

Rheological properties of branched polycarbonate prepared by an ultrasound-assisted intensive mixer

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Abstract

By combining ultrasonic energy which is essential for the chain scission of polymer molecules and a multifunctional agent (MFA) having double bonds at its ends, we were able to modify the molecular structure of polycarbonate (PC) from linear to a branched structure during melt processing. The three double bonds in chain ends of MFA were expected to act as sites for trapping macroradicals of PC during the course of ultrasound-assisted mixing process. The transformation of molecular structure of PC was confirmed by the measurements of rheological properties of the modified PC. After the ultrasonic irradiation of PC together with MFA, increase in complex viscosities and shear-thinning behavior were observed. The Cole-Cole plot and measurement of extensional viscosities revealed the characteristic features of branched structure with well-defined extensional behavior which is comparable to that of a commercial branched PC.

Keywords : branched polycarbonates, ultrasound, melt mixing, multifunctional agent

1. Introduction

The chain structure of polymeric molecules is an important characteristic of polymers. In the polymer industry, in-situ processing during polymerization or a post-processing is applied to alter the chain structure as an attempt to produce polymers with tailored properties. Among various methods to control the chain structure, ultrasound-induced polymer scission is a useful route which can either be used as a post-processing step or can be used during ultrasound-induced polymerization (Suslick and Price, 1999). In our previous studies (Kim *et al.*, 2002; Kim, 2004; Ryu *et al.*, 2004), we intended to induce degradation of polymer melts in a sonicated intensive mixer. 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 the process can be used to control the rheological properties of various polymers during the melt processing. In addition, since cleaving bonds can create reactive macromolecules (or macro-radicals), it was confirmed that direct mutual coupling between different macro-radicals is possible, thereby successful in-

situ compatibilization of immiscible polymer blends based on styrenics, polyolefins, and polycarbonate (PC) was achieved. In this study, we intended to apply the previous idea to the transformation of molecular structure from linear to branched one during melt processing of polycarbonate. Polycarbonate is one of the widely used engineering plastics due to its excellent toughness and heat resistance. Depending upon the required rheological properties, chain branching of PC has been practiced during polymerization process or through reactive extrusion, where branched PC's are prepared by reacting polyfunctional organic compounds with chemically treated PC derivatives (Kramer, 1972; De Bont and Hoeks, 1999; Marks *et al.*, 2000). Compared with the previous approaches, here we are introducing a relatively simple method by imposing ultrasound and a multifunctional agent (MFA) to produce branched PC. The MFA used in this study includes three arms and a double bond exists at the end of each arm. Thus, formation of branched structure is feasible when macroradicals of PC react with the end group of MFA. In fact, branched polypropylene was successfully generated by using the MFA under ultrasonic irradiation (Kim *et al.*, 2006). It was expected from this study that we may be able to provide a fundamental information associated with the development of a viable process of PC modification.

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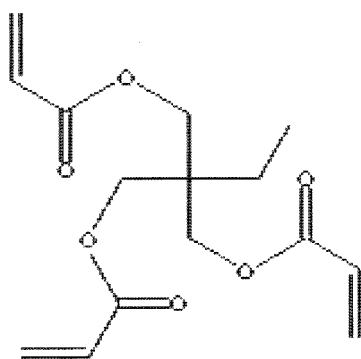


Fig. 1. Structure of MFA used in this study.

2. Experimental

2.1. Materials and sample preparation

The PC used was a low viscosity grade of Teijin in powder form. The MFA was Trimethylolpropane triacrylate purchased from Aldrich in liquid form and its chemical structure is demonstrated in Fig. 1. The concentration of MFA used was 3 and 5 phr, respectively. To compare the extensional properties of the branched PC made in this study, a commercially available grade (Samyang Co.) was evaluated as a reference.

