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Effect of ultrasonic wave on the degradation of polypropylene melt and morphology of its blend with polystyrene

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Abstract

A new method using high intensity ultrasonic wave has been developed for the degradation of polymer melt in an intensive mixer. For the effective transfer of ultrasonic energy, experimental apparatus was specially designed so that polymer melt can be in direct contact with the ultrasonic horn. In this research, we observed that the significant degradation of polypropylene (PP) melt in a mixer occurs due to the action of ultrasonic wave without any aid of additives or solvents. To compare the degradation efficiency of ultrasonic irradiation with that of peroxide, additional experiments were performed to practice the peroxide-aided degradation by mixing 1 part of dicumyl peroxide with PP in the mixer. It was also found that the direct sonication on polymer mixture in melt state reduces the domain sizes and stabilizes the phase morphology of the blend. It is suggested that ultrasound assisted melt mixing can lead to in situ copolymer formation between the components and consequently provide an effective route to compatibilize immiscible polymer blends. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ultrasounic wave; Degradation; In situ copolymer formation

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1. Introduction

High intensity ultrasonic waves are generally employed in the areas of cleaning, plastic welding, machining, etc. In addition to these conventional applications, numerous studies have suggested a new possibility as a useful way to induce mechano-chemical degradation in polymeric materials [1–4]. It was observed that if polymer solution is subjected to irradiation of high intensity ultrasonic waves, main-chain scission of polymer chains occurs and consequently the molecular weight is decreased [5]. The relevant mechanism for the observed phenomena is explained by the interaction of ultrasound and component molecules. In a liquid, upon irradiation of ultrasound, molecules are exposed to alternate compression and expansion modes, by which bubbles are formed and eventually collapsed. At the molecular level, this implies a rapid motion of solvent molecules to which the macromolecules embedded in the solvent cannot adjust. Thus, friction is generated which causes strain and eventually bond rupture in the macromolecules. According to this principle, most studies have concentrated on the effects of sonication on the degradation of polymers in solution [6].

In the present study, we intended to induce degradation in polymer melt without any solvents. An important consideration here was to investigate whether the ultrasound-aided degradation is possible during melt processing of polymer in a batch mixer. Provided the intended degradation is feasible, it is expected that this process can be used to control the rheological properties of polymers in the absence of other chemical agents. In addition, cleaving bonds can create reactive macromolecules (or macroradicals), which will react with other compounds to form copolymers that otherwise could not be readily obtained. This leads to an important consequence since in situ copolymer formation is an efficient path to compatibilize immiscible polymer blends and stabilize their phase morphology under successive processing.

In this study, polypropylene (PP) melts having different initial molecular weights were subjected to ultrasonic irradiation. As is well known, peroxide-aided degradation of PP is widely practiced for various purposes. Thus, it would be meaningful to compare the effectiveness of degradation between the present approach and the conventional method. For the in situ copolymer formation, polystyrene (PS) was melt mixed with PP under sonication. It was expected that

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the copolymer of PP and PS could be produced by coupling of the corresponding macroradicals. Such copolymers would play an important role in compatibilization of PP/PS blend during melt mixing.

2. Experimental

Two grades of isotactic PPs, designated as PP-H and PP-L, were used in this study. They were kindly supplied from Daelim Industrial Co. of Korea with a melt index (230 °C, 2.16 kg) of 60 (PP-H) and 800 (PP-L), respectively. PS was obtained by polymerizing styrene with azobisisobutyronitrile (AIBN) at 60 °C in bulk. The number average molecular weight of PS was 180,000 g/mol with a polydispersity index of 2.0 as determined by GPC. For the controlled degradation of PP by peroxide, 1 phr of dicumyl peroxide (DCP) was melt mixed with PP-L for 10 min at 180 °C. The processing speed was 120 rpm.

In order to impose ultrasonic wave during melt mixing, a specially designed ultrasonic horn was assembled with a Haake mixer. A schematic diagram of the sonicated mixer is shown in Fig. 1. For durable operation, an effective cooling accessory was necessary. The horn vibrated longitudinally at a frequency of 20 kHz with an amplitude of 30 μm. A 1.5 kW power supply with a piezoelectric converter was used. Each sample was prepared on a fixed volume basis of 70% and loaded at 200 °C with a rotor speed of 75 rpm, unless mentioned. Sonication times investigated were 10, 15, 20, 25 and 30 min. Various filling percentages and rotor speeds were used to observe the effect of energy density on the degradation behavior of polymer melt. Prior to mixing, samples were dried in a vacuum oven at 80 °C for 24 h.

