

Morphology and mechanical properties of LDPE/PS blends prepared by ultrasound-assisted melt mixing

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Abstract

Ultrasound-assisted melt mixing was applied to blending polystyrene (PS) and low density polyethylene (LDPE). The influence of the ultrasonic irradiation on the morphology and mechanical properties of the blends was investigated. It was observed that the domain sizes of the blend were significantly reduced and phase stability was well sustained even after a thermal treatment. Such morphological feature was consistent with the improvements in mechanical performance of the blends. The desirable results of ultrasonic compatibilization are mainly attributed to the in-situ formation of PS-LDPE copolymers as confirmed by a proper separation experiment. An important relationship between ultrasonic irradiation time and mechanical properties is revealed and an issue on the thermal stability of the blend is discussed.

Keywords : LDPE, PS, polymer blend, power ultrasound, in-situ compatibilization

1. Introduction

Polystyrene (PS) and polyethylene (PE) are widely used plastics. PS possesses high modulus and high tensile strength; however, it is brittle and easy to crack. On the other hand, PE shows high toughness and good impact performance even at low temperature. But, owing to the great differences in chemical structure, solubility and crystallinity, PS and PE are incompatible and their simple blends exhibit weak interfacial adhesion and inferior stability of the phase dispersion, leading to very poor mechanical properties (Lindsey *et al.*, 1981; Teh and Rudin, 1991).

Polymer blending is a useful approach for the preparation of new materials with specially tailored or improved properties that are often absent in the single component polymers. Enhanced properties of polymeric materials are achieved by developing multi-component system in the form of polymer blends composed of two or more homo-polymers (Paul and Bucknall, 1999). Final performance of polymer blends are closely related to their morphology and the evolution of phase morphology of polymer blends is influenced by numerous factors including type of imposed flow field (elongation or shear), interfacial tension, and the viscosity ratio of components (Wu, 1987; Favis and Therrien,

1991; Sundararaj *et al.*, 1995; Oh *et al.*, 2001). Since most of the polymer pairs exhibit weak interfacial interaction, which leads to a coarse morphology and poor mechanical properties, it is necessary to achieve compatibilization by adding a block or graft copolymer to the system, or by inducing chemical reaction between the components, leading to modification of the polymer interfaces in two-phase blends. However, these methods are often limited by the available reactivity of polymers and difficulty of the synthesizing block copolymers (Chen *et al.*, 2002).

In our previous study (Kim and Lee, 2002), we intended to induce degradation in polypropylene (PP) melt without any solvents. An important consideration was to investigate whether the ultrasound-aided degradation is possible during melt processing of polymer in a batch mixer. It was found that this process can be used to control the rheological properties of PP in the absence of other chemical agents. In addition, since cleaving bonds can create reactive macromolecules (or macroradicals), it was also expected and confirmed that direct mutual coupling between different radicals of PP and polystyrene (PS) is possible.

In this study, we attempted in-situ compatibilization of PS/LDPE by using high intensive power ultrasound during melt mixing in an internal mixer. By diversifying the combination of polymers to be processed, we tried to add further confirmation on the utility of the prepared method

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demonstrated previously (Ryu *et al.*, 2001; Xu *et al.*, 1999). A major purpose of this study was to investigate the effect of sonication time on the mechanical properties and morphology of PS/LDPE blends.

2. Experimental

2.1. Sonicated melt-mixing

Polystyrene (PS) and Low Density Polyethylene (LDPE) were supplied by LG chemicals. In order to impose ultrasonic wave during melt mixing, a specially designed ultrasonic horn was attached to Haake mixer. The horn vibrated longitudinally at a frequency of 20 kHz with amplitude of 15 μm . A 1.5 kW power supply with a piezoelectric converter was used. The on/off ratio of ultrasonic irradiation was fixed as 7:3. Prior to mixing operation, pure resins were dried in a vacuum oven at 70°C for 24 hours. Each sample was prepared on a fixed volume basis of 70% and mixing temperature was 180°C. The content of the blend was fixed as 80/20 (PS/LDPE) by weight fraction. Before the irradiation of ultrasound, preliminary mixing was carried out for 1 min to reach the molten state. As an indication for the viscosity variation induced by sonication, torque data were collected throughout the mixing process.