In order to impose ultrasonic wave during melting mixing, a specially designed ultrasonic horn was assembled with a Haake mixer (Haake Rheocord 600). 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, homo polycarbonate was dried in a vacuum oven at 80°C for 24 hours. Each sample was prepared on a fixed volume basis of 70% and mixing temperature was 230°C with 60 rpm. Before irradiation of ultrasound, preliminary mixing was carried out for 1 min to reach the molten state. Sonication time was set to 5 min and the on/off ratio of ultrasound irradiation was fixed as 7:3.

2.2. Measurements

The samples obtained from the internal mixer were dried at 125°C for 4 hours and compression-molded at 230°C for 5 min. The samples obtained from the internal mixer were compression-molded at 230°C for 5 min. Disk-shaped specimens with a thickness of 2 mm and a diameter of 25 mm were prepared. An ARES rotational rheometer (Rheometric Scientific) was used to measure the complex viscosity and complex modulus. The measurements of the dynamic viscosities were performed in a parallel-plate fixture (diameter=25 mm) with a gap distance of 1.2 mm. The strain was kept at 10% to ensure linear viscoelasticity. The frequency range was 0.1-500 rad/s, and the temperature was 230°C. The work was conducted under a nitrogen atmosphere to prevent degradation. The melt extensional

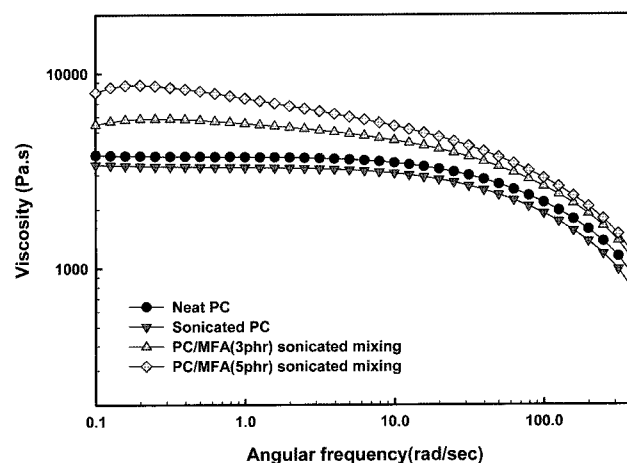


Fig. 2. Complex viscosities for neat PC and modified PC with multifunctional agent.

viscosity measurements were performed in a rotary clamp extensional rheometer (Rheometric Scientific). The temperature was 190°C and extensional rates were 0.01, 0.05, 0.1 and 0.3. Rectangular shaped samples (thickness=1 mm, length=5 cm, width=0.7 cm) were prepared by using compression molding.

FTIR spectra were obtained on a Shimadzu 8501 IR spectrometer with thin films of the samples. A TA instrument 2950 thermal analyzer was used to determine the thermal stability of the modified PC. Experiments were carried out on about 2 mg samples under nitrogen at a heating rate of 10°C/min up to 800°C.

3. Results and discussion

Fig. 2 shows the effect of sonication and addition of MFA on the complex viscosities of PC. Upon sonication of 5 min, the complex viscosities of pure PC were decreased, which reflects the chain scission of PC molecules proceeded during ultrasound-assisted melt processing. In principle, when polymer molecules are subject to ultrasonic irradiation, competition between chain scission and recombination exists. If recombination of PC macroradicals was predominantly occurred after chain scission, such reduction of viscosities would not be observed; accordingly it is inferred that chain scission prevails over recombination to some degree when PC molecules are under the influence of ultrasonic irradiation. In case of a PC molecule it is presumed that chain breakage was preferentially occurred at carbonate linkages simply because C-O bond energy is lowest (330 kJ/mol) along the main chain axis (Li and Huang, 1999). Although we did not conduct a rigorous element analysis, a partial support of this notion was obtained from an FTIR analysis for the sonicated PC and the result was compared with the neat PC in Fig. 3. For unequivocal comparison of the spectra, the

