E' + iE'' \quad 1.2.12$$

1.3. Molecular Interpretation of Viscoelasticity in Polymers

Although so far the discussion of viscoelasticity has been broadly directed at polymers, much of what has been said applies to other viscoelastic materials. It is now time to focus specifically on polymers and examine what it is about their molecular make-up which accounts for their viscoelastic behaviour.

Figure 1.3.1 is a schematic diagram showing the change in the storage modulus and loss tangent of a typical amorphous polymer as a function of temperature and time. The segments marked on the diagram correspond to the four states of polymers discussed earlier. It can be seen that there are no clear dividing lines between the four states, only a gradual change of behaviour. The following two sections look at the molecular explanation for this behaviour in terms of temperature and then time.

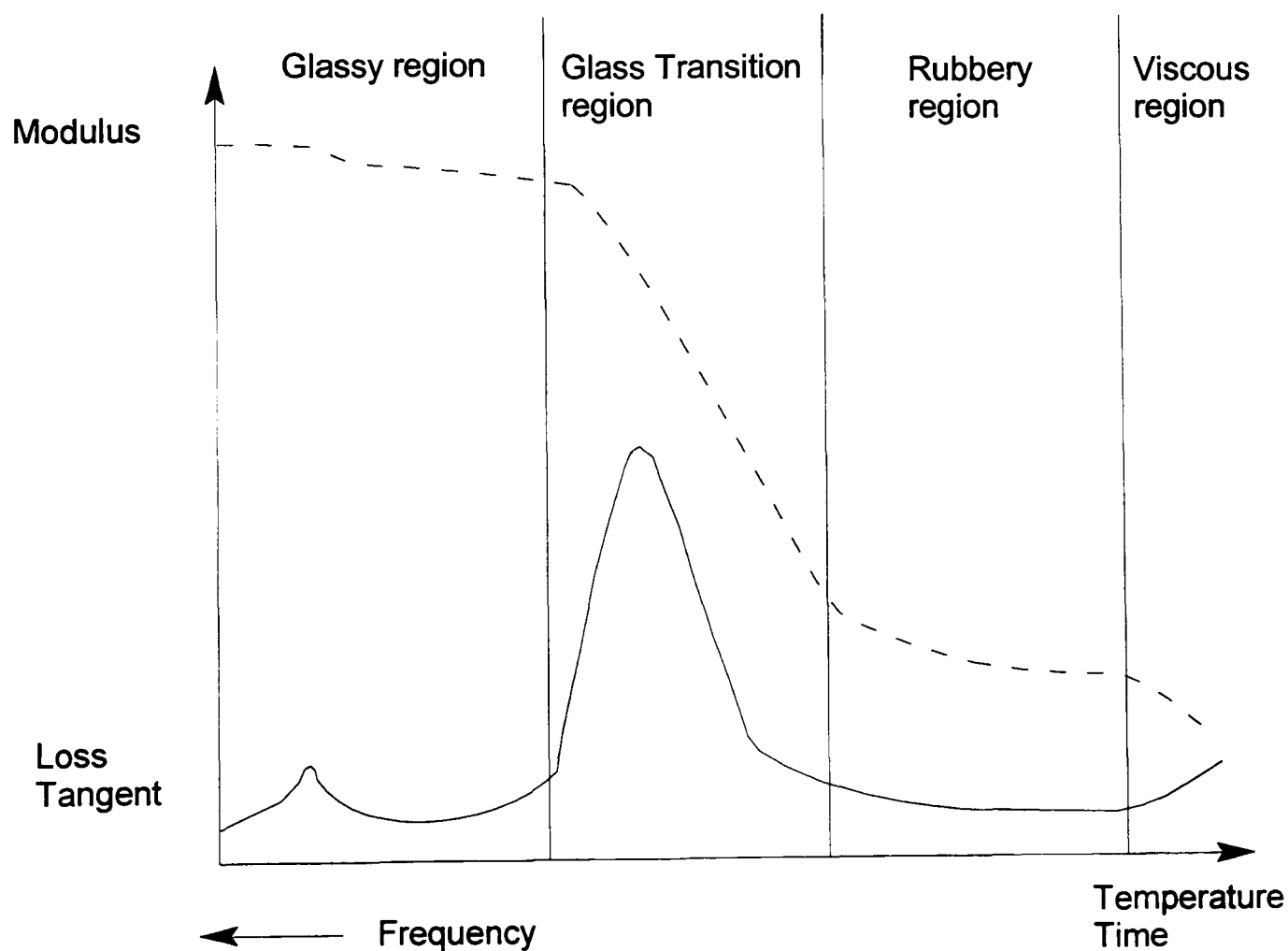


Fig 1.3.1 The temperature dependence of a typical amorphous polymer.

1.3.1. Temperature Dependence.

At the lowest end of the temperature scale the material is said to be glassy, implying hardness, brittleness and a high modulus (\approx GPa). The deformation energy loss in the material is negligible. In this region the thermal vibrational energy of the molecules is not large enough to overcome the energy barriers to facilitate movement of the segments of the polymer chain relative to each other. Hence the long polymer molecules are locked rigidly into fixed positions, or 'frozen' in. They vibrate around these fixed positions and only interact with their immediate neighbours in a similar way to common materials such as metals and ceramics. Because of this the material is relatively insensitive to the presence of cross-links.

Sometimes small peaks relating to secondary transitions can be seen, these are commonly of small magnitude, with minimal effect on the modulus. They are caused by the limited movement of side groups or the main chain. These include rotation of side groups such as methyl and 'Crankshaft' rotation of a small number of adjacent molecules in a chain (Boyer, 1963).

As the temperature of the polymer rises the molecules vibrate with increasing amplitude. The temperature at which the molecular chains have sufficient thermal energy to start short range movements is called the glass transition temperature or T_g . This movement of polymer chains is accompanied by a spectacular drop in the modulus of the material (3 orders of magnitude). The loss tangent similarly increases to a peak due to the increasing molecular friction. This zone of polymer behaviour is known as the leathery region as the material changes from a glass to a rubber.

As the temperature is further increased there comes a point when nearly all the polymer chain segments have gained enough energy to move and are free to change their configurational arrangements, at this point the modulus again becomes insensitive to temperature and is constant (\approx MPa magnitude). The loss factor diminishes after its

peak in the leathery region to a low value, although not as low as in the glassy region as there are frictional forces opposing the configurational changes. These features characterise the rubbery zone. The chain molecules are now free to take up many random arrangements. This leads on to the statistical theory of rubber-like elasticity which was postulated in the 1930's. The theory explains the large extensions which characterise polymers in this region and other thermal-mechanical effects peculiar to rubbers (Treloar, 1958).

Upon further heating a dramatic difference becomes apparent between cross-linked and uncross-linked polymers, whereas before their behaviour had been very similar. Firstly, considering the uncross-linked polymer: as the temperature increases the molecular motions become larger and larger so that eventually it is possible for molecules to slip past each other in a wholesale manner as their energy becomes greater than that of the local entanglements which up to now had served as temporary cross-links. This will eventually lead to the polymer being a viscous fluid. Not surprisingly this zone of polymer behaviour is known as the viscous region. This viscous state does not exist for the cross-linked polymer, although the modulus will in practice decrease slightly with increasing temperature. The cross-links keep the polymer together up to temperatures at which chemical degradation occurs.

1.3.2. Time and Frequency Dependence

It was mentioned that the state in which a polymer exists depends on the temperature of the experiment. This is true, but is only half of the truth because time is an equally important variable. Even at constant temperature different time scales will produce all the four states previously discussed. An everyday example is common glass which to our day to day perception (relatively fast time scale) appears as the archetypal hard and brittle solid, but given sufficient time (100's of years) will flow under its own weight just like a liquid. Glass windows from historic houses are often appreciably thicker

towards the bottom. So the arguments presented in terms of temperature can be reiterated in terms of time and frequency.

On the shortest of time scales the long polymer molecules have insufficient time to reorientate themselves substantially and react to stresses by distorting intermolecular distances. These small scale, high energy distortions have the effect of producing a high modulus, low loss material: a glass. If given sufficient time the molecules have the opportunity to change their configuration to relieve sites of particularly high stress, this opportunity to reconfigure the structure of the chain is the glass transition and is accompanied by a drop in modulus as well as an increase in the loss tangent of the material. At longer times the polymer molecules have time to reorganise themselves freely and can be considered as flexible chains. The effect of these motions are governed by the statistical theory of rubber elasticity. At still longer times the molecules have sufficient time to flow past each other and the material is in effect a viscous liquid.

1.3.3. Glass Transition Temperature.

From the preceding discussion the importance of the T_g or glass transition temperature is clear, as nearly all material properties change drastically at this point. Consider a soft lining material mounted on a rigid denture base. The glass transition of the lining material must be at or below mouth temperature if the material is to be considered soft, while the T_g of the denture base must be significantly higher than any temperature the material is likely to encounter in its lifetime or the denture is likely to soften and subsequently warp.

As noted by Ferry (1980) the use of the word 'transition' can lead to confusion. As the 'Glass transition temperature (T_g)' which is a single point (or very narrow region) on the temperature scale, is often muddled with the 'glass to rubber transition region' which is a larger temperature range pertaining to the leathery behaviour of the material.

1.3.4. Measurement of the Glass Transition

At the onset it must be recognised that the T_g is not simply a universal constant for a given material. Different methods of measuring T_g will invariably give different results, so that the '*... T_g is a property of an experiment as well as a material*' (Gee, 1970). The mode and parameters of the experimental procedure can have a dramatic effect on the T_g . The most common experimental techniques where by the T_g is determined are explained below.

Dilatometry is the classic and in principle the simplest experimental method for the determination of the T_g . The linear (α) or volumetric (v) expansion of the material in question is observed as it is cooled through its transition, a plot of the following kind is then seen:

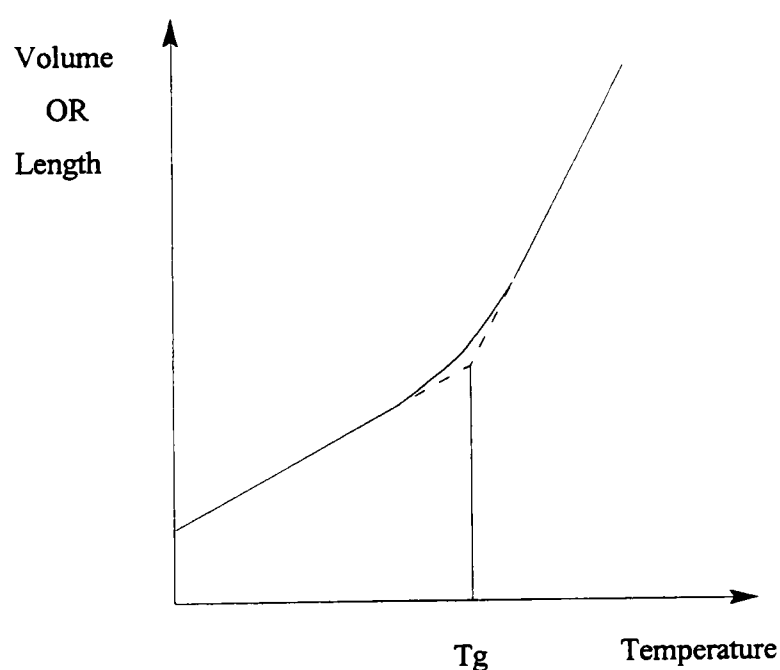


Figure 1.3.2 Expansion versus temperature for a typical polymer at its transition.

A discontinuity is seen in the expansion coefficient (either linear α or volumetric v .) which is taken as the T_g . The experimental value of the T_g thus obtained is still not a fixed quantity and is dependent on the rate of cooling (Gee, 1970). Generally the slower the experiment, the lower the value for the T_g .

Calorimetry can give similar results, although in this case the sample is heated through its T_g rather than cooled. In this case the heat capacity (C_p) is plotted against temperature where a discontinuity is seen at the T_g . Again the slower the experiment the lower the observed value of the transition temperature.

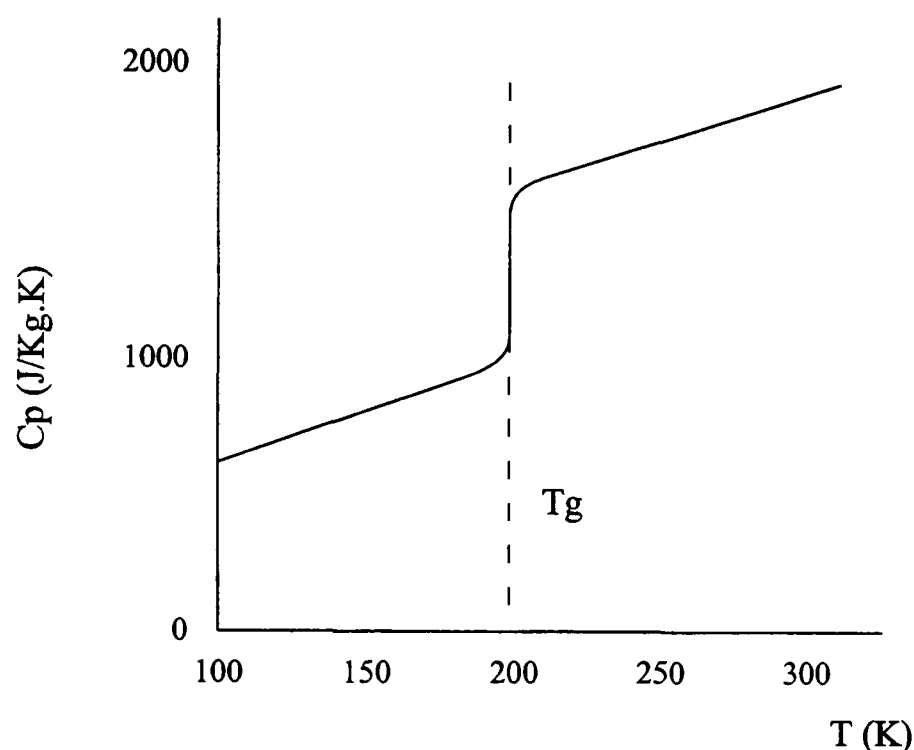


Figure 1.3.3. Heat capacity of amorphous polypropylene (Gee, 1970).

The dynamic viscoelastic behaviour of a material can be used to determine the T_g (ASTM. E 1640 - 94). Referring to the dynamic mechanical method used in this investigation, peaks in the loss modulus or the loss tangent can both be taken as indexes of the glass transition. The loss modulus peaks being at a lower temperature than the loss tangent. Again the results are affected by the rate of heating or cooling of the sample as before. In addition to which they are affected by the rate or frequency of the application of the loading. Dynamic methods invariably yield higher values of T_g than static methods such as calorimetry and dilatometry.

Dielectric relaxation is another technique for the study of transitions in polymers. Its principles are as follows. If a polymer is subjected to an electric field, any molecule with an asymmetrical distribution of positive and negative charge (i.e. pole) will tend to

align with the field. The scale of this polarisation phenomenon is measured by the dielectric constant of the material which is a macroscopic property. Any molecular rearrangement of the type seen during the glass transition is hence observed (Aklonis & MacKnight, 1983).

Other, more unusual, methods to determine Tg's can be derived from examining other material properties which also change at the Tg. These include optical properties, refractometry, craze relaxation, penetrometry, radiothermoluminescence, chromatography and buoyancy (Brandrup and Immergut, 1975).

It is clear that the rate of the experimental procedure can influence the results. These 'rate effects' fall into several categories. For example, fast heating or cooling rates may not allow time for temperature equilibrium within the sample, this is especially true for samples with large thermal inertia.

Experimental Method	Frequency (Hz)	Measured Tg (C)
Dielectrics method	1000	32
Mechanical vibration	89	25
Slow tensile	3	15
Dilatometry	0.01	7

Table 1.3.1 The dependence of the Tg of poly (3.3-bischloromethyloxacyclobutane) on the time scale of the experiment. (Sandiford, 1958)

The rate of application of the electrical or mechanical stimulus has a profound influence on the value of Tg obtained, static or slow methods always giving lower values. An indication of the effect of frequency is given by the results obtained by Sandiford in 1958, (table 1.3.1).

1.3.5. Theories of the Glass Transition

The glass transition temperature has been the subject of scientific debate since its existence was recognised. Many theories have tried to account for its subtleties from different perspectives. The theories can be classified according to the approach taken by the theoretician. Iso-viscous, Thermodynamic, Free volume, Relaxational and Statistical theories have all been proposed (Gee, 1970; Arridge, 1975). Here two of the best known and widely accepted theories are examined.

1.3.5a. Thermodynamic Theory.

Some early theories of the glass transition were based upon a thermodynamics approach, where the T_g has been likened to thermodynamic changes of state such as melting and vaporisation. These transitions are characterised by the equality of the Gibbs free energy (G) for the two phases at the transition temperature (i.e. melting or boiling point):

$$G_1 = G_2 \quad \text{and} \quad dG_1 = dG_2 \quad 1.3.1.$$

However the entropies (S) and volumes (V) of the phases are not equal and show a discontinuity:

$$S_1 \neq S_2 \quad \text{and} \quad V_1 \neq V_2 \quad 1.3.2.$$

But entropy and volume are both first order derivatives of the Gibbs free energy so that:

$$dG = -SdT + VdP \quad \Rightarrow \quad S = -\left(\frac{\partial G}{\partial T}\right)_P \quad 1.3.3.$$

$$\text{and} \quad \Rightarrow \quad V = \left(\frac{\partial G}{\partial P}\right)_T$$

So that melting and boiling can be referred to as 1st order transitions. Conversely for a 2nd order transition, the 2nd partial derivative of Gibbs free energy, such as the ones shown below show a discontinuity.

$$-\left(\frac{\partial^2 G}{\partial T^2}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \quad 1.3.4.$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P = \left(\frac{\partial V}{\partial T}\right)_P = \alpha V \quad 1.3.5.$$

Such that:

$$C_{p1} \neq C_{p2} \quad \text{and} \quad \alpha_1 \neq \alpha_2 \quad 1.3.6.$$

It is just this type of behaviour which is detected in dilatometric and calorimetric experiments. So that the T_g can be argued as a second order thermodynamic transition (Aklonis & MacKnight, 1983). This is not an entirely satisfactory explanation. For example the rate dependence of the T_g is in no way accounted for.

1.3.5b. Free Volume Theories.

In a previous section the T_g has been described as the point on the temperature scale where the thermal expansion coefficient (α) of a polymer* undergoes a discontinuity. This phenomena can be described in terms of the 'free volume' which is an ill defined but useful concept for the understanding of the glass to rubber transition (Ferry, 1980). The free volume can be loosely defined as the empty space in a sample of polymer, i.e. the space which is not occupied by polymer molecules. So that the total volume of a polymer (V) is the sum of the occupied (V_o) and free volumes (V_f):

* This phenomena does not belong exclusively to polymers, but occurs in any liquid which can be cooled, without crystallising, to a sufficiently low temperature.

$$V = V_o + V_f \quad 1.3.7.$$

Above the T_g the free volume is high enough for the polymer molecules to have room to move and make configurational adjustments. As the polymer is cooled there is a reduction in the free volume until the T_g , below which there is insufficient free volume and the molecules are cramped into immobility.

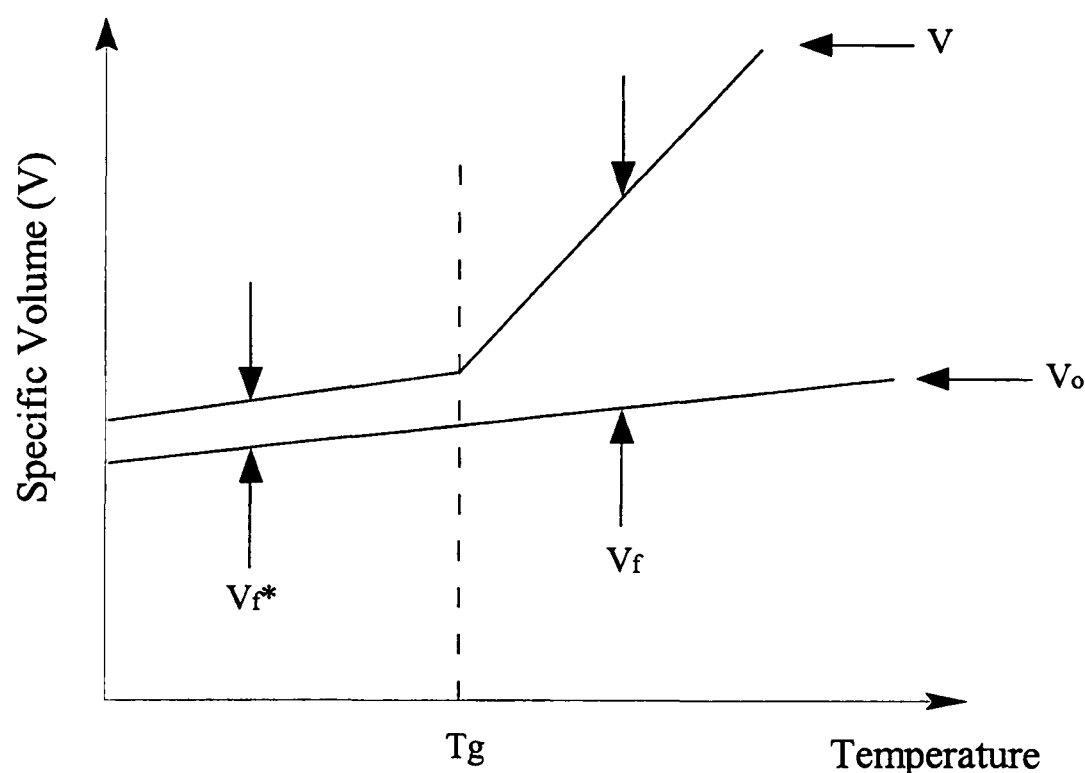


Figure 1.3.4. Diagrammatic representation of the change in volume and temperature for a polymer sample. (Young & Lovell, 1995)

In the above diagram the space between the two lines represents the free volume, being the difference between V_o and V . The free volume below T_g can to all intents and purposes be assumed to be a constant and is labelled in figure as V_f^* . The information about the free volume shown in figure 1.3.4. can be represented mathematically as a function of temperature by the following two expressions:

$$V_f = V_f^* \quad T < T_g$$

$$V_f = V_f^* + (T - T_g) \left(\frac{\partial V}{\partial T} \right) \quad T \geq T_g \quad 1.3.8.a,b$$

The fractional free volume is the ratio of the free to the total volume and is found to be a more useful quantity in practice ($f = V_f / V$). A similar constant f_g exists which is the ratio of V_f^* to the total volume. Thus dividing through by V we have:

$$f = f_g \quad T < T_g$$

$$f = f_g + \left(T - T_g \right) \alpha_f \quad T \geq T_g \quad 1.3.9.a,b$$

Where α_f (deg^{-1}) is the cubical thermal expansion coefficient of the free volume which will be given by the difference between the expansion coefficient of the glass and the rubber:

$$\alpha_f = \alpha_r - \alpha_g \quad 1.3.10$$

Related to the free volume concept is the WLF* equation. Although this principle was first developed by empirical curve fitting, it is now possible to derive it from free volume considerations. The simplest derivation involves using simple viscoelastic models (Young & Lovell, 1995). These models will be dealt with in some detail in the next chapter. For now the discussion is limited to a Maxwell model, consisting of an elastic spring and a viscous dashpot linked in series. The elastic component is designated to be temperature independent, while the viscosity of the dashpot does vary with temperature. The model has a relaxation time $\tau = \eta / E$ which itself is therefore temperature dependent. We can write:

* So called after its authors, Williams, Landel and Ferry (1955)

$$a_T = \frac{\tau(T)}{\tau(T_g)} = \frac{\eta(T)}{\eta(T_g)} \quad 1.3.11$$

Where a_T is defined in this case as the ratio of the two relaxation times, or as it turns out the ratio of any mechanical property such as modulus or viscosity. The relaxation times can be arbitrarily chosen, although for this argument T_g is used as a reference temperature. As was earlier mentioned in passing the concept of free volume is not limited to polymers and can equally well be applied to liquids. Doolittle (1951) studied the dependence of the viscosity of liquids on free volume and employed the following equation linking the two:

$$\ln \eta = \ln A + B(V - V_f) / V_f \quad 1.3.12.$$

A and B being empirical constants. The free volume term in this equation is then substituted for the fractional free volume term introduced earlier:

$$\ln \eta(T) = \ln A + B \left(\frac{1}{f} - 1 \right) \quad 1.3.13.$$

Which at T_g becomes:

$$\ln \eta(T_g) = \ln A + B \left(\frac{1}{f_g} - 1 \right) \quad 1.3.14.$$

Substituting our definitions of f and f_g (1.3.9) into the above two equations and subtraction gives us

$$\ln \eta(T) - \ln \eta(T_g) = \ln \left(\frac{\eta(T)}{\eta(T_g)} \right) = B \left(\frac{1}{f_g + \alpha_f (T - T_g)} - \frac{1}{f_g} \right) \quad 1.3.15.$$

Which can be rearranged, by using a single denominator and changing logarithmic bases to give:

$$\log \left(\frac{\eta(T)}{\eta(T_g)} \right) = \log a_T = \frac{-(B / 2.303 f_g)(T - T_g)}{f_g / \alpha_f + (T - T_g)} \quad 1.3.16$$

This last expression is in the form of the WLF equation. Which is normally written as

$$\log a_T = \frac{-C_1 (T - T_g)}{C_2 + (T - T_g)} \quad 1.3.17$$

When the WLF equation was originally introduced (Williams et al, 1955) it was thought that C_1 and C_2 were universal constants, with numerical values of 17.4 and 51.6 respectively (Williams et al, 1955). These constants have since been shown to vary slightly from polymer to polymer and a listing of these constants for some of the more common polymers can be found in Ferry (1980). Relating back to 1.3.17 C_1 and C_2 can be written in terms of the more fundamental quantities B , f_g and α_f .

$$C_1 = \frac{B}{2.303 f_g} \quad 1.3.18$$

$$C_2 = \frac{f_g}{\alpha_f} \quad 1.3.19$$

Similarly B , f_g and α_f are found experimentally to be near 1, 0.025 and 4.8×10^{-4} (K⁻¹), again their magnitudes found experimentally for different polymer systems can be found in the literature (Ferry, 1980).

1.3.6 The Effects of Chemical Structure

The effect and influence which the chemical structure and molecular architecture of a typical polymer chain can have on its T_g and other properties can be subdivided into three distinct factors (Boyer, 1963):

- Intermolecular forces
- Chain stiffness
- Geometry

Unfortunately the effect of the interaction of these factors on the mechanical properties of a polymer are not as yet an exact science, although the general trends involved are well understood. For a given system the effect produced by changing one of its structural variables on the physical properties are observed experimentally. Where possible empirical formulae are used to quantify the relationship, but these are usually approximate in nature and apply to a limited number of systems and conditions. The WLF equation being an atypical example in that its application is more widespread than most. Discussion on the effect of chemical structure and physical properties will then be qualitative rather than quantitative.

The basic requirement for any polymer with a low T_g is a flexible backbone as the ease with which main chain bonds rotate obviously increases chain mobility. Polyethylene with its carbon-carbon backbone has a T_g of -130°C* , the insertion of an oxygen atom into this arrangement raises polyoxyethylene's T_g by 60° to -70°C (Table 1.3.2).

* The T_g of Polyethylene is a matter of some contention because of the highly crystalline nature of this material.

Name	Tg (°C)
Polyethylene	-130
Polyoxyethylene	-70
Poly(p-xylylene)	80

Table 1.3.2. The effect on Tg from constituents of the polymer backbone (Young & Lovell, 1995).

The trend can be taken further by the addition of larger stiffer structures such as a p-phenylene ring into the polyethylene chain which gives poly (p-xylylene) a much higher Tg, at 80°C.

Side groups attached to the main chain backbone have an equally large influence associated with their bulkiness and affect on packing. Side groups generally tend to create more free volume by disrupting the packing of the main chain and thus lowering the Tg. Table 1.3.3. shows the Tg of a number of n-alkyl methacrylates whose esters contain 1-4, 6, 8 and 10 carbon atoms. A clear trend is observed as the higher methacrylates have progressively lower Tg's.

n-alkyl methacrylates	Methyl 1 C	Ethyl 2 C	Propyl 3 C	Butyl 4 C	Hexyl 6 C	Octyl 8 C	Decyl 10 C
Tg (°C)	115	62	38*	27	-5	-20	-70*

Table 1.3.3. Relationship between Tg and side groups in the methacrylate family (Ferry, 1980; *Braden et al 1997)

The effect of side groups is not always so clear cut, although they can create more free volume as just described; they can also make the back bone more cumbersome and less mobile if they are excessively bulky and inflexible. Such an affect can be seen in polystyrene, which has a Tg of 100°C incurred largely by having a phenylene ring as a

side group (See table 1.3.4.). Polar side groups also act to decrease the free volume by increasing the intermolecular forces and pulling the chains closer together. This effect can be demonstrated by examining two vinyl polymers: polyvinylchloride (PVC) and polypropylene. The only difference between the two are the side group; which are Cl in the former and CH₃ in the latter. This difference is enough to increase the T_g of polyvinyl chloride by 100°C to 81°C compared to polypropylene at -23°C. This effect is also demonstrated by other polar groups such as OH and CN .

Side Group (X)	CH ₃	Cl	Phenylene ring
Glass Transition (°C)	-23	81	100

Table 1.3.4. The effect of polar or bulky side group on the T_g of vinyl polymers of the type: (CH₂-CHX) where X is the side group in question (Young & Lovell, 1995).

The glass transition is usually insensitive to the molecular weight of a polymer at high molecular weights, but at lower molecular weights it falls with decreasing molecular weight. This is attributed to the increase in free volume associated with the chain ends. A low molecular weight polymer will have a higher number of chain ends per volume. These chain ends can move more freely as they are less restricted than central parts of a polymer chain. An equation of the following type is associated with this phenomenon (Brydson, 1975):

$$T_g = T_g^\infty - K \left(\frac{1}{M_n} \right) \quad 1.3.20.$$

Where the T_g rises proportionally to the reciprocal of the molecular weight (M_n), towards a maximum value (T_g[∞]) associated with infinite molecular weight. K being a positive constant for a given system.

Plasticisers or diluents are molecules of low molecular weight which are sometimes added to polymers to reduce the Tg. The effect of adding plasticisers is to reduce intimate contact between the polymer chains and hence increase free volume. The common analogy is to compare a plasticised and unplasticised polymer to spaghetti with or without butter, the plasticiser (butter) helping to lubricate the polymer network (Brown, 1988). A mathematical approach can be taken using the free volume theory, providing the effect of the two components are linearly additive. Then equation 1.3.9b can be rewritten as to take into account a system having a volume fraction of diluent:

$$f = f_g + V_p \left(T - T_{gp} \right) \alpha_{fp} + \left(1 - V_p \right) \left(T - T_{gd} \right) \alpha_{fd} \quad 1.3.21.$$

Where the subscripts p and d refer to the polymer and diluent respectively, and α_{fp} and α_{fd} are the coefficients of thermal expansion of the free volume in the polymer and diluent respectively. Invoking the free volume assumption that at $T = T_g$, $f = f_g$. The above equation can be rearranged to give the Tg of the whole material as a function of its polymer and plasticiser components (Akonis & MacKnight, 1983).

$$T_g = \frac{\alpha_{fp} V_p T_{gp} + \alpha_{fd} T_{gd} (1 - V_p)}{\alpha_{fp} V_p + \alpha_{fd} (1 - V_p)} \quad 1.3.22.$$

Copolymerisation of two or more homopolymers can have a number of effects on the Tg of the final material. In the case of a random copolymer where the constituents are well mixed one broad Tg will be seen at an intermediate value between the Tg's of the homopolymers. Free volume considerations of the type used in the discussion of plasticisers can be used to predict the behaviour of these systems. The trend observed for random copolymers of butadiene styrene experimentally is shown in figure 1.3.5.

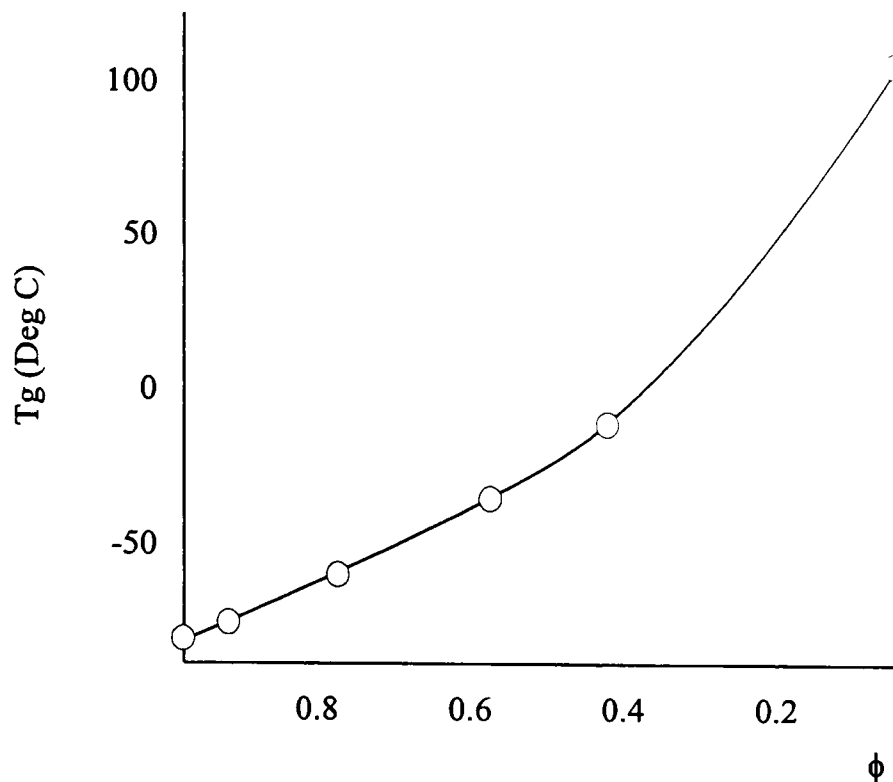


Figure 1.3.5. Glass transition of styrene-butadiene random copolymer. ϕ is the volume fraction of butadiene (Wood, 1958)

A block copolymer on the other hand will have two distinct T_g's close to the temperature of their respective homopolymer. This is because on the atomic level the monomers from the two systems have not mixed well and there are distinct areas dominated by one or the other.

Cross-links have the effect of binding polymer chains together and hence reducing free volume. For lightly cross linked systems the T_g is raised slightly. For increasingly heavily cross linked systems the T_g continues to rise but its effects virtually disappears as the chains are no longer able to make configurational readjustments. An example of this is 'Vulcanite' which is heavily cross-linked rubber occasionally used in dentistry as a denture base material. An investigation on the effect of cross-linking on T_g was carried out by Loshaek (1955), where he looked at PMMA cross-linked with various amounts (0 - 100%) of EGDM (Ethylene glycol dimethacrylate). This had the effect of raising the T_g from 108°C to 132°C. Loshaek recognised that the change in T_g was a function of a copolymerisation effect between the two materials, as well as a function of the cross linking itself. Particularly with the higher ratios of EGDM what is being measured is the T_g of EGDM copolymerised with small amounts of PMMA.

Fillers of many types, sizes and shapes can be used to modify and improve the properties of polymers. A filler being defined as a solid additive incorporated into the polymer (Brydson, 1975). There are however grey areas as the above definition can apply to plasticisers and copolymers for example. Hard inorganic reinforcing particulate fillers are popular in elastomers to improve tensile strength, modulus, abrasion and tear resistance. The particle size is an important factor, with large coarse particles having an adverse affect. The shape of the particle can also make an important contribution. Because of these many variations there is no universal relationships between fillers and the Tg. Any dependence of the Tg on fillers can be explained in terms of the mechanical properties of the filler, and its effect on chain mobility and free volume. Diametrically opposite to the above use of fillers, is the use of rubbery fillers in rigid materials to improve their toughness and impact strength*.

Other effects such as that of crystallinity or stereoisomerism which do not play a role in dental polymers and soft lining materials, which are in general atactic and amorphous (McCabe & Wilson, 1974) have been left out of this discussion. They can however be similarly treated in terms of packing efficiency and free volume.

* This type of 'filler' has been reported with high impact denture base materials (Clarke, 1988).

1.4. Materials Under Investigation

Table 1.4. summarises the commercial materials investigated in this report, together with their respective type, method of curing and manufacturer, as well as the abbreviated codes used to identify them in this report.

Material	Code	Type	Curing	Manufacturer
Super-soft, New	NS	Plasticised Acrylic	Heat	GC Laboratories Inc. Chicago. USA.
Super-soft, Old	OS	Plasticised Acrylic	Heat	Coe Laboratories Inc. Chicago. USA.
Futurasoft III	FS	Acrylic blend	Heat	Schultz Dental GmbH. Germany.
Molloplast B	MP	Heat cured Silicone	Heat	Karl Huber GmbH. Germany.
Flexibase	FB	Cold cured Silicone	Cold	Flexico Developments. Herts. UK.
Novus, Old	ON	Poly- phosphazine	Heat	Hygenic Corp. Ohio. USA.
Novus, New	NN	Poly- phosphazine	Heat	Hygenic Corp. Ohio. USA.
Triad resiline	TR	Light Cured	Light	Dentsply International Inc. USA.

Table 1.4.1. Commercial materials under investigation.

1.4.1. Acrylic Based Soft Lining Materials.

Acrylic polymers form an important part of dental materials in general and soft lining materials in particular. Of all the acrylics poly(methylmethacrylate) or PMMA is the most widely used, having applications as denture bases, artificial teeth, orthodontic appliances and of course as a component of acrylic soft lining materials. Soft acrylic materials are often supplied as powder/liquid systems. The powder commonly being polymer, while the liquid being a mixture of monomer, plasticiser and cross-linking agent. Upon mixing the two a dough is formed which is pressed into shape and then cured according to the manufacturer's instruction.

Material	Polymer	Monomer	% Plasticiser
Super Soft	PEMA	MMA	31.2
Palasiv 62	PEMA	BMA	24.9
Soft Nobilitone	PMMA	MMA	58.8
Virnia	PEMA	MMA, Ethyl acetate	36.2
Verno Soft	PEMA	EMA	39

Table 1.4.2. Typical plasticised acrylic soft lining materials. E : Ethyl, M : Methyl, B : n-Butyl, MA : methacrylate (Wright, 1981)

Table 1.4.2. lists a number of soft lining materials based on acrylic chemistry. As can be seen above they mostly incorporate methyl and ethyl methacrylate which have Tg's of 115°C and 62°C respectively (table 1.3.3). The implication being that at mouth temperature they are both stiff and show glassy characteristics and hence are not suitable as soft lining materials. This has prompted the need for plasticisers, of various types, the percentage of which are also shown in the above table. It can further be seen that there is a trend in the amount of plasticiser used to the Tg of the main material constituents. With 'Soft Nobilitone' (containing methylmethacrylate exclusively) needing a massive 58.8% plasticiser. While 'Palasiv 62' with its n-butyl methacrylate component, has the lowest amount of plasticiser (24.9%).

The viscoelasticity of three commercial acrylic systems was determined in this report. Two of them being different formulations of the same trade material 'Supersoft', these are labelled OS, referring to the older version (Wright, 1981) and the newer variety (NS). In these materials the powder component appears to be unchanged, being polyethylmethacrylate. Infra red analysis suggests that in the new formulation the liquid component has changed from being methyl to ethyl methacrylate with an undisclosed amount of plasticiser (Braden, 1996).

The third commercial acrylic material goes under the trade name of 'Futurasoft III' (referred to as FS). The powder is 80/20 butyl/ethyl methacrylate and the liquid is reported to contain a mixture of methyl, nonyl and tri-decyl methacrylate in undisclosed proportions (Wright, 1996). It is claimed that no plasticiser is used in this formulation, which seems to be confirmed by infra-red analysis. The composition of these three commercial soft liners are summarised in table 1.4.3.

Material	Powder	Liquid
OS	Poly(ethyl methacrylate)	methyl methacrylate, 31.2% Plasticiser: butyl phthalyl butyl glycollate
NS	Poly(ethyl methacrylate)	ethyl methacrylate, plasticiser.
FS	Poly(80/20 butyl/ethyl methacrylate)	methyl, nonyl and tri-decyl methacrylates.

Table 1.4.3. Summary of composition for acrylic soft lining materials tested.

The method of curing for the three materials was as follows. The powder and the liquid were measured in suitable proportions (4 ml of liquid to 5 grams of powder) and mixed well. Although care had to be taken not to introduce too many air bubbles into the mixture. This viscous mixture was then left to stand for a while so that a non-sticky, elastic paste was formed*. This paste was subsequently sandwiched between 2 flat metal plates, covered with acetate sheets to prevent paste adhesion (see figure 1.4.1). A 2mm thick aluminium 'spacer' was used in the shape of a window to produce samples of the required thickness. The mould and paste were slowly compressed under a hand operated press, till the excess material had flowed out, leaving a 2mm thick sample behind. This mould was subsequently removed from the press, placed into a standard dental flask and heat cured in water. The following heating regime was used as recommended by the

* FS was found difficult to work with as the mixture quickly solidified (i.e. short 'working time').

manufacturers: 30 minutes at 60-75°C, bring to boil over the next 30 minutes and continue boiling for a further 10 minutes. The flask was subsequently removed from the water and allowed to cool to room temperature. The flask and metal plates were removed and the acetate sheets gently peeled away, leaving the sample encased in the aluminum window. The sample (2 mm thick and approximately 40 by 60 mm in area) was cut out using a scalpel and subsequently used for the various tests which form the experimental section of this text.

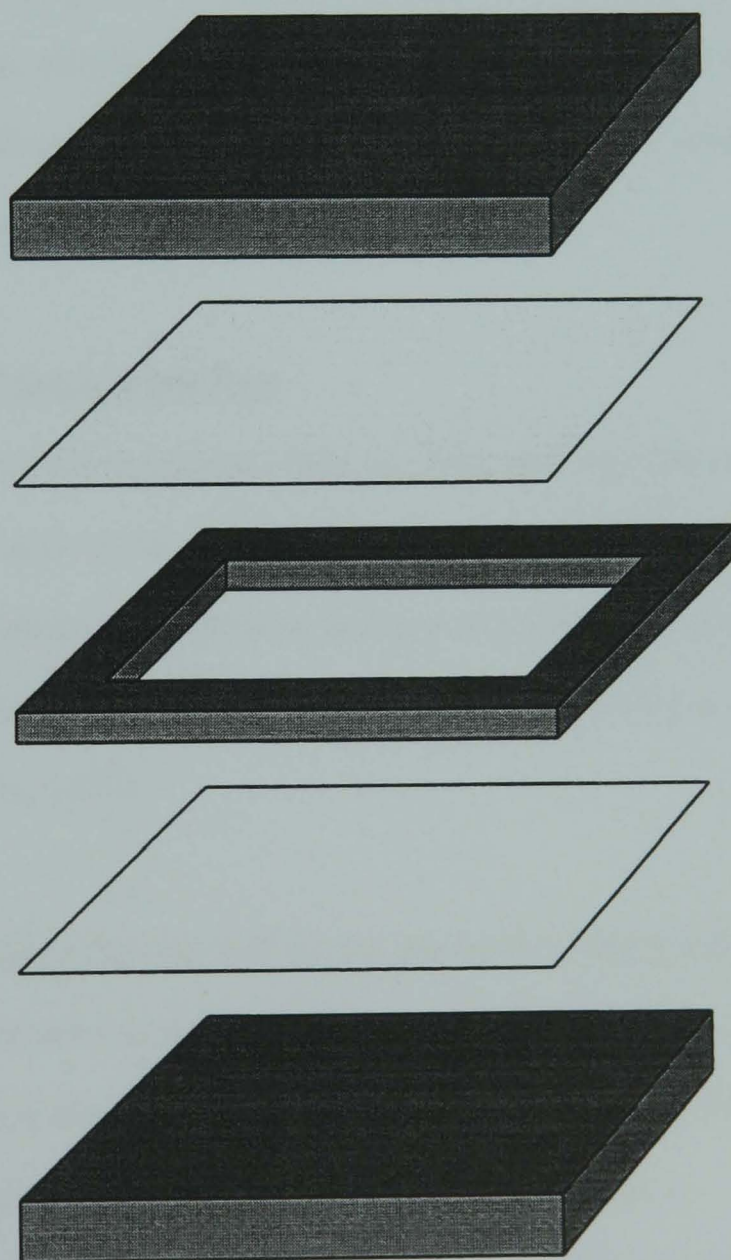


Figure 1.4.1. A diagrammatical representation of the 'sandwich' used to make soft lining samples. The aluminium window is enclosed between 2 steel plates, acetate sheets are used to prevent adhesion.

The biggest advantages associated with the soft acrylic materials is their mechanical strength, as well as their excellent adhesion to PMMA denture base, being of a similar chemical family. Their main short coming has traditionally been the loss of plasticiser, and associated hardening (Braden et al, 1995). Newer materials have either reduced, or completely eliminated the need for its use, as in the case of the experimental materials to be presented here.

There is another class of acrylic materials which are cured at room temperature, with the aid of a catalyst. The properties of the cold cure materials are generally inferior to those of the heat cured type, polymerisation often being less efficient with residual free monomer left over (Braden et al, 1997). None of the materials studied in this report are of the cold curing variety.

1.4.2. Silicone Soft Lining Materials

The two silicone materials mentioned here are both amongst the early commercially successful materials and can be neatly divided into two types with Molloplast B being a heat polymerising system and Flexibase being a room temperature curing system. The main component of both materials is silicone rubber whose T_g is 160°C below mouth temperature (McCabe, 1976).

Molloplast B is arguably the best soft lining material on the market (Wright, 1981; Collis, 1993). Its chemistry is very complex, with one of its components, RTV108 being a patented commercial material in its own right (Braden et al, 1997). Other components include PMMA, which is believed to help with the adhesion, γ -methacryloxypropyltrimethoxysilane and titanium dioxide in minute quantities*. The main advantage of this material is its low water uptake, but problems include poor tear strength, poor wettability and poor adhesion to polymethylmethacrylate denture base,

* There is to date some controversy over the exact composition of this material (Riggs, 1997).

although the adhesion is an improvement on other silicones available on the market (Braden et al, 1995).

This material (MP) is supplied as a one paste system which can be cured by heat or microwave. This paste was placed into the 2mm thick metal windows as described above and heat cured in water. The water was brought to boiling point from ambient temperature and left at 100°C for 2 hours. The composition of this paste is shown below.

Material	Quantity
General Electric RTV 108 (Acetoxy-cure silicone material)	720 parts
Poly(methyl methacrylate)	19.15 parts
γ -methacryloxypropyltrimethoxysilane	9.16 parts
Titanium dioxide + washung red	0.075 parts

Table 1.4.4. Composition of Molloplast B (Braden et al, 1997).

The other material, Flexibase, (FB) is also supplied as a paste, with the aid of a liquid catalyst (dibutyl tin dilaurate) this paste was cured (utilising a condensation reaction) at room temperature, and so is more convenient in that it has 'chair side' applicability. Its main component is α - ω -dihydroxy ended blocked poly(dimethyl siloxane) which is cross-linked by triethoxy silanol. A quantity of inorganic filler was also present (34.5%). FB has been noted in the past for its extremely high water uptake of up to 65% and associated poor dimensional stability (Wright, 1976). It also suffers from poor adhesion, wettability and low tear strength.

The curing of this material involved mixing together the polymer paste and catalyst in the recommended proportions. As was the case with FS, this material was found

difficult to work with due to the short working time, as the paste quickly solidified upon addition of the catalyst. The manufacturers recommend leaving the material overnight for complete curing.

1.4.3. Polyphosphazine Soft Lining Materials

This novel material sells under the name of 'Novus' (Gettleman et al, 1987). It is based on poly(fluoroalkoxy) phosphazine elastomer. The complete composition is listed in table 1.4.5.

Material	Role	Quantity
Polyphosphazine fluoroelastomer	Elastomer.	100 Parts
Trimethylopropane trimethacrylate	Cross-linker	18 Parts
Ethylene glycol dimethacrylate	Cross-linker	2 Parts
Poly(methyl methacrylate)	Filler	10 Parts
BaSO ₄	Radiopaque filler	15 Parts
Lauroyl peroxide	Initiator	1 Parts
CdSSe dark red	Pigment	0.2 Parts

Table 1.4.5. Composition of Novus (ON) (Braden et al, 1997).

The earlier version of this material (ON) had a characteristic look, with a speckled appearance caused by white particles. The formulation was later changed (here denoted as NN), it is believed by changing the initiator from lauroyl to benzoyl peroxide and eliminating the use of the PMMA filler (Gettleman, 1994). Both versions of the material were examined. The presence of the methacrylate groups confers good adhesion to the denture base, but the water absorption of the material is rather high (Collis, 1993).

Both materials were supplied as a one paste system which were heat cured in an identical fashion. This involved packing the material under pressure into a two

millimetre thick sheet (using the metal mould), and then heat curing it for two and a half hours at 74°C, followed by boiling for 30 minutes.

1.4.4. Light Curing Material

'Triad Resiline' (TR) is a light curing material, it is supplied as a one paste mixture. This is pressed into the required shape as before but then cured using light. This particular material was cured for 5 minutes on each side, while trapped between acetate sheets in a 2mm thick metal window, using the Triad curing unit. Light curing materials have the advantage over other materials in that they can be part cured in the mouth using a hand held light gun. This makes the process quicker and easier.

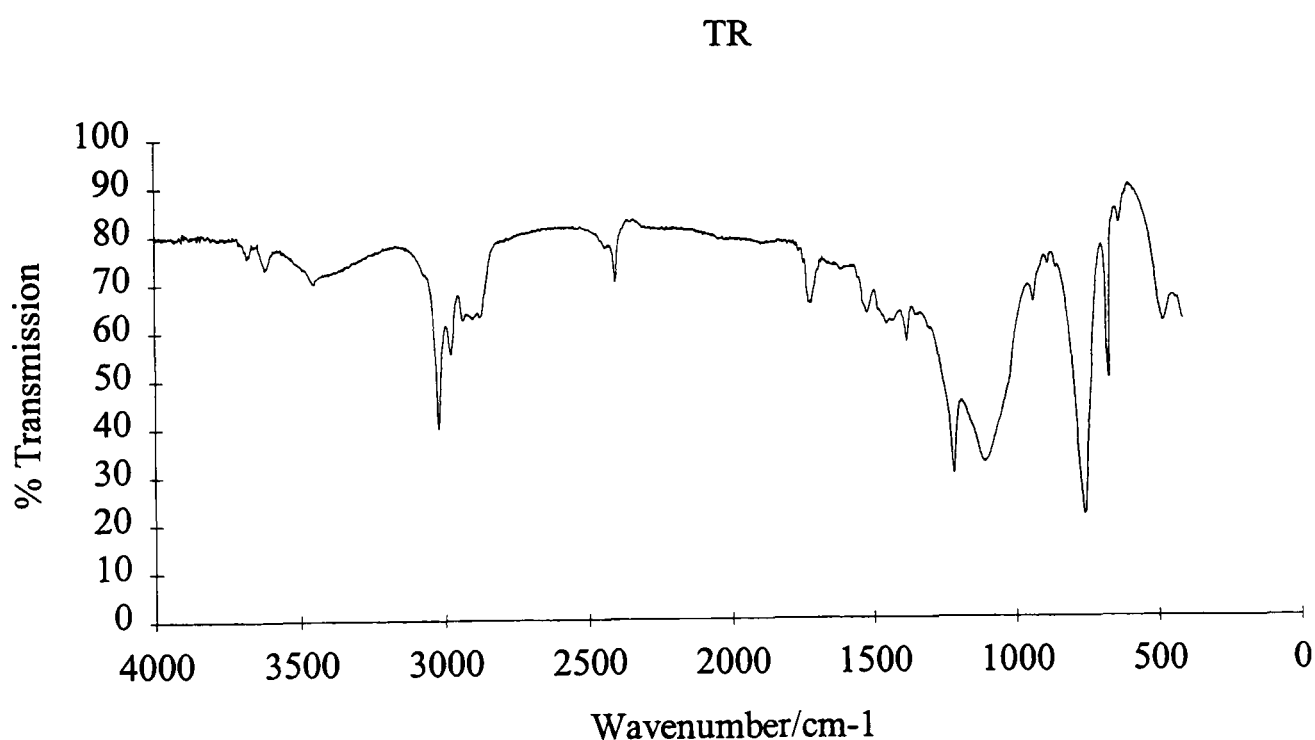


Figure 1.4.2. Infra-red spectrum of Triad (TR). Note ether band at 1100, isocyanate at 2400 (Braden, 1996).

Its exact chemistry is open to debate. It is believed to be a polyether-urethane dimethacrylate. Certainly the infra-red spectrum of this material (figure 1.4.2.) shows a major ether band, also the spectrum shows possible residual isocyanate groups (Braden, 1996). This is alarming as there is concern over the toxicity of isocyanates (Parker,

1982). A search of the literature did not reveal a reference to this material so its properties are largely unexplored.

1.4.5. Experimental Soft Lining Materials

In addition to the 8 commercial materials just described, 7 experimental materials developed at the Department of Biomaterials in Relation to Dentistry were also investigated. As has been mentioned previously the biggest problem with acrylic soft lining materials has always been instability in the mouth due to the leaching out of plasticisers. This has created the demand for a material with no plasticiser or one whose plasticiser does not leach out. The attempt to meet this need has resulted in two classes of experimental material (Parker, 1982; Parker & Braden, 1982): that of elastomer-methacrylate hybrids and acrylic based materials containing polymerisable plasticisers.

1.4.5a. Elastomer / Methacrylate Hybrids

The basic philosophy behind this type of material is to incorporate a polymer with a low glass transition (e.g. an elastomer) into a methacrylate system, thus creating a soft lining material with all the advantages of the current acrylic based materials without the need for plasticisation (Parker and Braden, 1990; Parker et al, 1996). The elastomers are either in pellet form, or in blocks which are cut into small pieces and then mixed with a methacrylate monomer prior to adding a cross-linking agent and an initiator. Initially butadiene styrene block copolymers were used, the range of elastomers used was later extended to include styrene-isoprene block copolymer and bromo-butyl rubber (Riggs, 1997). The elastomeric materials upon which the formulations are based are listed in table 1.4.6.

Material Code	Elastomer	Suppliers
BS	Butadiene-styrene block copolymer	Plascoats systems Ltd.
SI	Styrene-isoprene block copolymer	Shell chemical Ltd.
PB	Bromo-butyl rubber	Bayer AG.

Table 1.4.6. Elastomeric content of the Elastomer/Methacrylate soft lining materials.

In each case the elastomer was mixed in proportion with 2-ethylhexylmethacrylate monomer, lauryl peroxide initiator and ethyleneglycoldimethacrylate (EGDM) to act as a cross linker for the system (Supplied by Bonar Polymers Ltd). The ratio was 50 parts (by volume) monomer to 50 parts (by weight) elastomer with 1 part (volume) each of cross-linker and initiator*. This mixture was left to gel and subsequently cured by heat using conventional dental techniques. In this case the curing cycle involved bringing the dental flasks from ambient up to boiling point, and subsequently boiling for an hour.

1.4.5b. Polymerisable Plasticiser Acrylic Materials

The motivation behind this material is similar to that of the elastomer based systems i.e. to overcome the problems traditionally associated with the acrylic soft lining materials. However the concept used is quite different. In this class of materials the plasticising agent is a polymer of low molecular weight, which can not easily leach out of the material. To be an effective plasticiser the molecular weight of the diluent must be as low as possible, but not so low that the molecule can freely migrate. A monomer of low reactivity has to be used so that suitable oligomers are formed (Parker & Braden, 1982).

Four materials of this type were examined. The first one (PP) was developed by Parker (1982) and subsequently used in clinical trials where it was found to be unsuitable due to mechanical failure (Parker & Braden, 1989). The other 3 materials (C1, PE, PH), which are currently being developed are improvements on the previous generation of

* 1 ml equating to 1g

polymerisable plasticiser materials. The composition of the four materials, together with their codes are listed in table 1.4.7.

Code	Monomer	Cross-linker	Plasticiser
PP	1-Tridecyl MA 65	EGDM 5	EHM 30
C1	1-Tridecyl MA 70	EGDM 1	EHM 30
PE	2-Ethylhexyl MA 70	EGDM 1	EHM 30
PH	n-Hexyl MA 70	EGDM 0.5	EHM 30

Table 1.4.7. Liquid components and proportions (parts by volume) of the various polymerisable plasticiser systems (Parker & Braden, 1989; IRC Annual Report, 1996/97).

All the four materials were packed and cured as the conventional acrylic materials, in this case they were cured overnight in a pressure cooker at 2 bars and 85°C . In each case this consisted of mixing together the powder and liquid in the correct proportions. The proportions for these materials being 1.75 millilitres liquid to 1 gram of powder. The powder component of each system remained unchanged as 80/20 n-butyl/ethyl-methacrylate polymer (which contains approximately 1% residual benzoyl peroxide initiator). The composition of the liquids is listed in table 1.4.7. As can be seen three varieties of methacrylate monomer are used, with the same cross linker and plasticiser: ethylene glycol dimethacrylate (EGDM), and di-ethylhexylmalete (EHM) in various proportions.

1.5. Soft Lining Materials, Mastication and the Oral Environment.

Although soft lining materials are used extensively and have demonstrated clinical success, their exact mechanical function is not well understood. In particular, even though their function is clearly related to their viscoelasticity, it is unclear which range of these properties are clinically desirable (Braden et al, 1995). In this, a laboratory based investigation of the viscoelastic properties of soft liners, it therefore seems pertinent to ask: what effects do soft lining materials have on patients? and what is the relevance of their viscoelastic properties on these effects?

To attempt to answer these questions an overview of the clinical conditions and environment in which the materials operate is desirable. The following sections provide such an overview. In particular:

- The cushioning role of the mucosa and soft lining materials are looked at.
- The biomechanics of mastication in dentate patients and the subsequent effect on dentures and soft liners are examined.
- Alveolar bone loss and possible links to soft lining materials are examined.

1.5.1. Cushioning Effect of Oral Mucosa and Soft Liners.

The Oral mucosa can be subdivided into three regions (Moss-Salentijn and Hendricks-Klyvert, 1985) according to its function and properties. These regions are lining mucosa, masticatory mucosa and specialised mucosa. Specialised mucosa can be found covering the surface of the tongue only and its primary function is to taste. Lining mucosa covers the inside of the cheeks and the lips, the underside of the tongue as well as the floor of the mouth. It is characterised by its softness and mobility, which is attributed to the presence of a submucosa which attaches it to the underlying tissue (usually muscle).

The main interest here is however limited to the masticatory mucosa as its function is closely related to that of soft lining materials. Masticatory mucosa covers the area

surrounding the teeth and the roof of the mouth. A layer of submucosa is usually absent and a direct connection exists with the underlying tissues, i.e. bone. Masticatory mucosa is by and large resistant to movement and if healthy is mechanically strong enough to withstand most masticatory loading. Any prosthetic device which rests on the mucosa must rest exclusively on masticatory mucosa as only this type of mucosa meets the requirement for a stable and relatively unmovable surface.

The biological and mechanical properties of the mucosa were looked at by Kydd and Daly (1982). In particular they found that the mucosa showed evidence of time dependent, viscoelastic behaviour (Figure 1.5.1). Using a 10 minutes pressure pulse of 10g/mm^2 (in-vivo), an instantaneous elastic compression of 40% was seen. This was followed by a delayed elastic component of 10-20%. Upon release an instantaneous recovery is similarly followed by a delayed recovery which can last from 2 to 4 hours. Evidence of non-linearity was observed as doubling the magnitude of the load only served to produce an additional 5% change in the deformation.

