

Effect of viscosity ratio and AN content on the compatibilization of PC-SAN blends during ultrasound-assisted melt mixing

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Abstract

In this study, high intensity ultrasound was employed to induce mechano-chemical degradation during melt mixing of polycarbonate (PC) and a series of styrene-acrylonitrile (SAN) copolymers. It was confirmed that generation of macroradicals of constituent polymers can lead to in-situ copolymer formation by their mutual combination, which should be an efficient path to compatibilize immiscible polymer blends and stabilize their phase morphology in the absence of other chemical agents. Based on the effectiveness of the compatibilization by ultrasound assisted mixing process, we investigated the effects of viscosity ratio of PC and SAN and AN content in SAN on the compatibilization of PC/SAN blends. It was found that effectiveness of compatibilization is optimal when the AN content is in the range of favorable interaction with PC and the viscosity of the matrix is higher than that of the dispersed phase. In addition, changes in the interfacial tension between PC and SAN were assessed by examining relaxation spectra which were obtained from measuring rheological properties of ultrasonically treated blends.

Keywords : PC, SAN, polymer blend, ultrasound, compatibilization, interfacial tension

1. Introduction

Blend of PC (polycarbonate) and ABS (acrylonitrile-butadiene-styrene) is an important engineering plastic. Based on its excellent toughness, heat resistance and processability, it has been widely used in various parts for automobiles and appliances. Unlike most other recently developed polymer blends or alloys, to our knowledge, typical PC/ABS blends do not involve any compatibilizer, because the thermodynamic affinity of PC and SAN (styrene-acrylonitrile) copolymer, matrix of the ABS, is good enough to lead to adequate adhesion for the required mechanical strength (Keith *et al.*, 1984). However, due to the incomplete miscibility between PC and SAN, the blend often experiences significant changes in its phase morphology during compounding and injection molding, which results in phase coalescence and deterioration of mechanical properties (Quintens *et al.*, 1990a; 1990b; 1991).

In our previous study (Kim and Lee, 2002), we performed ultrasonic degradation of various thermoplastics in melt processing of polymer in a batch mixer. It was found that this

process can be used to control the rheological properties of polymers in the absence of solvent or other chemical agents. In addition, since cleaving bonds can create reactive macromolecules (or macroradicals), it was also confirmed from subsequent studies (Kim *et al.*, 2002; Ryu *et al.*, 2004; Kim, 2004) that direct mutual coupling between different radicals of constituent polymers is possible in blends of polypropylene (PP)/polystyrene (PS), PS/low density polyethylene (LDPE) and PC/SAN. 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 a series of styrene-acrylonitrile (SAN) copolymers and polycarbonate (PC). After confirming the effectiveness of ultrasound-aided compatibilization of PC/SAN as reported in a paper by Kim (2004), one of the major interests of this work was to investigate the effect of viscosity ratio between domain and matrix on the degree of compatibilization. Since the viscosity ratio always plays a critical role in mixing and compounding of polymer blends, it is necessary to explore such effect in the novel mixing environment, where additional energy is imposed by ultrasonic

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wave. For the fixed pair of a blend, viscosity ratio was controlled by simply changing the component polymers having different viscosities. Another purpose of this work was to study the effects of AN content in SAN on the degree of compatibilization. As reported by Keith *et al.* (1984), thermodynamic interaction between PC and SAN is strongly influenced by AN content of SAN and the interaction between the two is expected to be optimum when the AN level is around 25% in SAN. Thus, it is of particular interest to examine the contribution of thermodynamic factor in in-situ compatibilization of PC-SAN blends having various SANs of different AN contents. This is also an important issue in a commercial view of producing PC/ABS blend, since numerous grades of SANs with various AN contents are available for the blend with PC depending upon the final applications and required performance of the blends.

Within the available range of blend compositions, it is expected that we may be able to establish an improved understanding on the factors that influence the ultrasound-assisted compatibilization of polymer blends.

