

Development of Poly(methyl methacrylate)-Clay Nanocomposites by Using Power Ultrasonic Wave

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Abstract : Several methods have been used to synthesize polymer-clay nanocomposites. *In-situ* polymerization with clay belongs to a classical way to develop nano-structured materials, while melt intercalation is being recognized as another useful approach due to its versatility and environmentally benign character. In this research, we prepared polymer-clay nanocomposites based on the poly (methyl methacrylate) and organically modified montmorillonite via two-stage sonication process. According to the unique mode of power ultrasonic wave, the sonication during processing led to enhanced breakup of the clay agglomerates and reduction in size of the dispersed phase. Optimum conditions to form stable exfoliated nanocomposites were studied for various compositions and conditions. It was found that a novel attempt carried out in this study yielded further improvement in the mechanical performance of the nanocomposites compared to those produced by the conventional melt mixing process, as revealed by DMA, XRD and TEM. And rheological properties of nanocomposites were measured by ARES. As a result, sonicated PMMA-clay nanocomposites exhibits enhanced properties such as storage modulus and thermal stability than that of neat PMMA.

Keywords : poly(methyl methacrylate)-clay nanocomposites, ultrasonic wave, exfoliation.

Introduction

Recently, Polymer based nanocomposites are being recognized as a promising material derived from the ultra-fine inorganic particles with dimensions in the range of 1 to 10^3 nm that are dispersed in the polymer matrix homogeneously. Development of polymer/clay nanocomposites is on of the latest evolutionary step of polymer technology.¹ Also, polymer-clay nanocomposites have attracted considerable attention from governments, academic and industrial researchers because of their outstanding properties.

Up to date, a number of clays and polymers have been used in the synthesis of nanocomposites with great efforts to achieve nano-scale dispersion of the clays.^{2,3} The advantages of nanocomposites are characterized by high stiffness, strength, and modulus. Also, nanocomposites reveal superior barrier property, flame retardancy and transparency. In order to the advantage such benefits, it is important to consider and understand the numerous factors that affect exfoliation

of the clay. These factors include the exchange capacity of the clay, the polarity of the reaction medium, the chemical nature of the interlayer cations (e.g. onium ions), and thermodynamic and rheological interactions among the components. Among the several methods to produce nanocomposites, melt blending is particularly useful in terms of its compatibility with current polymer processing techniques and its environmentally benign character due to the absence of solvents.^{4,5}

In this study, we attempted a novel approach to overcome the limitations of existing methods. The sonication process using power ultrasonic wave was employed to enhance nano-scale dispersion during melt mixing of monomer, polymer and clay. According to the unique mode of power ultrasonic wave, we expected enhanced breakup of layered silicate bundle and further reduction in the size of dispersed phase with better homogeneity compared to the *in-situ* polymerization. It is known that ultrasound can initiate the radical polymerization of vinyl monomers and also it is able to carry out the controlled degradation of polymer molecules in solution. With regard to the origin of such effects, it is generally recognized that sonochemical reactions in liquid

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proceed by cavitation collapse of bubbles that are primarily induced by the alternating expansion and compression cycles of ultrasound traveling through the medium.⁶

Poly(methyl methacrylate)(PMMA) is a commercially important polymeric material with high light transparency and weather resistance.^{7,8} However, PMMA has relatively low heat-resistance and its heat deflection temperature is as low as 96 °C. Recently, further improvement in the heat-resistant property has been strongly desired and several attempts to improve the thermal property have been made for the PMMA resin. In order to improve the performance of PMMA, its nanocomposites with clay were prepared through in-situ polymerization and melt mixing under ultrasonic irradiation. For the effective mixing, a special intensive mixer equipped with ultrasonic generator was employed. The details of the mixer are found elsewhere.⁹⁻¹¹ As described above, according to the ultrasonic irradiation, the present method was expected to achieve effective breakup of the clay agglomerates and exfoliation of the silicate layers to yield useful PMMA-clay nanocomposite. It was of particular interest to investigate the effect of ultrasonic wave on the structure and the properties of resulting nanocomposites.