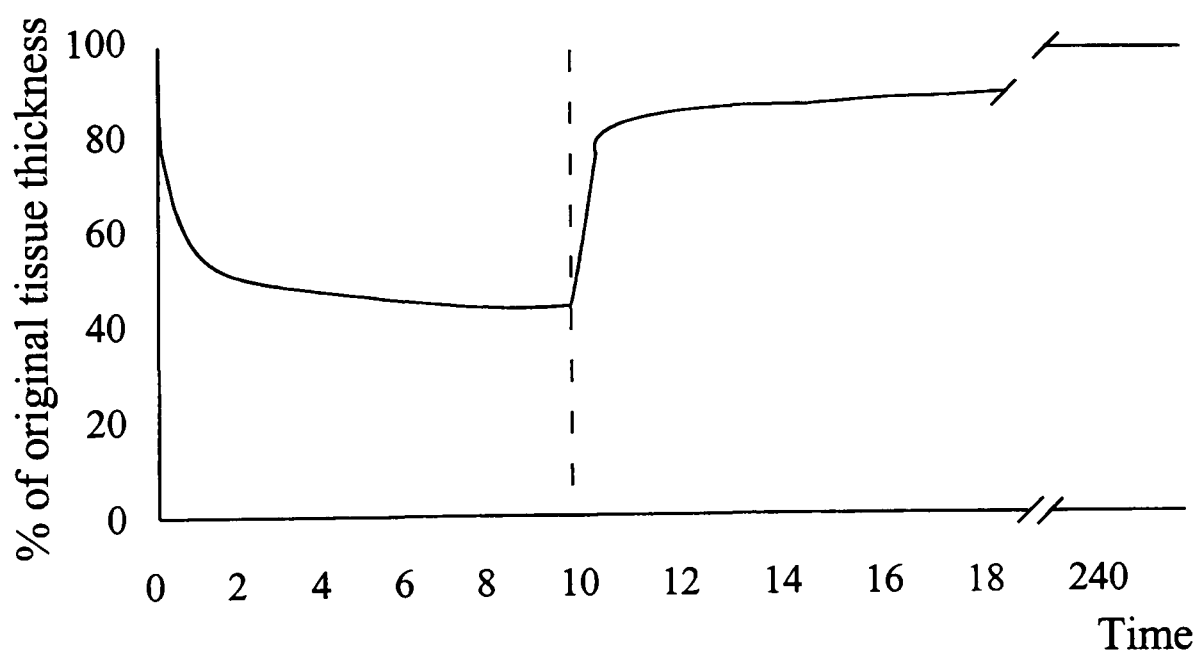


Figure 1.5.1. Typical behaviour of mucosa under constant load. Loaded for 10 minutes, and allowed to recover. (Kydd & Daly, 1982).

Age was seen to have a dramatic effect. Using a similar experiment as outlined above, the dependence of compression and recovery of the mucosa on the age of subjects was observed. The recovery in particular was seen to be strongly dependent on the age of the subject. See table 1.5.1.

Age	23	28	33	39	51	87	87
Compression	68%	61%	58%	53%	57%	49%	45%
Recovery	95%	90%	87%	86%	80%	61%	56%

Table 1.5.1. Effect of age on the deformation of the mucosa. The numbers represent the % of original thickness after compression for 2 minutes, and then the recovery after 1 hour. (Kydd & Daly, 1982).

The clinical significance of these results is that an elderly patient will take many hours to recover from moderate mechanical forces, whereas a young patient will only need a few minutes for the same amount of recovery. It is suggested by Kydd and Daly that in the case of an elderly patient wearing a denture over a period of several hours, a rest period of 2 days should be allowed before making impressions. In addition a low viscosity impression material should be used and it should be handled in such a way that the lowest possible force is transmitted to the mucosa. Several other authors (Tomlin et al, 1968; Inoue et al, 1985) have attempted to measure the viscoelastic properties of the oral mucosa. These will be dealt with in chapter 3 where a comprehensive survey of work carried out on the viscoelasticity of soft liners is undertaken.

It has been suggested that soft lining materials are essentially artificial mucosa prostheses and must attempt to mimic the viscoelastic properties of the biological tissue to be successful (Haykawa et al, 1994). In the authors own words: '*Soft lining materials are usually termed resilient liners. However, they should not have resiliency in the strict sense of the word. If the liner were truly resilient, the denture might tend to bounce away from the residual ridge with each application and release of masticatory force.*

For the soft liner to function as a shock absorber to ease masticatory loads, it is essential that the liner have the same viscoelasticity as the mucosa. A slow recovery following deformation under occlusal loading is more desirable than recovery that is instantaneously elastic.'

Other authors support this view point. Wagner et al (1995a): '*... the ideal soft liner would have a low storage modulus and a high damping factor.*' Although they warn that a high damping factor in a material might well lead to permanent deformation and therefore loss of fit.

This interpretation of the ideal viscoelastic properties of a soft lining material is however in direct contrast to that of other workers. Holt et al (1991) for example, correlated the 'Rebound Index' (a measure of resilience) with improved clinical performance in a small group of patients, while Wright (1976) indicates that the ideal viscoelastic requirement for a soft lining material is similar to that of a silicone rubber (i.e. highly resilient).

It seems clear that the ideal viscoelastic properties of the mucosa are open to debate, although what opinion there is seems to be divided into the two schools of thought outlined above. Unfortunately there has been little clinical, experimental or theoretical work carried out to elucidate which set of viscoelastic characteristics are ideal. A set of articles looking at the cushioning effect of soft lining materials are examined below. Although they do not provide a comparison between the different viscoelastic characteristics.

The load transmission properties of different thicknesses of mucosa on the underlying alveolar bone was investigated in an experimental in-vitro study by Schwarz (1992). His method was as follows: he obtained and machined ox bone into 2 mm thick plano-parallel sections. This was done as human post-mortem specimens were not available of

regular and sufficient dimensions. The soft lining material Flexibase (FB) was used as a mucosa substitute, as its mechanical properties are allegedly similar to those of the oral mucosa (Tomlin et al, 1968) He prepared the artificial mucosa in thicknesses ranging from 0.5 to 3 mm. Using spherical and cylindrical indentors the effect of the load bearing properties of the mucosa to the underlying bone was investigated. The author argues that the analytical benefits afforded by the use of this regular, and reproducible test regime, outweigh the advantages of a more realistic experiment of a similar nature. It was seen that as much as five times the load could be withstood by the bone before it was indented if the substitute mucosa was present. Not surprisingly the thicker the layer of artificial mucosa, the more energy was absorbed in its deformation. A layer 0.5 mm had only 20% of the effect of a 3 mm thick layer.

An early Finite Element Analysis (FEA) based study was carried out by Aydinlik et al. in 1980 looking at the effect of soft lining materials on the underlying tissues using a model of a partial lower denture. Elastic elements with the following material properties were used in the model.

Material	Elastic Modulus (MPa)	Poissons Ratio
Bone	19600	0.3
Acrylic Denture base	2350	0.29
Silicone lining material	1.38	0.49

Table 1.5.2. Material properties (Aydinlik et al, 1980).

The model did not include a mucosa and also did not take into account the effect of any viscoelasticity. A point load of 25 kg was applied to two dentures one with and the other without a soft liner. It was seen that the stress distribution was more uniform when the soft liner was introduced. The vertical displacement of the alveolar ridge was also reduced.

A more realistic study entitled: 'Effect of soft denture liner on stress distribution in supporting structures under a denture' used time dependent linear viscoelastic finite elements in its investigation (Kawano et al, 1993). Four 2-dimensional models were investigated; these included the standard case, where no soft lining was employed (A). Two models with the lining applied to the denture mucosa interface; in one case the lining extended to the periphery of the denture (B), in the other it did not (C). In the fourth model the lining was applied between the artificial teeth and the denture (D). Each model was deformed by a 50N vertical load set on the artificial teeth. Its time dependent response was observed in 0.1 second increments for a total of 3 seconds. The material properties assumed are listed in table 1.5.3.

Material	Mechanical Properties
Denture Base (PMMA)	Youngs Modulus, 1.96 GPa; Poissons Ratio, 0.3.
Soft Lining Material	E_m , 1.2 MPa; E_v , 3.1 MPa; η_m , 5430 MPa.s; η_v , 9.8 MPa.s
Mucosa	E_m , 1.1 MPa; E_v , 1.2 MPa; η_m , 250 MPa.s; η_v , 18 MPa.s
Bone	Youngs Modulus, 13.4 GPa; Poissons Ratio, 0.3.

Table 1.5.3. Material properties used in FEA. The viscoelastic properties of the mucosa and the soft lining material relate to those of a 4 element Voigt model. The soft lining material considered was 'Kurepeet' (Kawano et al, 1993).

The following conclusions were reached: if no soft lining material was used the greatest stress concentration was on the lingual slope of the residual ridge. The displacement of the denture increased after the addition of a soft lining material, the amount and direction of this displacement was dependent on the design of the denture. As expected the addition of a soft liner reduced the stress intensity at the load bearing areas, again according to the denture design. Model D showed the most uniform stress distribution in the soft tissues.

1.5.2. Biomechanics of the Masticatory Cycle, and the Effect of Soft Liners.

Mastication can be simply defined as the process of chewing food until it is reduced to small particles or 'pulp'. The large body of literature on the subject was reviewed in a set of three articles by Bates et al (1975a,b and 1976); looking in turn at the form, speed, rate, forces and efficiency of mastication.

The form of the chewing cycle is 'teardrop' in shape for people with healthy dentition and is essentially a two phased motion. From the open position the mandible is raised in a straight 'crushing' phase, which is followed by a sideways 'grinding' phase. In the last part of the chewing motion the mandible goes back to its original open position, this is sometimes called the preparatory phase.

Subjects tend to have a preference for one side of the mouth which they use for chewing. The choice of which side is associated with the state of the dentition, subjects choosing the side which gives them the best tooth contact. Where both sides are comparable they are used alternately, and the bolus of food is moved from side to side by the tongue. The dimensions of the cycle are normally half the maximum vertical and lateral possible movement of the mouth, and become smaller as chewing continues, and the food particles are reduced in size. Good dentures allow the patient to function in much the same way as subjects with natural teeth, although denture wearers have to use the tongue, lips and cheeks to control, stabilise and retain the denture (Bates et al, 1975a).

The speed of the mandible is not constant and varies in different parts of the chewing cycle. The mandible closes from an open position, in an upward direction and as contact is made the rate of closure dramatically decreases, and is usually accompanied by a pause during occlusion. The mandible then opens rapidly, usually at a faster rate than during the closing stroke, and gradually slows down as it nears the maximum opening position. Speed estimates range between 64 and 135 mm/s (Bates et al, 1975b).

Chewing rates exhibit a similarly large variation, ranging from 50 to 120 cycles per minute (0.8-2 Hz) have been reported, averaging at slightly over 1 cycle per second. There does not seem to be a noticeable change in the rate of chewing for people with and without dentures (Bates et al, 1975b).

The limiting factor which defines the forces developed during mastication is primarily the muscular power of the individual. Other factors include the pain threshold, and in denture wearers, the stability and retention of these devices. Forces developed in the mouth have been classified into two types: those developed due to a hard biting force in an empty mouth, termed the 'maximum biting force', the second group are those which occur during normal chewing of food. Again a large variation is seen clinically, with reported values of maximum biting forces* from 1 kg up to a massive 443 kg (Hagberg, 1987) being reported. More conservative estimates rate the maximum bite force between the first molars to be from 0.9 to 89.9 kg. The force which can be obtained between the incisors is much less ranging between 0.45 to 37.7 kg. The forces used in chewing are commonly much less than these maximum biting forces. Chewing forces between 0.3 to 7.2 kg are reported for people with their natural teeth (Bates et al, 1975b). Bite forces get progressively lower with short bounded saddle partial dentures, free end saddle dentures, and complete dentures. The exact amount of this reduction is again variable, but reductions of 5 or 6 times are reported (Zarb, 1982). Zarb also reported the mean denture bearing area to be 23 cm² in the maxilla and 12 cm² in the mandible for edentulous patients.

The efficiency of mastication can be assessed using fractional sieving, i.e. by examining the particle size distribution of food when chewed for a given number of strokes (Bates et al, 1976). Chewing gum is also occasionally used, the amount of sugar extracted over a time period or a number of strokes giving an indication of the effectiveness of

* Strictly speaking the unit of force is the Newton (N).

mastication. Following a similar trend to bite force, the efficiency is seen to decrease in patients with dentures compared to those with natural teeth. A relationship between bite force and effectiveness has been reported (Heath, 1982).

Such high variations in the biomechanical factors (frequency, force, etc.) of mastication are not surprising when one considers the many clinical, habitual and psychological factors which bear an influence, not to mention the widely differing testing methodologies which are employed in the literature.

The fact that soft lining materials have not been mentioned in the preceding discussion is because very few studies have attempted to quantify their biomechanical effect, although their potential relevance in terms of biting force and masticatory effectiveness have been noted (Heath, 1982; Zarb, 1982). Wright (1984) being an exception to this, although his results were inconclusive (Table 1.5.4). He used a strain gauge 'gnathometer' placed between the artificial first molar and premolar on each side to measure the maximum biting force. As can be seen the differences in maximum biting force between test groups are small compared to the experimental differences. Using sugar extraction from chewing gum as his criteria he also looked at masticatory effectiveness and found a more profound difference (although not quite statistically significant). The trend being that soft liners improve masticatory effectiveness.

Denture Type	Biting Force (kg)	Masticatory Effectiveness %
Lined with Molloplast B	4.97 ± 3.55	25.36 ± 7.75
Lined with other soft liner	4.58 ± 3.48	20.25 ± 7.85
Conventional denture	4.76 ± 3.75	19.14 ± 6.71

Table 1.5.4. Mean Maximum bite force and masticatory effectiveness for various denture configurations (Wright, 1984).

1.5.3. Alveolar Bone Loss and it's Relationship to Soft liners.

The loss of alveolar bone from the edentulous patient is a common and serious problem. Although the exact mechanism is not fully understood, several factors including age, sex, hormonal imbalance and nutritional deficiency are associated with it. The factors affecting bone loss were grouped into three broad categories by Atwood (1971). Biological factors just mentioned. Anatomical factors include size, shape and bone density of the ridge. Mechanical factors which include the prosthesis design and its effect on bite forces, their direction and duration.

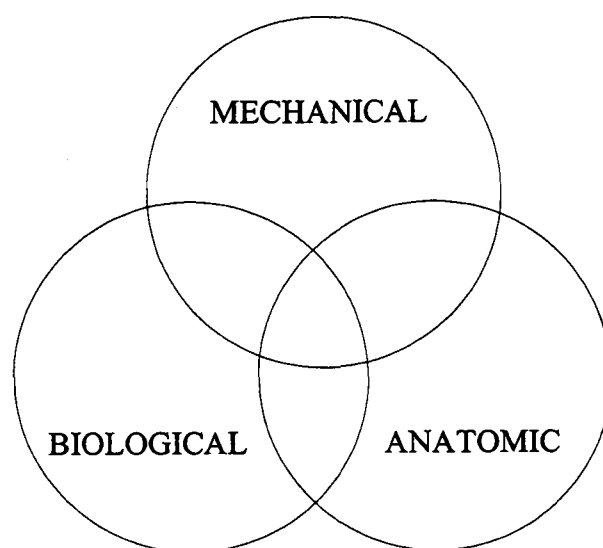


Figure 1.5.2. Co-factors affecting alveolar bone loss (Atwood, 1971).

Relating to denture biomechanics and soft lining materials it is the mechanical aspects which are of interest. In particular two mechanisms are important; these are occlusal trauma and disuse atrophy, termed 'abuse' and 'disuse' by Storer (1962a). Two recent papers have reviewed alveolar ridge resorption (Devlin & Ferguson, 1991; Klemetti, 1996). Their findings are discussed below.

After their review of the literature Devlin and Ferguson (1991) could not find any direct evidence linking bone resorption with occlusal trauma despite the traditional link between the two. They surprisingly found that the amount of time worn or quality of the denture (occlusal balance) had no effect on the amount of bone loss. They did find that the rate of bone loss was higher in the mandible compared to that in the maxilla. This

they attributed to the smaller area and hence higher stresses in the mandible; although they again found no data correlating denture bearing area to rate of bone resorption.

An increase in bone loss maybe analogous to disuse osteoporosis which can occur in any bone due to immobilisation or stress shielding (Devlin & Ferguson, 1991). Denture wearers have a well documented loss in biting force which can hence be linked with bone loss. This reduced force on the mandible may well result in the remodelling of the 'excess' bone until only a mechanically minimal amount is left. Against this argument stands the fact that the loss in the mandible seems to be greater, which is inconsistent with its smaller surface area and hence higher stresses. Also an equilibrium is not always reached as one would expect from this argument and the bone resorption process can continue for thirty years or more.

Devlin & Ferguson reached similar conclusions to that of Atwood (1971): that the mechanisms of bone loss are the superposition of various factors in particular local and systematic factors. Systematic factors can include age, sex and diet. Superimposed on these are local factors such as occlusal trauma and disuse atrophy.

More recently (1996) Klemetti reviewed the literature and in particular looked at the correlation between alveolar bone loss and osteoporosis. Based on this review it was concluded that masticatory forces were the dominant factor: *'occlusal forces must be considered to be the major cause of residual ridge resorption because these forces are able to cause rapid and thorough resorption without systemic bone loss, namely osteoporosis.'*

Although clinical evidence is not consistent and quiet often contradictory it seems at the very least plausible that occlusal trauma and bone disuse due to a loss in biting force can have an important effect on alveolar bone loss. Considering soft lining materials once again; one would intuitively expect that the use of soft lining materials would have a

positive effect on both occlusal trauma (by distributing biting force more evenly) and disuse atrophy (by increasing comfort, reducing pain hence increasing overall biting force). Some clinical evidence does indeed exist linking the use of soft liners and reduced bone resorption.

ElCharkawi and ElMahdy (1988) used a radiographic technique to look at residual ridge reduction. The subjects were 17 edentulous men whose last extraction had been 6-12 months previous to the trials. They all had a well developed residual ridge with firm healthy mucosa, no systemic diseases and no previous denture experience. These subjects were split into 3 groups. Group A given dentures lined at the mucosal interface. Group B given dentures lined between the acrylic teeth and the denture base and group C were used as controls with normal hard acrylic dentures. The lining material Molloplast B (MP) was used. Table 1.5.5 summarises their results:

	Man (A)	Max (A)	Man (B)	Max (B)	Man (C)	Max (C)
Average Ridge	0.1003	0.1446	0.088	0.1694	0.2553	0.2256
Reduction (mm)	<i>0.02262</i>	<i>0.0442</i>	<i>0.01907</i>	<i>0.0633</i>	<i>0.02333</i>	<i>0.03333</i>

Table 1.5.5. Average ridge reduction of the mandible and the maxilla after 6 months for various denture types (See text). Numbers in italic refer to the Standard deviation (ElCharkawi & ElMahdy, 1988).

As can be seen ridge reduction occurred in all three groups but was significantly lower for those patients wearing soft liners, although there was also no significant difference between the two methods of using the soft liner (A and B). It can also be noted that the use of a soft liner had a larger consequence for bone loss in the mandible which was seen to be significantly lower than in the maxilla. This is not consistent with other clinical studies looking at conventional denture types nor with the control group.

The correlation between the use of soft lining materials and reduced bone loss were also noted by Badawy & ElSherbiny (1992) although they were looking at different denture

types. Wright's (1994) observations also seem to agree with these findings over a longer time scale '*the mean mandibular residual ridge resorption over the 9-year period was very small.*' .

CHAPTER TWO

THEORY

2. Linear Viscoelastic Theory.

In an earlier section Hooke's law, Newton's law and the concept of viscoelasticity were introduced together with 3 common experimental techniques used to gauge it.

Viscoelasticity has been loosely defined as the property of a material exhibiting both elastic and viscous behaviour. This section attempts to take a more quantitative look at the subject. In order to make a mathematical approach practical, a number of assumptions have to be made. These are called the assumptions of linear viscoelastic theory and have been previously used in the study of dental materials (Clarke, 1988).

- Two types of deformation are involved. The total deformation is the summation of the viscous and elastic components considered separately.
- Only small strains and rates of strain are considered and the relationship between these and the stress is considered to be linear.

Newton's and Hooke's laws, as well as the other governing equations developed later in this chapter can be considered to be particular cases of the more general application of the linear viscoelastic equation of the following form:

$$A_0\sigma + A_1\frac{d\sigma}{dt} + A_2\frac{d^2\sigma}{dt^2} + \dots + A_n\frac{d^n\sigma}{dt^n} = B_0\varepsilon + B_1\frac{d\varepsilon}{dt} + B_2\frac{d^2\varepsilon}{dt^2} + \dots + B_n\frac{d^n\varepsilon}{dt^n}$$

2.1.

Where the A's and B's are constants for a particular case. For example in the case of a Hookian spring A_0 equals one, B_0 is the modulus of the spring and the higher A's and B's equate to zero.

2.1. Viscoelastic Models

Viscoelastic models are used to gain a greater insight into the behaviour of such systems. They can be broadly divided into two classes. The first type are called molecular models and as the name implies are concerned with the modelling of actual polymer molecules. The simplest of these look at the behaviour of isolated polymer molecules which can be treated as entropy springs, in a viscous environment of a solvent. Further complications arise when one considers the effect which polymer chains have on their neighbours, entanglements and cross-links (Aklonis & MacKnight, 1983; Ferry, 1980). Molecular models are outside the scope of this chapter whose attention is directed to viscoelastic mechanical models.

The second type of viscoelastic model are mechanical ones and are thus not strict representations of real microscopic processes in the polymer. They are however useful in that they provide an insight into the macroscopic behaviour of such systems. In addition to providing insight into viscoelastic behaviour these models have a number of theoretical and practical uses. As has been demonstrated they can be used in the derivation of theoretical concepts such as the WLF equation (Section 1.3.5). They are also often used to characterise viscoelastic materials for comparison or analysis, such as FEA (section 1.5.1).

2.1.1. Maxwell and Voigt Models Under Static Conditions

Two mechanical elements are commonly used to derive viscoelastic models. These are the weightless elastic spring representing an ideal Hookian solid and the viscous fluid in a piston or dashpot representing an ideal Newtonian fluid as discussed earlier. The simplest viscoelastic models involve one spring and one dashpot. These two elements can either be linked in series or parallel and give rise to two models: the Maxwell and the Voigt models respectively.

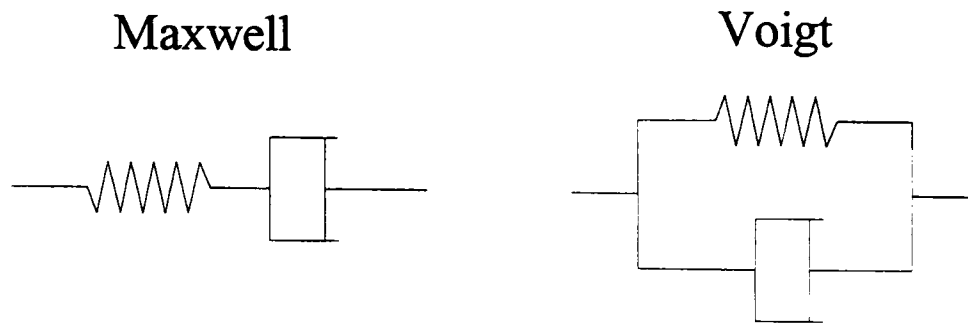


Figure 2.1.1. The Maxwell and Voigt elements.

The governing equations for these models together with their behaviour in creep and stress relaxation are derived in Appendix A and presented in table 2.1.1. Both the governing equations are 1st order linear differential equations and again can be thought of as particular cases of equation 2.1.

	Maxwell	Voigt
Governing Equation	$\frac{d\varepsilon}{dt} = \frac{1}{E} \times \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$	$\sigma = \frac{\varepsilon}{D} + \eta \frac{d\varepsilon}{dt}$
Creep Compliance	$D(t) = D + \frac{t}{\eta}$	$D(t) = D(1 - e^{-t/\tau})$
Stress Relaxation Response	$E(t) = E e^{-t/\tau}$	$E(t) = E$

Table 2.1.1. Maxwell and Voigt static behaviour.

The ratio of η/E is labelled τ and is known as the relaxation or retardation time of the model.

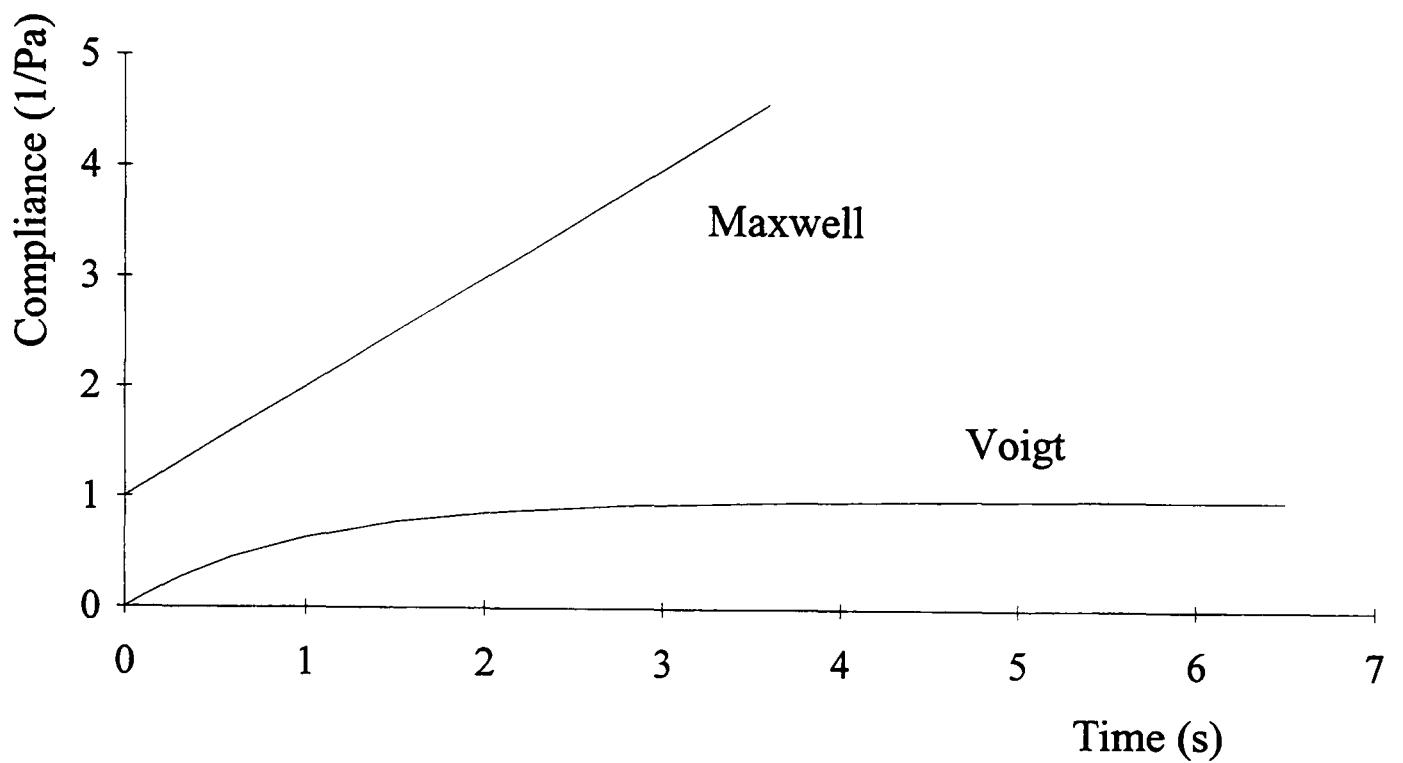


Figure 2.1.2. The time dependence of creep compliance of the Maxwell and Voigt elements. Note E and η are arbitrarily chosen to be unity for this representation.

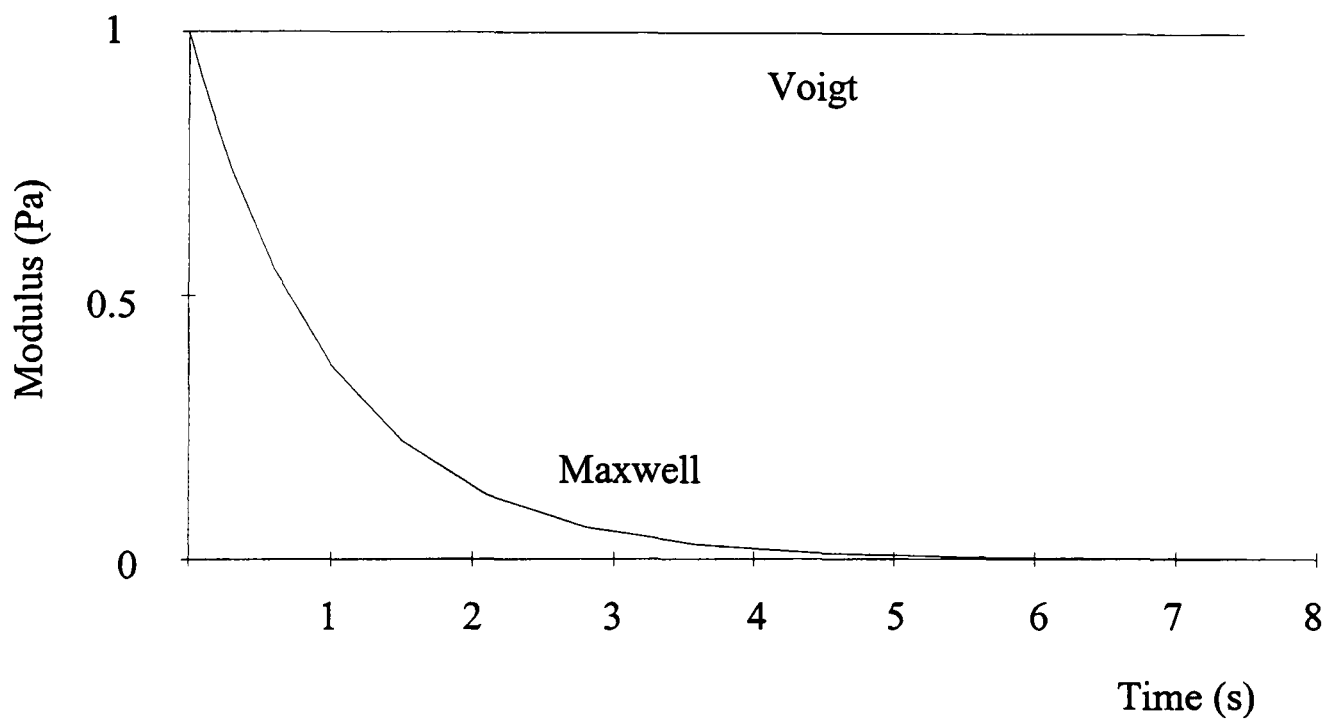


Figure 2.1.3. The Maxwell and Voigt elements in stress relaxation. E and η are again chosen to be unity.

Figure 2.1.2. shows the plot of the creep compliance functions of both elements as a function of time. The spring and dashpot constants have been arbitrarily set to 1 for this representation so that the relaxation time of the models is also 1 second. The compliance

of the Maxwell model is directly proportional to time as for a liquid although its intercept is the spring constant. At infinite time the model will have an infinite compliance. The Voigt element on the other hand has an exponentially decaying compliance and at infinite time will behave as a spring.

Figure 2.1.3. shows the behaviour of the Maxwell and Voigt models in stress relaxation. Just as the Maxwell element in creep was seen to behave as a Newtonian liquid, here we see the Voigt element in stress relaxation appearing as a Hookian spring, i.e. time independent. Again similarly the Maxwell model relaxes exponentially and has zero stiffness at infinite time.

Clearly the Maxwell model in creep, and the Voigt model in stress relaxation can be dismissed as representations of viscoelastic behaviour because they follow Newton's and Hooke's law respectively. The two models can approximate viscoelastic materials where their behaviour is exponential however (i.e. Maxwell in stress relaxation and Voigt in creep). In general however this does not provide a good representation for two reasons: firstly the behaviour of real materials can not be readily expressed in terms of a single exponential decay term. Secondly the creep compliance of a real system would not always decay to a fixed value such as that of the Voigt model, particularly if the material was uncross-linked. Similarly the relaxation modulus of a real material would not diminish to zero if the material was cross-linked as in the Maxwell model.

2.1.2. Maxwell and Voigt Models Under Dynamic Conditions.

The dynamic behaviour of the Maxwell and Voigt models are summarised in table 2.1.2.*

	Maxwell Model	Voigt Model
Complex Modulus (E^*)	$\frac{\tau\omega E}{\tau\omega - i}$	$E + i\eta\omega$
Complex Compliance (D^*)	$D - \frac{iD}{\tau\omega}$	$\frac{1}{E + i\eta\omega}$
Storage Compliance (D')	D	$\frac{D}{1 + \omega^2 \tau^2}$
Loss Compliance (D'')	$\frac{1}{\eta\omega}$	$\frac{D\omega\tau}{1 + \omega^2 \tau^2}$
Storage Modulus (E')	$\frac{E\tau^2 \omega^2}{1 + \tau^2 \omega^2}$	E
Loss Modulus (E'')	$\frac{E\tau\omega}{1 + \tau^2 \omega^2}$	$\eta\omega$
Loss Tangent ($\text{Tan } \delta$)	$\frac{1}{\omega\tau}$	$\omega\tau$

Table 2.1.2. The Dynamic behaviour of the Maxwell and Voigt models.

It is convenient to represent the Maxwell element by its dynamic modulus and the Voigt model by its dynamic compliance. Figures 2.1.4. and 2.1.5. are such representations.

Showing the normalised forms of these functions.

* Derived in appendix A.

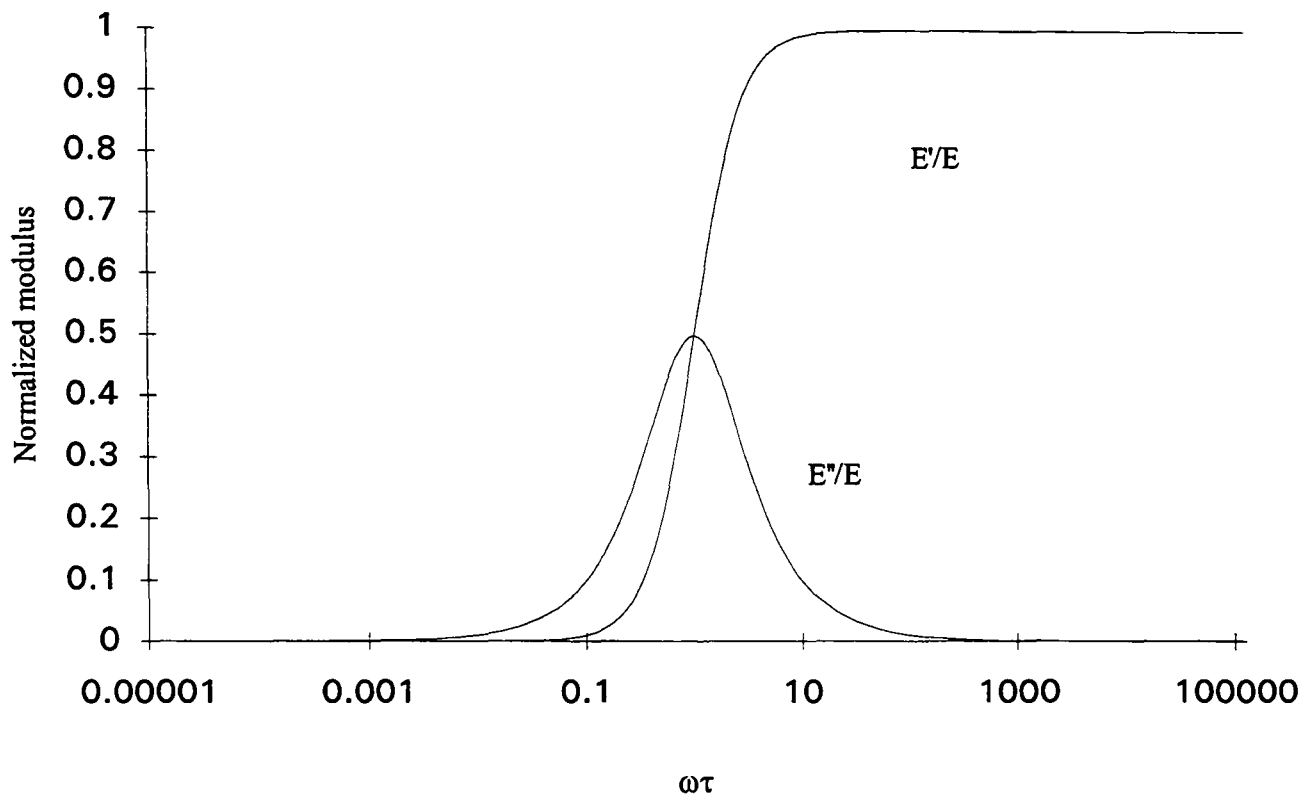


Figure 2.1.4. Dynamic modulus of a Maxwell element.

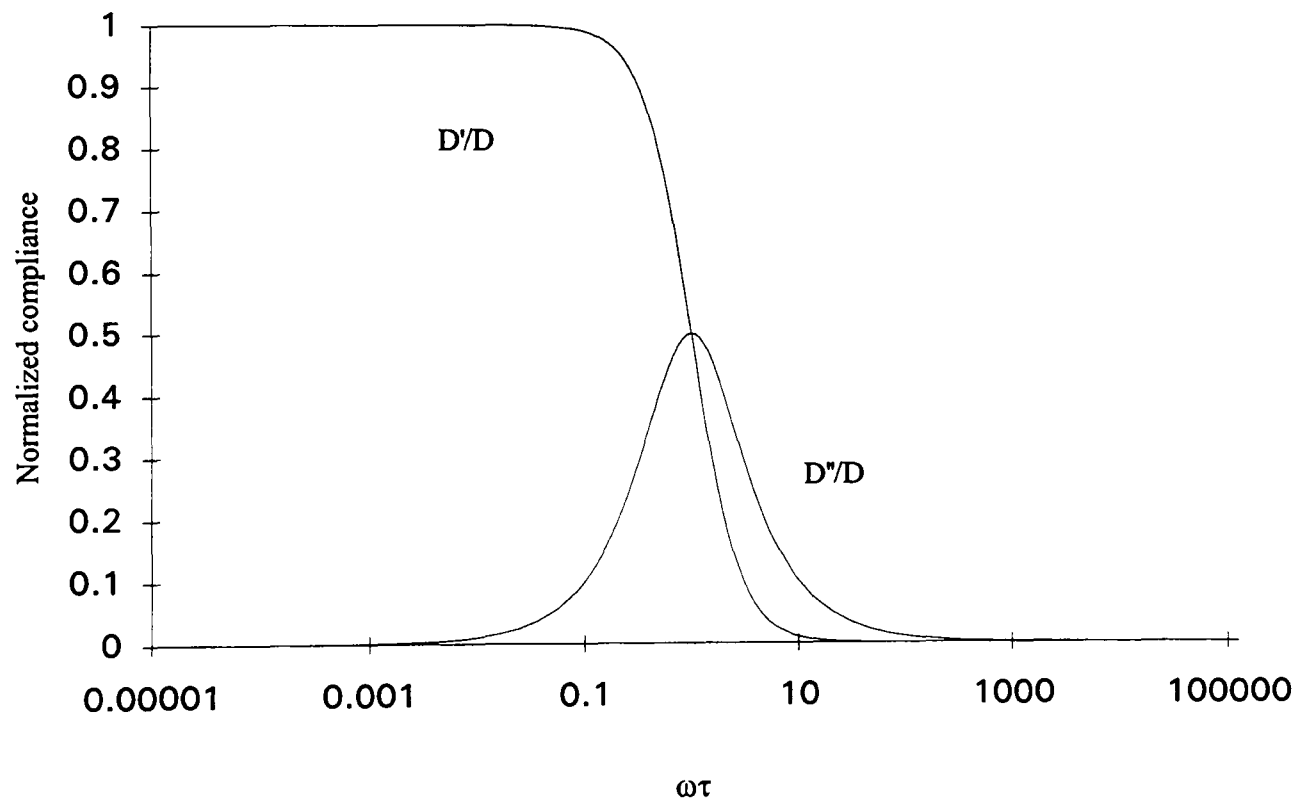


Figure 2.1.5. Dynamic compliance of a Voigt element.

For the Maxwell element it can be seen that the storage modulus is highly time dependent near $\omega\tau = 1$; at higher frequencies the modulus approaches the modulus of the spring in the model, while at lower frequencies the modulus approaches zero. The loss modulus of the model is zero at the high and low ranges of frequency but near $\omega\tau = 1$ is very frequency dependent and goes through a peak when the relaxation time of the model equals the reciprocal of the frequency. These functions are qualitatively good descriptions of real polymer systems, where the storage modulus falls abruptly at the glass transition to a frequency independently low value. Although in most polymers this is known as the rubbery plateau and the modulus is in the range of MPa and not zero. Largely because of this the loss tangent of the model is a very poor approximation to real systems. Rising to infinity at low frequencies, being equal to 1 at $\omega\tau = 1$, and shadowing the loss modulus function at high frequencies. This is clearly not realistic of a real polymer system.

Figure 2.1.5. shows the dynamic behaviour of a Voigt element. The D'/D plot shows that the faster the sample is deformed the stiffer it appears. The model is again sensitive in the region where $\omega\tau$ is around 1, at smaller or larger frequencies the model is not so sensitive. The plot of D''/D is identical to the E''/E plot for the Maxwell element and shows a maximum as the $\omega\tau$ term reaches 1. The loss tangent equals $\omega\tau$, which is again not very realistic for a polymer.

To summarise then it can be seen that the Maxwell and Voigt elements are similar in character and have similar shortcomings, not surprising perhaps considering that both are governed by equations of a similar form. The Voigt element providing a relatively better approximation in creep and the Maxwell being more useful in stress relaxation. Under dynamic excitation both models mimic to some extent the behaviour of real systems although the approximation is not in any way accurate.

2.1.3. The Four Element Model in Creep.

In hope of finding a better viscoelastic model additional elements can be added. Three element models can be built up by adding an extra spring or dashpot to a Maxwell or Voigt model. A common viscoelastic model is made up of a Maxwell and a Voigt model joint together in series (figure 2.1.6.) The behaviour of the four element model can be represented by the following second order differential equation*.

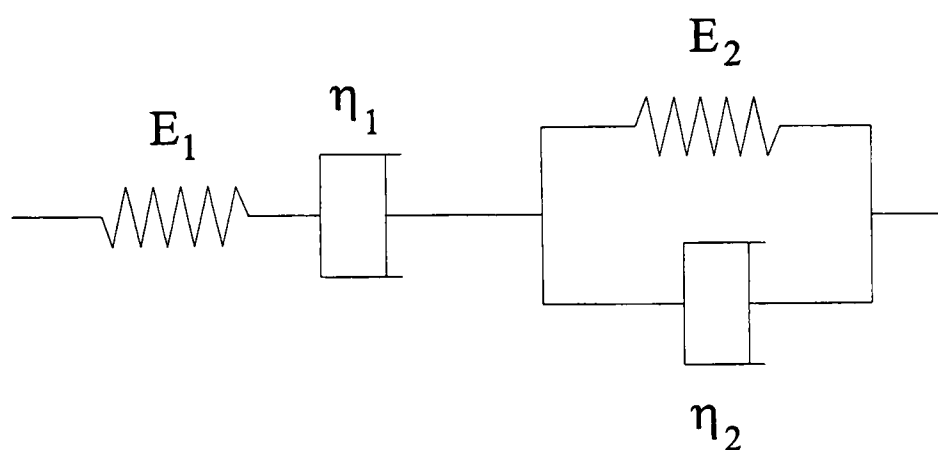


Figure 2.1.6. The four element model.

$$\frac{\eta_2}{E_1} \frac{d^2 \sigma}{dt^2} + \left(1 + \frac{E_2}{E_1} + \frac{\eta_2}{\eta_1} \right) \frac{d\sigma}{dt} + \frac{E_2}{\eta_1} \sigma = \eta_2 \frac{d^2 \varepsilon}{dt^2} + E_2 \frac{d\varepsilon}{dt} \quad 2.1.1.$$

The creep compliance of which can be shown to be of the following form.

$$D(t) = \frac{1}{E_1} + \frac{t}{\eta_1} + \frac{1}{E_2} \left(1 - e^{-tE_2/\eta_2} \right) \quad 2.1.2.$$

* As before derivation in Appendix A.

There are three distinct components to this equation. The first term is time independent and represent the instantaneous elastic response. The second term is directly proportional to time and can be regarded as the purely viscous part of the response. The third term is an exponential and although dominant at the beginning eventually decays to zero. This equation can in practice provides a good approximation for the behaviour of real materials and an example of its application has already been mentioned: when it was used by Kawano et al (1993) in a finite element study. Taking figures already introduced in table 1.5.3. as the representations of a soft liner and the oral mucosa we can use the above creep equation to obtain a plot of their time dependent creep modulus over a 30 second time period.

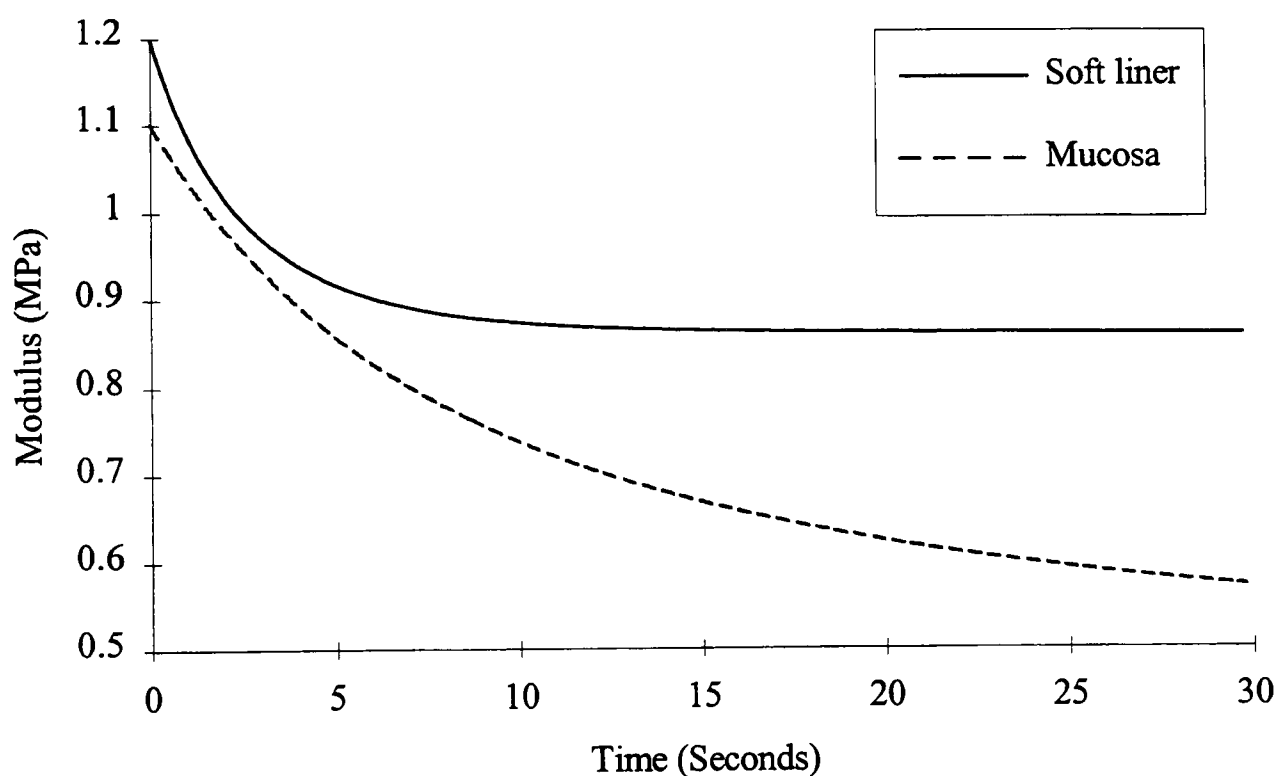


Figure 2.1.7. Creep behaviour of 4 element model. (from data of Kawano et al, 1993)

2.1.4. The Four Element Model Under Dynamic Excitation.

In dynamic conditions the following equations can be derived in terms of the 4 element model:

The overall modulus of the model:

$$E(t) = \frac{A}{\varepsilon_0} \cos \omega t + \frac{B}{\varepsilon_0} \sin \omega t \quad 2.1.3.$$

The storage modulus of the model:

$$E' = \frac{B}{\varepsilon_0} \quad 2.1.4.$$

The loss modulus of the model:

$$E'' = \frac{A}{\varepsilon_0} \quad 2.1.5.$$

and hence the Loss tangent:

$$\tan \delta = \frac{A}{B} \quad 2.1.6.$$

Where A and B are model parameters as defined below:

$$A = \frac{\eta_2 \varepsilon_0 \omega^3 \beta + E_2 \varepsilon_0 \omega \times \left(\gamma - \alpha \omega^2 \right)}{\beta^2 \omega^2 + \left(\gamma - \alpha \omega^2 \right)^2} \quad 2.1.7.$$

$$B = \frac{E_2 \varepsilon_0 \omega^2 \beta - \eta_2 \varepsilon_0 \omega^2 \times \left(\gamma - \alpha \omega^2 \right)}{\beta^2 \omega^2 + \left(\gamma - \alpha \omega^2 \right)^2} \quad 2.1.8.$$

and α , β , γ are in turn coefficients of the governing equation 2.1.1. such that:

$$\alpha = \frac{\eta_2}{E_1} \quad 2.1.9.$$

$$\beta = 1 + \frac{E_2}{E_1} + \frac{\eta_2}{\eta_1} \quad 2.1.10.$$

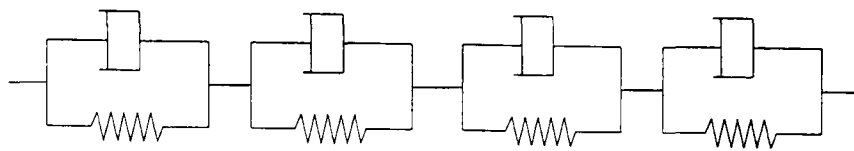
$$\gamma = \frac{E_2}{\eta_1} \quad 2.1.11.$$

The approximation of real materials provided by these equations is frankly disappointing. β in particular can easily take negative values, which is clearly meaningless for a modulus.

2.1.5. Spectral Models

As can be seen from Appendix A the increased sophistication of the four element model compared to the 2 element models has severely increased the size and complexity of the algebra. It is not common practice to analyse models more complex than the one just described as the mathematics soon becomes intractable. In the search for better mathematical representations of viscoelastic materials generalised Maxwell and Voigt models are the next step. It is possible to construct models of infinite size by adding Voigt and Maxwell models in parallel and series as depicted in figure 2.1.8.

Generalised Voigt model



Generalised Maxwell model

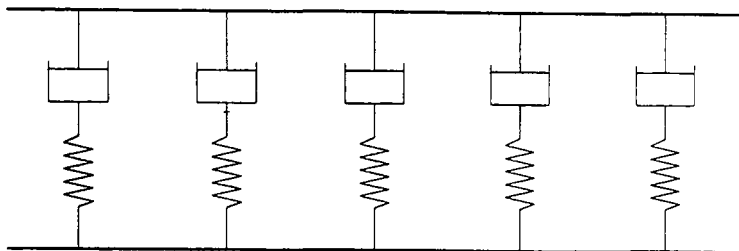


Figure 2.1.8. Generalised Voigt and Maxwell models.

For a series of n Maxwell or Voigt elements, table 2.1.3. shows that summing the stress relaxation and creep expressions respectively from 1 to n gives:

	Generalised Maxwell	Generalised Voigt
Creep	—	$D(t) = \sum_{i=1}^n D_i \left(1 - e^{-t/\tau_i} \right)$
Stress Relaxation	$E(t) = \sum_{i=1}^n E_i e^{-t/\tau_i}$	—
Storage Modulus/ Compliance	$E' = \sum_{i=1}^n \frac{E_i \tau_i^2 \omega^2}{1 + \tau_i^2 \omega^2}$	$D' = \sum_{i=1}^n \frac{D_i}{1 + \tau_i^2 \omega^2}$
Loss Modulus/ Compliance	$E'' = \sum_{i=1}^n \frac{E_i \tau_i \omega}{1 + \tau_i^2 \omega^2}$	$D'' = \sum_{i=1}^n \frac{D_i \tau_i \omega}{1 + \tau_i^2 \omega^2}$

Table 2.1.3. The generalised Maxwell and Voigt models.

As n tends towards infinity continuous spectra are produced and the summation signs can be replaced by integration signs. Below the results for the static cases are shown, similar results can be expected using the dynamic variables.

$$E(t) = \int_0^{\infty} E(\tau) e^{-t/\tau} d\tau \quad 2.1.12.$$

$$D(t) = \int_0^{\infty} D(\tau) \left(1 - e^{-t/\tau}\right) d\tau \quad 2.1.13.$$

where $E(\tau)$ and $D(\tau)$ are the continuous functions to replace the E_i 's and the D_i 's in the previous equations. It is conventional to represent these functions in terms of a logarithmic scale such that.

$$E(t) = \int_0^{\infty} \frac{H(\tau)}{\tau} e^{-t/\tau} d\tau = \int_{-\infty}^{\infty} H(\tau) e^{-t/\tau} d \ln \tau \quad 2.1.14.$$

Where $H(\tau)$ is the relaxation spectrum, and equals $\tau E(\tau)$. Similarly for the compliance function:

$$D(t) = \int_{-\infty}^{\infty} L(\tau) \left(1 - e^{-t/\tau}\right) d \ln \tau \quad 2.1.15.$$

Where $L(\tau)$ is the retardation spectrum.

It is possible to obtain viscoelastic functions (i.e. creep compliance, storage modulus etc.) from the relaxation and retardation spectrums using the above equations. The reverse process is not so easy however as the observed parameters E' , E'' etc. can not normally be represented analytically to sufficient accuracy (Ferry, 1980). It is therefore common practice to represent experimental data in terms of measured quantities in graphical or tabular form. The observed experimental results in this report are thus

depicted in this manner and no attempt is made to approximate them by mechanical models/mathematical functions.

CHAPTER THREE

LITERATURE SURVEY

3.1 Methods of measuring Viscoelasticity

This literature survey concerns methods of measuring the viscoelasticity of materials in general and soft lining materials in particular. The various methods used to investigate viscoelastic properties are often grouped together under their frequency range. This was carried out by Clarke in 1988, when he looked at the ways used to measure the viscoelastic properties of various materials related to dentistry.

Transient measurements.	Approx. Frequency range	Up to 1 Hz
Low frequency vibrations.	"	0.1 Hz to 50 Hz
Forced vibrations (Non-Resonance)	"	0.01 Hz to 100 Hz
Resonance of standing waves	"	20 Hz to 10^5 Hz
Wave propagation.	"	More than 10^5 Hz

3.1.1. Transient

Creep and stress relaxation experiments have already been described. These test can be performed for a full range of deformation modes including, shear, torsion compression, elongation and flexure. The mode studied being primarily governed by what the experimental data is to be used for, but also depending on the sensitivity of the equipment and the properties of the material. Tensile testing is the preferred method when dealing with highly extendible materials, for example.

Indentation tests, using indentors of various geometry's (cones, hemispheres, diamonds etc.) are sometimes used to give information about the time dependent mechanical behaviour of a material. The basic test consists of pressing the indenter against the test surface, the load is controlled and the size or depth of the indentation is measured. The main disadvantage of these techniques is that the area of contact between the indenter and the specimen does not remain constant, but is constantly changing. The basic viscoelastic properties can not be easily calculated using these techniques. As will be

seen transient tests form the bulk of viscoelastic research carried out on soft liners, mainly because of the ease and cost effectiveness of the technique.

3.1.2. Low Frequency Free Vibration

If a sample of material is displaced from its rest position, on its release free oscillation will ensue. The frequency of these oscillations and the rate at which they die is governed by viscoelastic theory. This is the idea behind the free vibration method. The main drawback with this group of methods is that the frequency of the vibration is not directly controlled by the user, but is related to the resonant frequency of the system. In particular the frequency is not held constant, and is subject to drift as the temperature and therefore the stiffness of the material is changed.

In the frequency region from 0.01 to 50 Hz the torsion pendulum is the most popular instrument. It is not normally possible to investigate higher frequencies, as the natural frequency of the apparatus interferes with the measurements. The instrument consists of two inertia bars suspended by metal wire, which are connected in series with samples of the test material. Knowing the inertia of the bars and the mechanical properties of the wire, the effect of the viscoelasticity of the sample on the oscillation of the system can be isolated and hence its shear modulus and loss tangent worked out. The temperature of the sample is normally controlled, providing a spectrum of thermal material properties. Difficulties can arise in the transition region, as the extremely 'lossy' nature of the materials makes accurate measurements very difficult.

Although by definition, not a free vibration technique, rebound resilience provides information on the viscoelasticity of a material. A round striker falls from a known height onto the sample which is maintained at a known temperature. The percentage of the rebound height gives information on the internal friction of the material. A wide temperature range can be easily scanned.

3.1.3. Forced Vibration

The forced vibration experiments are of particular interest as this is the method which is used in this report. The main attraction of the non-resonance vibration technique is that the frequency is continuously and accurately controlled through out the experiment.

Forced vibration techniques involve imposing a cyclic stress or strain on the sample and measuring the resulting strain or stress. It is the best method available for studying high loss materials as it has none of the inherent difficulties associated with the torsional pendulum and resonance methods.

3.1.4. High Frequency Resonance Methods

Resonance methods rely on standing waves of high frequency. The length of the standing waves decreases with increasing frequency until it is comparable with the dimensions of the sample. The sample is then a resonating system. The modes of vibration used are flexural, torsional and longitudinal, in order of increasing frequency. This method is characterised by the extremely low amplitudes of its vibration.

One manifestation of the resonance method is the vibrating reed, with a frequency range of 10 to 2000 Hz. This consists of a thin rectangular cross-section of the material, rigidly clamped at one end while the other end is excited over the frequency range. From the resonant curve of vibration versus frequency the modulus and loss factor of the material can be determined.

3.1.5. Wave propagation

The wave propagation method employs frequencies in the ultrasonic region, extending from 20 kHz upwards. In this range the wavelength of the stress wave is always smaller than the dimensions of the sample.

A comprehensive account of the various dynamic measurement systems has been given in Murayama (1978), Ferry (1980) and Read and Dean (1978). Clarke (1988) also

carried out a comprehensive survey of viscoelastic measurements, with a particular focus on dental materials.

3.2 Determination of the Viscoelasticity of Soft Liners

The bulk of the previous work carried out on the viscoelastic properties of soft lining materials and oral mucosa is presented in table 3.2.1.

Author	Title	Date	Methods
Storer	Resilient denture base materials. Part I. Introduction and laboratory Evaluation.	1962	Hardness test
Bates & Smith	Evaluation of indirect resilient liners for dentures: Laboratory and clinical tests.	1965	Hardness test
Tomlin et al	The thickness and hardness of soft tissues.	1968	Handheld probe.
Wilson & Tomlin	Soft lining materials: some relevant properties and their determination	1969	Creep
Braden & Clarke	Viscoelastic properties of soft lining materials	1972	Torsional pendulum
Going et al	Mouth guard materials: Their physical and mechanical properties.	1974	Hardness test
Suchatlampong	Some physical properties of four resilient lining materials	1975	Stress relaxation
Wright	Soft lining materials: their status and prospects	1976	Torsional pendulum
Manderson & Brown	A clinical and laboratory investigation of a new denture cleaner	1978	Rebound resilience
Duran et al	Viscoelastic and dynamic properties of soft liners and tissue conditioners	1979	Creep & Dynamic
Ellis et al	Variations in the elastic modulus of a soft lining material	1980	Transient
Clarke & Braden	Determination of viscoelastic properties of dental polymers by mechanical impedance measurements	1982	Mechanical Impedance
Robinson & McCabe	Creep and stress relaxation of soft denture liners	1982	Creep / Stress relaxation

Parker & Braden	New soft lining materials	1982	Torsional pendulum
Schmidt & Smith (a & b)	A six year retrospective study of Molloplast B lined dentures (Part I) (Part II)	1983	Hardness test
Inoue et al	Viscoelastic properties of oral soft tissue. 1. A method of determining elastic modulus of oral soft tissue.	1985	Handheld device
Kazanji & Watkinson	Influence of thickness, boxing, and storage on the softness of resilient denture lining materials.	1988	Hardness test
Parker & Braden	Soft prosthesis materials based on powdered elastomers.	1990	Torsional pendulum.
Graham et al	Clinical compliance of two resilient denture liners	1990	Indentation probe
Quadah et al	The effect of thermocycling on the hardness of soft lining materials	1991	Indentation probe
Holt et al	Force versus time profiles of selected heat-processed denture liners	1991	Transient
Dootz et al	Comparison of the physical properties of 11 soft denture liners	1992	Hardness test
Dootz et al	Physical property comparison of 11 soft denture lining materials as a function of accelerated ageing	1993	Hardness test
Jepson et al	Evaluation of the viscoelastic properties of denture soft lining materials.	1993	Hand held creep probe
Jepson et al	Age changes in the viscoelasticity of permanent soft lining materials	1993	Hand held creep probe
Kawano et al	Effect of soft denture liner on stress distribution in supporting structures under a denture.	1993	Finite element study.
Collis	Assessment of a recently introduced fluoroelastomeric soft lining material	1993	Hardness test
Hayakawa et al	The creep behaviour of denture supporting tissues and soft lining materials.	1994	Creep
Kalachandra et al	Characterisation of commercial soft liners by dynamic mechanical analysis.	1995	DMA

Jepson et al	A new temporary soft lining material	1995	Hand held creep probe
Wagner et al	Dynamic viscoelastic properties of processed soft dentures liners: Part I - Initial properties	1995	DMA
Wagner et al	Dynamic viscoelastic properties of processed soft dentures liners: Part II - Effect of ageing	1995	DMA
Kalachandra et al	Dynamic mechanical analysis and water absorption of some experimental soft lining materials	1996	DMA
Waters et al	Dynamic mechanical thermal analysis of denture soft lining materials	1996	DMA

Table 3.2.1. The Work surveyed in this review.

