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Extensional and Complex Viscosities of Linear and Branched Polycarbonate Blends

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Abstract: Blends of the linear bisphenol-A polycarbonate (L-PC) and randomly branched bisphenol-A polycarbonate (Br-PC), prepared by co-rotating twin screw extrusion, were investigated using differential scanning calorimetry (DSC), sag resistance time tester, extensional rheometry, and advanced rheometric expansion system (ARES). From the DSC results, the glass transition temperature (T_g) of the L-PC/Br-PC blend was increased with the increase of Br-PC in the blend, and the blend showed a single T_g , which suggests a miscible blend. The sag resistance time of the L-PC/Br-PC blend was increased with the increase of Br-PC in the blends. From the results of rheological measurements of the L-PC/Br-PC blends, the extensional viscosity and the complex viscosity of the blends were found to increase with the increase of Br-PC in the blends. The increase of extensional viscosity and complex viscosity was related with the increase of sag resistance time with the Br-PC in the L-PC/Br-PC blends.

Keywords : polymer blends, polycarbonate, extensional viscosity.

Introduction

Polycarbonate (PC) is a widely used engineering polymer and has an excellent mechanical properties, dimensional stability, heat resistance, and transparency. Since its introduction during the late 1950s, bisphenol-A polycarbonate has exhibited a substantial growth rate. So far, a variety of

new applications have been created by tailoring the base polycarbonate polymer with modification that enhance the end-use properties of the polymer.¹

Polycarbonate is divided into a linear and a branched polymer according to its structure, and these polymers show a different rheological behavior.² It has been reported that branching is a well-known structural modification of the polymers for the change of their rheological properties. Branched polymers are used for the applications characterized by extensional flow fields in the molten state such as

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extrusion coating, blow molding, foam extrusion, and melt phase thermoforming.³⁻⁵ Generally, branched polymer exhibits higher molecular weight than linear polymer, therefore it exhibits lower flowability. In order to compensate the low flowability of the branched polymer without loss of the characteristic of polymer, the blends of a linear and a branched polymer, each polymers have a same molecular composition, have been studied.

Several researchers have reported the rheological and mechanical properties containing polycarbonate blends. In the early studies from the same laboratory (Samyang R&D Center), Lyu *et al.*⁵ reported the mechanical and rheological behaviors of the linear and branched polycarbonate (Br-PC) blends and they showed that the mechanical properties were not changed regardless of the compositions of the linear and branched polycarbonate blends. However, the rheological properties are much more dependent on the composition of linear and branched polycarbonates in their blends than the mechanical properties. Kim *et al.*⁶ reported the molecular modeling of bisphenol-A polycarbonate and tetramethyl bisphenol-A polycarbonate. Kim *et al.*⁷⁻⁹ reported the thermal behavior and morphology of the blends of PC with poly (methyl methacrylate), poly(ethylene terephthalate), and poly (ϵ -caprolactone) blends. For the blends of PC and poly (styrene-*co*-acrylonitrile), Kim *et al.*¹⁰ reported the morphology and interfacial tension of the blends. In the study of blends of low density polyethylene (LDPE) with high density polyethylene, Cho *et al.*¹¹ reported that the melt strength of the blends was increased with increasing molecular weight of the LDPE.

In this study, rheological properties such as complex viscosity and extensional viscosity were studied by advanced rheometric expansion system (ARES) and extensional rheometer, respectively, for the L-PC/Br-PC blends. Also, the effect of branched polycarbonate on the glass transition temperature (T_g) and sag resistance time were studied by differential scanning calorimeter (DSC) and a custom-built sag tester, respectively. The rheological properties were compared with the results obtained from the sag resistance measurements.

Experimental

Materials. The polymers used in this study were obtained from commercial sources. The characteristics of the polymer

samples are shown in Table I. The linear polycarbonate (L-PC) and branched polycarbonate (Br-PC) were manufactured by Samyang-Kasei Co. Ltd, under the trade name of TRIREX 3022 and TRIREX 3026U, respectively.

Blend Preparation. To prepare melt-extruded blends with composition of 100/0, 95/5, 90/10, 80/20, 70/30, 60/40, 50/50, 20/80, and 0/100 L-PC/Br-PC, all polymers were dried in a vacuum oven at 120°C for 24 hr before use. Blends were prepared by co-rotating twin screw extruder (ZSK-25, Warner & Pfleiderer) which has a 25-mm inside diameter of the barrel. The temperatures of the extruder were set at 270°C in barrel zones and at 280°C in a die zone.

