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초음파가 가진되는 용융혼련에 의한 비상용계 고분자 블렌드의 상구조전개

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Evolution of Phase Morphology and In-situ Compatibilization of Polymer Blends During Ultrasound-Assisted Melt Mixing

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Introduction

High intensity ultrasounds, as compared with diagnostic ultrasounds, are generally at lower frequency where greater acoustic energy can be generated to induce cavitation in liquids. They are widely employed in the areas of biology, cleaning, plastic welding, and machining, chemical reactions, and so on. In addition to these conventional applications, numerous studies have suggested a new possibility as a useful way to induce mechanochemical degradation in polymeric materials (Price, 1992). It was observed that if polymer solution is subjected to the irradiation of high intensity ultrasonic waves, main-chain scission of polymer chains occurs and consequently molecular weight is decreased (Schnabel, 1981; Suslick, 1990).

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 dierect mutual coupling between different radicals of PP and polystyrene(PS) is possible. 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, we intended to expand our previous study by employing various pairs of immiscible blends based on PP, PS, polymethyl methacrylate(PMMA) and polycarbonate(PC) . A major interest of the present work was to investigate the effect of viscosity ratio between domain and matrix on the degree of compatibilization.

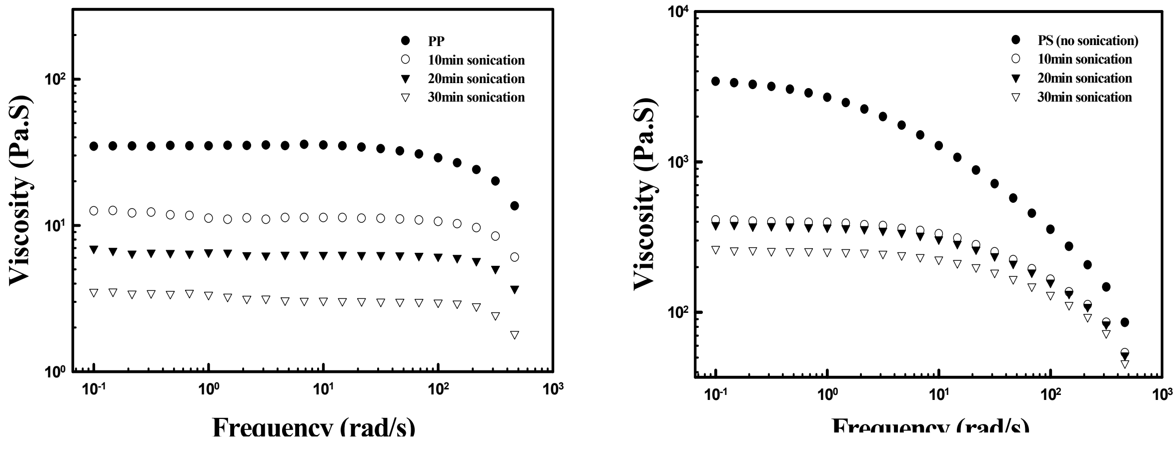
Experimental

The materials used in this study are all commercially available polymers and they are supplied in the form of powder or granule. 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 can be found elsewhere (Kim and Lee, 2002). For durable operation, an effective cooling accessory was necessary. The horn vibrated longitudinally at a frequency of 20 kHz with an amplitude of 23 ㎛. 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℃ with a rotor speed of 75 rpm unless otherwise mentioned. Before the irradiation of ultrasound, preliminary mixing was carried out for 2 min to reach the molten state. Sonication times investigated were 10, 20, 30 min.. The ultrasonic irradiation was imposed at 50% of the maximum output of the generator. Prior to mixing, samples were dried in a vacuum oven at 80^{o}C for 24 hrs.

Samples obtained from the internal mixer were compression molded to produce disk shaped specimens with 2.5 ㎜ in thickness and 25 ㎜ in diameter. 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.

