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Synthesis, thermal properties and applications of polymer-clay nanocomposites

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Abstract

Polymer-clay nanocomposites constitute a new class of materials in which the polymer matrix is reinforced by uniformly dispersed inorganic particles (usually 10 wt.% or less) having at least one dimension in the nanometer scale. Nanocomposites exhibit improved properties when compared to pure polymer or conventional composites, such as enhanced mechanical and thermal properties, reduced gas permeability, and improved chemical stability. In this work, the synthesis of poly(methyl methacrylate) (PMMA)/clay nanocomposites is described via two methods: in situ and emulsion polymerization. The in situ technique follows a two-step process: ion-exchange of the clay to make it hydrophobic, and polymerization after dispersing the functionalized clay in the monomer. The emulsion technique combines the two steps of the in situ method into one by conducting ion-exchange and polymerization in an aqueous medium in the same reactor. The clay (montmorillonite, MMT) is functionalized with a zwitterionic surfactant, octadecyl-dimethyl betaine (C18DMB). Partially exfoliated nanocomposite, observed by transmission electron microscopy (TEM), was obtained by emulsion polymerization with 10 wt.% clay. Glass transition temperature (T_g) of this nanocomposite was 18 °C higher than pure PMMA. With the same clay content, in situ polymerization produced intercalated nanocomposite with T_g 10 °C lower than the emulsion nanocomposite. The storage modulus of partially exfoliated nanocomposite was superior to the intercalated structure and to the pure polymer. Using nanocomposite technology, novel PMMA nanocomposite gel electrolytes were synthesized exhibiting improved ionic conductivity and stable lithium interfacial resistance. Nanocomposites can also be used for gas storage and packaging applications as demonstrated by high barrier polymer-clay films.

Keywords: Polymer-clay nanocomposites; Thermal properties; Montmorillonite; PMMA

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1. Introduction

Polymer composites are widely used in applications such as transportation, construction, electronics and consumer products. The properties of particle-reinforced polymer composites are strongly influenced by the dimensions and microstructure of the dispersed phase. Recently, there has been a growing interest in the development of polymer-clay nanocomposites [1–4]. Nanocomposites constitute a new class of material that involves nano-scale dispersion in a matrix. Nanocomposites have at least one ultrafine phase dimension, typically in the range of 1–100 nm, and exhibit improved properties when compared to micro- and macro-composites. Strong interfacial interactions between the dispersed clay layers and the polymer matrix lead to enhanced mechanical, thermal and barrier properties of the virgin polymer [1,2]. Since clay is hydrophilic, it is necessary to make it organophilic via cation exchange, typically with alkylammonium cations [3,4].

The synthesis of PMMA/clay nanocomposite has been reported very recently using a variety of surfactants, dispersion techniques and polymerization conditions. In this paper, we describe the synthesis of PMMA/clay nanocomposite via emulsion and in situ polymerization with 10 wt.% clay modified with zwitterionic surfactant, C18DMB. The paper focuses on the thermal and mechanical property reinforcement due to the morphology of the nanocomposites and also discusses their possible applications in batteries and packaging films.

2. Experimental

Clay montmorillonite (MMT) with a cation exchange capacity (CEC) of 0.9 mol/kg was provided by Southern Clay Products. MMA was purchased from Aldrich Chemical and the zwitterionic surfactant, C18DMB, was synthesized in

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the laboratory [5]. Hydrophilic MMT was ion exchanged with C18DMB as described in a previous paper [5]. In the case of the in situ method, the organophilic clay (10 wt.%) was dispersed in MMA, mixed by vortex, sonicated for 3 h and allowed to swell overnight. Approximately 0.1 wt.% of initiator 2,2-azobis (isobutyronitrile) (AIBN) was added to the sample and polymerized in an oil bath at 55 °C for at least 24 h. For the emulsion technique, 0.04 g of C18DMB was added to a dispersion containing 0.282 g of MMT in 30 ml of deionized water with constant stirring. Three ml of MMA monomer was added along with 0.1 wt.% of AIBN and the mixture was polymerized in an oil bath at 60 °C for 48 h.

