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Preparation and characterization of light-cured methacrylate/montmorillonite nanocomposites

Verónica Mucci, Javier Pérez and Claudia I Vallo*

Abstract

Polymer/clay nanocomposites were prepared from dimethacrylate monomers, commonly used in dental restorative resins, and an organically modified silicate (montmorillonite). The photopolymerization process was hardly affected by the presence of the silicate filler, and thus 2 mm thick samples containing 3 wt% clay were extensively cured. Transmission electron microscopy revealed that the montmorillonite platelets were either intercalated or exfoliated. Nevertheless, for all formulations, intermediate-sized aggregates of about 1 μm were present and their fraction increased as the amount of filler increased. The presence of the clay was found to have no major effect on the flexural modulus and compressive yield strength of the nanocomposites. Moreover, the water uptake of nanocomposites containing 3 wt% clay was about 10–15% higher than that of unfilled monomers. Modification of the clay surface with alternative organic cations is certainly necessary in order to achieve an optimal dispersion of the clay in the polymer matrix.

Keywords: nanocomposites; montmorillonite; methacrylates; photopolymerization; dental resins

INTRODUCTION

Visible light-curable polymeric composites are commonly used as filling materials for dental restorations. These materials contain 15–25 wt% of free radical-polymerizable methacrylate monomers and 75–85 wt% of a mixture of different inorganic fillers.[1] The polymerization of the methacrylate monomers is initiated by radical-forming photoinitiators which decompose under irradiation with visible light in the region of 450–480 nm (blue light).[2,3] Inorganic fillers of glass or quartz are added to improve the mechanical properties[1] and to reduce polymerization shrinkage of the composites.[4] Dental composites possess many advantages such as mechanical properties comparable to those of commercial dental amalgams and an excellent aesthetic quality. However, in aqueous environments they absorb water, which can lead to deterioration of their mechanical properties.

Polymer/clay nanocomposites have attracted significant research interest in the last few years due to the potential of enhanced mechanical and physical properties and reduced water sorption with incorporation of low clay concentrations.[5,6] The use of clay as a filler in dental resins has been recently reported.[7–9] The improved material properties have been attributed to polymer–clay interactions based on the inherent nanoscale dimensions of the clay platelets. Even if usual fillers, like alumina and silica, have been added successfully at the nanometric scale, laminate plate-like particles like mica and clay have shown the most promising results.[5]

The most widely used clay, montmorillonite (MMT), is composed of individual sheets, which are approximately 1 nm thick and vary in lateral dimension from 50 nm to several micrometres. Each platelet has a negative charge arising from isomorphous substitution in the lattice structure, which is compensated by naturally occurring cations that reside within the gallery (or interlayer) regions between the platelets. These cations can be exchanged with other cations under appropriate conditions, allowing the clay surface to be modified. The presence of organic cations in the galleries increases the compatibility between the normally hydrophilic clay surfaces and the surrounding monomer or polymer. Alkylammonium salts have been used to treat unmodified clay and the resulting organically modified clay is commonly termed organoclay. This process allows resin penetration between the clay layers, and thus clay dispersion into a polymer can be achieved. In contrast to the conventional inorganic fillers, the addition of a small amount of MMT can improve the properties to a satisfactory level because of the extremely large interface area provided by the nanosize particles of the suspended filler.

As mentioned above, current dental composite formulations have the drawback of high levels of water sorption. Generally, polymer/layered silicate nanocomposites are characterized by very strong reduction in water uptake.[5] This characteristic makes these materials very attractive for dental applications. The purpose of the study reported here was to examine the effect of the addition of clay to methacrylate monomers on water sorption and some selected mechanical properties. Various proportions of layered organic silicate were dispersed into

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* *Correspondence to: Claudia I Vallo, Institute of Materials Science and Technology (INTEMA), Universidad Nacional de Mar del Plata–National Research Council (CONICET), Av. Juan B Justo 4302, (7600) Mar del Plata, Argentina. E-mail: civallo@fi.mdp.edu.ar*

Institute of Materials Science and Technology (INTEMA), Universidad Nacional de Mar del Plata–National Research Council (CONICET), Av. Juan B Justo 4302, (7600) Mar del Plata, Argentina

dimethacrylate monomers commonly used for the preparation of dental restorative composites. The clay-filled dental monomers were prepared with the intention of their being used as matrices for light-cured dental composites. Additional inorganic fillers were not added in this study because their presence could mask the effect of the clay on the measured properties. The dispersion of the clay in the monomers was investigated using XRD and dynamic oscillatory shear experiments. Characterization of the polymerized clay-filled monomers was carried out by measuring water sorption as well as flexural and compressive properties. The degree of dispersion of clay in the polymerized resins was assessed using transmission electron microscopy (TEM).

EXPERIMENTAL

Materials and sample preparation

The methacrylate monomers used for the preparation of the nanocomposites were 2,2-bis[4-(2-methacryloxyethoxy)phenyl]propane (BisEMA; from Esstech, Essington, PA), triethylene glycol dimethacrylate (TEGDMA; from Sigma-Aldrich) and 1,6-bis(methacrylyloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA; from Esstech, Essington, PA). The structures of the monomers are shown in Fig. 1. The clay mineral was organophilic MMT from Southern Clay Products Inc. (Gonzales, TX) having the trade name of Claytone APA. It was received as a fine-particle powder. The organically modified silicate was produced by cation-exchange reaction between the silicate and dimethylbenzyl hydrogenated tallow ammonium chloride. TEGDMA is commonly used as a reactive diluent in high-viscosity monomers. In this study, undiluted UDMA and BisEMA were used. TEGDMA monomer was used in water sorption studies for comparison purposes.

