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Photopolymerization kinetics of PMMA/organoclay nanocomposites

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ABSTRACT

Organoclay/methyl methacrylate (MMA) nanocomposites were obtained by photopolymerization of the monomers in the presence of organomodified clays using thioxanthone (TX) and ethyl 4-(dimethylamino) benzoate (EDB) as photoinitiating system. The SWy-1 montmorillonite organoclays, SWy-1-C8 and SWy-1-C16, were prepared by ion exchange with octyltrimethylammonium bromide (C8) and hexadecyltrimethylammonium bromide (C16). The photopolymerization rates (R_p) for MMA with different organoclay loadings (0.25; 0.50 and 1.0 wt %) were determined by photodilatometry. The effect on the photopolymerization rate of organoclay concentration, organoclay species and solvent used for dispersion of organoclay were studied. The conversion of monomers with the nanocomposites increased up to 2.5 times with 1.0 wt% of organoclay loading. This behaviour could be attributed to the larger amount of initiator molecules in the microenvironment of the clay, resulting in a lower internal conversion rate of the excited initiator to the ground state, thus increasing the yield of the triplets and, consequently, that of free radicals. The presence of the modifying chain C16 reduces the photopolymerization rates when compared with C8. This decrease is most likely due to the C16 causing a larger increase in the interlayer than C8, enabling a higher mobility of the excited initiator. The R_p values for the nanocomposites prepared in acetonitrile were higher than when using ethanol.

KEYWORDS: organoclay/PMMA composites, nanocomposites, photopolymerization

INTRODUCTION

Nanocomposites formed from layered polymer-silicates exhibit exceptional properties. The study of these materials has increased in the last years due to a significant improvement in their properties such as thermal stability [1], mechanical properties [2, 3] and photooxidation stability [4]. Small concentrations of the mineral clay (<5%) are required to obtain improvements in these properties when compared to conventional composites [5].

In general, the preparation of polymer/clay nanocomposites involves the use of montmorillonite clays, like SWy-1 and others. These clays are smectites, formed by silicate sheets containing Mg or Al ions. The sheets are arranged parallely and may form piles with regular interlamellar spaces. It is within these interlamellar spaces that the organic ions might be placed, replacing the inorganic ions. Furthermore, the use of larger size organic ions can change the dimensions of the interlamellar spaces, allowing the incorporation of other species [6].

Polymer/clay species can be prepared by three different methods, namely, mixing the polymer with a suspension of the clay, melting this mixture, and polymerizing the corresponding monomer in the presence of the dispersed clay. For the first two methods, the clay and the polymer retain their structure. On the other hand, the polymerization in the presence of clay will change the overall structure of the system due to the delamination of the clay

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and the placement of the polymers around the individual platelets of the clay [7].

The use of organoclays, by increasing the interlamellar spaces and due to the hydrophobic character of the modifiers, allows a larger amount of the monomers to be placed in this microenvironment prior to the polymerization process. The light-induced polymerization is a preferential method for polymerization as it will not affect the distribution of the monomers in the clay microenvironments nor will it produce any direct effect on the structure of the species involved in the process [8].

In this work, the photopolymerization kinetics of MMA/organoclay montmorillonite with different organoclay contents (0.25; 0.5 and 1.0 wt%) was studied by dilatometry. The effects on the photopolymerization rate of the type of organoclay, its content and the solvent used to disperse them were evaluated by a factorial design.

MATERIALS AND METHODS

Materials

The Na^+-SWy-1 Mt was supplied by Source Clays Repository of the Clay Minerals Society, University of Missouri, Columbia, MI. The clay mineral was purified as described earlier [3]. Methyl methacrylate, thioxanthone and ethyl 4-(dimethylamino)benzoate were supplied by Sigma Aldrich and used as received. Ethanol, acetonitrile and tetrahydrofuran (THF, Tedia) were used as solvents in the synthetic and analytical procedures. SWy-1-C8 and SWy-1-C16 were prepared in our laboratory as previously described [3].

