HYBRID ORGANIC-INORGANIC NANOCOMPOSITES BASED ON POLY (HYDROXYETHYL METHACRYLATE) / SILICA (PHEMA/SIO$_2$)

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Abstract

Hybrid organic-inorganic nanocomposites were prepared through the simultaneous polymerization of 2-hydroxyethyl methacrylate and tetraethoxysilane (TEOS) by the sol-gel process. The resulting PHEMA/SiO_2 films (~ 1.5 mm thick) were rigid and optically transparent. The films were crushed into fine particles which were used as filler for light-cured dental composite resins based on methacrylate monomers. The presence of methacrylate groups in the PHEMA/SiO_2 particles improves their compatibility with the methacrylate monomer used as matrix of the composite resins. This facilitates the incorporation of high amount of filler into the resins. The composites containing particles based on PHEMA/SiO_2 offer the possibility of reduced polymerization shrinkage without severe reductions in flow characteristics of the prepolymerized resin. The amount of reinforcing filler in the final composite will be determined as a compromise between optimizing both the rheological properties and the volumetric shrinkage without jeopardizing the mechanical properties required by a particular application.

Keywords: Sol–gel, hybrid organic-inorganic, photopolymerization.

1. Introduction

Current dental composite resins have been developed to be used as restorative material and adhesives. However, there are some problems associated with the use of these materials that have not yet been solved. They involve the contraction resulting during polymerization of the methacrylate monomers, and their low wear resistance. During the last decade there have been many studies on the synthesis and preparation of novel filler particles, monomers, photoinitiators, and coupling agents to solve the aforementioned problems. According to a recent review [1], the most important advances in light-cured dental composites involve improvements in the reinforcing fillers, which have been reduced in size to produce materials that are more easily and more effectively polished. Due to the small particle size, i.e. large specific surface area, the interaction between the organic matrix and the surface of the particles is dramatically increased [2]. This raises the viscosity of the filled resins and reduces the attainable filler load. Thus, it is important to devise methodologies to introduce high amounts of inorganic fillers into resin composites. In this context, the preparation of silica nanoparticles in organic liquid media is particularly interesting.

Prepolymerized particles are very attractive for the preparation of dental compounds [3] and can be easily synthesized using the sol-gel method. The sol-gel process permits the incorporation of a highly crosslinked inorganic networks in organic monomers. This can be accomplished by direct reaction between orthosilicates with oligomers or organic polymers that can provide connectivity between the organic phase and the inorganic network that is formed by precipitation of SiO_2 in situ. Another way to obtain them is by the hydrolysis and condensation of alkoxysilanes containing a functional group which can be subsequently polymerized.

This combination of organic polymers with inorganic glass reduces the brittleness of pure inorganic glasses. SiO_2 acts as a reinforcing agent increasing both the hardness and the compressive strength of the polymerized resin. In addition, the presence of SiO_2 reduces the coefficient of thermal expansion of the material. The main factors that determine to what extent those properties can be improved are the mass fraction of filler particles and the adhesion between the silica and organic polymer [4].

The objective of this work was the synthesis and characterization of novel particles to be used as filler in light-cured dental restorative resins.

2. Methodology

2.1 Materials

The methacrylate monomers used for this study were 2,2-bis[4-(2-hydroxy-3- methacryloxyprop-1-

oxy)phenyl]propane (BisGMA, Esstech, Essington, PA), triethylene glycol dimethacrylate (TEGDMA, from Aldrich), 2,2-bis[4-(2-methacryloxyethoxy) phenyl]propane (BisEMA, Esstech, Essington, PA). One of the resins was formulated from blends of BisGMA and TEGDMA at mass fraction of 70:30. This resin was denoted BisTEG. All the resins were activated for visible light polymerization by the addition of 1 wt% camphorquinone (CQ, Aldrich) in combination with equimolar proportion of ethyl-4-dimethylaminobenzoate (EDMAB). 2-hydroxyethyl methacrylate (HEMA), tetraethoxysilane (TEOS), benzoyl peroxide (BPO), hydrochloride acid were purchased from Aldrich. The silica used in rheological studies, Aerosil OX-50 (Degussa Corporation), is an amorphous form of silicon dioxide prepared by a flame hydrolysis process. This silica is also referred to as pyrogenic or fumed silica. According to the manufacturers, the primary particles of the OX-50 silica are 50 nm in diameter and the BET surface area is ~50 m^2 g^{-1} [2]. The light source employed to cure the resins was a light-emitting diode unit (Ultralume2, Ultradent, USA) with a wavelength range of 410–530 nm and light irradiance of 400 $mWcm^{-2}$.

