

Evolution of phase morphology and in-situ compatibilization of polymer blends during ultrasound-assisted melt mixing

Hyungsu Kim*, Joung Gul Ryu¹ and Jae Wook Lee¹

Applied Rheology Center, Department of Chemical Engineering

Dankook University, Hannam-Dong, Yongsan-Gu, Seoul 140-714, Korea

¹Applied Rheology Center, Department of Chemical Engineering Sogang University,

1 Shinsu-Dong, Mapo-Gu, Seoul 121-742, Korea

(Received July 10, 2002)

Abstract

A series of thermoplastic polymers and their blends were melt-processed with high intensity ultrasonic wave in an intensive mixer. For the effective transfer of ultrasonic energy, an experimental apparatus was specially designed so that polymer melt can directly contact with ultrasonic horn. It was observed that significant variations in the rheological properties of polymers occur due to the unique action of ultrasonic wave without any aid of chemical additives. It was also found that the direct sonication on immiscible polymer blends in melt state reduces the domain sizes considerably and stabilizes the phase morphology of the blends. The degree of compatibilization was strongly affected by viscosity ratio of the components and the morphology was stable after annealing in properly compatibilized blends. 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.

Keywords : ultrasound, degradation, polymer blend, *in-situ* compatibilization

1. 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). 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. On 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 (Schnabel, 1981). Despite the potential uses of ultrasonic effect in modification of polymers, little attention has been focused on the sonicated melt processing except a number of reports by Tapel and Isayev (1988), Hong and Isayev (2001; 2002), and 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. 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 polycar-

*Corresponding author: hkim@dku.edu
© 2002 by The Korean Society of Rheology

bonate (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. From numerous studies (Manas-Zloczower and Tadmor, 1994), it is a well known fact that the viscosity ratio plays a critical role in mixing and compounding of polymer blends. Accordingly, it is of particular interest to explore such effect in the novel mixing environment, where additional energy is imposed by ultrasonic wave. For the fixed pair of a blend, viscosity ratio was controlled by simply changing the blend ratio of component polymers having different viscosities. An interesting question was also raised about the applicability of the present technique to the system containing a polymer made from condensation reaction rather than from free radical polymerization. In principle, the underlying mechanism of compatibilization is closely related to generation of macroradicals and their combination. Thus, it is worthy to examine such blend containing polycarbonate in a sonicated mixer. Within the available range of blend compositions, it is expected that we may be able to establish an improved picture of the factors that influence of ultrasonic wave in melt mixing of polymer blends.

2. Experimental

The materials used in this study are all commercially available polymers. They are supplied in the form of powder or granule and their details are summarized in Table 1.

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 15 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 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 ultra-

sonic irradiation was imposed at 50% of the maximum output of the generator. Prior to mixing, samples were dried in a vacuum oven at 80°C for 24 hrs.

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

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 10 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

Table 1. Polymers used in this study

Polymer	Designation	Source (Grade)	Molecular weight
Polypropylene	PP	Daelim (PP1386)	MI=200 (230°C, 2.16 kg)
Polystyrene	PS	LG (20 HRE)	
Poly(methyl methacrylate)	PMMA	LG (IH 830)	Mn=37,000 Mw=79,000
Polycarbonate	PC	Teijin (TPLLP)	11,000 20,000

