Study of Mechanical and Rheological Behaviors of Linear and Branched Polycarbonates Blends

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ABSTRACT: A study of the mechanical and rheological properties of linear and branched polycarbonates blends is presented. Phase separations of the blends were checked through DSC and SEM, and, subsequently, mechanical and rheological properties were investigated. Phase separations were not observed in the blends. The mechanical properties were examined through tensile, flexural, and impact tests. All the mechanical properties of the blends were relatively independent of the compositions. For study of the rheological properties, melt viscosity, storage and loss moduli, and melt tension of the blends with various compositions were examined at various temperatures. The dependence of the viscosity on the molecular weight was also studied. As the content of branched polycarbonate increases, the dependence of the viscosity on the molecular weight and the shear thinning behavior became more marked. Melt tensions were also increased as the branched polycarbonate content increased in the blends for all tested temperatures. In this study, the blend systems which have same mechanical properties but different rheological properties can be obtained through blending of linear and branched polycarbonates. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1814–1824, 2001

Key words: linear polycarbonate; branched polycarbonate; mechanical property; melt viscosity; melt tension

INTRODUCTION

Polycarbonate is one of the engineering plastics and it is widely used in the plastic industries. It is used in automobile parts, electrical parts, bottles, optical parts, sheets, and media materials for audio and visual systems. The main advantages of polycarbonate over other thermoplastics are dimensional stability, heat resistance, self-extinguishing characteristics, good electrical resistance and transparency, as well as high mechanical strengths.[1,2] Polycarbonate is an amorphous thermoplastic and it can be divided into linear and branched polycarbonates according to its structure.[3,4]

The flow and mechanical properties of a polymer depend upon its molecular weight and structure. Generally, low molecular weight polymers have a higher flow property than have high molecular weight polymers.[5–8] Linear and branched

polymers show different flow properties.[9–11] The flowability of linear polycarbonate depends on the molecular weight.[12] However, flowability of branched polycarbonate depends on the degree of

(a) Linear structure: TRIREX® 3022

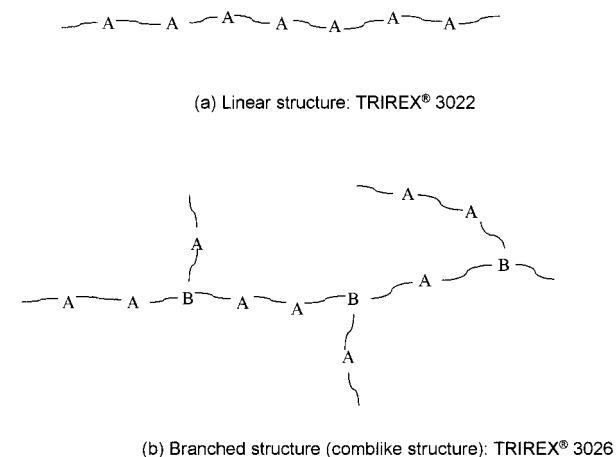(b) Branched structure (comblike structure): TRIREX® 3026

Figure 1 Schematic drawings of linear and branched polycarbonates that were used for blends: (a) linear structure: TRIREX® 3022; (b) branched structure (comblike structure): TRIREX® 3026.

Table I   Compositions of Linear and Branched Polycarbonates in Blends

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Linear polycarbonate (wt %)	100	95	90	85	80	75	70	50	30	25	20	15	10	5	0
Branched polycarbonate (wt %)	0	5	10	15	20	25	30	50	70	75	80	85	90	95	100

branching and the molecular weight.[13] Applications of polycarbonate in practical use are by blending with other polymers as well as by itself. A number of studies have appeared on the blend system of polycarbonate and other polymers such as ABS or SAN,[14–19] polyolefins,[18–23] polyesters,[24–28] polyamide, and poly(ε-caprolactone),[29] etc.[30–32] However, there are a few studies on the blend of linear and branched polycarbonates.[33,34] Hansen and Jansam[33] argued that the linear and branched polycarbonates blend has a higher melt elasticity than that of linear polycarbonate. Pham[34] suggested that the processability and physical properties can be improved through the blending of linear and branched polycarbonates.

In polymer processing operations, such as injection molding, blow molding, and sheet extrusion, appropriate rheological properties are required for their processes. The blend of linear and branched polycarbonates could improve the flow properties, melt elasticity, and melt tensions without deteriorating the mechanical properties. Thus, the purpose of this study was to present the characteristics of the rheological and mechanical properties of the linear and branched polycarbonate blend systems.

EXPERIMENTAL

Material and Specimen Preparation

We used two kinds of polycarbonates: linear (TRIREX® 3022) and branched polycarbonates

(TRIREX® 3026) supplied by Samyang Co. (Seoul, South Korea) for blending. The TRIREX® 3022 is a linear polycarbonate and is made by interfacial polymerization of bisphenol A and phosgene. The branched polycarbonate, TRIREX® 3026, is made by using a branching agent in bisphenol A and phosgene.[3,4] Figure 1 shows the schematic drawings of linear and branched polycarbonates: TRIREX® 3022 and TRIREX® 3026.[4] The molecular weights (M_w) of linear and branched polycarbonates that we used were 43,000 and 60,000, respectively. We mixed and blended linear and branched polycarbonates using an intermeshing corotating twin-screw extruder (ZSK25, Warner & Pfleiderer) which a 41 L/D and 25-mm inside diameter of the barrel. Table I shows the compositions of the linear and branched polycarbonates in the blends. Figure 2 shows the screw configuration and operational conditions of the ZSK25 twin-screw extruder for blending. The mixed and blended polycarbonates' strand from the extruder die was pelletized after it passed a water bath.