2.2. Measurements

In order to assure the formation of the PE-PS copolymer, the reaction products were put into a proper separation procedure, by which unreacted PS was separated from the mixture. After the mixing process, the samples were immersed into THF and filtered in order to extract PS. Then the remaining sample containing PE and PE-PS copolymer was washed by a Soxhlet extraction with THF for 48 hrs and dried in a vacuum oven at 343 K for 24 hr. The existence of PS units grafted to PE chains was inves-

tigated by Fourier transform infrared spectroscopy (FTIR, Shimadzu 8501).

For detail investigation on time dependency of mechanical properties, samples were collected in every 30 sec during 5 min of mixing. Mixing times were increased up to 20 min for the analysis of domain size variation. The domain size of the 80/20 (PS/LDPE) blends was investigated by SEM micrograph (HITACHI S-2500). These samples were prepared by quenching in the liquid nitrogen and subsequent fracturing. Standard specimens (ASTM D638) were used for tensile measurements. Tensile testing was performed in a materials testing machine (Lloyd Instruments, Model-LR5K), with a crosshead speed of 20 mm/min at room temperature. Notched Izod impact strength was determined by the impact tester (Ceast, Code 6545). In order to assure the *in-situ* compatibilization, the samples were put into a proper annealing procedure, where each blend was stored in an oven for 5 – 20 min at a temperature of 200°C and then poured into a bath of cold water to prevent further morphology change. By observing the changes in the domain sizes after the annealing, we can confirm the desired effect of compatibilization since significant coalescence is typically promoted in immiscible polymer blends during the thermal treatment. Plate-plate rheometer (ARES, Rheometrics Scientific) was used to measure the rheological behaviors of sonicated samples at 10% strain rate. The geometry was parallel plate with 25 mm diameter and 1.5 mm gap size. The frequencies were in the range of 0.1 ~ 400 rad/s. The thermal gravimetric analyzer (TGA, TA instrument. TGA 2950) was used to estimate the thermal stability of the blends.

3. Results and discussion

Fig. 1 shows torque variation measured during melt pro-

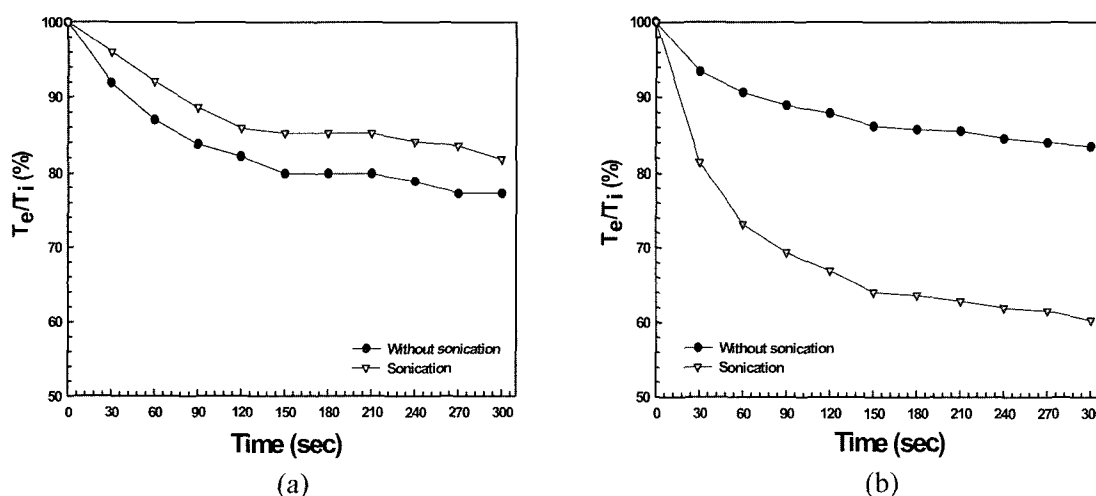


Fig. 1. Comparison of torque variations between simple mixing and sonicated mixing: (a) LDPE (b) PS (T_i = initial torque, T_e = torque measured during mixing).