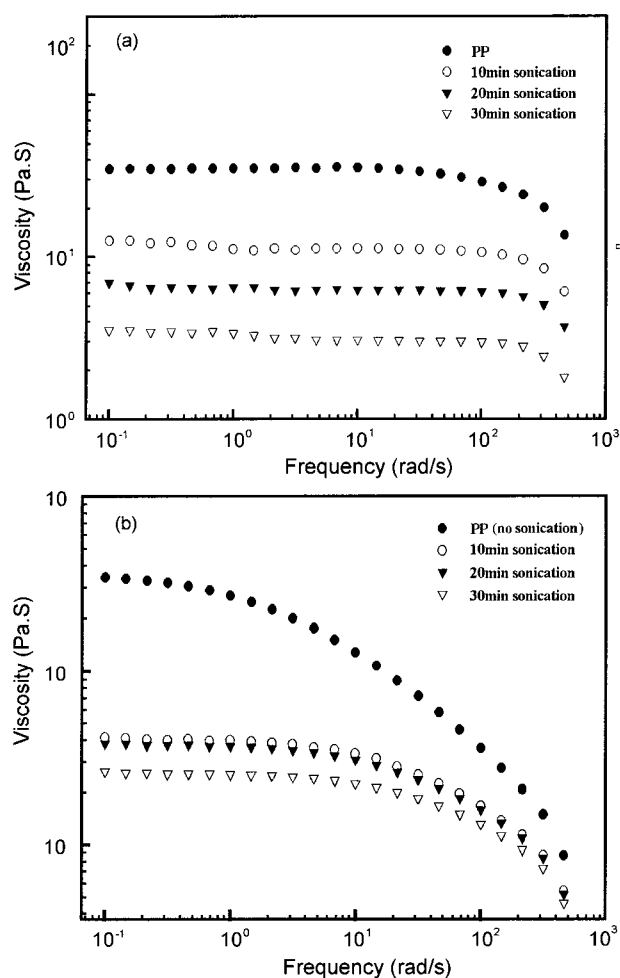


Fig. 1. Effect of sonication time on the viscosity of the polymer: (a) PP (b) PS.

confirm the desired effect since significant coalescence is typically promoted in immiscible polymer blends during the thermal treatment (Quintens *et al.*, 1990).

3. 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 facilitated by the well known mechanism of

β -scission (Moore, 1996), whereas competition between chain scission and recombination is operative under the ultrasonic irradiation of PS.

Fig. 2 describes the effect of ultrasonic irradiation on the morphology of the blend based on PP and PS. 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 in which numerous domains are agglomerated with wide size distribution, the sizes of dispersed phase in the sonicated blend are mostly uniform. Although the overall array of the domains appears to be more regular in Fig. 2(d), notable reduction in domain size is hardly observed for the prolonged sonication of 30 min and even somewhat larger domains are found. This is contrary to our early expectation of the present study since the input of ultrasonic wave was not effective to compatibilize the blend.