One of the first formal investigations of the properties of soft lining materials was carried out by Storer (1962a). He examined a range of materials (including Flexibase (FB)), using a variety of physical tests including: hardness, water absorption, abrasion resistance and bond strength. He used a British standard rubber hardness tester to measure the initial hardness of a materials as well as the effect of storage in water (at 37 °C for up to 30 months) on these properties. A range of properties were observed for different materials. In the case of FB an 18% increase in the hardness was observed over this time period. This was accompanied by a small amount of water uptake. In the clinical leg of this work (1962b) they found that 77% out of the 219 patients obtained relief when a soft lining material was used.

Bates and Smith (1965) also looked at the hardness and absorption (from various media including olive oil), as well as a range of other physical properties, for a number of soft lining materials (including FB and Molloplast (MP)) and tissue conditioners*. They used a spherical indenter to obtained hardness values although they used International rubber

* They made no distinction between the two. Wilson & Tomlin, 1969. Duran et al, 1979. Ellis et al, 1980. Graham et al, 1990. and others have also failed to make this distinction.

hardness degrees (IRHD). They noted that the hardness of the acrylic materials was more temperature dependent than that of the silicones. In the clinical part of their investigation they noted that 60% of the patients were more comfortable and had less pain. Although they identified a broad range of elastic and 'plastic' behaviour they could not identify an ideal range for these properties, as both were acceptable to patients.

In 1968 Tomlin et al made an *in vivo* study of the mechanical properties of soft oral tissues. The instrument used was a hand held force distance probe which was steadily pressed against the oral mucosa, until a maximum force of 5N was achieved, force and distance were recorded. Twenty five patients aged from 35 to 55 were selected, none of these patients had worn dentures and all had been edentulous for at least six months. The test consisted of pressing the probe in to the mucosa of the mandible at sites where the patients teeth had once been. The authors recognised, although did not take into account, the time dependent modulus of the mucosa. They concluded that although for some patients the thickness of the mucosa and its modulus were constant in all areas tested, in other patients considerable variations occurred in different areas of the same mouth. There was no correlation between thickness and the softness of the mucosa and both these factors could vary independently of each other. They did however find that 82% of the soft tissue tested was between 1.5-2.0 mm's thick and that 52% had a modulus of 2.0 MPa. The thickness values ranged from 1 mm to 3 mm while the modulus was found to be as low as 0.4 MPa.

Wilson and Tomlin made a study of the viscoelastic properties of 7 soft lining materials and tissue conditioners in 1969. They employed a creep test, with a stress pulse of 56 MPa for 1 minute and recorded the strain. Of the materials looked at FB and MP had the smallest resultant strain after one minute (4% & 5% respectively) and hence the lowest creep compliance's. They were also the only two materials to recover completely after 5 minutes. The recovery of the acrylic materials was much slower with some materials not having recovered even after 5 minutes.

Braden and Clarke (1972) were the first authors to study the viscoelasticity of soft lining materials under dynamic conditions. They realised the relevance of sinusoidal loading to the conditions in the mouth and used a torsional pendulum apparatus (free vibration) to study the materials. They studied a range of materials including the acrylic, Supersoft and the silicones, FB and MP. The temperature range studied was 20-45°C but the frequency drifted from 0.1 to 0.5 Hz, although an average of 0.25 Hz was assumed. Another problem with the torsional pendulum is associated with very lossy polymers. The $\tan \delta$ graphs failing to show a peak relating to the transition of the materials. The material properties determined were the shear storage modulus (G'), which for a rubber like material is three times the Young's modulus ($3G = E$)*, the dissipative component of the modulus (G'') and the loss tangent ($\tan \delta$). The authors concluded that a wide range of material properties existed in the soft liners; the shear storage modulus ranging from 0.2 to 1 MPa, and the loss tangent ranging from 1 to 0.012. The silicones were generally less lossy than their acrylic counterparts. Table 3.2. summarises the results obtained for Supersoft, FB and MP at 37°C.

Material	Shear Storage Modulus (MPa)	Loss Tangent
Supersoft	0.8	1
Flexibase	0.9	0.1
Molloplast	0.5	0.06

Table 3.2.2. Viscoelastic parameters for of selected materials at 37°C (Braden & Clarke 1972).

The physical and mechanical properties of mouth guard materials were the subject of a contribution by Going et al in 1974. Fifty seven mouth guard materials were investigated including natural rubber, PVC, soft acrylics and polyurethane based

* This assumes that the poissions ratio of the material is 0.5 which is true for most rubbers, but not necessarily true for polymers going through their transitions.

materials. A range of physical tests were carried out including tensile strength, elongation and water absorption. In relation to viscoelasticity, hardness measurements and impact energy tests were also carried out. The hardness tester was a 'Rex A durometer'. Readings were taken initially and after 15 seconds of contact to gauge the creep response of each material. A range of 'Rex A' hardness values in the region of 66-86 was seen with some materials being more time dependent than others. A rebound range of 22% to 74% was seen. Without adverse clinical data the authors concluded that all the mouth guards under investigation provided adequate protection.

Suchatlampong et al (1975) studied the compressive behaviour, as well as water uptake and solubility, of four soft lining materials, including the three just mentioned. The effect of sample thickness on compressibility was investigated, with the authors recommending a 2 mm thickness. The mechanical testing was transient in nature where the strain was specified and the stress examined. The viscoelastic nature of the materials was not considered however and stress relaxation during the loading cycle although recognised, was not taken into account. This had the effect of over testing the acrylic polymers which were more viscoelastic at test temperatures as they went through their T_g, as opposed to the silicones which were in the rubbery phase of their behaviour.

In 1976 Wright measured the viscoelasticity of a number of additional soft lining materials to those investigated by Braden and Clarke (1972) as well as carrying out water absorption and solubility experiments. He also investigated the optimum thickness of soft liners bonded to PMMA and recommended a layer 2-3 mm thick. Above this level any increase in thickness yielded an insubstantial increase in the softness of the sample.

The response of soft lining and other denture related polymers to various denture cleaners was investigated in 1978 (Manderson & Brown). They studied Supersoft and Molloplast B as well as other soft liners, tissue conditioners and denture base materials.

They looked at the rebound resilience of the materials using a simple pendulum which bounced off the samples. The percentage change of the resilience before and after immersion in cleaning fluids was measured. The fluids used were an acidic and an alkaline denture cleaner as well as water. It was seen that Supersoft's resilience increased the most (10.8-12.9%). Although the change was not particularly sensitive to the immersion fluid. Molloplast B also increased in resilience, but by a smaller margin, 1.8% in water and 3.5-5.0% when immersed in the denture cleansers. In contrast the cold cured silicone and the tissue conditioner both became more lossy, with 5.3-9.7% and 5.8-18.5% losses in resilience, respectively.

Duran et al (1979) made a study of three tissue conditioners and four soft liners including Supersoft. They used transient and dynamic methods of testing. The transient experiment took the form of a creep test. They derived a viscosity value by taking the value of the steady slope portion of the creep compliance versus time curve*. They also took their creep compliance value from the intercept of the same line on the y axis. Two different levels of loading were considered at 5.3 and 10.3 N, the larger load giving a lower value of compliance (i.e. stiffer). The compliance of Supersoft was seen to decrease over a 3 month period in water from 1.71 to 1.04 MPa⁻¹ for the larger load. This is a 40% increase. A smaller load was used for the tissue conditioners but they were still seen to be approximately 10 times less stiff than Supersoft. The dynamic test gave a modulus value of approximately 7.5 MPa for Supersoft which was significantly higher than that obtained by the creep test. The dynamic test however failed to notice any hardening after 3 months storage in water. Unfortunately important parameters of the dynamic method such as the frequency and mode of deformation were not enclosed so it is difficult to reach any quantitative conclusions.

In 1980 Ellis et al investigated the variations in elastic modulus of a tissue conditioner 'Coe-Soft', which they wrongly identified as a soft-lining material. The samples were

* Equivalent to the η_1 value of the 4element model in the theory chapter.

immersed in water, brine (artificial saliva) and 30% glucose solutions and the water uptake and compressive modulus were continuously monitored. The modulus readings were carried out at 37°C and took the form of an increasing stress whose corresponding strain was measured, from which a modulus value was calculated. In all cases the samples in solution lost weight as ethanol leached out of the material. It was seen that the diffusion was more pronounced in water than in artificial saliva or glucose solution. This was mirrored by the variations in modulus, as the samples held in water lost their compliance to a larger extent. Parallel to these laboratory tests a set of in vivo experiments were also carried out. Discs of the material were mounted on sheets of PMMA and held in an appliance in the mouth of 9 male volunteers. The overall age of the samples, 4-8 days and the total amount of time worn in the mouth were recorded. When not wearing the appliance the subjects were told to store the samples in water. Modulus results in the range $0.56 - 1.99 \times 10^5$ Pa were found, and it was concluded that the individual variations in saliva have a large influence on the ageing behaviour of the materials.

In 1982 Clarke and Braden sought to determine the viscoelastic properties of dental polymers by mechanical impedance measurements (High frequency resonance). The materials under investigation included Supersoft, Flexibase and Molloplast B. as well as a selection of hard denture base materials. This method of testing suffered from needing very large samples, these were 200 mm long and 9 mm in diameter, which were difficult to manufacture, especially for the soft materials. These rods were cemented onto the impedance head of the apparatus and excited through the frequency range of 0.02-20 kHz. The tests were all carried out at room temperature. From viscoelastic wave theory the modulus and loss tangents were calculated. The results were compared with torsional pendulum data (Braden and Clarke, 1972) and static test data. It was seen that the silicones were not as affected by this change in the time scale. Presumably because their T_g was far below the experimental temperature, but the acrylic whose T_g was close to room temperature had a large increase in modulus, indicating that at this frequency

the material was approaching the glassy state. For comparison the modulus of Perspex was also quoted.

Material	Torsional pendulum	Mechanical Impedance
Supersoft	0.0025	0.54 at 0.96 kHz
Flexibase	0.0028	0.0025 at 1 kHz
Molloplast B	0.0016	0.0094 at 1 kHz
Perspex	3.33	5.77 at 2 kHz

3.2.3. Young's Modulus (GPa) of various soft lining materials at room temperature (Clarke & Braden, 1982).

These mechanical impedance measurements while interesting are of limited clinical relevance as the temperature and frequency of the experiment are not those which are likely to be experienced in the body.

The creep and stress relaxation of three soft lining materials and a tissue conditioner were investigated by Robinson and McCabe in 1982. The materials (Molloplast B, Flexibase and Supersoft) were tested at room temperature; as processed and after a 3 month immersion in water at 37°C. Mechanical testing at room temperature detracts from the usefulness of the results as the materials are used at mouth temperature.

In the creep test, specimens were subjected to a 11.76 N stress pulse (98 kPa). Problems were encountered with the silicone materials. Due to imperfections with the sample geometry, a small pre-load (66 g) was applied for 30 seconds, the strain value zeroed and the full load subsequently applied. This was required for the silicones to bring them into uniform contact with the plates but not for the acrylic materials which flowed easily to give reasonable contact. The change of strain with time was noted after the application of this load and the creep compliance and hence the time dependent modulus was calculated. Some of their results are summarised in table 3.2.4.

Material	10 seconds	60 seconds	600 seconds
Supersoft (Dry)	2.4	1.5	1.2
Supersoft (Wet)	2.77	1.66	1.19
Molloplast (Dry)	3.5	3.5	3.48
Molloplast (Wet)	4.76	4.76	4.64
Flexibase (Dry)	2.38	2.34	2.3
Flexibase (Wet)	2.14	2.14	2.12

Table 3.2.4. Creep Modulus (MPa) carried out at room temperature (Robinson & McCabe, 1982)

The time dependent nature of the acrylic based material can be seen in contrast with the essentially elastic behaviour of the two silicone materials. For the stress relaxation experiment a constant strain value was not arbitrarily chosen, instead for each material the same value of strain observed at 10 seconds in the creep experiment above was selected. Supersoft relaxed by 80% in one minute, while Molloplast B and Flexibase relaxed by less than 10% and 20% respectively.

In 1982 Parker and Braden developed and tested two fundamentally different types of soft lining materials. These are the acrylics incorporating polymerisable plasticisers and powdered elastomers as described in section 1.4.5. They were tested by a torsional pendulum apparatus as used by Braden and Clarke in 1972. For the plasticised acrylic it was seen that by controlling the level of the plasticiser a wide range of viscoelastic properties could be engineered at any given temperature. For the powdered elastomer the values of storage shear modulus (3.3 MPa) and $\tan \delta$ (0.36) were obtained and compared with that of existing materials.

A double paper published by Schmidt and Smith (1983 a,b) concentrated on one soft lining material, Molloplast B, with liners being examined up to and after six years service. The first part was concerned with patient response with nearly all the patients

(93%) agreeing that the lining increased comfort. In the second part, which dealt with serviceability, the resilience of the liners was evaluated by a Shore durometer and compared with that of newly processed liners; in general the length of time in service did not have an appreciable effect on the hardness of the liner. The average reading from the Shore durometer was 55.8 and had a range from 36 to 72. The average thickness in the buccal shelf area was 2.8 mm and had a range from 1.5 to 5.8 mm. The dependency of hardness on thickness of liner was determined by making samples of various thicknesses. It was again seen that 2-3 mm was the ideal thickness for a soft liner as above this depth the softness was not very responsive to further increases in the thickness.

In 1985 Inoue et al published a paper on the mechanical behaviour of the oral soft tissue. They used a hand held device which could measure the force applied and the subsequent deflection of the soft tissues. Measuring the modulus at various anatomical landmarks for two patients (a man 44 years old, and a woman of 51 years) they found a range of values from 0.66 to 4.36 MPa. They did not take into account the time dependence of the mucosa's modulus.

Kazanji and Watkinson (1988a) studied the effect of thickness, storage and boxing in on the softness of 5 materials including Supersoft, Flexibase and Molloplast B. The testing equipment employed was a Shore durometer hardness tester. It was concluded that softness was a function of thickness and that a minimum thickness of 1.8 mm should be used in soft liners to provide adequate compressibility. Boxing in had a slight effect on the softness of the materials more so for Molloplast than Supersoft. After immersion in water for 6 months a familiar trend was observed as the acrylic became harder due to the leaching out of plasticiser, the silicone became softer.

In 1990 Graham et al studied the clinical compliance of two materials, one of which was a tissue conditioner. They failed to take into account the time dependency of the

properties of these materials. The testing apparatus was an indentation probe. To measure compliance, the material was indented to half of its measured thickness, and the force required to do this was recorded. The stress and strain, and hence the compliance of the material was calculated. The observed trend was a reduction in compliance for the materials over time, this reduction being similar in magnitude for both materials.

Also in 1990 Parker and Braden presented a further contribution to the work concerning soft liners based upon powdered elastomers and methacrylate monomers. The range of elastomers which these materials were based on included: natural rubber, butadiene styrene and butadiene acrylonitriles. These were mixed with a range of alkyl methacrylate (MA) monomers including 1-tridecyl MA, 2-ethylhexyl MA, 2-ethoxyethyl MA. The latter has since been found to be biologically suspect (Braden et al, 1995). The elastomers and the methacrylate monomers were mixed in various quantities to form doughs which were then cured by heat. A series of physical tests were then carried out including tensile, tear adhesion, water uptake and viscoelastic. For the latter they used a torsional pendulum as before to obtain values for G' , G'' and $\tan \delta$. A representative example of their results is presented in tables 3.2.5. and 3.2.6.

Powder/Liquid	Shear Storage Modulus (MPa)	Tan δ
0.3	27.8	0.37
0.4	15.4	0.39
0.45	12.5	0.39

Table 3.2.5. Effect of powder to liquid ratio on a natural rubber/2-ethoxyhexyl methacrylate system (Parker & Braden 1990).

% EGDM by Volume	Shear Storage Modulus (MPa)	Tan δ
30	12.10	0.25
20	6.66	0.31
10	2.20	0.36

Table 3.2.6. Effect of cross linking on viscoelastic properties of a butadiene acrylonitrile/2-ethoxyhexyl methacrylate system (Parker & Braden 1990).

From Table 3.2.5. it can be seen that as the rubber content of the sample increases the material becomes more compliant, although its resilience is not particularly affected.

From Table 3.2.6. it can be seen that increased cross linking has the effect of increasing the modulus but lowering the loss tangent of that particular system. Overall their experimental materials had a shear storage modulus ranging from 0.175-56.2 MPa and a loss tangent range of 0.13-0.42.

In 1991 Quadah et al made a study into the effect of thermocycling on the hardness of soft lining materials. The testing instrument was an indenter. Different loads were applied to different materials, due to the ranges of material stiffness, therefore it is not easy to compare the various materials to each other. It was concluded that thermocycling has a deleterious effect on the properties of all the materials. The relevance of the method of thermocycling is debatable. Control specimens were stored at 20°C while the trial specimens were taken from 18 to 53°C (average value of 35°C). It is well known that the diffusion of water is strongly related to temperature, with the diffusion coefficient, being a function of temperature. The relevance of thermocycling is therefore unclear, as the trial set of specimens are at a higher average temperature than the control ones. They would in any event be likely to interact with the water more quickly, with or without thermocycling.

In 1991 Holt et al published their research into the force versus time behaviour of 4 soft lining materials, two of which were silicone based (including Molloplast) and two of which were acrylic based (including Supersoft). Their research involved 9 patients who were not satisfied with the hard denture base due to 'soreness' and inability to chew a soft-solid diet. They each received a soft lined denture, lined with a 2 mm thick layer of silicone or acrylic based material. Each denture was tested before placement and re-tested after 7, 32 and 92 days of use. A mechanical indenter (3 mm diameter) was used at a test temperature of 37°C, to apply a perpendicular load to the lined surface of the denture. A pre-load of 0.09 kg was used for initial contact. At time t_0 the loading was started with an indentation speed of 0.02 in/min, this was over a duration of 2 minutes. The indenter was then held at this position for 1 minute, over which time the relaxation of the material was observed. After this, the material was unloaded at the same rate until the force reached zero. The parameters investigated were the loading time t_l (constant at 2 minutes), unloading time t_{ul} , F_{max} recorded at the end of the loading time and F_{min} recorded at the end of the relaxation time. From these quantities a 'Rebound index' was defined as the ratio of the forces F_{min}/F_{max} , multiplied by the ratio of the times t_{ul}/t_l multiplied by 100%. This is not a common viscoelastic quantity, but was here used to distinguish the time dependant behaviour of the materials. The silicone based materials were found to have a higher rebound index. Interviews with the patients seems to indicate a preference for the silicone based materials, both in terms of increased comfort and masticatory effectiveness. The authors, whilst appreciating that no single parameter can judge the success of a soft liner, never the less correlated the rebound index with improved clinical performance. The results at 7, 32 and 92 days were inconclusive.

Dootz et al (1992, 1993) made two studies of the physical properties of soft lining materials, the latter as a function of ageing. They looked at tensile strength, elongation, tear resistance and hardness of 11 materials including Supersoft, Molloplast and Novus. Hardness was determined using a Shore A hardness instrument on specimens 10 mm thick. Hardness values from 25 to 95 Shore A units were observed with an average of

58. Molloplast, Novus and Supersoft had a hardness of approximately 43, 50 and 80 respectively (Supersoft being the hardest material). A Similarly large range of other physical properties were also observed. In the second part of this study the samples were subjected to an accelerated ageing chamber. This involved 900 hours of exposure to an ultraviolet/visible light source at 43°C and 90% relative humidity. A programmed cycle of 18 minutes of distilled water spray was used during each 2 hour period. This had the effect of hardening Supersoft to 90 Shore A units. Novus was unaffected at 50 whereas Molloplast became softer at 35.

Jepson et al, (1993a) made an in depth evaluation of the viscoelastic properties of three materials, including Coe-soft (which they identified as a temporary material), Molloplast-B and Palasiv 62 (a heat cured acrylic). The viscoelastic properties of these materials were measured both clinically and in the laboratory using a hand held force/distance probe. This was similar to the type used by Tomlin et al, 1968. The test took the form of a rapid application of the load, which was then held constant. The penetration was noted as a function of this constant stress. This is synonymous with a creep test. It was noted that the rate of the application of the stress was an important parameter, but the probe did not lend itself to the easy control of this parameter. In any case the application of the load was achieved within 1 second in all cases and this was assumed rapid enough to eliminate the variability of the strain rate. A load of 4N (corresponding to a stress of 2.17 MPa) was used and it was held constant for at least 10 seconds. For each set of data the immediate deformation and the deformation after 10 seconds were noted. On the clinical side of the study 71 patients were given soft lined dentures. Three widely spaced sites were tested with the probe at 37°C. For Molloplast-B there was very little separation between the initial compliance (0.169 /Pa) and the delayed (10 seconds) compliance (0.180 /Pa) indicating the largely elastic nature of this material. For the acrylic material this was not the case with the initial compliance (0.211 /Pa) being a lot smaller than the delayed one (0.327 /Pa). A reasonable value for the thickness was concluded to be 2 mm as above this value there was not an appreciable

increase in compliance. For the laboratory based experiments, sample thicknesses from 1 to 5 mm were used. These basically confirm the results obtained on the clinical side, with the silicone proving to be more elastic than the acrylic material.

In the follow up from the previous study Jepson et al (1993b) related the effect of age on the viscoelasticity of the two permanent soft lining materials examined previously. The same methodology and equipment were used to test the viscoelasticity of these materials. On the clinical side of the study forty four patients were given dentures lined with either of the two materials. The thickness and compliance (both initial and delayed) of these materials was recorded over 18 months, although past 60 weeks the results were not reliable as the patient numbers had dropped to too low a value, because of soft lining failure. In fact at all times after the first set of data points were gathered (at time zero) a smaller population of data points were examined. If the results are compared at various times it must be assumed that these smaller data sets are a random sample of the first set. This is not necessarily a valid assumption as the failure of the materials can be clearly linked to their viscoelasticity. In the laboratory three batches of 1,2,3 and 4 mm thick samples of each material were stored in distilled water at 37°C. These were tested at a similar time scale to that used in the clinical study. It was concluded that the viscoelasticity of Molloplast B was virtually unchanged over time, whereas Palasiv 62 showed a marked reduction in initial and delayed compliance, both in the laboratory and clinical situation. The ageing was more rapid in the mouth as opposed to the laboratory.

Collis (1993) compared two of the materials examined in this report, namely Novus and Molloplast. He looked at both distilled water absorption at 37°C and hardness using an indenter. The hardness of both materials was initially identical, at 2.25 mm thick for example both materials were 60 IRHD. After 4 months in water it was seen that Molloplast was unaffected whereas Novus had a 5% water uptake and softened slightly (58 IRHD). Novus was also more affected by various denture cleaners.

The creep behaviour of denture-supporting tissues as well as a range of experimental soft liners was the subject of a contribution by Hayakawa et al in 1994. Their aims were to investigate the creep behaviour of the mucosa and to ascertain whether the character of the mucosa can be emulated by a soft lining material. A hand held loading and measuring device was used for the creep tests. The apparatus relied on air pressure, to apply the given load. A low pressure load was used to delicately bring the loading rod into contact with the material and then a high pressure creep load was applied through a 2 mm diameter piston. A valve was fitted to release the load instantaneously. To fix the device in place a resin plate was manufactured to sit on the hard palate of each patient. This plate had holes drilled into it at sites where the measuring device could be inserted and was manually held in place by the operator. A load of 0.1 kg was applied for 30 seconds, two minutes of recovery time were allowed after load removal, with the tests being repeated 10 times with at least 24 hours between tests. Displacements were measured as the instantaneous (S1), delayed elastic (S2), and viscous (S3) displacement*. Similarly the material behaviour upon recovery was divided into three parts, S1', S2' and S3'. The subjects investigated were 8 men with a mean age of 27 years. Young individuals were chosen so that the properties of healthy mucosa could be studied. The results were analysed using the creep curves and a four element model. Experimental materials consisted of a monofunctional monomer with a light polymerising initiator, while various amounts of cross linking agent and inorganic filler were used to control the properties. These materials were made into 2 mm thick samples and stored in air at 25°C for 24 hours before measurement using the apparatus previously described. The authors concluded that by controlling the degree of cross-linking and the amount of filler in the material its viscoelastic properties could be made to emulate those of the mucosa.

In 1995 Kalachandra et al characterised the dynamic viscoelastic properties of four commercial soft liners using a forced vibration, dynamic mechanical analyser of the

* See four element model in Chapter 2.

same type used in this investigation. Molloplast B, Novus and Supersoft were investigated. The tests were carried out on dry materials and after storage in water for up to 100 days. Each measurement was only carried out once. The samples were only 1.5 mm thick, less than the recommended thickness of 2 mm. They were cyclically compressed at 1 Hertz with a dynamic stress of 5 kPa amplitude using a 3 mm diameter flat tip probe. Superimposed on this was a static stress of 50 kPa to keep the samples in contact with the loading plates at all times. Each test run consisted of measurements whilst the specimens were taken from 5 to 95°C at the rate of 2.5°C per minute, from which plots of the storage modulus and $\tan \delta$ were obtained for all the materials in the wet and dry states. Their results at 37°C are summarised in table 3.2.7.

Material	E' (dry)	E' (wet)	Tan δ (dry)	Tan δ (wet)	% Uptake
Molloplast	4.8	5.1	0.005	0.005	0.5
Novus	6.2	3.5	0.12	0.1	34.0
Supersoft	10.0	8.0	1.25	1.25	5.0

Table 3.2.7. DMA properties of commercial soft liners (Kalachandra et al, 1995)

It was concluded that DMA was a useful tool for studying soft liners and that large differences in the physical properties were seen in the materials tested.

A new light cured temporary material (LiteLine) was investigated in vitro by Jepson et al in 1995 using similar equipment and methods as in their 1993 articles. It was seen that this material was harder than its competitors and that its compliance was little affected by the sample thickness. Furthermore, immersion in water had no significant effect on the compliance and elasticity of the material.

Wagner et al studied 12 commercial soft liners in 1995(a) using a custom made 'Viscoelastometer'. Samples of material (1.4 x 3 x 40 mm) were extended sinusoidally at

two temperatures (23 and 37 °C) and three frequencies (1, 5 & 10 Hz), further more each test was repeated 5 times and the results averaged. E', E'' and tan δ were calculated for these conditions. The results relating to Supersoft, Novus and Molloplast are summarised in three tables below*.

Frequency (Hz)	E' at 23°C	E' at 37°C	Tan δ at 23°C	Tan δ at 37°C
1	16.65	2.59	1.12	1.25
5	34.9	7.24	0.77	1.47
10	46.01	11.97	0.7	1.4

Table 3.2.8. Viscoelastic properties of Supersoft (Wagner et al, 1995a).

Frequency (Hz)	E' at 23°C	E' at 37°C	Tan δ at 23°C	Tan δ at 37°C
1	2.30	2.20	0.13	0.12
5	2.63	2.48	0.18	0.14
10	2.86	2.65	0.24	0.18

Table 3.2.9. Viscoelastic properties of Novus (Wagner et al, 1995a)

Frequency (Hz)	E' at 23°C	E' at 37°C	Tan δ at 23°C	Tan δ at 37°C
1	1.45	1.5	0.02	0.02
5	1.51	1.53	0.03	0.03
10	1.54	1.55	0.04	0.03

Table 3.2.10. Viscoelastic properties of Molloplast (Wagner et al, 1995a)

As would be expected the higher frequencies increased the stiffness of all three materials. The loss tangents of the latter two materials increased with frequency as they were shifted towards their glass transitions in the frequency domain. The opposite was true for Supersoft at 23°C as it was moved away from its T_g. At 37°C an inflection is

* The Storage modulus results are assumed to be in MPa although this is not specified in the article.

seen for the loss tangent of Supersoft indicating that at this temperature its T_g is between 1 and 10 Hz on the frequency domain. Relating to other materials investigated (i.e. apart from the above), at 1 Hz and 37°C a familiar large variation was seen in their properties, the E' for example ranged from 0.73 to 41.61.

The second part of this study (Wagner et al, 1995b) used a similar ageing technique to that of Dootz et al (1993), involving 900 hours of visible and ultraviolet light and distilled water sprays. Samples were tested at 1 Hz and 37°C. The following results were obtained. As can be seen Novus and Molloplast were comparatively unaffected, whereas Supersoft increased its stiffness by nearly 8 fold compared to that obtained in Wagner et al (1995a).

Material	E' (MPa)	Tan δ
Supersoft	20.1	0.93
Novus	2.6	0.13
Molloplast	1.2	0.05

Table 3.2.11. DMA properties of 3 commercial soft liners after accelerated ageing (Wagner et al, 1995b).

Kalachandra et al (1996) examined 5 experimental acrylic materials based on a butadiene styrene copolymer. Two different monomers, different levels of cross-linking agent (EGDM) and different initiators were used. Both DMA and water absorption properties were looked at, using similar techniques as before (Kalachandra et al, 1995). In the dry state the materials had a storage modulus ranging from 14 to 20.9 MPa, which after immersion in water had reduced for all the materials to 11.6 - 16.0 MPa, probably due to plasticisation effect of the water. This was confirmed by the glass transition of the five materials which also decreased in all cases from 20 - 9 when dry to 17 - 5°C after immersion. The loss tangent of the 5 materials mirrored this trend, decreasing from 0.21 - 0.37 in the dry state to 0.16 - 0.32 in the wet state. Of the five materials one had

the same composition as the BS material studied here and its properties at 37°C are listed in Table 3.2.12.

BS Material	Dry	Wet
E' (MPa)	20.9	16.0
Tan δ	0.37	0.29
Tg (°C)	20	17

Table 3.2.12. DMA and water absorption of BS material (Kalachandra et al, 1996).

Waters et al made a study of the dynamic viscoelastic properties of 6 permanent soft lining materials in 1996a. The specimens were cut into 10mm diameter, 3mm thick samples and subjected to sinusoidal shear deformation at 1 Hz, each reading was repeated 5 times. Measurements of G', G'' and tan δ were made at 30, 37, 50 and 70 °C. The results obtained for Supersoft, Flexibase, Novus and Molloplast at 37°C are presented here.

Material	G' (MPa)	Tan δ
Supersoft	0.311	1.078
Molloplast	0.439	0.066
Flexibase	0.509	0.158
Novus	0.355	0.117

Table 3.2.13. Shear storage modulus and the loss tangent of selected soft liners (Waters et al, 1996).

The results show that the acrylics have the highest loss tangent by far as would be expected. The relatively small difference in the modulus figures for the 4 materials is surprising and not consistent with some of the earlier work on this subject.

CHAPTER FOUR

INSTRUMENTATION: DYNAMIC MECHANICAL ANALYSIS

4.1. Introduction to the Apparatus

The bulk of the experimental work carried out in this thesis involves the measurement of dynamic viscoelastic parameters of various soft lining materials. The materials investigated in this report have already been outlined in section 1.4. While the principles behind dynamic viscoelastic measurements were dealt with in section 1.2.3. This chapter therefore focuses upon the instrumentation; this was the Perkin Elmer DMA-7* dynamic mechanical analyser. A summary of the important features of the instrument are presented here.

4.1.1a. The Hardware.

The DMA 7 instrument consists of four main components.

- *Linear force motor.* The force applied by the motor being proportional to the current supplied to the force coil. The current can take the form of DC (constant force), AC (sinusoidal force) or a combination of the two.
- *Linear variable differential transducer (LVDT).* The position transducer produces a voltage proportional to its deflection from a central null datum. The output of the LVDT can then be compared to the input of the force motor. The amplitude being related to the storage modulus E' and the phase lag to the loss modulus E'' .
- *Core rod and measuring system assembly.* The measuring systems allow loading of samples in various deformational modes and configurations, thus extending the application range of the instrument. A range of measuring systems are available and will be discussed in section 4.1.3.

*

DMA 7, Serial No 138656
Perkin Elmer
Post Office Lane B
Beaconsfield, Buckinghamshire
England HP9 1QA

- *Heating/Cooling system.* Low inertia, fast response furnace, enclosed in a cooling (liquid nitrogen) system.

A schematic diagram of the internal arrangements of the instrument is represented in figure 4.1.1. Figure 4.1.2. consists of a photograph of the instrument while Figure 4.1.3. is a close up of a representative measuring system.

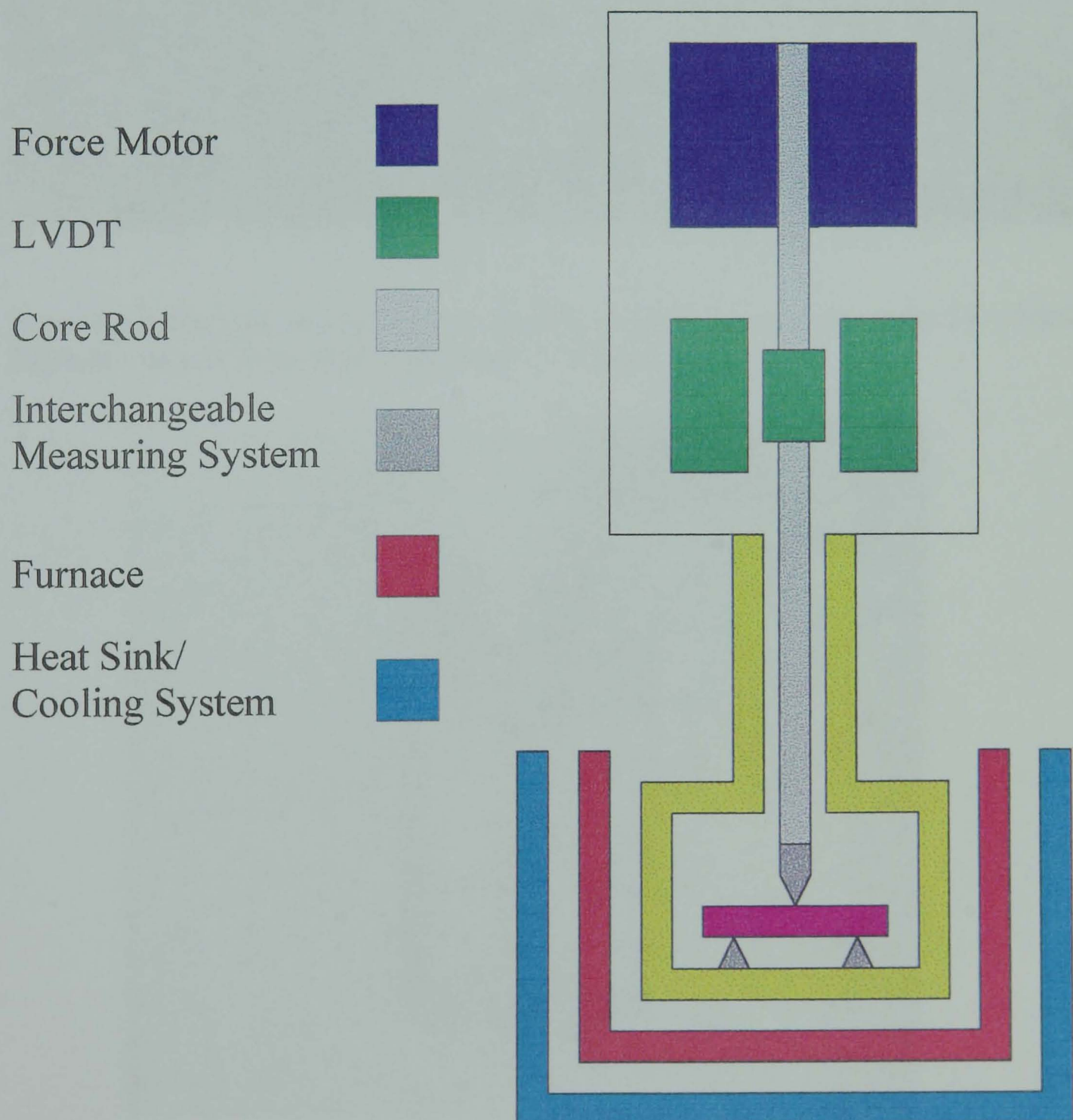


Figure 4.1.1. Schematic cross-section of the apparatus.



Figure 4.1.2. The instrumental set up consisting of DMA 7 connected via the TAC 7/DX Thermal Analysis Instrument Controller to Computer.

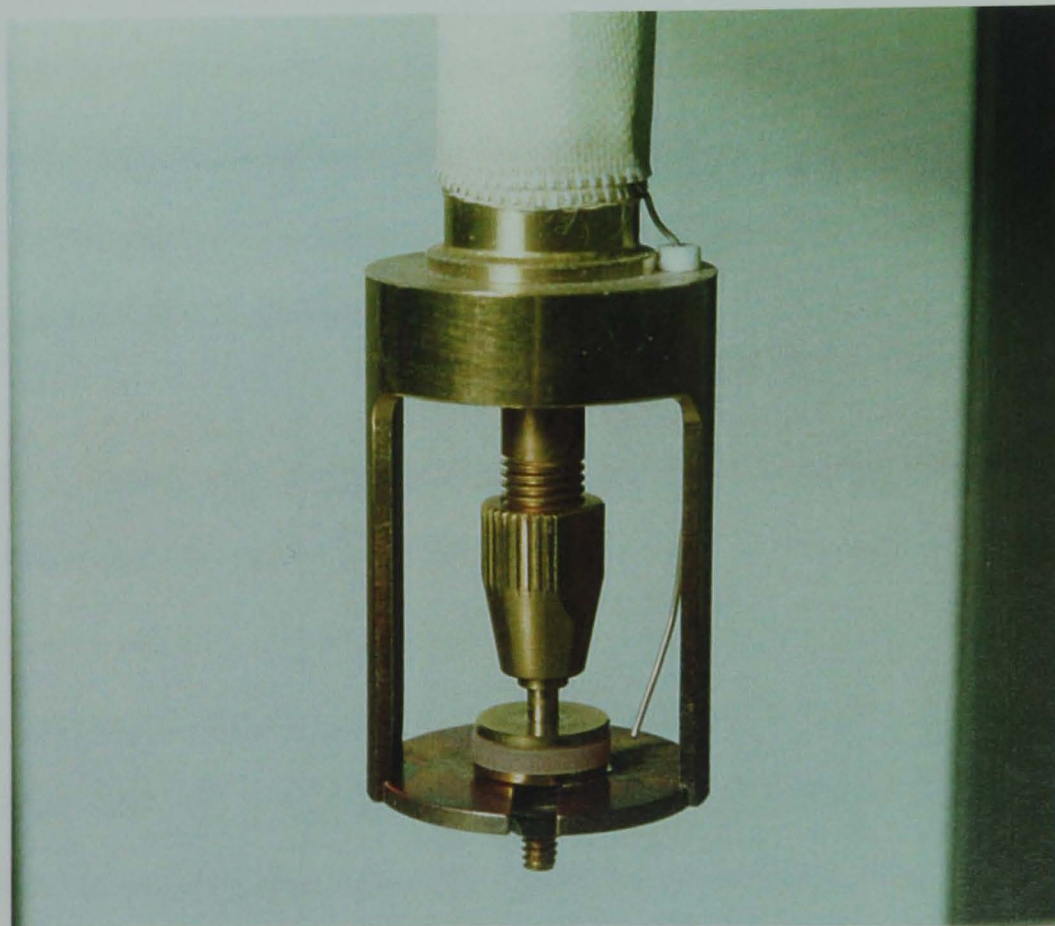


Figure 4.1.3. Close up of the 10 mm diameter Parallel Plate measuring system.

The instrumentation requirements include: 10 Amp, 240 Volt, high quality (low noise) electrical supply. Stable, vibration free, flat mounting surface. High purity, dry purge gas (Helium or Nitrogen) at constant pressure. Clean, relatively temperature stable and low humidity environment and an appropriate coolant, depending on the cooling system in use.

4.1.1b. The Measuring Systems

While the force motor and the LVDT are integral parts of the instrument a variety of interchangeable measuring systems are available to enable investigation of a range of materials with differing physical properties using a variety of deformational modes. These deformational modes include: three-point bending, extension, parallel plate, single and dual cantilever. One of the considerations for which choice of measuring system is used is that the forces provided by the instrument should convert into displacements of an appropriate magnitude which can be accurately measured*. For example, a steel rod under tension will not deform as much as it would in a three-point bend, if the same forces are used in both cases. An extension test therefore might not be satisfactory. Conversely it would not be appropriate to examine a rubber 'rod' under bending conditions as it would be too compliant (for example deform under its own weight), so that extension could be a better choice.

The 3-point bending system, such as incorporated in the instrument used by Clarke (1988) can be used to study materials with high modulus, including thermoplastics, composites, resins and polymers below their Tg's. The mode of deformation is flexure, the basic sample geometry can be a beam, including rods and tubes as well as sheet stock. Single and dual cantilever arrangements are available to study the behaviour of materials with a mid range of moduli. An extension analysis system is available to study materials of various modulus in tension, including fibres, hairs and standard tensile samples. Parallel plates are the measuring system of choice for viscous liquids and soft

* This topic is discussed at length in section 4.1.3.

solids. A range of plates is available from 1 to 20 mm in diameter. The measuring systems available are summarised below (table 4.1.1).

Measuring System	Deformation Type	Stiffness Range
Three-point bending	Flexural	High
Cantilever	Flexural	Mid-range
Extension	Tensile	Mid-range
Parallel Plate	Compressive	Low

Table 4.1.1. DMA Measuring Systems.

4.1.2. The Software: Modes of Operation.

The instrument is computer controlled and can be operated in a number of different modes. A mode of operation is defined by the software which runs it. In each mode a selected variable or variables are programmed while the other variables are held constant. The modes of operation include:

Temperature Scan Mode. In this mode the temperature is programmed over a specified range while the frequency and stress are held constant. The viscoelastic parameters of the specimen can thus be studied as a function of temperature. Transition temperatures such as the T_g can readily be identified. Temperature scan is the mode used in this work.

Time Scan Mode. In the time scan mode, temperature, frequency and stress are held constant, and the material properties are investigated over a period of time. This mode is useful for the study of curing behaviour in polymers.

Frequency Scan Mode. The frequency of the deformation is programmed over a given range while the temperature is held constant. This mode can be used to obtain

transitions in the frequency domain, as well as to obtain information on the molecular behaviour of a material.

Stress Scan Mode. In this mode the temperature and frequency are held constant while the stresses are linearly programmed. This mode can be used to obtain information on the linear viscoelastic region.

Creep-Recovery Mode. Several experiments are possible under this heading. In the creep test a load is applied instantaneously and held constant while in the recovery test a load is suddenly removed and the recovery response observed. Instead of applying an instantaneous load a facility exists for the introduction of a creep ramp, where the rate of the introduction of the load can be controlled.

Constant Force Mode. Only static forces are applied in this mode of operation. The temperature can be programmed over a range or held constant. Temperature or time dependent behaviour is characterised by the change in sample dimensions. This mode is used to look at softening points and expansion coefficients.

4.1.3. Fundamentals of DMA: Displacement, Force, Frequency and Temperature.

The forces and displacements that the sample under investigation experiences have to be kept within certain limits. The displacement amplitude is the most vital output signal, generated by the LVDT. The full amplitude range is 1-650 microns although amplitudes in the range 5-500 μm give the best results. The phase angle is also important, the amplitude and the phase angle interact in the following way: the limits for the accurate detection of amplitude and phase angle are 1 μm , and 0.5° respectively. If both the amplitude and the phase angle are below these limits then it is very difficult to obtain decent measurements. If only one is below the limit then good results can be obtained, but for best results they should both be above 1 μm and 0.5°, respectively (table 4.1.2.).

Measured Quantity	Amplitude < 1 μ m	Amplitude > 1 μ m
Phase lag < 0.5°	Poor	Good
Phase lag > 0.5°	Good	Excellent

Table 4.1.2. The dependence of data quality on the measured parameters.

To increase the displacement amplitude the dynamic stress has to be increased appropriately. The phase angle (loss) of a material can not be changed so readily. For a viscoelastic material, altering the frequency can change the phase angle.

Paradoxically the lower the phase angle the better the quality of the experiment. This is because the apparent phase angle during an experiment can be increased by poor sample mounting, loose probes, probe misalignment, etc. All of which lead to friction and damping losses measured by the instrument and hence an increase in the phase angle. Thus the apparent phase angle can be reduced by eliminating experimental error.

Figure 4.1.4. shows the results of a temperature run on the MB material. As can be seen the results of the storage modulus curve at less than -60°C is little more than noise, corresponding to a virtually undetectable amplitude. As the material softens slightly from -60 to -50°C, the amplitude increases slightly so that the storage modulus can be estimated, although excessive noise persists and the results are not ideal. From -50°C onwards there is a dramatic transition of the material, the amplitude rises rapidly and good results are obtained.

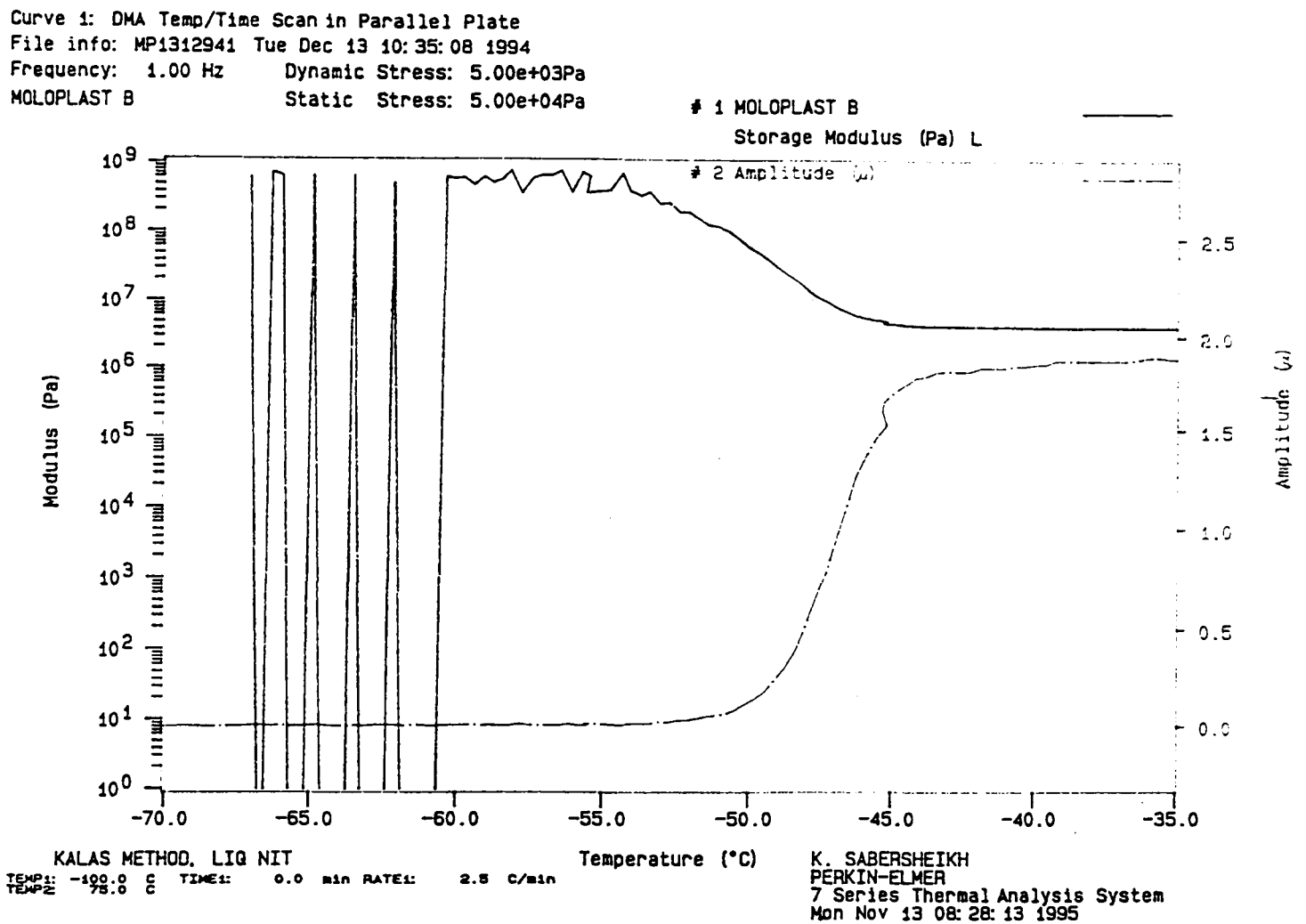


Figure 4.1.4. The effect of amplitude on the quality of the results.

The dynamic force must really be sufficient to produce an amplitude of at least 1 micron, but not greater than 650 microns as this is the maximum detection limit for the instrument. Also, to prevent the probe losing contact with the material and bouncing, a static force is superimposed on top of the dynamic force (see figure 4.1.5). The static force should be as low as possible, whilst still maintaining contact. An excessively large static force can lead to errors in the phase angle.

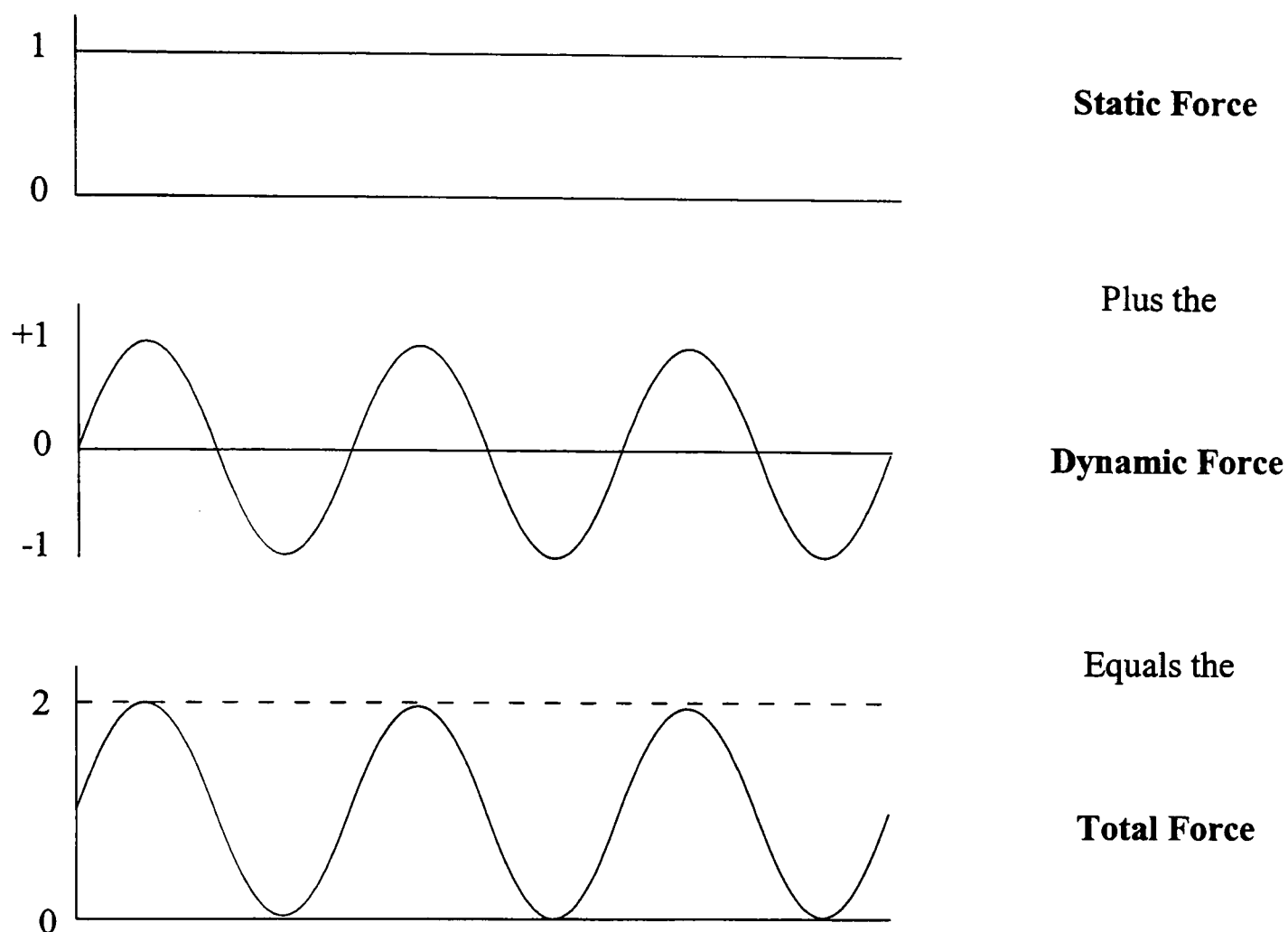


Figure 4.1.5. Total force on the sample.

The total force, i.e. the sum of the static and dynamic component available from the force motor is 2500 mN in compression and 1300 mN in extension. This, in conjunction with the various measuring systems already discussed, is theoretically sufficient to investigate materials in the modulus range of 10^3 to 10^{12} Pa. Difficulties arise when in the course of a single run the material properties change dramatically as in the case of polymers where the modulus changes spectacularly across a relatively small temperature spectrum. To accommodate this several force motor facilities are available:

Force Control. The force control is the default on the DMA 7. Both static and dynamic forces are maintained at fixed values throughout the experiment

Dynamic Control: Amplitude, Strain and Stress. In dynamic control the analyser keeps the amplitude, the strain or the stress at a constant level, depending on the respective

mode. This is accomplished by varying the dynamic force output of the motor. The application range of the instrument is thus extended.

Static Control: Position and Tension. A static force component is needed to keep the probe in contact with the sample at all times. Constant position and tension controls provide alternatives to static force control. In position control the static stress is varied during the course of a run to keep the position of the sample constant. For example if a fibre shrinks during the course of a run, the static force is increased to keep the fibre at its original length. The tension control applies a static force as a percentage of the dynamic force, enough to keep the sample and probe in contact.

The DMA has a frequency range from 0.01 to 51 Hz encompassing 258 delectable frequencies. If a specific frequency is not specified then frequency should be chosen to provide a reasonable phase angle. Problems can be encountered with the lower frequencies as the time between successive cycles becomes too large. At 0.01 Hz for example 100 seconds will elapse between each peak in the amplitude. Problems can also occur at the higher end of the frequency spectrum due to resonance. The resonant frequency of the instrument with no sample is 75 Hz which is well above the 51 Hz limit. The sample will modify this resonant frequency however. If the resonant frequency of operation is close to the operating frequency of the instrument then either the operating frequency or the sample dimensions have to be changed.

The sample and measuring system are held in a furnace enclosed in a liquid nitrogen/ice case as represented in figure 4.1.1. The temperature range of the instrument is thus -170 to 500°C. This can be extended by using different furnace and cooling systems. The rate of temperature change can be from 0.1 to 40°C per minute. The temperature rate should take into account the thermal inertia of the sample. The temperature of the sample will lag behind the temperature of the furnace, as it takes time for the sample to warm up.

4.2. Experimental Methodology

Initial work carried out was concerned with finalising the measuring system which was to be used. The dual cantilever measuring system was assessed for its suitability in studying soft lining materials. It was found not to be ideal as some of the materials being investigated were too soft at room temperature. Difficulty was experienced in mounting and clamping these compliant samples. Parallel plates were the measuring system actually used in this report. Using this geometry samples took the shape of flat disks which were held between two circular parallel plates and deformed in compression. Several sizes of plates were available ranging from 1 mm to 20 mm in diameter and again experimental work was carried out to evaluate an optimum size. The edges of the probes supplied with the instrument were machined so as to be rounded. This means that the actual area of contact was less than the nominal area of contact for small deformations. This ratio of actual area to apparent area is inversely proportional to the size of the probe. With the larger probes the difference between the two was negligible, while for the smaller probes it increased in magnitude. For larger deformations the smaller probes (1 and 3 mm probes in particular) were found to dig into the sample. Theoretically therefore the larger probes provided more accuracy. In practice however, the instrument could not always provide enough force and hence deformation to run the largest of the probes. So a compromise had to be reached. All the probes were tested, the 5 mm probes were found to give the most satisfactory results and so these were used.

Samples were cut out of 2mm sheets, whose manufacture was outlined in section 1.4.1. A cork borer of approximately 7mm internal diameter was utilised to cut the circular samples. The slight over lap (i.e. *diameter* of these samples was approximately 2mm larger than that of the probe) was required so that a 5 mm radius of material under compression could be guaranteed.

Work was then carried out to select suitable force controls. The force controls were initially used at the levels recommended by Kalachandra et al. (1995). This was not found to be ideal for the more temperature dependent materials however as the displacement amplitude was too small at lower temperatures (producing noisy results) and excessive at high temperatures (resulting in large amounts of strain). After extensive trial and error it was decided to opt for tension static control and dynamic strain control. That is to say the dynamic stress was designated to be kept at such a level to provide 0.5% strain in the sample. The static force was likewise kept at 105% of the dynamic force to prevent the loss of contact between the probe and the sample. The reasons for the selection of this method of force control were as follows: as will subsequently be apparent some of the materials investigated in this report have a 3 decade range in properties within the region of experimental interest. The best way of analysing these materials was found to be by keeping a constant level of strain through out. This means that at the high modulus range high stresses are imposed, these stresses fall proportionately as the material softens. A small level of dynamic strain was chosen for two reasons: one was to keep the materials in the linear viscoelastic region. The other reason was simply due to the maximum force limitations of the instrument. The static control was also chosen at a low value for similar reasons. Using the stress scan mode of the instrument it was verified that all the materials were in the linear viscoelastic region of their behaviour at 37°C and 1 Hz at up to 0.5% strain levels.

In the experiments the frequency of 1 Hz was used as a constant value. This was chosen as it approximates the frequency of mastication. The temperature range was similarly chosen to encompass those temperatures which are likely to be met in clinical applications (10°C to 70°C). A heating rate of 5°C per minute was found to be satisfactory.

For the sake of comparability all the materials in this investigation were subjected to the same test regime. A typical screen display from the DMA computer is presented in figure 4.2.1.

DMA7 TEMP/TIME SCAN METHOD			
Sample Parameters		Temperature Program	
Sample ID	Flexibase	Temp	Time
Comment	5mm, 0.5strain, 5%tension.	C	min
Operator ID	K. SABERSHEIKH		C/min
File Name	fb287951	1	10.0
Measuring System	Parallel Plate	2	70.0
Sample Geometry	Disc	3	-
Sample Height	2.136mm	4	-
Sample Diameter	5.000mm	5	-
Sample Zero	-2.452mm	6	-
DMA7 Parameters		7	-
Static Force	100.0mN	8	-
Dynamic Force	0.0mN		
Frequency	1.00Hz		
	DMA7 Program		
	Static Control	Tension	End Condition
	Static Setpoint	105%	Go To Initial
	Dynamic Control	Strain	Static On
	Dynamic Setpoint	0.500%	Dynamic On

Figure 4.2.1. Print out of a typical DMA method screen.

Each DMA run consisted of an initialisation process whereby the sample was carefully mounted* between the parallel plates and the sample chamber cooled down to its initial temperature of 10°C. Static and dynamic controls were then applied to the sample, run parameters were allowed to equilibrate. The run was subsequently started and the materials heated at 5°C per minute through the temperature range. A minimum of 3 repetitions were made for each material to get an idea of the reproducibility and accuracy of the experimental technique. The important parameters of the DMA test are summarised in table 4.2.1.

* Mounting of the sample is crucial as errors can easily occur due to poor mounting.

Experimental mode:	Temperature Scan.
Mode of deformation:	Compression between 5mm diameter parallel plates.
Sample geometry	Cylinder, 2mm nominal thickness.
Repetitions:	Minimum of 3.
Dynamic control	A dynamic strain of 0.5%.
Static control	A static force of 105% of the dynamic force.
Frequency	1 cycle per second (Hz).
Temperature range	10 - 70°C.
Heating Rate	5°C per minute.

Table 4.2.1. Summary of experimental parameters.

CHAPTER FIVE

RESULTS AND DISCUSSION

5. Introduction.

The results obtained during the current investigation are presented and discussed in this chapter*. These results are subdivided in the following two sections: work pertaining to materials in their initial state i.e. as processed, is found in section 5.1, and the effect of water absorption and ageing characteristics of these materials are subsequently dealt with in section 5.2.

