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Properties and Characterization of Organoclay/ Dimethacrylate Composites Obtained by In Situ Photopolymerization

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Summary: Composites of dimethacrylates/organoclay were obtained by *in situ* photopolymerization of Bis-GMA (Bisphenol A glycidyl methacrylate) and TEGDMA (tetraethyleneglycol dimethacrylate) in the presence of camphorquinone and DEEMA (2-(diethylamino)ethyl methacrylate). The composites contained up to 10% wt/wt of organoclays. Monomer conversion and polymerization kinetics were determined by real time Fourier-Transform Infrared Spectroscopy – Attenuated Total Reflectance (FTIR-ATR), and showed an increase of conversion with addition of the clay. The storage modulus E' of the composites also had a marked dependence on the composite composition and increased with addition of clay at all temperatures. T_g also increases with clay content. X-Ray Diffraction (XRD) analysis shows that the clay is completely exfoliated for the composites with a lower proportion of clay, whereas for larger clay/polymer proportions peaks corresponding to the interlamellar distance of the clay are still observed. This is probably due to the fact that the amount of monomers in the initial formulation was not sufficient to delaminate the clay. Scanning Electron Microscopy (SEM) images indicate a quite homogenous copolymer, with some clay aggregates that increase in size and number for the higher filler loadings in agreement with the XRD results.

Keywords: clay; composites; dimethacrylate-clay composites; photopolymerization; thermal analysis

Introduction

Dental composites consist of two main components, an organic matrix and an inorganic filler. The organic matrix is formed by free radical polymerization of dimethacrylates that are capable of rapid polymerization in the presence of oxygen and water, because the restorations are polymerized in situ in a tooth cavity. The most common dimethacrylate monomer used in current commercial dental composites is bis-glycidyl methacrylate, Bis-GMA. Advantages of using Bis-GMA over the first used small-sized dental monomers, such as methyl methacrylate, include less shrinkage, higher modulus and reduced toxicity due to its lower volatility and diffusivity into tissue.[1–4] These desirable properties of Bis-GMA are partially compensated by its relatively high viscosity, which does not permit the use of high amounts of filler. It is a common practice to use this monomer together with triethyleneglycol dimethacrylate, TEGDMA, a less viscous monomer as dilutant.[5] This organic matrix when without the addition of an inorganic filler shows a poor wear resistance. A wide range of fillers of various shapes and sizes is being used in varying combinations.

Clays have been recognized as potentially useful inorganic filler in polymers composites because of their high aspect ratio and lamellar morphology. Their

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addition to dental resins may lead to materials with improved wear resistance under masticatory attrition, among other advantages.[6] Layered silicate minerals belong to the structural group of swelling phyllosilicates or smectites, as montmorillonites (MMT). Smectite clays are a class of layered aluminosilicate minerals with a unique combination of swelling, intercalation and ion exchange properties that make them valuable nanostructures in diverse fields. These clays are characterized by a 2:1 structure with a central octahedral sheet sandwiched between two tetrahedral sheets. The distance between these layers is variable and depends on factors, such as water content, and the nature of the adsorbed material.[7] The layers are negatively charged due to the isomorphic replacement of some cations present in the clay structure by others of lower charge and similar size. The negative charge is normally balanced by hydrated cations placed in the interlayer spaces. These cations can be exchanged by others. The amount of the exchangeable cations is known as CEC (cation exchange capacity) and is commonly expressed in milliequivalents per 100 g of clay (mEq/100g clay).[8,9]

The untreated smectite mineral is strongly hydrophilic and hence, not suitable for the absorption of most organic molecules. A specific treatment of the naturally hydrophilic minerals is necessary to allow the sorption of organic materials and render them organophilic and compatible with polymers. Frequently this is performed introducing alkylammonium cations in the clay interlayers.[10,11]

Polymer-clay composites can be prepared in four ways: *in situ* polymerization,[12] intercalation from a polymer solution, direct intercalation of melted polymer, and sol–gel technology.[13] The direct intercalation of the organoclay into the melted polymer may produce undesirable thermodegradation of the organic surfactant. Solvent-based processes require the use of specific solvents that might evaporate during the relative long time required for swelling and exfoliation of the silicate plates. Additionally, it is sometimes difficult to find appropriate solvents for some polymer systems.