Experimental

Materials. PMMA in this study was obtained from LG Chemical of Korea and its commercial name is IH830. Methyl methacrylate (MMA) was purchased from Junsei chemical. Azo-bis-isobutyronitrile (AIBN) used as an initiator. All of them are used without purification.

Two organically modified clays (Cloisite 10A and 20A, respectively) were employed to combine with PMMA. They were supplied by Southern Clay Products, Inc (USA). At present, numerous grades of clays are commercially available and it is important to consider the influence of interlayer composition and structure on the formation of nanocomposites. Such issue would be fully investigated by having a wide range of clay collection. In our study, a rather limited choice was made as a model compound since major point was focused on the effect of power ultrasonic wave on the dispersion of clays in the polymer matrix.

Preparation. In first-stage, free radical polymerization of MMA with organically modified clay was carried out sonication for 10 min at room temperature in the presence of 0.1 phr AIBN. Although, as previously mentioned, ultrasonic wave can initiate radical polymerization, we used AIBN to accelerate the polymerization. Obviously, with AIBN alone, we cannot promote enough polymerization for successful hybrid formation under the given time and temperature. In the second-stage PMMA was melt mixed with the product of the first-stage. Melt mixing of the samples was performed in a sonicated mixer (Haake Rheomix 600) at a fixed volume basis of 70% filling and at a temperature of 230 °C. The rotor speed was set as 120 rpm and total mixing time

including sonication was 20 min. The total content of the clay was kept as 3 wt%. Schematic description of the present method is given in Figure 1. After the melt mixing, specimens required for subsequent characterization were prepared by compression molding in a hot press.

Characterization. To measure the change of gallery distance of the nanocomposites prepared from two-stage sonication process, we used an X-ray diffraction (XRD, Philips XPERT MPD). CuK α radiation generated at a voltage of 40 kV was used as an X-ray source. The sample-to-detector was 30 cm yielding an angular scan from 1.5 to 10 degrees (2θ). Samples were pellets with a smooth surface and a dimension of $1 \times 1 \times 0.1$ cm. Transmission electron microscopy (TEM, Hitachi H-600) was used to confirm the morphology of the nanocomposites. Since TEM is a powerful technique to study structure at and below the nanometer scale, it can be used to confirm results obtained by XRD about the organization of the clay layers in the matrix. Ultra-thin sections of the specimens were obtained by a microtome and observed without staining.

Dynamic mechanical analyzer (DMA, Dupont983) was used to assess the mechanical performance of the nanocomposites. The evaluation was made in the flexural mode at a fixed frequency of 10 Hz and the temperature was varied from 50 to 130 °C at a heating rate of 2 °C/min. The thermogravimetric analyzer (TGA, TA instrument. TGA 2950) was used to estimate the thermal stability of the composites. The measurements were carried out under N₂ flow at the heating rate of 20 °C/min in the temperature range of 30~600 °C. Also, the rheological properties of nanocomposites were measured at 230 °C by ARES (Rheometric Scientific). The geometry was parallel plate with 25 mm diameter and 1.5 mm gap size.

Results and Discussion

Structure and Morphology. The changes of the inter-layer distance in various nanocomposites were estimated from XRD by monitoring the position, shape and intensity of basal reflections corresponding to the silicate layers. The analysis is performed at low angle ($2\theta < 10^\circ$) in order to detect the (d_{001}) reflection and evaluate the d-spacing between the clay layers.

Figure 2 shows a series of XRD patterns of the C10A and PMMA/MMA-C10A. In case of the specimen obtained by simple mixing without sonication, new peaks located around $2\theta = 3.06^\circ$ and 5.74° were observed. When the sonication was imposed during the melt mixing, the peak positions were shifted to lower angle and the intensity of each peak was significantly reduced. Figure 3 shows a series of XRD patterns for C20A, and PMMA/MMA-C20A. Again, simple mixing after the first stage produced a similar result with that of C10A, while sonicated mixing eliminated the peak almost completely. According to most literatures, the ran-