cessing of LDPE and PS, respectively in the sonicated mixer. The relative percentages (T_e/T_i in graph) of torque values were calculated starting from a point (time zero) after the 1 min of preliminary mixing. In case of LDPE, compared with simple mixing, sonicated mixing yielded higher torque values, indicating that ultrasound-induced structural change was occurring in LDPE molecules. It is widely accepted that free-radical reactions contribute to PE crosslinking on gamma irradiation or peroxide incorporated shear mixing (Singh, 1999). A similar argument is pertinent here, as ultrasound passing through the molten medium induces generation of LDPE macroradicals and possibly other types of free-radical species such as allyl radicals, alkyl radicals and peroxy radicals, etc.. Accordingly, the observed torque rise is associated with ultra-

sound-induced crosslinking of PE chains. Contrary to PE, the level of the torque was lowered in PS, which is indicative of degradation of PS during sonication. The results found in Fig. 1 may be associated with the chain structure of the polymer under ultrasonic irradiation; according to the long chain branching in LDPE, crosslinking between macroradicals can be facilitated, while main chain scission prevails in linear chains of PS. These results constitute an important basis for in-situ compatibilization of LDPE/PS blends by confirming ultrasound-initiated generation of macroradicals of each component.

Figs. 2 and 3 depict the morphology of blends developed in simple mixing and ultrasound-assisted mixing, respectively. It is apparent from these figures that simple mixing yielded coarse morphology with large domain size, while

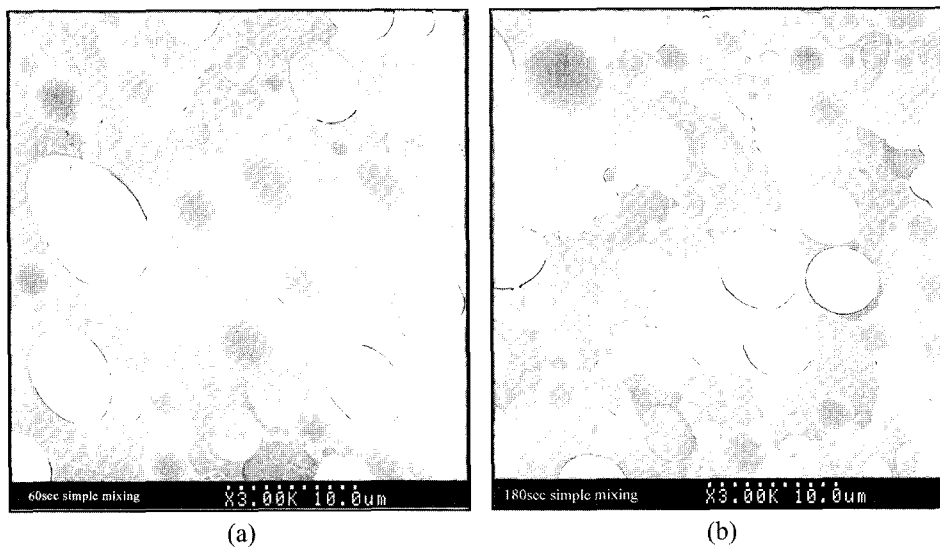


Fig. 2. SEM micrographs of PS/LDPE blends (simple mixing): (a) 1 min (b) 3 min.