Transmission electron microscopy (JEOL 1200 EX TEM) was used to investigate the nano-structure of PMMA nanocomposites. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 from 50 to 150 °C at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 2950. Samples of 10–15 mg were heated to 500 °C at a rate of 20 °C/min under nitrogen atmosphere. Dynamic mechanical properties were measured using a Dynamic Mechanical Thermal Analyzer (DMTA) from Rheometric Scientific. The samples (0.2 mm × 10 mm × 25 mm) were swept at 3 °C min^{-1} from 25 to 170 °C at a frequency of 1 Hz.

3. Results and discussion

PMMA/clay nanocomposites synthesized via emulsion and in situ polymerization were partially exfoliated and intercalated, respectively, as determined by TEM micrographs shown in Fig. 1. The zwitterionic surfactant in the emulsion polymerization acted as a stabilizer and as an intercalating agent allowing the polymerization of MMA within the clay interlayer spacing to form a partially exfoliated structure. In the in situ polymerization, the high viscosity of the dispersion slowed the cure inside the gallery layers as compared to the outside region leading to intercalated morphology.

DSC showed an 18 °C increase in the glass transition temperature (T_g) of the nanocomposite prepared by emulsion technique as compared to pure polymer (Table 1, Fig. 2). Also, the increase in T_g was higher than for the intercalated nanocomposite with 10 wt.% clay produced by the in situ method. In addition, the T_g was verified by DMTA through $\tan\delta$ (Table 1) showing similar increase as measured by DSC. The T_g increased by 16° and 8° for the partially exfoliated and intercalated nanocomposites, respectively. This increase in T_g is not only related to the nanocomposite morphology but also to its high molecular weight; partially exfoliated nanocomposite presented an average molecular weight of 930,000 versus 548,000 for intercalated nanocomposite, as reported in a previous paper [6].

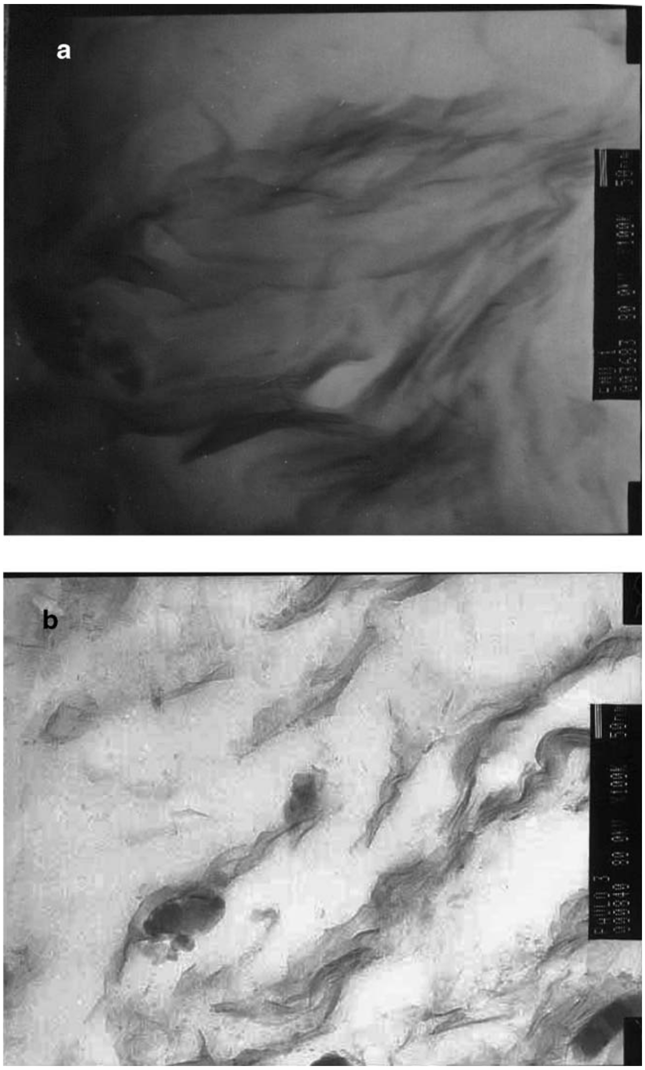

Fig. 1. TEM micrographs of PMMA/clay (10 wt.%) nanocomposites (a) partially exfoliated via emulsion polymerization and (b) intercalated via in situ polymerization.