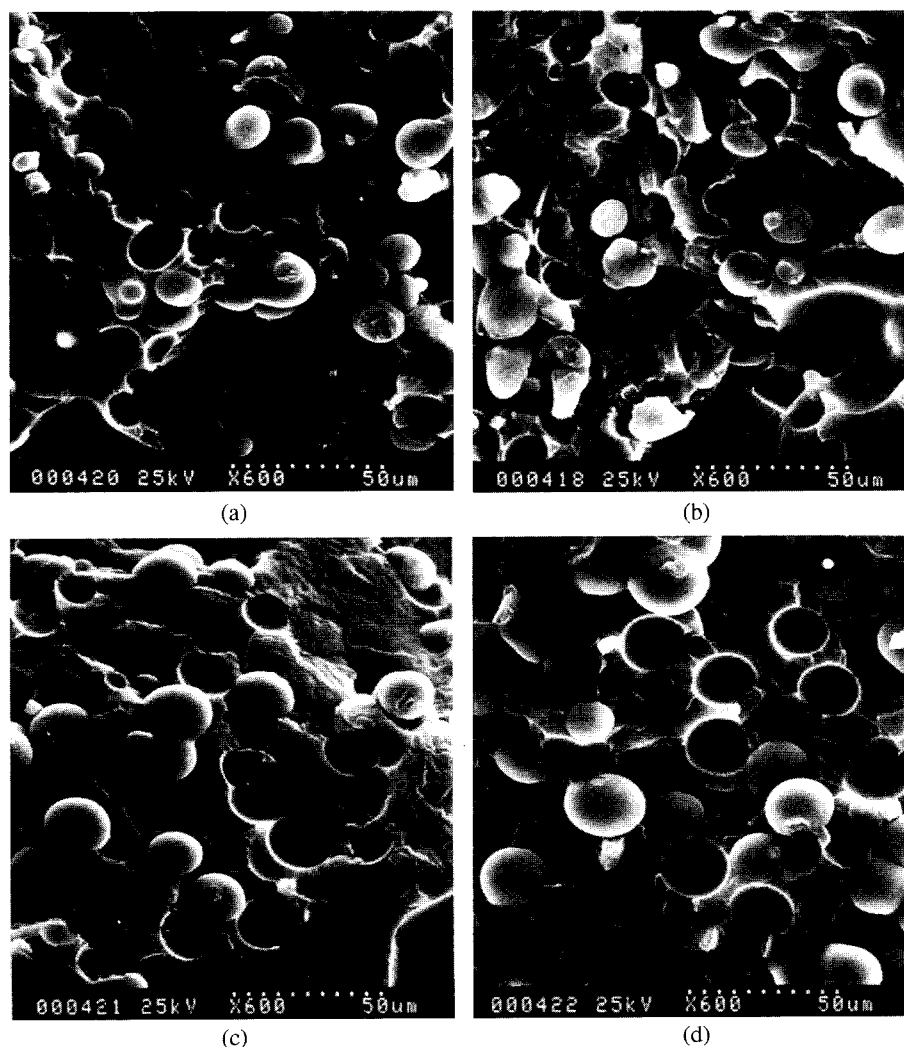


Fig. 2. SEM micrographs of PP/PS (7/3) blends; (a) simple mixing (10 min) (b) ultrasonic mixing (10 min) (c) ultrasonic mixing (20 min) (d) ultrasonic mixing (30 min).

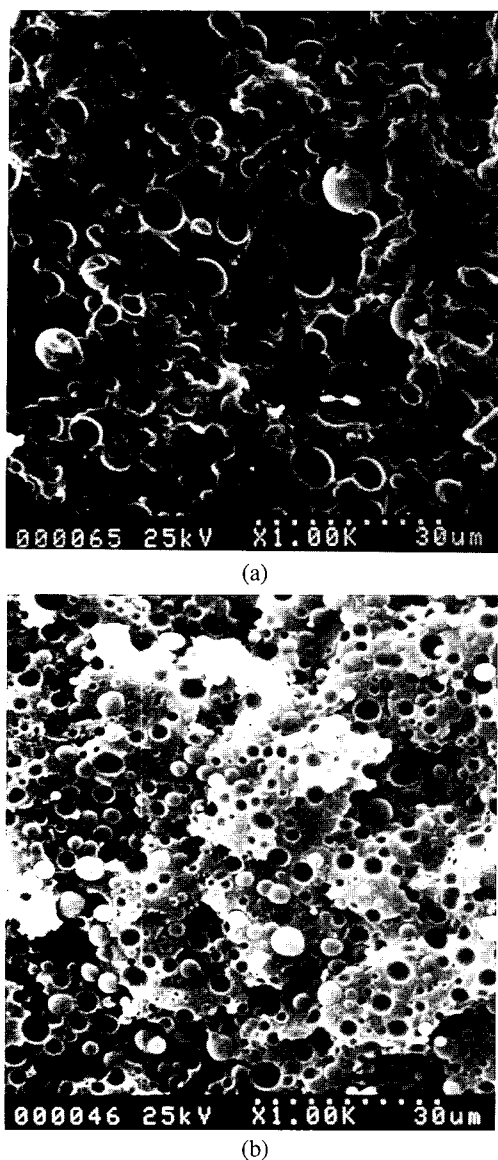


Fig. 3. SEM micrographs of PP/PS (2/8) blends; (a) simple mixing (b) ultrasonic mixing (Mixing time=30 min).