2. Experimental

The materials used in this study are all commercially available polymers 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. 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. Prior to mixing operation, pure resins were dried in a vacuum oven at 80°C for 24 hours to prevent hydrolytic degradation of PC during mixing process. Each sample was prepared on a fixed volume basis of 70%. The mixing temperature was 230°C and blend composition was fixed as 80/20(PC/SAN) by weight fraction. Before the irradiation of ultrasound, preliminary mixing was carried out for 2 min to reach the molten state and the sonication time was varied as 1, 3 and 5 min. Plate-plate rheometer (ARES,

Rheometrics Scientific) was used to measure the dynamic viscosities of sonicated samples. Experiments were carried out with 25 mm plate diameter, 1.5 mm gap distance, 10% strain rate, and 0.1~100 rad/sec frequency ranges. The morphology of the cross section of the blends prepared by cryogenic fracturing was examined by scanning electron microscope (SEM, HITACHI S-2500) at 20 kV accelerating voltage after platinum sputtering coating. The volume-average radius of droplets was determined from SEM pictures by using an image analysis technique. In order to assess the phase stability of sonicated blends, the changes in the morphology of the blends were investigated after annealing and remixing procedure, where a blend was stored in an oven for 10 min. at a temperature of 200°C and then reprocessed in the mixer for 5 min without sonication. After sampling in each step, all specimens were immediately poured into a bath of cold water to prevent further morphology change and investigated in SEM.

3. Results and discussion

Fig. 1 shows the complex viscosities of polymers used in

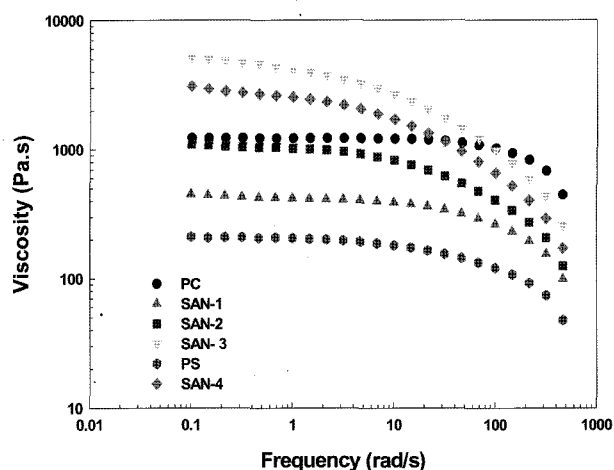


Fig. 1. Complex viscosity of the polymers used in this study.

Table 1. Materials used in this study

Polymer	Abbreviation	Source (Grade)	Molecular Weight	Copolymer composition (wt%)
Polycarbonate	PC	Teijin (TPLL)	Mn=11,000 Mw=20,000	
Poly (styrene-co-acrylonitrile)	SAN-1	Cheil Ind. Inc.	Mn=42,000 Mw=69,000	25% AN
	SAN-2	Cheil Ind. Inc.	Mn=53,000 Mw=96,000	24% AN
	SAN-3	Cheil Ind. Inc.	Mn=91,000 Mw=170,000	26% AN
	SAN-4	Cheil Ind. Inc.	Mn=59,000 Mw=116,000	40% AN
Polystyrene	PS	LG Chemicals (20 HRE)		0% AN