2.2 Synthesis of particles prepolymerized

($PHEMA/SiO_2$) hybrid organic-inorganic films were prepared by the polymerization of TEOS by the sol-gel method with acid catalysis. It is widely reported that when basic catalysis is used in the sol-gel method of TEOS the condensation step is highly favoured. This results in very condensed discrete particles and the polymerized material is opaque. On the other hand, the use of acid catalysis, favours the hydrolysis reaction, which leads to a fine structure of branched silicates and the resulting materials are transparent [4-6]. The general reactions involved in the sol-gel method are summarised as follows:

i) Hydrolysis

$$\equiv Si-O-C_2H_5 + H_2O \longrightarrow \equiv Si-OH + C_2H_5OH$$

ii) Condensation

$$\equiv Si-OH + OH-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + H_2O$$

and/or

$$\equiv Si-OH + C_2H_5-O-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + C_2H_5OH$$

If the reaction is complete, then the process can be expressed as:

$$Si(O-C_2H_5)_4 + H_2O \longrightarrow SiO_2 + 4\,C_2H_5OH$$

The synthesis of the ($PHEMA/SiO_2$) films was completed by the free-radical polymerization of hydroxyethyl methacrylate (HEMA) using benzoyl peroxide (BPO) as initiator.

The sol-gel polymerization of TEOS was catalysed by adding a mixture of water and HCl with the following molar ratios: [HCl]/[TEOS]= 1.85 10^{-2} and [H2O]/[TEOS]=2. The silica content of the resulting nanocomposites can be adjusted by varying the [HEMA]/[TEOS] ratio. A theoretical prediction of the silica content can be calculated by assuming that the sol-gel reactions are complete:

$$\frac{m_2}{m_1} = \left(\frac{1}{\omega} - 1\right)\frac{PM_{siO_2}}{PM_{TEOS}} \qquad (1)$$

Here m_1 and m_2 are the masses of TEOS and HEMA respectively, ω is the weight per cent of silica, and PMSiO2 and PMTEOS are the molecular weights of silica (60 g/mol) and TEOS (208 g/mol). Thus, Eq. (1) gives the masses of TEOS and HEMA to be used in the synthesis for a given weight per cent of silica in the films (ω). A typical preparative procedure of hybrid films can be described as follows. First, an HCl aqueous solution is prepared by mixing 10 g of distilled water with 0.51 g of concentrated hydrochloric acid solution: 37.0 per cent by mass. If 30 wt% silica content is expected for the resulting material then 0.95 g of the above solution are added to 5.2 g of TEOS under continuous stirring. Simultaneously, 3.5 g of HEMA and 0.07 g of BPO are mixed together. After having maintained both mixtures under stirring for 30 min, the HEMA-based mixture is added under stirring to the TEOS solution. The resulting mixture is kept under vigorous stirring for 30 min, then it is poured into a 10 cm diameter PTFE mould and is heated in a an oven at 60 ºC for 21 h, followed by 18 h at 90 ºC to initiate the free-radical polymerization of HEMA and to ensure a maximum conversion of double bonds. The resulting hybrid organic-inorganic films (~ 1.5 mm thick) were optically transparent and rigid. The films obtained were crushed into fine powder using an analytical mill (IKA-A-10, Teckmar, Cincinnati, USA); the particles obtained are called $PHEMA/SiO_2$.

2.3 Sample preparation

Experimental composites were prepared by incorporating 60 wt% of $PHEMA/SiO_2$ powder containing 50 wt% silica into both BisTEG and BisEMA methacrylate resins.

2.4 Characterization techniques

Diffuse reflectance infrared Fourier transform (DRIFT) spectral measurements were carried out with a Bruker IFS 25 Fourier transform infrared

spectrometer provided with a 'collector' diffuse reflectance accessory from Barnes Analytical/Spectra Tech. All spectra were recorded at 2 cm^{-1} resolution and with 128 scans.

The viscosity of pastes was measured at 30 ºC using an Anton Paar rheometer (Physica MCR-301) provided with a CTD 600 thermo chamber. A parallel-plate configuration (diameter D = 25 mm, gap H ~ 1 mm) was used in oscillatory mode in the frequency range 0.1–100 s^{-1}. All tests were performed using small strains to ensure the linearity of the dynamic response. Runs were repeated using different samples.