Polymerization

The photopolymerization rates of the monomers were evaluated by dilatometry, which is based on the specific volume change associated with the polymerization reaction [9]. The dilatometer consists of two capillaries (i.d. 0.18 cm) attached to a cylindrical reaction vessel (i.d. 2.2 cm, volume 8.5 mL), which was placed in a constant temperature bath (25 °C). The samples were irradiated with a 200 W Hg(Xe) lamp placed in an Oriel Universal Arc Lamp source. A monochromator set at 380 nm was placed between the lamp and the reaction cell. The R_P values were determined using equation 1

$$R_p = \frac{[M_t]}{t} \qquad \text{Equation 1}$$

$$[M_t] = \frac{\Delta V \text{x} C}{F \text{x} f} \qquad \text{Equation 2}$$

where $[M_t]$ is the MMA concentration, t is the irradiation time, ΔV is the contraction in volume of the capillary at time t, F is a factor related to the densities of the polymer and monomer in solution [$F = (d_p - d_m)/d_p$]; f is the volume fraction of MMA monomer in the solution; C corresponds to the monomer molar concentration (M^{-1}).

The polymerization quantum yields were determined using equation 3

$$\Phi_p = \frac{R_p}{I_\alpha} \qquad \text{Equation 3}$$

where I_a is the light intensity absorbed by the photoinitiator.

Photon flux was determined using a spectroradiometer SPR-01 Luzchem.

Characterization

The average molar weights (*Mn*) were determined using size exclusion chromatography (SEC) on a Shimadzu LC-20 AD chromatographic system with a Shimadzu RID-10A refractive index detector. The sample solutions were injected in a combination of two Styragel HR4 and two Styragel HR5 columns. THF was used as the eluent at a flow rate of 1 $mL.min^{-1}$. Narrow-distribution poly(methyl methacrylate) standards (American Polymer Standards Corp.) were used for calibration.

RESULTS AND DISCUSSION

The MMA conversion in the presence of SWy-1-C8 and SWy-1-C16 organoclays was determined by photodilatometry, and is shown in figure 1. In these experiments the MMA, TX and EDB concentrations were kept constant (4.7 M, 1.0×10^{-5} M and 2.0×10^{-2} M, respectively). Different clay loadings (from 0 to 1 wt%) were dispersed in two different solvents, acetonitrile and ethanol. The effects of clay type, clay content and solvent used to disperse the organoclays were studied.

Irradiation of the reaction mixture in acetonitrile for 4 h in the absence of the organoclay resulted in a conversion of 14%. When adding 1 wt% of SWy-1-C8, the conversion rose to 40% for the same irradiation time. In all cases, when organoclay was added to the MMA solution, the photoconversion was higher than in the pure solvent (ethanol or acetonitrile). Batista *et al.* (2011) observed similar results for the photopolymerization of styrenesulfonate in the presence of Laponite RD clay in aqueous solution [10].

The photopolymerization rate values (R_P) were obtained from the slopes of the plots in figure 1 and are show in table 1.

An increase in the photopolymerization rate was observed when increasing the organoclay content for all the systems (Figure 2). Rigoli *et al.* ascribed this increase in the photopolymerization rate to the larger concentration of photoinitiator in the microenvironments of the clays. In these more rigid microenvironments, the lower internal conversion rate from the excited state to the ground state of TX molecules, results in higher triplet and radicals quantum yields [11].

The length of the alkylammonium salts used as the modifying agent for the clay does not seem to contribute significantly in changing the R_P, as can be seen in figure 2. The presence of the C16 chain induces a small decrease in the polymerization rate compared to C8. This behaviour is due to the fact that the modification of the clay layers with C16 promotes a bigger interlayer basal spacing as previously described [4], allowing a greater mobility of the initiator in those microenvironments [12].

