Ultrasonic Effects on PP/PS/Clay Nanocomposites during Continuous Melt Compounding Process

Kyung Yl Kim,[1] *Dong Uk Ju,*[1] *Gi Joon Nam,*[2] *Jae Wook Lee**[1]

Summary: Polymer blend/clay nanocomposites were prepared by ultrasonic-assisted continuous extrusion process. This process was employed to enhance the compatibility between two polymers, and nano-scale dispersion between the polymer blend and organically modified clay. Materials were linear polypropylene and polystyrene with 3 phr loading of organophilic montmorillonite clay. The effectiveness of the proposed ultrasonic-assisted process on the polypropylene/polystyrene/clay nanocomposites was confirmed by rheological property measurements and structural analysis by scanning electron microscope and X-ray diffraction. The sonication during extrusion was effective in improving the compatibility between polypropylene and polystyrene. Also, it led to enhanced breakup of the clay agglomerates. The observed clay was in the exfoliated state from the X-ray diffraction analysis.

Keywords: extrusion; nanocomposite; polypropylene; polystyrene; ultrasonic wave

Introduction

Nanocomposites have become a new class of composites and attracted considerable attention from both academy and industry.[1–3] As results of the nanometer-scale dispersions, nanocomposites exhibit markedly improved mechanical, thermal, optical and physico-chemical properties compared with the conventional composites. As polypropylene (PP) and polystyrene (PS) are the most widely used commercial polymers, the hybridization of PP/PS blends with nano-structured ingredients should be effective implement in the commercial applications. The mainstream of manufacturing PP/PS/clay nanocompsites was by general compounding of polymer with clay in the presence of compatibilizer. In this case, the low molecular weight nature of compatibilizer such as maleic anhydride, acrylic acid etc. is apt to decrease the mechanical properties of nanocomposites. To surpass limitation of using compatibilizer, high intensity ultrasonic energy can be applied to intercalate the gallery space of the clay.

Ultrasonic waves are widely employed in the area of biology, cleaning, plastic welding, matching and chemical reactions and so forth. In addition to these conventional applications, numerous studies have been suggested to the new possibilities as a useful way to induce mechano-chemical degradation in polymeric materials.[4–11] In the previous study, high intensity ultrasonic wave in batch-type melt mixing led to stable morphology with reduced phase size of the domain in the PP/PS blend.[12] On extending the previous research, high intensity ultrasonic wave was applied to improve the compatiblity between PP and PS in the continuous extrusion process. The incresase of mechanical properties were monitored with the ultrasonic wave. Also, the effect of ultrasonic wave on enhancing nano-scale dispersion of polymer blends and organically modified clay in the PP/PS/clay nanocomposites were studied, compared to the conventional compounding method.

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Experimental Part

PS was obtained from LG Chem. Co. (Korea) and the grade is 20HRE. Homo polypropylene from Samsung-Total Co. (Korea) was used. The organically modified clay, Cloisite 10A, supplied by Southern Clay Prodcuts, were employed to the PP/PS blends. The organic modifier is dimethyl benzyl hydrogenated-tallow quaternary ammonium, and the modifier concentration is 125 meq/100 g clay. The content of clay was kept to 3 phr and polymer contents were calculated by weight percent in this study.

To impose ultrasonic wave during melt extrusion, the intermeshing co-rotating twin screw extruder (model TEK 25 from SM Platek Co., Korea) was specially designed.

Figure 1 shows a schematic diagram of the ultrasonic-assisted processing configuration used in this work. The horn vibrated longitudinally at a frequency of 20 kHz and the ultrasonic power of horn was 100 W. The extruder had 10 barrel sections and the ultrasonic waves were transmitted though the middle part of the barrel. The screw diameter is 25 mm and screw length/diameter ratio is 41. The temperature profiles were 160 (feeding zone), 190 (melting zone), and 210 °C (metering zone and die) with 50 rpm screw rate. Before irradiation of ultrasound, preliminary extrusion was carried out for 3 minutes to reach the stable state. For durable operation, an effective cooling accessory was equiped. Prior to extrusion operation, PP and PS were dried in a vacuum oven at 80 °C for 24 hours. After the melt compounding, specimens for characterization were prepared by compression molding in a hot press.

An ARES rotational rheometer (Rheometric Scientific) was used to measure the complex viscosities of PP/PS blends and PP/PS/clay composites.