Measurements of conversion versus time for resins prepared with CQ in combination with EDMAB were carried out in 2 mm thick and 10 mm diameter circular samples using near-infrared (NIR) spectroscopy with a Nicolet 6700 Thermo Scientific. The NIR spectra were acquired over the range 4500–7000 cm^{-1} from 28 co-added scans at 2 cm^{-1} resolution and an acquisition time of 120 s. Resins were sandwiched between two 2 mm thick glass plates separated by a 2 mm thick rubber spacer, which were tightly attached to the sample holder using small clamps. With the assembly positioned in a vertical position, the photoirradiation source was placed in contact with the glass surface. To obtain the double bond conversion as a function of the irradiation time, the samples were irradiated for specific time intervals and the spectra recorded. These spectra were corrected with the background spectrum collected through an empty mould assembly fitted with only one glass slide to avoid internal reflectance patterns. The conversion profiles were calculated from the decay of the absorption band located at 6165 cm^{-1} [7, 8]. Two replicates were used in the measurement of conversion.

The shrinkage development during photopolymerization was monitored by means of a Fizeau-type interferometric method. Details of the technique were reported elsewhere [9]. The technique enables quantitative measurements providing data for the continuous shrinkage evolution during photopolymerization. The light source employed in shrinkage studies was assembled from an LED (OTLH-0090-BU, Optotech Inc.), which functions in a continuous fashion. The emittance of this LED was centred at 470 nm and its irradiance was 12.8 $mWcm^{-2}$. The results are the average of five measurements.

Observations to examine the morphology of the composites by field emission scanning electron microscopy (FESEM) were carried out with a Zeizz-Supra 40 instrument at 5 kV. The surfaces of the samples were coated with a thin Au–Pt layer.

Flexural and compressive tests were carried out at room temperature with an Instron testing machine (model 4467) at a crosshead displacement rate of 2 mm min−1. The mechanical properties measured were the flexural modulus of elasticity (E) and the compressive yield strength (σy). E was measured in flexure using sample dimensions recommended by ISO 4049: 2000(E): (25±2) mm× (2±0.1) mm× (2±0.1) mm. Results were computed using the standard formula:

$$E = \frac{L^3 P}{4bd^3 y} \qquad \sigma_f = \frac{3P}{2bd^2}$$

where L is the length between the supports, P is the load, b is the width of the specimen, d is the thickness of the specimen, and y is the deflection at the centre. The results are the average of five measurements. Multifunctional methacrylates are brittle in nature; therefore, they are weak in tension but quite strong in compression and capable of yielding under uniaxial compression. Samples for compression testing were made by injecting the resins into polypropylene cylindrical disposable melds of 6 mm internal diameter (D). Samples were irradiated for 60 s on each side. After removal from the moulds, the compression specimens were machined to reach their final dimensions. Cylindrical specimens having an aspect ratio L/D of 1.5 were deformed between metallic plates lubricated with molybdenum disulfide. The deformation was calculated directly from the crosshead speed. True stress–deformation curves were obtained by dividing the load by the cross-sectional area. The yield stress was determined at the maximum load.

3. Results and discussion

The synthesized hybrid materials were transparent to the visible light indicating that there was no macroscopic (i.e., greater than the wavelengths of the visible light) organic–inorganic phase separation. Fig. 1 show that the powder obtained contained particles with a distribution bimodal of size, appear particles about 100 microns and more small; and its shape is irregular.

Fig. 2 gives a typical Drift spectrum for the powder containing 30 wt% silica. The broad band between 3000 and 3700 cm-1 is related to the stretching of OH group, bonded to carbon or silicon; the presence of bonds C-OH would corresponds to polymerized HEMA and Si-OH to the silica rich phase, both forming inter and intramolecular hydrogen bonds. The band at 970 cm^{-1} corresponds to the deformation of Si-OH bond. The band at 2900 cm-1 corresponds to the stretching C-H from poly (2-hydroxyethyl methacr-

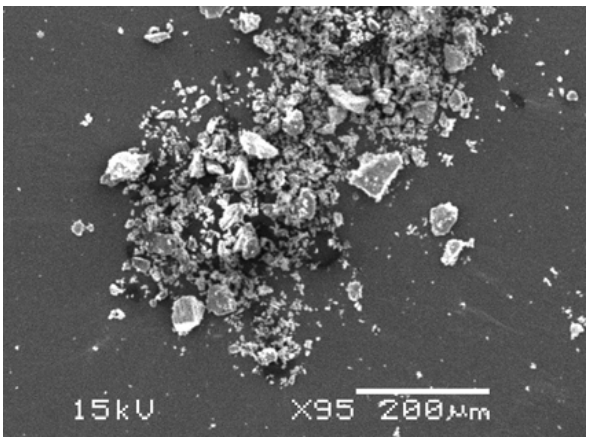

Fig. 1. Micrograph of the fine white powder obtained by crushing the hybrid organic-inorganic film.