Moreover, the solvents also showed an important role in the photopolymerization mechanism and rate values (R_P). Valandro *et al.* observed that during the photopolymerization of clay/PMMA mixtures,

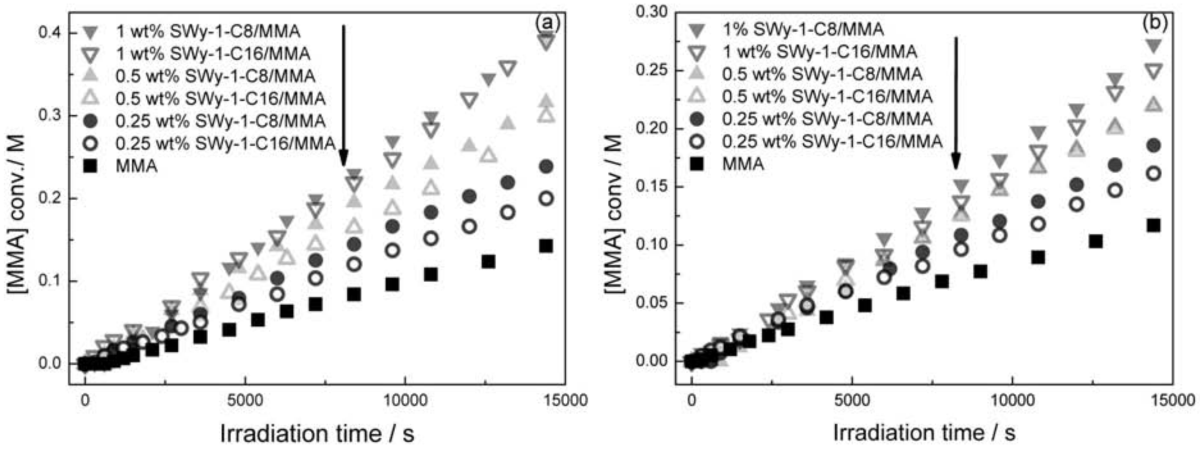

Figure 1. MMA conversion as a function of irradiation time in (a) ethanol and (b) acetonitrile.

Table 1. Polymerization rates (R_p) and quantum yields (Φ_p) for the photopolymerization of MMA photoinitiated by TX/EDB in the presence of organoclays SWy-1-C8 and SWy-1-C16.

	Photopolymerization in ethanol		**Photopolymerization in acetonitrile**	
	$R_p(10^{-5}\,M^{-1}s^{-1})$	Φ_p(mol Einstein^{-1})	$R_p(10^{-5}\,M^{-1}s^{-1})$	Φ_p(mol Einstein^{-1})
PMMA	0.82	418	1.04	776
PMMA + 0.25% SWy1-C8	1.30	663	1.68	1253
PMMA + 0.5% SWy1-C8	1.62	826	2.21	1649
PMMA + 1% SWy1-C8	1.85	943	2.97	2216
PMMA + 0.25% SWy1-C16	1.10	561	1.49	1111
PMMA + 0.5% SWy1-C16	1.46	744	2.09	1559
PMMA + 1% SWy1-C16	1.72	877	2.65	1977

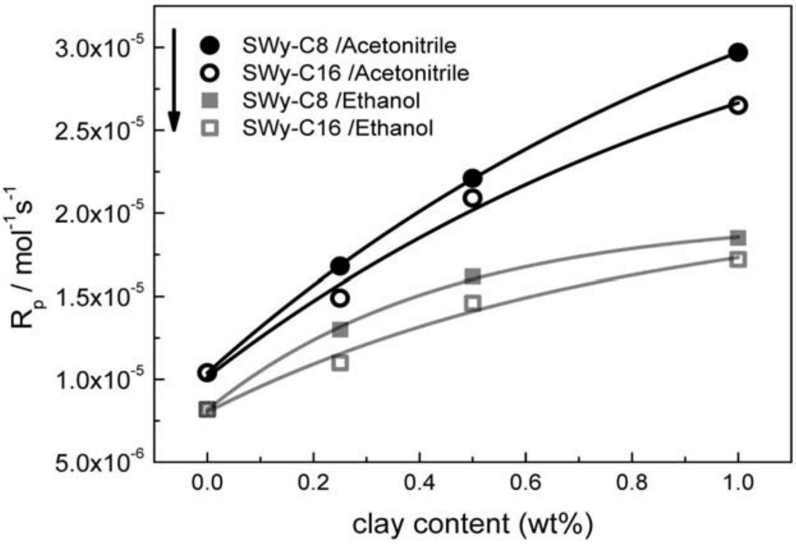

Figure 2. Dependence of photopolymerization rate on organoclay content.