The frequency range was 0.1–500 s^{-1}, and the temperature was 200 °C. The measurements of the dynamic viscosities were performed with a parallel-plate fixture (diameter = 2.5 mm), gap distance of 1.2 mm, and strain was kept 10% to ensure linear viscoelasticity.

The morphology of the PP/PS blends was examined with scanning electron microscopy (SEM; S-2500C, Hitachi) at 25 kV. The samples were gold-coated before the examination. The mechanical properties were measured using a universal testing machine at 25 °C according to ASTM D638, and the head speed was 50 mm/min.

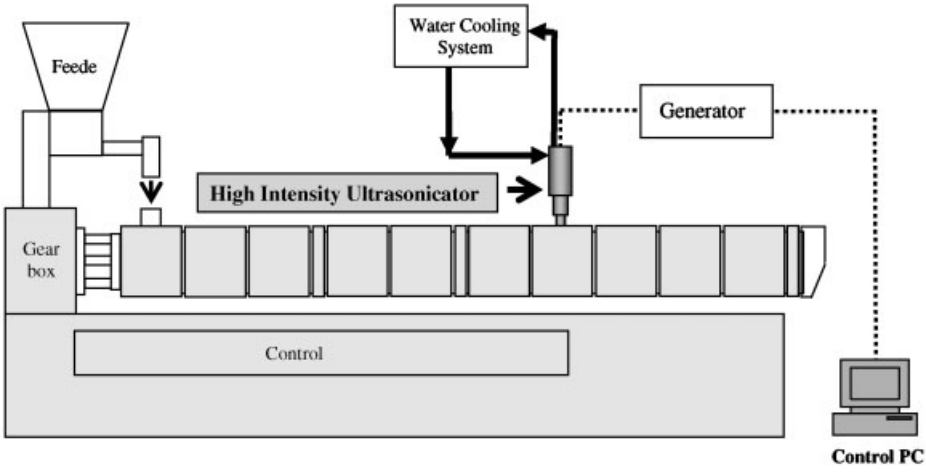

Figure 1.
Schematic diagram of twin screw extruder with high-intensity ultrasonic system.

Samples were prepared from 1.0 mm thick compression molding sheets, from which test specimens were cut using a die.

The analysis of delamination and dispersion of clay was carried out using X-ray diffraction (XRD, Rigaku D/Max-A). CuKα radiation ($\lambda = 1.540562$ Å), generated at a voltage of 40 kV was used as an X-ray source. The 2θ angles were varying between 1.5 and 10° at a scanning rate of 1°/min in order to measure the d_{001}-spacing between silicate layers.

A thermo gravimetric analyzer (TGA 2950, TA Instruments) was used to observe the thermal stability of PP/PS/clay nanocomposites.

The weight loss, which is the decomposition of organic materials due to the break of covalent bond at high temperature, was monitored with temperatures. The measurements were carried out under nitrogen flow at the heating rate of 20 °C/min in the temperature range of 30 ~ 600 °C.

Results and Discussion

Complex viscosities of PP/PS blends with and without sonication were represented in Figure 2. The complex viscosities of PP/PS = 25/75 and PP/PS = 75/25 lie between those of the neat PP and PS. When ultrasonic waves were dosed, the viscosities of PP/PS blends increased.

Figure 3 shows the SEM images of the PP/PS blends with and without sonication. The sonication led to decrease in the average domain size for each sample.

From the results of Figure 2 and Figure 3, it was believed that the in-situ copolymers between PP and PS macroradicals were formed during ultrasonic-assisted extrusion process.[12]

The formed copolymers at the interface would increase the interfacial viscosity by enhancing the entanglement between droplet and matrix.

The mechanical properties of PP/PS blends are represented in Table 1. The sonicated samples show 1 ~ 16% increases in stiffness, 5 ~ 8% increases in Young's modulus, and 12 ~ 25% increases in tensile strength.

To the author's knowledge, these increases of mechanical properties are unique properties by the formation of copolymers at the interface, and promise the effect of ultrasonic-assist during melt compounding.