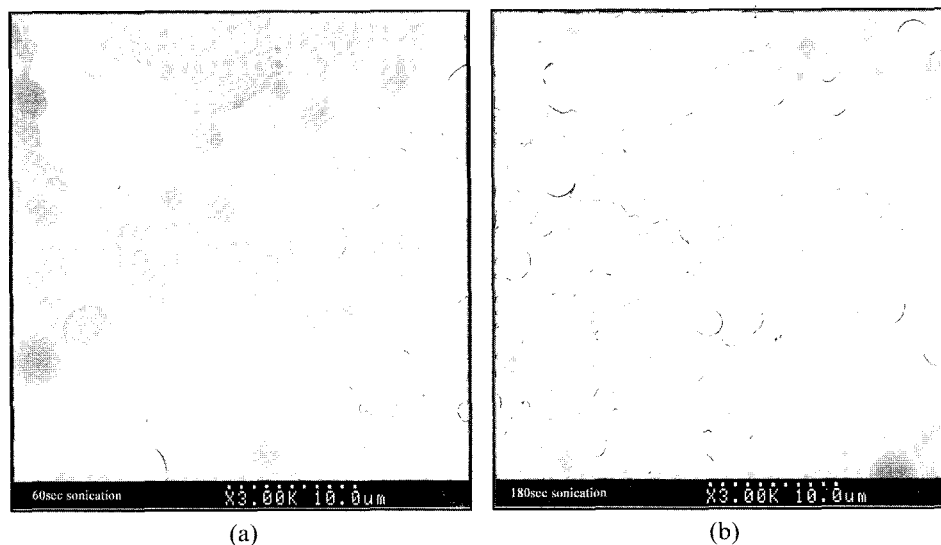


Fig. 3. SEM micrographs of PS/LDPE blends (sonicated mixing): (a) 1 min (b) 3 min.

more uniform dispersion and reduction of phase size were achieved by ultrasound-assisted mixing. In Fig. 4, average domain sizes were measured from the collection of SEM pictures and plotted as a function of mixing time. The data show that average particle sizes of the blends prepared by simple mixing were significantly increased especially for mixing times longer than 600 sec., whereas such serious enlargement of domains was not occurred in sonicated mixing, regardless of mixing duration. The enlargement of domains observed in simple mixing is the consequence of coalescence among domains, which is typically observed in melt mixing of immiscible blends. It is noted that the domain sizes of sonicated blend were fluctuating along with the sonication times, maintaining smaller sizes than those of simple blend. The trend found in Fig. 4 reveals that coalescence of the domains was inevitable due to the inherent incompatibility in PS/LDPE blend. Such tendency was successfully suppressed by sonicated melt mixing,

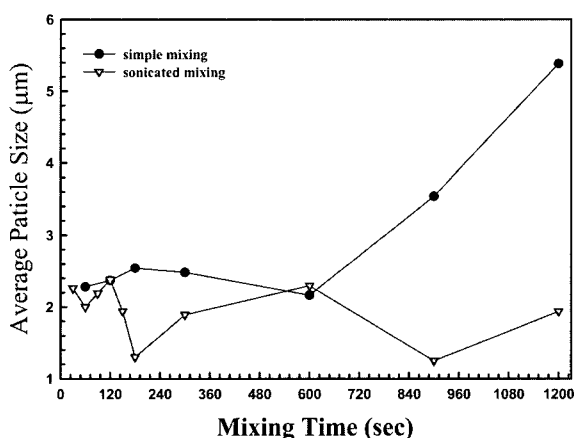


Fig. 4. Effects of power ultrasound on the particle size of PS/LDPE blends.

which is indicative of effective compatibilization. As demonstrated in previous papers (Chen *et al.*, 2002; Kim and Lee, 2002; Kim *et al.*, 2002), it is believed that ultrasonic irradiation promoted formation of LDPE-PS copolymers by mutual coupling of their macroradicals, which in turn acts as compatibilizing agents for the blends by lowering interfacial tension of the system and efficiently preventing coalescence of domains as well. Depending on the source of the radicals, either block or graft copolymers of PE and PS can be made by mutual combination of PE and PS macroradicals. Although exact distinction for the types of the copolymers is not available, an evidence for the copolymer formation was found in the FTIR analysis of samples prepared by removing ungrafted PS from the reaction products. As shown in Fig. 5, the C=C stretching vibrations of a PS benzene ring appeared at 1600 cm^{-1} , which confirms the existence of PS component grafted to PE chains. It is worthy to point out that the intensity of the characteristic

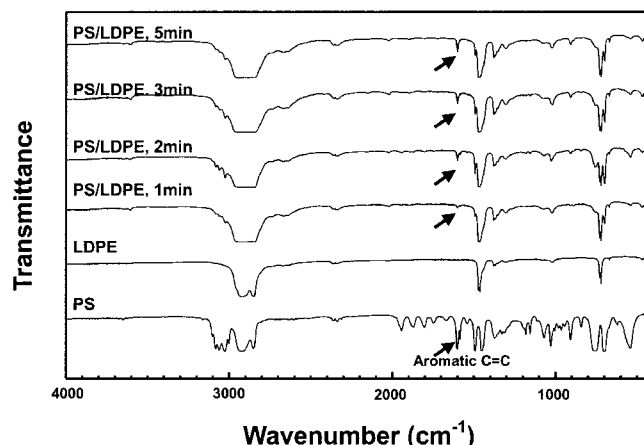


Fig. 5. FTIR spectra of LDPE, PS, and their blends for various sonication time (after 2 days of extraction).