Table 2. Average molecular weights for PMMA and nanocomposites.

	Synthesis in ethanol *Mn*	Synthesis in acetonitrile *Mn*
PMMA	199 000	135 000
PMMA + 1% SWy-1-C8	402 000	121 000
PMMA + 1% SWy-1-C16	385 000	163 000

the clay dispersed in ethanol inhibits the formation of head-to-head bonds and unsaturated chain-ends [3]. On the other hand, higher R_P values were obtained using acetonitrile as a solvent in the photopolymerization. This behaviour may be due to the higher chain transfer reaction rate, which is favoured in better solvents such as acetonitrile. This conclusion was corroborated by the molecular weight (*Mn*) determined for the nanocomposites containing 1 wt% of organoclays, which are larger than those of the polymers obtained by photopolymerizing pure MMA. The *Mn* values are shown in table 2.

The molecular weights (*Mn*) of the nanocomposites obtained in ethanol were higher (up to 3.5 times) compared to those prepared in acetonitrile. This effect can be ascribed to acetonitrile being a more suitable solvent than ethanol for the photopolymerization of SWy-1-C8/PMMA and SWy-1-C16/PMMA. According to Hansen's theory a solvent is appropriate if its Hansen parameters are within the solubility sphere of the polymer [13]. The radius of the Hansen solubility sphere (R) of PMMA is 8.6 Mpa [14]. Therefore, as can be seen in figure 3 acetonitrile (δ_P = 18.0 and δ_h = 6.1 (Mpa)^{½}), being inside the solubility sphere of PMMA (R = 8.6), is a better solvent for this polymer than ethanol (δ_P = 8.8 and δ_h = 19.4 (Mpa)^{½}) [15].

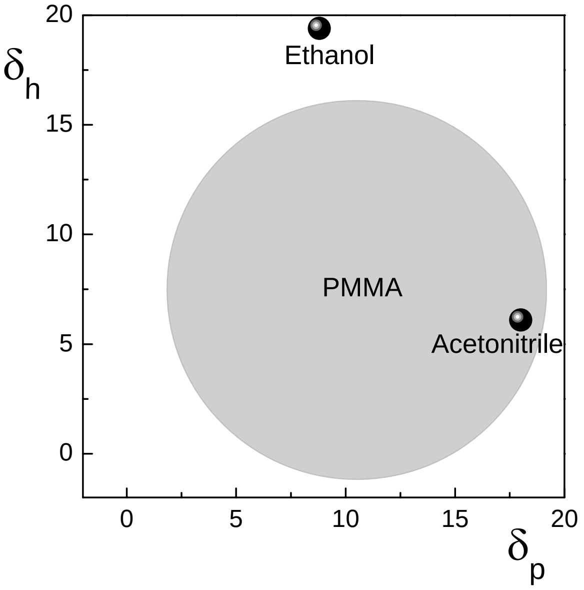

Figure 3. Hansen solubility sphere for PMMA.

On the other hand, the polarity of the solvent may also influence the polymerization rate, affecting the yield of triplet species, because of its effects on the energies of the electronic states and the photophysical properties of the carbonyl systems [16].

Analysing the results of polymerization quantum yields (Φ_p) shown in table 1, it was observed that the Φ_p using acetonitrile were approximately twice as high as in ethanol. It is worth noticing that the precipitation of PMMA was observed during the polymerization in ethanol. This behaviour may influence the amount of light absorbed from the reaction systems, leading to lower polymerization quantum yields.

Table 3. Factors studied in the factorial design 2^3.