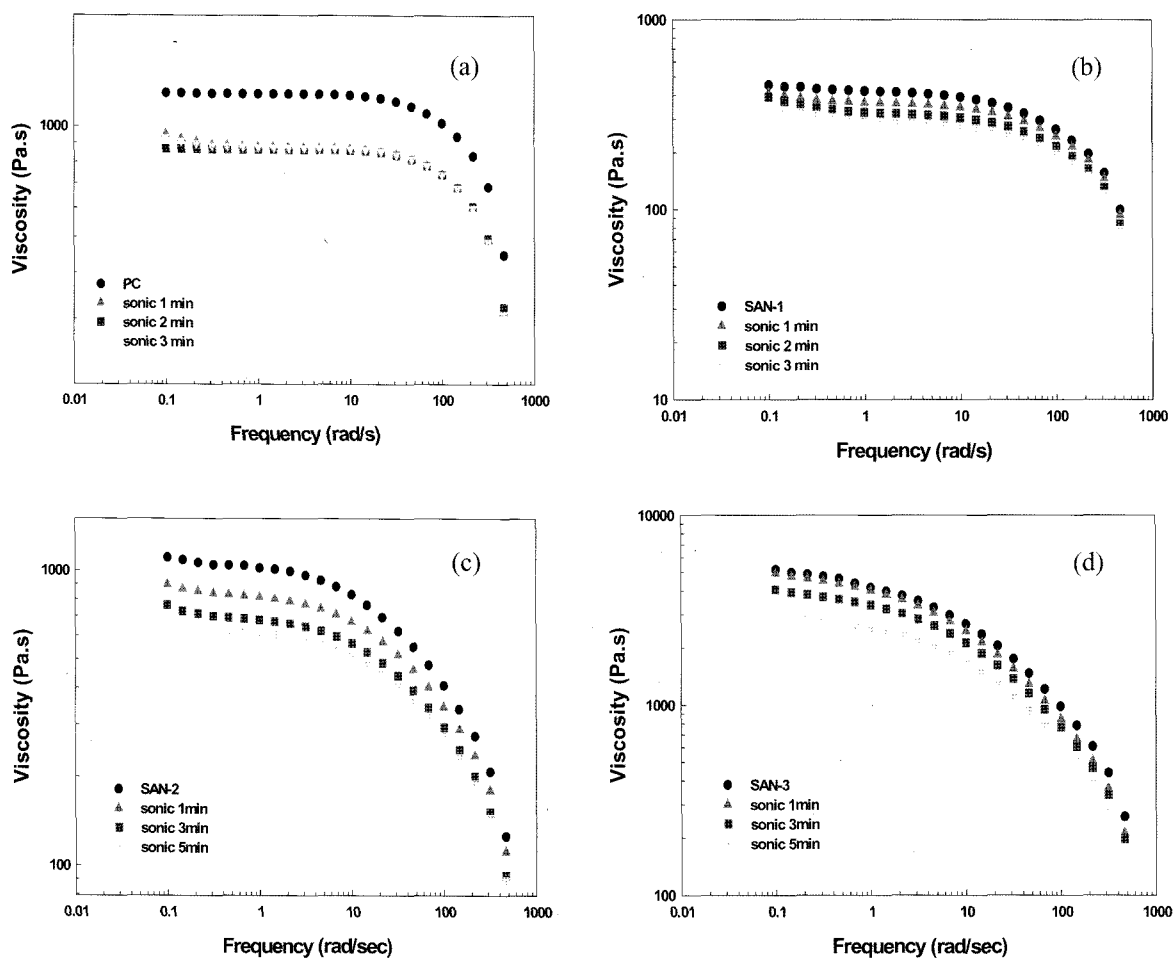


Fig. 2. Effect of sonication time on the viscosity of the polymer; (a) PC; (b) SAN-1; (c) SAN-2; (d) SAN-3.

this study. It appears that a wide range of viscosity is available to easily vary the viscosity ratio of PC and SAN copolymers. Fig. 2 shows effect of sonication time on the changes in complex viscosity of PC, SAN-1, SAN-2, and SAN-3, respectively. Although the data of PC and SAN-1 included in Fig. 2 have been reported previously (Kim, 2004), they are reproduced and compared here with other SAN copolymers to get a better picture on the degradation behavior of a series of SAN copolymers. It is clearly seen that the viscosities of both PC and SAN's decreased with increased sonication time. Within the given sonication times of 5 min, it appears that the degradation of SAN is proceeded in step with the sonication times, while that of PC is somewhat delayed after a significant drop in viscosities for 1 min of sonication. These results provide the evidences of chain scission in PC and SAN by ultrasonic wave during melt processing.