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. 3(b). The results shown in Figs. 2 and 3 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.

In compounding of immiscible polymer blends, the final phase size of the minor component is determined by numerous factors including viscosity ratio, interfacial tension and type of flow field, etc. In a given equipment, it has been reported and widely recognized that the best result of mixing is expected at a closely matched viscosity ratio (Wu,

1987). In the practice of polymer blending, difficulty of mixing may arise especially when the viscosity of the minor component is significantly higher than that of the matrix. This is simply because sufficient stress required for the breakup of the minor phase is not available in such case, although other causes may be involved due to the polymer viscoelasticity and complexity of the flow field during melt mixing.

In case of PP/PS blend, the average viscosity ratio of PS to PP is even more than 50 before ultrasonic irradiation and the comparable ratios are maintained for successive sonication (see Fig. 1). Thus, 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. Note that the magnification used in Fig. 3 is higher than that of Fig. 2.

In order to examine stability of the morphology developed from the ultrasonic mixing, samples were annealed during 10 min at 200°C and then viewed under a SEM. The results are shown in Fig. 4. It is 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.

Based on numerous studies (Makosko *et al.*, 1996; Sundararaj and Macosko, 1995; Utracki and Shi, 1992; Roland and Bohm, 1984), it is reported 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 (Roland and Bohm, 1984). According to the mechanism, when the dispersed droplets are brought close together by the flow field, the matrix film between the drops thins until the interface ruptures and then 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 (Quintens *et al.*, 1990; Lee and Kim, 1996). It is clearly indicated from Figs. 3 and 4 that both the stability of phase morphology and the reduction of phase size were achieved by ultrasonic-assisted mixing. Obviously such effects are ascribed to *in-situ* copolymer formation between PP and PS macroradicals occurs during sonication in the melt. 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 (Sundararaj and Macosko, 1995).

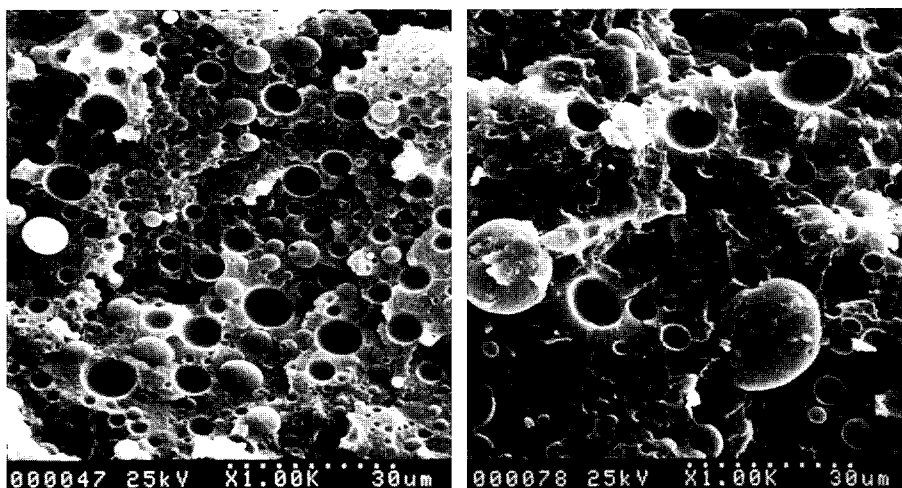


Fig. 4. Effect of annealing on morphology in PS/PP (8/2) system shown in Fig. 3: (left) ultrasonic mixing, (right) simple mixing.