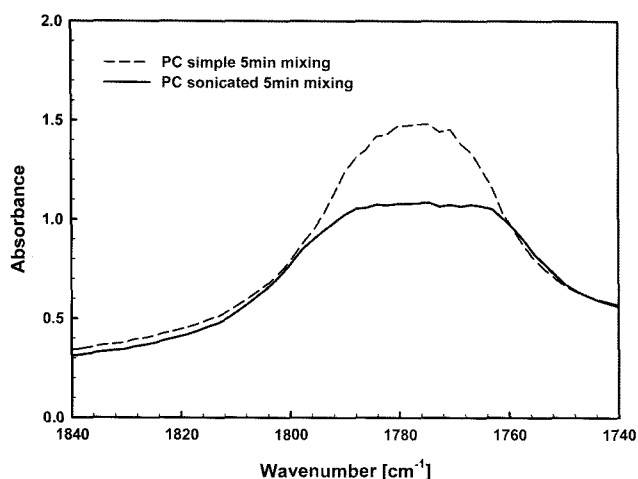


Fig. 3. FTIR results of neat PC and sonicated PC in the region of 1780 cm^{-1} .

spectra were normalized relative to the 1408 cm^{-1} , and curves were displaced vertically for clarity (Robertson, 2001). It is evident from Fig. 3 that the absorbance at 1780 cm^{-1} (indicative of carbonate linkage) was decreased after sonication, signifying breakage of carbonate linkage underwent during sonication. When 3 phr of MFA was added, on the other hand, the viscosities in the ranges under the frequency of $\sim 50\text{ rad/s}$ were higher than those of neat PC. Moreover, viscosity variation of sonicated PC with MFA was more sensitive to frequency change compared to Newtonian behavior of neat PC. Such effect became more significant when the concentration of MFA was increased. By adding 5 phr of MFA, the level of complex viscosities was higher than those of the others and shear thinning-tendency was more evident. It is well known that shear thinning in the shear viscosity is a reduction of the flow resistance due to the arrangement of the polymer molecules parallel to the flow direction. The degree of shear thinning is related to the structure of the molecules, molecular weight, molecular weight distribution and relaxation speed. Accordingly, by a simple examination of shear viscosity data, it is difficult to determine the structure of the molecules. Nevertheless, it was considered that the shear-thinning behavior displayed in the Fig. 2 is not a result of the increase in molecular weight which can be induced by a linear-type chain extension. Instead, it is more likely to be associated with the formation of the branched structure in PC molecules, according to the nature of MFA having a three-armed structure. The double bonds in chain ends of MFA were expected to act as sites for trapping macroradicals of PC during the course of ultrasound-assisted mixing process. This was verified by examining the variations of characteristic peaks of MFA in PC/MFA mixture. As shown in Fig. 4, the absorbance due to C-H stretching vibrations of vinyl group in the regions $3060\text{--}3040\text{ cm}^{-1}$ was decreased after sonication, while the

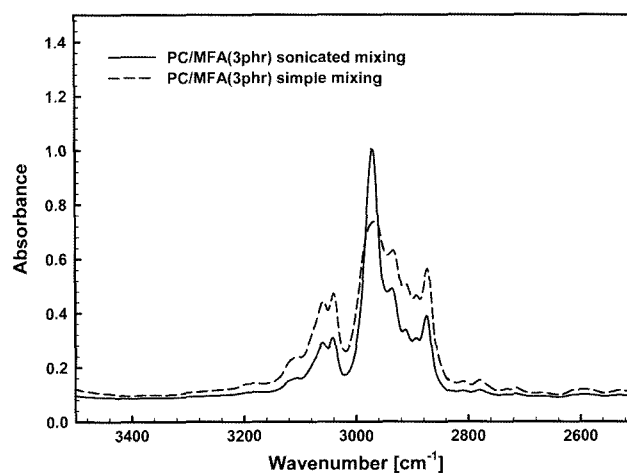


Fig. 4. FTIR results for PC/MFA prepared from simple mixing and sonicated mixing.

absorbance due to alkane C-H stretching vibrations at 2970 cm^{-1} was increased. Hence, shear-thinning can occur because entanglements of the branched polymers are more easily detached than the entanglements of the linear chains at the higher shear rates (Jacovic *et al.*, 1979). A similar result with present study has been reported in a study on the rheological behavior of linear and branched PC blends (Lyu *et al.*, 2001). The transformation of molecular structure of PC was further confirmed by following experimental results.