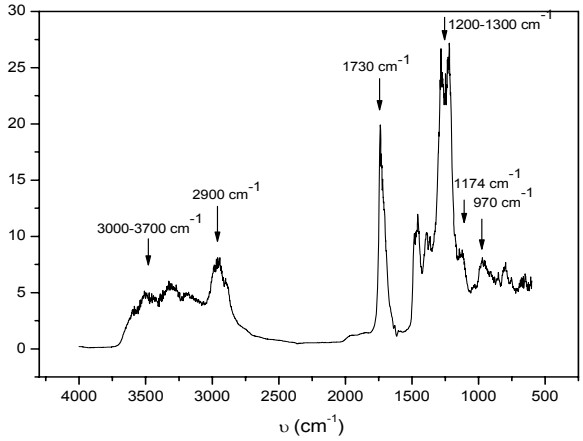

Fig. 2. Typical spectrum of PHEMA/SiO_2 hybrid powder containing 30 wt% SiO_2.

ylate). The band at 1730 cm^{-1} indicated the presence of the carbonyl group of the polymer. The double band between 1200 and 1300 cm-1 is the characteristic of the silica presence (Si-O-Si stretching) and finally, the band at 1174 cm^{-1} is the one corresponding to the stretching Si-O-C. This band has been attributed by Schylze et al. [10] to the condensation of the silica particles formed with the HEMA.

HEMA/SiO_2 films were crushed into fine powder and used as filler of methacrylate resins. A high proportion of particles could be incorporated into methacrylate monomers. Composite materials based on BisTEG or BisEMA monomers and different proportions of (PHEMA/SiO2) particles were prepared. Rheological characterization of the resulting pastes was carried out by dynamic oscillatory shear experiments. Fig. 3 shows the curves of storage and loss modulus and dynamic viscosity, as a function of the frequency for BisTEG and BisEMA resins filled with 60 wt% PHEMA/SiO_2 particles. Curves of BisTEG and BisEMA filled with 30% wt fumed nanosilica (Aerosil) are shown for comparison.

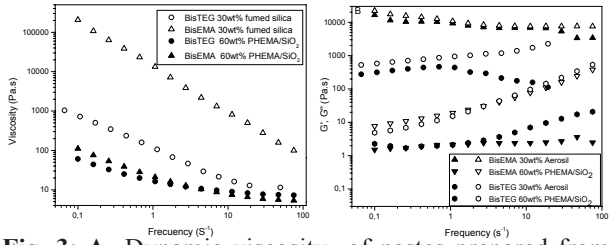

Fig. 3: A- Dynamic viscosity of pastes prepared from BisTEG and BisEMA resins filled with PHEMA/ SiO_2 prepolymerized particles. **B-** Storage (filled symbols) and loss modulus (hollow symbols) of pastes in A. The curve of suspension containing 30 wt% fumed nanosilica (Aerosil) in resins is shown for comparison.

Tests carried out on the neat resins (not shown here) showed that the resins behave as Newtonian liquids; i.e. the viscosity remains constant during the duration of the test [11]. However, the addition of fumed nanosilica results in a significant increase in the viscosity and a shear thinning behaviour is observed during the whole test. In contrast, a less marked effect of the filler on the dynamic viscosity in suspensions prepared with prepolymerized PHEMA/SiO_2 particles. The fumed nanosilica has a high surface area covered by silanol groups. Consequently, the particles easily adhere to each other through hydrogen bonding and form irregular agglomerations. This raises the viscosity of the filled resins and reduces the attainable filler load. Thus, it is important to devise novel methodologies to introduce high amounts of inorganic fillers into resin composites without jeopardizing the workability of the pastes. In this context, the synthesis of silica nanoparticles in organic liquid media by the sol–gel technique is especially interesting. Compared to mechanical dispersing techniques of silica-based nanoparticles the sol–gel technique is a very efficient chemical method for embedding silica particles in methacrylate resins. The polymeric methacrylate present in the PHEMA/SiO_2 hybrid particles improves the compatibility of the filler with the methacrylate monomer to be photopolymerized, resulting in enhanced wetting capabilities. Moreover, the relatively low viscosity in resins filled with PHEMA/SiO_2 prepolymerized particles enables the preparation of composites with a high filler load, thereby reducing the shrinkage of the dental composite during polymerization. In addition, favourable rheological properties of the uncured materials facilitate the handling and placement of the filling material in the desired location on a tooth.