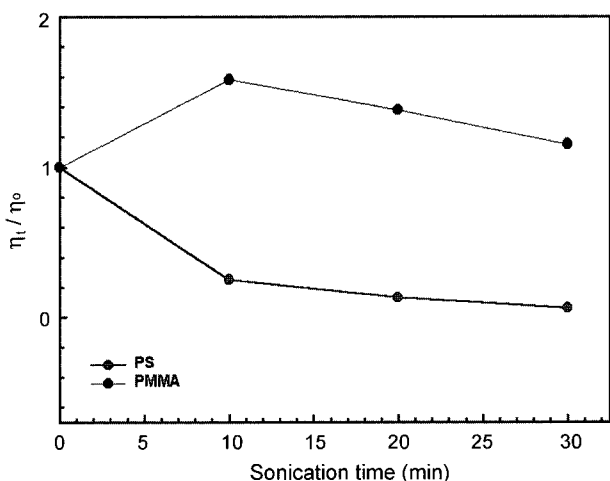


Fig. 5. Effect of sonication on the viscosities of PMMA and PS.

Fig. 5 shows the change in viscosities of PMMA after sonication. For a comparative illustration with the trend found in PS, relative viscosity (i.e., viscosity of sonicated sample over that of pristine one) was used. In Fig. 5, we see that viscosities of sonicated PMMA are higher than those of pristine PMMA at all sonication times within 30 min. This result suggests that crosslinking reaction occurred during sonicated melt mixing. As an attempt to clarify this issue, the composition of PMMA was examined by gas chromatography after pyrolysis. The result revealed that about 2% of methacrylate (MA) was included as a comonomer with methyl methacrylate. In this composition, crosslinking among the chains can occur if the macroradicals abstract tertiary hydrogen of MA (Saunders, 1988). Another feature in Fig. 5 is that the relative viscosity reaches a maximum value at around 10 min of sonication. We infer that crosslinking prevails up to a certain point and then again the network structure is disrupted

under the successive sonication.

Morphology of PMMA/PS system is displayed in Figs. 6 and 7. The matrix phase was PMMA in Fig. 6 and vice versa in Fig. 7. In both cases, simple mixing resulted in coarse morphology and the domain size increases as the mixing time increases. In Fig. 6, it is observed in sonicated blends that the morphology was stable to maintain reduced domain size, which is indicative of compatibilization. In contrast, however, increased sonication time was seen to lead to an increase in the average domain size when the matrix was PS, as presented in Fig. 8. It should be noted that the viscosity of PMMA at the processing range is about three-fold higher than that of PS and moreover the difference in the viscosities between the two becomes even more serious due to the opposite effect of sonication on each polymer (see Fig. 5). Figs. 6 and 7 again demonstrate the important role of matrix viscosity to compatibilize the blend and stabilize the morphology during ultrasound-assisted processing.

The effectiveness of the present technique was further assessed by employing the blends containing PC and PC and the results are shown in Fig. 8. It is consistently observed that sonicated mixing can improve the compatibility of PC/PS blend especially when PC (the higher viscosity component) constitutes the matrix phase. It is interesting to note that even a blend containing a polymer produced from condensation polymerization can be compatibilized by interactions between counter-macroradicals. In a practical sense, it would be worthwhile to apply present idea to PC/ABS (Acrylonitrile-Butadiene-Styrene) blend. Although it belongs to an important class of commercial material, due to its insufficient compatibility, some drawbacks such as unstable morphology and mechanical properties are still controversial in certain applications.

Obviously, complete understanding and prediction of mutual coupling between various kinds of macroradicals

