

Effect of Preshearing on the Structure and Properties of Poly(methyl methacrylate)/Clay Nanocomposite Panels

Kab-Jin Hwang, Dae Su Kim

Department of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk 361-763, South Korea

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ABSTRACT: The effect of preshearing resin mixtures prior to casting on the structure and properties of *in situ* polymerized poly(methyl methacrylate)/clay nanocomposite panels was investigated. The preshearing was performed with a mechanical stirrer and controlled by varying mixing time. The structure, thermomechanical, and optical properties of the panels prepared with differ-

ent preshearing times were analyzed by XRD, TEM, DMA, and UV/visible spectrophotometer. The properties of the panels increased with preshearing time because of improved intercalation and exfoliation of the clay. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2957–2960, 2008

Key words: PMMA; clay; nanocomposites; shearing

INTRODUCTION

Poly(methyl methacrylate) (PMMA)/clay nanocomposites have been extensively studied recently.^{1–11} Compared to neat PMMA the nanocomposites comprising nanometer scale silicate layers of clays showed significantly improved properties in stiffness, strength, thermal stability, and permeability. Pristine or organically modified clays have been successfully used to improve the properties of neat PMMA.

PMMA/clay nanocomposites are generally prepared by *in situ* polymerization^{1,3,4,7–11} or melt processing.^{6,10} The intercalation and exfoliation of clays would be significantly dependent on the processing methods as well as conditions, and affect considerably the structure and properties of the nanocomposites. Although a few studies^{10,12} on the processing of PMMA/clay nanocomposites had been reported, they mainly dealt with the effect of the two different processing methods on the structure and properties of the nanocomposites, together with partly dealing with the effect of shearing just in the case of melt processing. It is not easy to find previous studies dealing with the effect of shearing in the case of producing PMMA/clay nanocomposites via *in situ* polymerization. Therefore, in this study, we tried to investigate the effect of preshearing resin mixtures prior to casting on the structure and properties of an *in situ* polymerized PMMA/clay nanocomposite system. In the case of other polymer/clay nanocompo-

sites, the effect of shearing conditions on the structure and properties of the nanocomposites were reported in several studies^{13–18} for melt processing, and a few studies^{19–21} for *in situ* polymerization.

One of the major commercial PMMA products is a PMMA panel. Commercial PMMA panels are produced by casting and *in situ* polymerizing methyl methacrylate (MMA) syrup composed of MMA, PMMA, initiators, fillers, and additives.²² The properties of PMMA panels comprising clay would be affected by the intercalation and exfoliation of the clay, which would be determined by preshearing history of MMA syrup prior to casting. Therefore, the effect of preshearing MMA syrup prior to casting on the structure and properties of PMMA/clay nanocomposite panels were investigated in this study. The preshearing was performed with a mechanical stirrer and controlled by varying mixing time at a constant rotor speed.

EXPERIMENTAL

Materials

MMA and PMMA were provided by LG MMA, Korea. PMMA was used as a thickener for MMA to control the viscosity of MMA syrup adequate (about 1000 cP at room temperature) for commercial casting processes producing PMMA panels. The number-average molecular weight of the PMMA was 1×10^5 g/mol. Benzoyl peroxide (BPO) was used as a free radical initiator.

A commercial organoclay (Cloisite 25A, montmorillonite (MMT) modified with dimethyl hydrogenated tallow 2-ethylhexyl quaternary ammonium,

Correspondence to: D. S. Kim (dskim@chungbuk.ac.kr).

from Southern Clay Products, USA) was used because it was considered the most compatible to the MMA resin system among the commercial clays [from the most hydrophilic clay (Cloisite Na+) to the most organophilic clay (Cloisite 15A)] from the Southern Clay Products. When 3 phr (parts per hundred of the resin system) of each clay was mixed with the MMA resin system respectively, the mixture with Cloisite 25A appeared most homogeneous and showed the least settling down of clay after 24 h.