Results and Discussion

Fig. 1 shows how the complex viscosities of PP and PS are affected by irradiation of ultrasonic wave. It is consistent with the previous results (Kim and Lee, 2002) and clearly seen that the viscosities of both PP and PS decreased with increased sonication time. Within the available sonication times of 30 min, it appears that the degradation of PP is proceeded in step with the sonication times, while that of PS is somewhat delayed after a significant drop in viscosities for 10 min of sonication. The tendencies found in Fig.1 indicate that the degradation of PP chains are

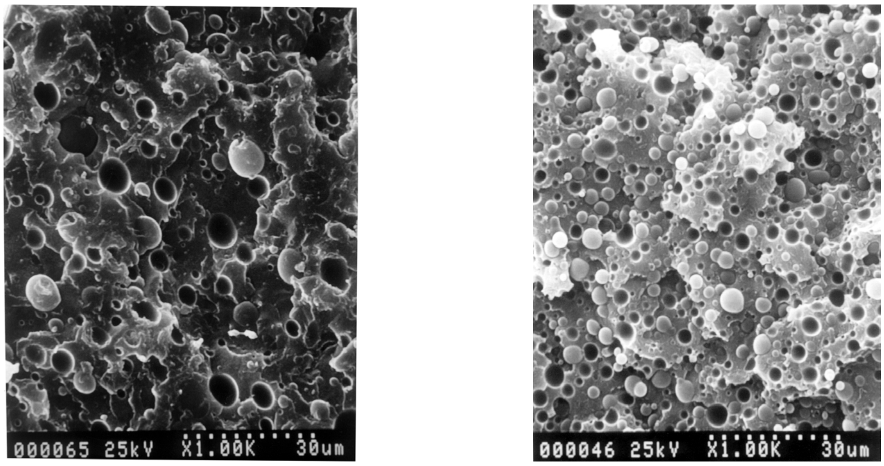


(a) (b)

Fig.1. Effect of sonication time on the viscosity of the polymer: (a) PP (b) PS

facilitated by the well known mechanism of β-scission, whereas competition between chain scission and recombination is operative under the ultrasonic irradiation of PS. The effect of ultrasonic irradiation on the morphology of the blend based on PP and PS was investigated. The blend ratio of PP/PS was kept as 7:3 in order to sustain the matrix phase as PP.

Compared to the simple mixing without sonication, notable reduction in domain size was hardly observed for the prolonged sonication of 30 min and even somewhat larger domains are found. Totally different results, however, were obtained by changing the matrix phase with PS. When the blend ratio of PP/PS was set as 2/8, the average domain size was significantly reduced, as shown in Fig. 2(b). The results shown in Fig. 2 reflects the fact that viscosity ratio between the major phase and the minor one also plays a critical role in sonicated mixing, as is typical in conventional melt blending of polymers.



(a) (b)

Fig.2 SEM micrographs of PP/PS(2/8) blends; (a)simple mixing (b) ultrasonic mixing . (Mixing time = 30 min)

When the PP is the matrix, difficulty in breakup of PS domains is encountered; and consequently the possibility for the combination of PP and PS radicals is greatly reduced. In other words, enough amount of copolymers can not be formed at the interface in such condition. On the contrary, if PS is the matrix, the dispersion process becomes more efficient so that the average domain size is smaller both in simple mixing and ultrasonic mixing. In order to examine stability of the morphology developed from the ultrasonic mixing, samples were annealed during 10 min at 200℃ and then viewed under a SEM. It was clearly seen that coalescence was significantly suppressed in the sonicated blend, while considerable increase in domain size was inevitable in the blend prepared from simple mixing. In addition to the case of PP/PS, consistent results were obtained from the blends of PMMA/PS and PC/PS.

Conclusions

By using high intensity ultrasonic wave, it was possible to induce chain scission or crosslinking of the polymers in melt state without any solvents or additives. 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 from the annealing experiments that copolymers of PP and PS were formed by combination of the corresponding macroradicals and consequently act as compatibilizers for the blend. It was consistently observed that it is desirable to keep the viscosity of the matrix higher than that of the domain for effective compatibilization. It is suggested 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.

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