5.1. Initial Viscoelastic Characteristics.

5.1.1. Acrylic Based Materials.

Futurasoft III (FS)

Figures 5.1.1. and 5.1.2. show the graphs of the storage modulus and loss tangent of the FS material as determined in this study using the DMA method just outlined. The graphs are typical of a polymer going through its glass transition. The modulus curve shows a dramatic drop (350 to 3 MPa) in stiffness across the 45°C temperature range shown here. The $\tan \delta$ curve has a peak at 36.8°C which can be used as a measure of the T_g^{**} . This material was the stiffest of the commercial heat cured acrylics as might be expected with regards to the absence of plasticisers in the system.

FS	E' (MPa)	S.D.	Tan δ	S.D.
37°C	19.7	1.63	1.47	0.01
22°C	209	9.06	0.779	0.04

Table 5.1.1. The viscoelastic properties of FS at mouth and room temperature.

* With the exception of some work concerning the frequency dependent characteristics of soft lining materials which is presented separately in the form of a minipaper in appendix B. This article was published in 1996, in the Polymers In Medicine and Surgery (PIMS) meeting abstract book (pp 301-308).

** In this report the peak in the loss tangent curve is used as the measure of the T_g following the trend made by other workers in the dental field (Clarke, 1988). The peak of the loss modulus (E'') and the extrapolated onset of the storage modulus drop can also be used (ASTM 1640 - 94). Although the T_g values obtained will not be consistent. The following order is generally observed:
 $T_g (E') < T_g (E'') < T_g (\tan \delta)$.

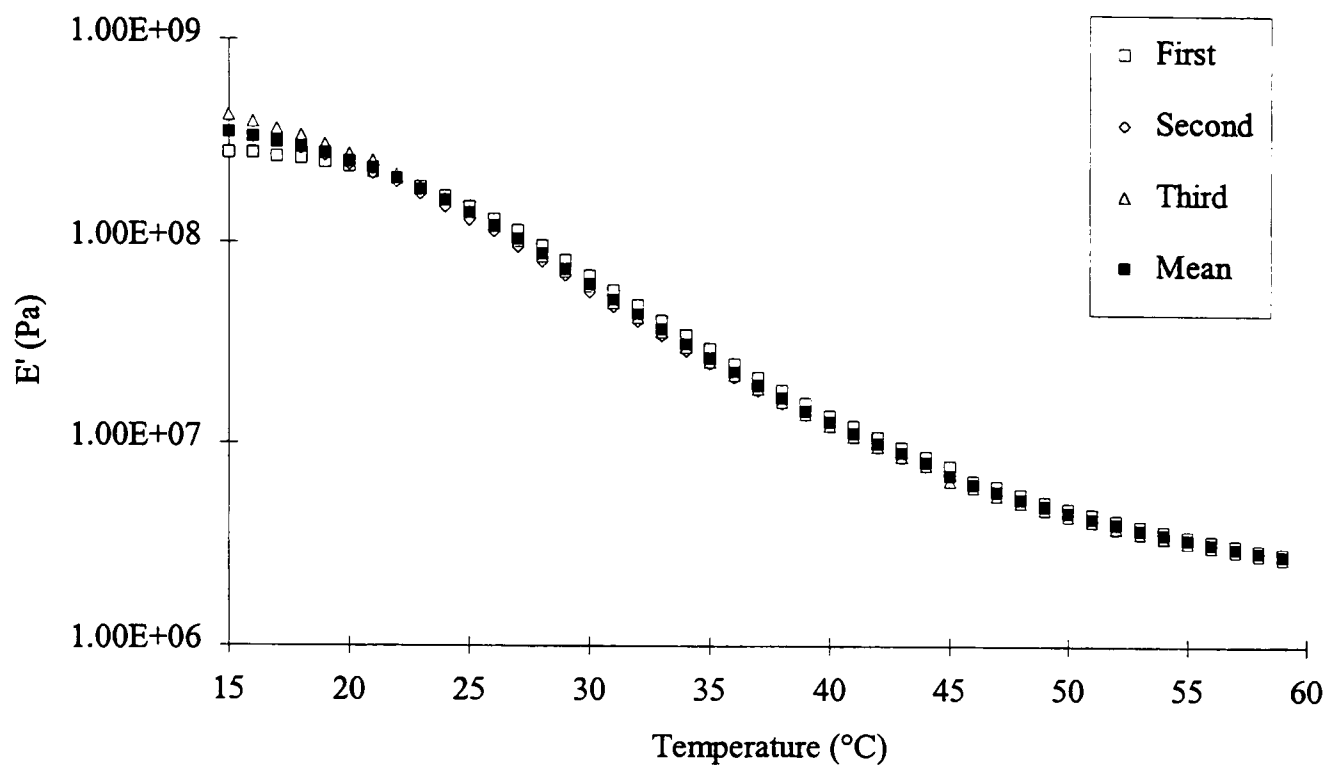


Figure 5.1.1. Storage modulus* of Futurasoft (FS).

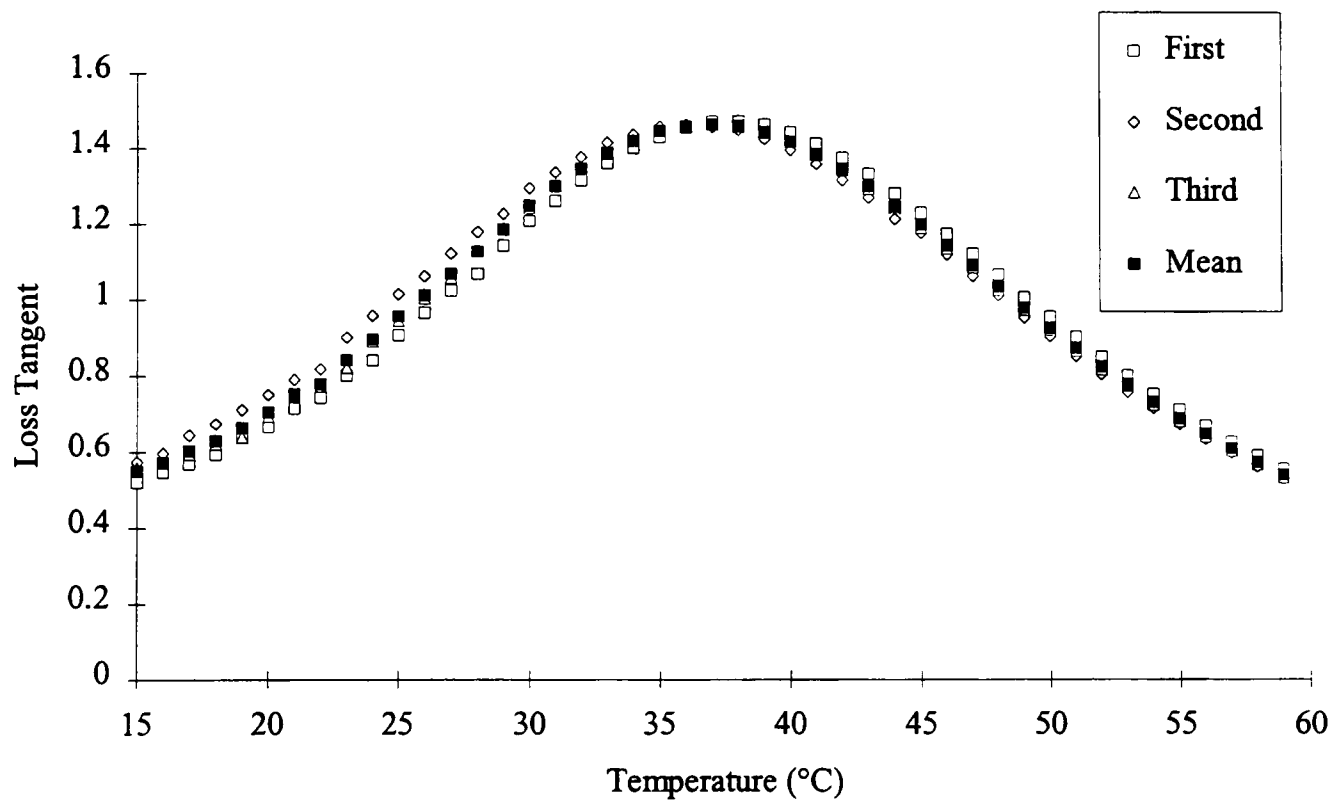


Figure 5.1.2. Loss Tangent of Futurasoft (FS).

* The DMA storage modulus graphs in this section are presented on a logarithmic scale for clarity and convenience.

As was discussed in section 1.4.1. this material is a mixture of methyl, ethyl, butyl, nonyl and tri-decyl methacrylates, the exact proportions of which are not known for certain. It was noted in table 1.3.3. that the first two constituents have Tg's above mouth temperature while the higher methacrylates have proportionately lower Tg's. The overall Tg of the material however is extremely close to its operating temperature (37°C). It is unclear whether this is by chance or design.

As far as the literature survey revealed the viscoelastic properties of this (FS) material have never been investigated before so that no comparisons with previous studies can be made.

Supersoft, new and old (NS & OS)

The viscoelastic properties of both materials are represented in figures 5.1.3. to 5.1.6. From these results alone it seems clear that the formulation of Supersoft has changed over the years. This is in spite of the fact that both the NS and OS materials were typical of the soft acrylics and had similarly shaped E' and loss tangent curves, indicative of polymers going through their glass transitions. The distinguishing difference between the two was the value of the glass transition. The new formulation of the material had its Tg at 37.8°C, a 7.7°C shift from the older version which had a Tg at 30.1°C. This glass transition shift corresponds to a three times increase in the stiffness for the new material from 5.87 to 16.8 MPa at mouth temperatures.

Infra red spectroscopy seems to suggest that there has been a change from methyl methacrylate to ethyl methacrylate in the liquid component of this material (Braden, 1996). Ethyl methacrylate has a lower Tg and is thus softer. If this was the only variation between the two materials one would expect NS to be softer than OS. In fact the opposite is true, it can be postulated however that the new version of the material has a reduced amount of plasticiser which has been facilitated by the change in the

monomer. There is indeed strong evidence of this reduction in the amount of plasticiser used; provided by the water absorption data presented in section 5.2.

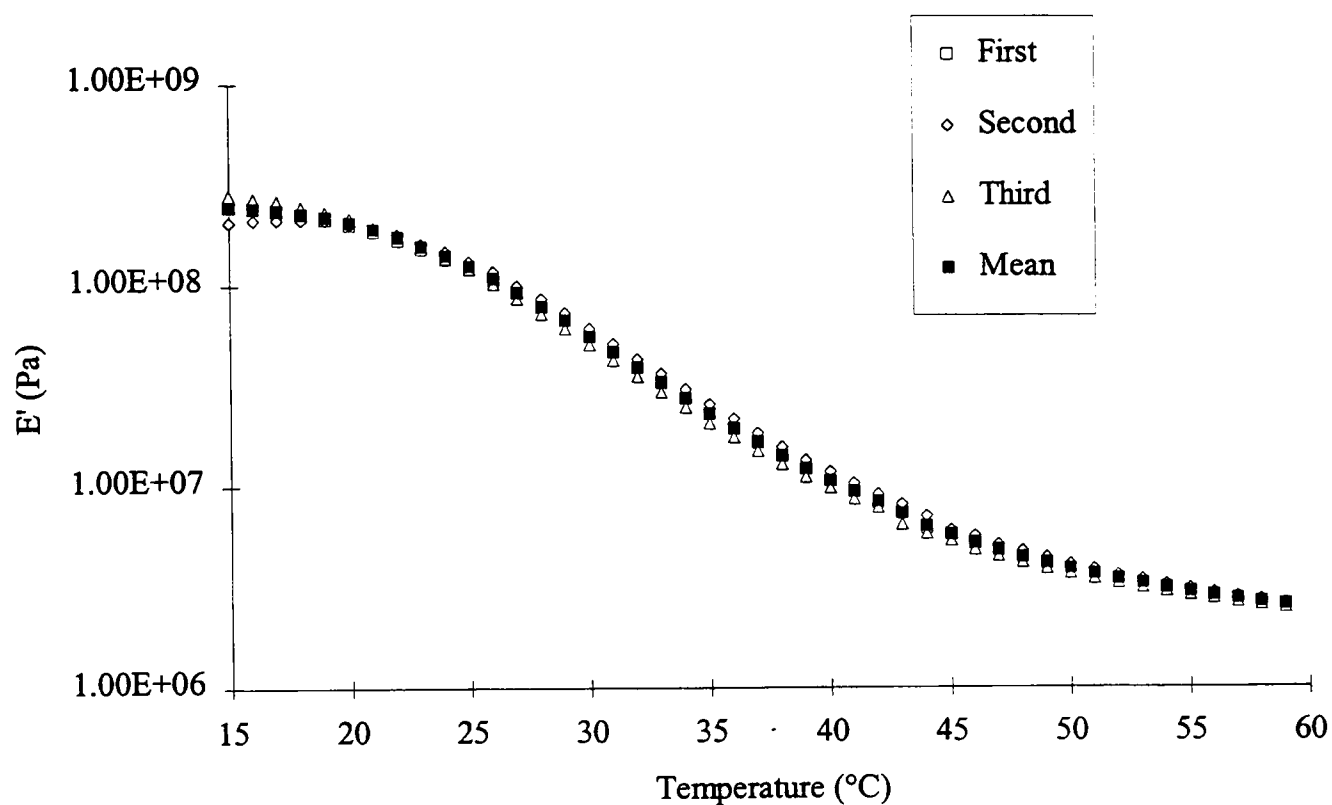


Figure 5.1.3. Storage modulus of Supersoft (NS).

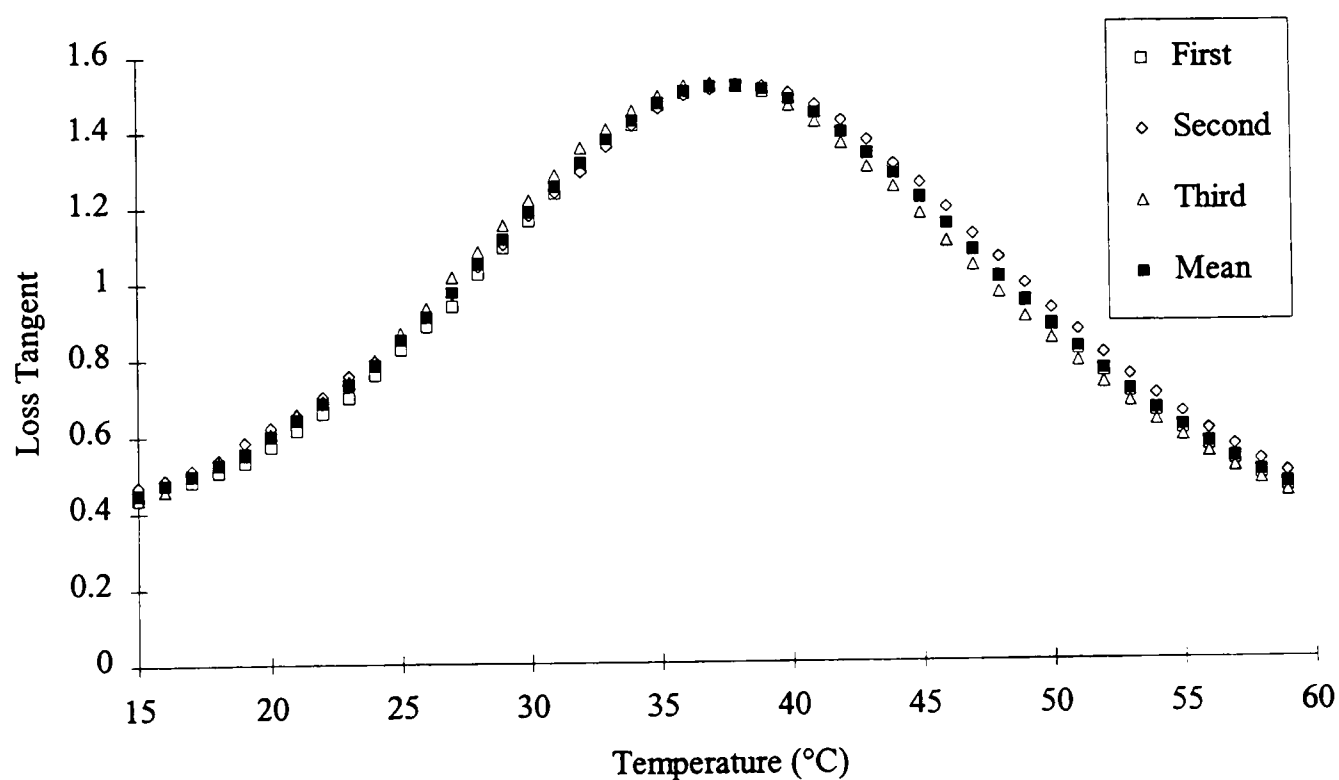


Figure 5.1.4. Loss Tangent of Supersoft (NS).

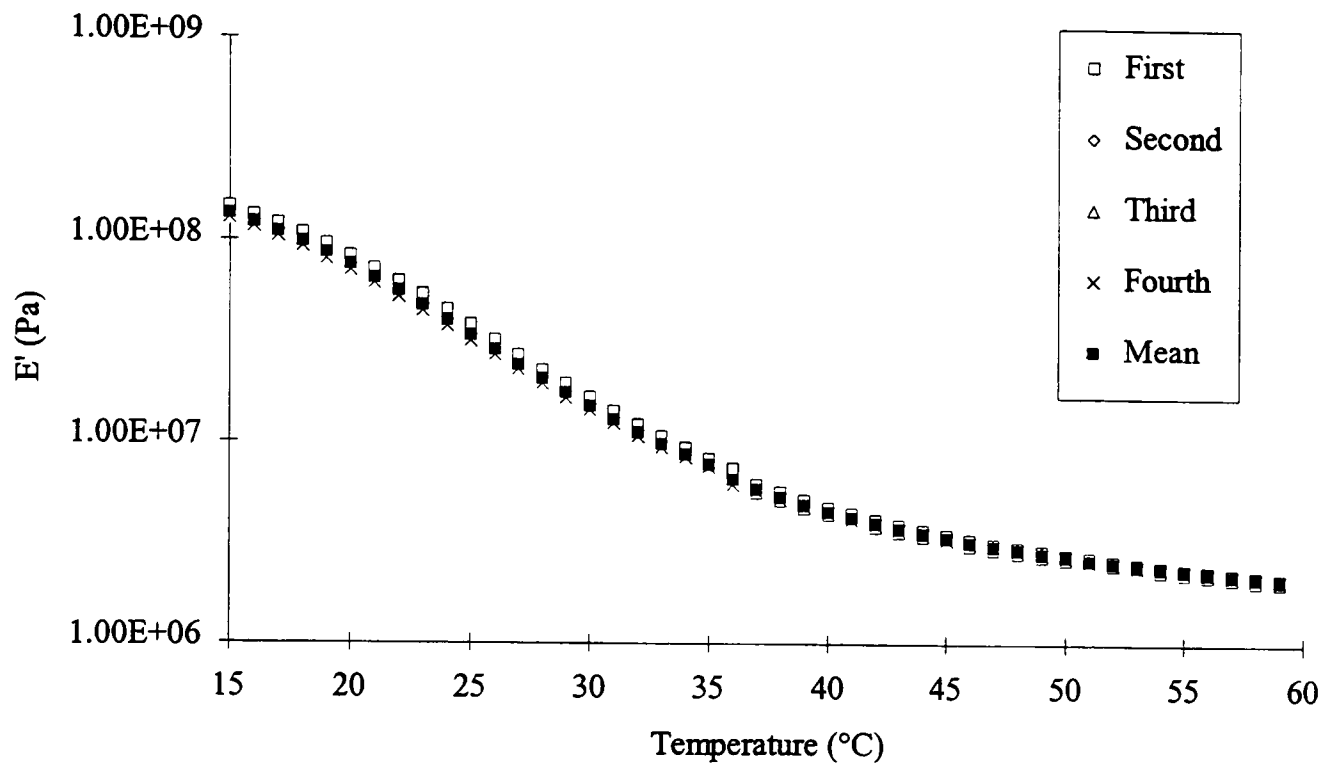


Figure 5.1.5. Storage modulus of Supersoft (OS).

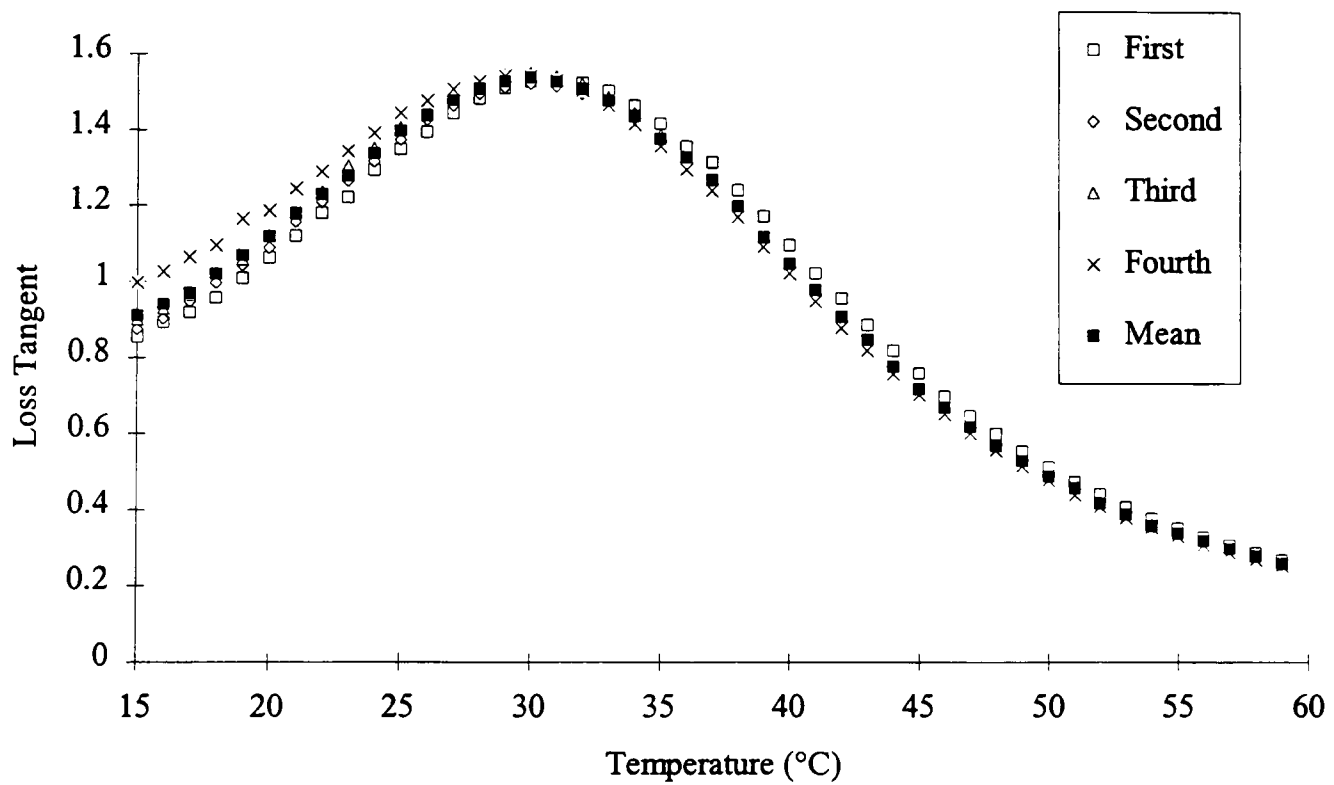


Figure 5.1.6. Loss Tangent of Supersoft (OS).

NS	E' (MPa)	S.D.	Tan δ	S.D.
37°C	16.8	1.76	1.52	0.01
22°C	176	6.43	0.685	0.02
OS	E' (MPa)	S.D.	Tan δ	S.D.
37°C	5.87	0.22	1.27	0.03
22°C	56.3	4.45	1.23	0.05

Table 5.1.2. The viscoelastic properties of NS and OS at room and mouth temperature.

The results for the two versions of the Supersoft material were compared with those obtained by other workers. It is uncertain which version of the commercial material each author is referring to, although the date of the publication and the ageing properties of the material provide some clues. Furthermore it is possible, and even probable, that the material formulation has changed more than once over the past 25 years since it was first tested by Braden and Clarke (1972).

In the investigation carried out by Waters et al (1996) Supersoft was measured as having a shear storage modulus of 0.311 MPa and a loss tangent of 1.078. Assuming the Young's modulus is 3 times the shear modulus* the material is still considerably softer than either NS or OS as observed in the present study. As will become apparent Waters and co-workers obtained comparatively lower modulus values for all the materials tested, and hence this systematic discrepancy must be attributed to the differences in the two instruments used.

* The assumption for arriving at $E = 3G$ is that the Poisson's ratio is 0.5 (i.e. the material is incompressible). This is based on a more fundamental equation from the theory of elasticity, i.e. $E = 2G(1 + \mu)$, (Tschoegl, 1989). The assumption of incompressibility although true for most polymers past their transition region (i.e. rubbers) is extremely doubtful for Supersoft, which is undergoing a transition in this temperature range.

Kalachandra et al (1995) obtained a figure of 10 MPa for the storage modulus and 1.25 for $\tan \delta$ for Supersoft* at 37°C and 1 Hz. This modulus figure is higher, and the loss tangent similar to the experimental data found in this investigation. One possible source of discrepancy is the difference in the motor controls used in the two investigations.

Whereas the sample is kept under a constant strain in this study, Kalachandra et al used two, seemingly arbitrary, values for the static and dynamic stress at 50 kPa and 5 kPa with the result that the strain imposed on the sample is constantly increasing during the temperature run. Because of this, and other reasons (outlined shortly), it is hard to make a direct comparison. Problems mentioned in chapter 4 concerning the use of a reasonable force to obtain an adequate amplitude are well exemplified by Kalachandra's results, as the modulus and $\tan \delta$ traces show substantial noise in the high modulus region where the analyser (the LVDT to be precise) is struggling to read the minimal amplitude.

Using a custom made analyser Wagner et al (1995a) observed a E' of 2.59 MPa and $\tan \delta = 1.25$ at 37°C and 1 Hz; and values of 16.65 MPa and 1.12 measured at 23°C and 1 Hz. These, and other values obtained in their study are again lower than the values obtained here, so this must again be due to a systematic difference between the two techniques. A likely cause of this is the deformational mode and geometry which in this case is the extension of a 1.4 x 3 x 40 mm strip.

Braden and Clarke (1982) tested Supersoft dynamically, but on a very different time scale. At room temperature and 0.96 kHz they found Supersoft to be much stiffer, 540 MPa. This compares to 56.3 and 176 MPa obtained in this investigation for OS and NS at similar temperatures but at a much slower time scale.

* It is believed that the author is referring to OS. This view is based on the fact that all the other materials tested by the author also have a higher modulus than was found in this report. There is however contrary evidence to this assumption (i.e. NS is being tested) provided by the ageing characteristics in section 5.2.

Also in 1982 Robinson and McCabe did some compressive creep tests on Supersoft. These were carried out at room temperature, so that these results are of limited clinical relevance. Their results clearly show the time dependent character of Supersoft with the creep modulus halving in magnitude as the time scale is changed from ten seconds to ten minutes. The 10 second value of the creep modulus was 2.4 MPa compared with the higher value of 56.3 MPa obtained in this report at 1 Hz. An increase in the modulus following a reduction in the time frame of the experiment is to be expected as this relates to the time dependent nature of this material.

Duran et al (1979) obtained a value of 7.5 MPa for the modulus of Supersoft using a dynamic method of undisclosed nature. They found this to be larger in magnitude than the creep compliance figure of 1.71 /MPa which they also measured.

Braden and Clarke used a torsional pendulum to study the viscoelasticity of Supersoft in 1972. They obtained a value of 0.8 MPa for the shear dynamic modulus of Supersoft, which implies a compressive modulus of 2.4 MPa. For the loss tangent a value of 1 was arrived at. Apart from the 'E = 3G' assumption; other sources of discrepancy between these results and the results in table 5.1.2. could be due to the lower frequency range (0.1 - 0.5 Hz) which would certainly have the effect of measuring an apparently lower modulus value. Additionally as was earlier noted the torsional pendulum is not an ideal instrument for studying lossy polymers going through their transition.

5.1.2. Silicone Based Materials.

Molloplast B (MP)

The DMA traces obtained for Molloplast B (Figures 5.1.7 and 5.1.8) are indicative of a rubber well beyond its glass transition. In this temperature range MP can therefore be considered as a temperature independent silicone based rubber. As would be expected of a rubber, the properties are marked by a low average modulus and loss tangent of 3.9

MPa and 0.027, respectively. The loss tangent was by far the lowest of any material analysed.

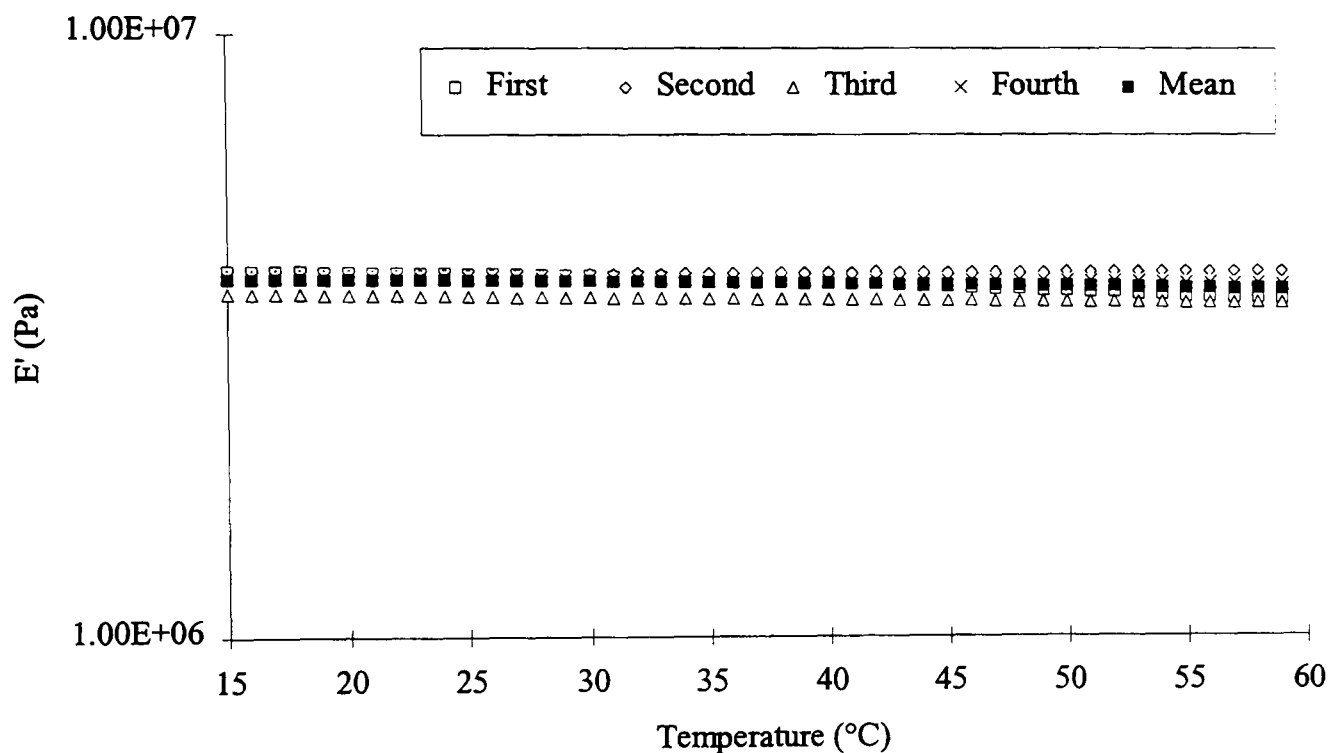


Figure 5.1.7. Storage modulus of Molloplast B (MP).

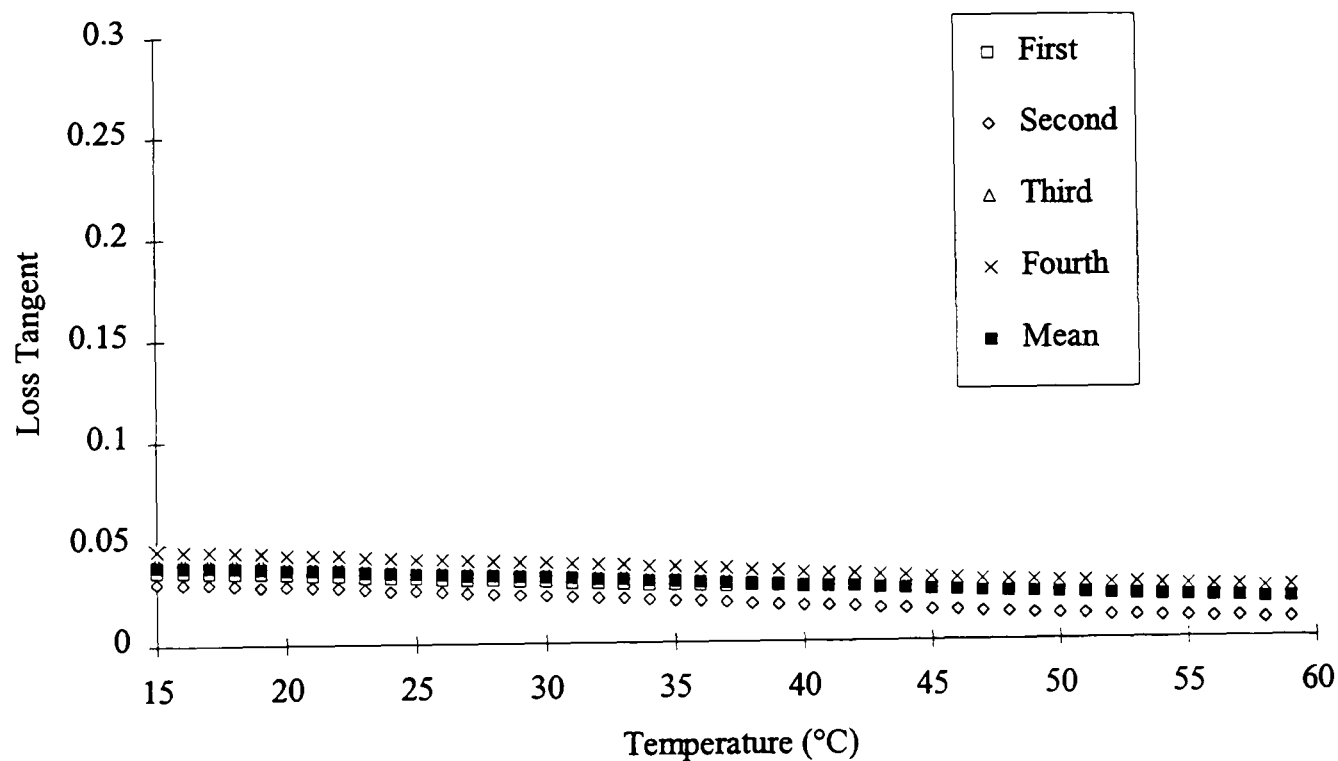


Figure 5.1.8. Loss tangent of Molloplast B (MP).

MP	E' (MPa)	S.D.	Tan δ	S.D.
37°C	3.87	0.16	0.029	0.007
22°C	3.91	0.15	0.036	0.007

Table 5.1.3. The viscoelastic properties of MP at room and mouth temperature.

Waters et al (1996) obtained a value of 0.439 MPa for the shear storage modulus of this material at 37°C and 1 Hz. Using the 'E = 3G' assumption, which is more applicable because of MP's rubber like nature, a value of 1.32 MPa can be obtained for the modulus. This is roughly 3 times lower than the value obtained here. The loss tangent value obtained by these authors is 0.066 which is conversely approximately 3 times higher than the value obtained here.

Wagner et al (1995a) obtained a value of 1.5 MPa for the modulus of this material and a loss tangent value of 0.02. The modulus is approximately two times lower than was found here while the loss tangent figure is approximately the same.

Kalachandra et al (1995) obtained a value of 4.8 MPa for the storage modulus and a value of 0.05 for the loss tangent (at 37°C and 1 Hz). These are similar in magnitude although larger than the values obtained here. Problems noted earlier with the constant force method used do not occur here mainly because the material is more compliant and not very temperature dependant as was the case with Supersoft.

Jepson et al (1993a) looked at the properties of Molloplast B using their force/distance probe. They found little difference between the initial and delayed compliance of Molloplast as would be expected. The actual values of modulus were 5.26 MPa and 5 MPa respectively. These are again somewhat higher than the values obtained here.

Braden and Clarke (1982) found a modulus of 9.4 MPa for Molloplast although at much higher frequencies. This increase in the modulus was relatively small compared with the one observed with Supersoft at these higher frequencies. This can be attributed to the fact that Supersoft is going through its transition.

Robinson and McCabe (1982) studied Molloplast B in creep conditions. Although this was not carried out at mouth temperature, the results are applicable in this case because of the temperature independence of the material. This reason coupled with the fact that the time difference, (i.e. the difference between 10 seconds and 1 Hz) has less of an influence on the 'low loss' silicones means that these results compare much better with the results given here. From the creep curves it can be seen that Molloplast B exhibits minimal time dependence after 10 seconds. Molloplast had a modulus of 3.5 MPa.

Using a torsional pendulum in 1972, Braden and Clarke obtained a 'compressive' storage modulus (using $E = 3G$) of 1.65 MPa for Molloplast B, and a loss tangent value of 0.06.

Flexibase (FB)

Similarly to Molloplast B, Flexibase is also in the rubbery zone of its behaviour. Unlike MP some activity of low magnitude can be seen in Figure 5.1.10. This was not generally reproducible however and because of its low magnitude no conclusions can be drawn. The modulus and the loss tangent have low values of 3.4 MPa and 0.11, respectively. Comparison with Molloplast B shows that this cold cured material has a lower modulus and a higher loss tangent than its rival.

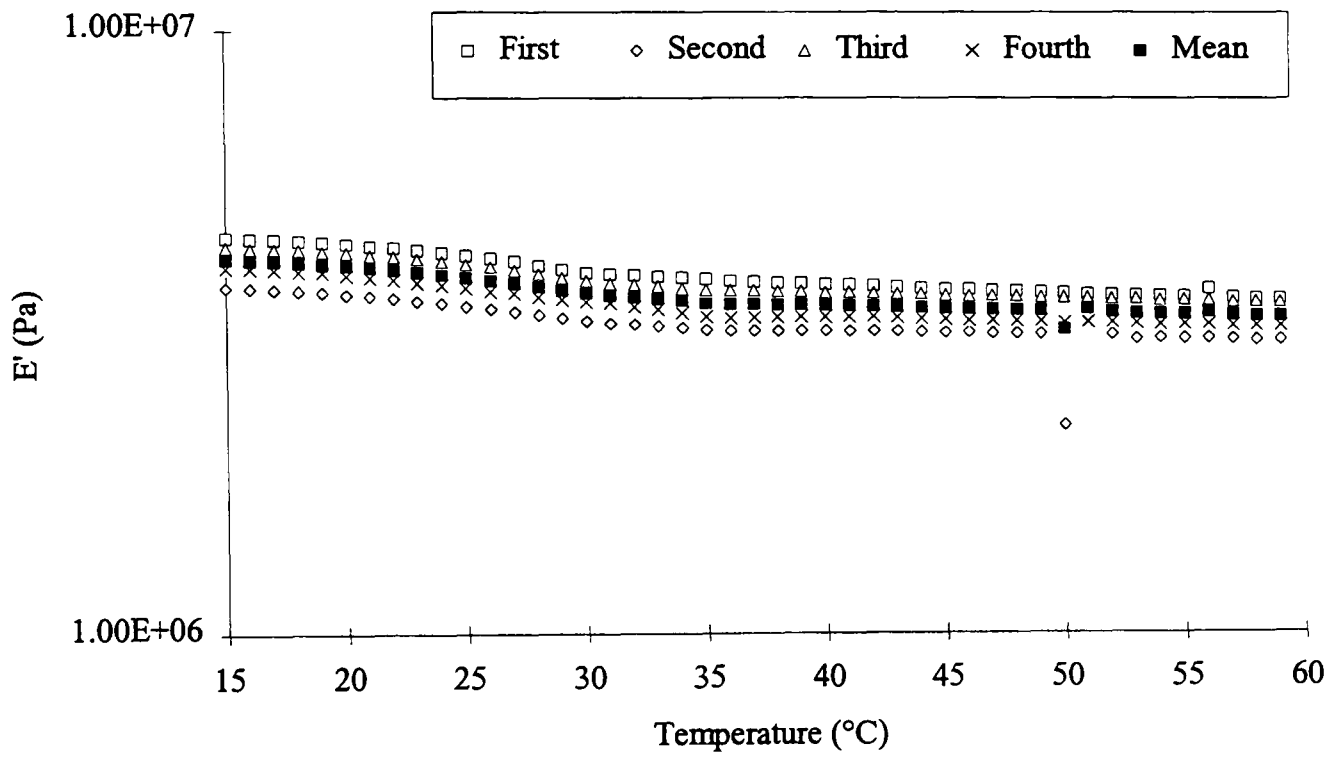


Figure 5.1.9. Storage modulus of Flexibase (FB).

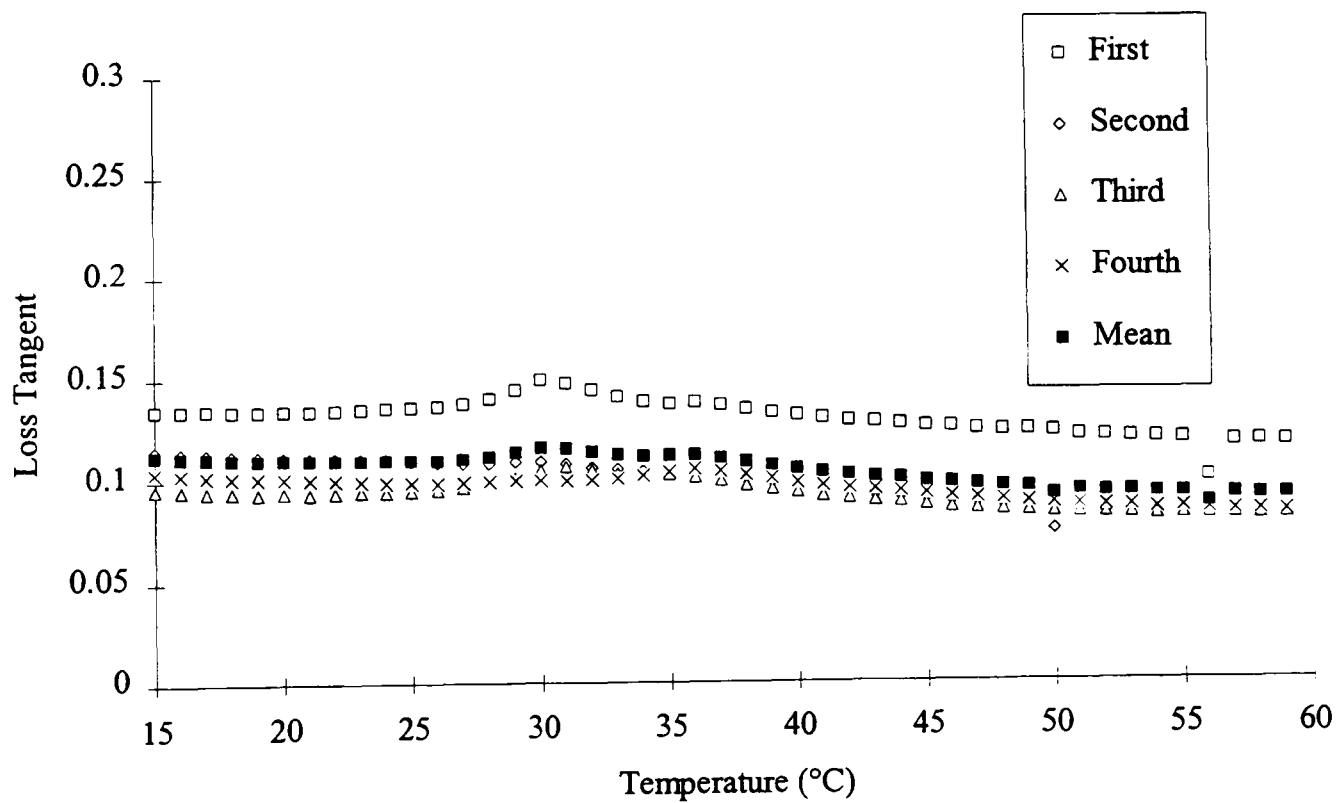


Figure 5.1.10. Loss tangent of Flexibase (FB).

FB	E' (MPa)	S.D.	Tan δ	S.D.
37°C	3.52	0.31	0.111	0.017
22°C	4.01	0.35	0.110	0.018

Table 5.1.4. The viscoelastic properties of FB at room and mouth temperature.

Waters et al (1996) obtained a value for G' of 0.509 MPa, and a loss tangent of 0.158 at mouth temperature and the same frequency as used here. This translates into a compressive modulus of 1.53 MPa, indeed FB was found by the authors to be the stiffest of the materials tested. As was the case with Molloplast B the modulus value is less than the one found here (less than half). The loss tangent value on the other hand was slightly larger than the one found here.

Braden and Clarke (1982) found Flexibase to have a modulus of 2.5 MPa using a high frequency method. This is lower than the value found here and significantly lower than the value found for MB in the same paper.

In the study mentioned earlier by Robinson and McCabe (1982) Flexibase was studied in creep conditions. Again although the tests were not carried out at mouth temperature, the results should be valid for this temperature independent material. Again Flexibase had a lower modulus (2.8 MPa) than was found for Molloplast B.

Using a torsional pendulum in 1972, Braden and Clarke obtained a compressive storage modulus (again using ' $E = 3G'$ ') of 2.7 MPa for Flexibase, and a loss tangent value of 0.4.

5.1.3. Miscellaneous Commercial Materials.

Novus (NN, ON)

The two formulations of polyphosphazine based material 'Novus' were investigated and compared. The two materials ON (old) and NN (new) were very similar in their viscoelastic characteristics, the only tangible difference being a slightly higher loss tangent in the older version of the material.

ON and NN were found to be viscoelastically similar to the silicone materials investigated in that they were all well above their glass to rubber transition, showing rubber like behaviour. They were more compliant than the silicones with the lowest modulus of any material tested here. The modulus was 3.02 and 2.79 MPa for new and old Novus, respectively at 37°C. The loss tangent was also on the low side with the range of 0.103-0.125 for the new and old.

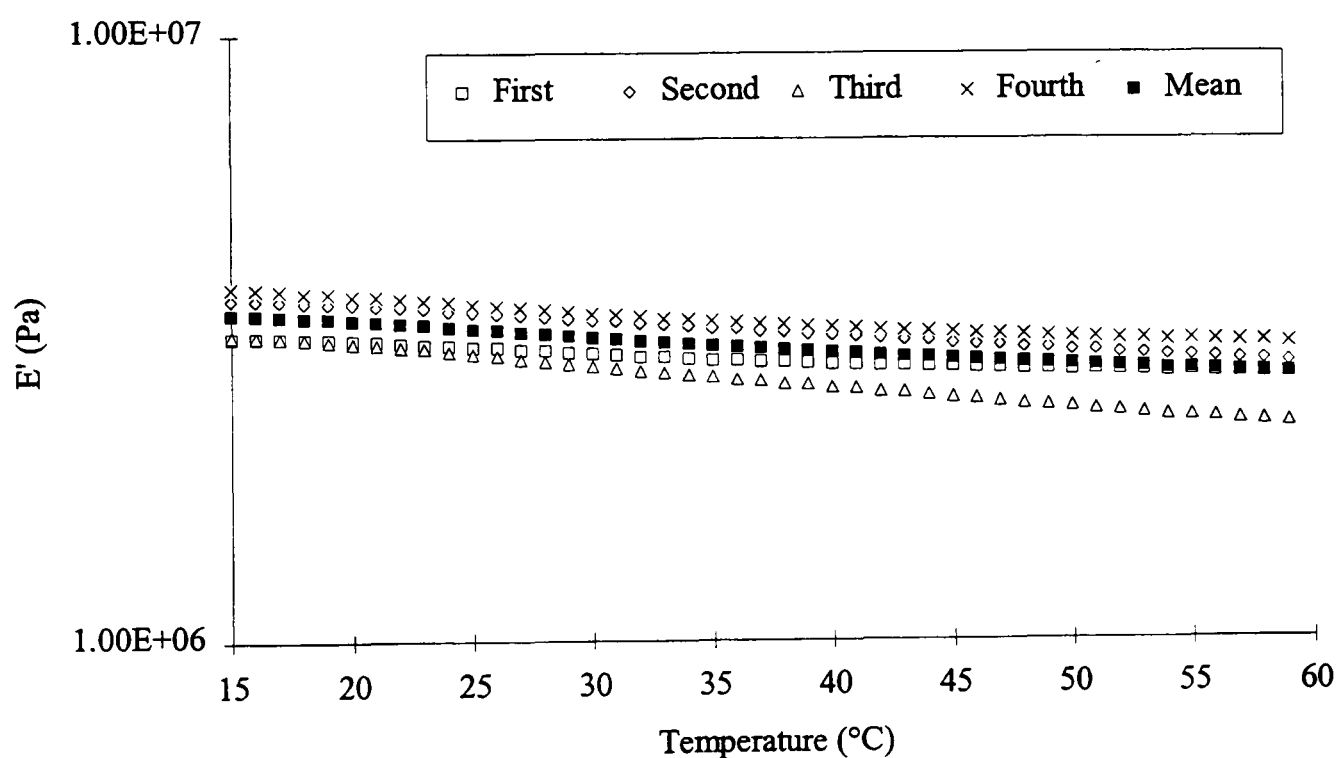


Figure 5.1.11. Storage modulus of Novus (NN).

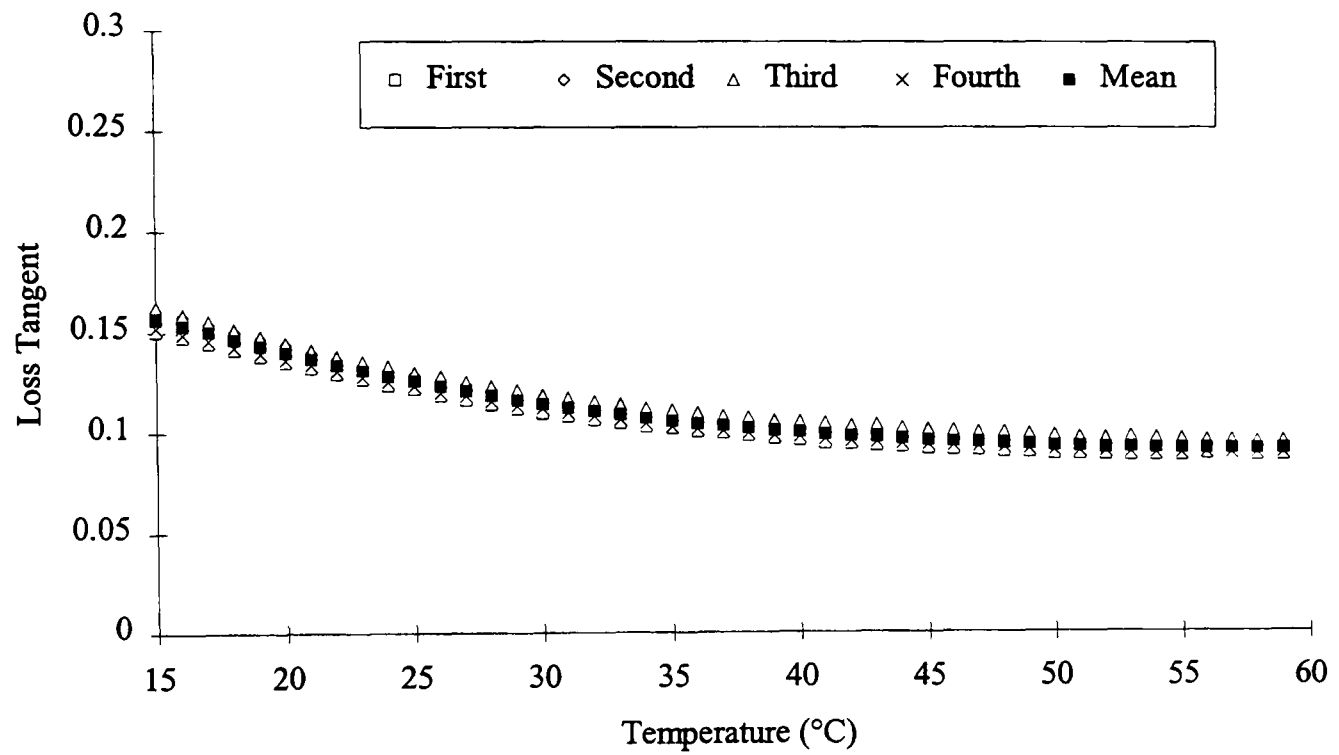


Figure 5.1.12. Loss Tangent of Novus (NN).

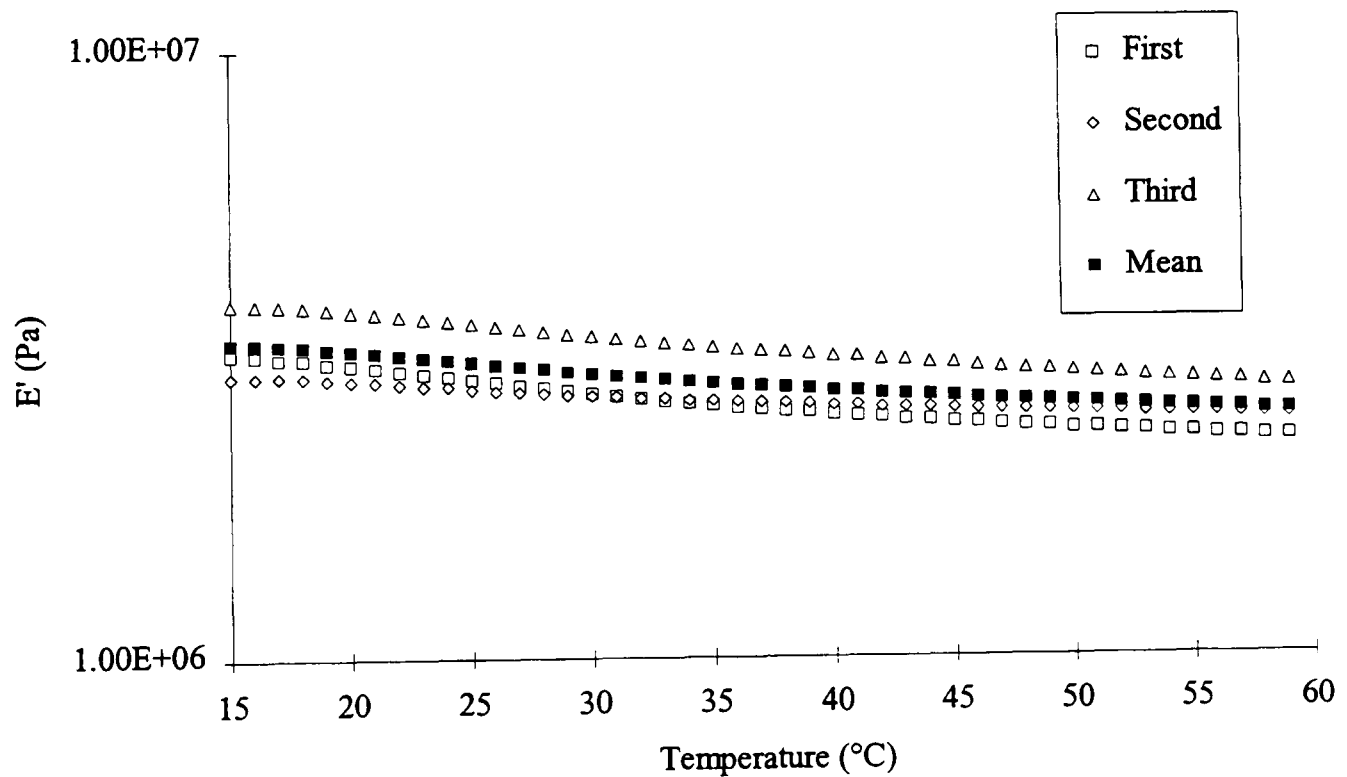


Figure 5.1.13. Storage modulus of Novus (ON).

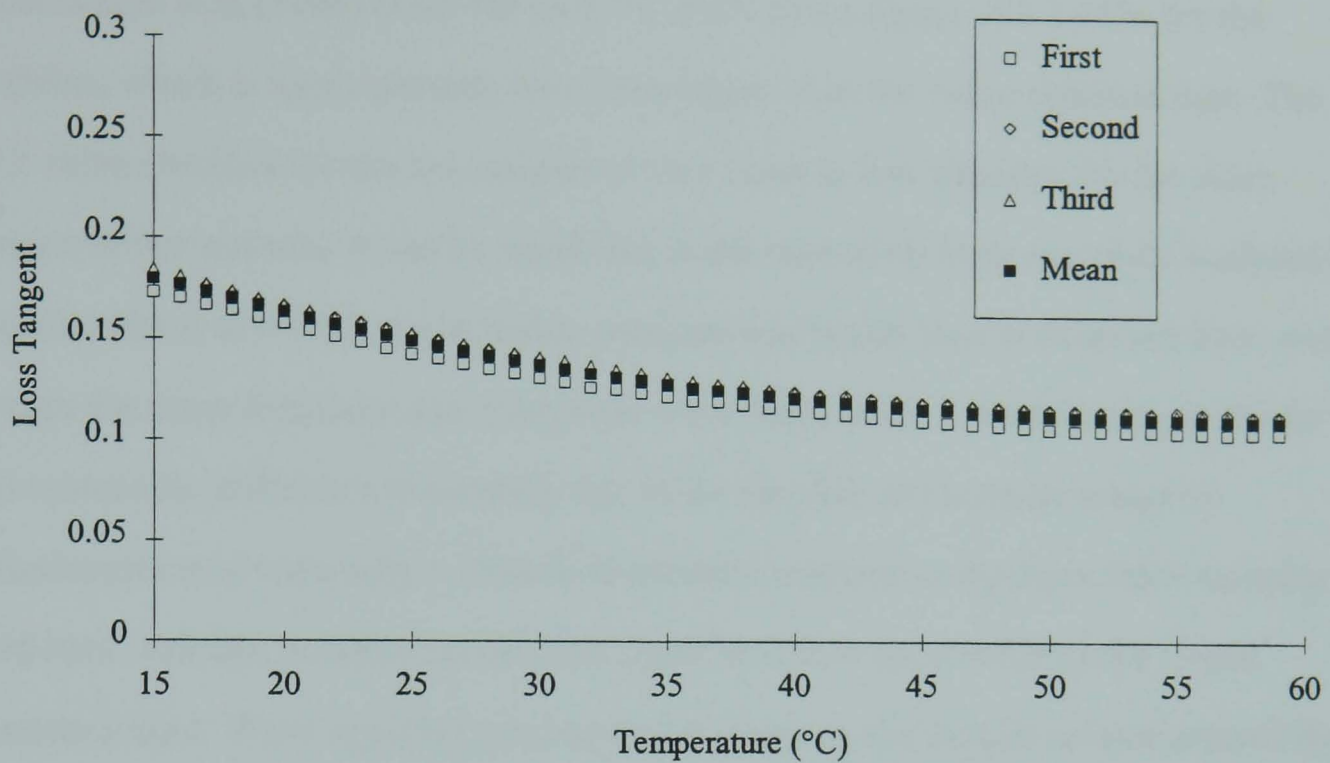


Figure 5.1.14. Loss tangent of Novus (ON).

NN	E' (MPa)	S.D.	Tan δ	S.D.
37°C	3.02	0.30	0.103	0.004
22°C	3.33	0.31	0.133	0.004
ON	E' (MPa)	S.D.	Tan δ	S.D.
37°C	2.79	0.35	0.125	0.005
22°C	3.14	0.45	0.157	0.005

Table 5.1.5. The viscoelastic properties of NN and ON at room and mouth temperature.

The results obtained by Waters et al (1996) follow a familiar trend in that the modulus value is smaller than the value obtained here ($G' = 0.355$ MPa, $\tan \delta = 0.117$ at 37°C and 1 Hz). It will be noted that all the modulus figures obtained by Waters et al (Table 3.2.13) are of a comparable magnitude. As noted earlier this is not consistent with the work of earlier researchers who have found a large spread of stiffness in these materials (e.g. Braden & Clarke, 1972).

Kalachandra et al (1995) observed (at 37°C and 1 Hz) a figure of 6.2 MPa for the modulus, which is approximately two times higher than the value obtained here. The 0.12 value obtained for the loss tangent is very close to that obtained for the older version of the material. It can be noted that in the case of all three materials analysed by Kalachandra et al (1995), the modulus obtained was higher than is observed here, even though the same technique and instrument were being used. A contributing factor for this systematic difference is certainly due to the fact that the samples tested by Kalachandra et al were only 1.5mm in thickness compared to the 2mm thick samples used here. Another possible explanation could be due to the smaller probe (3mm diameter) used. When applying a compressive stress on the sample an area around the sample is also deformed and contributes to the apparent modulus of the sample. This contribution would be relatively larger, for a smaller probe. This being the case, an apparently stiffer material would be expected to be observed by using the smaller probes.