Complex viscosities of PP/PS/clay composites with and without sonication were represented in Figure 4. As ultrasonic was dosed, the complex viscosities increased especially at low frequency ranges. The reason for this was believed to the increase

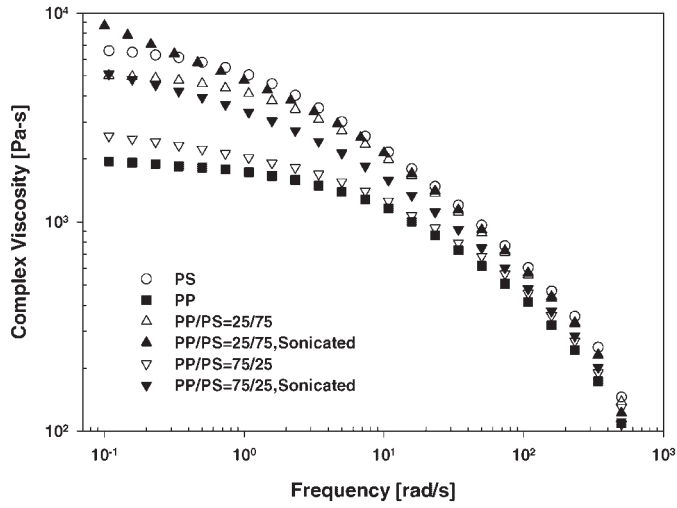

Figure 2.
The effect of ultrasonic dosage on the complex viscosities of PP/PS blends.

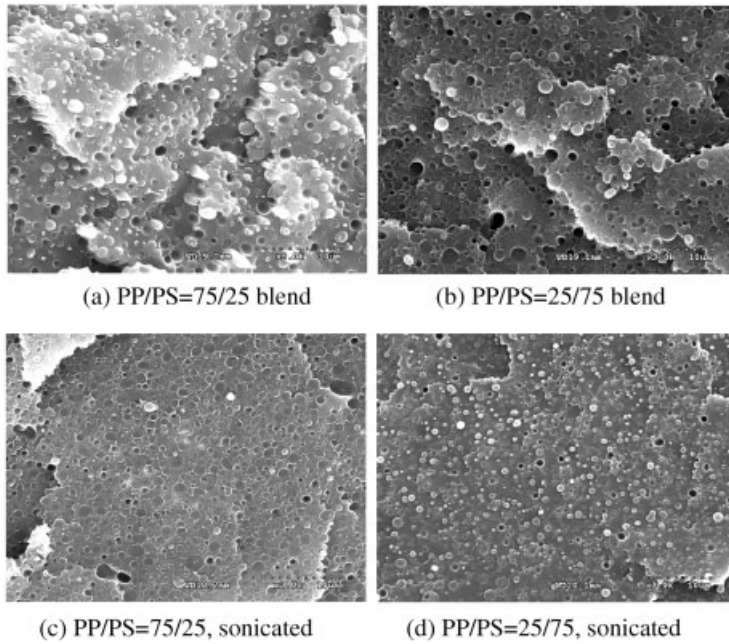

Figure 3.
SEM morphologys of PP/PS blends with the effect of ultrasonic dosage.

Table 1.
Mechanical properties of PP/PS blends with and without sonication.

	Stiffness [kN/m]	Young's Modulus [MPa]	Tensile Strength [MPa]
PP/PS = 75/25	202.5	792.0	29.8
PP/PS = 75/25,Sonicated	203.8	855.6	33.3
PP/PS = 25/75	209.6	1077.5	25.0
PP/PS = 25/75,Sonicated	242.8	1124.4	31.2

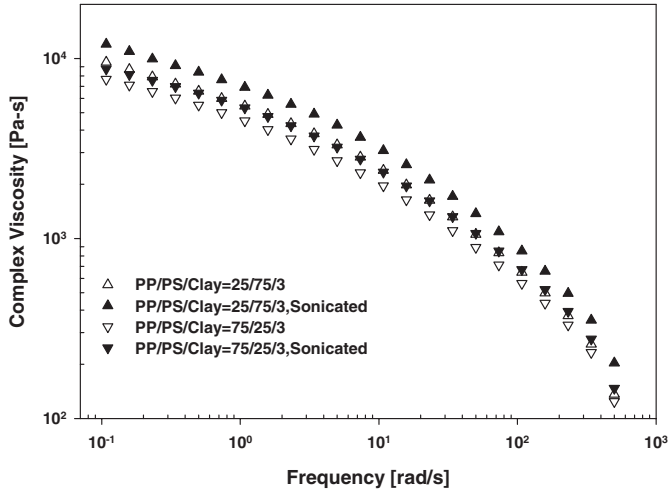

Figure 4.
The effect of ultrasonic dosage on the complex viscosities of PP/PS/clay composites.