The effects of sonication time and viscosity ratio on the average domain size of the PC/SAN (80/20) blends are displayed in Fig. 3. In order to clearly elucidate the effect of viscosity ratio, it is important to use SAN copolymers having similar AN content, so that we can minimize the influ-

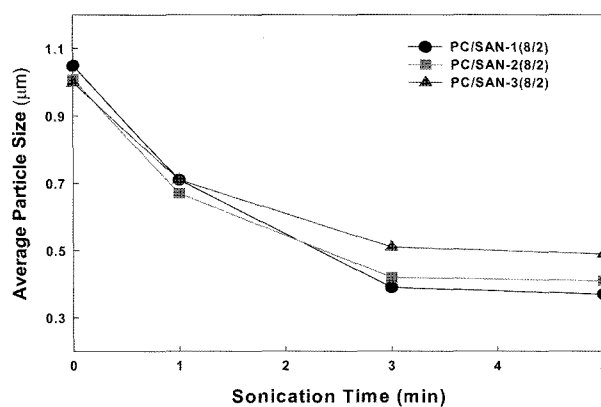


Fig. 3. Effect of sonication time on the average particle size of PC/SAN blends.

ence caused by different interfacial activities. This can be done by comparing SAN-1, SAN-2 and SAN-3, in which the AN content in SAN copolymers is around 25%. It is observed in Fig. 3 that a notable decrease in the average domain size for each sample is occurred within 3 min of sonication and the change in phase size was only marginal

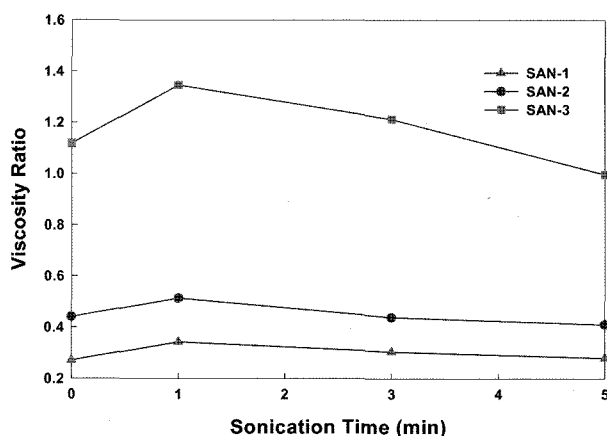


Fig. 4. Effect of sonication on the variation of viscosity ratios (viscosities measured at shear rate of 68 s^{-1}).

for further sonication. For the fixed sonication time, as we increase the viscosity of SAN for the fixed matrix of PC, the domain sizes were gradually increased. 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 a practical aspect of polymer blending, difficulty of mixing may arise especially when the viscosity of the minor component is 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 PC/SAN-3 blend, the viscosity ratios measured at 68 s^{-1} , which is the average shear rate of mixing condition, are greater than 1, while those of the other blends are far less than 1. (see Fig. 4) Thus, when SAN-3 is the minor phase, relative difficulty in breakup of the domains is encountered; and consequently the possibility for the combination of PC and SAN radicals may be lower than the other two. In other words, enough amount of copolymers can not be formed at the interface in such condition. On the contrary, if SAN-1 or SAN-2 is the minor phase, the dispersion and mutual combination between the components can be facilitated so that the average domain size becomes smaller. The effect of viscosity ratio on the effectiveness of ultrasound-assisted compatibilization was consistently observed in studies with other pairs of polymer blends. The case of PP/PS is one of the obvious example (Kim *et al.*, 2002), where the successful compatibilization in ultrasound-assisted mixing was achieved only when the viscosity of the matrix was higher than that of the minor phase; domain size of PP/PS blend was little changed by extended sonication time up to 30 min in the reversed case.