On the other hand, solvent-free light-curable formulations, made of a photoinitiator, an acrylate-functionalized oligomer and the mineral filler, are perfectly stable in the dark, thus allowing enough time for the monomers to penetrate deeply into the organophilic clay lattice which may ultimately fall apart. A short light exposure will generate free radicals capable of initiating polymerization of the acrylate double bonds, forming a three-dimensional polymer network. This *in situ* light-curing technology offers a number of advantages for the synthesis of composites material, like for example, control of the swelling time to ensure perfect penetration of monomers into the interlayer of the clay.[14] Furthermore, the *in situ* polymerization in the clay interlayer will provide an homogenous distribution of clay layers in the polymer matrix, leading to the formation of polymer/clay nanocomposites.[15]

It has been shown that silicate fillers do not affect at all the polymerization process of multifunctional acrylates containing small amounts of organophilic clays and produce highly crosslinked polymers. Therefore few millimeter thick samples can be cured within seconds by a frontal light-induced polymerization.[16]

In this study, composites of TEGDMA/BisGMA copolymers (TB) and organoclays with different clay loading (0.5, 2.0, 5.0 and 10% w/w) were prepared by *in situ* photopolymerization. The photopolymerization kinetics as a function of clay loading was studied by FTIR Spectroscopy with Attenuated Total Reflection (ATR) and the obtained composites were characterized by DSC, TG, DMA, XRD and SEM.

Experimental Part

Materials and Methods

Dimethacrylates used were Tetraethyleneglycol Dimethacrylate (TEGDMA, Aldrich Chem. Co.) and Bisphenol A glycidyl methacrylate (Bis-GMA, Aldrich Chem. Co.). They were used as received without further purification. The composites were prepared from mixtures of TEGDMA and Bis-GMA in a weight ratio 50:50 (w/w) with an organoclay (C16-montmorillonite), prepared as described in a previous report,[17] using SWy-1 (Source Clays, Clay Minerals Soc.) and hexadecyltrimethylammonium bromide (Aldrich Chem. Co.). The clay loadings used were in the range 0.5–10% w/w. The mixtures of monomers and organo-clay were kept under agitation in the dark by 72 h. For *in situ* polymerization 0.5 wt % of camphorquinone (CQ) and 0.5 wt % of 2-(diethylamino)ethyl methacrylate 99% (Sigma-Aldrich Chem. Co.) were added as photoinitiator and co-initiator, respectively. The mixtures were stored in the dark until the photocuring process was initiated.

Dynamic Mechanical Analysis

The samples used in DMA analysis were prepared in a Teflon mould [$10 \times 5.5 \times 1.0$ mm] and photocured for 100 s with a UltraBlue IS 600 mW light emitting diode (DMC Instruments – Brazil), set at 3 mm from the sample. The unit emitted radiation mainly in the 475 ± 15 nm range, where CQ also absorbs ($\lambda_{max} = 470$ nm, $\varepsilon = 3.8 \times 10^4$ cm^2 mol^{-1}).[18,19]

A dynamical mechanical analyser DMA 242C (Netzsch Instr., Germany) was used to measure the mechanical properties of samples of the TB/clay composites. Dynamical mechanical analysis was performed in the -50 to 250 °C temperature range at a heating rate of 2.0 °C min^{-1} using tension mode at the fixed frequency of 1 Hz. Liquid nitrogen was used to cool the sample as well as to provide an inert atmosphere for the analysis. The loss modulus (E''), storage modulus (E') and the loss tangent (*tan* δ, ratio of loss to storage modulus) were recorded as function of temperature, and the glass transition temperatures (T_g) were obtained from the maxima of the loss tangent versus temperature curves.

Thermogravimetry (TG) Experiments

Samples for TG analysis were prepared in a mould of 10 mm-diameter and a 1 mm-depth on a Teflon plate. The appropriate mixture of monomers, photoinitiator and co-initiator and clay were irradiated in the same way as described above.

TG/DTG experiments were performed using a TA Instruments SDT-Q600 Simultaneous Thermogravimetric Analyzer, using an alumina sample holder under nitrogen atmosphere at a flow rate of 100 mL min^{-1} in the temperature range 25–700 °C, at a heating rate of 10 °C min^{-1}. The mass of the samples was approximately 7 mg. The TG and DTG curves were analyzed with Universal Analysis 2000 v. 4.1D program from TA Instruments.