The organic–inorganic hybrid films synthesized by the sol– gel route were milled down and used as filler in light-cured composites. Fig. 4 shows the conversion of methacrylate groups versus irradiation time in experimental composites. The polymerization of dimethacrylate monomers in the absence of

external heating leads to glassy resins in which only part of the available double bonds are reacted [12]. Before reaching complete conversion, the vitrification phenomenon decelerates the reaction to hardly perceptible rate.

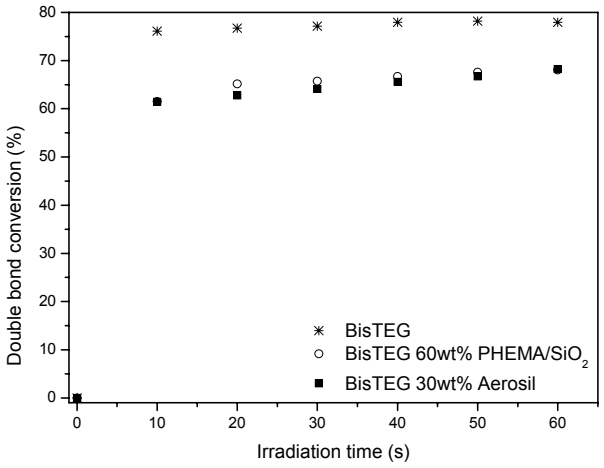

Fig. 4: Conversion of methacrylate groups versus irradiation time in experimental composites. The unfilled resin is shown for comparison.

It is worth noting that the photo-polymerization of filled systems can occur at low polymerization rate when large filler particles scatter, reflect or absorb the incident light required to initiate photopolymerization. Fig. 4 shows that the degree of polymerization of composites prepared with 30 wt% Aerosil particles is similar to that reached in the composite containing 60 wt% prepolymerized particles. The similarity among these curves indicates that the penetration of visible radiation into the 2-mm thick sample is not reduced significantly by the presence of the filler. It is worth mentioning that the amount of polymerizing monomer in the filled resin is greater than that in the unfilled resin. Consequently, the temperature reached during polymerization in the unfilled resins is higher than that in the composites. A higher sample temperature increases the mobility of the reaction environment (i.e. monomer, radical, and polymer) and consequently increases the reaction rate parameters. Thus, the greater double bond conversion in unfilled resins is attributed to thermal effects.

Fig. 5 shows the shrinkage over time during photopolymerization of composites prepared with different containing fillers.

Cure shrinkage is highly undesirable in numerous applications because it impairs dimensional control and causes poor surface finish in moulded polymers; it also generates setting stresses in highly filled systems. In the particular case of methacrylate resins used in dental composites, they tend to build-up residual

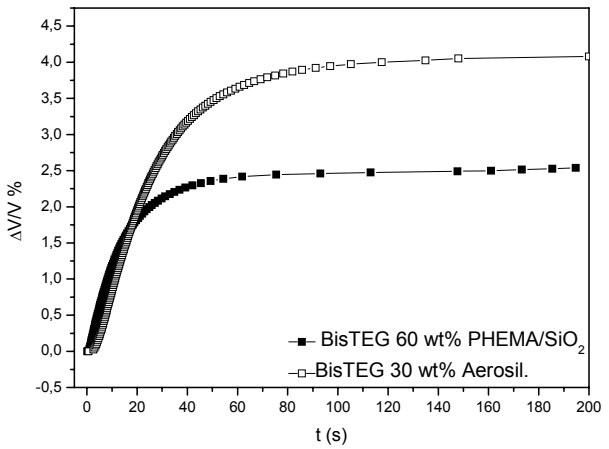

Fig. 5: Volumetric shrinkage versus irradiation time measured in experimental composites containing different type and amount of filler particles.

stresses induced by shrinkage during polymerization. When composite restorative material is placed and cured in the confined setting of a cavity preparation, its tendency to shrink can generate stresses that are high enough to break the bond of the composite to the surrounding tooth structure. The resulting gaps have been found to lead to marginal staining, sensitivity, and recurrent caries [13].