Thermal Analysis. Thermal properties of all the samples were measured calorimetrically with a Perkin-Elmer DSC model DSC-7. Blend samples were heated in a nitrogen atmosphere from 30°C to 250°C at a heating rate of 20°C/min and cooled to 30°C for the second scan. And then, the second scan was measured from 30°C to 250°C at a heating rate of 20°C/min, and the data were acquired.

Sag Resistance Time. A custom-built sag tester was used to compare the sag resistance of the specimen made from the L-PC/Br-PC blends. The specimens for sag resistance test were prepared using a injection molding machine (Battenfeld UNILOG 2040). Once the predetermined oven temperature (200°C) is reached, the specimen is placed on a supporting jig in the oven and the time is recorded when the center of specimen sags to 10 mm distance. Sagging time was monitored by a laser beam installed to give a precise-out of the time required for specimens to sag a specified distance.

Extensional Viscosity. Measurement of the uniaxial extensional viscosity at constant strain rate was carried out using Meissner type extensional rheometer at 220°C. Rodlike specimens, which were prepared by cooling the extruded strand with a 9 cm length and 2 mm diameter, have been used for elongational measurement. In this experiment, the stress growth curves were recorded in an uniaxial extension rate at 0.5 s⁻¹. A detail description and discussion of the reliability of the extensional rheometer were given in the previous paper.^{12, 13}

Complex Viscosity. Dynamic shear tests were carried out on an Advanced Rheometric Expansion System (ARES) in oscillatory shear at 7% strain with a parallel plate arrangement with 25 mm in diameter and 2 mm gap setting. A strain sweep test was performed on each of the samples to

Table I. Characteristics of the Polymer Samples Used in This Study

Polymer	M_w^a	M_n^a	MWD	MI ^b (g/10 min)	T_g^c (°C)
Linear polycarbonate (L-PC)	23,000	9,800	2.3	12.2	148.5
Branched polycarbonate (Br-PC)	30,000	15,000	2.0	2.5	151.9

^aMeasured by GPC.

^bMelt Index, measured with 1.2 kg at 300°C.

^cMeasured by DSC.

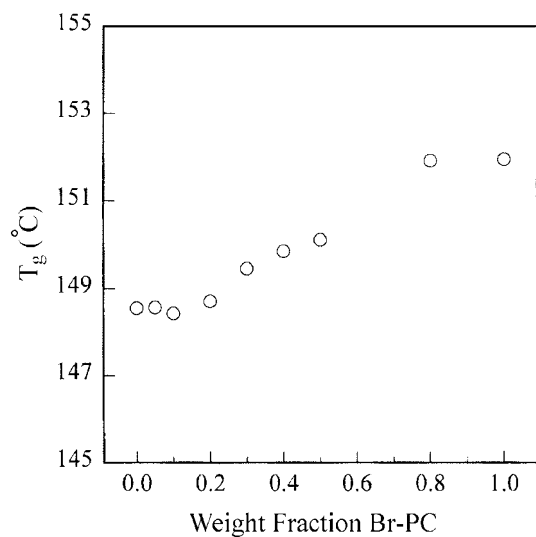


Figure 1. Glass transition temperature of L-PC/Br-PC blends.

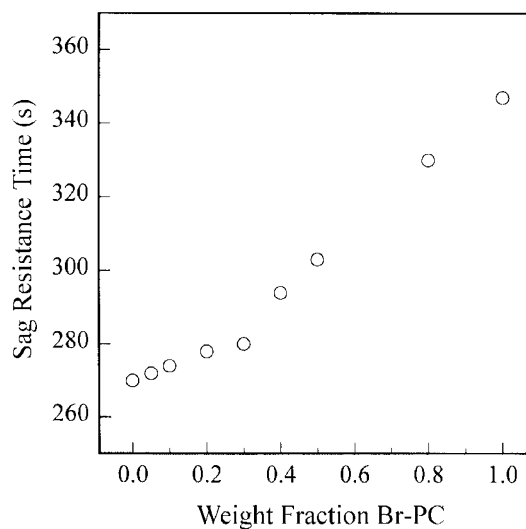


Figure 2. Sag resistance time of L-PC/Br-PC blends at 200°C.

ensure that the measurements were made within the linear viscoelastic range. The frequency sweeps from 0.01 to 0.1 were carried out at 260°C.

Results and Discussion

Thermal Analysis. Thermal behavior of the L-PC/Br-PC blends was studied using differential scanning calorimetry (DSC). Figure 1 shows the glass transition temperature (T_g) of the L-PC/Br-PC blends with blend composition of 100/0, 95/5, 90/10, 80/20, 70/30, 60/40, 50/50, 20/80, and 0/100 L-PC/Br-PC blends. From Figure 1, the T_g of the blends increases from 148.5 to 151.9°C with the Br-PC. This behavior indicates that the branched PC in the blends, which have a higher molecular weight, reduce the chain mobility of the blend in a glass transition temperature region. From Figure 1, we can see single T_g for the various compositions of the blends of L-PC and Br-PC, which suggests a miscible polymer blend.