The clay was incorporated into the liquid methacrylate monomers and exposed to ultrasound (40 kHz, 160 W, TESTLAB ultrasonic bath, model TB04, Buenos Aires, Argentina) for a period of 8 h. The clay-modified monomers were activated for visible light polymerization by the addition of 1 wt% camphorquinone (Aldrich) in combination with equimolar amounts of ethyl-4-dimethylaminobenzoate (EDMAB; Aldrich). 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 mW cm^{-2}.

Characterization techniques

XRD was used to analyse the morphology of the materials and to determine the interlayer spacing between stacked clay platelets. The study was done using a Phillips PW1710 X-ray diffractometer equipped with a Cu Kα radiation source of wavelength 1.54 Å operated at 45 kV and 30 mA. The diffraction spectra were recorded in the reflection mode over a 2θ range of 2–45° in steps of 0.035° using a rate of 4° min^{-1}.

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. Background spectra were recorded using dry KBr powder. Results reported were the average of 32 scans for transmission mode, while 500 scans, of both the sample and reference, were averaged in DRIFT mode to improve the signal-to-noise ratio. In both cases, further increases of the number of scans did not change the spectral appearance. Conversion of the DRIFT signal to Kubelka Munk units was done using commercial software from Bruker.

The viscosity of monomer/clay suspensions was measured at 30 °C using an Anton Paar rheometer (Physica MCR-301) provided with a CTD 600 thermo chamber. A parallel-plate configuration (diameter $D = 25$ mm, gap $H \approx 1$ mm) was used in oscillatory mode in the frequency range 0.1–500 s^{-1}. All tests were performed using small strains to ensure the linearity of the dynamic response. All runs were repeated using different polymeric samples.

Measurements of conversion *versus* time for resins prepared with camphorquinone/EDMAB were carried out with 2 mm thick and 1×1.5 cm^2 rectangular samples using near-infrared (NIR) spectroscopy with a Genesis II Mattson FTIR (Madison, WI). The NIR spectra were acquired over the range 4500–7000 cm^{-1} from 16 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. In order 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}. Two replicates were used in the measurement of conversion.

Water sorption tests were carried out according to the method described in ISO 4049:2000(E) (dentistry-polymer-based filling and restorative materials). Specimen discs 12 mm in diameter and 1 mm in thickness were fabricated in a Teflon mould between two glass slides. They were irradiated for 60 s on each side. In order to avoid complications arising from the leaching of residual monomer, the specimens were post-cured at 100 °C for 2 h, after which they were placed at 37 °C in triple-distilled water. The specimens were periodically removed, mopped dry and weighed. This was continued until a constant weight was attained. Four discs were prepared for each resin.

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 (σ_y). E was measured in flexure using sample dimensions recommended by ISO 4049:2000(E): (25 ± 2) mm $\times$ (2 ± 0.1) mm $\times$ (2 ± 0.1) mm. Results were computed using the standard formula

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

where E is the Young's modulus, 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. Like other brittle materials, they are weak in tension but quite strong in compression and capable of yielding under uniaxial compression. Therefore, the yield strength was determined in compression. Samples for compression testing were made by injecting the resins into polypropylene cylindrical disposable moulds of 6 mm internal diameter (D). Samples were irradiated for 60 s on each side. After removal from the moulds,

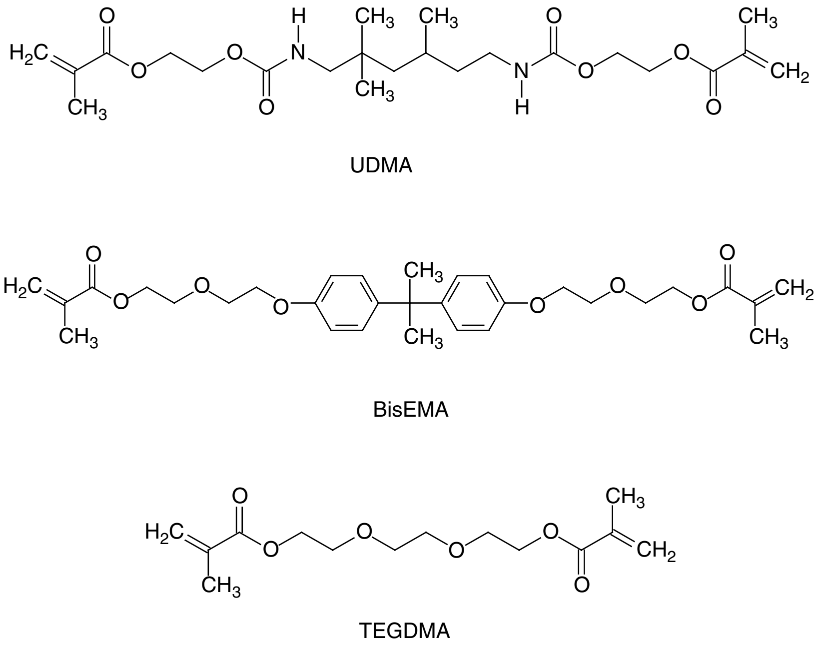

Figure 1. Monomers used for the preparation of nanocomposites.