From Fig. 5, it is seen that the shrinkage can be reduced depending on the filler content. The substitution of resin with no shrinkable particles leads to lower shrinkage stress and internal mechanical stress in the composite resin. The composites prepared from PHEMA/SiO2 prepolymerized particles offer the possibility of reduced polymerization shrinkage without severe reductions in flow characteristics of the precured polymers. It should be pointed out that silica-based particles also decrease the coefficient of thermal expansion and improve thermal conductivity. Both parameters also affect the shrinkage process [9].

Mechanical characterization of the experimental composites was carried out by measuring selected flexural and compressive properties. The applied load versus strain curves in flexural tests of both neat BisTEG resin and filled composites exhibited a linear relationship over the whole range of strain and all specimens fractured catastrophically in the linear regime (curves not shown here). In these curves, the fracture of the neat BisTEG resin occurs after an important degree of deformation. Conversely, the addition of filler to the neat resin results in a limited ability of the composites to undergo deformation under compressive load. The curves corresponding to the composite resins show an important nonlinear response after reaching the maximum stress and before the final fracture of the material. After reaching

the maximum stress there is a short plateau, during which the propagation of existing cracks occurs. At this point, the contribution of the particles to load carrying is dramatically reduced. The early failure of the material can be attributed to the brittle nature of the filler particles that are not strongly bonded to the matrix. Similar behaviour was reported by Marcovich et al. [14] in resin–sisal and wood flour composites made from unsaturated polyester thermosets. Table 1 summarizes the flexural modulus (E) and compressive yield strength (σy) of experimental composites prepared from BisTEG resin and PHEMA/SiO2 prepolymerized particles.

Table 1. Flexural modulus (E), Flexural strength (σf) and Compressive yield strength (σy) of composites prepared with PHEMA/SiO_2 prepolymerized particles and commercial silica Aerosil.

Filler	E (GPa)	σf (MPa)	σy (MPa)
No filler (neat BisTEG resin)	3.4 (±0.2)	145 (±22)	108 (±5)
30 wt% Aerosil	3.6 (±0.2)	99 (±16)	45 (±12)
60 wt% PHEMA/SiO_2	3.2 (±0.7)	54 (±12)	60 (±15)

The compressive yield strength of the neat BisTEG resin was determined from the maximum in the load versus deformation curve while those of the composites were calculated from the maximum value of load at rupture. It can be seen that the flexural modulus of experimental composites were similar to that of the unfilled resin. The flexural strength values (σf) of experimental composites (Table 1) fulfil the requirements of the International Standard for polymer-based filling and restorative materials (ISO 4049:2000(E)). This standard recommends a flexural strength greater than 50 MPa for Type 2 restorations. The high data scatter observed in flexural strength values (Table 1) is associated to a brittle rupture of the test specimens [12, 15]. Brittle fracture occurs due to the propagation of a crack in the material. Flaws of variable sizes, shapes, and orientations with respect to the applied load are possible. Hence, variable crack sizes and their orientations with respect to the applied load can account for the observed scatter of fracture strengths, when nominally identical specimens are tested under nominally identical loading conditions. The addition of PHEMA/SiO_2 prepolymerized particles results in a reduction in the compressive strength compared with that of the unfilled BisTEG resin, which indicates that the particles act more as fillers than as reinforcements. Similarly to the trend observed in flexural strength values, the high data scatter in compressive strength values (Table 1) is associated to a brittle rupture of the test specimens. The amount of reinforcing filler in the final composite will be set as a compromise between optimizing both the rheological properties and the volumetric shrinkage without jeopardizing the mechanical properties required by a particular application.

The fracture surfaces of the specimens prepared with both resins were analysed by FESEM. Visual examination of the fracture surfaces of the neat resin revealed that the crack showed flat propagation with a brittle aspect. FESEM micrograph of the non reinforced resin (not shown here) revealed a very smooth ‘‘mirror-like’’ zone which is associated with rapid crack propagation regions. Conversely, fracture surfaces of composites were macroscopically very rough and three-dimensional, which is indicative of considerable crack branching.

