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The effect of addition of acrylic acid and thioglycolic acid on the nanostructure and thermal stability of PMMA–montmorillonite nanocomposites

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ABSTRACT

Poly(methyl methacrylate) (PMMA)/organophilic montmorillonite (OMMT) nanocomposites were synthesized by the in situ free radical bulk polymerization of methyl methacrylate. The effect of small amount of acrylic acid as the co-monomer and thioglycolic acid as the chain transfer agent on the nanostructure of these nanocomposites was investigated by X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS) analyses. No reflection was discernible in the XRD patterns of all samples. In SAXS experiments, a great amount of small clay montmorillonite aggregates (less than 40 Å) were observed. The acrylic acid used as the co-monomer increased the affinity between the montmorillonite and the polymer, resulting in better dispersion of the montmorillonite particles. The glass transition temperature of the nanocomposites was evaluated by differential scanning calorimetry (DSC) and the thermal stability was investigated by thermogravimetric studies (TGA). As expected, the presence of the montmorillonite increased the glass transition temperature. The thermal stability of nanocomposites was distinctly higher than of pure PMMA and was increased by the presence of small amounts of acrylic acid as the co-monomer.

1. Introduction

Poly(methyl methacrylate) (PMMA) is an important thermoplastic material, which presents interesting characteristics such as high transparency, high strength and dimensional stability. Because of these outstanding properties, PMMA is widely used as transparent covers for several purposes including special devices for electronic industries. However, its poor heat resistance, brittleness and stress cracking in most organic solvents limit its application. The dispersion of small amounts of montmorillonite within the PMMA matrix has been considered a very promising strategy for improving thermal stability and barrier properties without losing its optical properties (Gilman, 1999). The enhancement of these properties is based on the ability of the polymer chains to penetrate into the interlayer spaces of the montmorillonite yielding separated platelets, giving rise to the as-called nanocomposites with intercalated and/or exfoliated structures. This process is usually possible for several monomers and polymers because the cations which naturally reside within the interlayer space regions can be easily exchanged by large, organic cations, increasing the organophilic character of the montmorillonite (Tjong, 2006; Goettler et al., 2007; Liu, 2007; Pavlidou and Papaspyrides, 2008). The intercalated structure consists of a well ordered multilayered structure of silicate containing polymer chains inserted into the interlayer, whereas a complete exfoliated structure presents individual silicate layers, homogeneously dispersed inside the polymer matrix. In practice, exfoliated structures are very rare even using strongly organophilic montmorillonite.

The best way to prepare PMMA-based nanocomposites with a high degree of intercalation/exfoliation is through the in situ lamellar polymerization of methyl methacrylate (MMA). In this procedure, the clay minerals are swollen by the liquid monomer or its solution, whose polymerization inside the interlayer spaces expands the distance between the silicate layers and leads to an exfoliation of the particles. The in situ polymerization has been performed in bulk (Okamoto, et al., 2000, 2001; Su and Wilkie, 2003; Wei'an et al., 2003; Xie et al., 2003; Zhang et al., 2003; Qu et al., 2005; Stadtmueller et al., 2005; Ratinac et al., 2006; Yoon et al., 2007), in solution (Chen et al., 1999; Li et al., 2003; Wang et al., 2005), and emulsion (Lee and Jang, 1996; Choi et al., 2001; Essawy et al., 2004; Meneghetti and Qutubuddin, 2004; Yeh et al., 2004). The emulsion polymerization has been carried out in the presence of pristine montmorillonite (Lee and Jang, 1996; Choi et al., 2001) or alkyl ammonium and alkyl phosphonium montmorillonites (Yeh et al., 2004). The bulk and solution polymerization processes are usually performed in the presence of the organo-montmorillonite to improve its compatibility with the monomer and facilitate the diffusion of the monomer into the interlayer spaces.

The degree of exfoliation can also be improved by using montmorillonite modified with a quaternary ammonium salt containing a free radical initiator moiety (Huang and Brittain, 2001), or a vinyl group, which acts as a co-monomer during the in situ interlamellar polymerization of MMA (Zhang et al., 2003; Ratinac et al., 2006). The

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use of a small amount of polar co-monomers in the in situ polymerization of MMA was also reported by Okamoto et al. (2001) as a way to improve the degree of dispersion and intercalation in the corresponding nanocomposites. They have used N,N-dimethylaminopropyl acrylamide, N,N-dimethyl-aminoethyl acrylate and acrylamide as the co-monomers and observed a greater exfoliation degree when acrylamide was used as the co-monomer.

The use of acrylic acid as the co-monomer is also a good strategy for improving the interaction between the PMMA chains and the clay mineral surface, through hydrogen bonds. The carboxyl groups in the corresponding nanocomposite can also impart better compatibility with other polymer systems such as epoxy resins (Zaioncz et al., 2007).

The present paper aims studying the effect of small amounts of acrylic acid as the co-monomer and thioglycolic acid as the chain transfer agent on the degree of intercalation/exfoliation of PMMA-based nanocomposites prepared by in situ interlamellar polymerization. For this purpose, a commercial organophilic montmorillonite (OMMT), Viscogel B8, was swollen by the monomers. The bulk polymerization was performed in the presence of an organic initiator. The degree of intercalation/exfoliation was investigated by wide angle X-ray diffraction (WAXS) and small-angle X-ray scattering (SAXS). A stacked-disc model was adapted from the literature (Porod, 1982; Hanley et al., 1997; Hernandez et al., 2007) to estimate the average size of the OMMT aggregates dispersed in the PMMA matrix. The thermal stability of PMMA-based nanocomposites was also discussed focusing the effect of the acrylic acid as the co-monomer and thioglycolic acid as the chain transfer agent.