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. The results are the average of five measurements. All test specimens were photopolymerized in ambient at room temperature (20 ± 2 °C). A set of test specimens was also post-cured at 130 °C for 2 h.

Observations to examine the morphology of the nanocomposites were carried out with a JEOL 100 CX II TEM instrument at 100 kV. Samples were sectioned using an LKB ultramicrotome with a diamond knife.

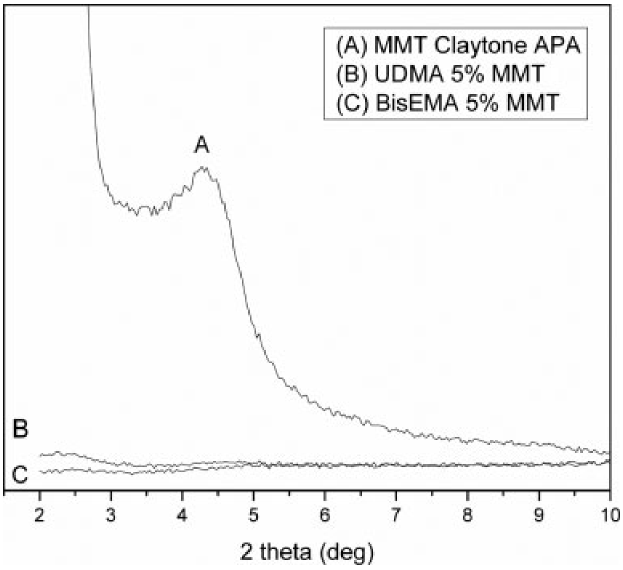

Figure 2. XRD curves of Claytone APA organoclay and nanocomposites prepared with 5 wt% of organoclay.

RESULTS AND DISCUSSION

Nanocomposite preparation and evaluation of clay dispersion using XRD

Nanocomposite preparation was carried out using the *in situ* intercalative polymerization method.[5,10,11] In this technique, the layered silicate is swollen within the liquid monomer so polymer formation can occur between the intercalated sheets. The replacement of inorganic exchange cations by organic ions on the gallery surfaces of clays not only serves to match the clay surface polarity with the polarity of the monomer, but it also expands the clay galleries. This facilitates the penetration of the polymer precursors between the clay layers. The intercalation of the monomer/polymer usually increases the interlayer spacing, in comparison with the spacing of the organoclay used, leading to a shift of diffraction peaks towards lower angles. The angle and layer spacing values are related through the Bragg relation: $\lambda = 2d \sin\theta$, where λ is the wavelength of the X-ray radiation used in the diffraction experiment, d is the spacing between diffractional lattice planes and θ is the measured diffraction angle. XRD experiments were performed to determine the quality of the clay dispersion in the various formulations. Figure 2 shows the diffractograms for the formulations prepared with 5 wt% of Claytone APA in BisEMA and UDMA monomers. The organoclay shows a peak at about 4.3° indicating that the clay has a layered structure with a d spacing (d_{001}) of 20.5 Å. The absence of the d_{001} peak in the traces of the nanocomposites (Fig. 2) means that the monomers penetrate between the clay platelets, thereby increasing the spacing between the layers, or the nanocomposite no longer shows ordering. In order to confirm if exfoliation was achieved, TEM was performed; these results are presented in a subsequent section.

The *in situ* intercalative polymerization technique is commonly used for the preparation of clay-based nanocomposites.[5,10,11] However, some studies have shown that ultrasound treatments

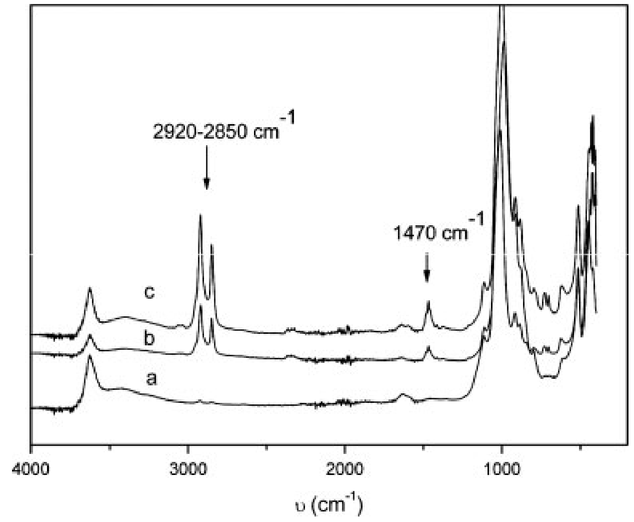

Figure 3. DRIFT spectra of (a) unmodified MMT (Na-MMT), (b) as-received Claytone APA organoclay and (c) Claytone APA organoclay after 8 h ultrasound treatment.