Figs. 6 A–E show micrographs of composites prepared from BisEMA and 60 wt% PHEMA/SiO_2 particles. No significant differences among micrographs from BisTEG and BisEMA were observed. Fig. 6 A is a panoramic view showing that he PHEMA/SiO2 particles are well dispersed within the monomer and no aggregates are observed. The rough fracture surface in Figs. 6 B and C is due to the crack propagation in layers of material below and above the main crack plane. The rough structure with prominences and depressions caused by variations in the crack propagation can be seen above and below the main crack plane. Ridges are formed by the merging of two crack planes at slightly different levels. This occurs when the crack front passes around a particle, splitting the crack, which then travels on two different planes. The bifurcated crack merges again after passing the particle forming a ridge. Bonding between filler particles resin is poor. This is revealed by the smooth appearance of some filler particles shown protruding above the fracture plane of the methacrylate matrix. Figs. 6 D and E correspond to magnifications of the region of Fig. 6 C. The crack propagated through a PHEMA/SiO_2 prepolymerized particle, and the silica particles generated by the hydrolysis and condensation of TEOS can be clearly seen. This micrographs confirm the brittle nature of the prepolymerized particles prepared by the sol–gel process.

4. Conclusions

PHEMA/SiO_2 hybrid organic–inorganic nanocomposites were prepared through the simultaneous polymerization of HEMA and TEOS. PHEMA/SiO2 nanocomposites were obtained as monolithic and transparent films disks, which were crushed into fine

