

## Ultrasonic degradation of polypropylene and its application for the development of PP based copolymer and nanocomposite

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### Abstract

Thermoplastic nanocomposites based on the copolymers of polypropylene (PP)-polystyrene (PS) and organically modified montmorillonite (org-MMT) were produced by using power ultrasonic wave in an intensive mixer. Owing to the unique action of the ultrasonic wave, free radicals of styrene monomers and macroradicals of PP were generated, by which copolymers of PP and PS were formed. Another important aspect of using ultrasonic wave during the mixing process was to enhance nano-scale dispersion of org-MMT by destructing the agglomerates of org-MMT in the polymer matrix. Optimum conditions for the in-situ copolymerization and melt intercalation were studied with various concentrations of styrene monomer, sonication time and different kinds of clay. 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.

### 1. Introduction

In recent years, there have been many attempts to develop nanocomposites of layered silicates and polymer matrix as an advanced plastic material. (Alexandre and Dubois, 2000). At the early stage of the development, the formation of nanocomposites was mostly conducted via solution method. More recently, however, directly melt intercalation is being recognized as a promising approach due to the facts that it can be performed by using conventional polymer mixing or extrusion processes and it is environmentally benign.

In this study, a novel attempt to produce a nano-structured material was made by employing power ultrasonic wave during melt mixing in an intensive mixer. It is well known from the studies on the ultrasound assisted chemical reactions that the use of ultrasound offers various benefits including higher yield, reaction rate, and purity. (Price, 1992). Along with the synthesis of low molecular mass compounds, an application of sonochemical effect in polymer system has yielded a variety of useful consequences.

For example, ultrasound can initiate the radical polymerization of vinyl monomers and also it is able to carry out the controlled degradation of polymer molecules in solutions. With regard to the origin of such effects, it is generally recognized that sonochemical reactions in liquid

proceed by cavitation collapse of a bubble that is primarily induced by the alternating expansion and compression cycles of ultrasound traveling through the medium. Upon the collapse of a bubble, the local temperature is increased up to 5000K, which enables decomposition of molecules and then leads to the formation of free radicals.

Moreover, when macromolecules are under sonication in the liquid phase, they are subject to shock waves emanated from the collapse of the cavity. On the molecular level, this implies a rapid motion of solvent molecules to which the macromolecules embedded in the solvent cannot adjust. At this stage, macromolecules are sufficiently strained and consequently macroradicals are produced (Schnabel, 1981).

The main objective of the present research is to utilize the unique effects of the ultrasonic wave in copolymerization of a polymer with a different monomer. In addition, another important role of ultrasonic wave relates to the useful mixing element for ultra-fine dispersion of layered silicates in the thermoplastic matrix. In a sense, aside from its much higher frequency, the role of the ultrasound as a mixing element may be analogous to the effect of kneading blocks in a twin-screw extruder, which is also characterized by compression and expansion actions.

In order to perform the copolymerization, we adopted the mixtures of polypropylene (PP) and styrene monomer and for the hybrid formation, organically modified montmorillonites (org-MMT) were introduced during the copolymerization in a special intensive mixer equipped with

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ultrasonic generator. The details of the mixer are found elsewhere. (Yoo *et al.*, 1999). As described above, according to the ultrasonic irradiation, it is expected that both styrene radicals and PP macroradicals be generated to form both homopolymer of PS and copolymer of PP and PS. At the same time, effective breakup of the org-MMT agglomerates and delamination of the silicate layers would be facilitated by the exceptional vibration of the ultrasonic wave.

## 2. Experimental

PP used in this study was a commercial product (PP1386) made by Daelim Industrial Co. of Korea with a melt index of 200 (230°C, 2.16 kg). Styrene monomer (SM) was purchased from Junsei chemicals and used without purification.

Two org-MMTs (Cloisite 10A and 20A) were supplied by Southern Clay Products, Inc, USA. The Cloisite 10A (C10A) has a dimethyl hydrogenated-tallow benzyl ammonium as a organic modifier with a cation exchange capacity of 125 meq/100 g, while Cloisite 20A (C20A) has a dimethyl hydrogenated-tallow ammonium as a organic modifier with a cation exchange capacity of 95 meq/100 g. Prior to the melt mixing, org-MMT was premixed with SM for 30 min at room temperature. Melt mixing and synthesis of the samples was performed in an intensive mixer (Haake Rheomix 600) at a fixed volume basis of 70% filling and at a temperature of 180°C. The rotor speed was set as 75rpm and total sonication and mixing times were 20 min. In every case, the composition of the sample was fixed as 80/15/5 of PP/SM/org-MMT in weight basis.