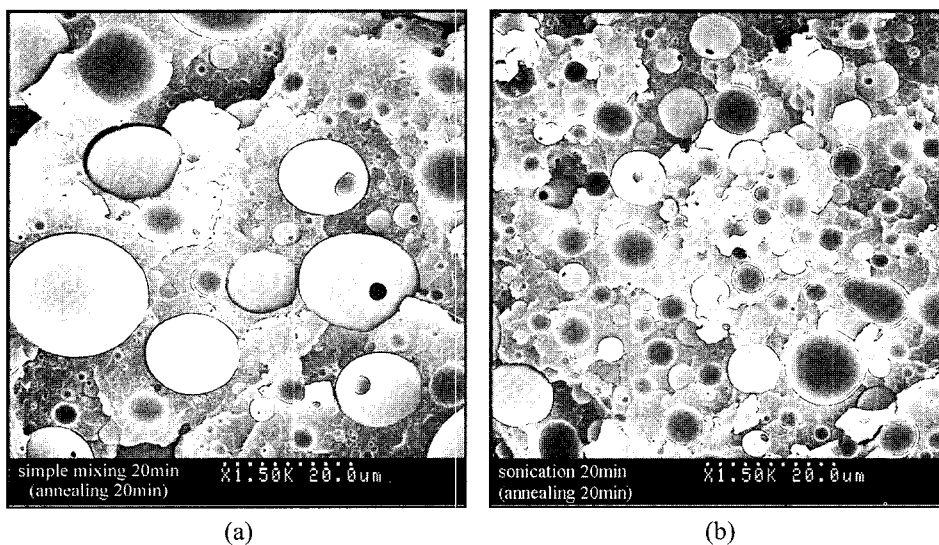


Fig. 6. SEM micrographs of PS/LDPE blends after annealing of 20 min: (a) simple mixing (b) sonicated mixing.

peak increases as the sonication time increases, which is of critical importance in the interpretation of mechanical property data, as will be discussed later.

In order to further confirm the stability of the morphology of sonicated blends, samples were annealed during 20 min at 200°C, and the results are shown in Fig. 6. It is clearly seen that coalescence was considerably suppressed in the sonicated blend, while the domains were considerably enlarged in the blend prepared from simple mixing. Copolymers formed at the interface would in principle increase the interfacial viscosity by enhancing the entanglement between domain and matrix. Accordingly, the coalescence can be prevented by steric interactions which limit the drainage of matrix fluid, as reported elsewhere (Sundararaj and Macosko, 1995).

The effect of sonication time on the mechanical properties of the blends is demonstrated in Fig. 7. For those blends formed from simple mixing, impact strength was little affected by the increase of mixing time. By contrast, impact strength appears to be dependent on the sonication time; maximum value was obtained at 180 sec throughout

