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SYNTHESIS AND CHARACTERIZATION OF POLY (METHYL METHACRYLATE)/MONTMORILLONITE NANOCOMPOSITES BY EMULSIFIER-FREE EMULSION POLYMERIZATION

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PMMA/clay nanocomposites are prepared by emulsifier-free emulsion polymerization. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the distribution of clay in the polymer matrix and observe the morphology of the resulting nanocomposites, respectively. The exfoliated nanocomposites were successfully prepared up to 10 wt% pristine Na^+-MMT incorporation. Compared to neat PMMA, the glass transition temperature and storage modulus of PMMA/clay nanocomposites became higher without significant increase in refractive index. PMMA/clay nonocomposites were found to retain over 70% of transparency, which is important for optical applications.

Keywords: emulsifier-free emulsion polymerization; nanocomposite; PMMA; refractive index; transparency

1. INTRODUCTION

Poly (methyl methacrylate) (PMMA), typical transparent amorphous polymer, has been widely used as core materials of plastic optical fiber (POF) as well as optical lenses [1,2]. Although PMMA has certain advantages including good flexibility, lightweight, and low processing cost over

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conventional inorganic glasses, its temperature resistance needs to be enhanced without sacrifice of optical properties since the use of PMMA as POF core materials in harsh environments such as under the hood application is considered.

Polymer nanocomposites have been prepared using various inorganic fillers in order to increase several properties like heat resistance, mechanical strength and impact resistance [3 ∼ 5]. There are two distinct nanostructures identified in these nanocomposites: intercalated and exfoliated (or delaminated) [6 ∼ 8]. The intercalated nanocomposites are well-ordered multilayered structures where the extended polymer chain is inserted into the gallery space between parallel individual clay layers, and the distance between the adjacent clay layers is about 2–4 nm. The exfoliated or delaminated nanocomposites result from the weak intercalation between the individual clay layers and the adjacent layers cation [9], where the individual layer is not parallel to each other so that they are well dispersed in polymer matrix. Until now, many polymer/clay nanocomposites were prepared through an in situ intercalative polymerization initiated by chemical initiators and almost none by heat or radiation. However, in order to achieve a good dispersion of the inorganic compound and increase interfacial adhesion between the polymer and the mineral, techniques for synthesizing colloidal nanocomposites made of inorganic particles surrounded by polymers have been developed.

PMMA nanocomposites offer the potential for reduced gas permeability, improved physical performance, and increased heat resistance without significant reduction in optical clarity. It was reported that the optical clarity of polycarbonate was not diminished significantly in silicate nanocomposites [10]. The manufacture of PMMA/clay nanocomposites using a polymerization reaction to enhance the performance of PMMA was reported in literature [11,12]. The emulsion polymerization technique has been extensively used to make nono-particle and nanocomposites [13 ∼ 16]. In this study, we attempted to synthesize PMMA/clay nanocomposites with improved heat resistance using emulsifier-free emulsion polymerization in order to minimize decreased light scattering loss caused by addition of surfactant.

2. EXPERIMENTAL

Materials

MMA (Aldrich) was purified with inhibitor remover for removing hydroquinone and monomethyl ether hydroquinone and stored at $-10^{\circ}C$ before polymerization. Na^{+}- MMT (Southern clay) with a cation exchange capacity (CEC)of 92.6 meq/100 g was used without further purification.

Potassium persulfate (KPS, Aldrich) and methyl alcohol (Daejung chemicals) of pure grade were used as received.

Synthesis of PMMA/Clay Nanocomposites

The certain amount of clay dispersed in 240 ml of de-ionized water was placed in three-necked round bottom flask equipped with a condenser, a nitrogen inlet, and a mechanical stirrer, The mixture was stirred at 400 rpm for 2hr under N_2 atmosphere and gradually heated to 80°C. 30 g of MMA was added through addition funnel and, 10 g of 1.5 wt% aqueous solution of KPS was injected into the reactor, followed by further reaction at 80°C for 6 hr. The emulsion was poured into excess amount of methyl alcohol to precipitate it out. The crude product washed extensively with de-ionized water was collected using centrifuge and dried by freeze-dryer (EYELA, FD-5N) for 3 days.

Characterization of the PMMA/Clay Nanocomposites

Wide-angle X-ray diffraction (XRD) patterns were obtained using X-ray diffractometer (Mac Science, MXP 18A-HF) equipped with graphite mono-chromatized Cu-Kα radiation ($\lambda = 0.154178$ nm). The accelerating voltage was 40 kV and the current was 100 mA. The scanning range was 1.8-10° with a scanning rate of 1°/min.

The morphology of nanocomposites was observed using transmission electron microscopy (Philips, CM 30T) technique, where specimens of 60nm thickness were prepared with ultra-microtome apparatus (Leica, Reichert Ultracuts 702501).

Dynamic mechanical thermal analysis (DMTA) was carried out on a Rheometric Scientific, PL-DTMA MK III. The examination for sample of $10 \times 30 \times 2$ mm was made in the three-point bending mode at a fixed frequency of 10 Hz and the temperature range from 40 to 180°C at the heating rate of 2°C/min.