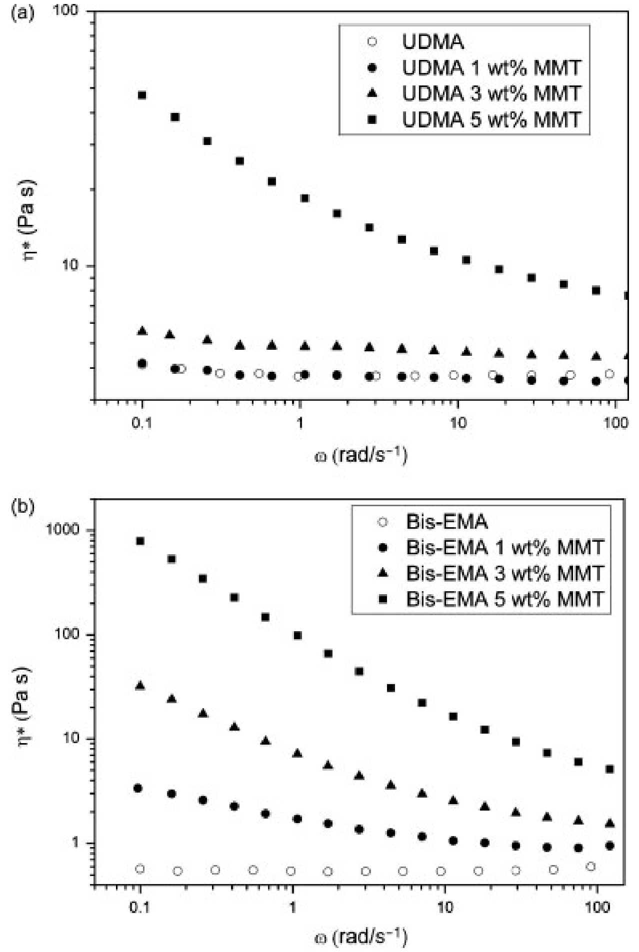

Figure 4. Viscosity of suspensions prepared with various amounts of filler in (a) UDMA and (b) BisEMA.

can lead to a degradation or scission of the organic functional groups at the surface of the nanoclay platelets,[12,13] which would decrease the hydrophobicity of the clay and consequently the clay/monomer compatibility. In order to assess the stability of the organic groups of the MMT during sonication, a suspension of 7 wt% MMT in ethanol was subjected to ultrasound treatment at 30 °C. After 10 h sonication, the MMT was extracted by centrifugation and dried at 60 °C for 24 h. Figure 3 shows DRIFT spectra of the MMT after 10 h sonication in ethanol. The bands at 2920 and at 2850 cm^{-1} are assigned to C–H stretching of the CH_3 and CH_2 groups, respectively. The absorption band at 1470 cm^{-1} is associated with the bending modes of the vibration of CH_2 groups.

Comparison of the sonicated MMT and non-sonicated MMT spectra indicates that the ultrasound treatment does not affect appreciably the alkylammonium ions present in the organically modified MMT.

Viscosity of suspensions

The rheological characterization results of the liquid suspensions made from BisEMA and UDMA monomers with various proportions of MMT are summarized in Fig. 4. The measurements were carried out in the linear viscoelastic range, using small strains. Figure 4(a) shows the dynamic viscosity of the samples prepared with UDMA as a function of the frequency for various MMT concentrations. The neat UDMA monomer and suspensions prepared with 1 or 3 wt% MMT behave as Newtonian liquids; i.e. the viscosity remains constant during the duration of the test. Formulations having low clay content exhibit viscosity values similar to that of the neat resin. However, at 5 wt% MMT a significant increase in the viscosity and a shear thinning behaviour are observed during the whole test. The low-frequency viscosity increases to a value about 14 times higher than that of the neat monomer and 2 times higher at the highest frequency. In contrast, Fig. 4(b) shows a more marked influence of the filler in suspensions prepared with BisEMA. The neat BisEMA monomer clearly shows Newtonian behaviour displaying a viscosity independent of the shear rate. Conversely, the clay-modified BisEMA suspensions show a shear thinning behaviour even at low filler concentrations. The addition of a small amount of MMT (1 wt%) is sufficient to increase the low-frequency viscosity to a value about 5 times higher than that of the neat mixture and 1.6 times higher if the high-frequency range is considered. Similarly, the addition of 5 wt% MMT increases the low-frequency viscosity to a value about 1500 times higher than that of the neat mixture and 10 times higher for the high-frequency range.

Many studies have reported that exfoliation or even intercalation of clay leads to a strong viscosity increase. In fact, the viscosity change was reported to be highly related to the degree of exfoliation achieved. Gopakumar *et al.*[14] have demonstrated that exfoliation of clay/polypropylene composites leads to a more significant increase of complex viscosity compared to composites which remain unexfoliated. According to those authors, this viscosity change is evidence of improved surface area/adhesion between the polymer matrix and the exfoliated clay. Yudin *et al.*[15] have shown that a significant viscosity increase of oligoimide/MMT is observed after the application of strong shear flow fields which led to a partial exfoliation of the MMT. Landry *et al.*[12] studied the degree of dispersion of MMT in different acrylate monomers (1,6-hexanediol diacrylate and tripropylene glycol diacrylate). Different degrees of exfoliation were produced by dispersing the MMT using four different methods: high-speed mixing, ball milling, bead milling and three-roll milling. The authors found that the higher the degree of exfoliation the higher the viscosity of the suspensions.