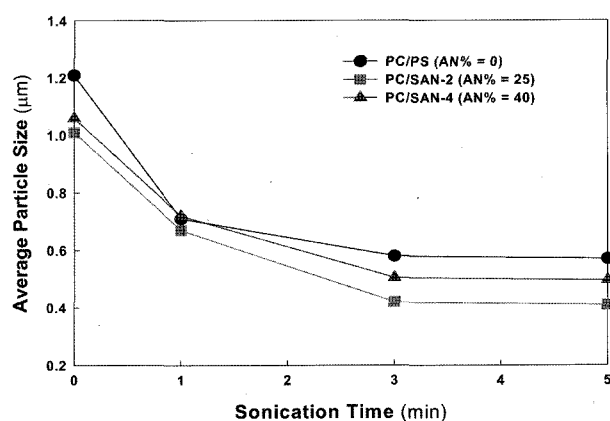


Fig. 5. Effect of AN content in SAN on the average particle size of PC/SAN blends.

In Fig. 5, the effect of AN content in SAN on the average particle size of PC/SAN blend is displayed. For this examination, it is important to keep the viscosity ratio less than one so that the rheological condition is satisfied for effective mixing. Among the selected pairs of PC with PS (0% AN), SAN-2 (25% AN) and SAN-4 (40% AN), it appears that blend of SAN-2 which was expected to provide the most favorable interaction with PC, gives the best result. The changes in average particle size shown in Fig. 5 reflect the role of thermodynamic interaction in determining final domain size of sonicated PC/SAN blends; since the order of average particle size in the blends is in accordance with that of interaction parameter between SAN and PC (Keith *et al.*, 1984). Nevertheless, it is important to note that ultrasound-assisted compatibilization is operative for PC/SAN pairs having AN content even beyond the range of optimum interaction. Accordingly, it should be emphasized that ultrasound-assisted mixing can overcome possible drawbacks such as reduced interfacial adhesion and deterioration of mechanical properties caused by insufficient thermodynamic interaction. This becomes an important issue especially when SAN with high AN content needs to be selected to enhance the chemical resistance of PC/ABS blend.

In order to examine the stability of the morphology for sonicated blend, samples were annealed during 10 min at 200°C , which was followed by remixing of 5 min without sonication, and the results are shown in Fig. 6. It is clearly seen that coalescence was significantly suppressed in the sonicated blend and phase stability is well maintained even after remixing of the annealed sample, while considerable increase in domain size was inevitable 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

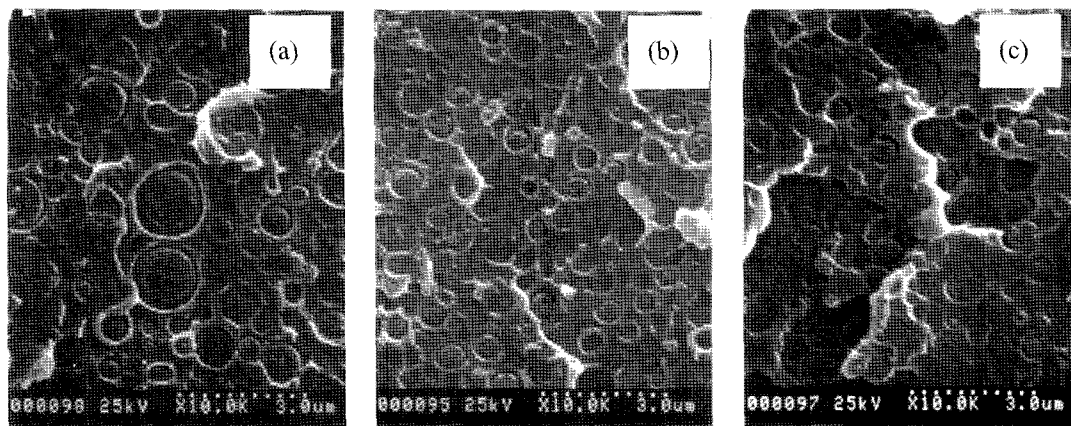


Fig. 6. SEM pictures from annealing test of PC/SAN-1 blends; (a) simple mixing, (b) sonication 3 min, (c) 5 min remixing (without sonication) after annealing.

pointed out earlier (Kim, 2004).