Thermal degradation can be monitored by TGA, and the behavior is shown in Fig. 3 for pure PMMA and the nanocomposites. Hirata et al. [7] reported that two main reaction stages take place during degradation of PMMA in nitrogen atmosphere. The first stage, which can be divided into two steps, represents decomposition of weak head-to-head linkages and impurities for the range between 160 and 240 °C, and decompo-

Table 1
DSC, TGA, and DMTA analysis of nanocomposites

Type of nanocomposite	Nano-structure	T_g, °C (DSC)	T_g, °C (DMTA)	T, °C for 20 wt.% loss	Storage modulus at 80 °C (GPa)
Pure PMMA	–	104.6	129.3	321.6	1.81
PMMA with 10 wt.% C18-MMT (in situ)	Intercalated	112.0	137.1	382.6	2.84
PMMA with 10 wt.% MMT and 1.5 wt.% C18DMB (emulsion)	Partially exfoliated	122.6	145.2	358.2	2.50

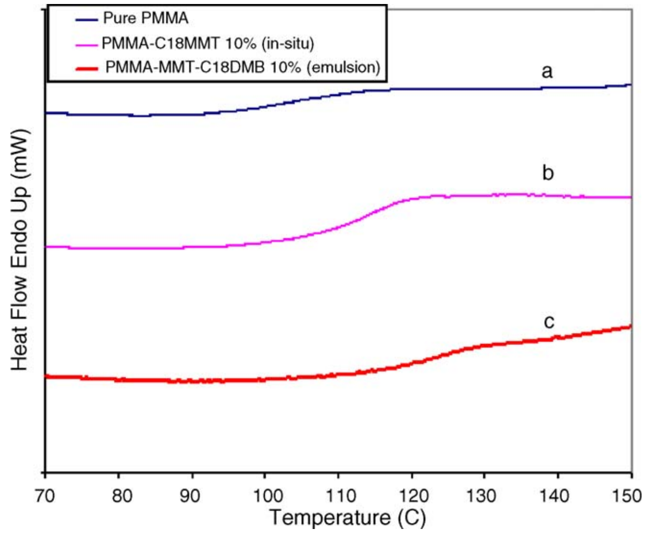

Fig. 2. DSC scans of (a) PMMA, and PMMA/clay (10 wt.%) nanocomposites via (b) in situ and (c) emulsion polymerization.

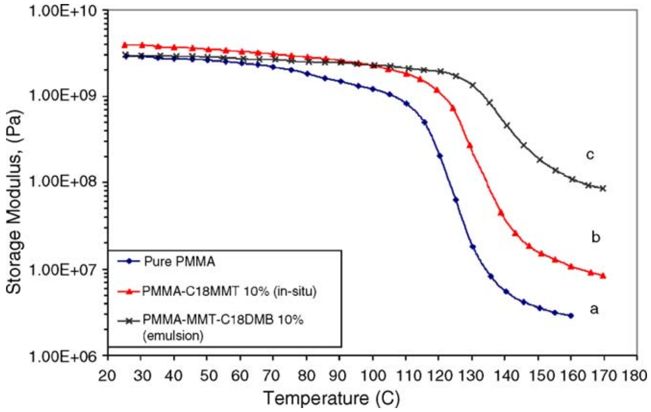

Fig. 4. DMTA scans of (a) PMMA, and PMMA/clay (10 wt.%) nanocomposites via (b) in situ and (c) emulsion polymerization.

sition of PMMA chain-ends around 290 °C. The second stage, between 300 and 400 °C, represents random scission of the polymer chains. In Fig. 3, pure PMMA displays these two reaction stages, while the nanocomposites display only the second stage indicating random scission decomposition. PMMA/clay nanocomposites showed improved thermal stability when compared to the pure polymer. TGA indicated an increase of 37 and 61 °C in the 20 wt.% decomposition temperature for the nanocomposites prepared by emulsion and in situ polymerization, respectively. The reason for lower increase in the emulsion nanocomposites is probably due to excess surfactant present in the polymer emulsion powder.