Samples obtained from the internal mixer were compression molded to produce disk shaped specimens with a thickness of 2.5 mm and diameter of 25 mm. Advanced Rheometrics Expansion System (ARES, Rheometrics Co.) using the dynamic oscillatory mode with parallel plate fixture of 25 mm was employed to measure the complex viscosities ($\eta^*(\omega)$) at wide ranges of frequencies (ω). A scanning electron microscope (SEM, Jeol JSM-840A) was used to investigate the morphology of the blends after the fracture surface of the specimen was coated with a thin layer of gold.

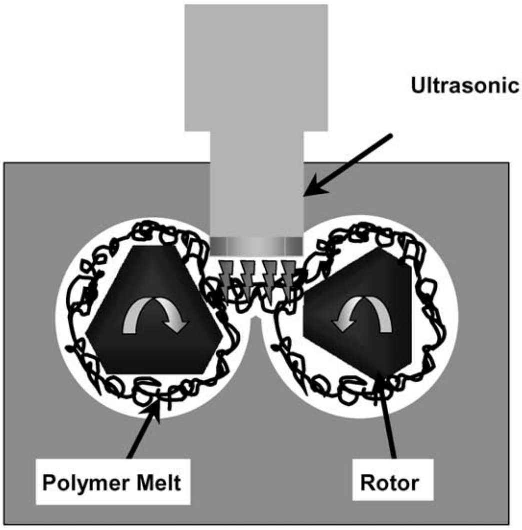

Fig. 1. Schematic description of the intensive mixer equipped with an ultrasonic horn.

In order to assure the formation of the PP–PS copolymer, the reaction products were put into a proper separation procedure, by which PS homopolymer (or free PS) and PP–PS copolymer were separated. After mixing, the samples were immersed in THF and filtered in order to extract the free PS. The sample of PP–PS copolymer was washed by a Soxhlet extraction with THF for 24 h and dried in a vacuum oven at 343 K for 24 h. The existence of PS units grafted to PP chains was investigated by Fourier transform infrared spectroscopy (FTIR, Shimadzu 8501).

3. Results and discussion

Fig. 2 shows the way in which the complex viscosities of the polymers are affected by irradiation of ultrasonic wave. Here, the viscosity ratios of sonicated polymer to the neat one, which were measured at a frequency of 10 rad/s, were plotted as a function of time in order to trace the evolution of degradation. It is clearly seen that the viscosities of both PPs decreased with increase in sonication time. In case of PP-L, it appears that the ratios are higher than those of PP-H, for the given sonication times. From the trend shown in Fig. 2, it is worthy to note that the degradation rate was influenced by the molecular weight of the sample, since increased mobility of the macromolecules favors harmless energy dissipation. In other words, the influence of the characteristic movements in ultrasonic wave is relatively weak and the efficiency of degradation is limited in case of low viscosity matrix. Of considerable relevance to the present discussion is the effect of the relaxation time of the melt.

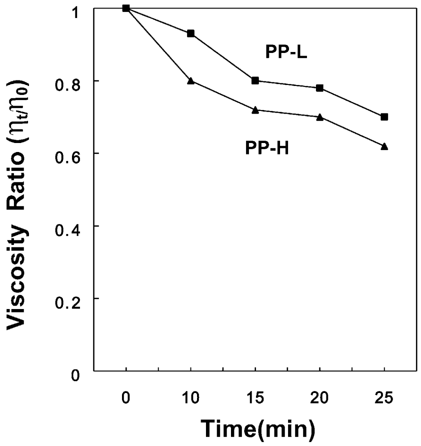

Fig. 2. Viscosity ratios versus sonication time for PP-L and PP-H.

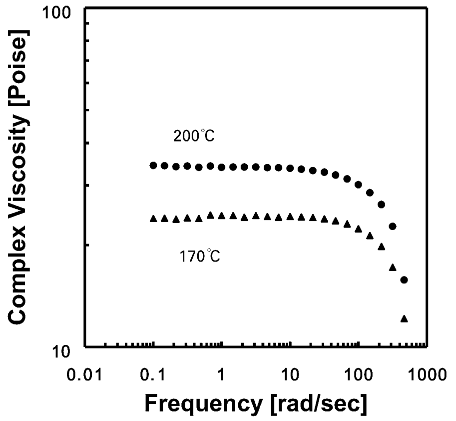

Fig. 3. Effect of mixing temperature on the viscosity of PP-H after 10 min of sonication (rotor speed = 90 rpm).

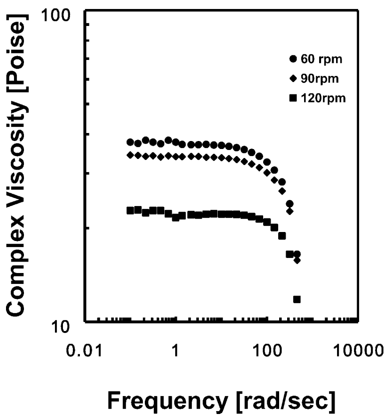

Fig. 4. Effect of rotor speed on the viscosity of PP-H after 10 min of sonication.