FTIR-ATR Spectroscopy

The degree of conversion of the monomers and the polymerization kinetics were evaluated by FTIR spectroscopy with Attenuated Total Reflection (ATR).[20–23] Infrared spectra were recorded on a Bomem100 (MB Series) spectrometer with a Golden Gate single reflection diamond ATR unit (Specac, Co) with a spectral resolution of 8 cm^{-1}. One drop of the mixture of the monomers was placed on the internal reflectance crystal where total internal reflection occurs, and irradiated with the same source used for preparing the samples for DMA analysis. The degree of conversion was determined from the ratio of the absorption peak areas of the aliphatic C=C absorption (at ~1635 cm^{-1}) to aromatic carbon-carbon absorption (at ~1608 cm^{-1}) between the cured (A) and uncured (A_0) copolymers according to[24,25]

$$DC(\%) = 100 - \left\{ \frac{A(1635)}{A_0(1635)} \times \frac{A_0(1608)}{A(1608)} \right\} \times 100$$

where A_{1635} and A_{1608} are the areas of the 1635 and 1608 cm^{-1} peaks, respectively.

The same procedure was used to determine photopolymerization conversions using the kinetic software (Bomem-GRAMS, ABB). The resolution used was

16 cm^{-1} that allows acquisition of approximately 48 spectra. The light beam was aligned to place the ATR crystal at the centre, and the start of irradiation was synchronized with the start of the FTIR data collection. The samples were irradiated for 40 s and the absorbance was monitored at 1635 and 1608 cm^{-1}.

Morphological Characterization

The surface morphology of composites was determined by scanning electron microscope (SEM). To obtain the microscopic images the composite powder was deposited on aluminium stubs with a carbon tape. Samples were coated with gold film. SEM analyses were performed on a LEO 440 SEM, at 2.7×10^{-6} torr and 20 kV.

The basal distance of the organoclay and the composites was determined by X-ray diffraction (XRD). The XRD data were collected on an Enraf-Nonius Kappa CCD diffractometer (Cu, radiation $\lambda = 0.154$ nm) at 50 kV, 100 mA.

Results and Discussion

Photopolymerization

The FTIR-ATR spectra showed a decrease of the aliphatic C=C absorption band at ~1635 cm^{-1}, whereas the aromatic carbon-carbon band at ~1608 cm^{-1} remained constant.

The degree of conversion of monomers in the composites increased from 43 to 51%, with increasing clay loadings, as can be seen in Figure 1. This increase is most likely due to the presence of more initiator in the more rigid microenvironment of the clay, which results in a lower internal conversion rate of the excited initiator to the ground state, thus increasing the yield of triplets and, consequently, that of free radicals.[26] The addition of an inorganic salt to the reacting mixture ($BaSO_4$) had practically no effect on conversion and kinetics, suggesting that there is no effect due to the scattering and/or reflection by the solid particles.

Figure 1 also shows that approximately half of the monomers remain unreacted and that a significant proportion of the photopolymerization occurs during the first 50 s of irradiation.

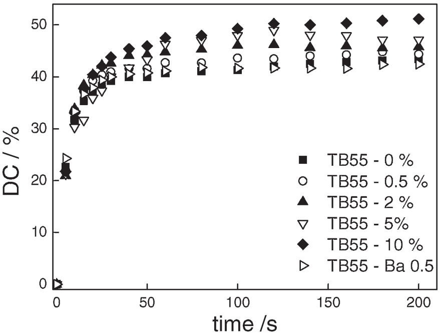

Figure 1.

Degree of conversion of the composite at different clay loadings.

Thermomechanical Behaviour

Figure 2 shows the temperature dependence of the storage modulus E' for the pure copolymer and the copolymer with different clay loadings. A decrease of E' can be observed over practically the whole temperature range (−150 to 250 °C), except around 100 °C. This increase can be associated with the presence of a second thermal polymerization process that involves the residual monomers, increases crosslinking of the composite and leads to a higher storage modulus. The increase of the E' over the whole temperature range when adding more than 2% clay indicates that the polymer is re-enforced by the filler and

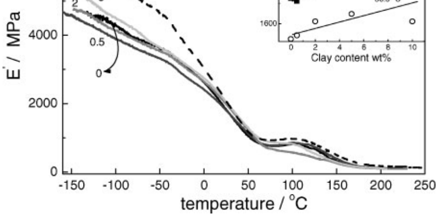

Figure 2.