Fig. 5 shows Cole-Cole plots of the modified PC and neat PC. It appears that at a given G'' , G' s of the PC modified by MFA and ultrasound are higher than those of neat PC. It is also noted from Fig. 5 that the increase in G' was only marginal for the PC prepared from mixing 3 phr of MFA without sonication (designated as simple mixing in the figure). It is emphasized that a sonicated mixing played a critical role in the formation of the branched

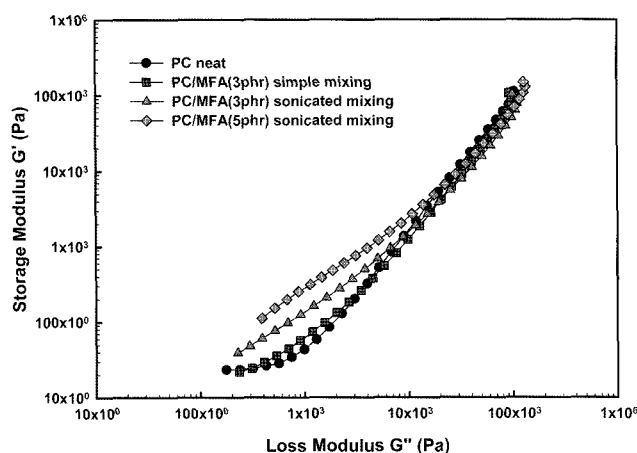


Fig. 5. Cole-Cole plot for neat PC and modified PC with multifunctional agent.

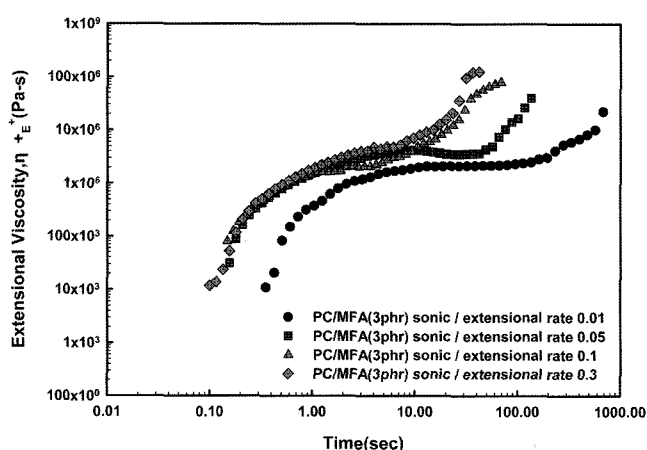


Fig. 6. Extensional viscosity of PC/MFA (3 phr) for various extension ratios (Temperature=190°C).

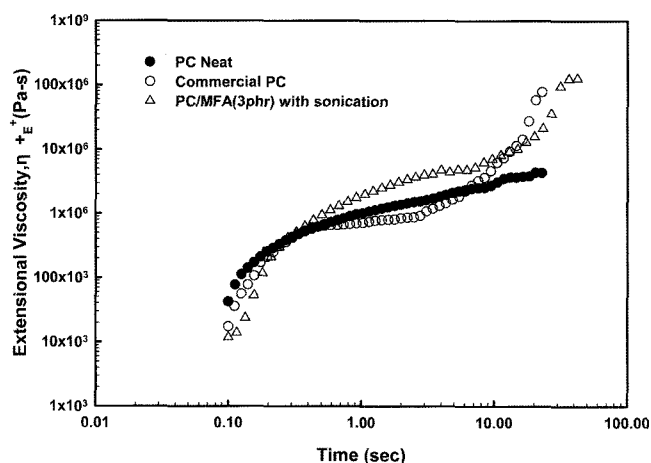


Fig. 7. Comparison of extensional viscosity for neat PC, PC/MFA (3 phr) and a commercial grade of branched PC at an extension ratio of 0.3 (Temperature=190°C).