Preparation of nanocomposite panels

At first homogeneous MMA syrup was prepared by mixing 75 g of MMA and 25 g of PMMA at 60°C for 2 h with a mechanical stirrer (Lab-stirrer PL-S41 equipped with a general 4-bladed propeller stirrer, Poonglim, Korea) rotating at about 200 rpm. 3 phr of the clay was loaded into the MMA syrup, and the MMA/clay syrup was presheared with the stirrer rotating at about 1000 rpm for 10, 20, and 30 min, respectively. After loading 0.3 phr of BPO into the syrup it was mixed further for 5 min at about 1000 rpm and cast into a glass mold with a silicone rubber spacer. It was *in situ* polymerized at 80°C for 2 h and then demolded to obtain PMMA/clay nanocomposite panels for characterization.

Characterization

XRD analysis of the PMMA/clay nanocomposite panels was performed with the XDS2000 X-ray diffractometer (Scintag, Cupertino, CA) with Cu K α radiation (wavelength = 0.15418 nm).

TEM images of the panels were obtained using a transmission electron microscope (TEM, JEOL JEM-2020, JEOL, Tokyo, Japan). Samples were prepared by slicing the panels into about 80-nm thick slices.

The DMA 2940 (TA Instruments, New Castle, DE) was used to measure the dynamic mechanical properties of the panels. Specimens were prepared by cutting the panels into rectangular pieces with dimensions of 35 mm \times 13 mm \times 3.2 mm. DMA was performed in a single cantilever mode at 1 Hz from room temperature to 200°C.

A UV/visible spectrophotometer (Shimadzu UV-1601, Kyoto, Japan) was used to measure the transparency of the panels.

RESULTS AND DISCUSSION

Structure of the nanocomposite panels

The XRD curves for the clay and the PMMA/clay nanocomposite panels are shown in Figure 1. The peak centered at $2\theta = 4.1^\circ$ on the XRD curve for the clay is due to diffraction at the (001) surfaces of sili-

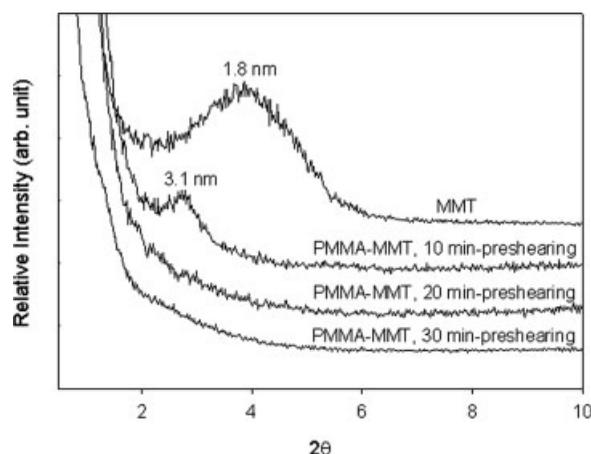


Figure 1 XRD curves of the clay and PMMA/clay nanocomposite panels.

cate layers. According to the Bragg's equation, $2d \sin\theta = n\lambda$, the corresponding d -spacing for the peak is 1.8 nm. However, the peak for the panel of 10-min preshearing was observed at $2\theta = 2.8^\circ$, which corresponds to the d -spacing of 3.1 nm. This result means that intercalation between silicates layers of the clay was improved by the preshearing. Even though both 20-min and 30-min preshearing led to the peak disappearance, it was noticeable that the XRD curve for 30-min preshearing shifted further to left (the lower angle region), compared to the curve for 20-min preshearing, due to improved intercalation and exfoliation of the clay. The XRD analysis clearly showed that the intercalation and exfoliation of the clay increased with preshearing time. Prolonged high shear levels have also promoted the intercalation and exfoliation of clays in the unsaturated-polyester/clay¹⁹ and epoxy/clay^{20,21} nanocomposites.

The TEM images for the panels are shown in Figure 2. The dark lines in the images correspond to the cross sections of silicate layers. Compared to the image for 10-min preshearing, the image for 30-min preshearing clearly shows improved intercalation and exfoliation of the clay.

Thermomechanical properties of the nanocomposite panels

Figure 3(a,b) shows the storage modulus and $\tan \delta$ of the PMMA/clay nanocomposite panels, respectively. The moduli of the nanocomposite panels were slightly higher than that of neat PMMA panel like the results of other studies.^{3,4,8,23} But the effect of preshearing time on the modulus of the nanocomposite panel in glassy state was almost negligible because the constitution of each nanocomposite panel was the same. Compared to neat PMMA panel, the damping property of the nanocomposite panel of 20-min or 30-min preshearing was slightly improved.