Storage modulus E' as a function of temperature for composites with different clay loadings. Inset: E' at 25 and 36.5 °C for the composites.

retains more elastic energy. This can be seen in the inset to Figure 2, which shows that the storage moduli for the composites with various clay content at 25 and 36.5 °C. Similar behaviour has been found for UDMA/TEGDMA copolymers filled with silica[27] and strontium aluminosilicate.[28] Addition of clay to the composites also results in higher storage moduli.

Figure 3 shows the loss tangent (tan δ) as function of temperature for the composites with different clay loadings. Two peaks with maxima around 70 and 150 °C (T_{g1} and T_{g2}, respectively) are present. The transition at the lower temperature T_{g1}, can be due to a second phase originated by the thermal polymerization of pendant unreacted methacrylate double bonds within the vitrified network. Similar effects have been observed in the thermal analysis and post-polymerization behaviour of TB copolymers.[29,30] On the other hand, the T_{g2} corresponds to the true glass transition of the specimen cured during the DMA test. It can be observed that the increase of the clay content promotes higher values of T_{g2}. Although there is a certain scatter of the T_g values as a function of clay content (probably due to a dispersion of the DMA data), it can be seen from the inset in Figure 3 that there is a general increase in the glass transition temperature. From there, it can be deduced that the properties of the composites are improved with respect to those of the pure copolymer when adding the clay. Similar results were observed when silica was added to dental resins.[27]

Figure 4 shows the DTA curves for the different polymer/organoclay composites. For all systems studied there is a slight loss of mass of about 3% until 250 °C, which might be due to the evaporation of residual solvent or decomposition of uncured monomers. The most significant decomposition starts around 250 °C and is characterized by three peaks with maxima at 290, 365 and 420 °C, respectively. The two peaks at lower temperature were assigned to the decomposition of unreacted monomers, and the scission of smaller products linked to the ends of the polymer chains. The third stage is associated with the general decomposition of the polymers to form lower molecular weight species.[31] The addition of clay reduces the relative importance of the first two peaks.

Structural Analysis

X-ray diffraction (XRD) was used to identify intercalated structures and to determine the interlayer spacing. The interlayer distance was calculated using the Bragg equation ($n\lambda = 2d \times \sin\theta$), where λ is the wavelength of the X-ray, d is the interlayer distance and θ is the angle of the

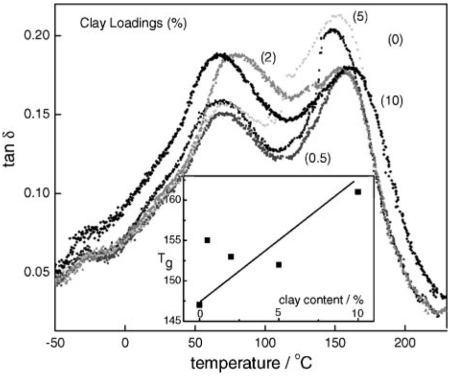

Figure 3.
Tan δ as function of temperature for composites with different clay loadings. Inset: dependence of the T_g with clay content in the composites.

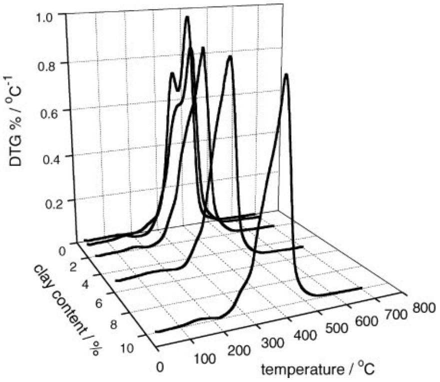

Figure 4.
DTG curves for composites with different clay contents.