The value of storage modulus observed by Wagner et al (1995a) is 2.20 MPa at 1 Hz and 37°C. This is again lower than the value observed here.

Triad Resiline (TR)

As stated before the chemistry of this material is not known for certain. Its viscoelastic characteristics are shown in Figure 5.1.15 and 5.1.16. Triad had its transition at sub zero temperatures (as might be expected from a polyether based material) and showed no transitions in the region studied. At mouth temperatures its behaviour is largely temperature independent. The value of the modulus was rather high for a soft lining material at 16.0 MPa. The loss tangent of the material was in contrast fairly low at 0.133.

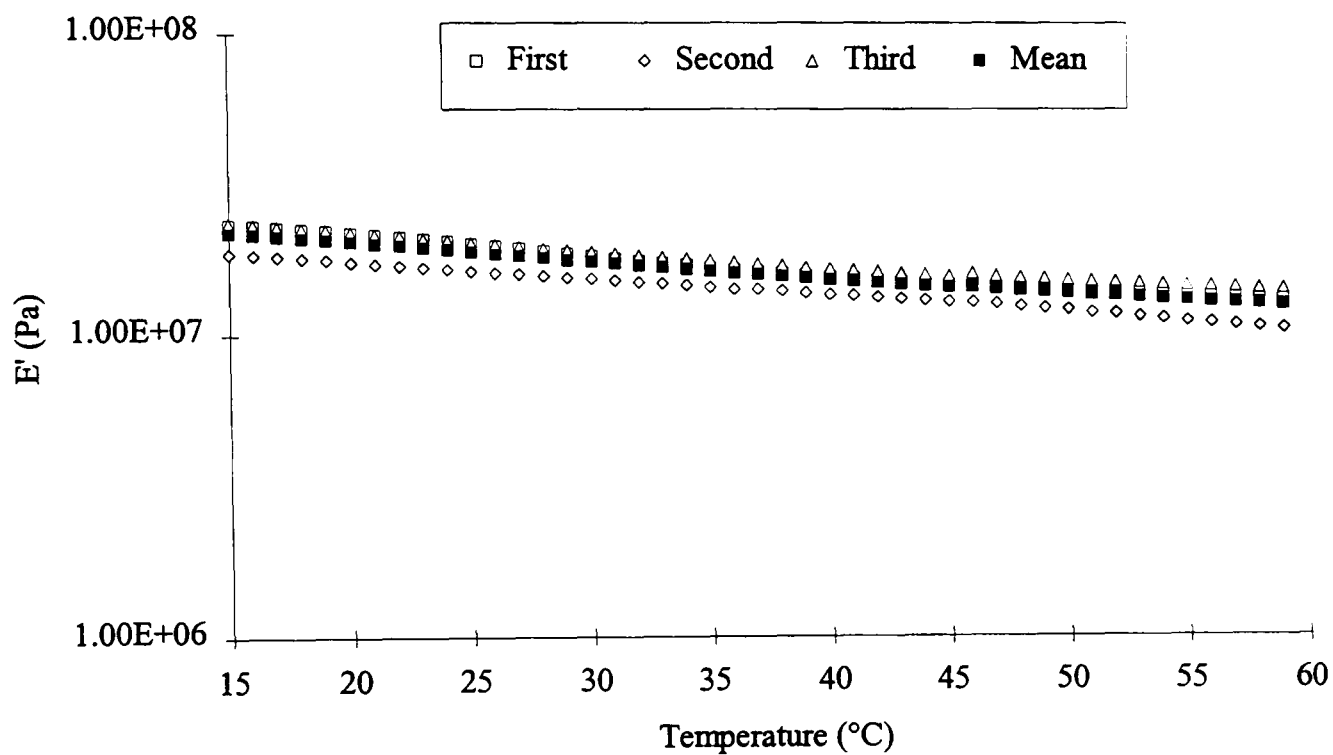


Figure 5.1.15. Storage modulus of Triad (TR).

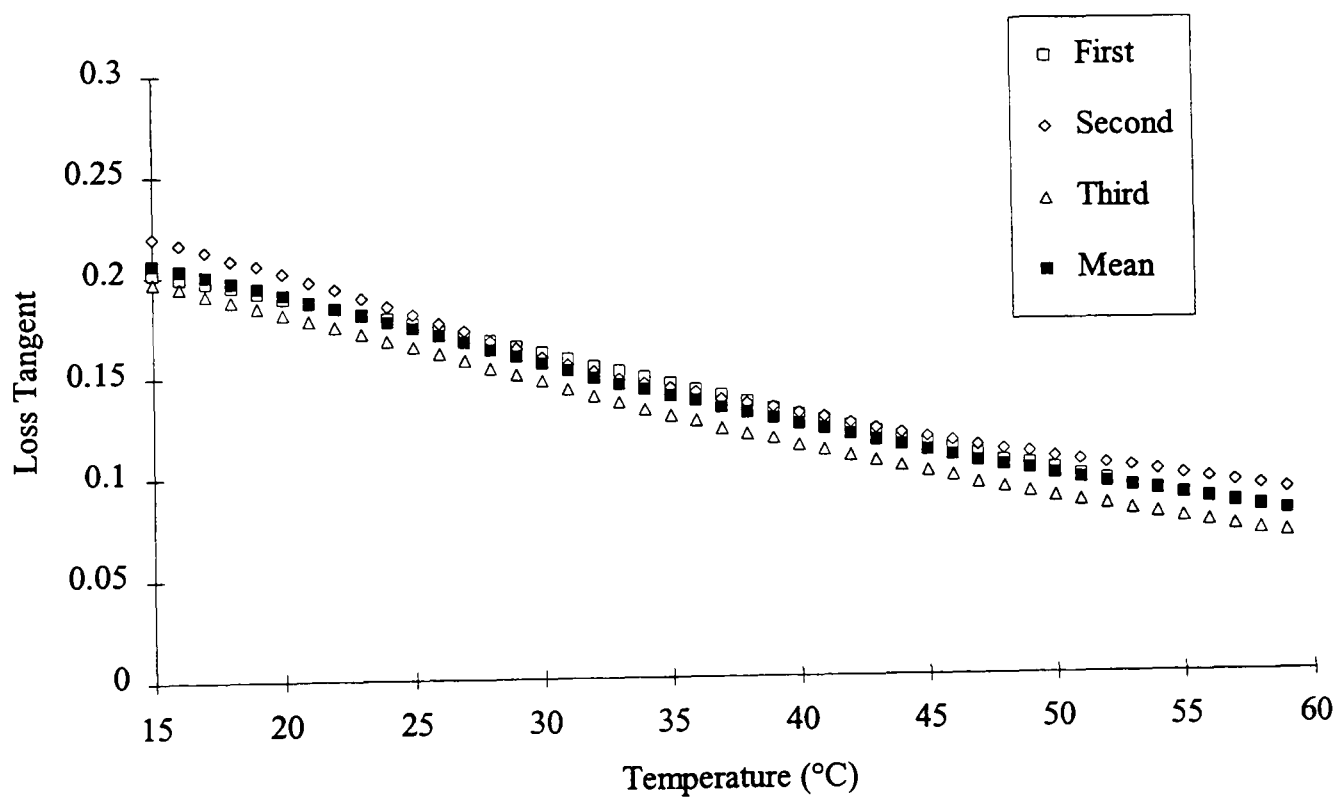


Figure 5.1.16. Loss tangent of Triad (TR).

TR	E' (MPa)	S.D.	Tan δ	S.D.
37°C	16.0	1.56	0.133	0.01
22°C	19.9	2.49	0.184	0.01

Table 5.1.6. The viscoelastic properties of TR at room and mouth temperature.

This material has not been previously studied and no comparisons can therefore be made.

5.1.4. Experimental Materials.

Elastomer / Methacrylate Hybrids (BS) (SI) (PB)

The viscoelastic properties of the elastomeric based experimental materials (see 1.4.5a for composition) are presented in figures 5.1.17. to 5.1.22. The storage modulus and the loss tangents of these materials at room and mouth temperature are summarised in table 5.1.7. The viscoelastic properties of all three materials are dominated by a broad, shallow peak of small magnitude in their loss tangent curve near mouth temperature. This is due to the methacrylate (i.e. 2-ethylhexylmethacrylate) phase of these materials*. It can be deduced from this peak that the methacrylate and elastomeric phases of these materials form distinct areas dominated by one or the other. i.e. elastomerically rich areas with a low Tg and methacrylate rich areas with Tg's in the temperature range of interest.

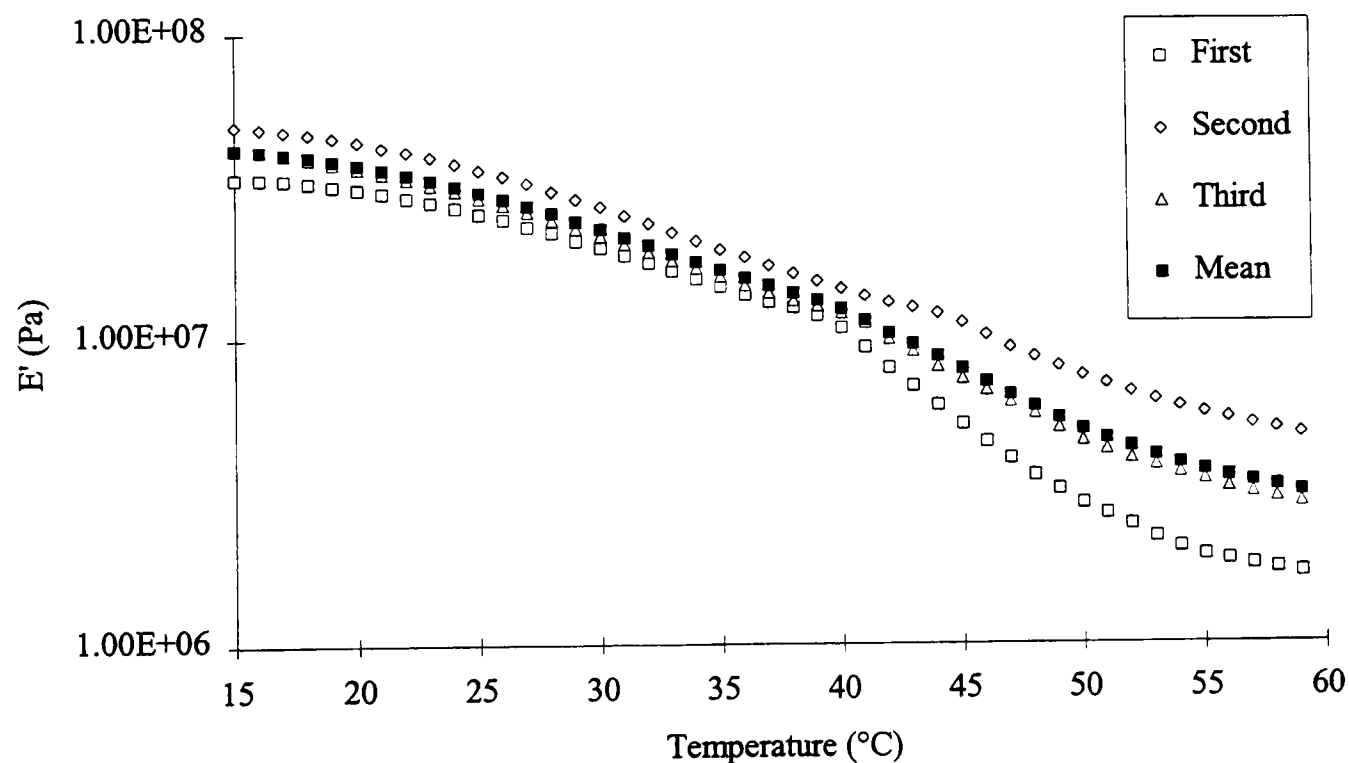


Figure 5.1.17. Storage modulus of experimental BS material.

* The Tg of 2-ethylhexyl methacrylate is actually quoted at a lower temperature of -10°C (Braden et al, 1997).

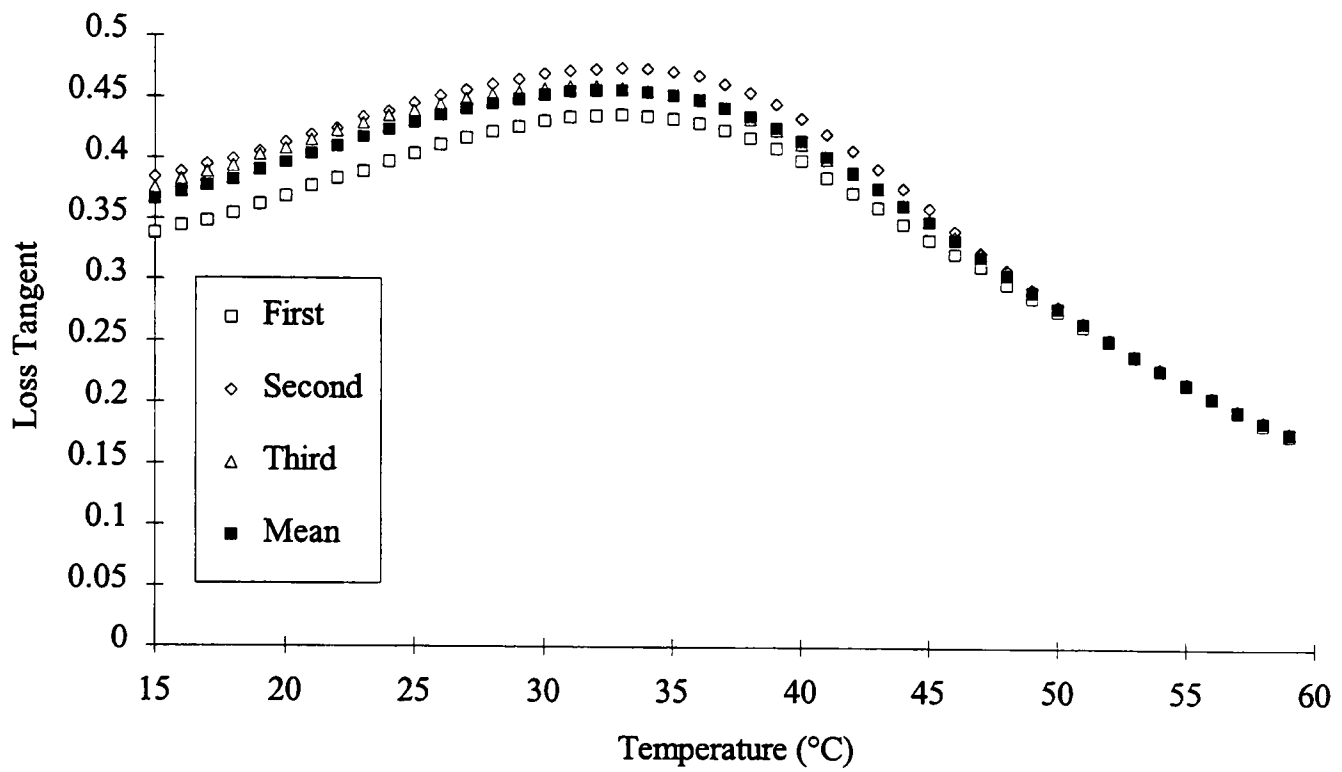


Figure 5.1.18. Loss tangent of experimental BS material.

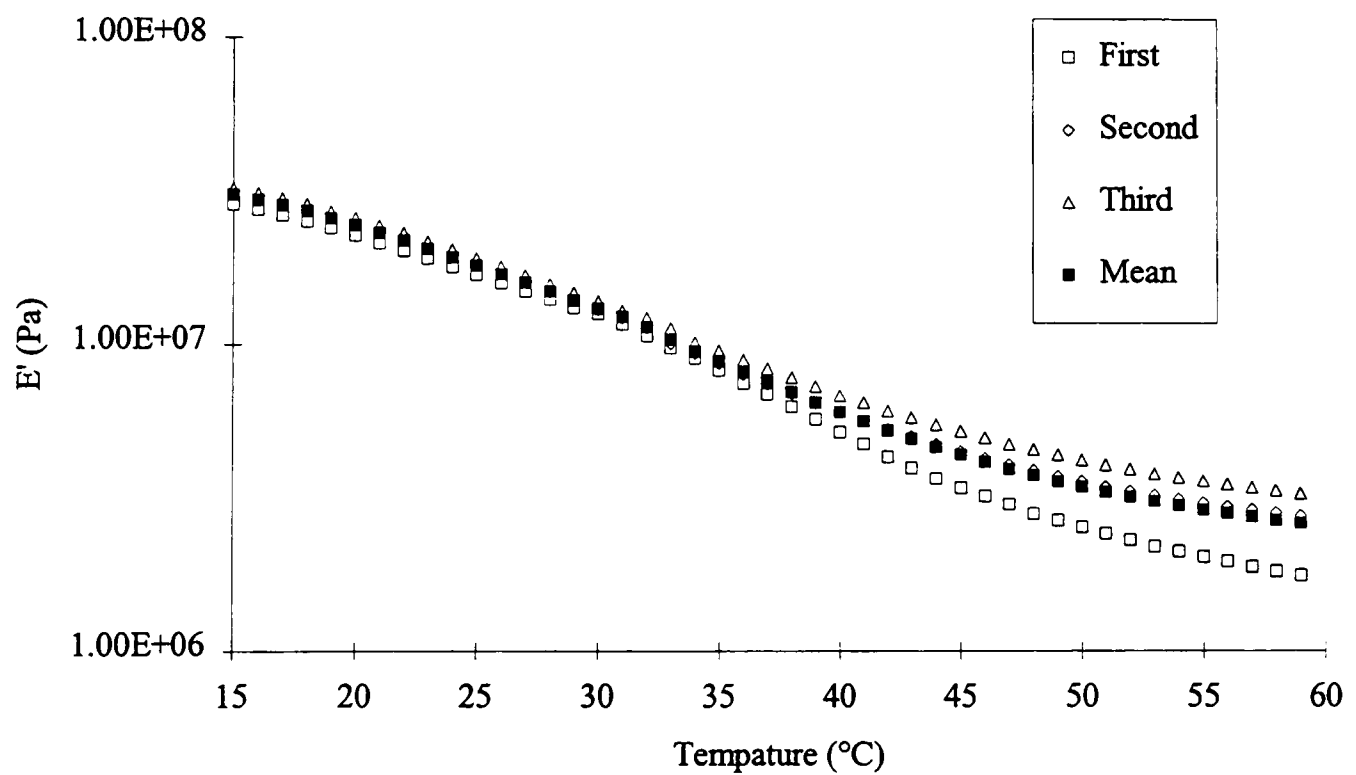


Figure 5.1.19. Storage modulus of experimental SI material.

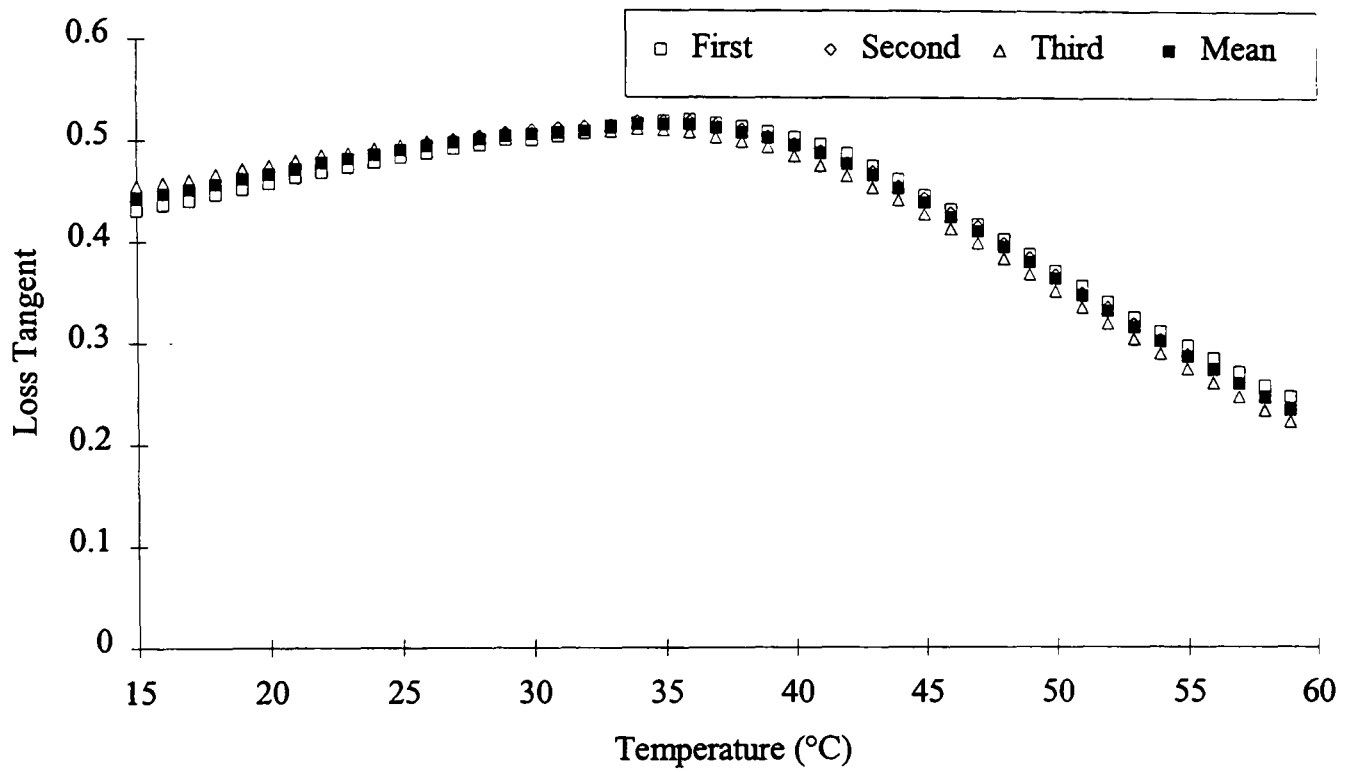


Figure 5.1.20. Loss tangent of experimental SI material.

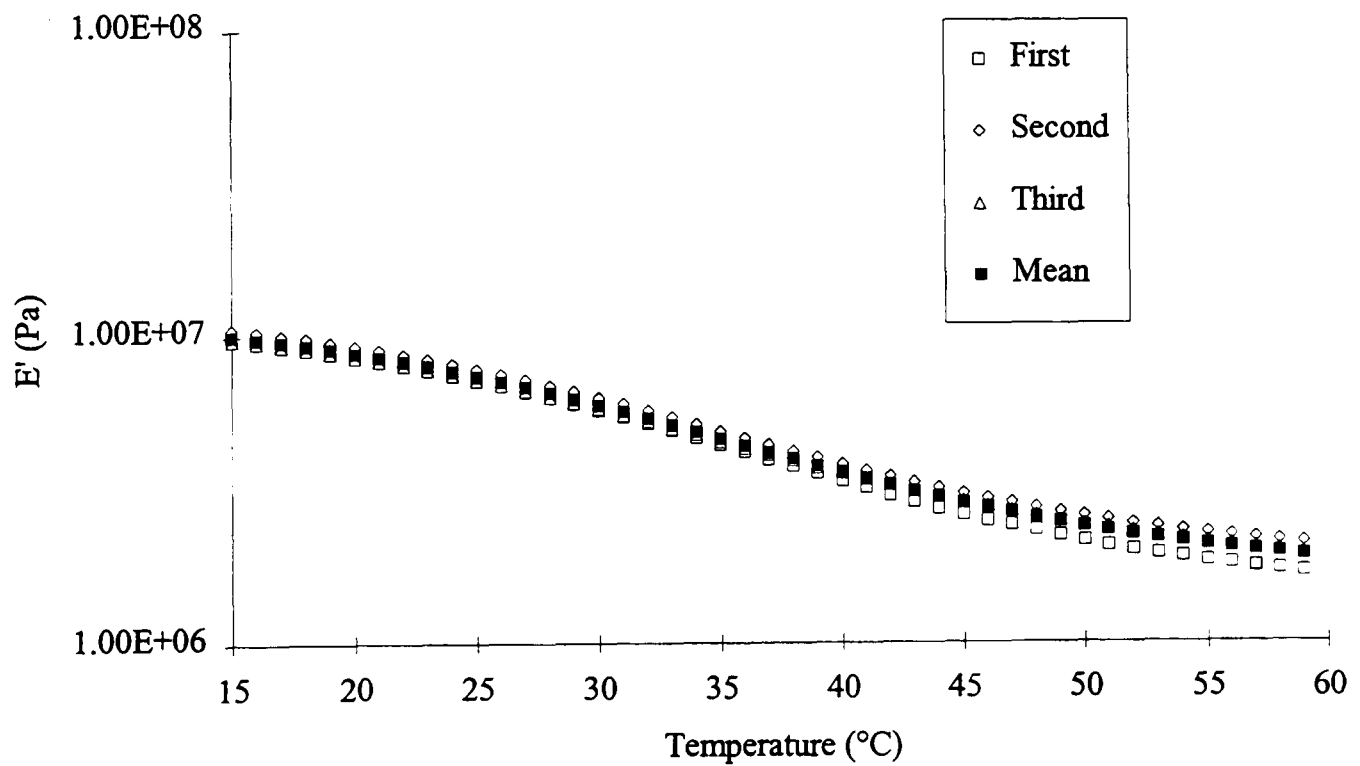


Figure 5.1.21. Storage modulus of experimental PB material.

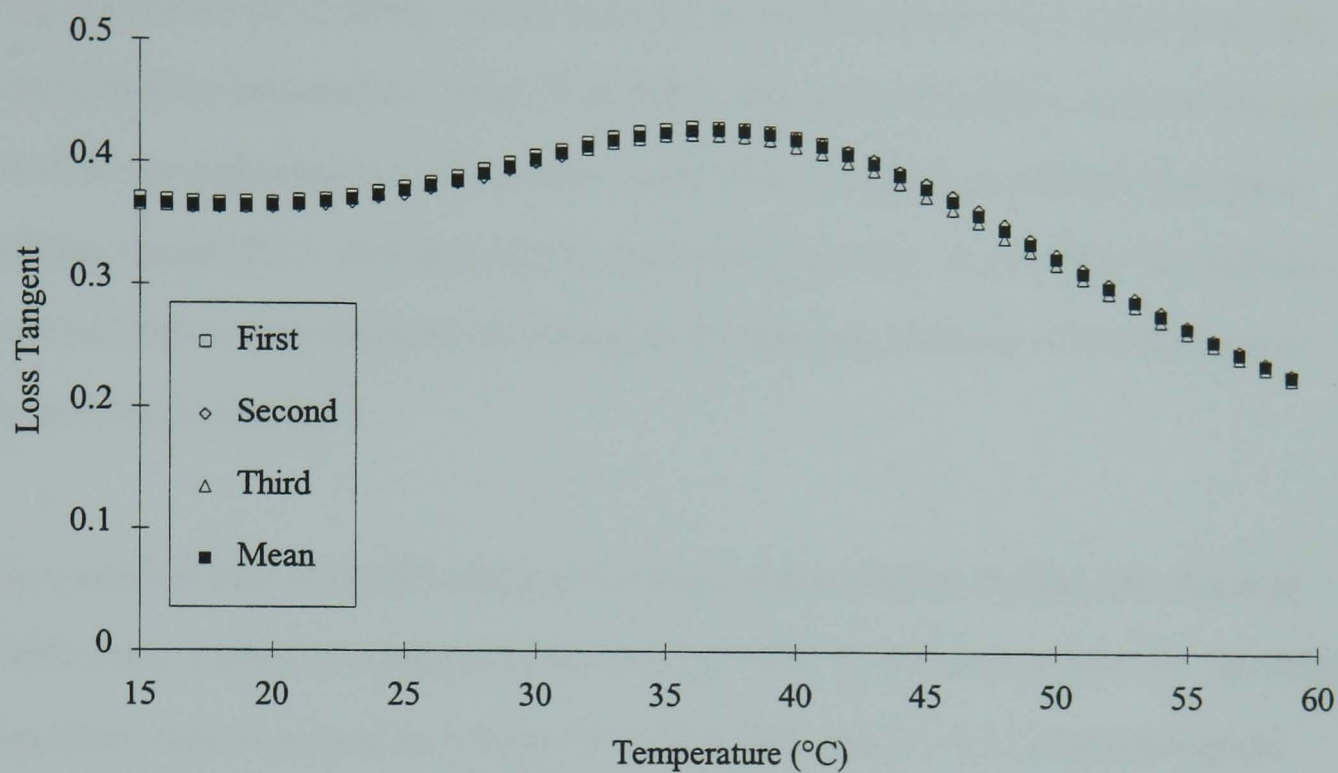


Figure 5.1.22. Loss tangent of experimental PB material.

BS	E' (MPa)	S.D.	Tan δ	S.D.
37°C	15.0	2.25	0.445	0.019
22°C	34.7	6.12	0.411	0.023
SI	E' (MPa)	S.D.	Tan δ	S.D.
37°C	7.54	0.75	0.514	0.008
22°C	21.9	1.44	0.478	0.008
PB	E' (MPa)	S.D.	Tan δ	S.D.
37°C	4.15	0.24	0.429	0.004
22°C	8.25	0.42	0.368	0.003

Table 5.1.7. The viscoelastic properties of BS, SI and PB at room and mouth temperature.

As can be seen the loss tangents of all three materials are very similar (at 37°C). The modulus on the other hand encompasses a relatively wide range, with the PB material being the softest (4.15 MPa), the BS material being the stiffest (15.0 MPa) while the SI material has an intermediate value (7.54 MPa). The glass transitions of these soft lining materials are surprisingly in the reverse order which would be predicted from these stiffness values (32.7, 34.9 and 36.5°C respectively for BS, SI and PB). The stiffness of these soft liners must therefore be related to the inherent stiffness of the elastomeric phase of each material.

The viscoelasticity of the BS material has been studied before by Kalachandra et al (1996) using a similar technique to that used in 1995 by the same author. Its viscoelastic properties were measured as follows: $E' = 20.9$ MPa, $\tan \delta = 0.37$ at physiological temperatures. The storage modulus in this case was higher than the value measured here as is consistent with Kalachandra's method i.e. thinner samples and smaller probe.

Polymerisable plasticiser based materials (PP) (CI) (PE) (PH)

The exact composition of these polymerisable plasticiser based materials was given in table 1.4.7. The DMA traces for this class of experimental materials are similar in nature and show typical plots for an acrylic soft lining material; with the maximum in the loss tangent curve peaking near mouth temperature. The peaks though are universally shorter and slightly broader than those obtained for the other plasticised acrylics. This can be attributed to a distribution of sizes of the plasticising oligomers, with the smaller ones contributing to the early part of the transition and the larger ones coming into effect at some higher temperature.

The plots of these polymerisable plasticiser based materials are shown in figures 5.1.23 to 5.1.30 with table 5.1.8 summarising the results at room and mouth temperatures.

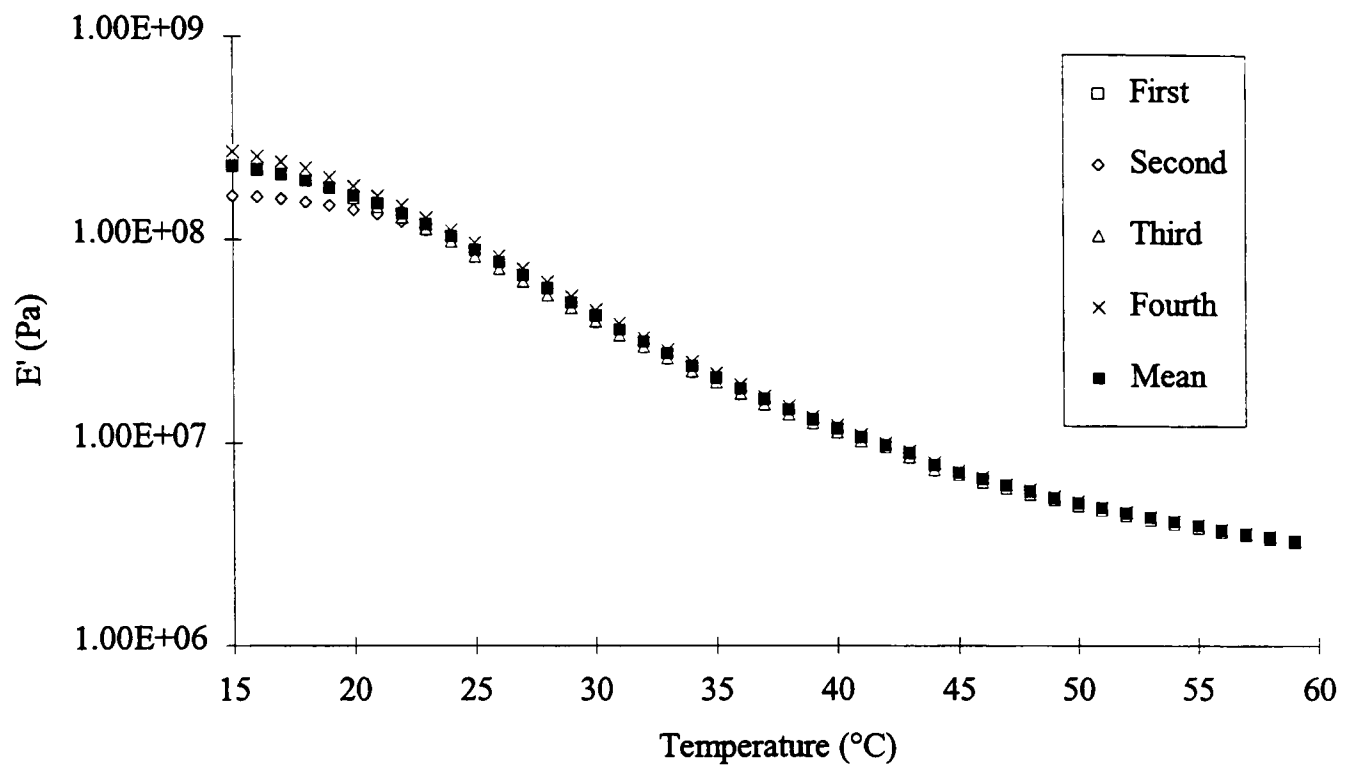


Figure 5.1.23. Storage modulus of experimental PP material.

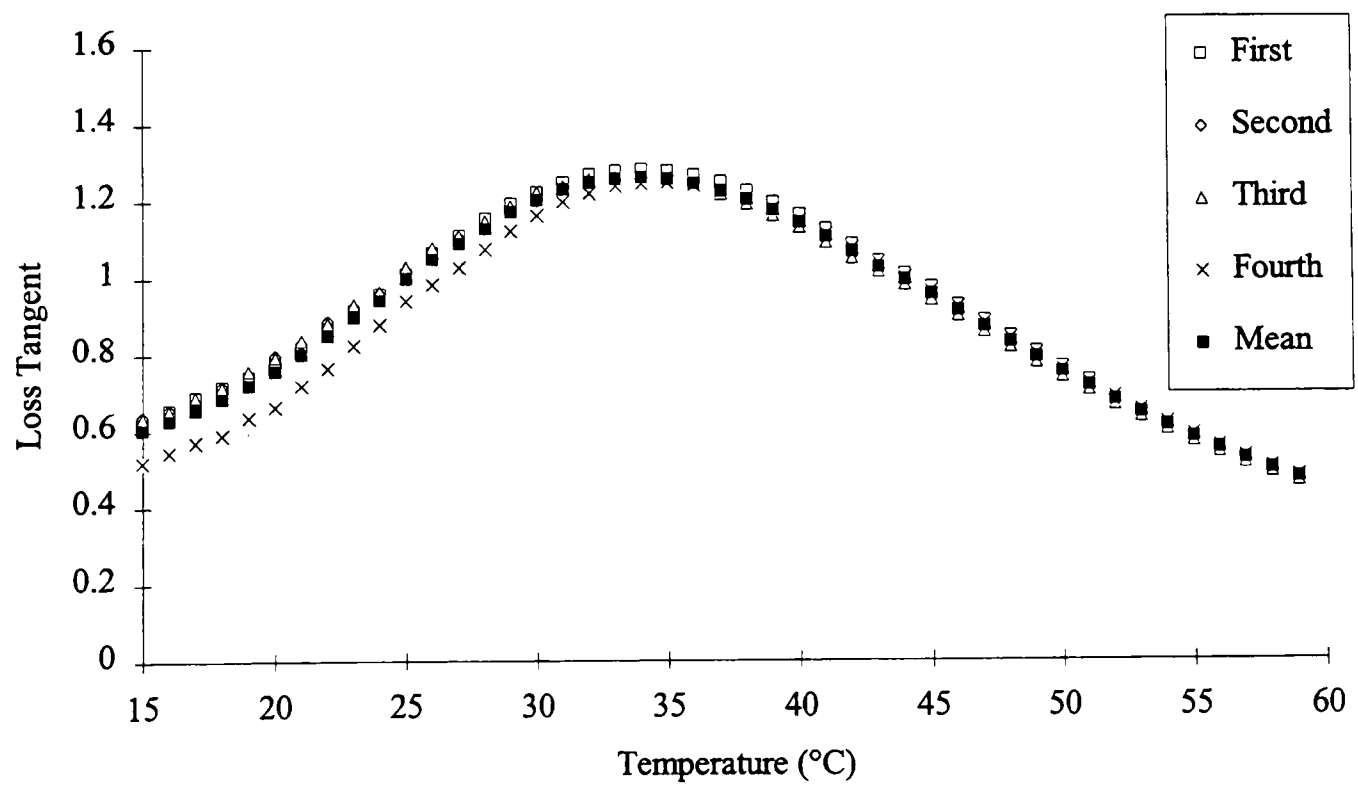


Figure 5.1.24. Loss tangent of experimental PP material.

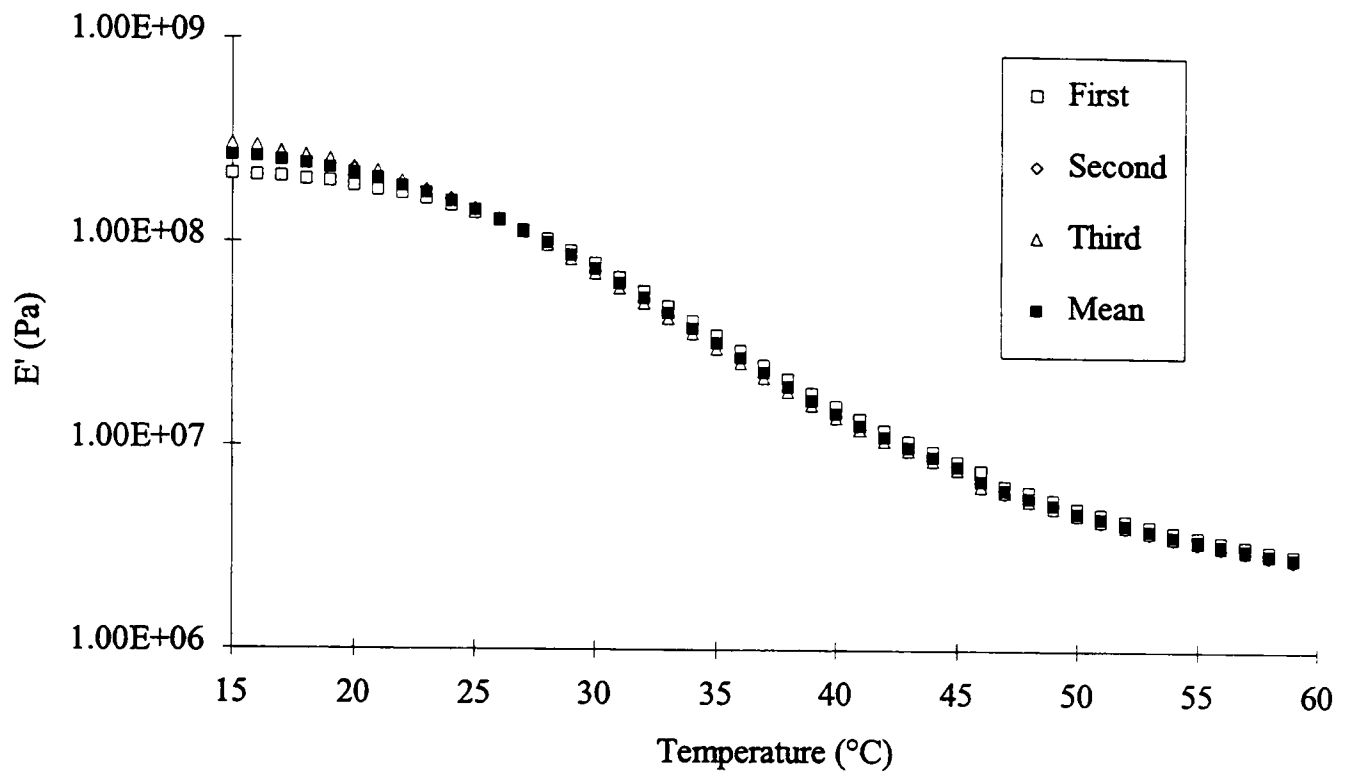


Figure 5.1.25. Storage modulus of experimental C1 material.

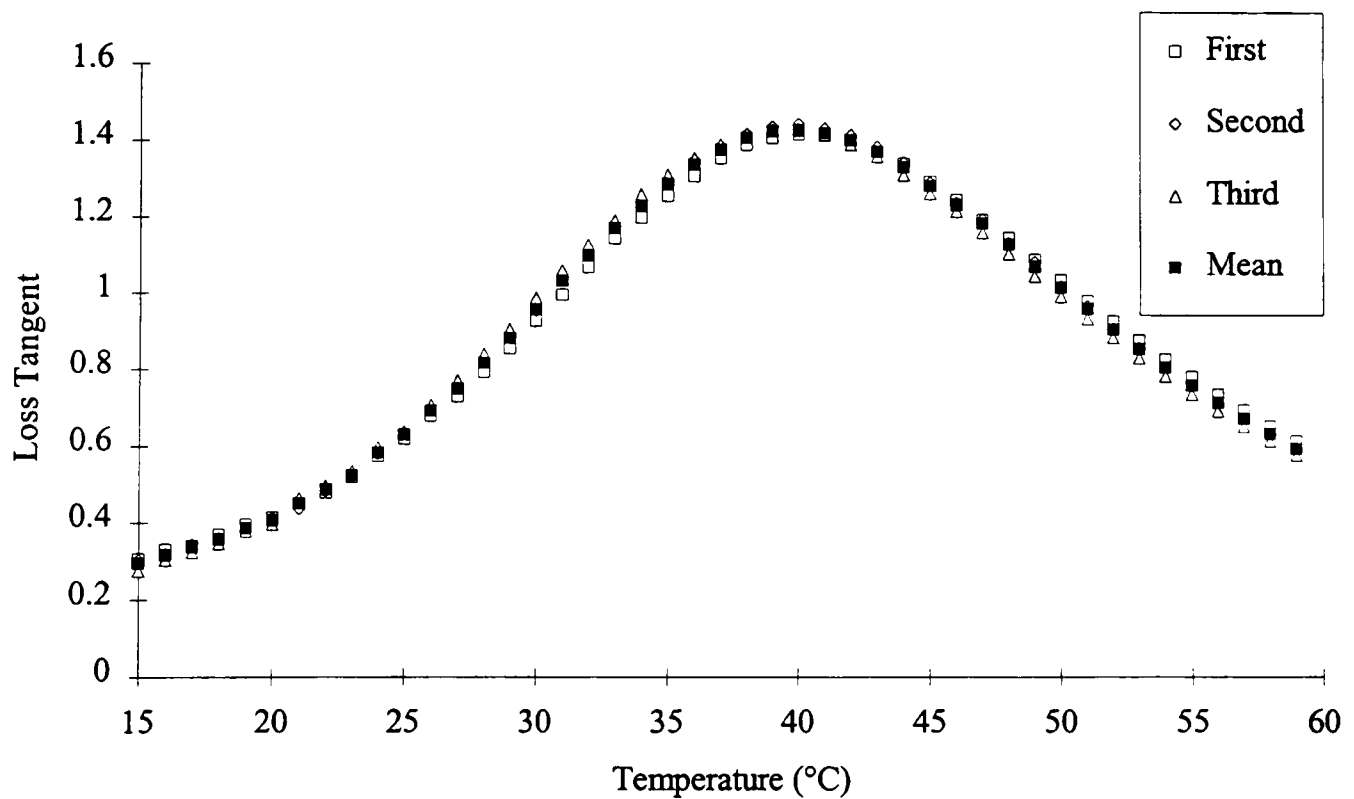


Figure 5.1.26. Loss tangent of experimental C1 material.

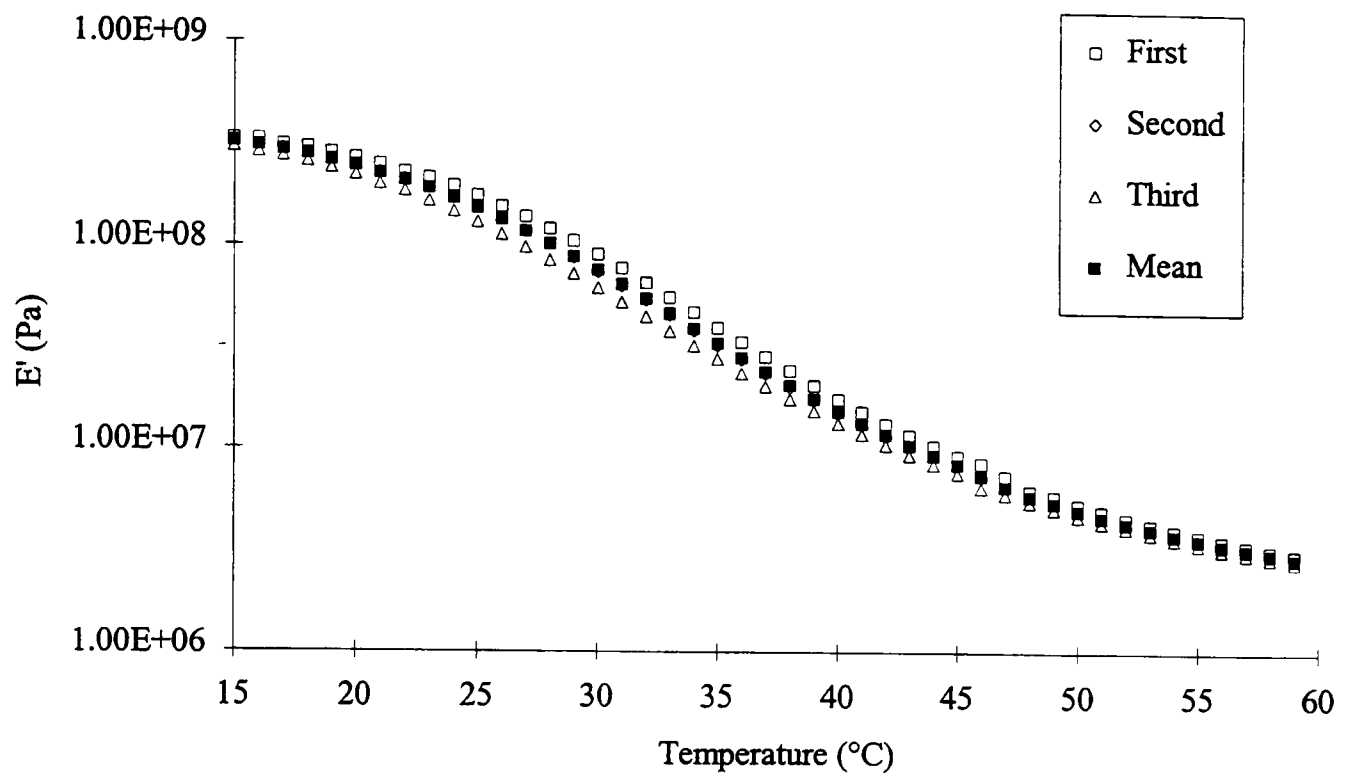


Figure 5.1.27. Storage modulus of experimental PE material.

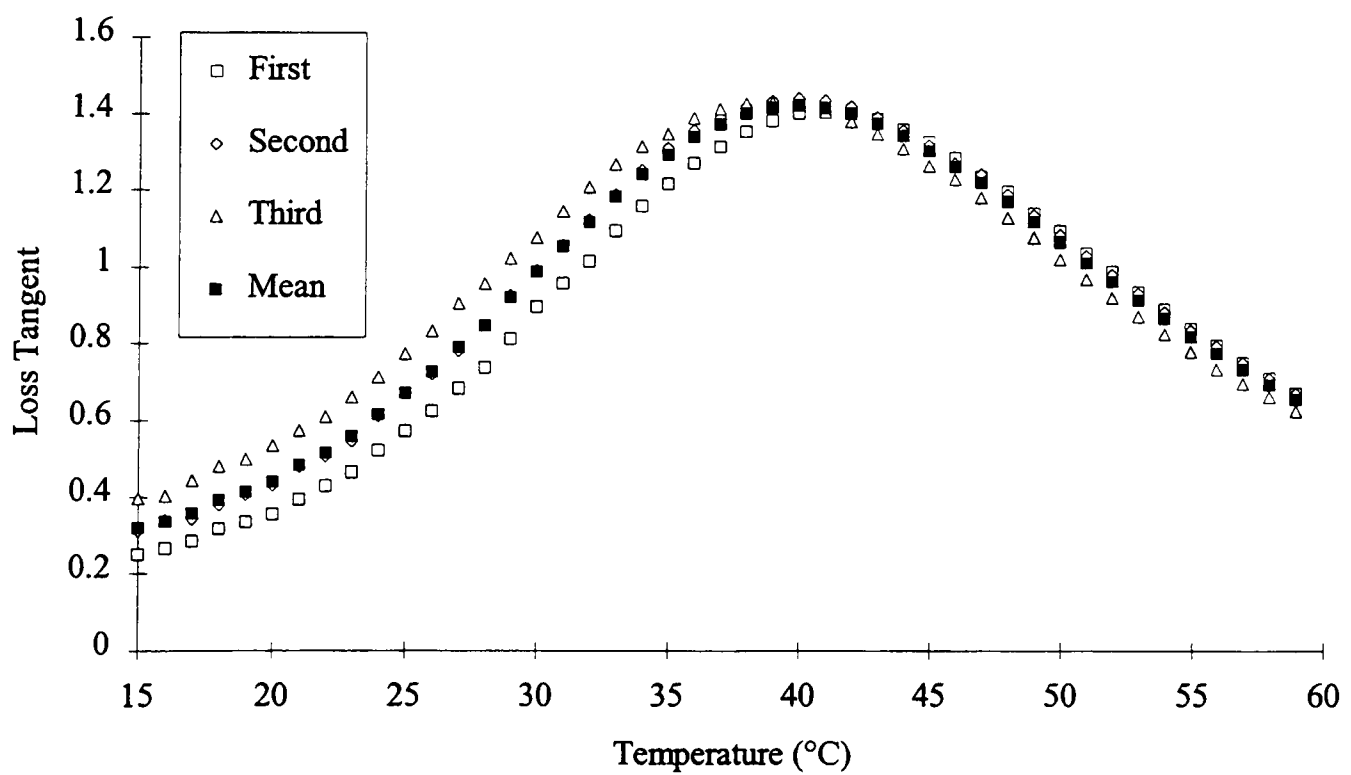


Figure 5.1.28. Loss tangent of experimental PE material.

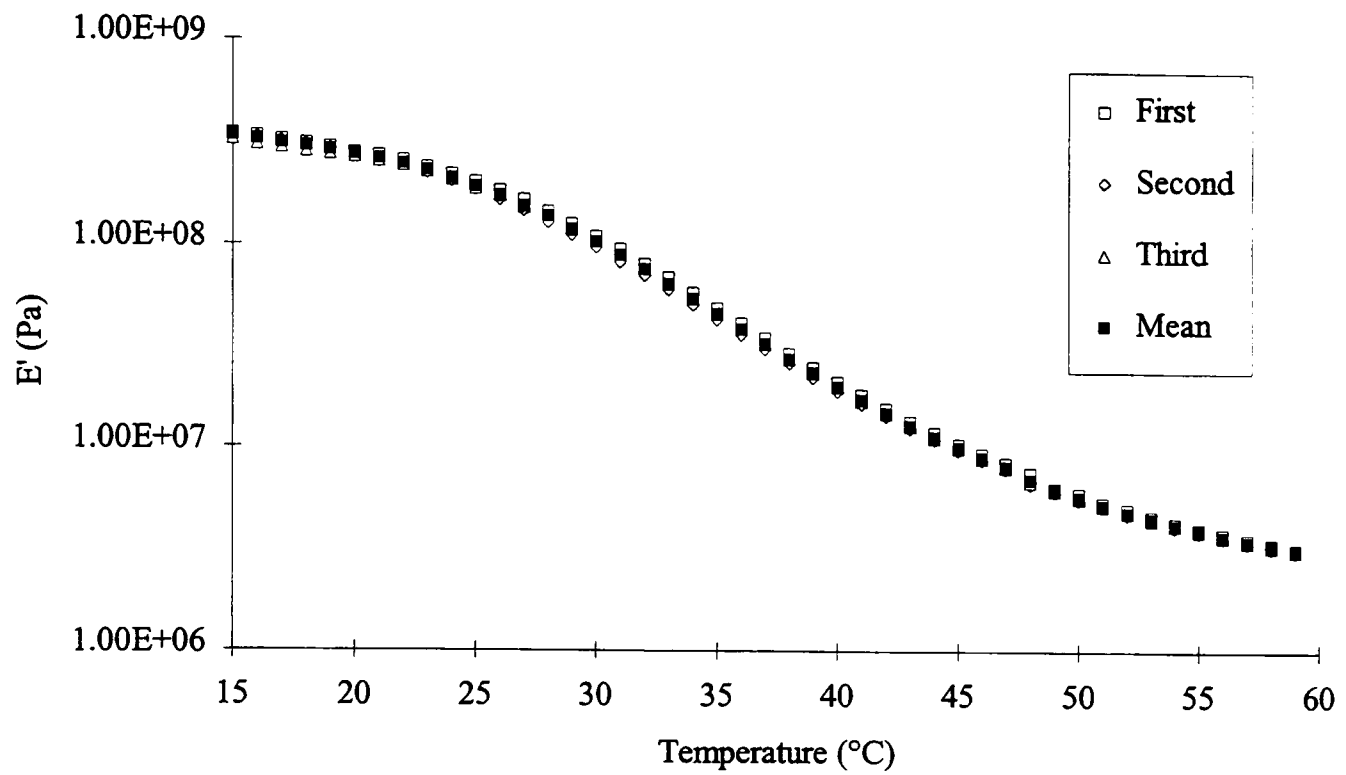


Figure 5.1.29. Storage modulus of experimental PH material.

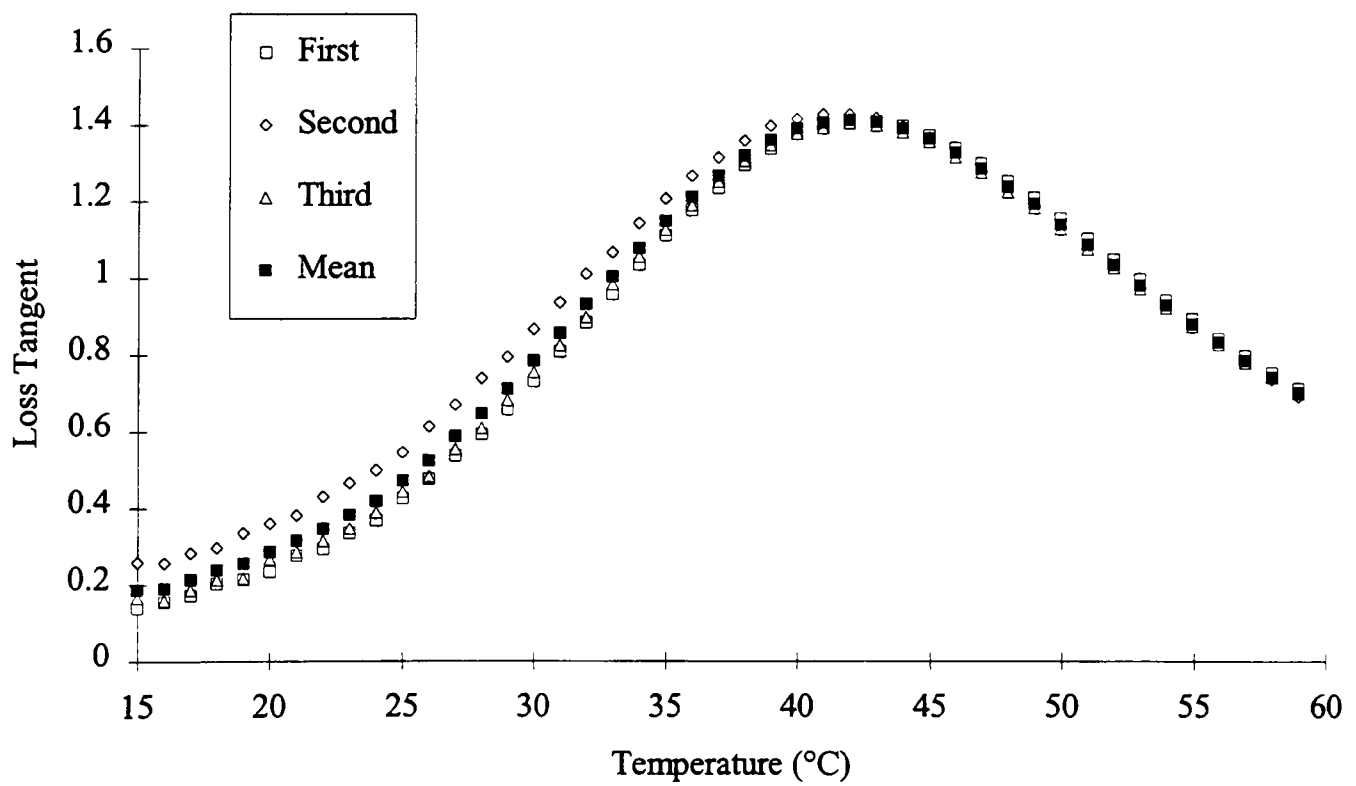


Figure 5.1.30. Loss tangent of experimental PH material.

PP	E' (MPa)	S.D.	Tan δ	S.D.
37°C	16.6	0.69	1.23	0.02
22°C	136	11.58	0.851	0.06
C1	E' (MPa)	S.D.	Tan δ	S.D.
37°C	23.6	1.79	1.38	0.02
22°C	191	14.16	0.487	0.01
PE	E' (MPa)	S.D.	Tan δ	S.D.
37°C	24.6	4.20	1.38	0.05
22°C	210	22.16	0.516	0.09
PH	E' (MPa)	S.D.	Tan δ	S.D.
37°C	33.1	2.17	1.27	0.04
22°C	251	7.19	0.348	0.07

Table 5.1.8. The viscoelastic properties of PP, C1, PE and PH at room and mouth temperature.

In these four polymerisable plasticiser materials the stiffness corresponds to the T_g^* . PH for example has the highest glass transition and the highest modulus, PE being next in line with stiffness and T_g , etc. In fact overall C1, PE and PH are the stiffest of all the materials tested in their natural state. This increase in stiffness of C1, PE and PH relative to the PP material is possibly due to the relative decrease in the amount of plasticiser used in these three materials.

It is not possible to predict the T_g 's of these materials with any degree of accuracy (based upon their compositions) although the trends observed can largely be accounted for. One would expect a material containing 2-ethylhexyl methacrylate to have a lower glass transition compared to one containing hexyl methacrylate, due to the increased

* The T_g 's of these materials are as follows: PP : 34.0°C, C1 : 39.8°C, PE : 40.1°C, PH : 42.0°C. These and all the other T_g 's for all the materials tested are summarised in table 5.3.1.

bulkiness of the former; this is observed by comparing PE and PH. Similarly one would expect C1 to have a lower T_g for similar reasons.

By virtue of the fact that these are experimental materials, there has been no previous work carried out on their viscoelastic characteristics. It is therefore not possible to compare these results with the work of others.

5.2. Ageing Characteristics.

In this section the effect of ageing on the viscoelastic characteristics of the soft liners were investigated. A variety of methods are described in the literature to study the durability of soft lining materials. These include dedicated ageing machines (Dootz et al, 1993); storage in water, and other media, e.g. denture cleaners (Bates & Smith, 1965; Manderson & Brown, 1978; Kalachandra et al, 1995); thermal cycling (Quadah, 1991); as well as clinically based experiments (Jepson et al, 1993b). Of the laboratory techniques, storage in water at 37°C is one of the most common, probably because of the ease, and reproducibility of the technique.