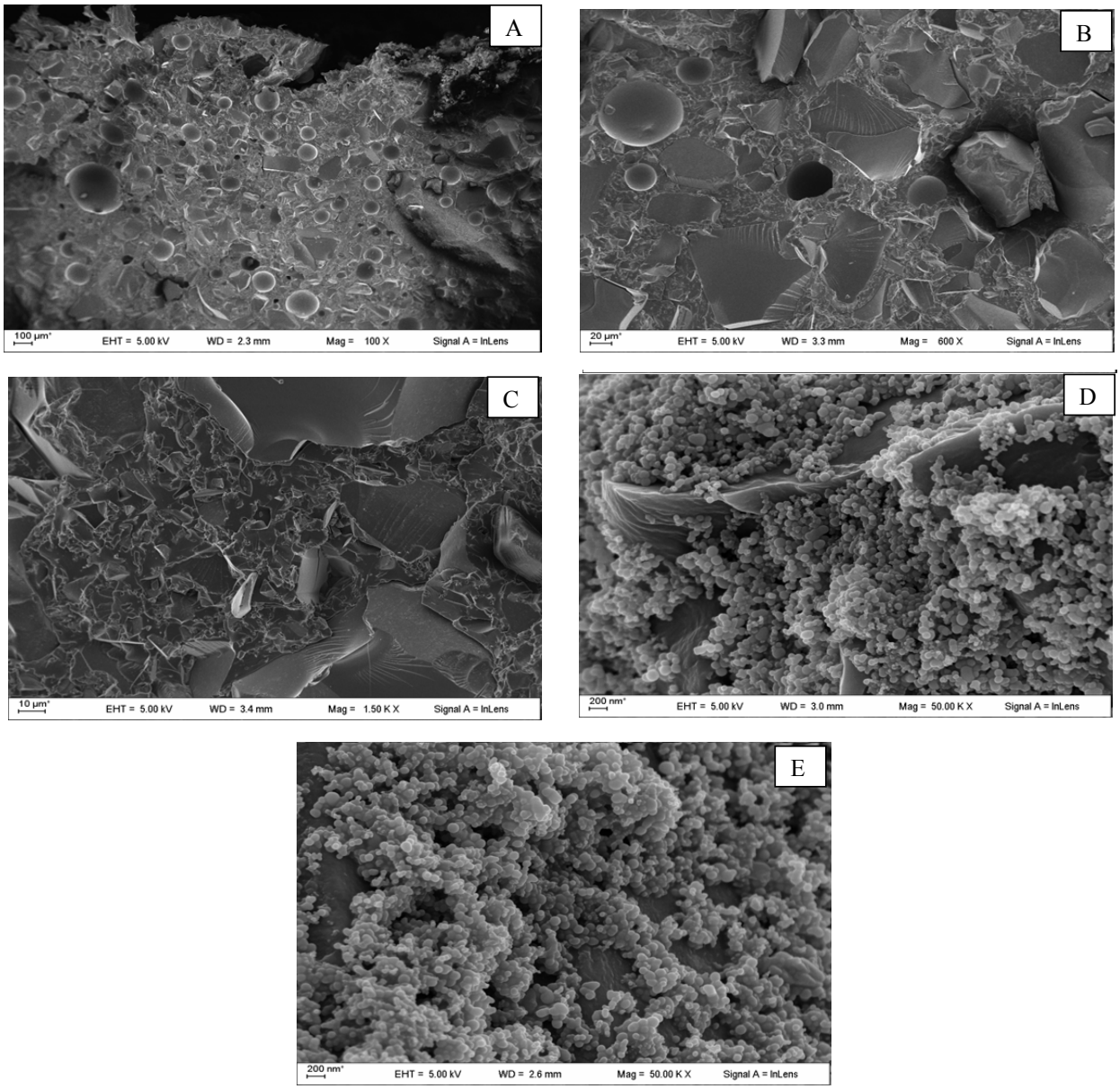

Fig. 6: FESEM micrograph of the composites containing 60 wt% PHEMA/SiO_2 prepolymerized particles in BisTEG (A,B,E) or BisEMA (C,D). A is a panoramic view. B and C are micrograph at higher magnification showing that the fracture surface was very rough and three-dimensional. D and E show that the crack propagated through a PHEMA/SiO_2 prepolymerized particle and the silica particles generated by the hydrolysis and condensation of TEOS can be clearly seen.

powder and used as filler of methacrylate resins. The methacrylate groups present in the PHEMA/SiO_2 particles improves the compatibility of the filler with the methacrylate monomer to be photopolymerized, resulting in enhanced wetting capabilities. The relatively low viscosity in resins filled with PHEMA/SiO_2 prepolymerized particles enables the preparation of composites with a high filler load, thereby reducing the shrinkage of the dental composite during polymerization. The composites prepared from PHEMA/SiO_2 prepolymerized particles offer the possibility of reduced polymerization shrinkage without severe reductions in flow characteristics of the precured polymers.

References:

1. **Ferracane J,** "Resin composite-state of the art", *Dental Materials,* **27** (2011), 29-38.
2. **Kristen S, Zhang K, Antonucci J,** "Systematic variation of interfacial phase reactivity in dental nanocomposites", *Biomaterials,* **26** (2005), 5095-5103.
3. **Kim K, Kim Y, Okuno O,** "Microfracture mechanisms of composite resins containing prepolymerized particles fillers", *Dental Materials Journal,* **19** (2000), 23-33.
4. **Landry C, Coltrain B, Brady B,** "In situ polymerization of tetraethoxysilane in poly(methyl methacrylate): morphology and dynamic mechanical properties", *Polymer,* **33**(1992), 1486-1495.

5. **Brinker C, Keefer K, Schaefer D, Ashley C,** "Sol-gel transition in simple silicates", *Journal Non-Crystalline Solids,* **48** (1982), 47-64.
6. **Pope E, Mackenzie J,** "Sol-gel processing of silica. II. The role of the catalyst", *Journal Non-Crystalline Solids,* **87** (1986), 185-198.
7. **Schroeder W, Arenas G, Vallo C,** "Monomer conversion in a light-cured dental resin containing 1-phenyl-1,2- propanedione photosensitizer", *Polymer International,* **56**(2007), 1099-1105.
8. **Schroeder W, Vallo C,** "Effect of different photoinitiator systems on conversion profiles of a model unfilled light-cured resin", *Dental Materials,* **23** (2007), 1313-1321.
9. **Mucci V, Arenas G, Duchowiczc R, Cook W, Vallo C,** "Influence of thermal expansion on shrinkage during photopolymerization of dental resins based on bis-GMA/TEGDMA", *Dental Materials,* **25** (2009), 103–114.
10. **Schulze K, Zaman A, Söderholm K,** "Effect of filler fraction on strength, viscosity and porosity of experimental compomer materials", *Journal of Dentistry*, **46** (2003), 333-350.
11. **Lemon M, Jones M, Stansbury J,** "Hydrogen bonding interactions in methacrylate monomers and polymers", *Journal of Biomaterials Research Part A,* 2007, 734-746.
12. **Vallo C,** "Residual monomer content in bone cements based on poly(methyl methacrylate)", *Polymer International,* **49**(2000), 831-838.
13. **Condon J, Ferracane J,** "Reduced polymerization stress through non-bonded nanofiller particles", *Biomaterials,* **23**(2002), 3807-3815.
14. **Marcovich N, Ostrovsky A, Aranguren M, Reboredo M,** "Resin–Sisal and Wood Flour Composites Made from Unsaturated Polyester Thermosets", *Composite Interfaces,* **16** (2009), 639-657.
15. **Giannotti M, Galante M, Oyanguren P, Vallo C,** "Role of intrinsic flaws upon flexural behaviour of a thermoplastic modified epoxy resin", *Polymer Testing,* **22** (2003), 429-437.