The samples for FTIR analysis were mixed with KBr power and pressed into pellets. Wave numbers scanned range from 4000 to 500  $\text{cm}^{-1}$ . X-ray diffraction (XRD) measurements were performed to verify the structure of the nanocomposites. All the samples were prepared by compression molding at 180°C after the melt mixing. The sample-to-detector was 30 cm yielding an angular scan from 1.5 to 20 degrees ( $2\theta$ ). Transmission electron microscopy (TEM, Hitachi H-600) was used to confirm the morphology development estimated by XRD. Ultra-thin sections of the specimens were obtained by a microtome and observed without staining.

Dynamic mechanical analyzer (DMA, Dupont 983) 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 30 to 130°C at a heating rate of 2°C/min. The thermal gravimetric analyzer (TGA, TA instrument. TGA 2950) was used to estimate the thermal stability of the composites.

The measurements were carried out under  $\text{N}_2$  flow at the heating rate of 20°C/min in the temperature range of 30–600°C. Also the rheological properties of nanocom-

posites were measured at 180°C by ARES (Advanced Rheometric Expansion System). The geometry was parallel plate with 25 mm diameter and 1.5 mm gap size.

## 3. Results and Discussion

### 3.1. Structural and morphological analysis

The changes of the interlayer distance in various nanocomposites were estimated from XRD by monitoring the position, shape and intensity of basal reflections corresponding to the silicate layers.

Fig. 1 shows a series of XRD patterns of the C10A and PP/C10A/SM. In case of the specimen obtained by simple mixing without sonication, new peaks located around  $2\theta = 2.23^\circ$  and  $5.04^\circ$  were observed. Since the shift of the peak of C10A ( $2\theta = 4.58^\circ$ ) to the lower angle side indicates the increase in gallery height of the org-MMT ( $d_{001}$ ), it is clear that simple melt mixing yielded a nanocomposite with intercalated structure, which would be presumably induced by thermal polymerization of styrene monomers within the interlayer of the org-MMT.

When the mixture was processed with sonication, however, the peak at lower angle disappeared, which suggests that exfoliated nanocomposite has been formed. It is important to note that conventional polymerization of styrene with C10A method led only to intercalated structure (Doh and Cho, 1998), while the imposition of ultrasonic wave facilitated delamination process of layered silicates to achieve exfoliation. Of course, the decrease in molecular weight of PP and copolymer formation between PP and PS are also responsible for the presented phase structure of the nanocomposite. In principle, low molecular weight species can more easily penetrate into the interlayer of org-MMT; and as the styrene monomers are polymerized, the compatibility problem between PP and PS becomes dominant,

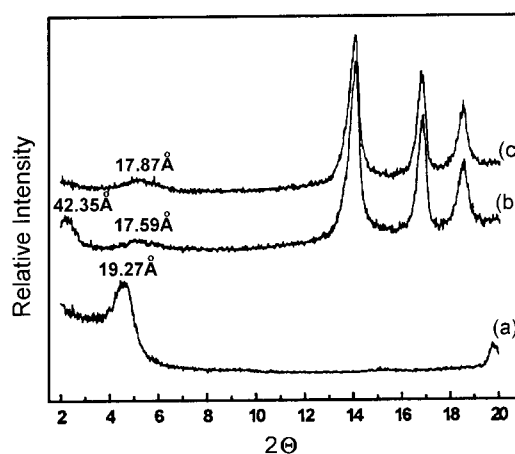


Fig. 1. XRD patterns of corresponding components and nanocomposites: (a) C10A (b) PP/C10A/SM (without sonication) (c) PP/C10A/SM (sonication).

which can be readily solved by the copolymer formation. Accordingly, evolution of stable phase morphology is possible in the proposed scheme. The result on the copolymer formation will be discussed later of this section.

The weak high-angle peak is not considered as the  $d_{002}$  reflection of the intercalated organosilicate, since the peak does not correspond to the scattering angle two times that for the first peak. Instead, it is considered as a shift of the characteristic peak of neat C10A, which is mainly due to its structural instability.

In fact, it has been reported that the interlayer structure of C10A may collapse from the bilayer arrangement of alkyl chains to monolayer one during annealing or melt processing (Yoon *et al.*, 2001).