Sag Resistance Time. Figure 2 is presented the sag resistance time versus Br-PC content of the blend. From Figure 2, as the content of the Br-PC increases, the sag resistance time of the blends increases from 270 to 347 sec. For conventional PC, the sag resistance time depends mainly on the molecular weight and molecular structure. Br-PC in the blends acts like a reinforcing linkage over the matrix chain entanglements, reducing the chain mobility, and prolong the relaxation time of the blends.⁴ By increasing the extent of entanglement, the long branched chains are effective in retarding the biaxial extensional flow and thus the sag resistance is enhanced. Therefore, by adding Br-PC in the L-PC, it is observed from Figure 2 that the L-PC/Br-PC blend shows synergistic increases in sag resistance time.

Extensional Viscosity. The extensional viscosity of the

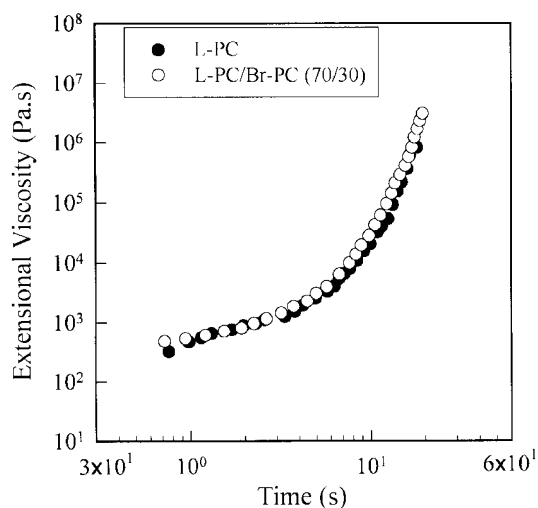


Figure 3. Extensional viscosity curves of L-PC and L-PC/Br-PC(70/30) blends at 220°C.

70/30, 20/80 L-PC/Br-PC blend, and Br-PC are shown in Figures 3-5, respectively. The extensional viscosity curve of the L-PC is added in Figures 3-5 in order to compare the strain-hardening behavior with the L-PC/Br-PC blends. Strain hardening is based on a comparison of the stress in start-up flow with that predicted by the theory of linear viscoelasticity. If the stress increased more rapidly than would be predicted by the linear theory, the material is said to be strain hardening.¹⁴ In general, polymers with a significant degree of long branching exhibit marked extension thickening compared with a linear polymer.

In Figures 3-5, extensional viscosities of the L-PC/Br-PC blends are increased with increasing the Br-PC content, 8.2×10^5 (100/0), 3.1×10^6 (70/30), 6.6×10^6 (20/80), and $2.6 \times$

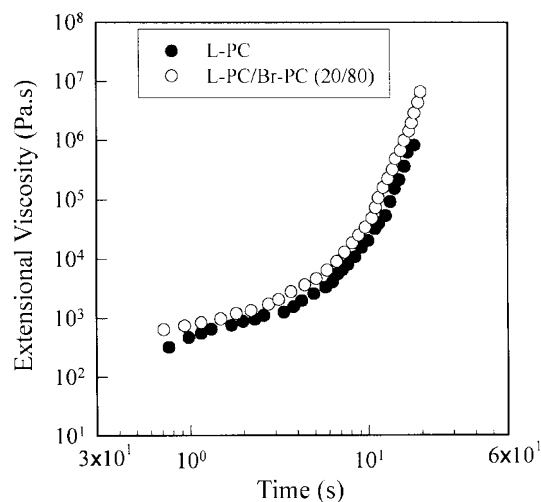


Figure 4. Extensional viscosity curves of L-PC and L-PC/Br-PC(20/80) blends at 220 °C.

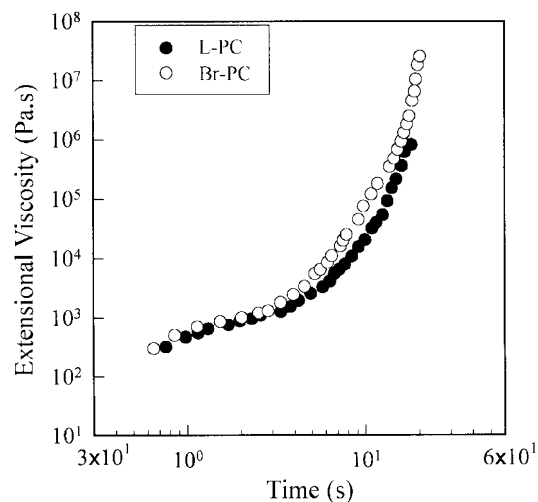


Figure 5. Extensional viscosity curves of L-PC and Br-PC at 220 °C.