It has been reported by Gramespacher and Meissner (1992) that it is possible to infer interfacial tension between polymers forming an inhomogeneous polymer blend using small amplitude oscillatory shear (SAOS). In their work, a constitutive equation was developed for an emulsion based on the work of Choi and Schowalter (1975) and on a linear mixing rule, which considers the complex shear modulus of a blend as a combination of the contribution of the shear moduli of the viscoelastic phases plus the contribution of the interface. An informative article on the relevant subject has been recently published by Sung *et al.* (2004), where the evaluation of interfacial tension by rheological measurements for binary blends was proven to be a reliable method. Here, we obtained relaxation spectra from rheological measurements and adopted a set of equations associated with Choi and Schowalter model to estimate the interfacial tension of sonicated blends of PC/SAN, and the results are demonstrated in Fig. 7. As expected and observed from SEM results, interfacial tension of PS/SAN

is reduced with increased sonication time. The interfacial tension decreases very rapidly for sonication time ranging from 0 to 3 min and then levels off to a saturation value between 0.5 and 1.0 mN/m. The values of the interfacial tension shown in Fig. 7 are in good agreement with those reported by Kim *et al.* (2004), where the effect of a compatibilizer on the interfacial tension of PC and SAN was estimated by imbedded fiber retraction technique. From the comparison of the interfacial tension data, it is interesting to note that the degree of compatibilization achieved by present route is comparable to that found in the incorporation of 5 wt% tetramethylpolycarbonate-*block*-SAN copolymers as a compatibilizer.

4. Conclusions

By using high intensity ultrasound, it was possible to induce chain scission of PC and SAN copolymers in melt state without any solvents or additives. In melt mixing of the PC/SAN blend, irradiation of ultrasound led to in situ compatibilization of PC/SAN blends. Identifying stable nature of the phase morphology with reduced domain size after annealing and remixing tests manifested the established effectiveness of ultrasound-assisted compatibilization in PC/SAN blends. The viscosity ratios of PC and SAN played an important role in in-situ compatibilization during sonicated mixing. It was desirable to keep the viscosity of matrix higher than that of the domain for effective compatibilization. In addition to the viscosity ratio, final domain sizes were also affected by AN content in SAN; the smallest size was attained with a SAN having favorable interaction with PC. Although an optimum selection of SAN copolymer can be made, it is emphasized that ultrasound-assisted compatibilization of PC/SAN blends is in effect for a wide range of AN content in SAN regardless of its favorable interaction with PC.

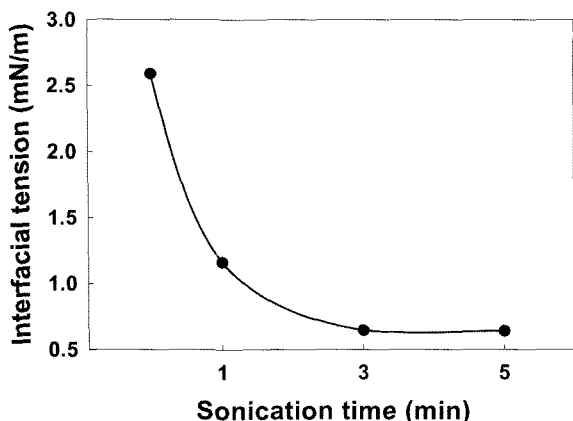


Fig. 7. Effect of sonication time on the interfacial tension of PC/SAN-1 blend.

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