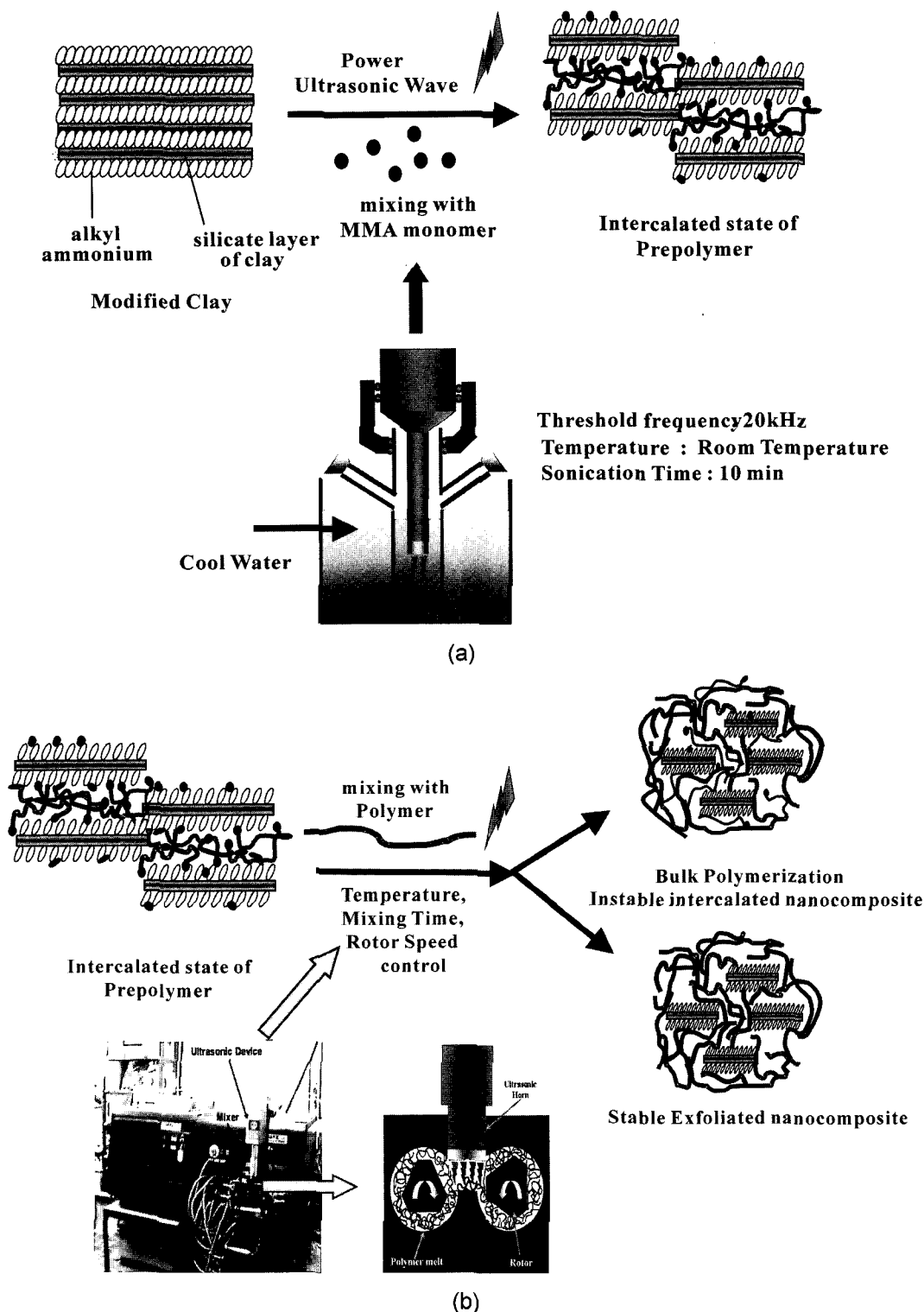


Figure 1. Schematic diagram of PMMA/clay nanocomposites by two-stage sonication process; (a) First-stage and (b) Second-stage.

domized array of clays is identified by observing the intensity of the peak. Also, disappearance or reduction of the peak indicate the changes in phase structure toward exfoliated structure.