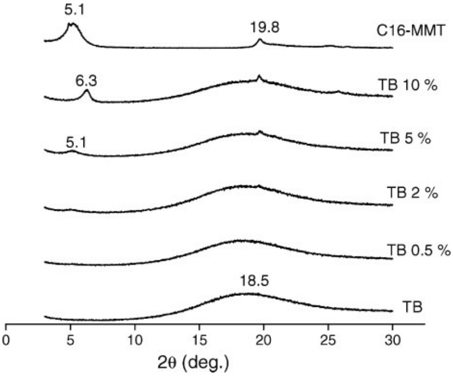

Figure 5.
X-ray diffractograms of organo-MMT, pure TB copolymer and composites of TB/organo-MMT.

incident radiation. Figure 5 shows XRD scans of the pure organoclay, the pure TB copolymer and the TB/organoMMT composites. The organo-MMT shows peaks at $2\theta = 5.1^\circ$, which corresponds to a basal spacing of 1.73 nm, as well as a peak around 19.8°. The pure copolymer has the characteristic peak of polymers at $2\theta = 18.5^\circ$. The analysis of the composites with clay loading ranging from 0.5 to 2.0% w/w, does not show the peak attributed to the d_{001} distance, suggesting that the layer spacing remains. However, the peak corresponding to the d_{001} distance can be observed for loadings of 5 and 10% w/w of clay, suggesting that part of it remained aggregated, possibly because the concentration of monomers was not sufficient to completely delaminate the clay.

Figure 6 shows SEM images obtained for the copolymer TB and the TB/organo-clay composites. Considering that single clay layers are not detected by this technique, the images suggest that the composite with low clay loading (0.5% w/w) is homogeneous indicating efficient dispersion of the clay in the monomers before polymerization. When increasing the clay loading, it is possible to observe the presence of tactoids with increasing sizes. These results are in agreement with the XRD data, suggesting a less efficient intercalation of monomers in the interlayer of clay when the proportion of clay in the polymerization formulation is higher.

Conclusion

Composites of dimethacrylates/organoclay with up to 10% wt/wt of organoclay were obtained by *in situ* photopolymerization of Bis-GMA- TEGDMA in the presence of camphorquinone (CQ) and DEEMA. The

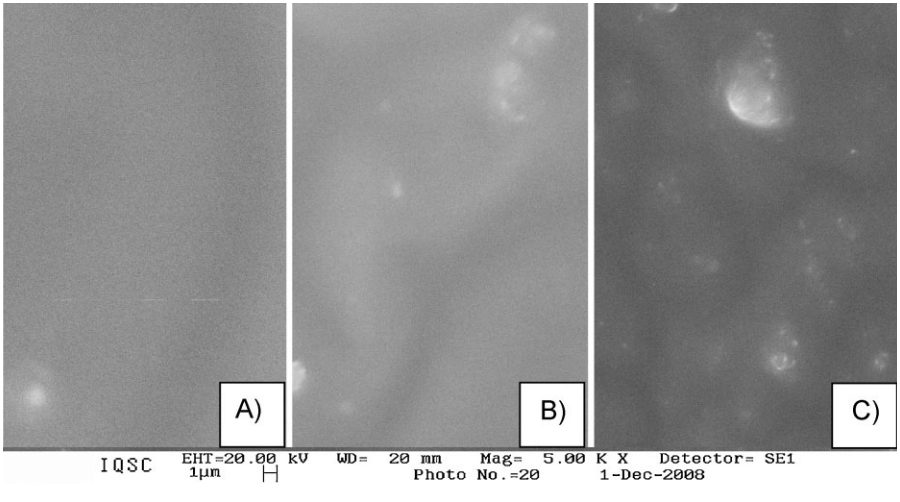

Figure 6.
SEM images of TB/organo-MMT composites with clay loadings of 0.5 (A), 5.0 (B) and 10% (C).

addition of organoclay to the copolymers had the following effects:

- increase of the monomer conversion, as determined by real time FTIR-ATR.
- increase of the storage modulus E' of the composites at all temperatures.
- increase of the glass transition temperature with clay content.
- exfoliation of the clay at low clay/polymer ratios, as determined by XRD analysis. At higher proportions the peaks corresponding to the interlamellar distance of the clay are still observed.
- formation of a homogenous copolymer, with the presence of clay aggregates at the higher filler loadings.

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