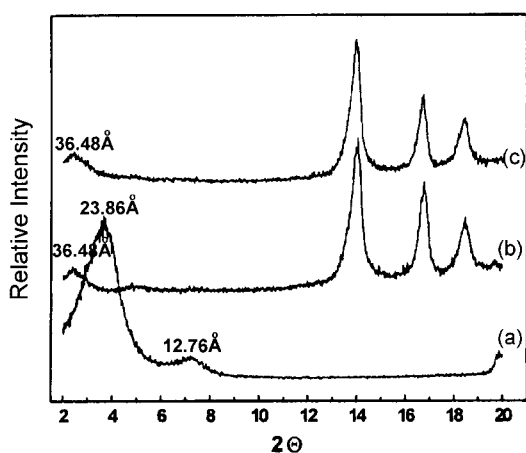


Fig. 2. XRD patterns of corresponding components and nanocomposites: (a) C20A (b) PP/C20A/SM (without sonication) (c) PP/C20A/SM (sonication).

Fig. 2 shows a series of XRD patterns of the C20A, and PP/C20A/SM. In neat C20A, two peaks corresponding to the basal reflections of ( $d_{001}$ ) and ( $d_{002}$ ) planes are observed, respectively. Upon mixing with PP and styrene without sonication, intercalated structure was evolved, as revealed by a new peak around  $2\theta=2.42^\circ$ . Compared to the nanocomposite containing C10A, however, the increase in  $d_{001}$  is relatively small and moreover, sonication did not alter the phase structure of the nanocomposite into the exfoliated one. The reasons for the difference between results shown in Fig. 1 and Fig. 2 may be manifold; but one definite origin stems from the miscibility of styrene and organic chains of the org-MMT. In C10A, the chemical structure of the interlayer is more similar to styrene than that in C20A; consequently the penetration of styrene monomers into the gallery is superior in the former. This suggests that an optimum combination of effective mixing and the interaction between monomer and silicate layer is the prerequisite for the exfoliated nanocomposite.

As an attempt to verify the existence of PP-PS copolymer, the samples after melt mixing were immersed into THF and filtered in order to extract the free PS. Thus the free PS and PP-PS copolymers were separated. The sample of the PP-PS copolymer was washed by a Soxhlet extraction with THF for 24 hr and dried in a vacuum at 343 K for 24 hr. Then the existence of PS was estimated by FTIR analysis by detecting the absorption of  $700\text{ cm}^{-1}$ , which is assigned to CH bending vibration of a PS benzene ring.

The phase structure investigated by XRD was further confirmed by TEM observation. As presented in Fig. 3, the nanocomposite of C10A exhibits better dispersion than that of C20A.

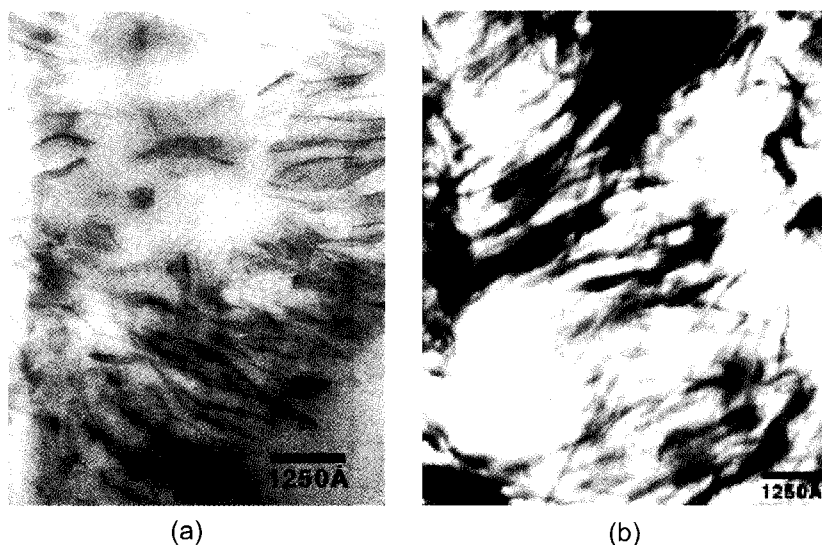


Fig. 3. Transmission Electron Micrographs of nanocomposites: (a) PP/C10A/SM (b) PP/C20A/SM (Both samples were obtained by sonication for 20 min.).

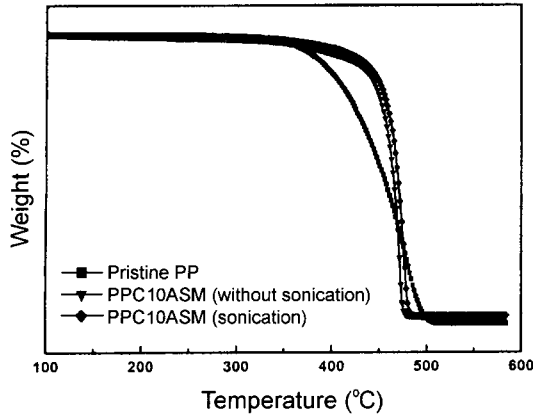


Fig. 4. Thermogravimetric analysis curves obtained under nitrogen for neat PP and nanocomposites.