The peaks found at lower angles indicate that the increase of the d_{001} of C10A occurred by polymerization of MMA within the C20A interlayer of clay. We presume that such intercalation was facilitated in part by the perturbations

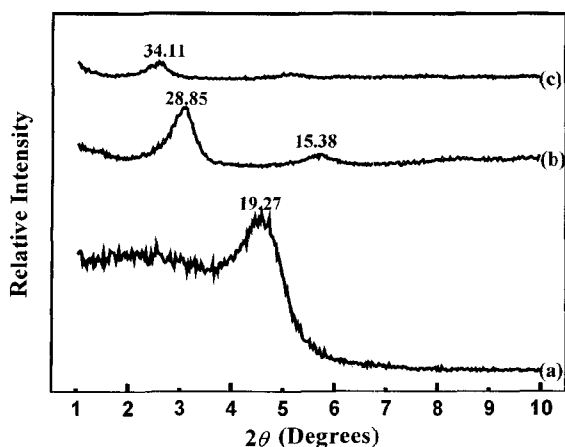


Figure 2. XRD patterns of the clay and nanocomposites; (a) C10A, (b) PMMA/C10A (without sonication), and (c) PMMA/C10A (sonication).

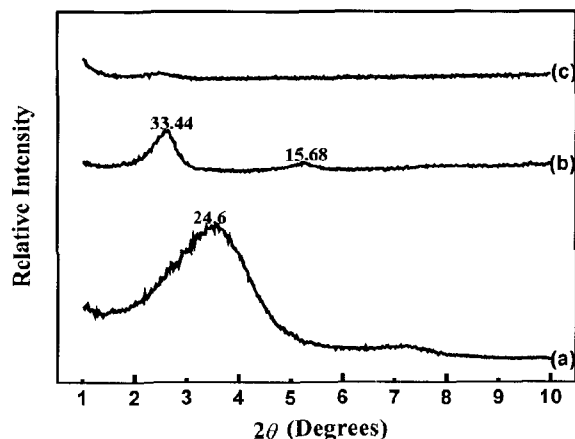


Figure 3. XRD patterns of the clay and nanocomposites; (a) C20A, (b) PMMA/C20A (without sonication), and (c) PMMA/C20A (sonication).

originated from strong sound stream because sufficient polymerization without sonication would not be available at such limited time and low temperature. Besides this desirable consequences, decrease in the interlayer distance was accompanied as revealed by the peaks appeared at higher angles than those of pristine clays in both. They are not considered as the d_{002} reflection of the intercalated organo-silicate, since the peak does not correspond to the scattering angle two times that for the first peak in each case. Instead, it is considered as a shift of the characteristic peak of neat clay, which is mainly due to its structural instability. The thermal stability of each clay was evaluated by TGA and the results are given in Figure 4. As can be expected from the figure, there is a possibility that the organic molecules may be degraded or exuded out of the gallery during melt mixing at the processing temperature. By these reason, decrease of

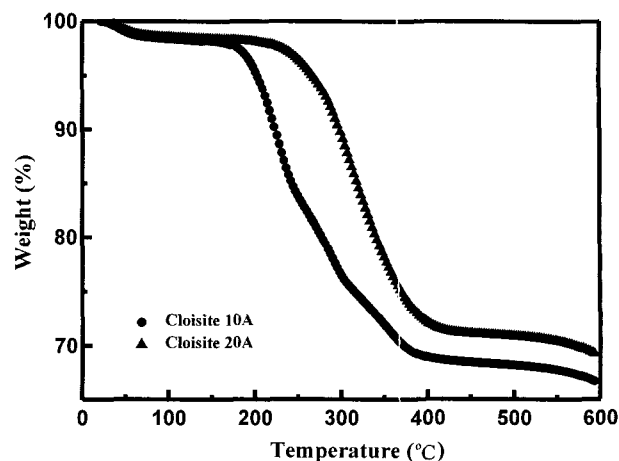


Figure 4. Thermogravimetric analysis curves of pristine clay (C10A and C20A).

interlayer distance becomes inevitable. In fact, a similar issue has been raised in a study by Yoon *et al.* that the interlayer structure may collapse from the bilayer arrangement of alkyl chain to monolayer one during annealing or melt processing.¹²