Dynamic mechanical analysis was used to measure the viscoelastic properties of the polymer nanocomposites as a function of temperature. The storage modulus is shown in Fig. 4 for pure PMMA and PMMA/clay nanocomposites formed via in situ and emulsion polymerization. The modulus increased with addition of clay as expected: at 80 °C storage modulus increased from 1.81 GPa for PMMA to 2.50 GPa and to 2.84 GPa for emulsion and in situ nanocomposites, respectively. The lower modulus for the emulsion nanocomposite versus the in situ can, again, be due to excess surfactant present in the emulsion product which acts as plasticizer. At temperatures higher than 100 °C, the partially exfoliated sample showed higher storage modulus than the intercalated structure. The rubbery plateau modulus for partially exfoliated nanocomposite was over 30 times higher than pure PMMA, and 10 times higher than the intercalated nanocomposites. Thus, the dispersion of the clay nano-structure in the polymer matrix affects the resulting thermo/mechanical properties of the nanocomposite.

Using nanocomposite technology, a novel polymer nanocomposite gel electrolyte was developed for lithium battery application, consisting of 30% PMMA/clay nanocomposite, 46.5% ethylene carbonate (EC) and 19% propylene carbonate (PC) as plasticizer, and 4.5% lithium perchlorate ($LiClO_4$). Fig. 5 shows ionic conductivity versus temperature for the electrolytes with different clay content. As the clay concentration increased up to 1.5 wt.%, the room temperature conductivity increased to a maximum of 8×10^{-4} S/cm, and then decreased with 3 wt.% clay to 4.5×10^{-4} S/cm. The PMMA nanocomposite gel electrolyte also demonstrated a stable lithium interfacial resistance over a

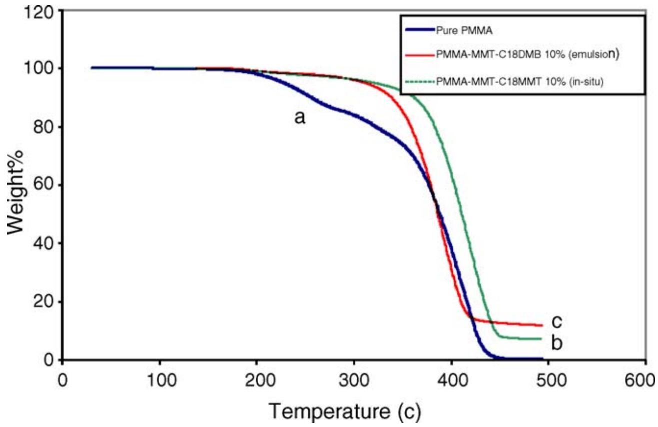

Fig. 3. TGA of (a) PMMA, and PMMA/clay (10 wt.%) nanocomposites via (b) in situ and (c) emulsion polymerization.

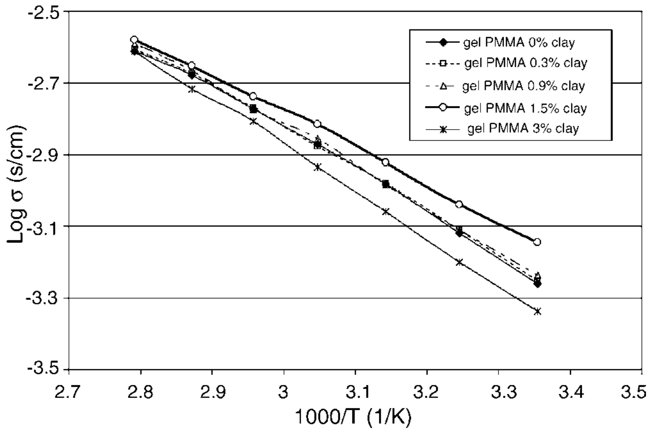

Fig. 5. Ionic conductivity vs. temperature for PMMA gel electrolytes with different clay concentrations [8].