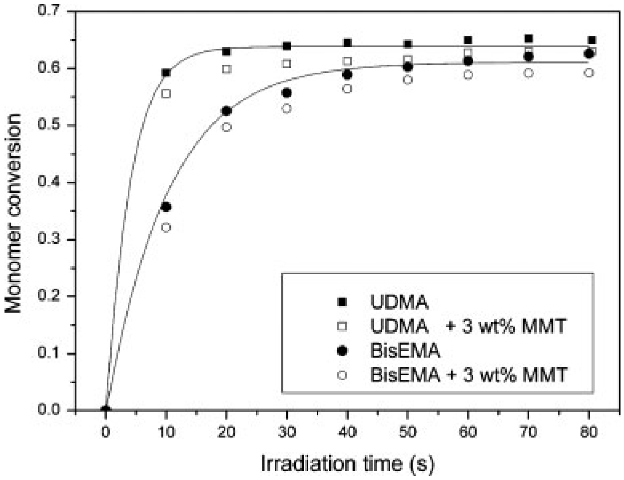

Figure 5. Monomer conversion *versus* irradiation time.

Table 1. Flexural modulus (*E*) and compressive yield strength (σ_y) of nanocomposites prepared using BisEMA[a]

MMT (wt%)	*E* (GPa) (NP)	*E* (GPa) (PC)	σ_y (MPa) (NP)	σ_y (MPa) (PC)
0	1.25 (±0.12)	1.85 (±0.10)	44.52 (±2)	72.3 (±1)
1	1.21 (±0.11)	1.84 (±0.10)	38.19 (±2)	68.5 (±2)
3	1.13 (±0.08)	1.89 (±0.07)	35.88 (±2)	76.3 (±5)
5	1.33 (±0.12)	2.15 (±0.12)	35.04 (±3)	69.1 (±4)

[a] PC, post-cured at 130 °C; NP, without post-curing treatment.

Table 2. Flexural modulus (*E*) and compressive yield strength (σ_y) of nanocomposites prepared using UDMA[a]

MMT (wt%)	*E* (GPa) (NP)	*E* (GPa) (PC)	σ_y (MPa) (NP)	σ_y (MPa) (PC)
0	2.01 (±0.09)	2.33 (±0.08)	78.32 (±2)	109.71 (±1)
1	1.93 (±0.11)	2.3 (±0.14)	69.68 (±3)	111.16 (±2)
3	1.85 (±0.08)	2.2 (±0.12)	71.52 (±2)	108.14 (±2)
5	1.83 (±0.12)	2.45 (±0.15)	56.35 (±2)	100.43 (±1)

[a] PC, post-cured at 130 °C; NP, without post-curing treatment.

Assuming that the viscosity increase is directly related to the level of exfoliation and intercalation of the clay in the monomers, the results presented in Fig. 4 suggest that the clay is dispersed at a greater extent in formulations prepared with BisEMA compared with that prepared with UDMA.

Photopolymerization of clay-loaded monomers

The photopolymerization of filled systems can occur at low polymerization rate when large filler particles scatter, reflect or absorb the incident light required to initiate photopolymerization. The effect of the presence of clay on the polymerization profiles was assessed by measuring the monomer conversion *versus* irradiation time. Figure 5 shows the conversion curves for formulations prepared with 3 wt% MMT. The addition of the organoclay to the liquid resins is found to hardly affect the degree of polymerization of BisEMA and UDMA monomers, irradiated under the same conditions and using the same amount of photoinitiator as in the clay-free monomers. The similarity between these curves indicates that the penetration of visible radiation into the 2 mm thick sample is not reduced significantly by the presence of the organoclay. It also means that the mineral filler does not act as a radical scavenger or a proton trap. Similar trends have been reported by Decker *et al.*[11] for clay-based nanocomposites prepared with polyester-acrylate or polyphenoxy-acrylate oligomers.

Mechanical properties

Tables 1 and 2 summarize the flexural modulus (*E*) and compressive yield strength (σ_y) of the materials prepared with BisEMA and UDMA, respectively. The polymerization of dimethacrylates in the absence of external heating leads to glassy resins in which only some of the available double bonds are reacted. Before the completion of conversion, the vitrification phenomenon decelerates the reaction to a hardly perceptible rate.[16] The presence of non-reacted monomer can have a plasticizing effect on the polymer, thereby altering the physical and mechanical properties of the hardened material.[17] The post-curing treatment at 130 °C increases monomer conversion and reduces the plasticizing effect of the non-reacted monomer on the mechanical behaviour of the nanocomposites.[17] Thus, the higher values of flexural modulus and compressive strength of samples subjected to a post-curing treatment are attributed to a reduced amount of non-reacted monomer.[16] The decrease in σ_y with filler content in the nanocomposites without post-curing treatment is associated with a reduced penetration of visible radiation into the 10 mm long compression specimens due to the presence of the clay. In contrast, for the nanocomposites post-cured at 130 °C, no significant differences in σ_y of samples containing different clay content are observed. When strength testing of brittle materials is performed, the sample size has a large influence on the measured value.[18,19] This means that a minimum number of specimens should be tested in order to obtain a proper estimation. As a compromise between minimizing both the dispersion of the evaluation method and the experimental effort, the use of a minimum number of 20 specimens has been suggested.[18,19] Flexural strength values are not reported here because the values averaged from five sample specimens result in an important data scatter and do not describe properly the statistical distribution of flexural strength.