Absorbance was measured between 300 nm and 800 nm at a spectral bandwidth of 2 nm on a UV/VIS Spectrophotometer (JASCO, V-530). The film thickness was 200 μm. Abbe refractometer was used to measure refractive index of the nanocomposites.

3. RESULTS AND DISCUSSION

Before entering into the discussion of intercalation behavior of the PMMA/clay nanocomposites, thermogravimetry analysis was conducted to prove the presence of silicate layers in the composites prepared by emulsion polymerization.

The XRD patterns of the PMMA/clay nanocomposites in Figure 1 show that the typical d_{001} peak of clay featuring intergallery distance of silicate layered structure was intensively suppressed when emulsifier-free emulsion polymerization was conducted. Although much lower angle measurement was not performed yet, it is proposed that highly intercalated or even exfoliated condition of layered silicate can be achieved through PMMA polymerization.

In Figure 1, TEM micrographs, showing the highly dissociated silicate layers well dispersed in PMMA matrix, of the nanocomposites prepared by emulsifier-free emulsion polymerization strongly support the XRD result.

Clarity or transparency of the materials is of critical importance in optical applications. In Figure 2, the results of UV/VIS measurement were shown. The nanocomposites show somewhat higher absorbance than that of neat PMMA, Which is, however, well below the limit for transparency. Especially in the case of nanocomposites prepared by emulsifier-free emulsion polymerization the sample shows much lower absorbance at 540 nm (ASTM D1003) than the nanocomposites by conventional emulsion polymerization. This implies that nanocomposite formation under emulsifier-free condition is highly favorable to reduce the absorbance of UV/VIS region of interest. Figure 3 shows the DMTA traces of neat PMMA and PMMA/clay nanocomposites. Neat PMMA has a maximum of tan δ (T_g)at 118°C, while the nanocomposites show higher T_g with much lower damping, implying well dispersed silicate nanoplatelets in PMMA matrix

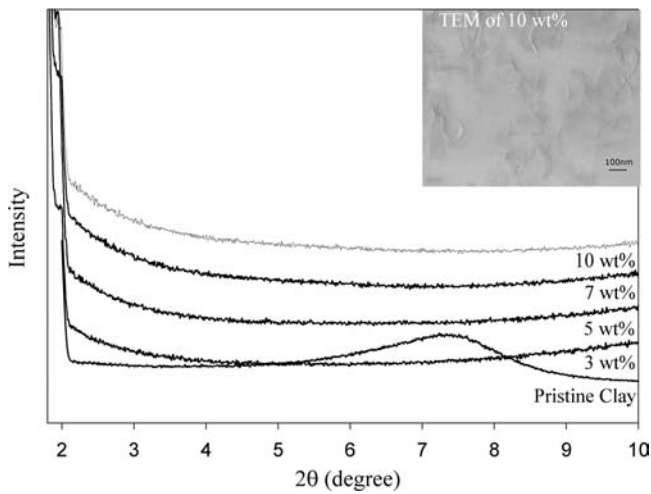

FIGURE 1 XRD pattern and TEM(10 wt%)of the PMMA/clay nanocomposites.