It is important to note, however, that the undesirable structural variation was removed during the process of sonicated melt mixing. Furthermore, the imposition of ultrasonic wave in the mixer yielded exfoliated structure especially in the composite containing C20A, while free radical polymerization of MMA with clays in the first stage led only to intercalated structure. As noted earlier, ultrasonic wave applied in the first stage would help uniform dispersion of clay in the reaction medium. However the present result denotes that further improvement in the nano-scale dispersion of clays was achieved due to the synergistic effect of high shear and ultrasonic wave in a sonicated intensive mixer. The reason for the difference between C10A and C20A in the phase structural is explained by considering the relevant principle in a thermodynamic sense. In principle, polymer-clay hybrid formation occurs if the free energy change, ΔG , associated with separation of the silicate layers and incorporation of polymer chains from the bulk is negative. During intercalation, the polymer chains that are initially in an unconstrained environment must enter the constrained environment of the narrow silicate interlayer, where as the organic chains gain configurational freedom as the interlayer distance increases. Based on this rationale, for successful hybrid formation, it is critical to have an initial interlayer structure that results in a maximum increase in entropy of the organic chains to compensate the penalty of polymer confinement. In present case, the initial interlayer distance of C20A is higher than that of C10A (24.60 Å vs 19.27 Å). By this reason, it is considered that the exfoliation is more easily promoted in PMMA/C20A system, provided little difference

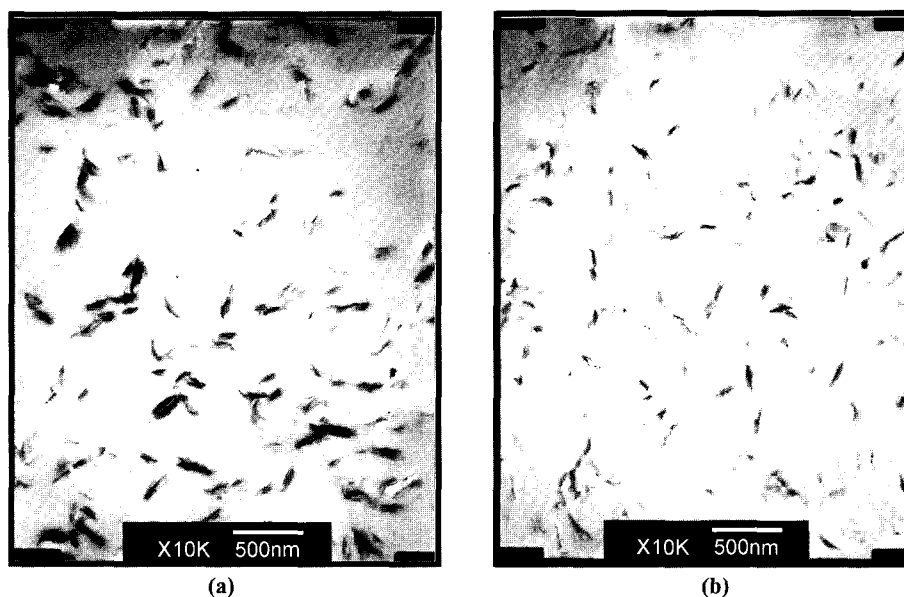


Figure 5. Transmission electron micrographs of PMMA/C20A ($\times 10,000$); (a) without sonication and (b) sonication (Both samples were obtained by mixing for 20 min).