This is precisely the method used in this thesis. Samples of material were prepared as before in the shape of 2mm thick discs approximately 7 mm in diameter. These were weighed (± 0.0002 g) initially and inserted into capped glass specimen containers filled with distilled water. These glass tubes were kept in an oven thermally controlled at 37°C ($\pm 1^\circ\text{C}$). After a nominated period of such storage (reported here up to a year) a set of 3 samples for each material were removed, re-weighed and subsequently tested using the DMA technique outlined previously. The changes in the storage modulus and loss tangent at 37°C as well as the Tg of the material at each time interval are reported here. The change of sample weight after each storage period is also given; with weight gain and loss being reported as positive and negative as might be expected.

In addition to this investigation of 'wet' samples, a set of samples were removed after a years immersion in distilled water. These were subsequently dried in an oven at 37°C, weighed and dynamically tested as before. This was done to investigate the solubility of the materials after a year and by comparison with the 1 year old 'wet' samples to elucidate the effect which the presence of water was having on the materials. Note that a positive weight change here indicates a weight loss whereas a negative weight change indicates a weight gain.

The effect of storage in an aqueous environment on soft lining materials has been extensively investigated in the past (Braden & Wright, 1983; Kazanji & Watkinson, 1988(b); Parker & Braden, 1989). The situation is often complicated as a number of contributing cofactors are occurring simultaneously, as noted by Braden and Wright (1983): *"Soft lining materials undergo two processes when immersed in water. Plasticiser and other soluble materials are leached out into the water, and water is absorbed by the polymer. The balance between these two processes affects both compliance and dimensional stability of the materials."*

This report will not concern itself with the mechanisms and theories of water absorption, particularly as the subject has very recently been the focus of an extensive study in this department (Riggs, 1997). The main mechanisms for the uptake of water in soft lining materials, as is pertinent to their viscoelastic properties, are briefly re-iterated here. For a more involved and mathematical treatment of the subject the above text should be consulted.

Water uptake is primarily governed by a diffusion process similar to the classic laws which govern heat conduction in solids. Fick's first law describes the rate of diffusion (F or flux) as being proportional to the concentration (i.e. c) gradient, D being the diffusion coefficient. Analogously the rate of heat flow into a material (Q) is proportional to the temperature (T) gradient, where k is the thermal conductivity.

$$F = -D \frac{\partial c}{\partial x} \quad \text{Diffusion of water.} \quad 5.2.1.$$

$$Q = -k \frac{\partial T}{\partial x} \quad \text{Conduction of heat.} \quad 5.2.2.$$

This relatively simple relationship rarely applies to soft lining materials however due to complications introduced by the presence of water soluble impurities in the polymer matrix. When these impurities are reached by the diffusing water they dissolve and form

droplets of solution. By a process of osmosis these droplets grow in size as the diffusing water is absorbed by them. This process of growth is opposed however by the elastic forces of the polymer matrix restraining the droplet size.

The magnitude of these elastic restraining forces are obviously connected to the mechanical properties of the material. In a strong material the size of the droplets and therefore the total uptake will be small as the droplets will be constrained in size; conversely, in a weaker material the droplets can grow indefinitely, possibly leading to the formation of cracks within the material.

Furthermore it should be noted here that for our purposes the water content of a polymer sample can be regarded as existing in two states* : bound water and free water. Bound water is closely bonded to the polymer chains; an example of this would be water attracted to hydrophilic parts of a polymer chain such as an OH group. Free water, as the terminology implies, is relatively free in that it is not actually bound to the polymer, an example of this can be water contained within a growing droplet or free volume within the polymer.

* This is a matter of some debate (Riggs, 1997)

5.2.1. Acrylic Based Materials.

Futurasoft III (FS)

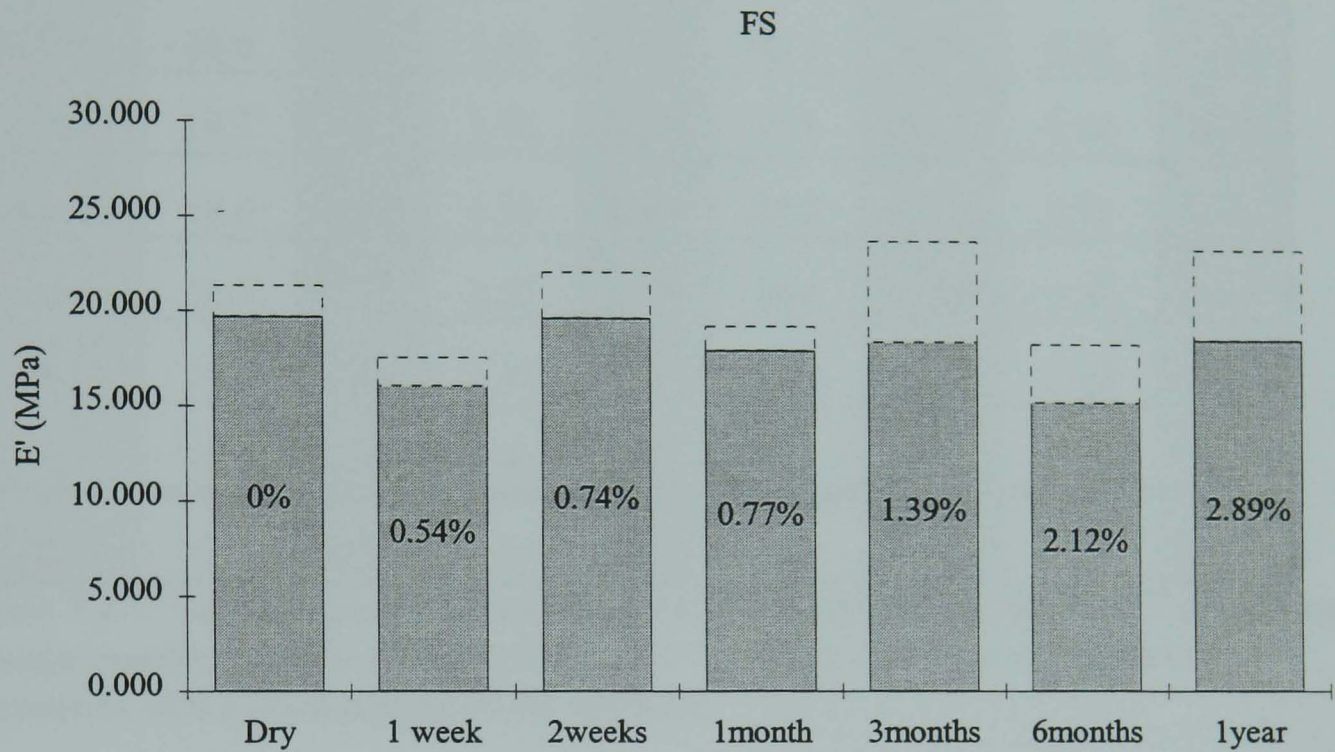


Figure 5.2.1. Variations in the storage modulus (at 37°C, 1Hz) of FS against time together with variations of sample weight.

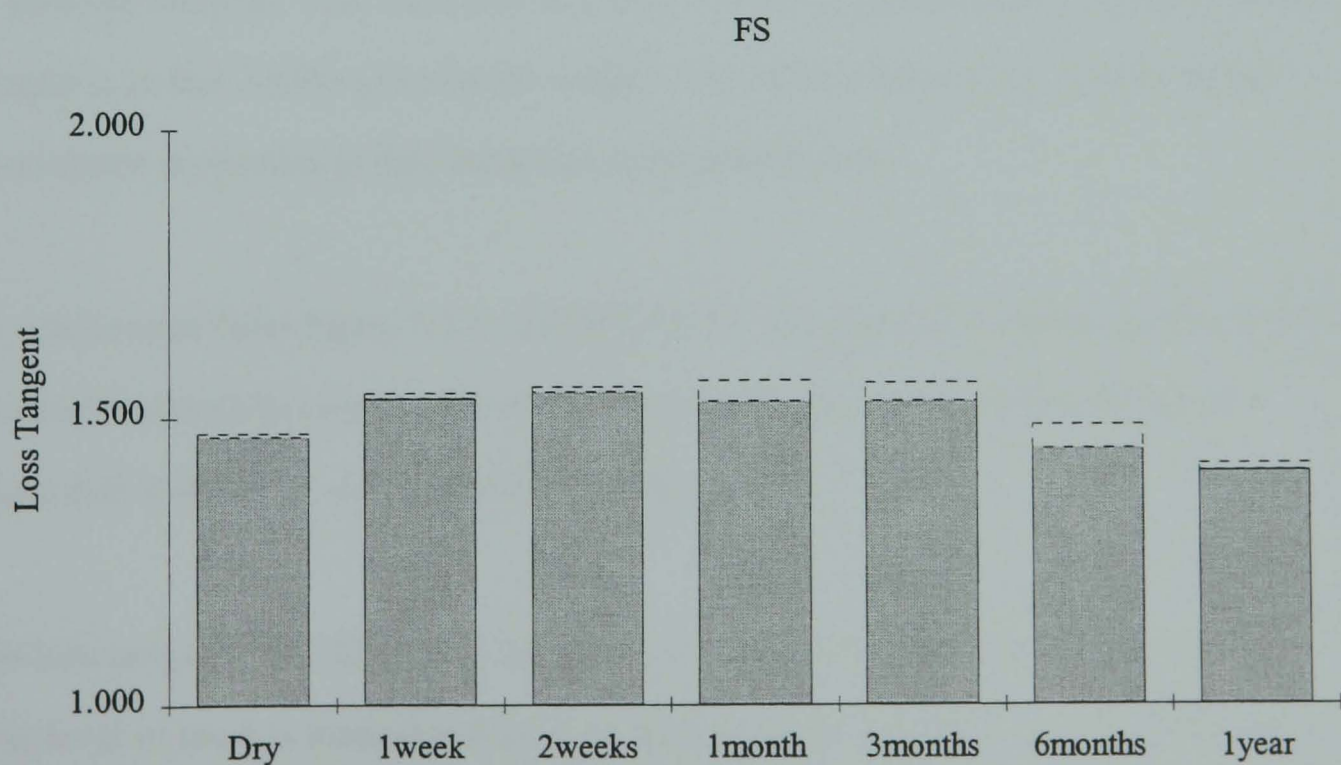


Figure 5.2.2. Variation of $\tan \delta$ with respect to time for FS.

	E' (MPa)	S.D.	Tan d	S.D.	Tg (°C)	S.D.	Weight (%)	S.D.
Dry	19.7	1.63	1.47	0.01	36.8	0.70	0.0	-
1 week	16.0	1.53	1.53	0.01	36.4	0.71	0.54	0.23
2 weeks	19.7	2.42	1.54	0.01	37.5	0.81	0.74	0.04
1 month	18.0	1.30	1.53	0.04	37.2	0.13	0.77	0.06
3 months	18.4	5.35	1.53	0.03	36.6	1.83	1.39	0.06
6 months	15.2	3.10	1.44	0.04	37.0	1.43	2.12	0.46
1 year	18.6	4.79	1.41	0.01	38.3	1.94	2.89	0.02
1 year D	31.4	10.59	1.35	0.08	41.2	1.81	0.76	0.18

Table 5.2.1. Ageing data for FS including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation. Last row of the table is concerned with a dried sample of the material.

It will be seen that this material had the lowest water uptake of all the acrylic materials tested here, gaining 2.89% weight over a year. Also after a year 0.76% of the initial weight of this material was lost due to leaching out of extractable (low molecular weight or soluble) material. This indicates that after a year the actual amount of water in the sample is in fact 3.65% of its initial weight. The effect of this water uptake on the viscoelastic properties of this material is discussed below.

As can be seen from figure 5.2.1. and table 5.2.1. the change in storage modulus of this material is somewhat erratic. Hence with the relatively high standard deviations associated with the E', a clear trend is not apparent.

The loss tangent data (figure 5.2.2.) shows an initial rise after a week in storage to 1.53. This level of tan δ is maintained for time periods up to 3 months, but the latter two readings i.e. 6 and 12 months, show a gradual decrease. As will be seen shortly this type

of behaviour is mirrored by all* of the acrylic based materials including NS and PP. A possible explanation is given here assuming that the presence of water or soluble impurities has the affect of raising the loss tangent of the material. This explanation also relies on the dual processes of water uptake and loss of leachable material. The water uptake is likely to be dominant initially as the intake of water has to precede the leaching out of plasticiser. This can be translated into the initial increase in the loss tangent (up to 1 week). Then follows a period of time when the two processes of uptake and leaching approximately cancel each other out, leading to a stable loss tangent (up to 3 months). Finally a (6 and 12 months) period ensues in which the latter process of leaching is in the ascendance.

As for the storage modulus, not much information can be gleaned from the Tg of the material because of the small overall change and relatively large standard deviations.

The one year old, dried material was seen to be, stiffer, with a higher Tg and lower loss tangent than any of the preceding results. This is no doubt due to the loss of water and leachable material (plasticisation).

* OS being an exception, due to its highly plasticised nature.

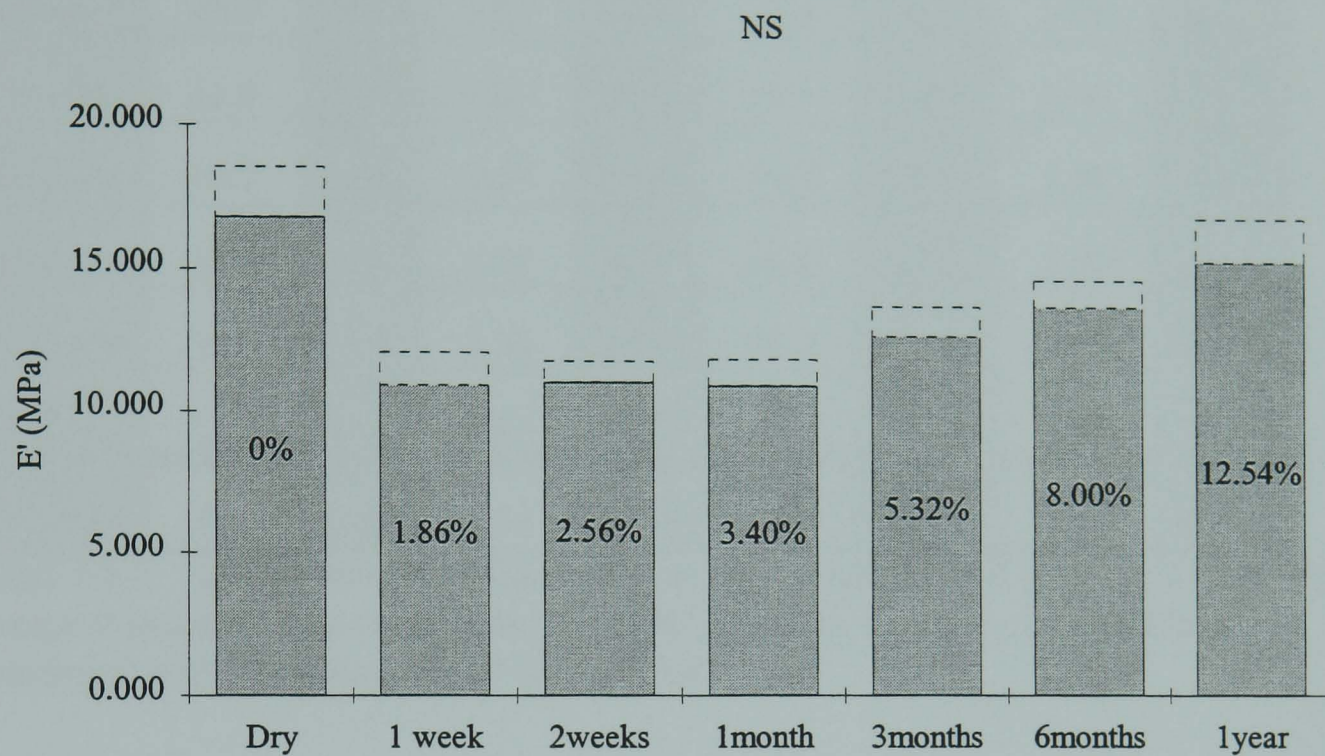
Supersoft, new and old (NS & OS)

Figure 5.2.3. Variations in the storage modulus (at 37°C, 1Hz) for NS, plotted against time. Together with variation of sample weight %.

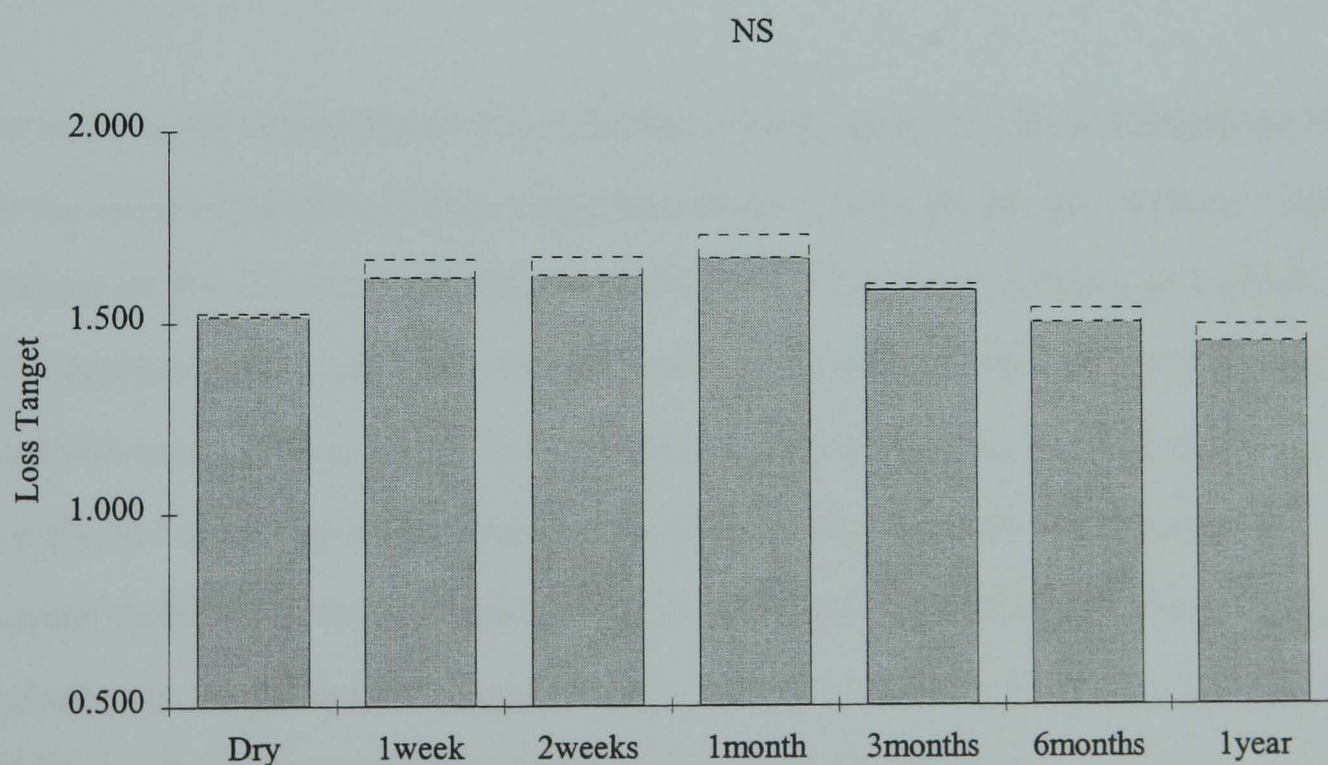


Figure 5.2.4. Variations in the loss tangent (at 37°C, 1Hz) for NS after storage.

	E' (MPa)	S.D.	Tan d	S.D.	Tg (°C)	S.D.	Weight (%)	S.D.
Dry	16.8	1.76	1.52	0.01	37.9	0.45	0.0	-
1 week	10.9	1.17	1.62	0.05	35.9	0.66	1.86	0.22
2 weeks	11.0	0.75	1.63	0.05	35.7	0.36	2.56	0.31
1 month	10.9	0.94	1.67	0.06	36.8	0.10	3.40	0.26
3 months	12.7	1.06	1.59	0.02	36.8	0.63	5.32	0.12
6 months	13.7	0.95	1.50	0.04	38.2	0.38	8.00	0.56
1 year	15.3	1.52	1.45	0.05	39.9	0.14	12.50	0.41
1 year D	47.0	0.94	1.14	0.05	44.7	0.02	2.00	0.04

Table 5.2.2. Ageing data for NS including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation. Last row of the table is concerned with a dried sample of the material.

Samples of this material had increased their weight by 12.5% after a year's immersion in water, taking into account the 2.0% loss of leachable material this translates into a 14.5% percent water gain.

The loss tangent values (figure 5.2.4.) follow a similar pattern to those outlined for FS and the same explanation of their occurrence holds. Unlike the storage modulus values obtained for FS, the results obtained for NS (figure 5.2.3.) show a clear trend which is again explained by considering the dual processes of water uptake and extraction of low molecular weight components. To re-iterate in terms of modulus, the drop in the modulus at 1 week can be explained by the initial intake of water. The period of constant modulus can be explained by a balance of water uptake against the leaching out of plasticiser. While from 3 months onwards the leaching out of plasticiser dominates over the intake of water and hence the material gradually hardens.

Tests on the samples of dried material after 1 year show the extent of the role played by the plasticisers (including water) on the material.

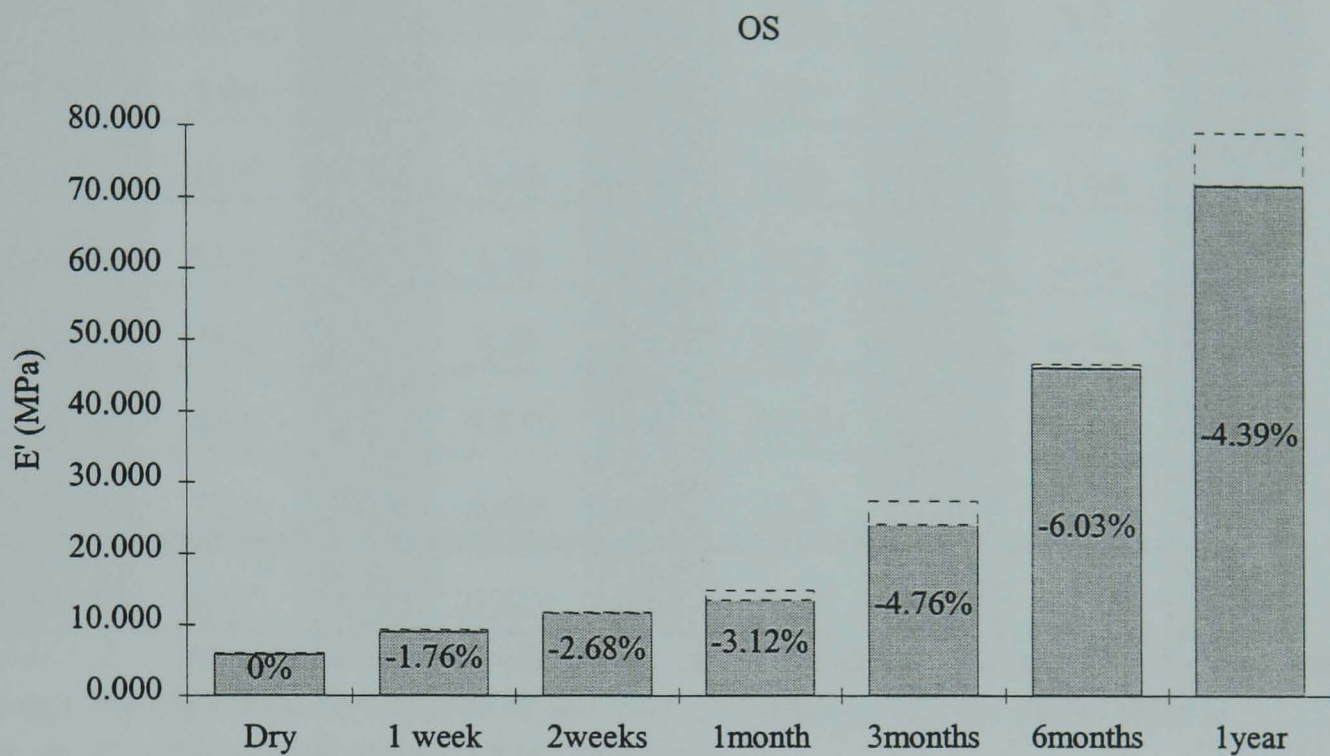


Figure 5.2.5. Variations in the storage modulus (at 37°C, 1Hz) for OS, plotted against time. Together with variation of sample weight %.

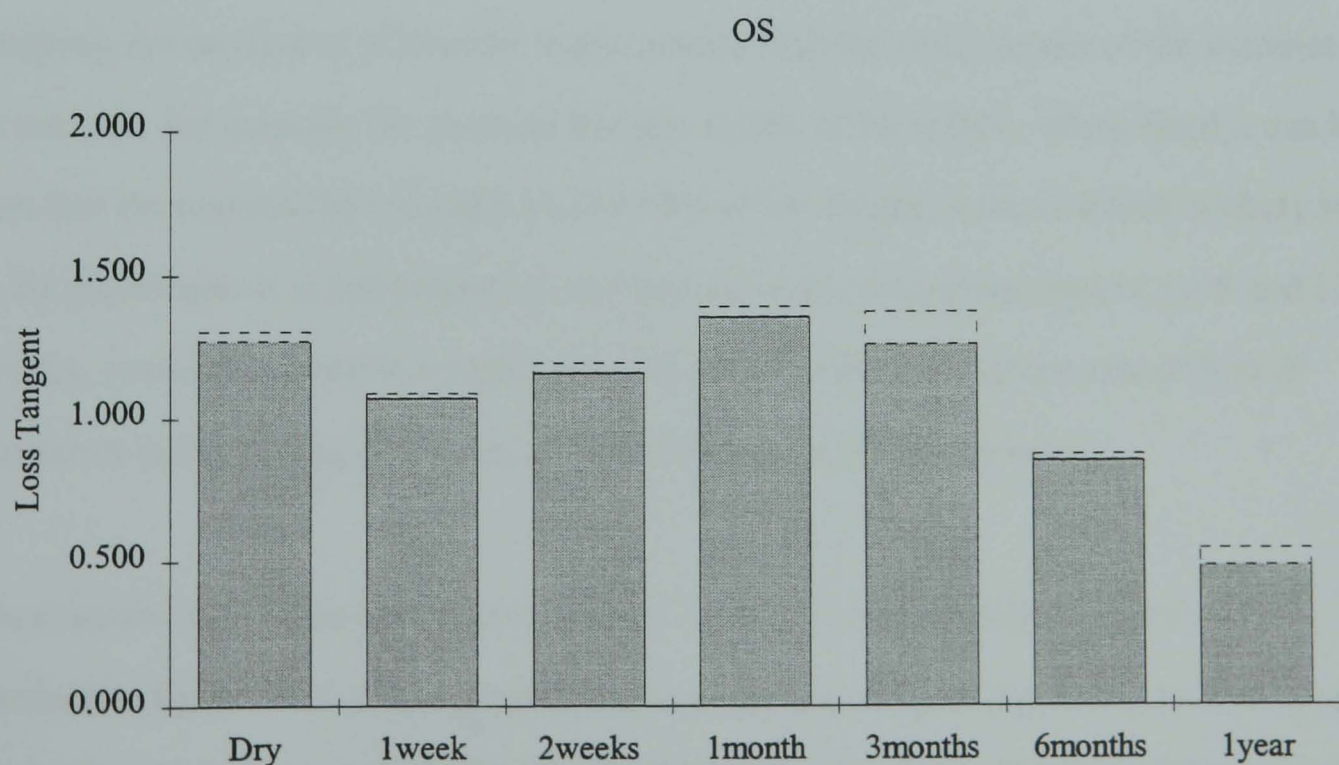


Figure 5.2.6. Variations in the loss tangent (at 37°C, 1Hz) for OS, plotted against time.

	E' (MPa)	S.D.	Tan d	S.D.	Tg (°C)	S.D.	Weight (%)	S.D.
Dry	5.87	0.21	1.27	0.03	30.1	0.53	0.0	-
1 week	9.04	0.31	1.07	0.02	30.9	0.22	-1.76	0.27
2 weeks	11.6	0.17	1.16	0.04	35.2	0.71	-2.68	0.11
1 month	13.5	1.42	1.35	0.04	37.3	0.36	-3.11	0.33
3 months	24.2	3.35	1.26	0.12	40.2	0.73	-4.76	0.04
6 months	46.4	0.57	0.850	0.02	47.0	0.19	-6.03	0.19
1 year	72.3	7.47	0.480	0.06	52.8	0.73	-4.39	0.39
1 year D	93.7	50.00	0.227	0.04	64.0	0.59	13.58	0.38

Table 5.2.3. Ageing data for OS including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation. Last row of the table is concerned with a dried sample of the material.

The water uptake of this material is very different to that of the previous two materials examined, in that at each time scale the material is losing weight. This is attributed to the large amounts of plasticiser in this material: 31.2%, (Wright, 1981). So that at each weighing the amount of plasticiser lost is greater than the water intake of the material. At one year for example the material has lost 4.39% of its weight. When dried it can be seen that the material has actually lost 13.58% of its weight, most of which is likely to be the plasticiser. It is interesting to note that the water absorption figures for 6 and 12 months, showing a relative weight gain. This is an indication that the rate of loss of plasticiser is decreasing compared to the water uptake of the material.

The dramatic rise in modulus (from 5.86 to 72.3 MPa) is a reflection of this loss of plasticiser (figure 5.2.5.). The general shape of the loss tangent graph (figure 5.2.6.) can be explained by the overall shift of the Tg of the material from 30.1 to 52.8°C, such that as the peak of the loss tangent approaches 37°C (towards 1 month) an increase is seen,

followed by a decrease as the Tg travels beyond mouth temperature with the continuing loss of plasticiser.

Wagner et al (1995b) used a 'Weather-Ometer' instrument to age their samples. This involved 900 hours of exposure to visible and ultraviolet light as well as periodic spraying with distilled water. The clinical significance of this unusual ageing regime is open to debate. However the effect of the ageing was certainly pronounced as Supersoft increased its storage modulus from 2.6 to 20.1 MPa, an approximately eight fold rise. The loss tangent was also affected falling from 1.25 to 0.93.

Kalachandra et al (1995) investigated Supersoft after a hundred days immersion in distilled water at 37°C and found its water absorption to be 5.0%, this is consistent with the new formulation of the material (NS) as tested in the present study*. This is contrary to the assumption taken in 5.1.1. concerning this paper i.e. that the material tested by Kalachandra et al is OS. This latter assumption was made based upon the test geometry favoured by Kalachandra et al, which had the effect of overestimating the stiffness of samples compared with the method used in this report. Based on this contrary evidence it is plausible that the result presently discussed is erroneous, and that OS is in fact being studied. Two points are in favour of this assumption: a) Kalachandra et al do not repeat their work. b) the water uptake results of Kalachandra et al come under suspicion in section 5.2.3 where the material NN is being considered.

Robinson & McCabe (1982) studied Supersoft after immersion in water for 3 months. The soft liner was seen to harden slightly in this time period, with its 10 second creep modulus increasing (2.4 to 2.77 MPa). This slight increase is smaller than the trend observed here.

* Although the water uptake data of Kalachandra et al (1995) have been known to be inconsistent (Gettleman, 1994) and the authors did not do repeats, to check the validity of their work.

The water uptake of Supersoft was looked at by Wright (1976) by immersion in distilled water, although over a longer period of time (up to approximately 2 years). Very similar characteristics were observed by Wright (i.e. a maximum weight loss of $\approx -5\%$). In particular the weight gain trend observed here between 6 months and 12 is also shown, and is seen to continue.

5.2.2. Silicone Based Materials.

Molloplast B (MP)

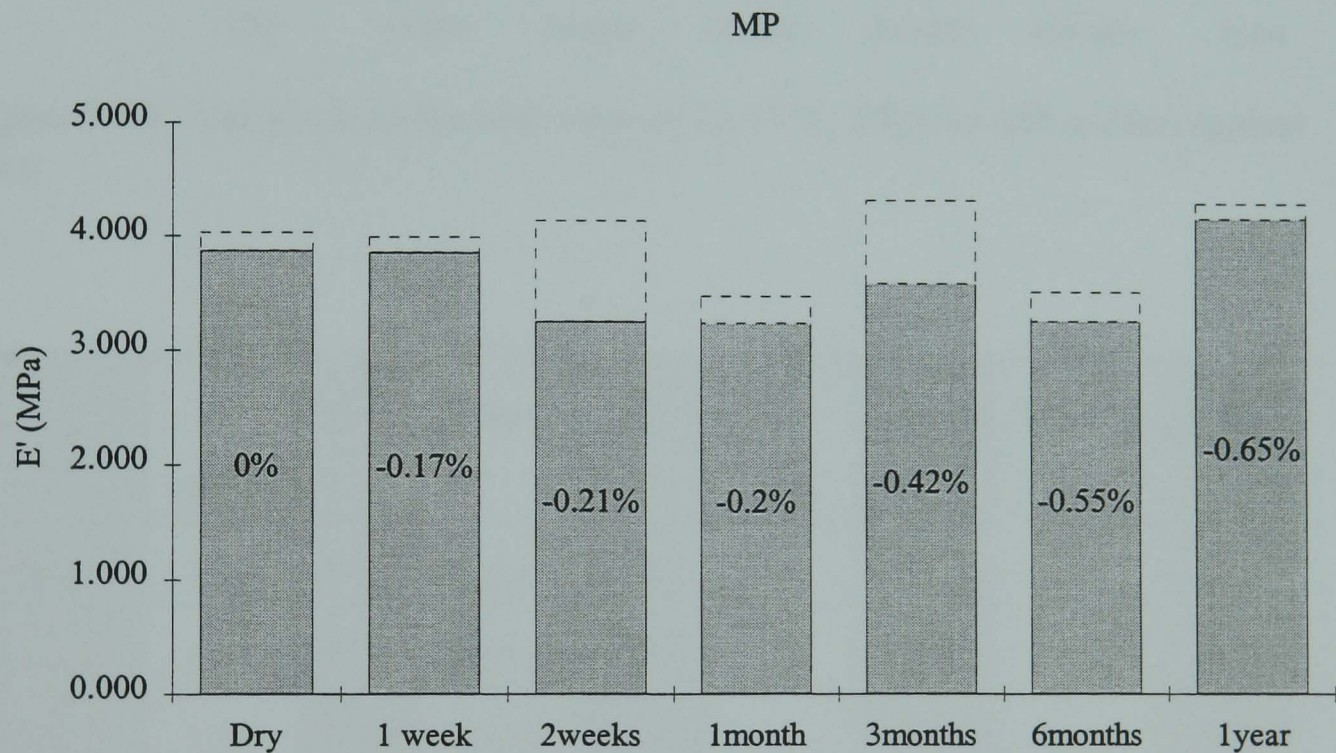


Figure 5.2.7. Variations in the storage modulus (at 37°C, 1Hz) for MP, plotted against time. Together with variation of sample weight %.

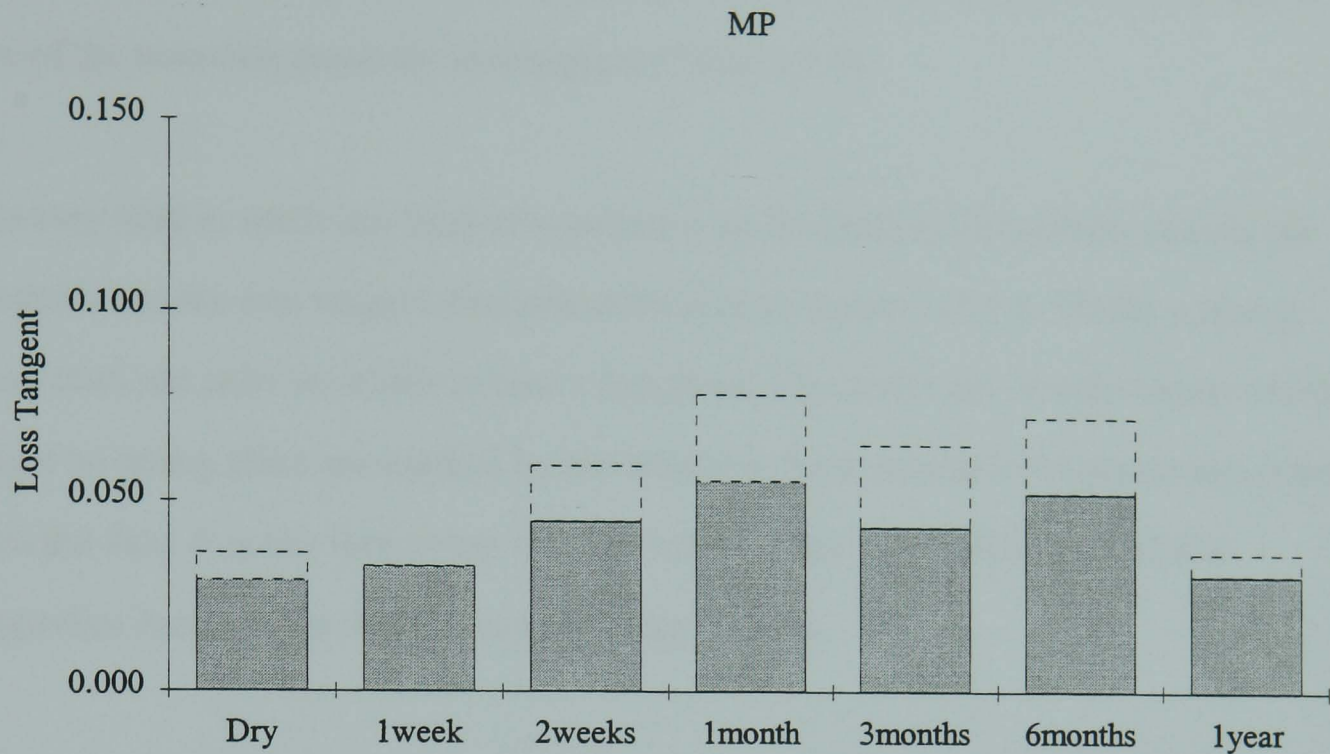


Figure 5.2.8. Variations in the loss tangent (at 37°C, 1Hz) for MP, plotted against time.

	E'	S.D.	Tan d	S.D.	Tg	S.D.	Weight	S.D.
	(MPa)				(°C)		(%)	
Dry	3.87	0.16	0.029	0.007	-	-	0.0	-
1 week	3.86	0.14	0.033	0.000	-	-	-0.17	0.25
2 weeks	3.26	0.88	0.045	0.015	-	-	-0.21	0.21
1 month	3.24	0.24	0.056	0.023	-	-	-0.20	0.00
3 months	3.59	0.74	0.044	0.022	-	-	-0.42	0.11
6 months	3.26	0.26	0.052	0.020	-	-	-0.55	0.17
1 year	4.17	0.14	0.031	0.006	-	-	-0.65	0.09
1 year D	3.25	0.74	0.053	0.023	-	-	0.91	0.07

Table 5.2.4. Ageing data for MP including storage modulus, loss tangent and weight change together with the associated standard deviation. Last row of the table is concerned with a dried sample of the material.

This material was seen to lose a small amount of weight throughout the period of water storage. This was however of low magnitude and MP had the lowest water uptake of any of the materials presently investigated (Table 5.2.4).

It is very hard to reach any kind of conclusion on the basis of the activity seen in the modulus and the loss tangent data presented here in figures 5.2.7-8. Firstly a strong trend does not exist on which to base a hypothesis. Secondly any (weak) trends which might be taking place are masked by the relatively large standard deviations associated with the data. It is fair then to say that this material had very stable viscoelastic properties during these water absorption experiments.

Wagner et al (1995b) using their 'Weather-Ometer' instrument to age their samples found MP to be relatively stable. The storage modulus changing from 1.5 to 1.2 MPa, and the loss tangent increasing from 0.02 to 0.05 after the ageing process.

Using a similar ageing technique as used here, Kalachandra et al (1995) examined the viscoelastic properties of MP. They found a slight rise in E' (4.8 to 5.1 MPa), but found the loss tangent to be unaffected.

Jepson et al (1993b) looked at the change in the viscoelasticity of MP, in both clinical and laboratory based experiments. They found the properties of the material to be independent of immersion in distilled water or clinical use.

Of the soft liners examined by Robinson & McCabe (1982) the largest effect was observed in Molloplast B (after 3 months immersion in water). The modulus of the material increased from 3.5 to 4.76 MPa. This is not consistent with the results obtained here.

Wright (1976) looked at the water uptake of MP. He found it to have a very low water uptake, as was the case here. This figure was positive however.

Flexibase (FB)

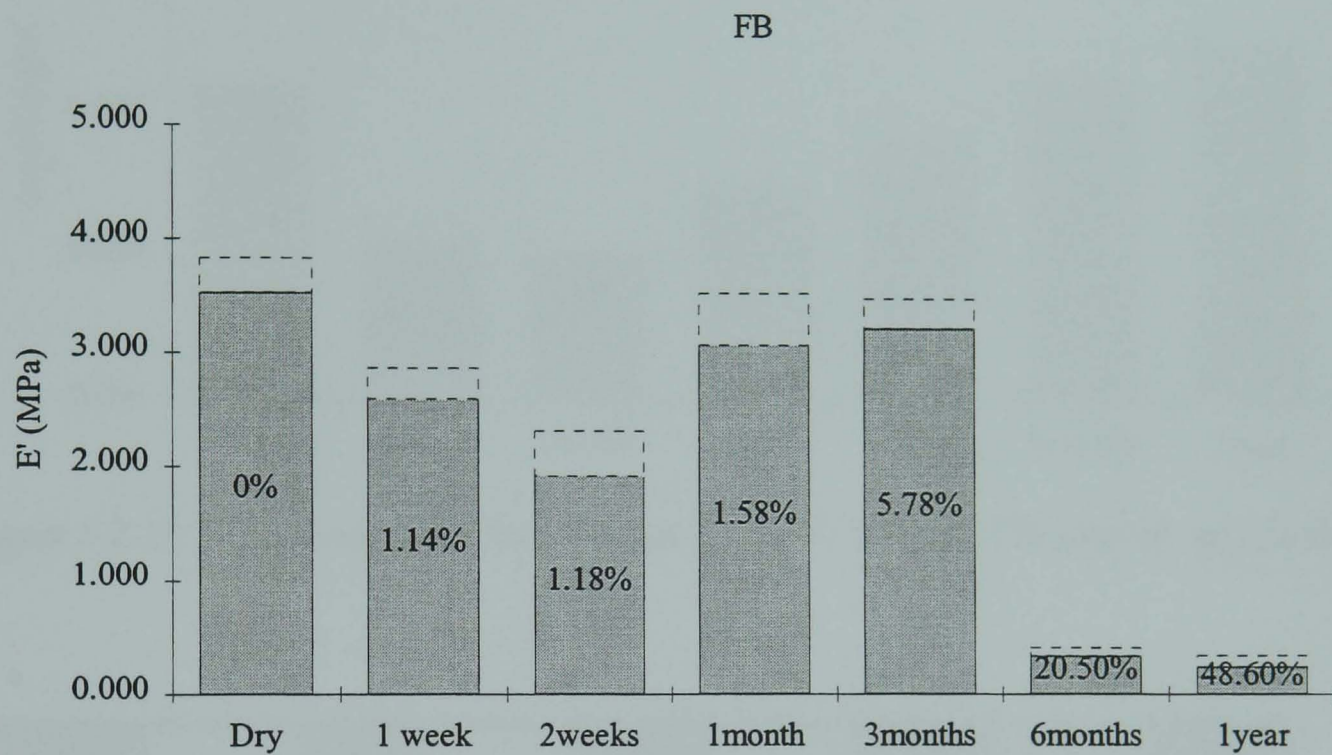


Figure 5.2.9. Variations in the storage modulus (at 37°C, 1Hz) for FB, plotted against time. Together with variation of sample weight %.

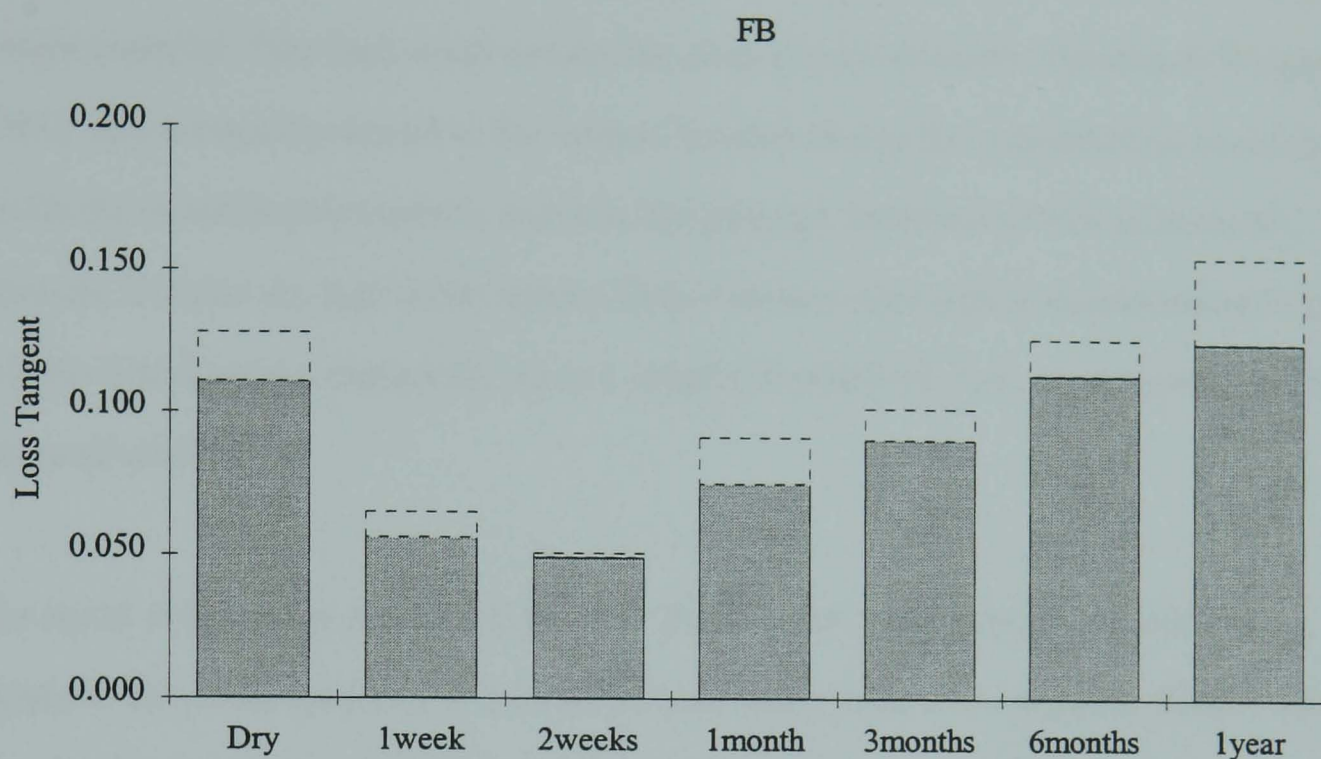


Figure 5.2.10. Variations in the loss tangent (at 37°C, 1Hz) for FB, plotted against time.

	E' (MPa)	S.D.	Tan d	S.D.	Tg (°C)	S.D.	Weight (%)	S.D.
Dry	3.52	0.31	0.111	0.017	-	-	0.0	-
1 week	2.59	0.27	0.056	0.009	-	-	1.14	0.12
2 weeks	1.91	0.40	0.049	0.002	-	-	1.18	0.08
1 month	3.07	0.46	0.075	0.016	-	-	1.58	0.34
3 months	3.22	0.26	0.091	0.011	-	-	5.78	0.22
6 months	0.338	0.07	0.114	0.013	-	-	20.54	0.50
1 year	0.242	0.10	0.126	0.030	-	-	48.57	3.11
1 year D	0.257	0.10	0.105	0.031	-	-	-4.52	0.25

Table 5.2.5. Ageing data for FB including storage modulus, loss tangent and weight change together with the associated standard deviation. Last row of the table is concerned with a dried sample of the material.

In direct contrast to MP, this silicone based material had a huge water uptake of nearly 50% after a years storage in water (table 5.2.5). After the same period the material also lost 4.52% of its weight due to the leaching out of soluble impurities and low molecular weight material. This high water uptake has been observed before (Braden & Wright, 1983), and is possibly linked to the ethanol formed during the condensation reaction by which the material polymerises; and also the inherent weakness of this cold cured material. Despite the high water uptake from 6 months onwards, it is interesting to note that the initial uptake (especially up to 1 month) is relatively low, in comparison with other materials.

The result of this huge amount of water in the polymer after 6 and 12 months was a dramatic fall in the modulus to 0.24 MPa, less than 1/10th of the original (figure 5.2.9). This is almost certainly due to the internal damage done to the polymer by the growth of water droplets. Some of these droplets were in fact large enough to be visible on the surface of the material. The presence of such large amounts of water in the polymer has also had the affect of raising the loss tangent to 0.126 (figure 5.2.10).

It is interesting to note that water, as a material in its own right, would have an infinite loss tangent, because as a liquid it has a negligible ability to store deformational energy. Yet even though after a year the sample contains nearly 50% water, its loss tangent is only slightly higher (14%) than in its initial condition. This indicates that the water is by and large not free to move around in the sample, as any movement would lead to frictional losses and hence an increase in loss tangent.

The earlier stages of the storage modulus and loss tangent behaviour are more difficult to explain. The early drop (1-2 weeks) in the modulus can be due to the loss of extractable matter. This is backed up by the fall in the loss tangent in the same time period. At 1 and 2 months, the rise in the modulus of the material can be explained by a similar reinforcement argument as will shortly be described for the NN material. The

final catastrophic drop in the modulus is due to the irreversible breakdown of the polymer matrix and the formation of cracks by the continual growth of the droplets. Subsequent drying of the material after a year in water did not have a large effect on its storage modulus, indicating that the damage to the polymer matrix is permanent.

Robinson & McCabe examined the viscoelastic properties of FB in 1982. They found a slight decrease in its 10 second creep modulus (2.38 to 2.14 MPa) after 3 months storage in water.

The huge water uptake (maximum $\approx 65\%$) of this material was also observed by Wright (1976).

Storer (1962a) observed an increase in hardness after a period of 30 months in water, indicating that the formulation has changed over the last 35 years.

5.2.3. Miscellaneous Commercial Materials.

Novus (NN)

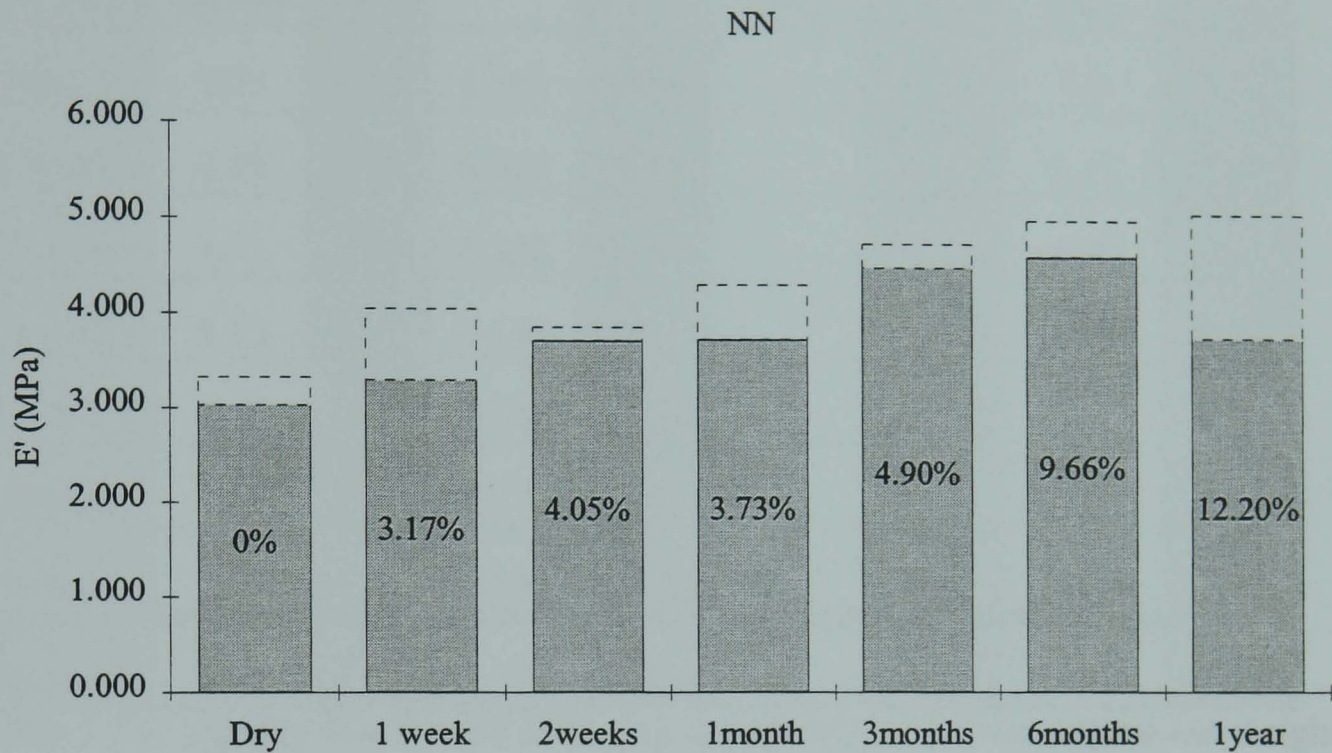


Figure 5.2.11. Variations in the storage modulus (at 37°C, 1Hz) for NN, plotted against time. Together with sample weight %.

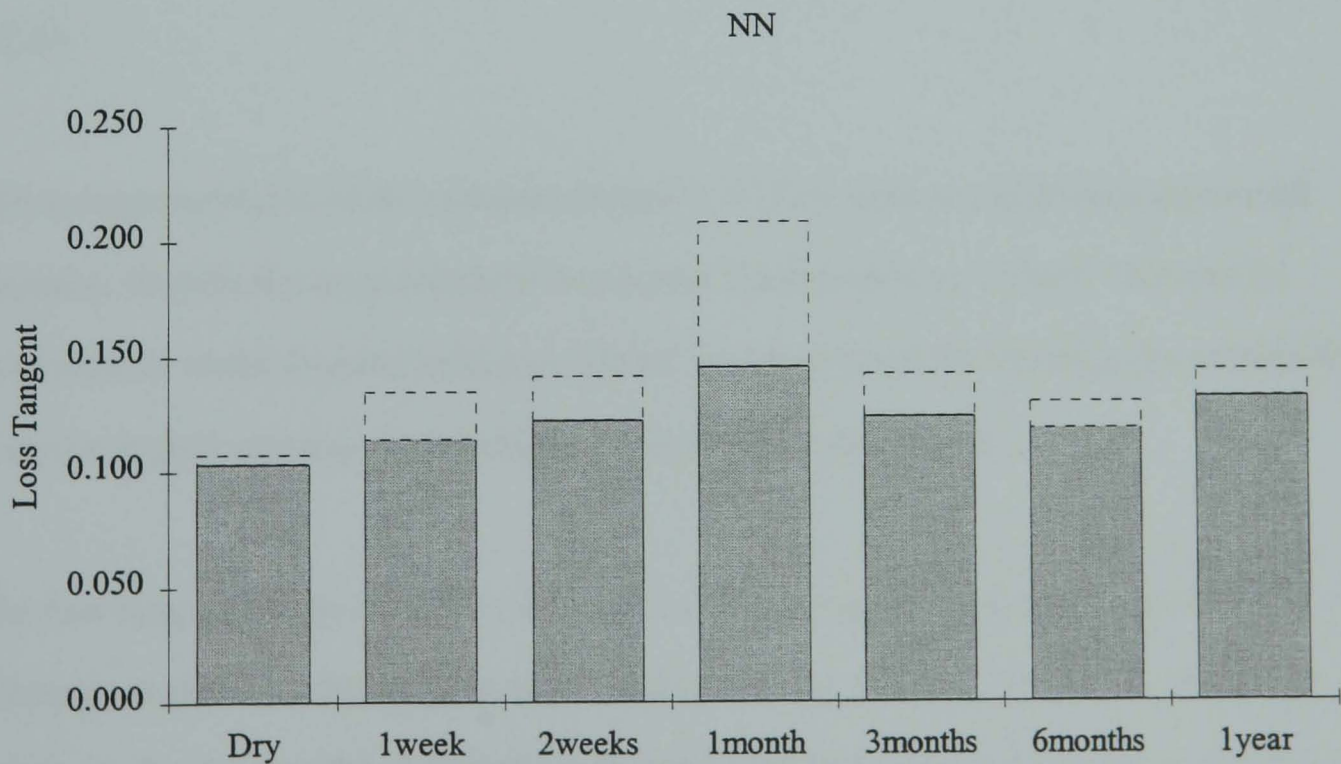


Figure 5.2.12. Variations in the loss tangent (at 37°C, 1Hz) for NN.

	E' (MPa)	S.D.	Tan d	S.D.	Tg (°C)	S.D.	Weight (%)	S.D.
Dry	3.03	0.30	0.103	0.004	-	-	0.0	-
1 week	3.29	0.76	0.114	0.021	-	-	3.17	0.10
2 weeks	3.71	0.15	0.122	0.019	-	-	4.05	0.07
1 month	3.73	0.58	0.145	0.063	-	-	4.90	0.18
3 months	4.49	0.25	0.124	0.019	-	-	7.05	0.10
6 months	4.61	0.38	0.118	0.012	-	-	9.66	0.15
1 year	3.76	1.30	0.132	0.012	-	-	12.20	0.25
1 year D	2.64	1.16	0.120	0.019	-	-	0.13	0.10

Table 5.2.6. Ageing data for NN including storage modulus, loss tangent and weight change together with the associated standard deviation. Last row of the table is concerned with a dried sample of the material.

The water uptake of this material is relatively high at 12.2% after a years storage in water. The loss of weight after desorption on the other hand is fairly low at 0.13% (table 5.2.6).

The storage modulus of the material (figure 5.2.11) is seen to experience an overall increase, despite the large standard deviations (particularly at 1 year). This can be attributed to water droplets acting as 'fillers' in the material by stressing the surrounding polymer matrix and therefore stiffening the polymer as a whole.

The loss tangent of the material (figure 5.2.12) also experiences an overall increase, although in this case the trend is even weaker and the standard deviations are larger (particularly at 1 month). Again the increase in the loss tangent does not corrolate with

the volume of water present in the material, for the same reasons previously mentioned in relation to FB.

Wagner et al (1995b) again using their 'Weather-Ometer' instrument found Novus to be fairly stable, with the storage modulus increasing from 2.2 to 2.6 MPa after ageing. The loss tangent was relatively unaffected however (0.12 to 0.13). This increase in modulus is similar to that seen here, although in this investigation the loss tangent shows a more pronounced increase.

Kalachandra et al (1995) investigated this material, using a similar technique to that used here. They however report the water uptake of this material to be 34% after a hundred days. This does not compare well with the 7% value found here after 3 months, or the 6-12% uptake mentioned by Gettleman (1994), or the 5% measured by Collis (1993), although slightly different methods were used. The change in the viscoelastic properties does not compare well either, with a reported reduction in E' from 6.2 to 3.5 MPa after one hundred days.