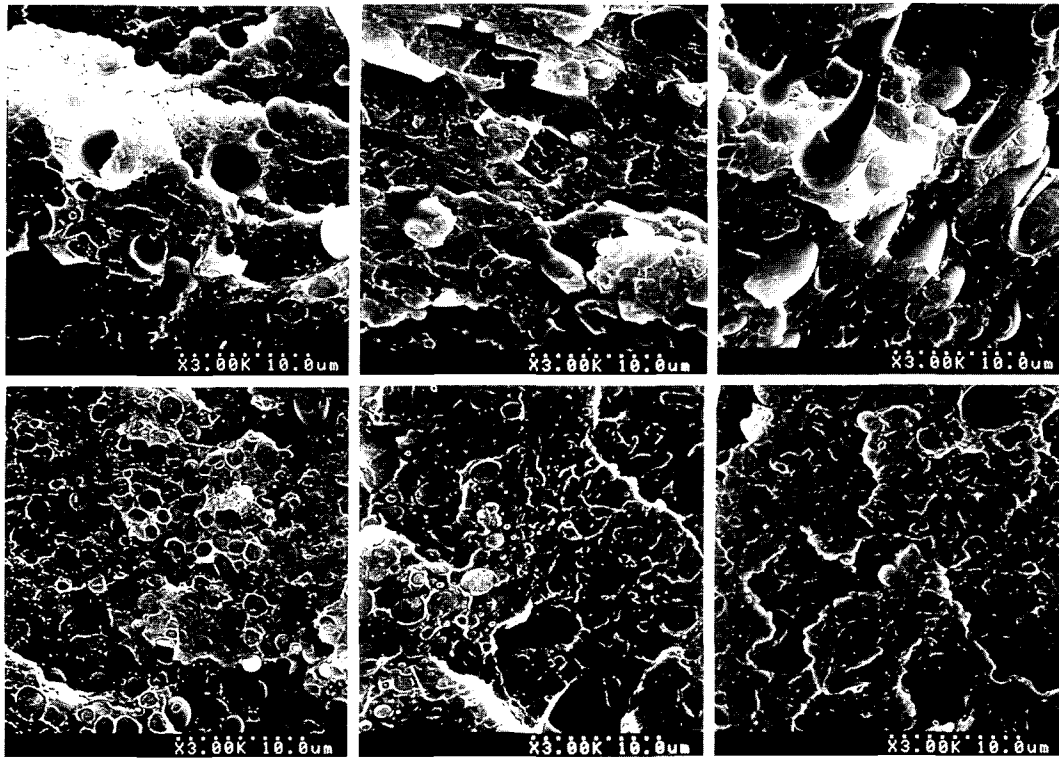


Fig. 6. SEM micrographs of PMMA/PS (7/3) blends: (top) simple mixing, (bottom) ultrasonic mixing (Mixing time=10, 20, 30 min, from left to right).