Since the relaxation time is temperature dependent, this could be manifested by the experiment conducted at a different temperature for 10 min of sonication. As shown in Fig. 3, the viscosities of PP-H were further reduced when the processing temperature was lowered to 170 °C. An important consideration here is the underlying mechanism of ultrasonic degradation in polymer melt. As described earlier in Section 1, the main impetus for the ultrasonic degradation in polymer solution is ascribed to the cavitational effects initiated in the liquid phase. In melt processing of polymers without any solvents, however, such a consequence is hardly expected. Accordingly, we propose a plausible mechanism in conjunction with the viscoelastic nature of polymer melt. As noticed from the given frequency of the ultrasonic wave, the time between successive expansion and compression is considerably less than the order of the relaxation time of the melt (typically order of few seconds at the processing temperature) [7]. Thus, the melt, unable to relax between successive ultrasonic waves, experiences a stepwise increasing stress and eventually the chains break. Based on this rationale, retarded degradation at higher melting temperature is explained by reduced relaxation time of the melt. A similar issue has been raised in a study on the dispersion characteristics of polymer blends by using the enhanced mixing simulator (EMS). In EMS, the Couette type flow is combined with the periodic cross flow, generated by the reciprocal movement of two pistons. The evolution of dispersive mixing was strongly dependent on the frequency of the stroke [8].

Fig. 4 describes the effect of rotor speed on the efficiency of ultrasonic degradation. As the rotor speed is increased, the viscosities decrease. In addition, the viscosity ratio increased from 0.75 to 0.92 when the filling percentage was varied from 50 to 90; this is because the energy density decreases as the filling percentage becomes higher. It seems that overall degradation is in part facilitated by the additional energy uptake from the shearing action.

Fig. 5 demonstrates the change in viscosity of PP-L caused by the addition of 1 phr of DCP during melt mixing. For a comparison with the present method, the data for PP-L sonicated during 15 and 25 min were plotted together. For the given sonication capability in this study, it is noted that comparable or more effective degradation is possible by irradiating ultrasonic wave. Of course, the resulting viscosity reduction from each degradation scheme depends on either the available energy density or the amount of peroxide.

The SEM images of the PP-H/PS (30/70) blends that were sonicated for various times are shown in Fig. 6. It was observed that the increased sonication time leads to a decrease in the average domain size for each sample. In contrast, as shown in Fig. 7, a SEM image of the sample from simple mixing for 30 min revealed a coarse morphology with agglomerated structure. Based on numerous studies [9–12], it is generally recognized that the morphology development in immiscible blends accompanies coalescence of discrete domains. The qualitative aspect of flow induced coalescence in immiscible polymer blends is well described by a three-step mechanism [13]. According to the mechanism, when the dispersed droplets are brought close together by the flow field, the matrix film between the drops becomes thinner until the interface ruptures and then

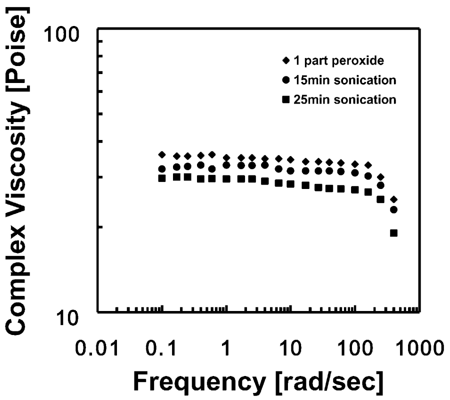

Fig. 5. Comparison between peroxide-aided degradation and ultrasonic degradation of PP-L.