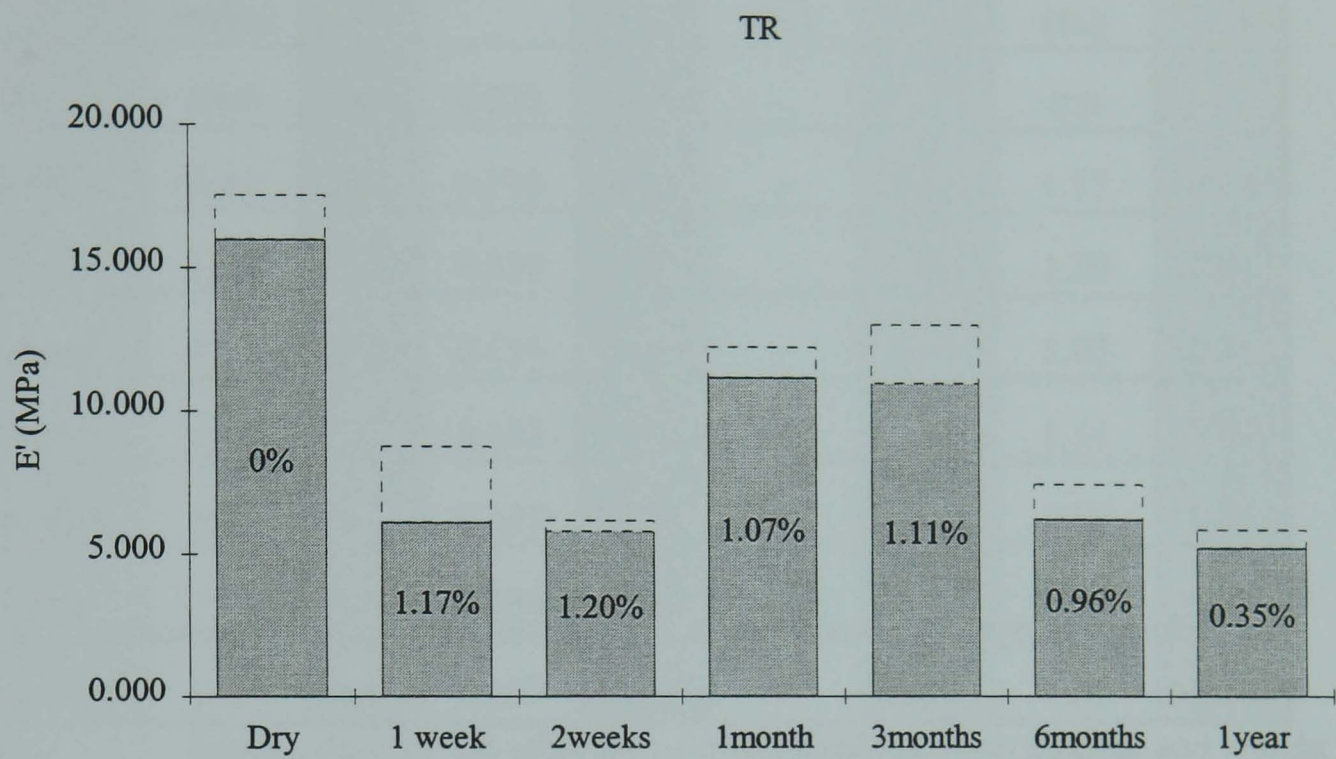
Triad Resiline (TR)

Figure 5.2.13. Variations in the storage modulus (at 37°C, 1Hz) for TR, plotted against time. Together with sample weight %.

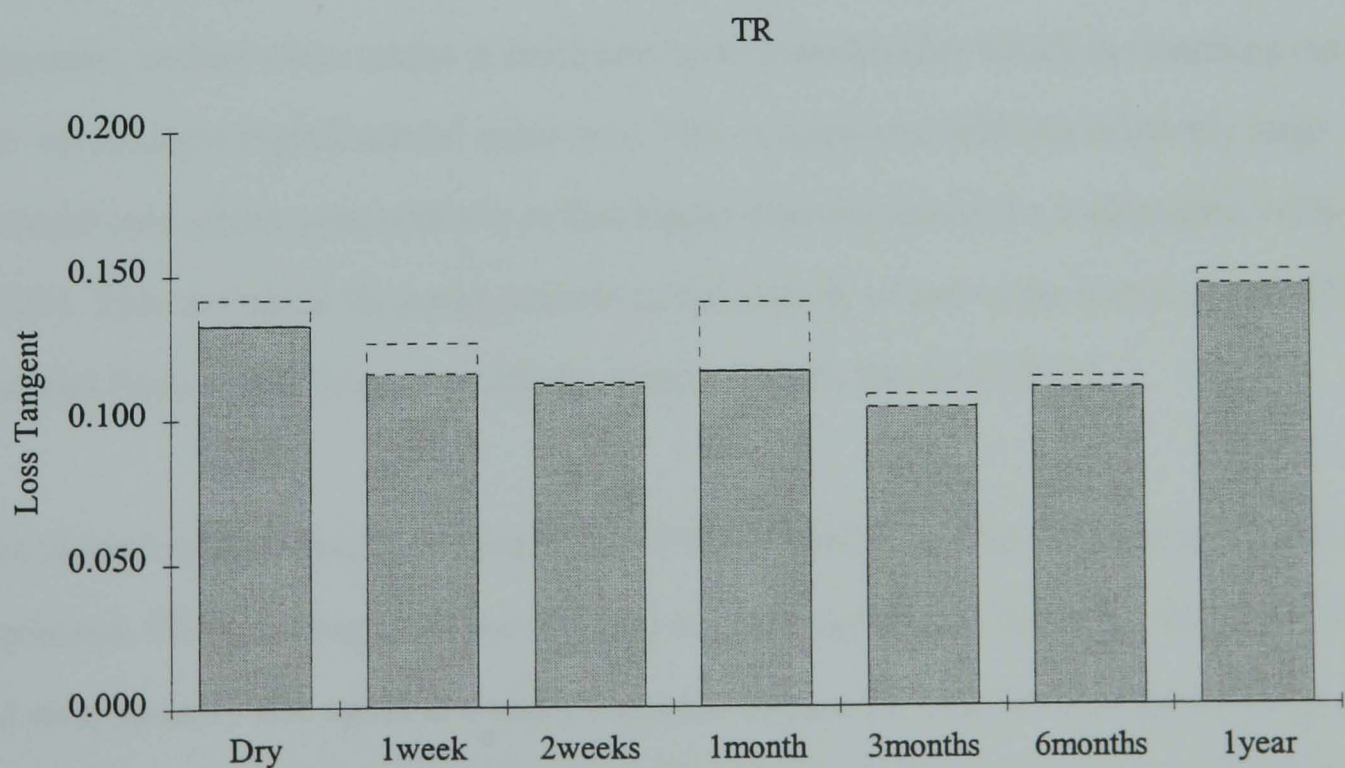


Figure 5.2.14. Variations in the loss tangent (at 37°C, 1Hz) for TR.

	E' (MPa)	S.D.	Tan d	S.D.	Tg (°C)	S.D.	Weight (%)	S.D.
Dry	16.0	1.56	0.133	0.01	-	-	0.0	-
1 week	6.11	2.66	0.116	0.01	-	-	1.17	0.11
2 weeks	5.80	0.40	0.112	0.00	-	-	1.20	0.01
1 month	11.2	1.08	0.116	0.02	-	-	1.07	0.11
3 months	11.0	2.07	0.103	0.01	-	-	1.11	0.09
6 months	6.25	1.23	0.110	0.00	-	-	0.96	0.01
1 year	5.26	0.66	0.146	0.01	-	-	0.35	0.23
1 year D	6.54	0.51	0.207	0.02	-	-	1.32	0.35

Table 5.2.7. Ageing data for TR including storage modulus, loss tangent and weight change together with the associated standard deviation. Last row of the table is concerned with a dried sample of the material.

The water uptake characteristic of this material (as seen in table 5.2.7.) appeared very complicated, rising to a maximum figure of 1.20% over the first 2 weeks and then gradually falling over the year. This can be explained using the dual intake/leaching out argument, so that water intake is dominant up to 2 weeks after which the leaching out of low molecular weight material takes over. This is consistent with the relatively large material loss after a year which is in fact bigger than the maximum weight gain value at 1.32%. This is a cause for some concern as the toxicity of one of the components of this material (isocyanate) is open to debate, Parker (1982), Braden (1996)*.

The change in the viscoelastic properties of this material over the year can not be easily explained. The loss tangent of the material is seen to gradually fall in the first 3 months, but subsequently rise again at 6 and 12 months (figure 5.2.14). The storage modulus of the material (figure 5.2.13) falls dramatically after the initial immersion (1st and 2nd

* A copy of a letter from Professor M. Braden, voicing concern was sent to the MDA (Medical Devices Agency), this is enclosed in Appendix C.

week); is then seen to rise (1 and 3 months) and finally fall again (6 and 12 months). This erratic behaviour is obviously connected to the intake of water and large amount of leaching (probably due to inefficient light polymerisation). It is however impossible to reach firm conclusions on the exact nature of the phenomenon based up on the strength of the immediate evidence.

5.2.4. Experimental Materials.

Elastomer / Methacrylate Hybrid (BS)

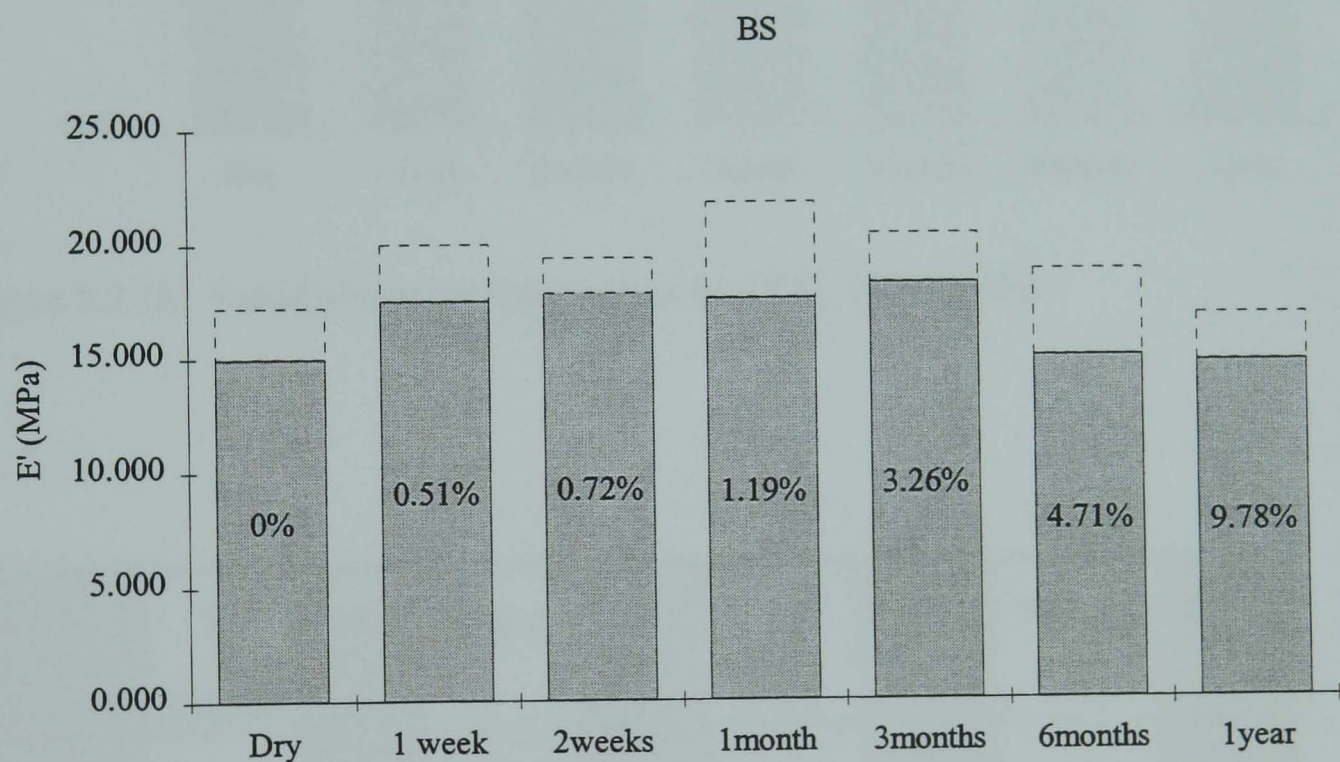


Figure 5.2.15. Variations in the storage modulus (at 37°C, 1Hz) for BS, plotted against time. Together with sample weight %.

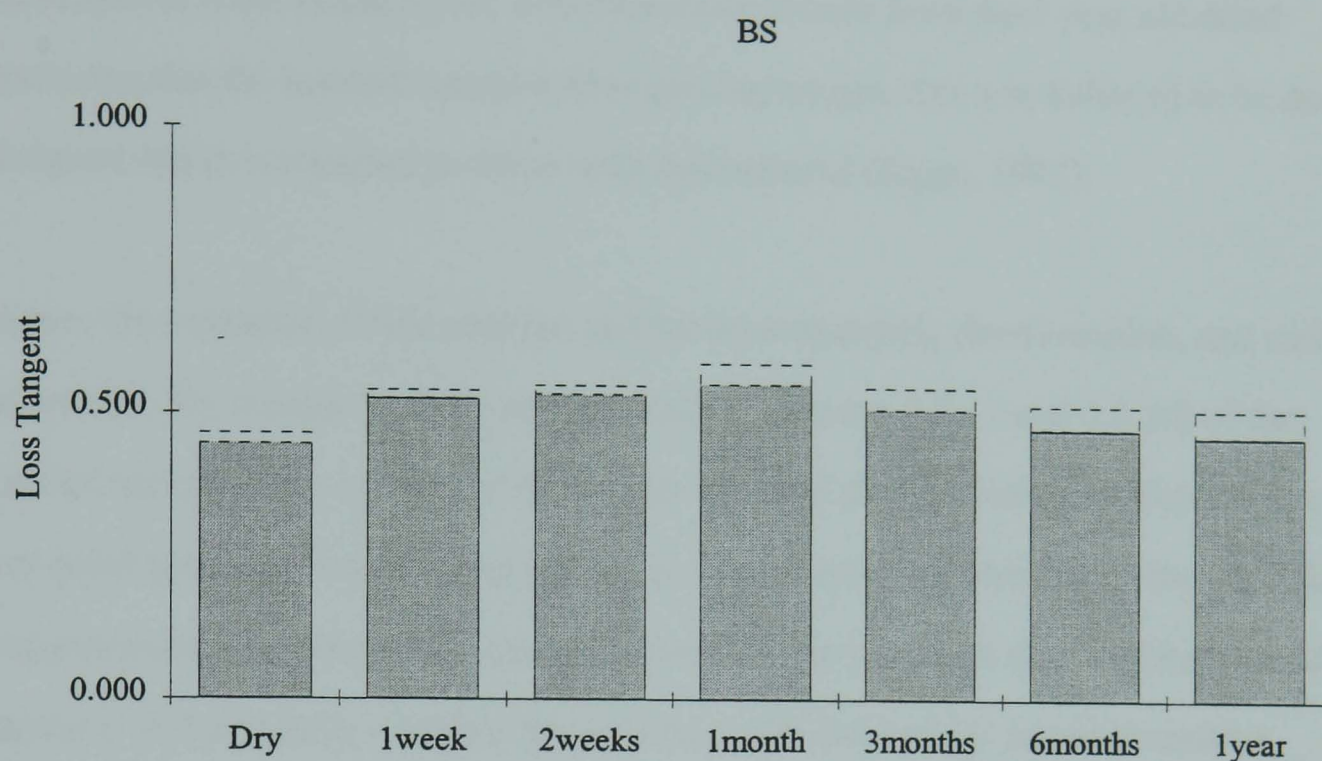


Figure 5.2.16. Variations in the loss tangent (at 37°C, 1Hz) for BS.

	E' (MPa)	S.D.	Tan d	S.D.	Tg (°C)	S.D.	Weight (%)	S.D.
Dry	15.0	2.25	0.445	0.02	32.7	0.79	0.0	-
1 week	17.5	2.51	0.526	0.02	33.9	1.12	0.51	0.11
2 weeks	17.9	1.58	0.534	0.02	32.8	0.75	0.72	0.19
1 month	17.6	4.22	0.553	0.04	33.9	0.66	1.19	0.08
3 months	18.3	2.17	0.511	0.04	33.8	0.71	3.26	1.90
6 months	15.0	3.84	0.478	0.04	33.2	0.76	4.71	1.06
1 year	14.8	2.09	0.466	0.05	32.1	0.26	9.78	2.04
1 year D	11.6	5.22	0.415	0.07	35.3	2.51	-0.49	0.59

Table 5.2.8. Ageing data for BS including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation. Last row of the table is concerned with a dried sample of the material.

The water uptake of the BS material reaches a maximum of 9.78% after a years immersion in water (table 5.2.8). It is interesting to note from the 1 year old dried specimens that the material samples have gaining weight, this was believed to be due to oxidation which is a known problem with this material (Riggs, 1997).

Despite the oxidation of this material and the accompanying discolouration, and surface-hardening*, the storage modulus and loss tangent (figures 5.2.15 and 5.2.16) of the material are relatively constant over the year of water storage, both of which show a very small peak at 2 weeks, 1 and 3 months. This unexpected stability of the viscoelastic characteristics is believed to be related to the fact that oxidation after the time period of interest is still primarily a surface phenomenon. The bulk of the material remains unaffected after 1 year's storage.

* The samples felt 'embrittled' by hand.

Polymerisable plasticiser (PP)

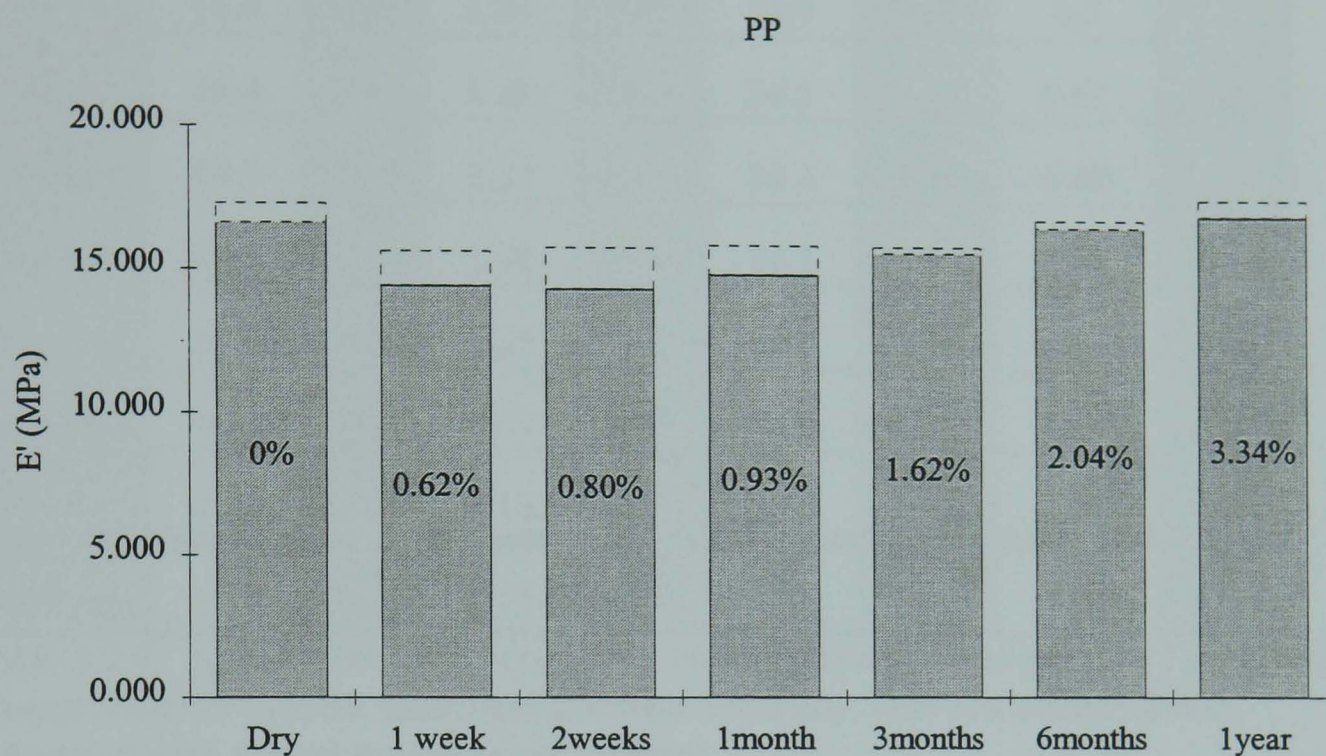


Figure 5.2.17. Variations in the storage modulus (at 37°C, 1Hz) for PP, plotted against time. Together with sample weight %.

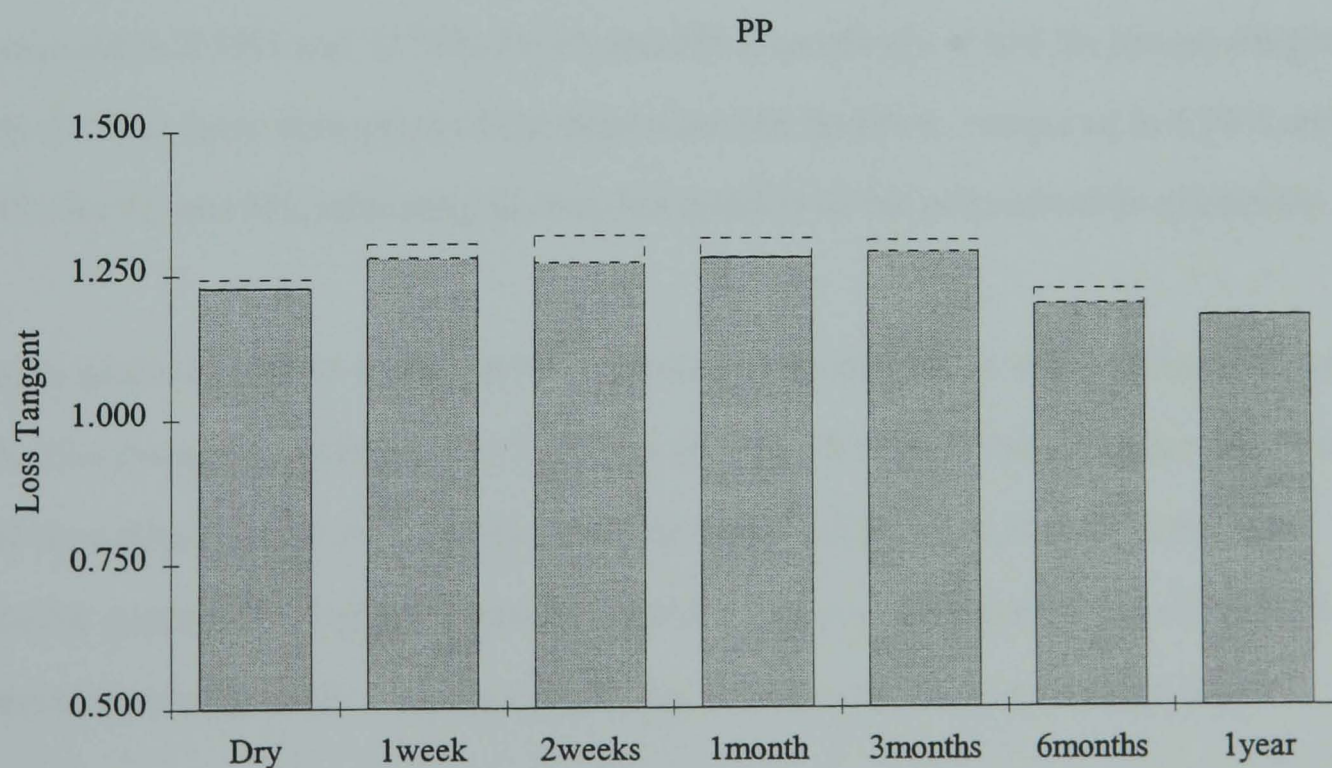


Figure 5.2.18. Variations in the loss tangent (at 37°C, 1Hz) for PP.

	E' (MPa)	S.D.	Tan d	S.D.	Tg (°C)	S.D.	Weight (%)	S.D.
Dry	16.6	0.69	1.23	0.02	34.0	0.64	0.0	-
1 week	14.4	1.21	1.28	0.03	34.1	0.47	0.62	0.00
2 weeks	14.3	1.45	1.27	0.05	34.3	1.10	0.80	0.09
1 month	14.9	1.03	1.28	0.03	34.1	0.79	0.93	0.08
3 months	15.6	0.23	1.29	0.02	34.5	0.89	1.62	0.06
6 months	16.5	0.27	1.20	0.03	35.8	0.13	2.04	0.35
1 year	16.9	0.58	1.18	0.00	35.8	0.69	3.37	0.48
1 year D	25.7	1.35	1.17	0.02	38.3	0.46	0.58	0.19

Table 5.2.9. Ageing data for PP including storage modulus, loss tangent, Tg and weight change together with the associated standard deviation. Last row of the table is concerned with a dried sample of the material.

The uptake of this material (as seen in table 5.2.9.) follows a qualitatively familiar trend to that of NS and FS, although in magnitude it is approximately 3 times smaller than NS and a fraction greater than FS at each time span. The weight gain after a year is 3.37% compared to 2.89% and 12.50% for FS and NS respectively. It had the lowest weight loss (0.58%) upon desorption of the three materials however, compared to 0.76% and 2.0% for FS and NS, indicating the non-leachability of the polymerisable plasticiser.

Again qualitatively the viscoelastic behaviour of this material is very similar to that of NS. The storage modulus (figure 5.2.17) is seen to fall slightly initially after immersion and then subsequently rise slightly. The loss tangent (figure 5.2.18) also follows a familiar pattern of a slight increase followed by a period of consistency and finally a reduction in magnitude. The same explanations as given earlier apply here also.

5.3. General Discussion and Clinical Implications.

The values of storage modulus and loss tangent at 37°C as well as the glass transition of the materials investigated in this report are summarised in table 5.3.1. As can be seen a huge range exists in the viscoelastic properties of these materials. The storage modulus of the commercial materials has a range from 2.79 to 19.7 MPa representing a seven fold difference. The loss tangent similarly ranges from 0.029 to 1.52 a fifty fold range. Similarly large ranges have been reported by other authors who have attempted a comparison (Braden & Clarke, 1972).

	E' (MPa)	S.D.	Tan δ	S.D.	Tg (°C)	S.D.
FS	19.7	1.63	1.47	0.01	36.8	0.701
NS	16.8	1.76	1.52	0.01	37.9	0.449
OS	5.87	0.22	1.27	0.03	30.1	0.532
MP	3.87	0.16	0.029	0.007	-	-
FB	3.52	0.31	0.111	0.017	-	-
NN	3.02	0.30	0.103	0.004	\approx -31*	-
ON	2.79	0.35	0.125	0.005	-	-
TR	16.0	1.56	0.133	0.01	\approx -52*	-
BS	15.0	2.25	0.445	0.019	32.7	0.790
SI	7.54	0.75	0.514	0.008	34.9	1.081
PB	4.15	0.24	0.429	0.004	36.5	0.446
PP	16.6	0.69	1.23	0.02	34.0	0.640
C1	23.6	1.79	1.38	0.02	39.8	0.605
PE	24.6	4.20	1.38	0.05	40.1	0.827
PH	33.1	2.17	1.27	0.04	42.0	0.579

Table 5.3.1. Summary of results at physiological conditions.

* From Appendix B.

The experimental materials were found to have a modulus range from 4.15 to 33.14 MPa and a loss tangent range of 0.429 to 1.38. The modulus range of most of the polymerisable plasticiser based materials was found to be higher than the commercial materials, while the properties of the elastomer based materials were in the mid range of the commercial materials.

Overall the materials investigated can be split into three groups according to their viscoelastic properties: leathery, rubbery and miscellaneous.

Acrylic based materials including FS, NS, OS, PP, C1, PE and PH are dominated by the fact that their glass transitions lie at or near mouth temperature. This has several implications: at their operating temperature materials are at their most 'dead' and leathery, thus dissipating most of their deformational energy as heat (loss tangent range 1.23 - 1.52). On the whole these materials are the stiffest soft liners, and with the exception of the heavily plasticised OS (5.87 MPa), have a higher modulus range than the other materials tested (16.8 - 33.1 MPa). They are also very temperature dependent and a relatively small change in temperature (and therefore frequency) will make a noticeable difference in their stiffness.

The MP, FB, NN, ON are characterised by the fact that their T_g is well below 0°C. At mouth temperatures they are rubbery, characterised by low values of modulus (2.79 - 3.87 MPa) and loss tangent (0.029 - 0.125). Their properties are independent of temperature and they will retain their viscoelastic properties over most of the temperatures which they are likely to encounter in the mouth.

The BS, SI, PB and TR materials don't easily fit into either of the above characterisations. The elastomeric/acrylic (BS, SI, PB) materials have properties in the mid range of the two above groups with E' in the range of 4.15 - 15.0 MPa and loss

tangents in the range 0.429 - 0.514. This average range of values is not surprising when one considers that they are hybrids containing the two material groups just discussed i.e. elastomers, with sub-zero Tg's and acrylics with ambient Tg's. The TR material has unusual viscoelastic characteristics compared to the other materials tested here. Although it is temperature independent, with a low loss tangent (0.133) and low Tg (-52 °C), it demonstrates a relatively high stiffness (16.0 MPa).

Given such a large spread, both in the stiffness and resilience of the available soft liners, it is surprising that there is no overall preference by patients or clinicians for a given set of viscoelastic characteristics (Braden et al, 1995). A major cause of this apparent indifference is likely be linked to the similarly large variations which are observed in the mechanical properties of mucosa (Tomlin et al (1968), Kydd & Daly (1982), Inoue et al (1985)). Another probable reason is that the viscoelastic properties, whilst the most important as far as the biomechanical function of the material is concerned (primarily to protect the mucosa), are only one out of many criteria from which the materials must be judged. Other parameters including the cost, tear strength, wear resistance, etc.(see section 1.1.3.) must also be taken into consideration.

As far as the question of the ideal viscoelastic properties of a soft lining material, what consensus there is in the literature can approximately be divided in two opposing schools of thought. While some authors (Holt et al, 1991) express a preference for a compliant, low loss material (typical of the silicones); others advocate a material which emulates the viscoelastic properties of the mucosa (Haykawa et al, 1994) and has a low modulus and low resilience, (Wagner et al, 1995a). Virtually no work has attempted to quantify the effect which the presence of a soft liner has on the biomechanics of mastication. What work there is on this topic (Wright, 1984) has largely concentrated on one material, and has not attempted to compare different soft lining materials on grounds of their respective viscoelastic properties. In conclusion it is not possible at the present time to recommend a set of viscoelastic characteristics as ideal. Although this is

an area which begs further investigation particularly as there is strong evidence of a link between the cushioning effect of soft lining materials and a reduction in alveolar bone loss (ElCharkawi & ElMahdy, 1988).

From a purely conceptual and therefore speculative stand point the following observations can be made, although even this approach is hindered by the fact that the exact mechanism by which soft lining materials operate is open to debate (Braden et al, 1995):

The loss tangent of a material is linked to its energy dissipating quality and hence the 'leathery' acrylics will offer the most protection in this respect. However, they are on the whole stiffer than the mucosa (0.66-4.36 MPa; Inoue et al, 1985) which may be considered as a negative point. From the point of view of manufacture and handling their temperature dependence can be viewed as an advantage because the clinician can manipulate their properties. At lower temperatures for example these materials are likely to be hard enough to be easily trimmed and polished.

The second set of viscoelastic characteristics discussed above (i.e. rubbery) are the most compliant of the materials tested and in fact have a stiffness range comparable to that reported for the mucosa (see above). They have very high resilience, which might prove to be a disadvantage in terms of their energy dissipative quality as well as a 'bounce' effect. Although in some application such as that of retention (see figure 1.1.2.) high resilience could prove to be an asset.

The experimental elastomeric/acrylic based materials showed great promise in that they combined to some extent the best features offered by the above materials in that they were relatively soft (particularly PB) with a high rate of energy dissipation. The reverse was true of the TR material which exhibited a low level of energy loss and a high modulus.

Ageing behaviour of soft lining materials

The water absorption properties of 7 commercial materials and 2 experimental materials have been discussed and their viscoelastic characteristics as well as their weight gain/loss and solubility are summarised in table 5.3.2.

	E' (MPa)	S.D.	Tan δ	S.D.	% Wt	S.D.	% Slb	S.D.
FS	18.6	4.79	1.41	0.01	2.89	0.02	0.76	0.18
NS	15.3	1.52	1.45	0.05	12.50	0.41	2.00	0.04
OS	72.3	7.47	0.480	0.06	-4.39	0.39	13.58	0.38
MP	4.17	0.14	0.031	0.006	-0.65	0.09	0.91	0.07
FB	0.242	0.10	0.126	0.030	48.57	3.11	4.52	0.25
NN	3.76	1.30	0.132	0.012	12.20	0.25	0.13	0.10
TR	5.26	0.66	0.146	0.01	0.35	0.23	1.32	0.35
BS	14.8	2.09	0.466	0.05	9.78	2.04	-0.49	0.59
PP	16.9	0.58	1.18	0.00	3.37	0.48	0.58	0.19

Table 5.3.2. The viscoelastic properties of some soft lining materials after a years storage in water (values at 37°C, 1Hz). %Wt refers to weight gain/loss, %Slb refers to solubility.

It is unclear whether a given change in the viscoelastic properties of soft liners will have an adverse or beneficial effect on the patient. Of the materials tested above only two showed a change in viscoelasticity which was larger than the spread already existing in the commercial materials. This includes OS which hardened substantially (5.87 to 72.3 MPa) due to the extraction of plasticiser, and FB whose modulus reduced dramatically (3.52 to 0.242 MPa) due to excessive water uptake (48.57%). The change induced in the loss tangent of the materials was not so dramatic, even in materials with a massive water uptake (FB). This was initially surprising, when one considers that water as a liquid would have an infinite loss tangent. It can be deduced however that the water inside

these materials is essentially immobile, as any movement would lead to frictional losses and hence a high loss tangent.

The new generation of the acrylics has overcome the need for high levels of plasticisation. NS proved to be much more stable in water due to a reduction in the amounts of plasticiser used. FS appears to have eliminated the need of plasticiser altogether, while new experimental materials PP utilise a polymerisable plasticiser. The heat cured silicone (MP) was the most stable in water in contrast with its cold cured counterpart. The polyphosphazene material (NN) had a fairly high water uptake but this did not have a large or adverse effect on its viscoelastic properties. The TR material was found to lose 1.32% of its weight in water after a year, this is of concern as the material is believed to contain isocyanates. The experimental BS material was seen to oxidise in water, although this did not affect its viscoelastic properties. It was concluded that the oxidation was primarily occurring on the surface and the bulk of the material was not affected in the time period of the study.

5.4. Sources of Error, Reproducibility and Limitations.

Having presented and discussed the experimental work carried out for this thesis, it seems pertinent to finish the discussion by addressing some of the problems, sources of experimental error and limitations of the study.

Using the DMA method outlined in chapter four, reproducible results were obtained for all materials under the majority of test conditions. Each experiment was repeated at least 3 times and the mean and standard deviation calculated. One of the largest sources of error in these experiments was found to be due to poor sample mounting. A manifestation of this inferior mounting was regions in the sample-plate interface which were not in intimate contact. This could either be due to parallel plate misalignment i.e. the plates not being quite parallel or similarly the two surfaces of the sample not being parallel; secondly imperfections on the surface of the samples could produce the same type of error. In either case the apparent surface area at the interface would be less than the nominal area (5mm diameter). The effect of this reduced area of contact is a sample which is apparently not as stiff. Therefore a lower modulus is reported for the material. Two points are worth mentioning: firstly imperfections such as these can only ever have the effect of under-estimating the modulus of the materials; secondly this problem is likely to be more pronounced for stiffer and/or less viscous materials which would have less ability to flow at the interface and hence achieve a more intimate contact area.

One of the assumptions of the stress analysis associated with the DMA is that the stress field within the sample is uniform. This is an idealisation of the real situation, however as dispersions of the stress patterns are bound to occur with finite strains. For example, compression of a rubber disc whose loaded sides are rigidly bonded* will produce a combination of compressive and shear strains. The shear strains being at their greatest at the edges and leading to a bulging or barrelling effect.

* This is an extreme case of frictional contact, i.e. infinite friction.

For the case where a rubber cylindrical disc is rigidly bonded, Gent and Lindley (1959) derived the following equation linking the apparent modulus E_a to the real modulus E via the shape factor S .

$$E_a = E (1 + 2S^2) \quad 5.4.1.$$

Where the shape factor is the ratio of one loaded surface to that of the free surface. This simple equation can not be applied here because the soft lining materials are not bonded to the parallel plates but are free to move within the bounds of their frictional characteristics. Also the above equation refers to rubbers which can be thought of as being essentially incompressible (Poissons ratio ≈ 0.5) which again does not necessarily apply to soft lining materials. The non-uniformity of the strain field while appreciated is here neglected and is assumed to be negligible at low strains (0.5%).

Other possible sources of errors include differences in the thickness of individual specimens. Although all the specimens were nominally 2mm thick, processing variations are to be expected. The softness of a layer of soft lining material is known to be dependent on its thickness and so variations in thickness are bound to give variations in results. Similarly, any inhomogeneity in the samples will be a source of error. This could include factors such as polymer rich phases in powder/liquid systems or elastomer rich areas in the experimental elastomeric materials. Inconsistencies in the heating rate and the associated feedback control were occasionally observed and would have a ~~dele~~-terious effect on results. The stress history of the sample could also make a difference. To minimise this effect the samples were always handled in the same manner and care was taken not to over stress them.

Comparison with other recent work on soft lining materials using the forced vibration dynamic mechanical technique (i.e. Kalachandra et al (1995), Wagner et al (1995a), Waters et al (1996)) has indicated that the use of DMA in this application should be

regarded as being comparative rather than absolute in nature. In particular, even when important test parameters such as time and frequency (37°C, 1 Hz in these cases) are kept constant, different instruments using different testing methodologies will obtain different results. Sources of discrepancies include the deformational mode and geometry of the sample, although other factors such as the stress/strain levels, heating/cooling rates and inherent design variations in the instruments are also liable to make an important contribution. This conclusion, i.e. that DMA is a comparative rather than absolute technique has also been reached in other DMA based work looking at widely different biomaterial systems (Nazhat, 1997).

CHAPTER SIX

CONCLUSIONS AND FUTURE WORK

6.1. Conclusions

The forced vibration dynamic mechanical method has been successfully used to fulfil the aims and objectives of this study. Namely to investigate and characterise the viscoelastic properties of commercial and experimental dental soft liners at masticatory temperatures and frequencies. However DMA is best considered as a comparative rather than absolute technique as there are many possible sources of output variability, based upon the experimental methodology and instrumentation.

The principle advantages of the forced, non resonance vibration method over other methods of measuring viscoelasticity is that the frequency and temperature of the experiment can be accurately and easily controlled, and hence can be chosen to be physiologically relevant. In particular some of the earlier workers in this field have studied these materials under different time and temperature conditions and assumed their results to be clinically relevant. This, whilst partially valid for the temperature independent polymers can lead to misleading results for materials which are going through a transition in the time/temperature domain of interest.

The commercial materials studied covered a 7 fold modulus range, from 2.79 to 19.7 MPa and a 50 fold range in the loss tangent going from 0.029 to 1.52. The materials were divided into three types according to their viscoelastic nature. The first group covers the acrylic based polymers, which were characterised by having their glass transition near mouth temperature. They were therefore stiff, lossy and temperature dependent. The second group included the silicone based soft lining materials as well as recently introduced polyphosphazine systems. These materials had their Tg's at much lower temperatures. They were characterised by having a low modulus and high resilience, as is typical of rubbers. Furthermore their viscoelastic properties were relatively constant at and near mouth temperatures. The third group contained materials which did not conform to either of the above. These included a range of experimental materials, based upon an acrylic/elastomeric system, which were characterised by

having a small transition corresponding to the methacrylate phase near mouth temperature. The modulus and loss tangent of these materials were in the mid range of the materials studied. One light curing polyether based material was characterised by its temperature independence, low loss and high stiffness.

The storage of soft liners in distilled water for up to a year and its effect on their viscoelastic properties was also examined. Many types of behaviour were observed, although only two materials exhibited a change in their viscoelastic characteristics which was greater than the overall spread already described. So that the stiffness range of the materials after a year in water was 0.242-72.3 MPa, a 300 fold range. The loss tangent was not affected to such an extent; surprising as water has an infinite loss tangent when considered as a material in its own right.

Based on the literature however it is impossible at the present time to say which of these materials has ideal viscoelastic properties. This is probably based on the fact that viscoelasticity is one of many competing requirements for a soft liner; but is also due to the large variations which are seen in the mechanical condition of patients mucosa's.

6.2 Future Work

An investigation of this kind cannot hope to address all the issues and problems presented by its subject matter. In particular a number of relevant and important points have been left unanswered by the current investigation. Some of these are discussed below.

Although the viscoelasticity of a range of experimental and commercial materials has been characterised into several distinct groups, important questions such as: the ideal range of properties which are acceptable/desirable; the effect of these properties on the biomechanics of mastication; and the exact mechanism by which soft lining materials work are not clearly understood. The answer to these questions are likely to be found in a clinically based investigation looking at the effect of different kinds of soft lining material on patient acceptability, the biomechanical parameters of mastication and alveolar bone loss. Considering the amount of research which has gone into the viscoelasticity of soft liners and the biomechanics of mastication; it is surprising that very few authors have attempted to tie the two together. This is particularly important as there is strong evidence of a link between the resorption of alveolar bone and the use of soft lining materials.

Water uptake studies were undertaken over a one year period. Extension of this time span to 5 years would be informative as the expected life of the hard denture base is of this order. Furthermore water uptake although relevant, can never simulate the oral environment where saliva maintains functional lubrication. However artificial saliva could be used to provide a more realistic alternative to distilled water.

There is much scope for further work to tie in the chemical composition and viscoelastic properties of commercial and experimental materials discussed in this report. In particular this study has largely concentrated on physiological temperatures and frequencies. Whereas at lower temperatures the Tg's, and secondary transitions of all the

materials could be elucidated. In particular there is room for the investigation of the viscoelastic properties of individual constituents of the experimental materials, (i.e. elastomers or methacrylates) and their effect on the main material, with the aim of tailoring viscoelastic properties to a specific range. Different methods of measuring the T_g (e.g. DSC and dielectrics) could also be used and compared.

REFERENCES

ASTM. D 4092 - 90. Standard terminology relating to dynamic mechanical measurements on plastics.

ASTM. E 1640 - 94. Standard test method for assignment of the glass transition temperature by dynamic mechanical analysis.

AIKEN.A. (1988) A physico-chemical and biological study of systems based on poly(2 ethoxy ethyl methacrylate) for use in oral and maxillofacial surgery. PhD, University of London.

AKLONIS.J.J. MACKNIGHT.W.J. (1983) Introduction to polymer viscoelasticity. Wiley-Interscience Publication.

ARRIDGE. R.G.C. (1975) Mechanics of polymers. Clarendon Press. Oxford.

ATWOOD.D.A. (1971) Reduction of residual ridges: A major oral disease entity. J Prosthet. Dent. **26**: 266-279.

AYDINLIK.E. AKAY.H.U. (1980) Effect of a resilient layer in a removable partial denture base on stress distribution to the mandible. J Prosthet Dent. **44**: 17 - 20.

BADAWY. M.S. EL-SHERBINY. N. (1992) Effect of using soft liner on bone density around the abutments supporting complete lower overdenture. Egypt Dent J. **38**: 105-112.

BASCOM. P.E. (1966) Resilient denture base materials. J Prosthet Dent. **16**: 646-649.

BATES.J.F. SMITH.D.C. (1965) Evaluation of indirect resilient liners for dentures: Laboratory and clinical tests. J Amer Dent Assoc. **70**: 344-353.

BATES.J.F. STAFFORD.G.D. HARRISON.A. (1975a) Masticatory function- a review of the literature (I) The form of the masticatory cycle. *J Oral Rehabil.* **2**: 281-301.

BATES.J.F. STAFFORD.G.D. HARRISON.A. (1975b) Masticatory function- a review of the literature (II) Speed of movement of the mandible, rate of chewing and forces developed in chewing. *J Oral Rehabil.* **2**: 349-361.

BATES.J.F. STAFFORD.G.D. HARRISON.A. (1976) Masticatory function- a review of the literature (III) Masticatory performance and efficiency. *J Oral Rehabil.* **3**: 57-67.

BERNHAUSEN. E.R. (1971) Resilient materials used between the teeth and the denture base: A preliminary report. *J Prosthet Dent.* **25**: 258-264.

BOYER.R.F. (1963) The relation of transition temperatures to chemical structure in high polymers. *Rubb. Chem. Tech.* **36**: 1303-

BRANDRUP.J. IMMERGUT.E.H. (1975) *Polymer handbook*, 2nd Ed. Wiley-Interscience Publication.

BROWN.D. (1988) Resilient soft liners and tissue conditioners. *Brit Dent J.* **164**: 357-360.

BRADEN.M. (1971) The rheology of dental tissue conditioners. *Rheol Acta.* **10**: 86-

BRADEN.M. CLARKE.R.L. (1972) Viscoelastic properties of soft lining materials. *J Dent Res.* **51**: 1525-1528.

BRADEN.M. WRIGHT.P.S. (1983) Water absorption and water solubility of soft lining materials for acrylic dentures. *J Dent Res.* **62**: 764-768.

BRADEN.M. WRIGHT.P.S. PARKER.S. (1995) Soft lining materials - a review. *Eur J Prosthodont Rest Dent.* **3**: 163-174.

BRADEN.M. (1996) Personal Communication.

BRADEN.M. CLARKE. R.L. J.NICHOLSON. PARKER.S. (1997) *Polymeric Dental Materials.* Springer. Germany.

BROWN. D. (1988) Resilient soft liners and tissue conditioners. *Brit Dent J.* **164**: 357-360.

BRYDSON. J.A. (1975) *Plastics materials.* 3rd Ed. Newnes-Butterworths. London.

CLARKE.RL. BRADEN.M. (1982) Determination of viscoelastic properties of dental polymers by mechanical impedance measurements. *J Dent Res.* **61**: 1245-1249.

CLARKE. R.L. (1978) *The visco-elastic properties of some dental materials.* MPhil Thesis University of London.

CLARKE. R.L. (1988) *The visco-elastic nature of polymers related to dentistry.* PhD Thesis University of London.

COLLIS.J. (1993) Assessment of a recently introduced fluoroelastomeric soft lining material. *Int J Prosthodont.* **6**: 440-445.

DAVIDSON. C.L. BOERE.G. (1990a) Liquid-supported dentures. Part I: Theoretical and technical considerations. *J Prosthet Dent.* **63**: 303-306.

DAVIDSON. C.L. BOERE.G. (1990b) Liquid-supported dentures. Part II: Clinical study, a preliminary report. *J Prosthet Dent.* **63**: 434-436.

DEVLIN. H. FERGUSON (1991) Alveolar ridge resorption and mandibular atrophy. A review of the role of local and systemic factors. *Brit Dent J.* **170**: 101-104.

DOOLITTLE. A.K. (1951) Studies in newtonian flow. II. The dependence of the viscosity of liquids on free-space. *J Appl Phys.* **22**: 1471-1475.

DOOTZ.E.R. KORAN.A. CRAIG.R.G. (1992) Comparison of the physical properties of 11 soft denture liners. *J Prosthet Dent.* **67**: 707-712.

DOOTZ.E.R. KORAN.A. CRAIG.R.G. (1993) Physical property comparison of 11 soft denture lining materials as a function of accelerated aging. *J Prosthet Dent.* **69**: 114-119.

DURAN.R.L. POWERS.J.M. CRAIG.R.G. (1979) Viscoelastic and dynamic properties of soft liners and tissue conditioners. *J Dent Res.* **58**: 1801-1807.

EICHARKAWI. G.H. EIMAHDY. A.S. (1988) The effect of resilient layer and occlusal reactive complete dentures on the residual alveolar ridge. *J Prosthet Dent.* **59**: 598-602.

ELLIS.B. LAMB.D.J. AL-NAKASH.S. (1980) Variation in the elastic modulus of a soft lining material. *Brit Dent J.* **149**: 79-82.

FERRY.J.D. (1980) *Viscoelastic properties of polymers.* 3rd Ed. Wiley, New York.

GEE.G. (1966) The thermodynamic analysis of the effect of pressure on the glass temperature of polystyrene. *Polymer*. **7**: 177-191.

GEE.G. (1970) The glassy state in polymers. *Contemp Phys*. **11**: 313-334.

GENT A.N. LINDLEY P.B. (1959) The compression of bonded rubber blocks. *Proc Inst Mech Engrs*. **173**: 111-117.

GETTLEMAN.L. GERBERT.P.H. (1987) Soft denture liner. U.S. Patent 4,661,065.

GETTLEMAN.L. (1994) Personal communication.

GOING.R.E. LOEHMAN.R.E. CHAN.M.S. (1974) Mouthguard materials: Their physical and mechanical properties. *J Amer Dent Assoc*. **89**: 132-138.

GONZALEZ.J.B. LANEY.W.R. (1966) Resilient materials for denture prostheses. *J Prosthet Dent*. **16**: 439-444.

GRAHAM.B.S. JONES.D.W. THOMSON.J.P. JOHNSON.J.A. (1990) Clinical compliance of two resilient denture liners. *J Oral Rehabil*. **17**: 157-163.

HAGBERG.C. (1987) Assessments of bite force: A review. *J of Craniomandibular Disorders: Facial and Oral Pain*. **1**: 162-169.

HAYKAWA.I. HIRANO.S. KOBAYASHI.S. NAGAO.M. MASUHARA.E. (1994) The creep behavior of denture-supporting tissues and soft lining materials. *Int J Prosthodont*. **7**: 339-347.

HEATH.M.R. (1982) The effect of maximum biting force and bone loss upon masticatory function and dietary selection of the elderly. *Int Dent J.* **32**: 345-356.

HOLT. R.A. ZYLINSKI. C.G. DUNCANSON. M.G. (1991) Force versus time profiles of selected heat-processed denture liners. *Int J Prosthodont.* **4**: 164-168

INOUE.K. ARIKAWA.H. FUJII.K. SHINOHARA.N. KAWAHATA.N. (1985) Viscoelastic properties of oral soft tissue. 1. A method of determining elastic modulus of oral soft tissue. *Dent Mater J.* **4**: 47-53.

IRC ANNUAL REPORT. (1996-1997) In print.

JEPSON.N.J.A. McCABE.J.F. STORER.R. (1993a) Evaluation of the viscoelastic properties of denture soft lining materials. *J Dent.* **21**: 163-170.

JEPSON.N.J.A. McCABE.J.F. STORER.R. (1993b) Age changes in the viscoelasticity of permanent soft lining materials. *J Dent.* **21**: 171-178.

JEPSON.N.J.A. McCABE.J.F. BASKER. R.M. (1995) A new temporary soft lining material. *J Dent.* **23**: 123-126.

KALACHANDRA.S. MINTON.R.J. TAKAMATA.T. TAYLOR.D.F. (1995) Characterization of commercial soft liners by dynamic mechanical analysis. *J Mater Sci: Mater in Medicine.* **6**: 218-222.

KALACHANDRA.S. XU.D. PARKER.S. RIGGS.P. TAYLOR.D.F. BRADEN.M. (1996) Dynamic mechanical analysis and water absorption of some experimental soft lining materials. *J Mater Sci: Mater in Medicine.* **7**: 237-240.

KAWANO.F. KORAN. A. ASAOKA.K. MATSUMOTO. N. (1993) Effect of soft denture liner on stress distribution in supporting structures under a denture. *Int J Prosthodont.* **6**: 43-49.

KAZANJI.N.M.M. WATKINSON.A.C. (1988a) Influence of thickness, boxing and storage on softness of resilient denture lining materials. *J Prosthet Dent.* **59**: 677-680.

KAZANJI.N.M.M. WATKINSON.A.C. (1988b) Soft lining materials: their absorption of, and solubility in, artificial saliva. *Brit Dent J.* **165**: 91-94.

KLEMETTI.E. (1996) A review of residual ridge resorption and bone density. *J Prosthet Dent.* **75**: 512-514.

KREYSZIG.E. (1985) *Advanced engineering mathematics.* 6th Ed. John Wiley & Sons.

KYDD. W.L. DALY. C.H. (1982) The biologic and mechanical effects of stress on oral mucosa. *J Prosthet Dent.* **47**: 317-329.

LAMMIE.G.A. STORER.R (1958) A preliminary report on resilient denture plastics. *J Prosthet Dent.* **8**: 411-424.

LOSHAEK.S. (1955) Crosslinked polyers. II. Glass temperatures of copolymers of methyl methacrylate and glycol dimethacrylates. *J Poly Sci.* **15**: 391-404.

MANDERSON.R.D. BROWN.D. (1978) A clinical and laboratory investigation of a new denture cleaner. *J Dent.* **6**: 222-228.

MATTHEWS.E. (1945) Soft resin lining for dentures. *Brit Dent J.* **78**: 140.

McCABE.J.F. (1976) Soft lining materials: composition and structure. *J Oral Rehabil.* 3: 273-278.

McCABE.J.F. (1990) *Applied dental materials.* 7th Ed. Blackwell Scientific Publications.

McCABE. J.F. WILSON.H.J. (1974) Polymers in dentistry. *J Oral Rehabil.* 1: 335-351.

McKINSTRY.R.E (1991) Microwave processing of permanent soft denture liners. *Compend Contin Educ Dent.* 12: 32-37.

MEARS.P. (1965) *Polymer structure and bulk properties.* Von-Nostrand Co. Ltd. London.

MOSS-SALENTIJN.L. HENDRICKS-KLYVERT.M. (1985) *Dental and oral tissues an introduction.* 2nd Ed, Lea and Febiger.

MURAYAMA. T. (1978) *Dynamic mechanical analysis of polymeric material.* Materials Science Monographs, vol 1. Elsevier. Amsterdam.

MURRAY. C.G. (1979) A resilient lining material for the retention of maxillofacial prostheses. *J Prosthet Dent.* 42: 53-57.

NAZHAT.S.N. (1997) *Dynamic mechanical characterisation of hydroxyapatite reinforced biomedical composites.* PhD Thesis University of London.

OKPOJO. A.O. BRADEN.M. (1993) Development of a novel audiological clinical material. *Biomaterials.* 14: 21-25.

PARKER. S. (1982) The development and evaluation of new elastomeric prosthetic materials. PhD Thesis. University of London.

PARKER.S. BRADEN.M. (1982) New soft lining materials. *J Dent.* **10**: 149-153.

PARKER.S. BRADEN.M. (1989) Water absorption of methacrylate soft lining materials. *Biomaterials.* **10**: 91-95.

PARKER.S. BRADEN.M. (1990) Soft prosthesis materials based on powdered elastomers. *Biomaterials.* **11**: 482-490

PARKER.S. RIGGS.P. KALACHANDRA.S. TAYLOR.D. BRADEN.M (1996) Effect of composition on the mechanical properties and water sorption of a butadiene/styrene copolymer-methacrylate monomer soft lining material. *J Mater Sci: Mater in Medicine.* **7**: 245-250.

POLYZOIS.G.L (1992) Light cured combination obturator prosthesis. *J Prosthet Dent.* **68**: 345-347.

QUDAH.S. HARRISON.A. HUGGETT.R. (1990) Soft lining materials in prosthetic dentistry: a review. *Int J Prosthodont.* **3**: 477-483.

QUDAH.S. HUGGETT.R. HARRISON.A. (1991) The effect of thermocycling on the hardness of soft lining materials. *Quintessence Int.* **22**: 575-580.

READ.B.E. DEAN. G.D. (1978) The determination of the dynamic properties of polymers and composites. Adam Hilger Ltd.

RIGGS.P.D. (1997) The water uptake of experimental soft lining materials. PhD Thesis. University of London.

ROBINSON J.G. McCABE.J.F. (1982) Creep and stress relaxation of soft denture liners. *J Prosthet Dent.* **48**: 135-141.

SANDIFORD. D.J.H. (1958) Polymer from oxacyclobutanes, II the laboratory-scale evaluation of the polymers from 3.3-bischloromethyloxacyclobutane. *J Appl Chem.* **8**: 188-

SCHMIDT. W.F. SMITH.D.E. (1983a) A six year retrospective study of Molloplast-B lined dentures. Part I: Patient response. *J. Prosthet. Dent.* **50**: 308-313.

SCHMIDT. W.F. SMITH.D.E. (1983b) A six year retrospective study of Molloplast-B lined dentures. Part II: Liner serviceability. *J Prosthet Dent.* **50**: 459-465.

SCHWARZ. W.D. (1992) Effect of loading on a substitute oral mucosa and underlying bone. *Biomaterials.* **13**: 1039-1042.

STORER.R. (1962a) Resilient denture base materials. Part I. Introduction and laboratory Evaluation. *Brit Dent J.* **113**: 195-203.

STORER.R. (1962b) Resilient denture base materials. Part II. Clinical trial. *Brit Dent J.* **113**: 231-239.

SUCHATLAMPONG.C. DAVIES.E.H. VON FRAUNHOFER. J.A. (1975) Some physical properties of four resilient lining materials. *J Dent.* **4**: 19-27.

SUCHATLAMPONG.C. DAVIES.E. VON FRAUNHOFER. J.A. (1986) Frictional characteristics of resilient lining materials. *Dent Mater.* **2**: 135-38.

TOMLIN.H.R. WILSON H.J. OSBORNE.J. (1968) The thickness and hardness of soft tissues, a preliminary clinical survey. *Brit Dent J.* **124**: 223-226.

TRELOAR.L.R.G. (1958) *The physics of rubber elasticity.* Oxford University Press.

TSCHOEGL.N.W. (1989) *Phenomenological theory of linear viscoelastic behaviour.* Springer-Verlag. Germany.

TWITCHELL. H. (1869) Improvement in dental plates. U.S. Patent No. 88 682.

WAGNER. W.C. KAWANO. F. DOOTZ. E.R. KORAN. A (1995a) Dynamic viscoelastic properties of processed soft dentures liners: Part I - Initial properties. *J Prosthet Dent.* **73**: 471-477.

WAGNER. W.C. KAWANO. F. DOOTZ. E.R. KORAN. A (1995b) Dynamic viscoelastic properties of processed soft dentures liners: Part II - Effect of aging. *J Prosthet Dent.* **74**: pp 299-304.

WATERS. M. JAGGER. R. WILLIAMS. K. JEROLIMOV. V. (1996) Dynamic mechanical thermal analysis of denture soft lining materials. *Biomaterials.* **17**: 1627-1630.

WATTS.D.C. (1994) Elastic moduli and viscoelastic relaxation. *J Dent.* **22**: 154-158.

WATT .D.M. (1957) Cleft palate in edentulous patients. *Brit Dent J.* **102**: 253-267.

WILLIAMS. M.J. LANDEL. R.F. FERRY. J.D. (1955) The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. *J Amer Chem Soc.* **77**: 3701-3706.

WILSON.H.J. TOMLIN.H.R. (1969) Soft lining materials: some relevant properties and their determination. *J Prosthet Dent.* **21**: 244-250.

WOOD. L.A. (1958) Glass transition temperature of copolymers. *J Poly Sci.* **28**: 319-330.

WRIGHT .P.S. (1976) Soft lining materials their status and prospects. *J Dent.* **4**: 247-256.

WRIGHT .P.S. (1980a) A Physico-chemical study of soft lining materials for acrylic dentures. PhD thesis, University of London.

WRIGHT .P.S. (1980b) The effect of soft lining materials on the growth of *Candida albicans*. *J Dent.* **8**: 144-145.

WRIGHT.P.S. (1981) Composition and properties of soft lining materials for acrylic dentures. *J Dent.* **10**: 210-223.

WRIGHT.P.S. (1984) The success and failure of denture soft lining materials in clinical use. *J Dent.* **12**: 319-327.

WRIGHT.P.S. (1994) Observations on long-term use of a soft-lining material for mandibular complete dentures. *J Prosthet Dent.* **72**: 385-392.

WRIGHT.P.S. (1996) Personal communication.

YOUNG. R.J. LOVELL. P.A. (1995) Introduction to polymers. 2nd Ed. Chapman & Hall. London.

ZARB. G.A. (1982) Oral motor patterns and their relation to oral prostheses. J Prosthet Dent. 47: 472-478.

APPENDIX A

DERIVATIONS

The Maxwell Model

The Maxwell model consists of one spring and one dashpot connected together in series. In this arrangement the force across the spring is equal to the force across the dashpot and the total force on the system. The total displacement on the other hand is equal to the sum of the displacements on the spring and dashpot respectively, so that:

$$\sigma = \sigma_s = \sigma_d \quad 1.$$

$$\varepsilon = \varepsilon_s + \varepsilon_d \quad 2.$$

Differentiating equation 2. gives:

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_s}{dt} + \frac{d\varepsilon_d}{dt} \quad 3.$$

Stating Hooke's law across the spring and then differentiating yields:

$$\frac{d\sigma_s}{dt} = E \frac{d\varepsilon_s}{dt} \quad 4.$$

So that the total stress across the system can be written

$$\frac{d\sigma}{dt} = E \frac{d\varepsilon_s}{dt} \quad 5.$$

Applying Newton's law across the dashpot gives:

$$\sigma_d = \eta \frac{d\varepsilon_d}{dt} \quad 6.$$

Combining equations 3, 5 and 6 gives the governing equation for the Maxwell element:

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \times \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad 7.$$

The ratio of η/E is the definition of τ and is known as the relaxation time of the model.