Factors	(-)	(+)
1 - Organoclay species	SWy-1-C8	SWy-1-C16
2 - Organoclay concentration	0.25 wt%	1.0 wt%
3 - Solvent	Ethanol	Acetonitrile

Table 4. Design matrix and response of 2^3 factorial design experiments for the photopolymerization of MMA/organoclay systems.

Run	1	2	3	R_P ($\times 10^{-5}$ $M^{-1}s^{-1}$)
1	-1	-1	-1	1.30
2	+1	-1	-1	1.10
3	-1	+1	-1	1.85
4	+1	+1	-1	1.72
5	-1	-1	+1	1.68
6	+1	-1	+1	1.49
7	-1	+1	+1	2.97
8	+1	+1	+1	2.65

Statistical evaluation of the influence of different factors

The effect of changing various photopolymerization parameters on the polymerization rates was evaluated using a typical 2^3 factorial design. These parameters are the organoclay species (SWy-1 clay modified with C8 or C16 alkyl chains), the organoclay concentration and the solvent used for the dispersion of the organoclay for photopolymerization of the material. These factors and the evaluated levels are shown in table 3.

Table 4 shows the design matrix for the 2^3 factorial experiments for the photopolymerization rate (R_P).

In the normal probability plot (Figure 4), the runs for which the effects deviated from the normal probability straight line (defined as zero effect) are considered to be the significant factors for the system. In the experiments performed, experiments 2 and 3, in which only the organoclay concentration and the solvent were changed, are those with larger deviation from the zero line. On the other hand, it was found that the organoclay species, SWy-1-C8 or SWy-1-C16, has a lesser influence on the photopolymerization rate. Also, as seen in the figure, there is no significant

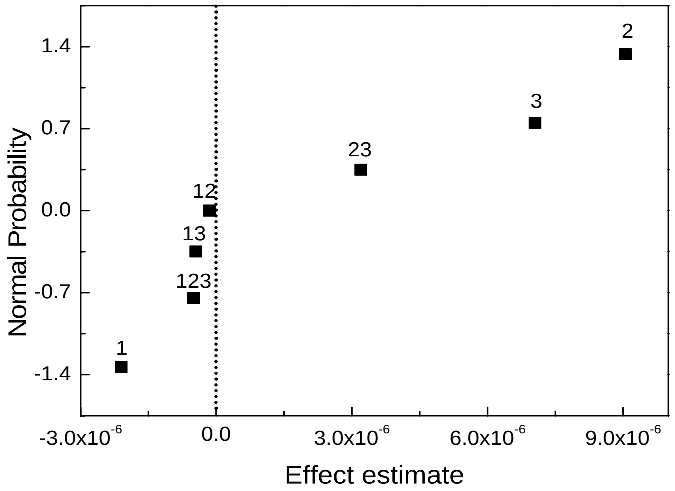

Figure 4. Normal probability plot of the effects on photopolymerization rates.

interaction between the different factors. Thus, the influences of the studied parameters for R_P are in the order (from highest to lowest): organoclay concentration > solvent > organoclay species.

CONCLUSION

The photopolymerization of MMA was studied in the presence of two organoclays with different length of organic chains (SWy1-C8 and SWy1-C16). The photopolymerization of monomers in the presence of organoclays occurs with larger rates and higher quantum yields due to the larger concentration of monomers in the hydrophobic microenvironments. At the same time, the process promotes the delamination of the organoclay sheets to form organoclay/polymer nanocomposites.

Slightly faster polymerization rates were found for organoclays with larger organic chain, that is, the rate of formation of SWy1-C8 is faster than that of SWy1-C16. The use of acetonitrile renders better results than with ethanol, due to the fact that the former is a better solvent for the polymer.

The effects of the organoclay species (SWy1-C8 or SWy1-C16), its concentration (0.25 or 1 wt%) and the solvent used (acetonitrile or ethanol) were evaluated using a 2^3 factorial design statistical methodology. The results showed that that the relative importance of these parameters on the rate of photopolymerization were in the order organoclay concentration > solvent > organoclay species.

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CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest related to the research reported in this paper.

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