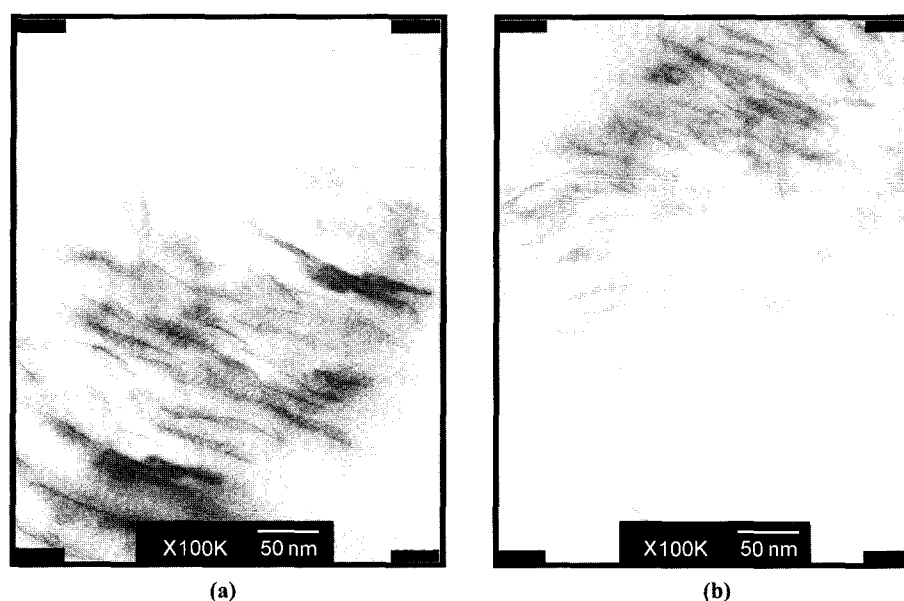


Figure 6. Transmission electron micrographs of PMMA/C20A ($\times 100,000$); (a) without sonication and (b) sonication (Both samples were obtained by mixing for 20 min).

in the thermodynamic affinity between the components of each system exists.

The phase structure investigated by XRD was further confirmed by TEM observation. As shown in Figure 5, the nanocomposites by sonication process (Figure 5(b)) exhibits better dispersion of silicate layers in polymer matrix than that of simple mixing process (Figure 5(a)). The product obtained from simple mixing process shows partial agglomeration of silicate layers in polymer matrix. On the other

hand, the product by sonication process shows enhanced dispersion of silicate layers in polymer matrix. In developing polymer based nanocomposites, the major interest is often focused on the achievement of intercalated or exfoliated structure itself. However, in terms of the product quality when molded, it is of considerable importance to keep uniform dispersion of clays throughout the whole specimen. We were able to manifest the beneficial effect of sonication on the overall uniformity dispersion by carefully examining

numerous positions of the sample under investigation.

Higher magnifications of the TEM pictures are displayed in Figure 6 to more clearly show the state of dispersion and phase morphology. The Figure 6(b) has more regular and clearly defined silicate layers than that of Figure 6(a).

Thermal, Rheological, and Mechanical Properties. Comparisons of thermal degradation behaviors of neat PMMA with its nanocomposites are shown in Figure 7. It demonstrates that the PMMA/C20A nanocomposites has better thermal stability than that of pure PMMA. About 60 ~70 increase in decomposition temperature was observed when PMMA was hybridized with C20A. In Figure 8, complex viscosity (η^*) of PMMA was compared with these of neat PMMA. The melt viscosity of pure PMMA increased substantially was incorporation of the clay. This viscosity enhancement is caused by the interaction and dispersion of clay in the polymer matrix that appears to provide resistance

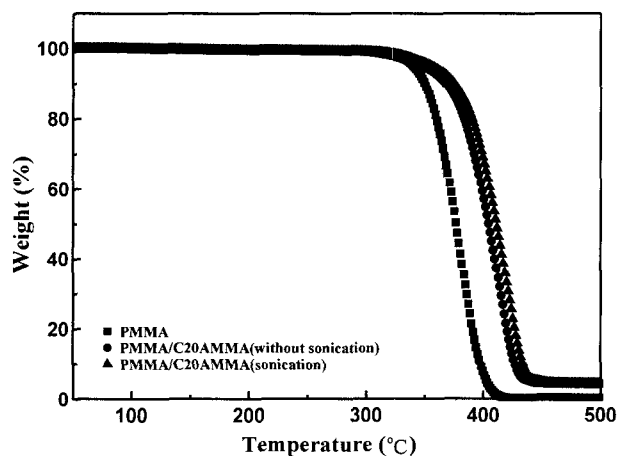


Figure 7. Thermogravimetric analysis curves obtained under nitrogen for neat PMMA and its nanocomposites.