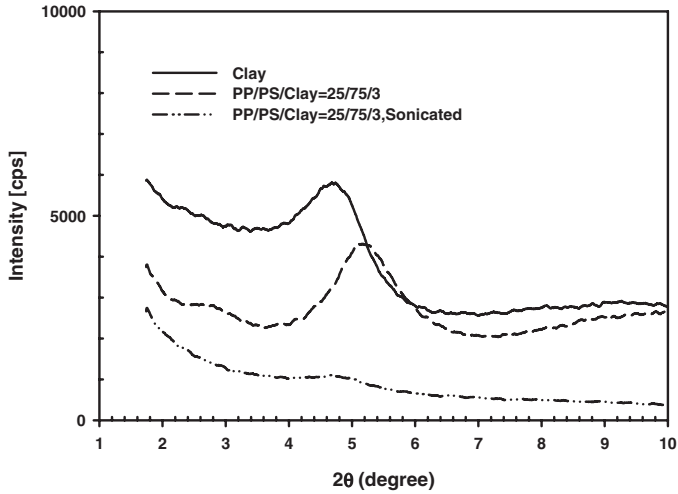

Figure 5.
XRD patterns of PP/PS/clay composites with and without sonication.

of interfacial energy due to the finely exfoliated nanoparticles with ultrasonic waves.

The dispersibilities of the clay layers in the PP/PS matrix were observed by XRD. Figure 5 shows the XRD patterns of Cloisite 10A, simply compounded and sonic dosed PP/PS/clay = 25/75/3 composites. Compared with Cloisite 10A, the simply compounded composite had the silicate layers still keep an ordered multi-layer structure. However, there were no peaks in the XRD patterns of the ultrasonic dosed PP/PS/clay composite. This indicates that the proper sonication during continuous extrusion could effectively exfoliate the layered clay without any compatibliizer.

Figure 6 represents the TGA analysis of simply compounded PP/PS/clay composite and sonicated PP/PS/clay nanocomposites.

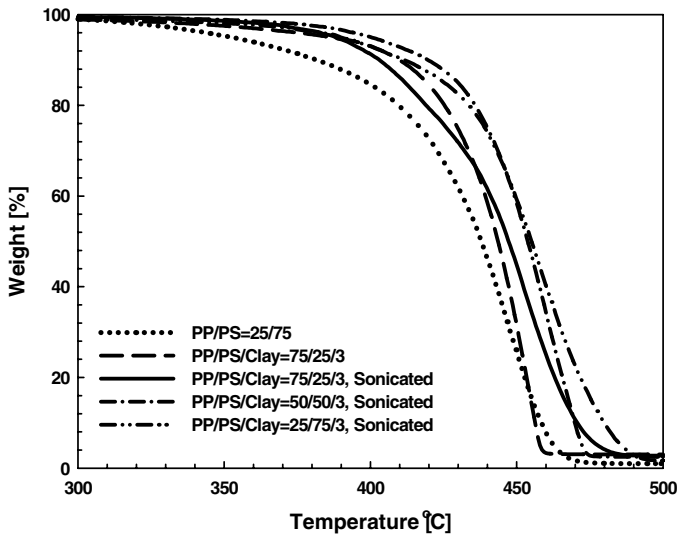

Figure 6.
TGA plots for PP/PS/clay composites with and without sonication.

In most cases, the incorporation of clay into the polymer matrix was found to enhance thermal stability. The clay acted as a heat barrier, which enhanced the overall thermal stability of the system, as well as assisted in the formation of char after thermal decomposition. The thermal stabilities of sonicated PP/PS/clay nanocomposites were enhanced compared to that by the simple extrusion. The increase of onset temperature of the degradation was around 10–20 °C higher for sonicated PP/PS/clay composite.

Conclusions

PP/PS/clay nanocomposites were successfully obtained by the continuous compounding with high intensity ultrasonic waves. The sonic wave was dosed during extrusion process and provided an effective route to accomplish the nano-scale dispersion of the layered silicates in the PP/PS/clay nanocomposites. From the rheologial property, mechanical property, XRD pattern, morphological and thermal stability measurements, the sonication was effective in enhancing the interfacial interaction between the immiscible polymer blend, breakup of the clay agglomerates, and as a result, exfoliated the clay layers in the PP/PS matrix.

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