2. Experimental

2.1. Materials

The organoclay (OMMT) used in this work was Viscogel B8, supplied by Bentec Rheological Additives (Livorno, Italy). This is a montmorillonite modified with octadecylammonium salt. Methyl methacrylate (MMA) and acrylic acid (AA) (Fig. 1) were purchased from Methacryl do Brasil (São Paulo, Brazil) and were distilled under reduced pressure. Azo-bis-isobutyronitrile (AIBN) from Merck, used as free radical initiator, was recrystallized from methanol/water. Thioglycolic acid (TA) (Fig. 1) (from Aldrich) was used as the chain transfer agent without purification.

2.2. Synthesis of PMMA–OMMT nanocomposites

Different amounts of OMMT were dispersed into 20 g (0.5 mol) of MMA (series **M**) or 20 g (0.5 mol) of MMA and 0.4 g (4 mmol) of AA (series **A**) under intensive stirring at room temperature for 24 h. After achieving complete dispersion of the OMMT, 0.61 g (1 mmol) AIBN was added under stirring and N_2 atmosphere. The polymerization was performed at 50 °C for 24 h and completed at a temperature of 85 °C for 1.5 h. Nanocomposites consisted of lower PMMA molar mass were also prepared by adding 0.34 g (4 mmol) of thioglycolic acid in the reaction medium containing the organo-montmorillonite dispersed into MMA/AA monomers (series **B**). The resulting nanocomposites were dispersed in acetone, precipitated with methanol, filtered and dried under vacuum at 60 °C. (Table 1) The amount of montmorillonite in each sample was determined by thermogravimetry analysis.

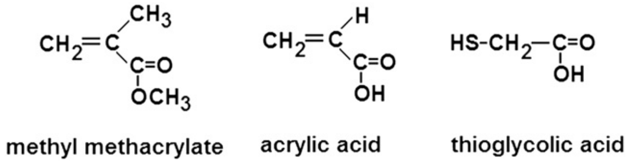

Fig. 1. Chemical structures of the monomers and reagent.

Table 1
Composition of PMMA–clay nanocomposites prepared by in situ bulk polymerization.

Compound code	Feed composition (g)				OMMT content in the composite[a] (%)
	MMA	AA	TG	OMMT	
M_0	100	0	0	0	0
M_1	97.5	0	0	2.5	3.1
M_2	95	0	0	5.0	5.0
M_3	90	0	0	10	15.5
A_0	100	2	0	0	0
A_1	97.5	2	0	2.5	3.2
A_2	95	2	0	5.0	4.4
A_3	90	2	0	10	11.4
B_0	100	2	1.7	0	0
B_1	97.5	2	1.7	2.5	3.5
B_2	95	2	1.7	5.0	7.3
B_3	90	2	1.7	10	13.0

[a] OMMT content determined from the residue obtained from thermogravimetry analysis.

2.3. Characterization

Molar mass and molar mass distribution were determined by Size Exclusion Chromatography (SEC) using a 600 module system from Water Associates equipped with a refractive index detector model 2414. Microstyragel columns with 10^2, 10^3 and 10^4 porosity were employed. The nanocomposites were extracted in a Sohxlet extractor for 48 h with tetrahydrofuran as the solvent. The extracted fraction in THF was precipitated with methanol and re-dissolved in tetrahydrofuran at a concentration of 0.1 g/100 mL. The molar mass of the extracted fraction was determined using a calibration curve obtained from polystyrene standards.

X-ray diffraction patterns (XRD) were recorded on a DMAX-RC (Miniflex) X-ray diffractometer (Rigaku Co., Tokyo, Japan), equipped with Cu Kα radiation source operating at 40 kV and 100 mA. The scanning rate was 2 °C min^{-1}.

The thermal stability was measured by thermogravimetry analysis in a TA Q50 thermogravimetric analyzer. Samples of 20 mg were heated to 600 °C at a heating rate of 20 °C/min under N_2 atmosphere.

The thermal properties of the composites were measured by differential scanning calorimetry (DSC) in a Perkin-Elmer DSC-7 calorimeter at a heating or cooling rate of 20 °C min^{-1} under a N_2 atmosphere between 35 and 160 °C. The samples were heated, cooled and re-heated again and the glass transition temperature (Tg) was recorded from the second heat scanning.

The nanostructural investigation of the composites was performed by small-angle X-ray scattering (SAXS). The SAXS measurements were performed at room temperature using the beam line of National Synchrotron Light Laboratory (LNLS), Campinas, Brazil. This beamline was equipped with an asymmetrically cut and bent silicon (111) monochromator that yielded a monochromatic ($\lambda = 1.608$ Å) and horizontally focused beam. The patterns were acquired for scattering vectors (q) in the range 10^{-2} Å^{-1} $< q <$ 0.12 Å^{-1}. The scattering intensity $I(q)$ was plotted as a function of the modulus of scattering vector, $q = (4\pi/\lambda)$sin (<theta>/2), where <theta> is the scattering angle. The scattering intensity was normalized by subtracting (background scattering) and sample thickness. Each SAXS pattern corresponds to a data collection time of 900 s.

3. Results and discussion

3.1. Structural investigation

The qualitative evaluation of the dispersion of the montmorillonite particles in PMMA–OMMT was performed by XRD. Fig. 2 compares the XRD patterns of the OMMT and the PMMA-based nanocomposites (Series **M**, **A** and **B**). The pure OMMT showed a basal reflection at $2\theta = 3.52°$ corresponding to a basal spacing $d_2 = 25$ Å. In addition, a