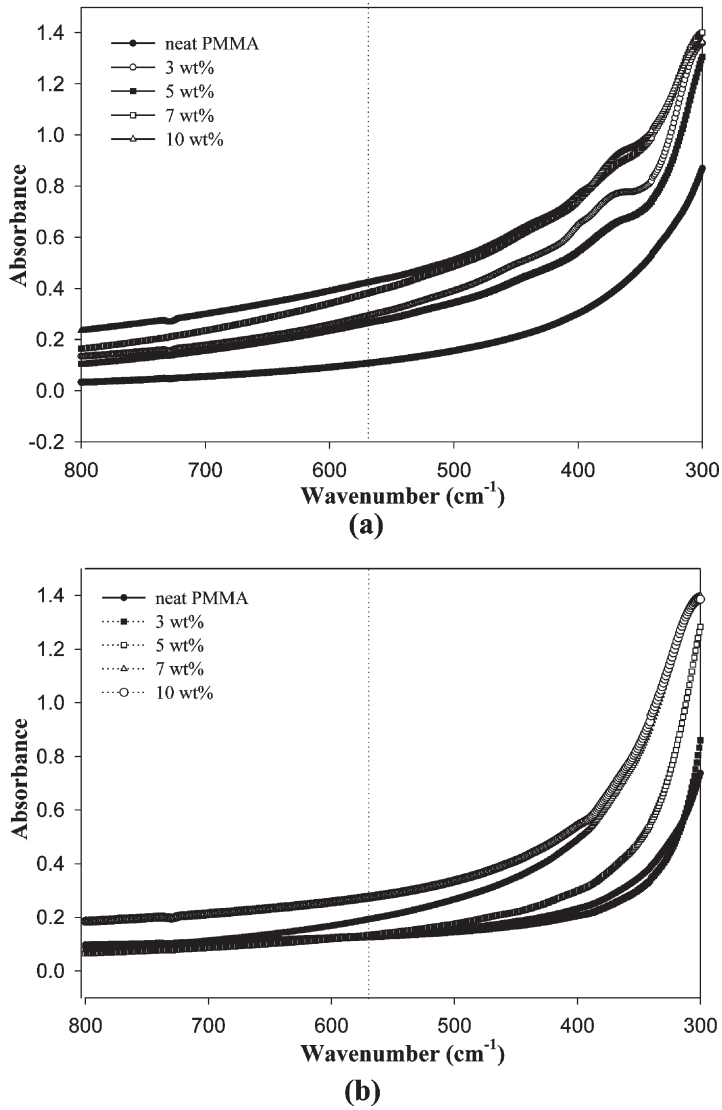

FIGURE 2 UV/VIS spectrograph of the PMMA/clay nanocomposites by (a) conventional emulsion polymerization and (b) emulsifier-free emulsion polymerization.

effectively suppress the mobility of PMMA chains. Especially the decrease of damping appeared proportional to the amount of clay up to 3 wt%, and further increase of clay up to 10 wt% provide no more contribution in decreasing PMMA damping, which means clay of no more than 5 wt% is

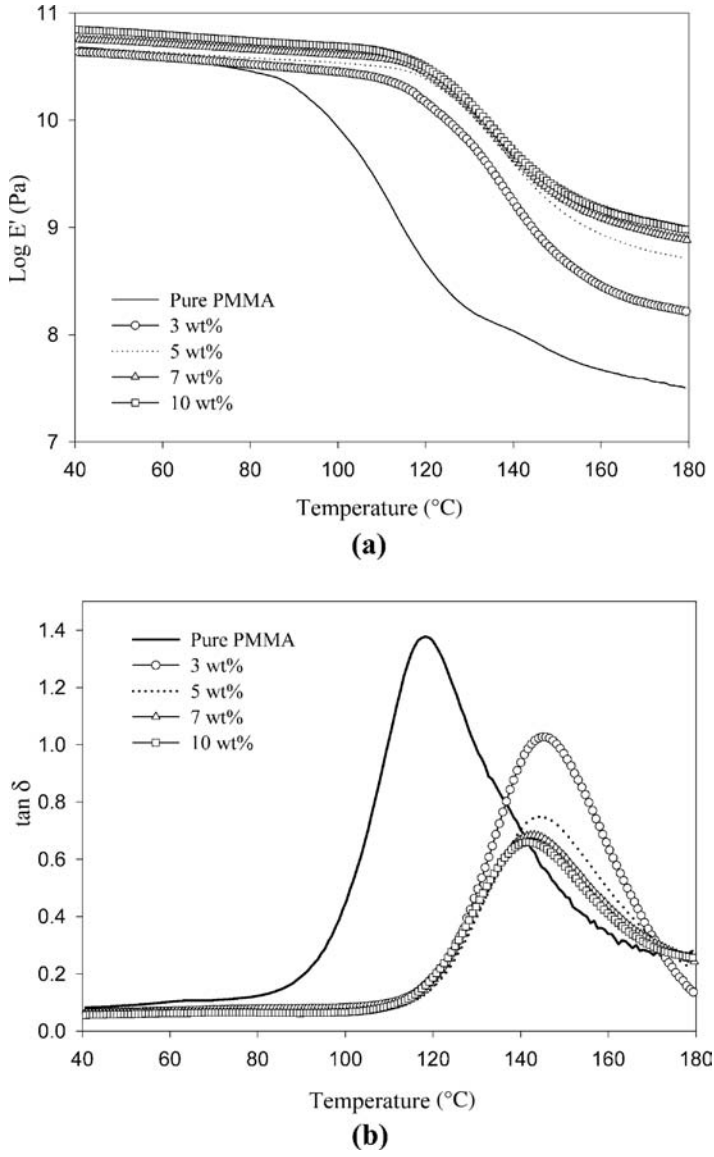

FIGURE 3 Dynamic mechanical thermal analysis results of neat PMMA and PMMA/clay nanocomposites with varying clay content. (a) storage modulus (b) tan δ.

enough to improve PMMA matrix once nano-sized dispersion of clay is established. Refractive index of PMMA/clay nanocomposites retained a steady value as the clay content increased.

4. CONCLUSION

PMMA/clay nanocomposites were successfully prepared by emulsifier-free emulsion polymerization. XRD and TEM analysis indicated that exfoliated structures were achieved by emulsifier-free emulsion polymerization. Both T_g and storage modulus of PMMA/clay nanocomposites were enhanced as clay content increased. The composite containing 10 wt% clay yielded absorbance and refractive index, respectively, of 0.29 (29%, transparency 71%) and 1.4920. The well-dispersed PMMA/clay nanocomposites retained good optical properties as deduced by UV/Vis spectrograph and refractive index.

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