In general, the addition of an organically modified layered silicate into a polymer matrix results in significant improvements of Young's modulus.[5] For example, Gorrasi *et al.*[20] reported an increase from 216 to 390 MPa for a polycaprolactone nanocomposite containing 10 wt% ammonium-treated MMT, while in another study,[21] Young's modulus was increased from 120 to 445 MPa with addition of 8 wt% ammonium-treated clay in a polycaprolactone. However, exceptions to this general trend have been reported. In crosslinked polyester-based nanocomposites, the modulus decreases with increasing clay content; in fact, a marked decrease for a 2.5 wt% nanocomposite was observed.[5] Results obtained in the present study and presented in Tables 1 and 2 show that the presence of various proportions of MMT has no significant effect on flexural modulus and compressive strength, irrespective of the monomer used as a matrix. An analysis of results reported in the literature indicates that improvements in the flexural properties are achieved in polymers having relatively low modulus values (of the order of 0.2–0.4 GPa). However, in high-modulus polymers (of the order of 2 GPa) the improvements are not marked.

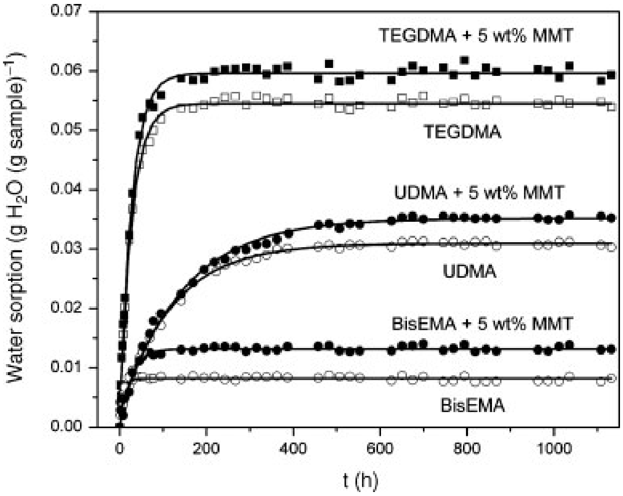

Figure 6. Water sorption *versus* time.

Water sorption of nanocomposites

The water sorption for the pure monomers and nanocomposites containing 5 wt% clay were evaluated by calculating the weight gains due to uptake of water at 37 ± 1 °C. The highly hydrophilic TEGDMA monomer was also tested for comparison purposes. As shown in Fig. 6, the water uptake is increased by about 10–15% by the presence of MMT. Generally, polymer/layered silicate nanocomposites are characterized by very strong enhancements of their barrier properties. Polymers ranging from epoxies and good sealants (like siloxanes) to semi-permeable (e.g. polyureas) and highly hydrophilic (e.g. poly(vinyl acetate)) are all improved up to an order of magnitude by low clay loadings.[5] On the other hand, Picard *et al.*[22] studied the water transport of polyamide 6-based nanocomposites prepared by melt blending. The authors reported that the water uptake still increased with clay content but seemed to depend much more on the clay dispersion state. In particular, XRD analysis gave clear evidence of the increase of the clay basal interplatelet spacing in clay aggregates when the respective nanocomposites films were immersed in liquid water. The clay aggregates were then able to swell when the matrix was itself highly swollen. The clay dispersion state was then a key parameter for the control of the water sorption. Similarly, Gorrasi *et al.*[20] studied the vapour barrier properties of polycaprolactone/MMT nanocomposites. Those authors found that microcomposites as well as intercalated nanocomposites had diffusion parameters very near to that of polycaprolactone, while the exfoliated nanocomposites had much lower values, even at low MMT content. Only in the case of exfoliated samples can the inorganic platelets dispersed in a non-ordered distribution constitute a barrier to the path of the water molecules.

The modification of the MMT by cation-exchange reaction between the silicate and dimethylbenzyl hydrogenated tallow ammonium chloride generally leads to a decrease of the clay hydrophilicity. However, results presented in Fig. 6 show that the clay interaction towards water is not totally annihilated. This may be attributed to the presence of silanol groups on the edges of the silicate layers, and the swelling ability of the organo-modified clays in water.[23]

Transmission electron microscopy

Depending on the nature of the components used (layered silicate, organic cation and monomer) and the method of preparation, three main types of composites may be obtained. When the monomer is unable to intercalate between the silicate sheets, a phase-separated composite is obtained, whose properties stay in the same range as those of traditional microcomposites. In addition to this classic family of composites, there are two types of nanocomposites. The first is an intercalated structure in which polymer chains are intercalated between the silicate layers resulting in a multilayer morphology built up with alternating polymeric and inorganic layers. Second, when the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained.

TEM was employed to assess the dispersion of clay in the various formulations and to probe the structure of the methacrylate/clay nanocomposites. TEM images shown in Figs 7 and 8 reveal that the layered silicate is swollen within the liquid monomer, which increases the interlayer spacing. Figures 7 and 8 show the presence of stacked silicate layers, which consist of parallel individual layers that are randomly distributed. In some regions, the clay nanolayers are not uniformly dispersed in the polymer matrix, but intercalated or aggregated as tactoids. Figures 7(c) and 8(b) show the clay separated into long tactoids with a length of about 0.5 μm and thicknesses ranging from about 100 to 200 nm. Nevertheless, for all formulations, even at low clay loading, intermediate-sized aggregates of about 1 μm can be observed and their fraction increases as the amount of filler increases. From the TEM studies, it emerges that the prepared nanocomposites consist of a combination of intercalated and exfoliated structures in combination with medium-sized agglomerates. Figures 7(d) and 8(d) show that the aggregates in nanocomposites prepared from BisEMA are smaller than those in nanocomposites prepared from UDMA. These results are consistent with the rheological behaviour of suspensions prepared with BisEMA and UDMA. In particular, a much less significant fraction of medium-sized agglomerates is evidenced in BisEMA, which results in a more significant increase in viscosity compared with UDMA (Fig. 4).