structure and thereby physically connected structure was promoted by branched chains, which resulted in increase of dynamic storage modulus, as addressed by Hingmann and Marzinke (1994).

Extensional behavior of the modified PC was investigated by measuring extensional viscosities. The results are demonstrated and compared with a commercial branched PC in Figs. 6 and 7, respectively. As shown in Fig. 6, the extensional viscosities gradually increased along with the extension rates exhibiting strain-hardening behavior. Again, the tendency found in Fig. 6 provides another evidence relating to the branched chain structure. When an extensional force is exerted to the polymer molecules, molecules tend to arrange parallel to the direction of force during extension. In this process, branched polymer molecules require a higher force than do the linear chains since branched chains exert hindrance on the movement (Lyu *et al.*, 2001). At a loading of 3 phr MFA into PC, sonicated

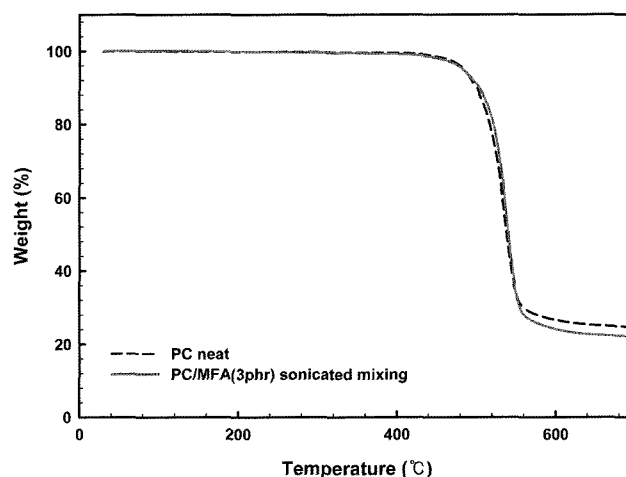


Fig. 8. TGA data for neat PC and modified PC.

PC exhibited a comparable level of extensional performance with a commercial grade of branched PC for the extension rate of 0.3, as demonstrated in Fig. 7.

Since, in principle, radical species are generated to achieve transformation of molecular structure, one may suspect that such radicals may affect somewhat adverse effect in the thermal stability of the modified PC. It was found from TGA analysis that the thermal stability of the modified PC is even superior or at least comparable to that of neat PC, as displayed in Fig. 8. Thus, the present method seems to be safe to preserve the thermal stability of neat PC.

4. Conclusions

By using intensive ultrasonic wave, it was possible to generate macroradicals of PC and induce combination between macroradicals and chain ends of MFA. By combining appropriate intensity of ultrasound which is essential for the chain scission of polymer molecules and a multifunctional agent having double bonds at its ends, we were able to modify a linear chain into a branched structure. The double bonds of MFA were expected to act as sites for trapping macroradicals of PC during the course of ultrasound-assisted mixing process. The measurements of rheological properties confirmed that the modified PC had a nonlinear branched structure. Unlike a typical PC or simply mixed PC with a multifunction agent in which a typical Newtonian behavior was apparent, the sonicated PC with a multifunction agent represents shear thinning behaviors in its viscosities at low frequencies. Formation of the branched structure was further confirmed from the tendency found in Cole-Cole plot and the comparison of extensional behavior with a commercial branched PC. It is suggested that ultrasound-assisted process can provide an effective route to transform the molecular structure of polymers during melt processing.

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