10^7 (0/100) Pa.s, respectively. From the results, strain hardening behavior is observed not only in the Br-PC but also in the L-PC/Br-PC blends. As the Br-PC content is increased in the L-PC/Br-PC blend, strain hardening behavior is observed more predominantly. Long branched chain extends the entanglement of the polymer, which retards the extensional flow of the polymer in a melt state.^{15,16} Therefore, it is suggested that the branched PC increases the extensional viscosity in the L-PC/Br-PC blends. The increase in extensional viscosity is related with the increase of sag resistance time with the Br-PC in the L-PC/Br-PC blends.

Complex Viscosity. Figure 6 is presented the complex viscosity of the L-PC/Br-PC blends with the blend compo-

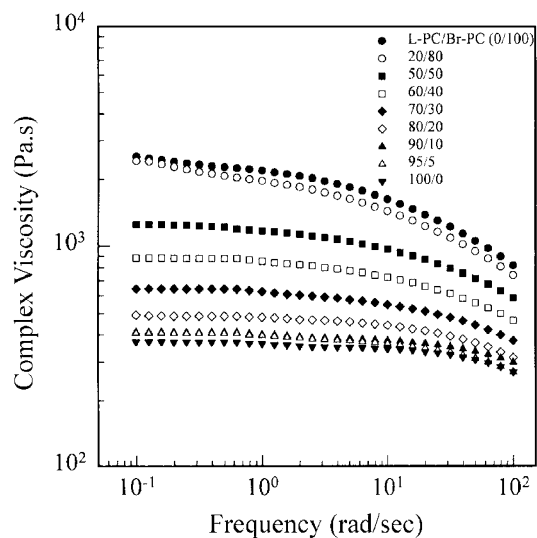


Figure 6. Complex viscosity curves of L-PC/Br-PC blends at 260 °C.

sition of 100/0, 95/5, 90/10, 80/20, 70/30, 60/40, 50/50, 20/80, and 0/100 L-PC/Br-PC. From Figure 6, the complex viscosity increases with the increase of Br-PC in the blends. As the content of the Br-PC increases, the differences of the viscosities depending on frequencies become larger. And the complex viscosity of the blends, which has a higher Br-PC content at high frequency, decreased more sharply than that of the blends, which has a lower Br-PC content. This behavior is related to the shear thinning effects of the blends, and the degree of shear thinning is related to the structure of the molecules, molecular weight, and relaxation of the blend.^{14,17}

Long chain branching in polycarbonate enhances melt elasticity at low shear rates and increases shear thinning at somewhat high shear rates.⁵ These phenomena have been advantageous for blow molding applications where enhanced elasticity gives rise to a good melt strength of the polymer and shear thinning allows for ease of the processing.^{1,2} High molecular weight or branched molecules of the Br-PC have less relaxation or diffusion speed compared with low molecular weight or linear molecules of the L-PC, and this gives a higher shear thinning behavior of the L-PC/Br-PC blends at high shear rates.

From Figures 2 and 6, it is shown that the sag resistance time and complex viscosity of the L-PC/Br-PC blends are increased with the increase of the Br-PC in the blend. The long branched chains in the Br-PC enhance the complex viscosity of the L-PC/Br-PC blends, by retarding the biaxial extensional flow. From the results of complex viscosity and sag resistance time, it is suggested that the increase in sag resistance time is related to the increase of the complex viscosity as well as the extensional viscosity of the L-PC/Br-PC blends.

Conclusions

Thermal and rheological properties of the L-PC/Br-PC blends were studied. In the thermal analysis, it was observed that the T_g was increased from 148.5 to 151.9 °C with the increase of Br-PC in the blend. Also, the blends showed a single T_g , which suggests a miscible blend of L-PC and Br-PC. From the results of sag resistance time of the L-PC/Br-PC blends, the sag resistance was enhanced with the increase of Br-PC in the blends.

From the results of rheological properties of the L-PC/Br-PC blends, the increase in extensional viscosity and the complex viscosity were observed with the Br-PC in the L-PC/Br-PC blends. This increase in viscosity is mainly attributed to the long branched chains in the Br-PC of the L-PC/Br-PC blends, by retarding the biaxial extensional flow. The increase of extensional viscosity and complex viscosity was related with the increase of sag resistance time with the Br-PC in the L-PC/Br-PC blends.

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