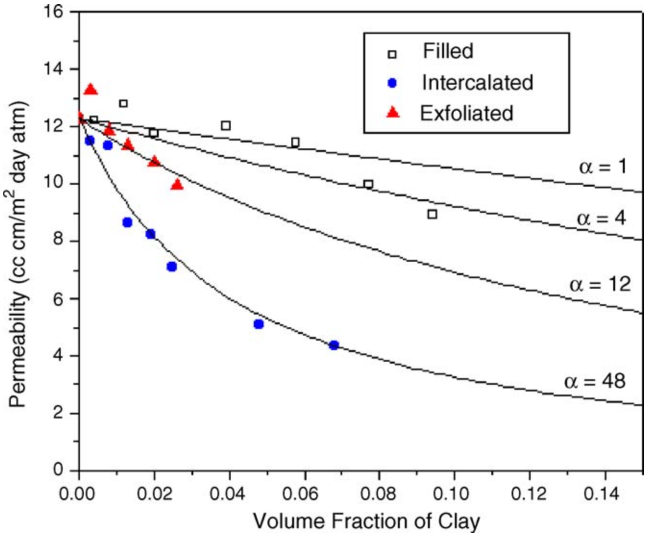

Fig. 6. Oxygen permeability of PS/clay nanocomposite films fit with Nielsen model [10].

three-week storage time, which is a key factor for use in electrochemical applications. The gel was sandwiched between two lithium electrodes and their surfaces remained perfectly shiny over this period.

Finally, polymer-clay nanocomposites can also be used for packaging or storage tank applications in which the nanodispersed clay layers reduce the permeability of the polymer matrix. The presence of silicate layers in nanocomposites increases the diffusion distance by creating a tortuous path which the diffusing species must traverse. Polystyrene (PS)/clay nanocomposites have been synthesized via in situ polymerization, with two different types of organoclays which resulted in exfoliated or intercalated morphology. Fig. 6 illustrates the oxygen permeability of these PS/clay films as a function of volume fraction of filler for systems with untreated clay (filled) and for intercalated and exfoliated structures. The permeability strongly depends on the morphology of the nanocomposites. The permeability decreased by more than 60% over pure PS for the intercalated nanocomposite with 0.07 volume fraction of clay. The exfoliated system did not reduce the permeability as much as the intercalated one and the filled system with untreated clay offered very poor gas barrier improvement. The data was fit with Nielsen model [9] to estimate the clay aspect ratio from the permeability trends of these nanocomposites.

4. Conclusions

The synthesis of PMMA/clay nanocomposites via emulsion and in situ polymerization resulting in partially exfoliated and intercalated nanocomposites, respectively, was described. The different morphologies of the nanocomposites resulted in significant thermo/mechanical property improvements in comparison to the pure polymer. Partially exfoliated nanocomposite exhibited T_g 18 °C higher than PMMA and 10 °C higher than intercalated system as determined by DSC. Dynamic Mechanical Thermal Analysis also verified similar T_g increase. The decomposition temperature measured by TGA for 20 wt.% loss increased to 358° and 382° for nanocomposites via emulsion and in situ polymerization, respectively. The storage modulus of the partially exfoliated nanocomposite was superior to the intercalated structure at higher temperatures and to the pure polymer; the rubbery plateau was over 30 times higher for the emulsion product than for pure PMMA. Using PMMA/clay nanocomposite, a novel polymer gel electrolyte was synthesized with improved ionic conductivity and stable lithium interfacial resistance, which could be used for battery applications. Other potential applications for these nanocomposites are in film packaging and gas storage. PS/clay nanocomposites demonstrated significant reduction in permeability, over 60%, with less than 10 vol.% clay.

Acknowledgements

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