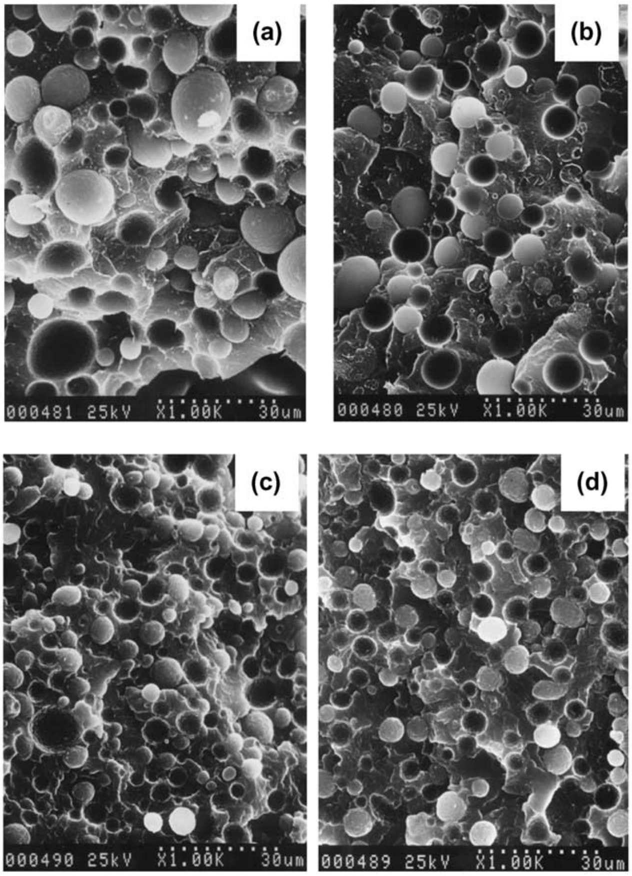

Fig. 6. SEM micrographs of PP-H/PS (30/70) blends. The sonication time was: (a) 0 min, (b) 10 min, (c) 20 min, and (d) 30 min.

coalescence occurs. Prevention of coalescence is of paramount importance in processing of immiscible blends, since mechanical properties of molded articles are significantly deteriorated unless the phase morphology is properly stabilized [14–17]. It is clearly seen from Figs. 6 and 7 that both the stability of the phase morphology and the reduction of phase size were achieved by ultrasonic-assisted mixing.

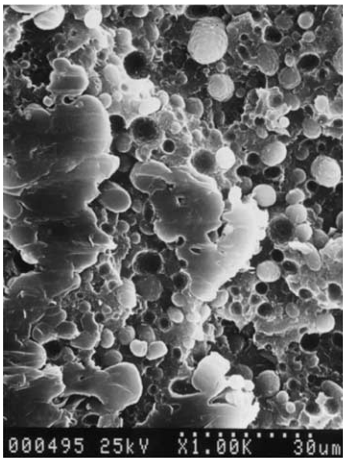

Fig. 7. SEM micrograph of PP-H/PS (70/30) blend obtained from simple mixing of 30 min.

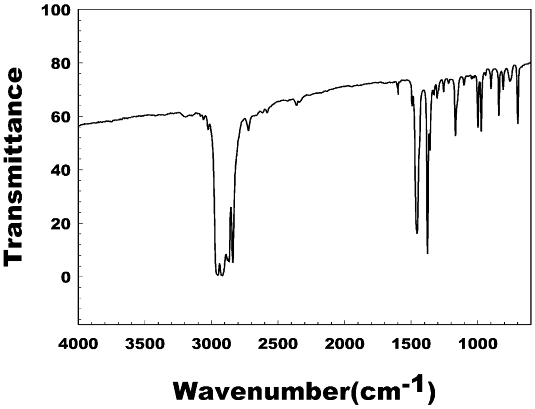

Fig. 8. FTIR spectra of PP–PS copolymer obtained from 30 min sonication of PP/PS blend.

Obviously, such effects are ascribed to the in situ copolymer formation between PP and PS macroradicals that occur during sonication in the melt. Copolymers formed at the interface, in principle, would increase the interfacial viscosity by enhancing the entanglement between domain and matrix. Accordingly, the coalescence can be prevented by limiting the drainage of matrix fluid [18]. 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 free PS from the sonicated mixture of PP and PS. As shown in Fig. 8, the CH bending vibration of a PS benzene ring appeared at 700 cm^{-1}, which confirms the existence of PS component grafted to PP chains [19].

4. Conclusions

By using high intensity ultrasonic wave, it was possible to induce chain scission of the polymers in melt state without any solvents or additives. Depending on the available energy uptake, the extent of the degradation appears to be practically acceptable, compared to the peroxide-aided degradation of PP. Obviously, numerous factors including de-excitation by recoupling of macroradicals or generation of radical species via chemical route are involved in ultrasonically assisted melt processing. Accordingly, it would be a difficult task to fully understand the results found from the current study. Nevertheless, we believe that the visco-elastic nature of the polymer melts plays an important role in ultrasonic degradation.

In melt mixing of the PP/PS blend, irradiation of ultrasonic wave led to stable morphology with reduced phase size of the domain. It is inferred that copolymers of PP and PS were formed by combination of the corresponding macroradicals and consequently act as compatibilizers for the blend. It is emphasized that ultrasonically assisted melt processing would offer an efficient route to control the rheological properties of polymers or to compatibilize immiscible polymer blends, which are not readily compatibilized otherwise.

Acknowledgements

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