The organically modified silicate used in this study was produced by cation-exchange reaction between the silicate and dimethylbenzyl hydrogenated tallow ammonium chloride. Despite such surface modification, it is still relatively difficult to achieve the exfoliated (homogeneously dispersed) structure that is thought to yield maximum enhancement of physical and mechanical properties. Ion exchanging aliphatic cations within the gallery region increases compatibility and monomer absorption; however, it is not sufficient to exfoliate clay in bulk polymerized methacrylate/MMT composites. The surface modification of MMT with alternative organic groups is certainly necessary in order to achieve more exfoliated methacrylate/clay nanocomposites compared with those obtained from conventional organoclays. Results reported recently for the modification of MMT with various organic groups encourages further research.[24–26]

CONCLUSIONS

Clay-based nanocomposites were prepared using the *in situ* intercalative polymerization method. The mineral filler was incorporated into the liquid methacrylate by ultrasound treatments over a period of 8 h.

The rate of photopolymerization in 2 mm thick layers was not substantially reduced upon adding 3 wt% clay to BisEMA or UDMA as compared to the unfilled formulation. The MMT platelets were either packed together in a disordered arrangement (intercalated morphology) or dispersed as isolated nanoparticles

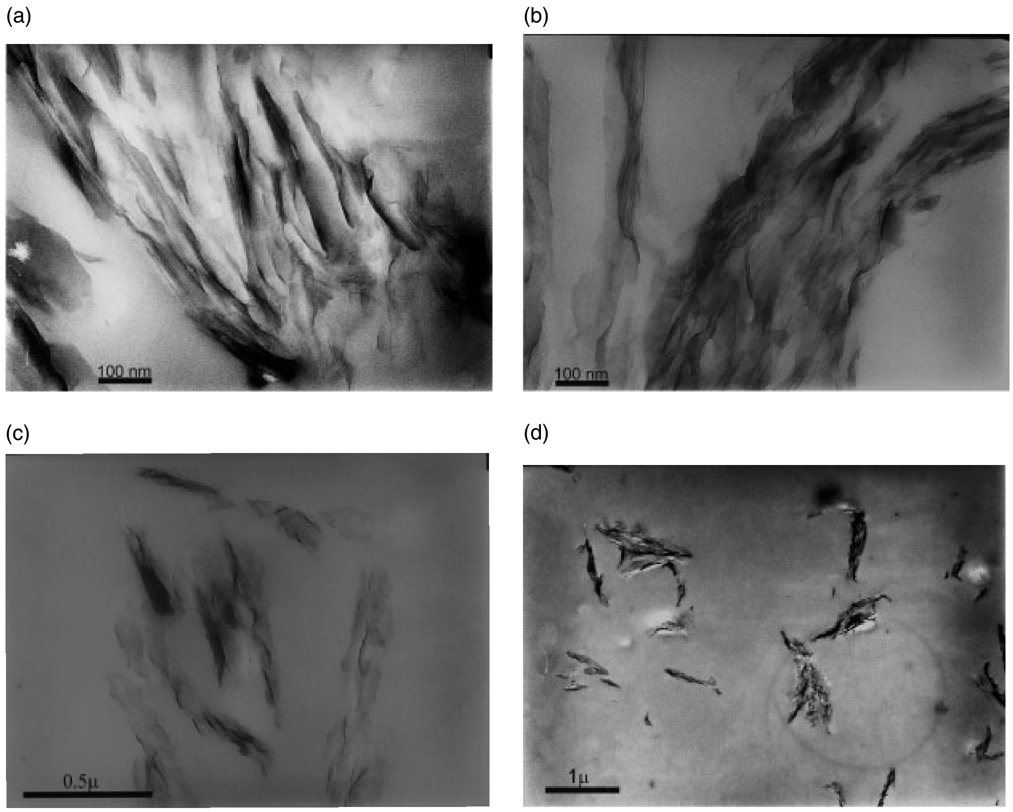

Figure 7. TEM images for the formulation prepared with (a, b) 2 wt% of clay in BisEMA and (c, d) 5 wt% of clay in BisEMA.