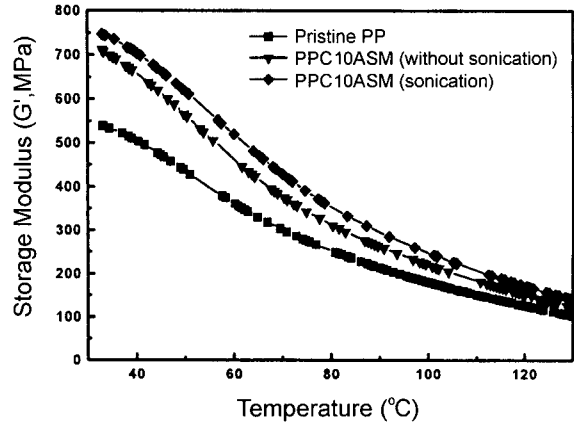
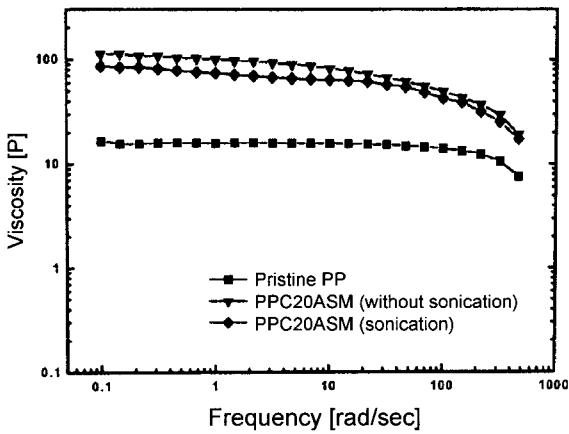
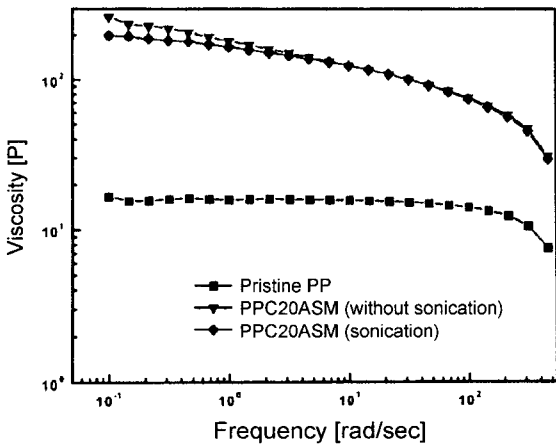


Fig. 6. Storage modulus (G) for PP and nanocomposites.



(a)



(b)

Fig. 5. Complex viscosity ( $\eta^*$ ) for PP and nanocomposites.

### 3.2. Thermal, rheological, and mechanical analyses

A comparative thermal gravimetric analysis (TGA) of neat PP and nanocomposites is shown Fig. 4. It is evident that the thermal stability of PP is greatly improved by nano-scale dispersion of silicate layers.

Fig. 5 (a) and (b) represent the complex viscosity behavior of neat PP and various nanocomposites. The melt viscosities of nanocomposites are higher than that of neat PP and they slightly exhibit shear-thinning behavior at low frequency. It is noted that the nanocomposites made by sonication show lower viscosity than that produced by simple melt mixing. Evidently, this reflects the fact that PP molecules were degraded by ultrasonic wave, as mentioned earlier.

As can be expected from the evaluation of the nanocomposites produced in this study, the storage modulus of the nanocomposites is significantly improved compared to the case of neat PP as shown in Fig. 6.

### 4. Conclusions

As a novel route to develop thermoplastic nanocomposites, our laboratory adopted an intensive mixer equipped with power ultrasound. During the melt mixing, it was possible to precede both copolymerization of PP with styrene and nano-hybridization with organically modified clays. The expected roles of the ultrasonic wave were to initiate free radical copolymerization by inducing chain scission of PP molecules and to facilitate the delamination process of layered silicates. It was found that sonicated mixer successfully generated exfoliated nanocomposite provided sufficient interaction between monomer and organic chains of the interlayer is available.

As a result, the nanocomposites produced in this study revealed enhanced thermal stability and mechanical performance.

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