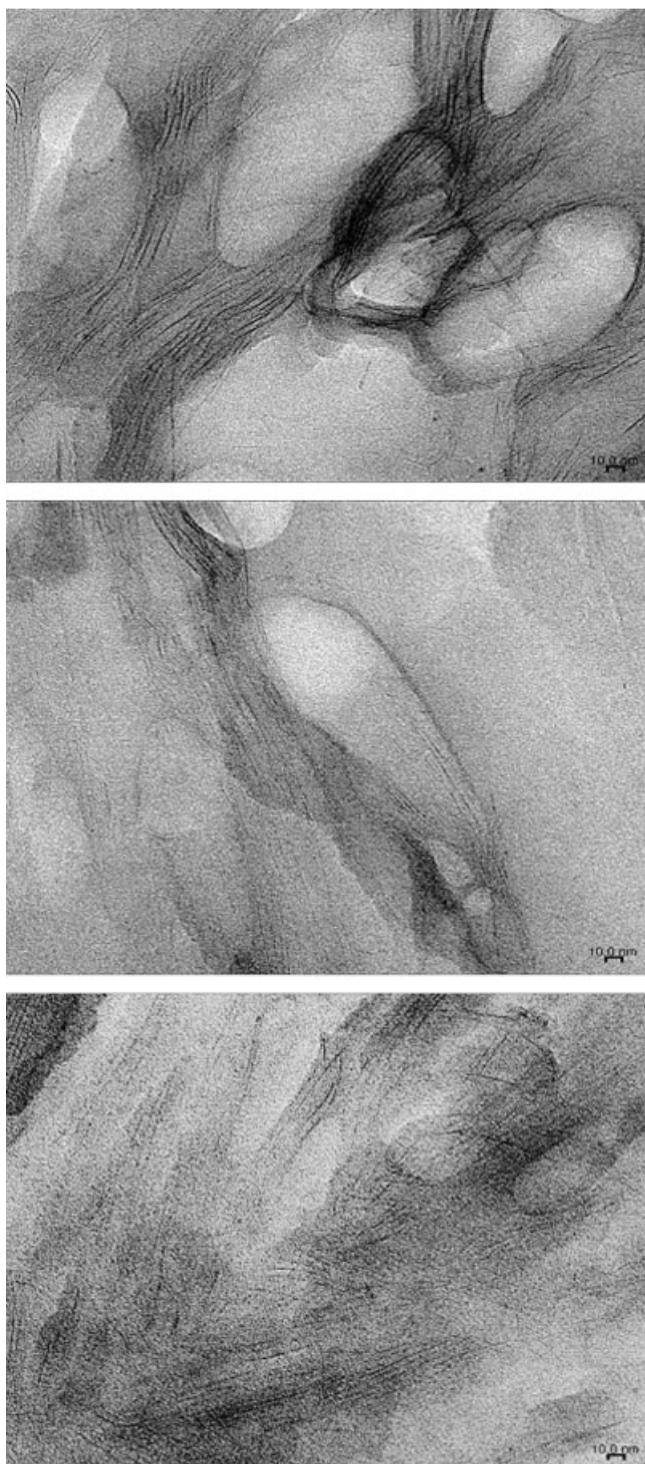


Figure 2 TEM images of the PMMA/clay nanocomposite panels, top: 10-min preshearing, center: 20-min preshearing, bottom: 30-min preshearing. The scale bars in the images are 10 nm.

Generally, the damping property of polymer composites with hard inorganic fillers is inferior to that of corresponding neat polymers.²⁴ However, in the case of polymer nanocomposites with exfoliated silicate layers, the damping property can be slightly

increased because individual silicate layers are somewhat flexible as shown in the TEM images. The nanocomposite panel of 10-min preshearing did not show the improvement because enough exfoliated structure was not developed yet.

The glass transition temperature of the nanocomposite panel, determined by taking the temperature of maximum $\tan \delta$, increased considerably with preshearing time, 129°C for 10-min preshearing, 141°C for 20-min preshearing, and 144°C for 30-min preshearing, and was significantly higher than that of neat PMMA panel (125°C). This result was considered due to improved intercalation and exfoliation of the clay with preshearing time because molecular mobility of polymer chains could be considerably reduced by well-intercalated and exfoliated silicate layers. The glass transition temperature of the PMMA panel could be considerably increased by incorporating the clay and preshearing the MMA/clay syrup sufficiently prior to casting.