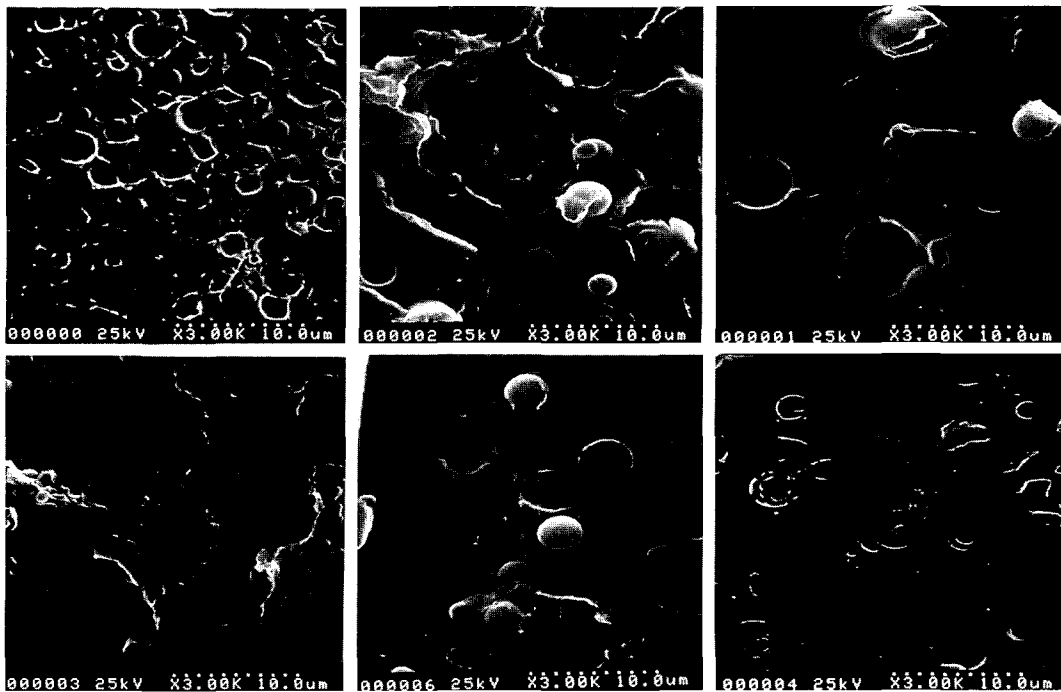


Fig. 7. SEM micrographs of PMMA/PS (3/7) blends: (top) simple mixing, (bottom) ultrasonic mixing (Mixing time=10, 20, 30 min, from left to right).

are not easy tasks according to the complicated nature of the relevant processes. Nevertheless, it is suggested that the

present method can be applied to wide range of multi-component systems provided the formation of macrorad-

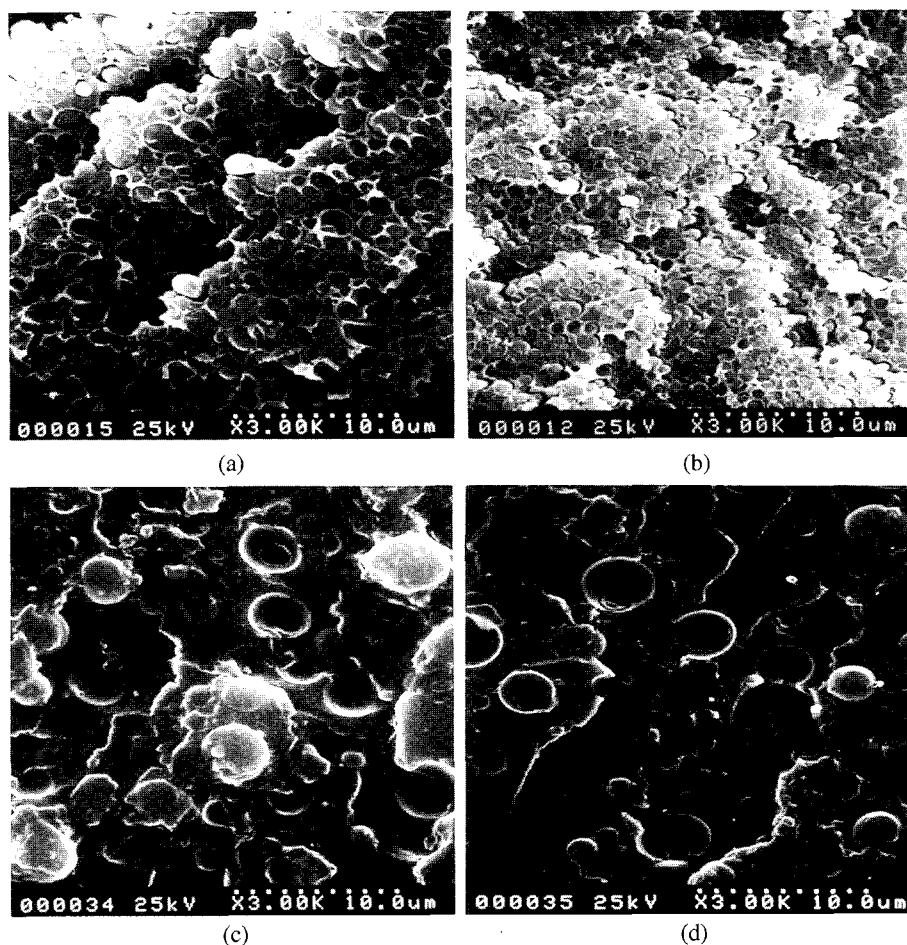


Fig. 8. SEM micrographs PC/PS blends: (top) PC/PS=7/3, (bottom) PC/PS=3/7; (left) simple mixing, (right) ultrasonic mixing (Mixing time=10 min).

icals and favorable interactions between them are feasible.