Maxwell Model in a Creep Experiment

In a creep experiment the stress is constant and so equation 7. immediately simplifies to:

$$\frac{d\varepsilon}{dt} = \frac{\sigma_0}{\eta} \quad 8.$$

This reduced form is an expression of Newton's law for liquids. Continuing the analysis we integrate from time zero to time t

$$\int_{\varepsilon(0)}^{\varepsilon(t)} d\varepsilon = \frac{\sigma_0}{\eta} \times \int_0^t dt \quad 9.$$

gives:

$$\varepsilon(t) = \varepsilon_0 + \frac{t\sigma_0}{\eta} \quad 10.$$

Dividing through by the stress (which is constant) leads to an expression in terms of compliance's, where D is the compliance of the spring and D(t) is the compliance of the model.

$$D(t) = D + \frac{t}{\eta} \quad 11.$$

Maxwell Model in a Stress Relaxation Experiment

In this case the rate of strain is zero so that the governing equation becomes

$$0 = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad 12.$$

Substituting in the relaxation time and then integrating from 0 to t gives:

$$\left[\ln \sigma \right]_{\sigma_0}^{\sigma_t} = \left[\frac{t}{\tau} \right]_0^t \quad 13.$$

This can be written as

$$\ln \sigma(t) = \ln \sigma_0 - \frac{t}{\tau} \quad 14.$$

Exponentiation of this function gives

$$\sigma(t) = \sigma_0 e^{-t/\tau} \quad 15.$$

This expression can be made in terms of modulus by dividing by the constant strain.

$$E(t) = E e^{-t/\tau} \quad 16.$$

Where E is the modulus of the spring and E(t) the modulus of the Maxwell element.

Maxwell Model Under Dynamic Loading

Now consider the Maxwell model and a sinusoidal strain.

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \times \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad 7.$$

$$\varepsilon = \varepsilon_0 \sin \omega t \quad 17.$$

by differentiation of equation 17 and substituting into 7 we have:

$$\varepsilon_0 \omega \cos \omega t = \frac{1}{E} \frac{d\sigma}{dt} + \frac{1}{\eta} \sigma \quad 18.$$

This is an equation of the form $y' + p(x)y = r(x)$ where $y = \sigma$, $x = t$, $p(x) = E / \eta$, and $r(x) = E\omega\varepsilon_0 \cos \omega t$ and for which we can quote the general result for a first order differential equation (Kreizig, 1985):

$$y(x) = e^{-h} \left[\int e^h r dx + c \right], \quad h = \int p(x) dx \quad 19.$$

h can easily be calculated

$$h = \int \frac{E}{\eta} dt \quad \Rightarrow \quad h = \frac{Et}{\eta} \quad 20.$$

using the integration factor we have:

$$\sigma = e^{-Et/\tau} \left[\int e^{Et/\tau} \times E \cos \omega t dt \right] \quad 21.$$

The term in the brackets has to be integrated by parts as follows:

$$\int e^{Et/\tau} \cos \omega t = e^{Et/\tau} \times \sin \omega t \times \omega^{-1} - \frac{E}{\eta \omega} \int e^{Et/\tau} \sin \omega t dt \quad 22.$$

Calling the left hand side I and integrating the right hand side again we have

$$I = e^{Et/\tau} \sin \omega t \times \omega^{-1} - \frac{E}{\eta \omega} \left[\left(-e^{Et/\tau} \cos \omega t \times \omega^{-1} \right) + \frac{E}{\eta \omega} \int e^{Et/\tau} \cos \omega t dt \right]$$

23.

Now I appears on both sides of the equation and we can write:

$$I \left[1 + \frac{E^2}{\eta^2 \omega^2} \right] = \frac{1}{\omega} \left(e^{Et/\tau} \sin \omega t + \frac{E}{\eta \omega} e^{Et/\tau} \cos \omega t \right)$$

24.

All that remains now is to simplify this:

$$\frac{1/\omega}{1 + \frac{E^2}{\eta^2 \omega^2}} \Rightarrow \frac{\frac{\eta^2 \omega}{2 \cdot 2}}{\frac{\eta^2 \omega}{2 \cdot 2} + E^2}$$

25.

$$I = \frac{\frac{\eta^2 \omega}{2 \cdot 2}}{\frac{\eta^2 \omega}{2 \cdot 2} + E^2} \times e^{Et/\tau} \left(\sin \omega t + \frac{E}{\eta \omega} \cos \omega t \right)$$

26.

We can now back track to equation 21 and substitute our integration into it:

$$\sigma = \frac{E \varepsilon_0 \eta^2 \omega^2}{\eta^2 \omega^2 + E^2} \left(\sin \omega t + \frac{E}{\eta \omega} \cos \omega t \right)$$

27.

This represents the in and out of phase components of the Maxwell model. So that substituting for the relaxation time ($\eta = E\tau$) in the sine terms gives the storage modulus:

$$E' = \frac{\sigma}{\varepsilon_0} = \frac{E\eta^2 \omega^2}{\eta^2 \omega^2 + E^2} \Rightarrow \frac{E\tau^2 \omega^2}{1 + \tau^2 \omega^2} \quad 28.$$

Similarly for the cosine term, we get the loss modulus.

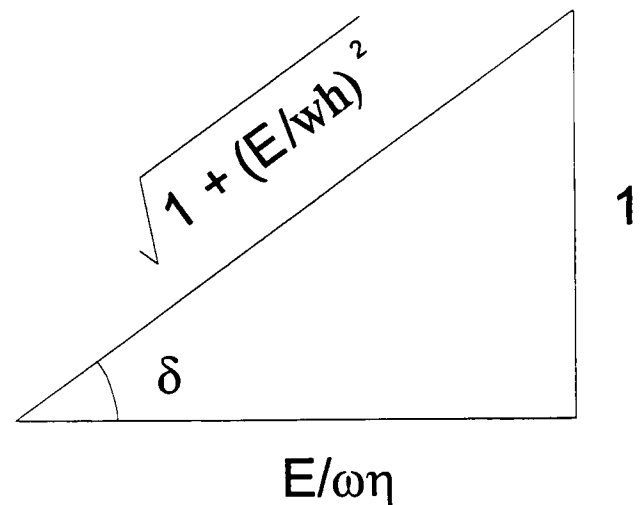
$$E'' = \frac{\sigma}{\varepsilon_0} = \frac{E\eta^2 \omega^2}{\eta^2 \omega^2 + E^2} \times \frac{E}{\eta\omega} \Rightarrow \frac{E\tau\omega}{1 + \tau^2 \omega^2} \quad 29.$$

and by our definition (equation 1.2.9.) $\tan \delta$ can be written down

$$\tan \delta = \frac{1}{\omega\tau} \quad 30.$$

Going back to equation 27 and taking a different route a useful equation can be derived in terms of δ the phase difference.

Taking the sine and the cosine terms as the respective sides of a right angled triangle and using pythagoresees theorem we can get the following diagram. From this we can read off $\sin\delta$ and $\cos\delta$



$$\sin \delta = \frac{E/\eta\omega}{\sqrt{1 + E^2/\eta^2 \omega^2}} \quad \cos \delta = \frac{1}{\sqrt{1 + E^2/\eta^2 \omega^2}} \quad 31.$$

Using the standard trigonometric identity: $\sin(A+B) = \sin(A)\cos(B) + \sin(B)\cos(A)$

where $A = \omega t$ and $B = \delta$

$$\sigma = \frac{E \varepsilon_0 \eta^2 \omega^2}{\eta^2 \omega^2 + E^2} \times \sqrt{1 + \frac{E^2}{\eta^2 \omega^2}} \times \left(\frac{1}{\sqrt{1 + \frac{E^2}{\eta^2 \omega^2}}} \sin \omega t + \frac{E/\eta \omega}{\sqrt{1 + \frac{E^2}{\eta^2 \omega^2}}} \cos \omega t \right)$$

32.

$$\sigma = \frac{E \varepsilon_0}{\frac{E^2}{\eta^2 \omega^2} + 1} \sqrt{\frac{E^2}{\eta^2 \omega^2} + 1} \times \sin(\omega t + \delta)$$

33.

The dynamic modulus is then given by

$$E(t) = \frac{\sigma}{\varepsilon_0} = \frac{E}{\sqrt{\frac{E^2}{\eta^2 \omega^2} + 1}} \times \sin(\omega t + \delta)$$

34.

Maxwell Model Under Dynamic Loading Using Complex Notation

Although the complex notation has already been introduced, its use has not yet been demonstrated. Starting again with the governing equation and a statement of the sinusoidal loading in complex notation, we differentiate to get.

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \times \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

7.

$$\sigma = \sigma_0 e^{i\omega t} \Rightarrow \frac{d\sigma}{dt} = \sigma_0 i\omega e^{i\omega t} \quad 35.$$

substituting the above, the governing equation becomes.

$$\frac{d\varepsilon}{dt} = \sigma_0 e^{i\omega t} \left(\frac{1}{\eta} + \frac{i\omega}{E} \right) \quad 36.$$

and hence

$$\varepsilon = \sigma_0 \left(\frac{1}{\eta} + \frac{i\omega}{E} \right) \times \int e^{i\omega t} dt \quad 37.$$

The integration gives

$$\varepsilon = \sigma_0 \left(\frac{1}{\eta} + \frac{i\omega}{E} \right) \times \frac{e^{i\omega t}}{i\omega} \quad 38.$$

Taking the stress term to the LHS gives the dynamic compliance

$$D^* = D + \frac{D}{i\tau\omega} = D - \frac{iD}{\tau\omega} \quad 39.$$

The convergence of this viscoelastic compliance to a modulus can be easily done.

$$E^* = \frac{1}{D - iD/\tau\omega} = \frac{\tau\omega E}{\tau\omega - i} \quad 40.$$

using complex conjugates E^* can be split into its real and imaginary parts.

$$E^* = \frac{\tau\omega E}{\tau\omega - i} \times \frac{\tau\omega + i}{\tau\omega + i} = \frac{\tau^2 \omega^2 E + i\tau\omega E}{\tau^2 \omega^2 - i^2} \quad 41.$$

$$E^* = \frac{E\tau^2\omega^2}{1+\tau^2\omega^2} + \frac{i\tau\omega E}{1+\tau^2\omega^2} \quad 42.$$

The storage modulus being the real, and the loss modulus being the imaginary components, as in equations 28 and 29. Comparison of the algebra when using complex notation (in the frequency domain) with the involved mathematics used when dealing in the time domain shows the elegance of the complex notation.

The Voigt Model

As depicted in figure 2.1.1. the Voigt element again consists of a Hookian spring and a Newtonian dashpot, but this time arranged in parallel. This arrangement leads us to the two following observations as the displacement of both elements is equal and the force across them is additive

$$\varepsilon = \varepsilon_s = \varepsilon_d \quad 43.$$

$$\sigma = \sigma_s + \sigma_d \quad 45.$$

The stress on each element is known, so that the governing equation can easily be written out:

$$\sigma = \frac{\varepsilon}{D} + \eta \frac{d\varepsilon}{dt} \quad 46.$$

Voigt Model in a Creep Experiment

For the case when stress is constant, the integration factor (equation 19) has to be used again. The first step is to isolate the rate of strain term in the governing equation.

$$\frac{d\varepsilon}{dt} + \frac{\varepsilon}{\tau} = \frac{\sigma_0}{\eta} \quad 47.$$

then as before use the integrating factor, this time h is t/τ

$$\varepsilon = e^{-t/\tau} \left[\frac{\sigma_0}{\eta} \times \int_0^t e^{t/\tau} dt \right] \quad 48.$$

integration and substitution of the limits gives

$$\varepsilon = \frac{\sigma_0 \tau}{\eta} e^{-t/\tau} \left(e^{t/\tau} - 1 \right) \quad 49.$$

$$\frac{\varepsilon}{\sigma_0} = \frac{\tau}{\eta} - \frac{\tau}{\eta} e^{-t/\tau} \quad 50.$$

So that the creep compliance works out to be.

$$D(t) = D(1 - e^{-t/\tau}) \quad 51.$$

Voigt Model in Stress Relaxation.

As the rate of strain is zero the governing equation simplifies to

$$\sigma = \frac{\varepsilon}{D} \quad 52.$$

Voigt Model Under Dynamic Excitation.

This time opting for the complex notation initially we write down the governing equation and the sinusoidal loading.

$$\sigma = \varepsilon E + \eta \frac{d\varepsilon}{dt} \quad 53.$$

$$\varepsilon = \varepsilon_0 e^{i\omega t} \Rightarrow \frac{d\varepsilon}{dt} = \varepsilon_0 i\omega e^{i\omega t} \quad 54.$$

Substituting in the strain and the rate of strain we have

$$\sigma = E\varepsilon_0 e^{i\omega t} + i\eta\varepsilon_0 e^{i\omega t} \quad 55.$$

Dividing through by the strain we arrive at the viscoelastic modulus of the material from which its storage and loss modulus as well as the loss tangent can be found.

$$E^* = E + i\eta\omega \quad 56.$$

$$E' = E = \frac{\eta}{\tau} \quad 57.$$

$$E'' = \eta\omega = E\tau\omega \quad 58.$$

The dynamic viscoelastic properties of a Voigt element are normally expressed in terms of the compliance's rather than modulus, the transformation is simply achieved:

$$D^* = \frac{1}{E^*} = \frac{1}{E + i\eta\omega} \quad 59.$$

Using the complex conjugate we can further simplify to get

$$D^* = \frac{1}{E + i\eta\omega} \times \frac{E - i\eta\omega}{E - i\eta\omega} = \frac{E - i\eta\omega}{E^2 + \eta^2\omega^2} \quad 60.$$

from this the storage and loss compliance's can also be written down.

$$D^* = \frac{E}{E^2 + \eta^2\omega^2} - \frac{i\eta\omega}{E^2 + \eta^2\omega^2} \quad 61.$$

$$D' = \frac{D}{1 + \omega^2\tau^2} \quad 62.$$

$$D'' = \frac{D\omega\tau}{1 + \omega^2\tau^2} \quad 63.$$

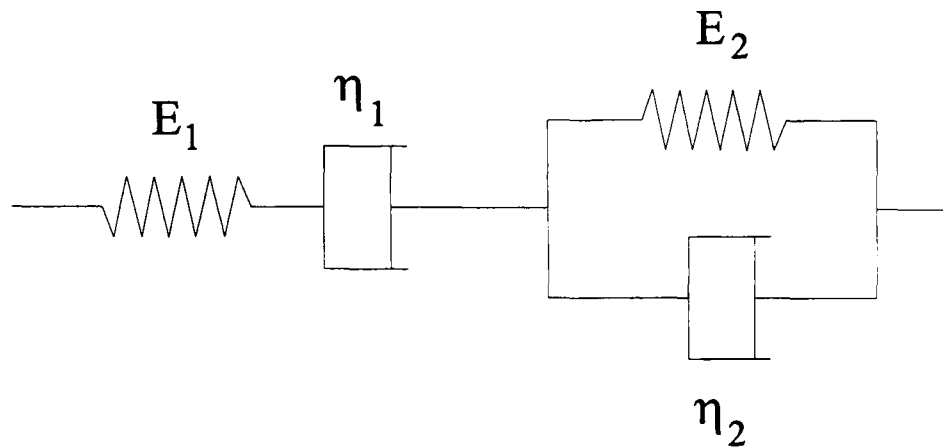
and similarly the loss tangent can be stated.

$$\text{Tan}\delta = \omega\tau$$

64.

The Four Element Model.

The four element model consists of a Maxwell and a Voigt element joint together in series.



In this arrangement the total displacement of the system is equal to that of the Maxwell Spring (ϵ_1), Maxwell dashpot (ϵ_2) and the Voigt element (ϵ_3).

$$\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3$$

65.

$$\frac{d\epsilon}{dt} = \frac{d\epsilon_1}{dt} + \frac{d\epsilon_2}{dt} + \frac{d\epsilon_3}{dt}$$

66.

For the Voigt model we can write

$$\sigma = E_2 \epsilon_3 + \eta_2 \frac{d\epsilon_3}{dt}$$

67.

$$\frac{d\sigma}{dt} = E_2 \frac{d\epsilon_3}{dt} + \eta_2 \frac{d^2 \epsilon_3}{dt^2}$$

68.

And similarly for the Maxwell element

$$\frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} = \frac{1}{E_1} \times \frac{d\sigma}{dt} + \frac{\sigma}{\eta_1} \quad 69.$$

Using equation 65 this can be rewritten:

$$\frac{d\varepsilon_3}{dt} = \frac{d\varepsilon}{dt} - \left[\frac{1}{E_1} \times \frac{d\sigma}{dt} + \frac{\sigma}{\eta_1} \right] \quad 70.$$

Differentiating equation 69 will result in

$$\frac{d^2\varepsilon_3}{dt^2} = \frac{d^2\varepsilon}{dt^2} - \left[\frac{1}{E_1} \times \frac{d^2\sigma}{dt^2} + \frac{1}{\eta_1} \frac{d\sigma}{dt} \right] \quad 71.$$

Equations 69 and 70 can be substituted into 67 to give:

$$\frac{d\sigma}{dt} = E_2 \left\{ \frac{d\varepsilon}{dt} - \left[\frac{1}{E_1} \times \frac{d\sigma}{dt} + \frac{\sigma}{\eta_1} \right] \right\} + \eta_2 \left\{ \frac{d^2\varepsilon}{dt^2} - \left[\frac{1}{E_1} \times \frac{d^2\sigma}{dt^2} + \frac{1}{\eta_1} \frac{d\sigma}{dt} \right] \right\} \quad 72.$$

This can be rearranged to a more convenient form:

$$\frac{\eta_2}{E_1} \frac{d^2\sigma}{dt^2} + \left(1 + \frac{E_2}{E_1} + \frac{\eta_2}{\eta_1} \right) \frac{d\sigma}{dt} + \frac{E_2}{\eta_1} \sigma = \eta_2 \frac{d^2\varepsilon}{dt^2} + E_2 \frac{d\varepsilon}{dt} \quad 73.$$

Or:

$$\alpha \frac{d^2 \sigma}{dt^2} + \beta \frac{d\sigma}{dt} + \gamma \sigma = \eta_2 \frac{d^2 \varepsilon}{dt^2} + E_2 \frac{d\varepsilon}{dt} \quad 74.$$

Where

$$\alpha = \frac{\eta_2}{E_1}, \quad \beta = 1 + \frac{E_2}{E_1} + \frac{\eta_2}{\eta_1}, \quad \gamma = \frac{E_2}{\eta_1} \quad 75, 76, 77.$$

2.1 The 4 Element Model in Creep.

Although the governing equation for the four element model can be solved (under creep conditions: rate of stress equals zero) it is easier by far to derive it by considering the creep behaviour of the different components of the system. For the Maxwell model this was earlier worked out to be:

$$\varepsilon(t) = \frac{\sigma_0}{E_1} + \frac{t\sigma_0}{\eta_1} \quad 78.$$

and similarly for the Voigt model

$$\varepsilon(t) = \frac{\sigma_0}{E_2} \left(1 - e^{-tE_2/\eta_2} \right) \quad 79.$$

The two strains are linearly additive so that the creep response of the four element model can be expressed as:

$$\varepsilon(t) = \frac{\sigma_0}{E_1} + \frac{t\sigma_0}{\eta_1} + \frac{\sigma_0}{E_2} \left(1 - e^{-tE_2/\eta_2} \right) \quad 80.$$

2.1 The Four Element Model Under Dynamic Excitation.

$$\alpha \frac{d^2 \sigma}{dt^2} + \beta \frac{d\sigma}{dt} + \gamma \sigma = \eta_2 \frac{d^2 \varepsilon}{dt^2} + E_2 \frac{d\varepsilon}{dt} \quad 74.$$

As before for a sinusoidal excitation:

$$\varepsilon = \varepsilon_0 \sin \omega t \quad 81.$$

$$\frac{d\varepsilon}{dt} = \varepsilon_0 \omega \cos \omega t \quad 82.$$

$$\frac{d^2 \varepsilon}{dt^2} = -\varepsilon_0 \omega^2 \sin \omega t \quad 83.$$

So that equation 74 becomes:

$$\alpha \frac{d^2 \sigma}{dt^2} + \beta \frac{d\sigma}{dt} + \gamma \sigma = \varepsilon_0 \left\{ E_2 \omega \cos \omega t - \eta_2 \omega^2 \sin \omega t \right\} \quad 84.$$

For a second order differential equation of the above configuration a solution of the following type can be assumed:

$$\sigma = A \cos \omega t + B \sin \omega t \quad 85.$$

So that:

$$\frac{d\sigma}{dt} = \omega (-A \sin \omega t + B \cos \omega t) \quad 86.$$

$$\frac{d^2 \sigma}{dt^2} = \omega^2 (-A \cos \omega t - B \sin \omega t) \quad 87.$$

Substituting these three equations into 84:

$$\begin{aligned} & \alpha\omega^2(-A\cos\omega t - B\sin\omega t) + \beta\omega(-A\sin\omega t + B\cos\omega t) + \gamma(A\cos\omega t + B\sin\omega t) \\ & = \varepsilon_0 E_2 \omega \cos\omega t - \varepsilon_0 \eta_2 \omega^2 \sin\omega t \end{aligned}$$

88.

And then collecting the Cosine and Sine terms we get the two following expressions:

$$-\alpha\omega^2 A + \beta\omega B + \gamma A = E_2 \varepsilon_0 \omega \quad 89.$$

$$-\alpha\omega^2 B - \beta\omega A + \gamma B = -\eta_2 \varepsilon_0 \omega^2 \quad 90.$$

This can be rearranged to give

$$A\left(\gamma - \alpha\omega^2\right) + \beta\omega B = E_2 \varepsilon_0 \omega \quad 91.$$

$$B\left(\gamma - \alpha\omega^2\right) - \beta\omega A = \eta_2 \varepsilon_0 \omega^2 \quad 92.$$

Equation 91 can be written so as to isolate B and similarly from equation 92 A can be derived:

$$B = \frac{E_2 \varepsilon_0 \omega - A\left(\gamma - \alpha\omega^2\right)}{\beta\omega} \quad 93.$$

$$A = \frac{\eta_2 \varepsilon_0 \omega^2 + B\left(\gamma - \alpha\omega^2\right)}{\beta\omega} \quad 94.$$

Putting equation 93 into 94 gives A.

$$A = \frac{\eta_2 \varepsilon_0 \omega^2 + \frac{E_2 \varepsilon_0 \omega - A \left(\gamma - \alpha \omega^2 \right)}{\beta \omega} \left(\gamma - \alpha \omega^2 \right)}{\beta \omega} \quad 95.$$

$$A \beta^2 \omega^2 = \eta_2 \varepsilon_0 \omega^3 \beta + \left\{ E_2 \varepsilon_0 \omega - A \left(\gamma - \alpha \omega^2 \right) \right\} \times \left(\gamma - \alpha \omega^2 \right) \quad 96.$$

$$A \beta^2 \omega^2 = \eta_2 \varepsilon_0 \omega^3 \beta + E_2 \varepsilon_0 \omega \times \left(\gamma - \alpha \omega^2 \right) - A \left(\gamma - \alpha \omega^2 \right)^2 \quad 97.$$

$$A \left(\beta^2 \omega^2 + \left(\gamma - \alpha \omega^2 \right)^2 \right) = \eta_2 \varepsilon_0 \omega^3 \beta + E_2 \varepsilon_0 \omega \times \left(\gamma - \alpha \omega^2 \right) \quad 98.$$

$$A = \frac{\eta_2 \varepsilon_0 \omega^3 \beta + E_2 \varepsilon_0 \omega \times \left(\gamma - \alpha \omega^2 \right)}{\beta^2 \omega^2 + \left(\gamma - \alpha \omega^2 \right)^2} \quad 99.$$

And similarly B can be worked out:

$$B\beta\omega = E_2\varepsilon_0\omega^2\beta - \left[\frac{\eta_2\varepsilon_0\omega^2 + B(\gamma - \alpha\omega^2)}{\beta\omega} \right] (\gamma - \alpha\omega^2) \quad 100.$$

$$B\beta^2\omega^2 = E_2\varepsilon_0\omega^2\beta - \eta_2\varepsilon_0\omega^2 \times (\gamma - \alpha\omega^2) - B(\gamma - \alpha\omega^2)^2 \quad 101.$$

$$B \left(\beta^2\omega^2 + (\gamma - \alpha\omega^2)^2 \right) = E_2\varepsilon_0\omega^2\beta - \eta_2\varepsilon_0\omega^2 \times (\gamma - \alpha\omega^2) \quad 102.$$

$$B = \frac{E_2\varepsilon_0\omega^2\beta - \eta_2\varepsilon_0\omega^2 \times (\gamma - \alpha\omega^2)}{\beta^2\omega^2 + (\gamma - \alpha\omega^2)^2} \quad 103.$$

To summarise then the sinusoidal stress and strain of the 4 element model can be expressed as:

$$\varepsilon = \varepsilon_0 \sin \omega t \quad 81$$

$$\sigma = A \cos \omega t + B \sin \omega t \quad 85$$

dividing equation 85 by ε_0 gives the overall modulus of the whole model so that:

$$E(t) = \frac{A}{\varepsilon_0} \cos \omega t + \frac{B}{\varepsilon_0} \sin \omega t \quad 104.$$

So that the dynamic viscoelastic parameters of the four element model are:

$$E' = \frac{B}{\varepsilon_0} \quad 105.$$

$$E'' = \frac{A}{\varepsilon_0} \quad 106.$$

$$\tan \delta = \frac{A}{B} \quad 107.$$

The Boltzmann Superposition Principle

Boltzmann's principle of superposition is a powerful tool in viscoelasticity theory.

Consider for now a creep compliance.

$$\varepsilon(t) = \sigma_0 D(t) \quad 108.$$

Where the stress σ_0 is applied instantaneously and then kept constant and D is the compliance. Imagine a similar experiment where the instantaneous stress σ_1 is applied, not at time 0 but at some arbitrary time u_1 . Then a similar equation can be written

$$\varepsilon(t) = \sigma_1 D(t - u_1) \quad 109.$$

Boltzmann's superposition principle states that if the two stresses σ_0 and σ_1 are applied at times $t = 0$ and $t = u_1$ respectively, then the two stresses act independently and the two strains add linearly, such that

$$\varepsilon(t) = \sigma_0 D(t) + \sigma_1 D(t - u_1) \quad 110.$$

or for a general case involving n strains at different times.

$$\varepsilon(t) = \sum_{i=1}^n \sigma_i D(t - u_i) \quad 111.$$

replacing the summation with an integration as n tends towards infinity we get:

$$\varepsilon(t) = \int_{-\infty}^t \frac{\partial \sigma(u)}{\partial u} D(t - u) du \quad 112.$$

It is important to note that t has become the fixed time of the observation of the experiment. The variable u is used as an account of the stress history. Similarly a stress relaxation experiment can be dealt with using the Boltzmann superposition principle.

This results in an equation of the form:

$$\sigma(t) = \int_{-\infty}^t \frac{\partial \varepsilon(u)}{\partial u} E(t - u) du \quad 113.$$

The implicit assumption of Boltzmanns principle being that of linearity.

APPENDIX B

THE VISCOELASTIC FREQUENCY RESPONSE OF SOFT PROSTHETIC MATERIALS.

THE VISCOELASTIC FREQUENCY RESPONSE OF SOFT PROSTHESIS MATERIALS.

K.Saber-sheikh, R.L.Clarke.*

ABSTRACT

In dentistry soft lining materials are used primarily to provide a cushion between the hard denture base and the soft tissue of the mouth, where their primary aim is to distribute the given masticatory load evenly. Their viscoelastic properties are of obvious interest.

This paper investigates the frequency dependence of the loss tangent of a number of commercial soft lining materials as well as PMMA in the frequency range 0.1-30 Hz, using the dynamic mechanical method. The peak in the loss tangent is used as an index of the Tg for these materials. Using an Arrhenius relationship the activation energies are calculated.

For the soft lining materials glass transitions ranged from -50 to +40 °C and the activation energies ranged between 100-200 kJ/mol. For PMMA the Tg was found to be 125°C but a low value of activation energy at 346 kJ/mol was found.

1. INTRODUCTION

Soft lining materials have an important role in dentistry when treating patients suffering from trauma or loss of the mucosal tissue due to age, Lammie & Storer(1). In these cases treatment is provided by lining the fit surface of the hard denture base with a soft polymer. The soft lining material has a dual role in that it absorbs some of the masticatory energy which might otherwise damage the mucosa, it also distributes the masticatory load evenly. The viscoelastic nature of these materials governs these functions and hence has been the subject of study over the years, Braden & Clarke(2), Clarke & Braden(3), using various techniques.

Dynamic mechanical analysis (DMA) is the ideal way of studying soft lining materials because it mimics the deformations encountered in the mouth (chewing forces). When a viscoelastic material is put under sinusoidal excitation part of the stress is found to be in phase with the strain leading to E' the storage modulus, and part is found to be out of phase leading to E'' the loss modulus. E''/E' is the loss tangent Tan δ . The peak in the loss tangent can be used as a measure of the glass transition temperature.

* IRC in biomedical materials, QMW, Mile end campus, London E1 4NS.
Department of biomaterials in relation to dentistry, LHMC, Turner St, London, E1 2AD.

This paper sets out to investigate the dynamic mechanical properties of several commercial soft liners, with the specific aim of investigating the frequency dependence of transitions, mainly the glass transition, and hence obtaining activation energies using an Arrhenius relationship.

2. MATERIALS AND METHODS

2.1. Materials

In all four materials were tested. These include 3 commercial soft lining materials, Braden et al(4), and Poly(methylmethacrylate), PMMA. A denture base material 'Trevalon' (Dentsply, UK) was used, which comprises of cross linked PMMA and some ethyl methacrylate. The reason for studying PMMA was that, unlike the soft lining materials, the dynamic viscoelastic properties of PMMA have been extensively studied over the years, Clarke (5), Clarke (6). Hence the results obtained by the present experimental technique and the instrumentation could be compared with previous work.

The soft lining materials tested here include 'Super-soft' (GC America Inc, USA). This is a traditional material based on plasticised acrylic. The other two materials represent recent developments in this field: 'Novus' (Hygenic Corporation, USA) is based on polyphosphazine elastomer mixed with a methacrylate monomer, Braden et al (4). 'Triad Resiline' (Dentsply, UK) is a light cured material, having the advantage of convenience over its competitors in that it can be partially cured in the mouth. It is believed to be similar in chemistry to the light cured impression elastomer 'Genesis'. This material is based on a polyether reacted with a di-isocyanate.

All four materials were manufactured into flat 2mm thick sheets using the standard dental procedures. This entailed packing and following the specific heating cycle for the heat cured materials. Triad was cured according to the manufacturers instructions using a light curing unit.

2.2. Instrument

This work has been carried out on a Perkin Elmer DMA 7 instrument. This is a forced vibration dynamic mechanical analyser, which has the advantage of keeping the frequency constant while the temperature of the material sample is being altered.

The instrument has a frequency range of 0.01 to 51 Hz. The lowest frequencies were not used however as the time between successive cycles and hence data points is very long (100 seconds for the lowest frequency) and hence not practical. Problems can also occur at the high end of the frequency spectrum as the resonant frequency of the instrument is approached.

The parallel plates measuring system was used where the material under investigation is sinusoidally deformed in compression between two circular parallel plates. This closely mimics mastication.

2.3. Experimental procedure

To obtain information on the transitions the materials were tested on a wide temperature range from -150 °C to 200°C. At the lower end of the temperature range all the soft lining materials were hard and glassy with moduli in the GPa range. Hence the 1mm diameter probe was used to provide a measurable deformation.

A range of discrete frequencies were studied from 0.1 to 30 Hz. For each frequency the results were repeated 3 times. An average value for the peak of the loss tangent curve was taken, this was used as a measure of the Tg. These results are summarised in Table 1. Figures 1,3,4,5 show the dependence of Tan δ on frequency for each material.

A relationship exists linking frequency to the transition temperature, Clarke (6), Boyer (7).

$$f = Ae^{-E/RT} \quad \Rightarrow \quad \ln f = \ln A - E / RT$$

Where f is the frequency, A is a constant, E is the activation energy, R is the universal gas constant (R = 8.314 J/mol°K) and T is the absolute temperature. Using this relationship activation energies of the transitions were calculated. In Figures 2 and 6 1/Tg is plotted against the frequency on a logarithmic scale.

3. RESULTS

Frequency (Hz)	PMMA	PMMA (Clarke, 1989)	Super-soft	Novus	Triad Resiline
0.1	125.0 ± 3	120.0 ± 3	-	-	-
0.3	129.0 ± 0.5	123.0 ± 3	-	-	-
1	132.0 ± 0.5	126.0 ± 0.5	29.0 ± 1	-31.0 ± 0.5	-52.0 ± 2
3	136.0 ± 1	129.0 ± 0.5	36.0 ± 1	-27.0 ± 0.5	-48.0 ± 0.5
10	142.0 ± 0.5	133.0 ± 0.5	37.0 ± 2	-21.0 ± 1	-43.0 ± 2
30	148.0 ± 0.5	137.0 ± 0.5	42.0 ± 4	-15.0 ± 1	-39.0 ± 0.5

Table 1 Glass transitions, Tg (°C)

Figure 1 Variation of Tan δ with frequency for PMMA, and modulus curve at 30 Hz.

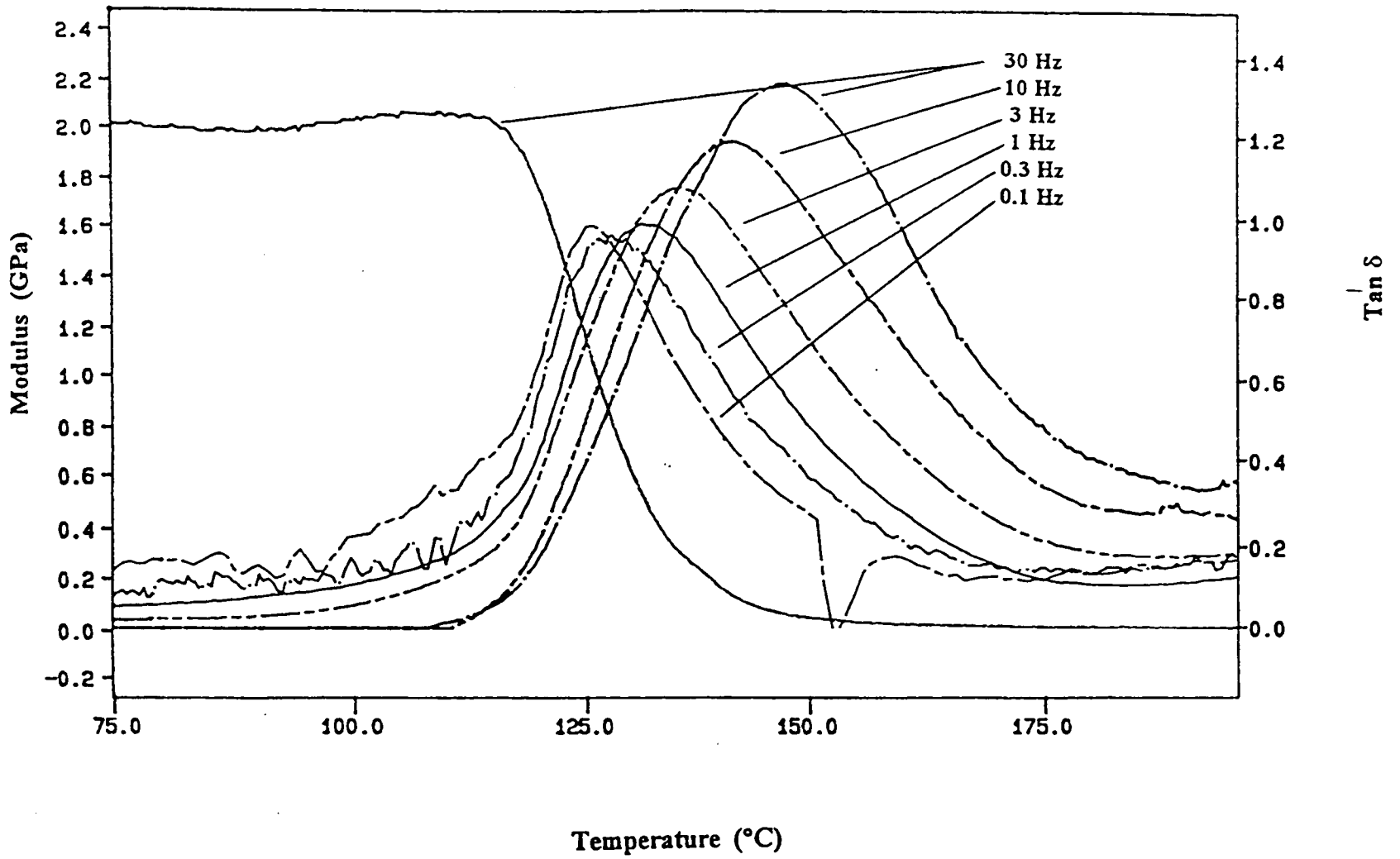


Figure 2 Activation energy plot for PMMA, comparison with previous study (Clarke, 1989).

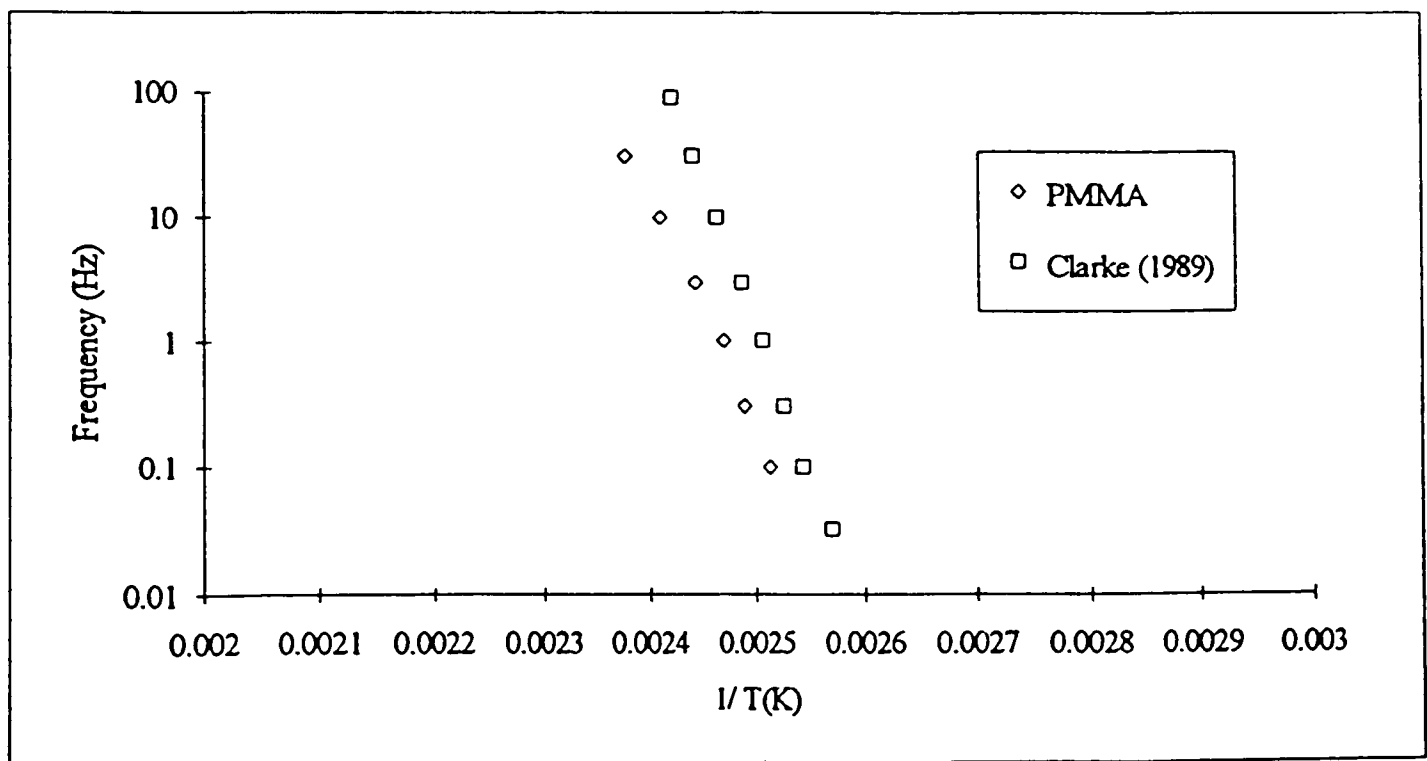


Figure 3 Variation of Tan δ with frequency for Super-soft.

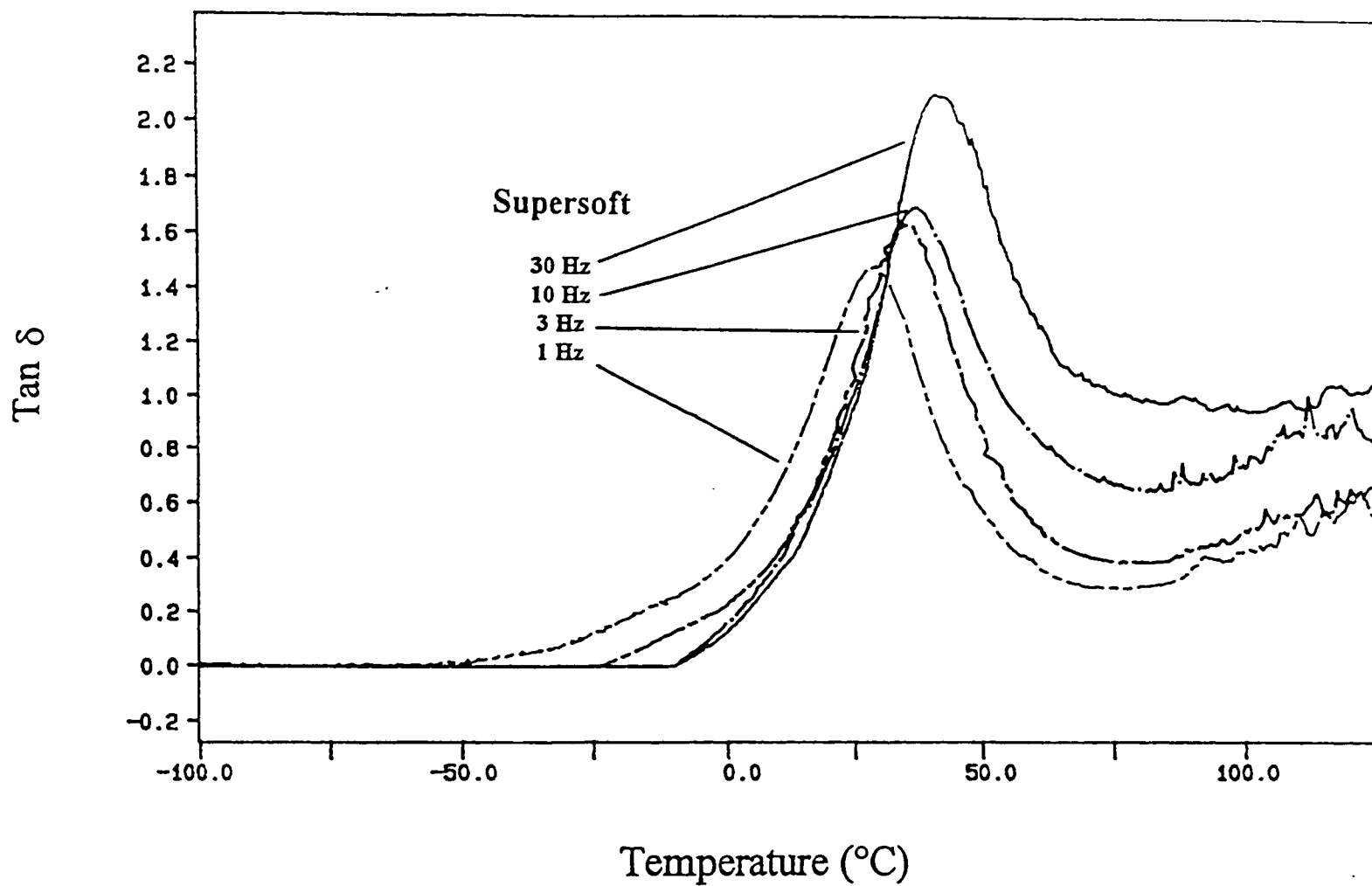


Figure 4 Variation of Tan δ with frequency for Novus.

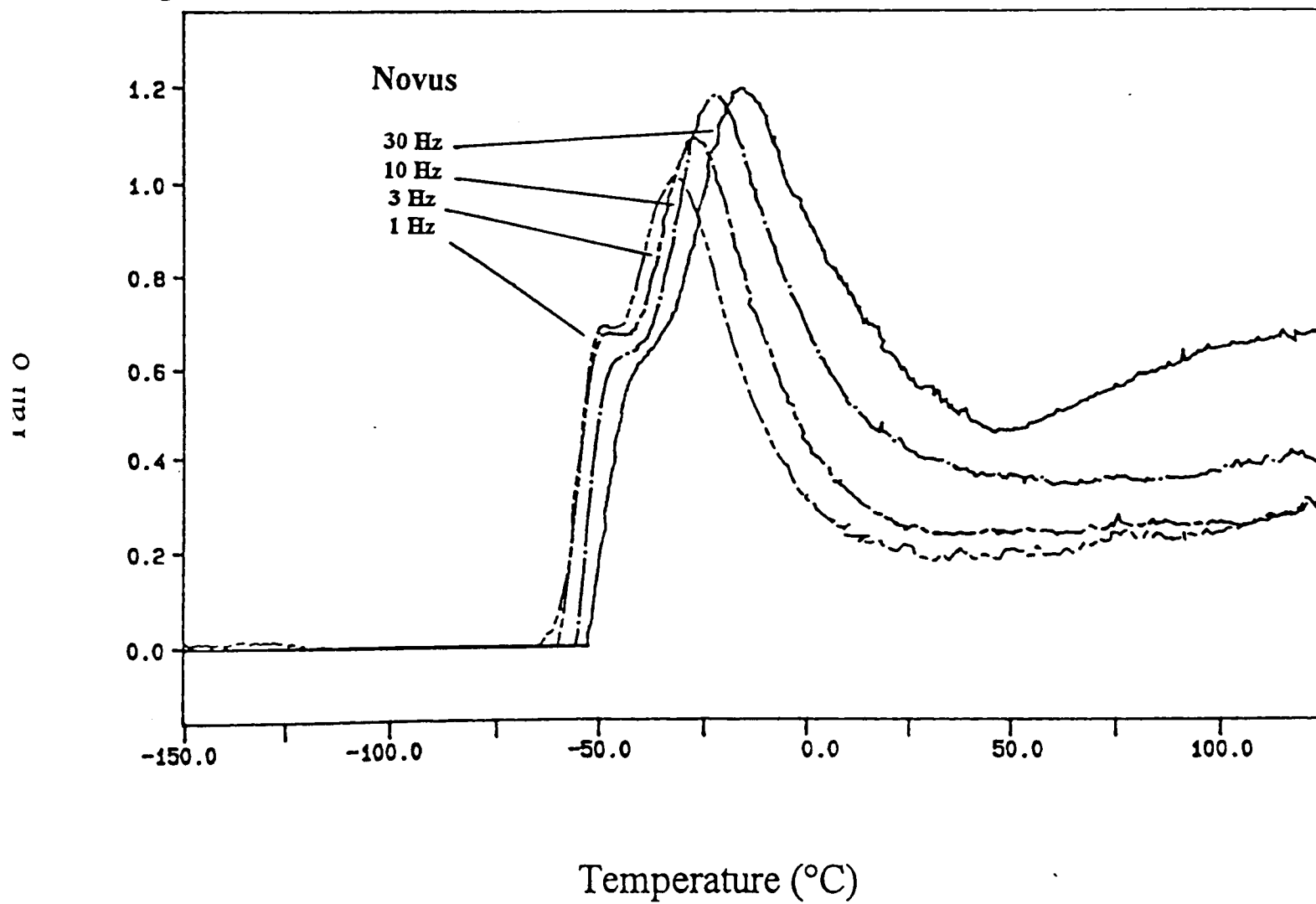


Figure 5 Variation of Tan δ with frequency for Triad Resiline.

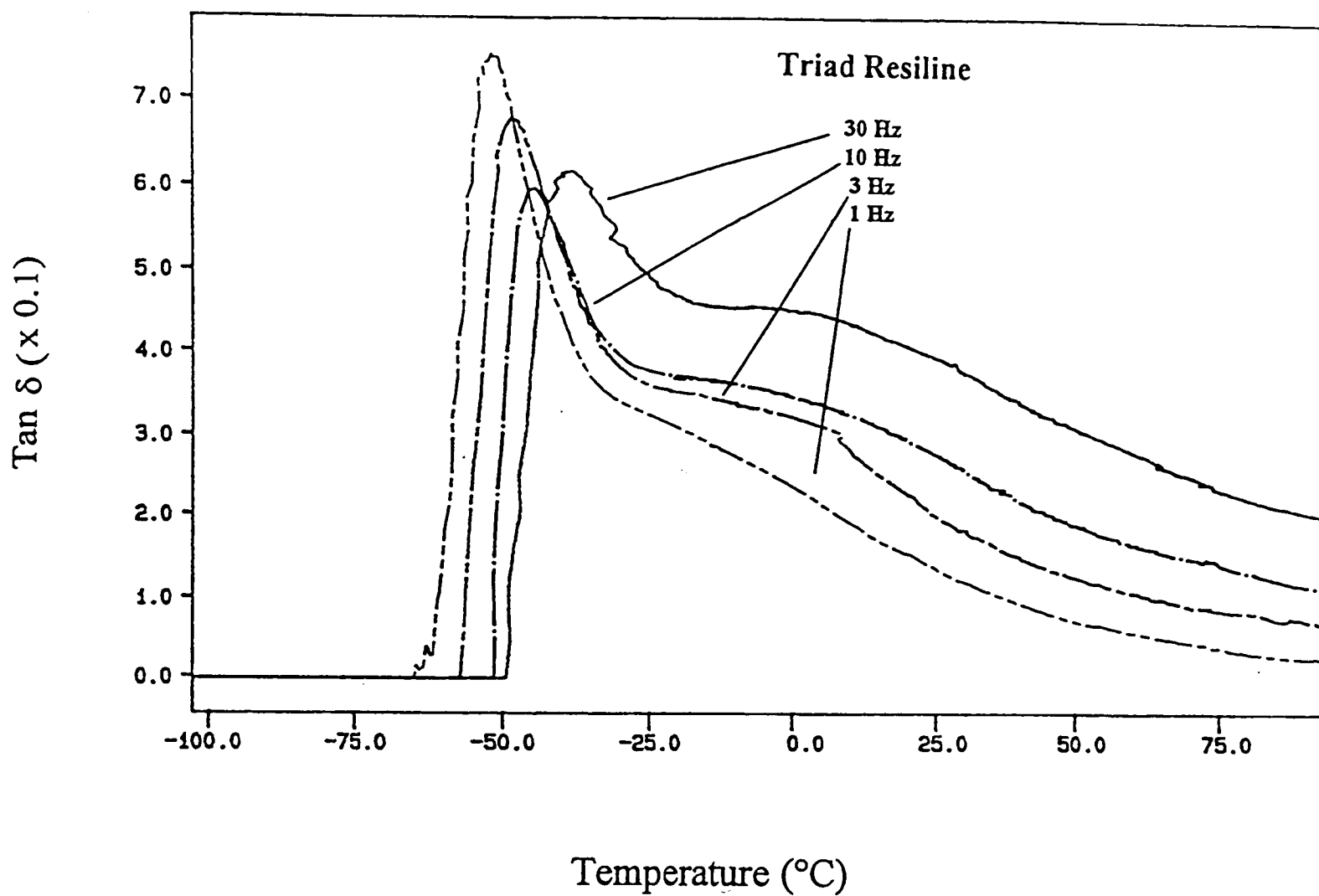
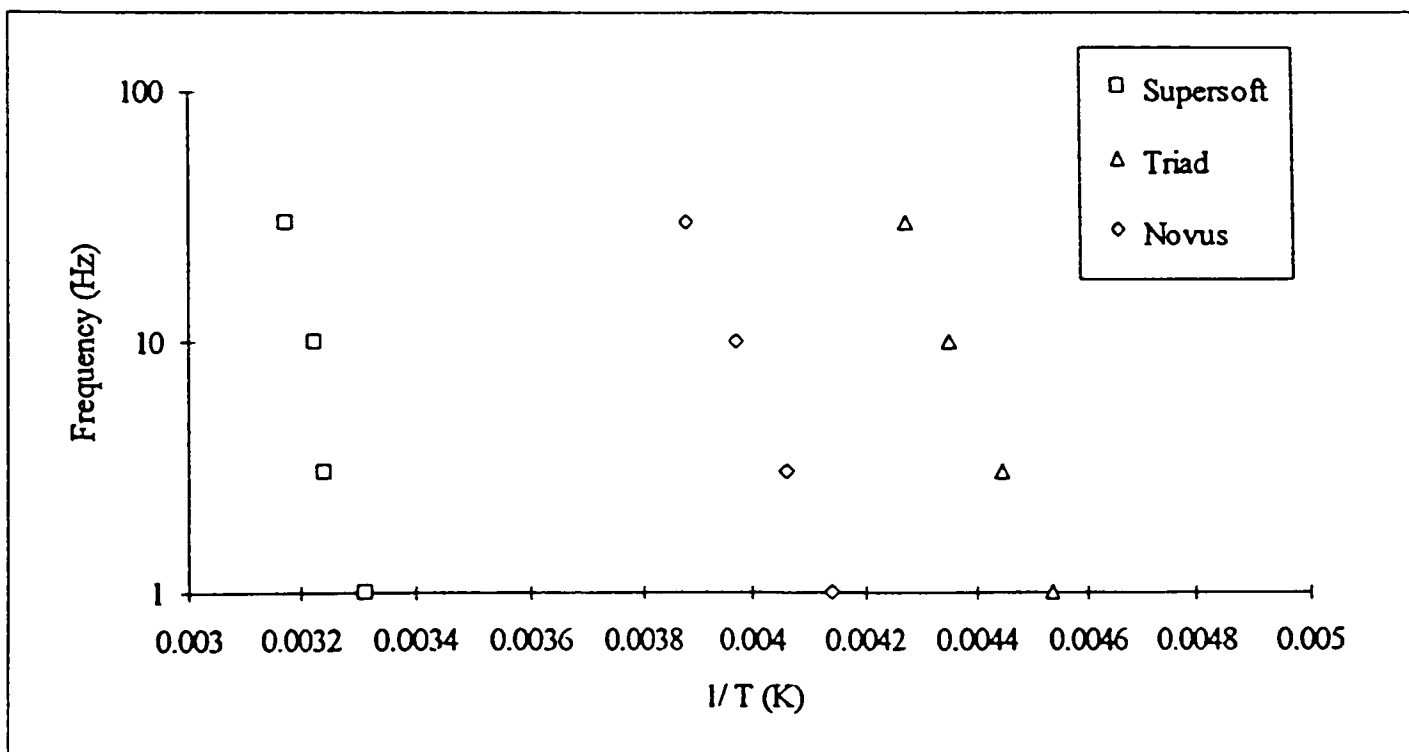


Figure 6 Activation energy plot for the soft lining materials.



4. DISCUSSION

The results obtained for Trevalon compared favourably with previous work carried out by Clarke in 1989(5), (Table 1). The Tg values were 5-10 °C higher than those found by Clarke. The difference in Tg between the two studies can in part be explained by the heating rate, which was 5°C/min in this study and 4°C/min in the previous study.

The lower frequency results suffered from excessive noise (Figure 1). This is partly due to the long time interval between data points. This meant that the lowest two frequencies were not used for the soft lining materials.

The rate of change of Tg with frequency was also higher than that found by Clarke, manifesting itself in a shallower gradient in Figure 2. This was reflected in an activation energy of 345.7 kJ/mol (regression coefficient 0.994). This was compared with an activation energy of 442 kJ/mol obtained by Clarke. The differences in the two techniques must account for this discrepancy, where Clarke used 3 point bending as opposed to a compression test. Further work is needed to elucidate the problem.

Table 1 shows that the glass transition of all the soft materials. Not surprisingly, these are lower or similar to temperatures at which the materials are used (mouth temperatures). The glass transition of Super-soft in particular occurs approximately at mouth temperature which accounts for the 'leathery' or 'lossy' nature of this material. The other two materials are well past their transitions and hence are rubbery.

Figure 3 shows the frequency dependence of Tan δ , and Figure 6 shows the activation energy plot for Super-soft. The linear dependence of $1/T_g$ and $\ln f$ was the poorest for this material (regression coefficient 0.972) An activation energy of 205 kJ/mol was calculated.

Figure 4 shows the behaviour of Novus, the main glass transition peak being at -31 C. It has a shoulder which represents the β transition approximately 20C lower. At the higher frequencies this becomes less distinct, so that no exact values for it could be calculated and hence no activation energies. The main transition however has an activation energy of 110.4 kJ/mol (regression coefficient 0.999).

Figure 5 depicts Triad resiline which also seems to have a secondary transition masked by the Tg. In this case it appears after the glass transition and hence can not be a β transition. The second transition appears to move away from the Tg with increasing frequency. It was again difficult to closely study this transition because it was very close to the Tg. For the main transition a value of 109 kJ/mol (regression coefficient 0.999) was calculated for the activation energy.

The activation energies found for the soft lining materials fit the data compiled by Boyer (7) pp1369. Where a plot of activation energy against glass transition temperature for a wide range of different polymers systems seem to lie on a common curve.

Out of the two activation energies found for Trevalon, Clarke's result corresponds more closely to this curve.

5. CONCLUSION

The Dynamic mechanical method has been successfully used to study the glass to rubber transitions of a number of soft denture lining materials.

A large discrepancy was seen for the activation energy of Trevalon compared with a previous study. The possible sources of this discrepancy deserve further investigation.

ACKNOWLEDGEMENTS

Sponsored by the IRC in Biomedical materials and Bonar Polymers Ltd.

SYMBOLS

PMMA	Poly(methyl methacrylate)
T _g	Glass transition temperature
Tan δ	Loss tangent

REFERENCES

- (1) Lammie GA, Storer R, 'A preliminary report on resilient denture plastics' J.Prof.Dent. Vol 8, 3, pp 411-424. 1958.
- (2) Braden M, Clarke RL, 'Viscoelastic properties of soft lining materials' J. Dent. Res. Vol 51, 6 pp1525-1528. 1972.
- (3) Clarke RL, Braden M, 'Determination of viscoelastic properties of dental polymers by mechanical Impedence measurements' J. Dent. Res. Vol 61 11 pp 1245-1249. 1982.
- (4) Braden M, Wright PS, Parker S, 'Soft lining materials- A review' Eur. J. Rest. Dent. Vol 3, 4 , pp 101-112.
- (5) Clarke RL, 'Dynamic mechanical thermal analysis of dental polymers. I.Heat cured poly(methy methacrylate)-based materials' Biomaterials 1989, Vol 10. pp 494-498.
- (6) Clarke RL, 'The viscoelastic nature of polymers related to dentistry', PhD thesis, University of London, 1988
- (7) Boyer RF, 'The relation of transition temperatures to chemical structure in high polymers' Rubb. Chem. Tech. Vol 36 1963

APPENDIX C

***LETTER TO THE
MEDICAL DEVICES AGENCY***

14th July 1996

Mr Jeremy Tinkler,
Medical Devices Agency,
Implants and Materials Section,
Department of Health,
Hannibal House,
Elephant and Castle,
London SE1 6 TQ

Dear Jeremy,

Re: TRIAD RESLINE - DENTSPLY LTD

I am sorry to trouble you again, on a matter quite unrelated to earlier correspondence. (Incidentally, I am most grateful for all the help that we are getting on our new materials from you and your colleagues.)

TRIAD RESLINE is a photo-polymerising soft-lining material, presumably an adjunct to TRIAD photo-polymerising denture base material. One of our Phd students is working on soft lining materials, and has been studying TRIAD RESLINE. Amongst other things, he got its Infra-red spectrum, a copy of which I enclose, and I would draw your attention to the band at $\sim 2400\text{cm}^{-1}$. This is fairly unambiguously the isocyanate group.

I suspect that this material is like their photo-polymerising impression material GENESIS, (not available in the UK as far as I know.) This is, to quote " a polyether urethane methacrylate."

The enclosed IR spectrum would support this, and one can make a fair guess of how they make it, by coupling the terminal OH groups of a polyether to hydroxyethylmethacrylate via a di-isocyanate.

Unfortunately, they have not got rid of all their isocyanate. Clearly in time this will hydrolyse to a primary amine, but that itself could be a worry.

My first action was to contact Dentsply, and I enclose the correspondence; I have heard nothing since the letter from Morton Jarvis.

It could be that I am worrying needlessly, but it would seem irresponsible to ignore the finding, in the light of episodes like that of BONELOC and Silicone Breast Implants, so I am formally reporting it to the Department.

Kind regards,
Yours sincerely