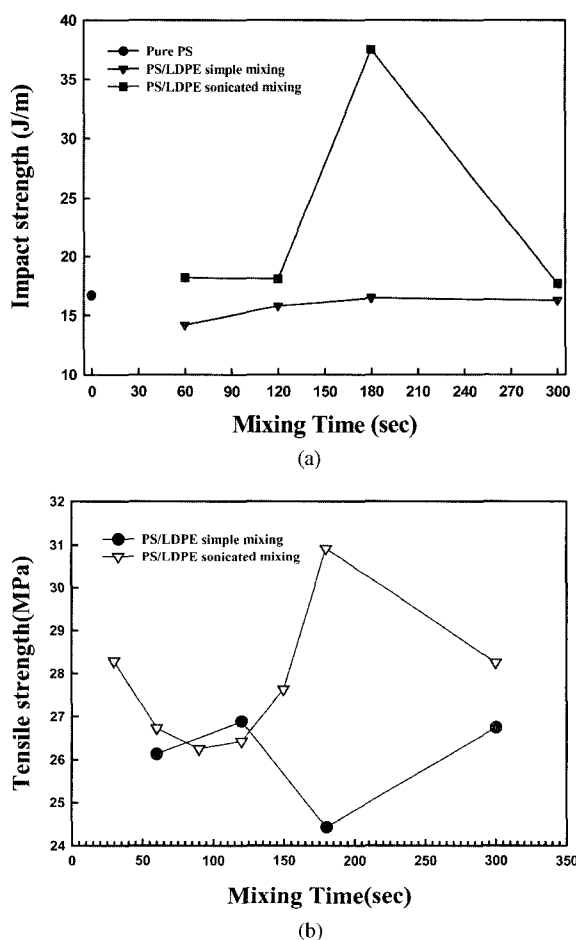


Fig. 7. Effects of power ultrasound on the mechanical properties of LDPE/PS blends: (a) Impact strength (b) Tensile strength.

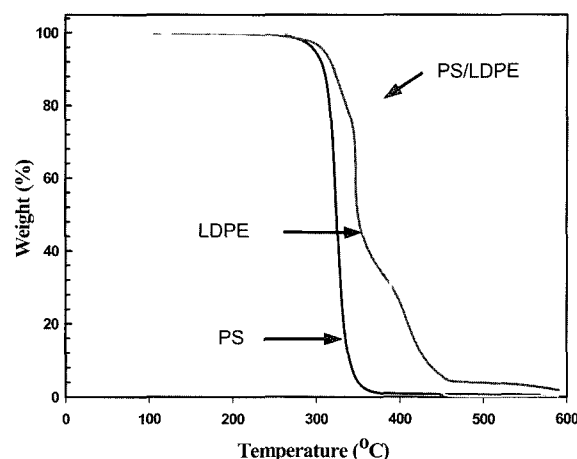


Fig. 8. TGA data for LDPE, PS and LDPE/PS blend (3 min sonication).

300 sec of sonication. During the early period of sonicated mixing, tensile strength was decreased within 100 sec, but it started to increase and reached a maximum value around 180 sec of sonication. The observed time dependency of the mechanical properties reflects the characteristic feature of ultrasonic compatibilization: Enough amount of macroradicals should be generated for the sufficient copolymer formation, meanwhile, excessive chain breakage can cause reduction in mechanical strength by lowering entanglement density of the entire system. Accordingly, it is considered that the optimum sonication time for the improvement of mechanical properties is associated with the combined effect of chain scission and recombination of dissimilar radicals under sonication. Along with the morphology analysis, investigation of the mechanical properties strongly supports that copolymers of LDPE-PS fortify the PS/LDPE interphase leading to blend compatibilization.

TGA data of LDPE, PS and their blend are demonstrated in Fig. 8, where sonicated blend reveals greater thermal stability compared to neat polymers. Based on the fact that the underlying mechanism of ultrasonic compatibilization is attributed to mechanochemical degradation of polymer chains, one might be concerned with deterioration of thermal stability after ultrasonic treatment of the blends. However, no such adverse effect is found, as shown in Figure 8. The remarkable improvement of thermal stability in sonicated LDPE/PS blend is mainly ascribed to partial crosslinking of LDPE chains and their coupling with PS chains as well.

4. Conclusions

By using high intensity ultrasonic wave, it was possible to induce chain scission of PS or crosslinking of LDPE in melt state without any solvents or additives. In melt mixing of the PS/LDPE blend, irradiation of ultrasonic wave led to

generation of PS-LDPE copolymers by combination of the corresponding macroradicals, as identified from FTIR after a proper separation procedure. It was revealed from the morphology analysis and mechanical testing that the blend of PS and LDPE was successfully compatibilized by imposition of ultrasonic energy during melt mixing process. Under the given sonication environment, maximum mechanical properties of sonicated blends were obtained for a specific sonication time which enables well-balanced degradation for sufficient copolymer formation within the limit of mechanical strength of polymers. It was also emphasized that thermal stability of the PS/LDPE blend was ameliorated by ultrasonic irradiation, which is of critical importance in practical application of polymeric materials.

It is suggested that ultrasonically assisted melt processing would offer an efficient route to control the rheological properties of polymers and to compatibilize immiscible polymer blends without the aid of compatibilizers.

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