Optical properties of the nanocomposite panels

One of the excellent properties of PMMA panels is its transparency. So it has been recommended

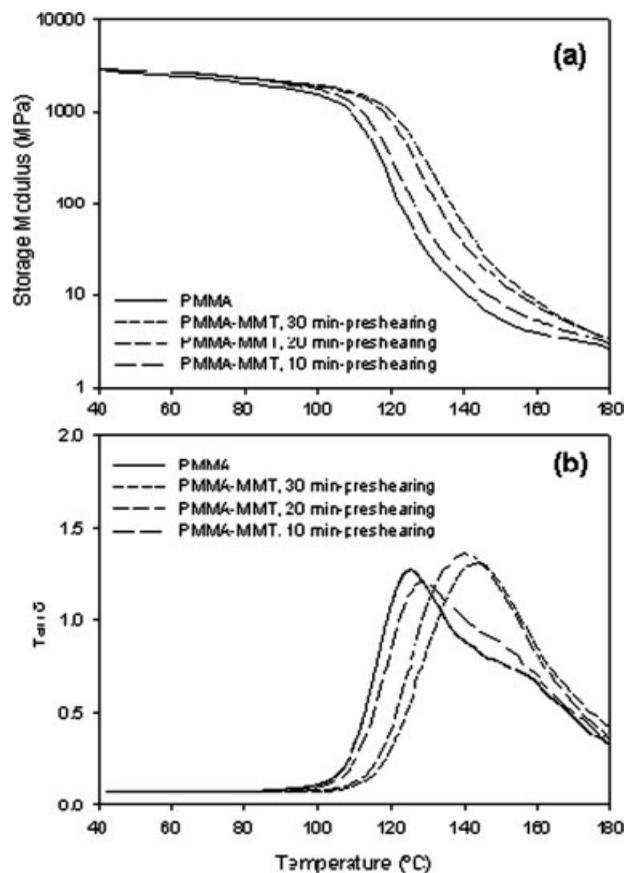


Figure 3 Effect of preshearing time on the storage modulus (a) and $\tan \delta$ (b) of the PMMA/clay nanocomposite panels.

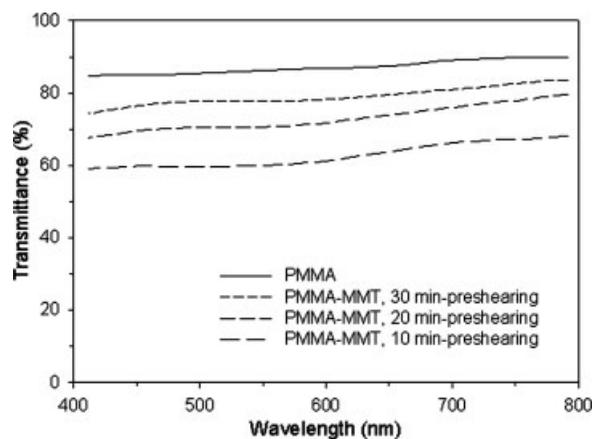


Figure 4 Effect of preshearing time on the transmittance of the PMMA/clay nanocomposite panels.

improving the properties of PMMA panels without considerably deteriorating the excellent transparency. Figure 4 shows the visible-light transmittance of the panels. Although the transparency of the nanocomposite panels was worse than that of neat PMMA panel, it increased significantly with preshearing time because of improved intercalation and exfoliation of the clay. The film obtained from the poly(amic acid)/clay nanocomposite formulation with clay 3 wt % was also very transparent because of its exfoliated structure.²⁵

CONCLUSIONS

The PMMA/clay nanocomposite panels with different preshearing histories were prepared via *in situ* polymerization and their structure and properties were investigated. The XRD curves and TEM images of the nanocomposite panels showed improved intercalation and exfoliation of the clay with preshearing time. Because of the structural change with preshearing time, the glass transition temperature and transparency of the nanocomposite panels also significantly increased with preshearing time. In conclusion, it was very important for the performance

of the PMMA/clay nanocomposite panels to control processing conditions.

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