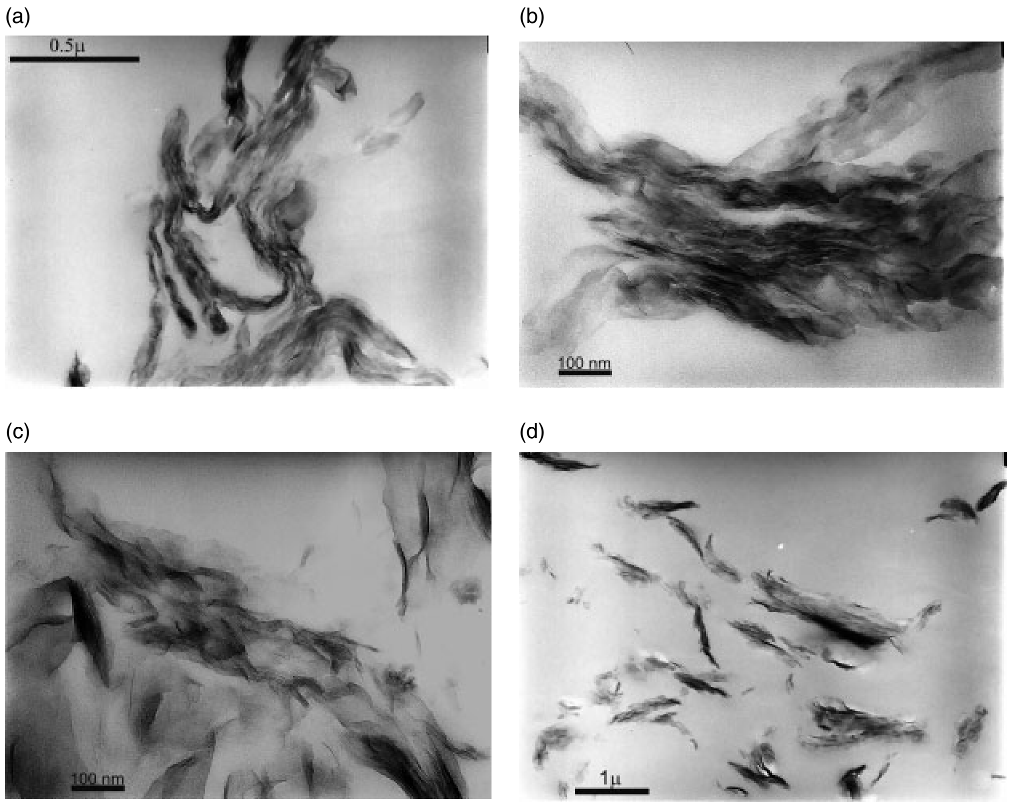

Figure 8. TEM images for the formulation prepared with (a, b) 2 wt% of clay in UDMA and (c, d) 5 wt% of clay in UDMA.

(exfoliated morphology). Nevertheless, for all formulations, even at low clay loading, intermediate-sized aggregates of about 1 µm were present and their fraction increased as the amount of filler increased. They were found to have no major effect on the elastic modus and compressive yield strength of the methacrylate-based nanocomposites. Moreover, the water uptake of the nanocomposites containing 3 wt% clay was about 10–15% higher than that of unfilled monomers. Thus, the nanocomposites failed to live up to expectations, failing to show improvements in mechanical properties, and having poor water uptake behaviour. Modification of the clay surface treatment is certainly necessary in order to increase the compatibility between the clay and the surrounding monomer and to achieve an optimal dispersion of the clay in the polymer matrix.

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REFERENCES

1 Klapdohr S and Moszner N, *Monatshefte für Chemie* **136**:2145 (2005).
2 Schroeder W, Arenas G and Vallo C, *Polym Int* **56**:1099 (2007).
3 Schroeder W and Vallo C, *Dental Mater* **23**:1313 (2007).
4 Mucci V, Arenas G, Duchowiczc R, Cook WD and Vallo C, *Dental Mater* **25**:103 (2009).
5 Pavlidoua S and Papaspyrides CD, *Prog Polym Sci* **33**:1119 (2008).
6 Kabiri K, Mirzadeh H, Zohuriaan-Mehr MJ and Daliri M, *Polym Int* **58**:1252 (2009).
7 Atai M, Solhi L, Nodehi A, Mirabedini S, Kasraei S, Akbari K, *et al*, *Dental Mater* **25**:339 (2009).
8 Dowling AH and Fleming GJP, *J Dentistry* **35**:309 (2007).
9 Discacciati JA and Lambert Oréfice R, *J Mater Sci* **42**:207 (2007).
10 Ding Q, Liu B, Zhang Q, He Q, Hu B and Shen J, *Polym Int* **55**:500 (2006).
11 Decker C, Keller L, Zahouily K and Benfarhi S, *Polymer* **46**:6640 (2005).
12 Landry V, Riedl B and Blanchet P, *Prog Org Coat* **62**:400 (2008).
13 Kost J, Leong K and Langer R, *Proc Natl Acad Sci USA* **86**:7663 (1989).
14 Gopakumar TG, Lee JA, Kontopoulou M and Parent JS, *Polymer* **42**:5483 (2002).
15 Yudin VE, Divoux GM, Otaigbe JU and Svetlichnyi VM, *Polymer* **45**:1086 (2005).
16 Vallo CI, *Polym Int* **49**:831 (2000).
17 Vallo CI, *J Biomed Mater Res Appl Biomater* **53**:717 (2000).
18 Vallo CI, *Polym Test* **21**:793 (2002).
19 Giannotti MI, Galante MJ, Oyanguren PA and Vallo CI, *Polym Test* **22**:429 (2003).
20 Gorrasi G, Tortora M, Vittoria V, Pollet E, Lepoittevin B, Alexandre M, *et al*, *Polymer* **44**:2271 (2003).
21 Tortora M, Vittoria V, Galli G, Ritrovati S and Chiellini E, *Macromol Mater Eng* **287**:243 (2002).
22 Picard E, Gérard JF and Espuche E, *J Membr Sci* **313**:284 (2008).
23 Picard E, Gauthier H, Gérard JF and Espuche E, *J Colloid Interface Sci* **307**:363 (2007).
24 Akat H, Tasdelen MA, Du Prez F and Yagci Y, *Eur Polym J* **44**:1949 (2008).
25 Owusu-Adom K and Guymon CA, *Polymer* **49**:2636 (2008).
26 Chen WC, Lai SM and Chen CM, *Polym Int* **57**:515 (2008).