4. 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. The viscosities of PP and PS were significantly decreased by sonication, while those of PMMA were increased due to the presence of comonomer which is capable of crosslinking.

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. The common features identified from the foregoing results on various blends including PMMA/PS and PC/PS emphasize the fact that viscosity ratio plays a critical role in in-situ compatibilization during sonicated mixing. 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.

Acknowledgements

This study was supported by research grants from the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC), an official KOSEF-created engineering research center (ERC) at Korea University, Seoul, Korea.

References

- Chen, G., S. Guo and H. Li, 2002, Ultrasonic improvement of rheological behavior of polystyrene, *J. Appl. Polym. Sci.* **84**, 2451.

- Hong, C.K. and A.I. Isayev, 2001, Continuous devulcanization of carbon black-filled NR vulcanizates, *J. Appl. Polym. Sci.* **79**, 2340.
- Hong, C.K. and A.I. Isayev, 2002, Continuous devulcanization of NR/SBR blends, *J. Appl. Polym. Sci.* **83**, 160.
- Kim, H. and J.W. Lee, 2002, Effect of ultrasonic wave on the degradation of polypropylene melt and morphology of its blend with polystyrene, *Polymer* **43**, 2585.
- Macosko, C.W., P. Guegan, A.K. Khandpur, A. Nakayama, P. Marechal and T. Inoue, 1996, Compatibilizers for melt blending: Premade block copolymers, *Macromolecules* **29**, 5590.
- Manas-Zloczower, I. and Z. Tadmor, 1994, *Mixing and Compounding of Polymers*, Hanser, Munich.
- Moore, E.P. Jr., 1996, *Polypropylene Handbook*, Hanser, Munich.
- Price, G.J., 1992, *Current Trends in Sonochemistry*, RSC.
- Quintens, D., G. Groeninckx, M. Guest and L. Aerts, 1990, Mechanical behavior related to the phase morphology of PC/SAN polymer blends, *Polym. Eng. Sci.* **30**, 1474.
- Quintens, D., G. Groeninckx, M. Guest and L. Aerts, 1990, Phase morphology coarsening and quantitative morphological characterization of a 60/40 blend of PC and SAN, *Polym. Eng. Sci.* **30**, 1484.
- Roland, C.M. and G.G.A. Bohm, 1984, Shear-induced coalescence in two-phase polymeric systems. I. Determination from small-angle neutron scattering measurements, *J. Polym. Sci.* **22**, 79.
- Saunders, K.J., 1988, *Organic Polymer Chemistry*, 2nd ed., Chapman and Hall, New York.
- Schnabel, W., 1981, *Polymer Degradation*, Hanser, Munich.
- Sundararaj, U. and C.W. Macosko, 1995, Drop breakup and coalescence in polymer blends: The effects of concentration and compatibilization, *Macromolecules* **28**, 2647.
- Suslick, K.S., 1990, *Ultrasound: Its chemical, Physical and Biological effects*, VCH, New York.
- Tapale, M. and A.I. Isayev, 1998, Continuous ultrasonic devulcanization of unfilled NR vulcanizates, *J. Appl. Polym. Sci.* **70**, 2007.
- Utracki, L.A. and Z.H. Shi, 1992, Development of Polymer Blend Morphology During Compounding in a Twin-Screw Extruder. Part I: Droplet Dispersion and Coalescence-A Review, *Polym. Eng. Sci.* **32**, 1824.
- Wu, S., 1987, Formation of dispersed phase in incompatible polymer blends: interfacial and rheological effects, *Polym. Eng. Sci.* **27**, 335.