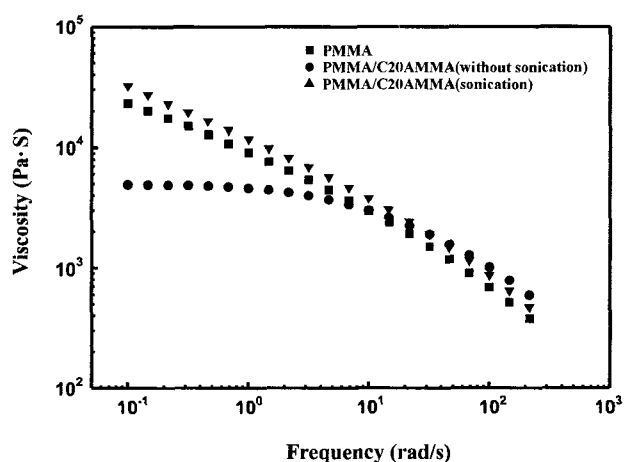


Figure 8. Complex viscosity (η^*) for PMMA and PMMA/C20A nanocomposites.

to flow and deform the molten polymer. In addition, unlike pure PMMA, both intercalated and exfoliated nanocomposites exhibit shear-thinning behavior at low shear rates, while similar shear dependency is apparent at high shear rate.

As pointed out from a recent paper^{13,14} the shear-thinning is considered to be due to the orientation of the silicate layers under shear. Another point that should be addressed in Figure 2 is that the melt viscosities of exfoliated system are lower than those of intercalated one. This seems somewhat unusual; since the increased interaction between the clay and polymer matrix may lead to increase of melt viscosity in exfoliated nanocomposites. Due to the lack of comparable data, exact interpretation is not available at present case. Nevertheless, we believe that the lower viscosities are closely related with the mechanochemical degradation of PMMA molecules that is mainly induced by ultrasonic irradiation during melt mixing.

In fact, we found that polymer can be degraded in various degrees by the action of ultrasonic wave.¹⁵ Although only slight difference were observed in decomposition temperatures and melt viscosities of the two nanocomposites having different phase structures, the considerable improvement of storage modulus in exfoliated nanocomposite is evident as demonstrated in Figure 9. Despite the possible loss in modulus due to the degradation of PMMA, exfoliation of clays in the matrix resulted in desirable mechanical performance.

Conclusions

PMMA/Clay nanocomposites were successfully prepared by in-situ polymerization and melt mixing with ultrasonic irradiation. We realized that the sonication imposed during melt mixing provided an effective route to accomplish the nano-scale dispersion of the layered silicates in polymer-clay nanocomposites. Accordingly, the synthesized nanocomposites via two-stage process revealed superior thermal

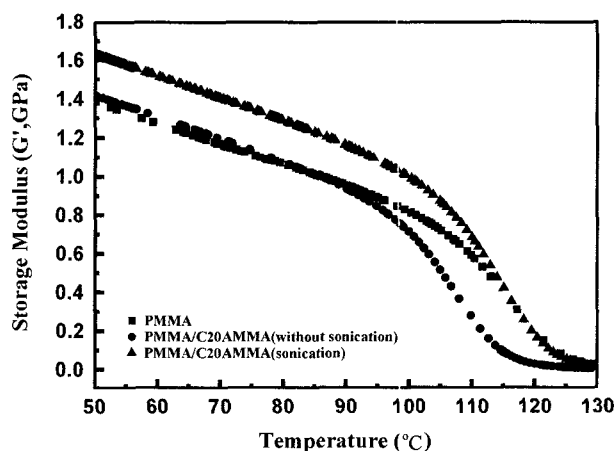


Figure 9. Storage modulus (G') for PMMA and PMMA/C20A nanocomposites.

stability and mechanical performance compared to simple melt mixing process. It was found that sonicated mixer successfully generated exfoliated nanocomposite with a clay having proper interlayer distance to compensate the entropy penalty of the polymer molecules.

In addition to the exfoliated structure, it is important to note that the overall homogeneity of the composite was also superior to those formed by typical compounding processes, which greatly affects the performance of the nanocomposites.

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