Tensile, flexural, and impact tests specimens were prepared by injection molding for the tests of mechanical properties. The injection-molding machine that we used was a Battenfeld machine (75
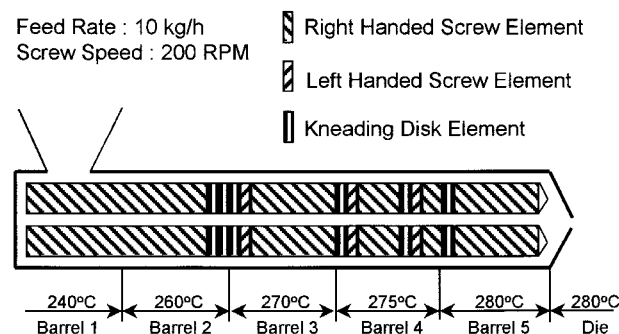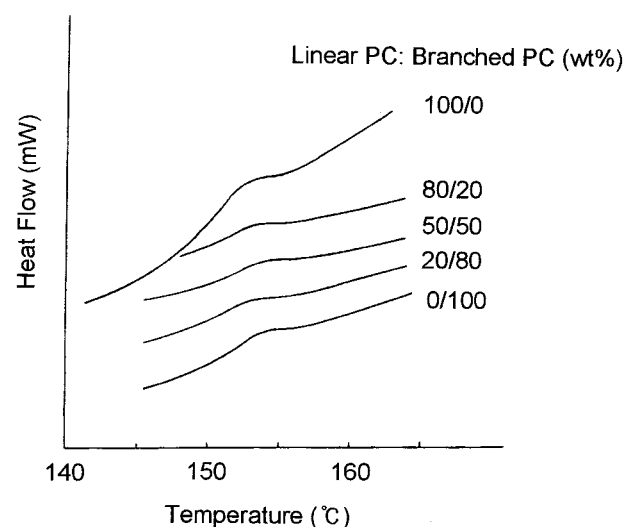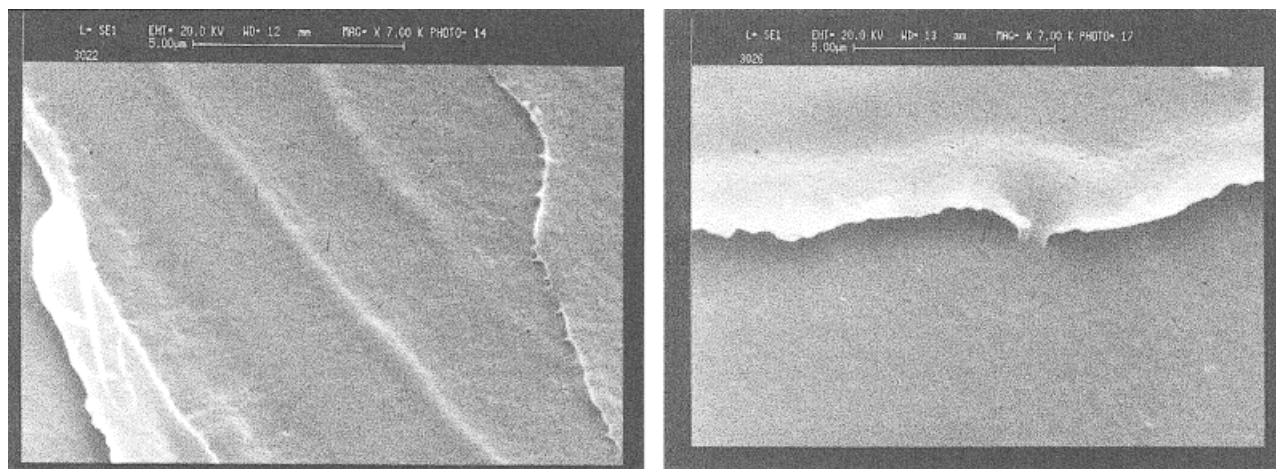

Figure 2   Schematic drawing of ZSK25 (intermeshing co-rotating, Warner & Pfleiderer) twin-screw extruder and operational conditions for the blends of linear and branched polycarbonates.

Figure 3   DSC traces of linear and branched polycarbonates blends.

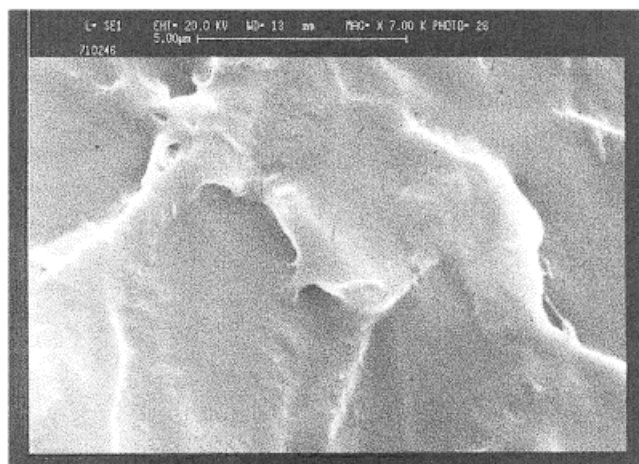(a) Linear polycarbonate

(b) Branched polycarbonate

(c) Polycarbonates blend
Linear PC : Branched PC (wt%)=50:50

Figure 4   SEM photographs obtained from fractured cross section of linear, branched polycarbonates and their blends: (a) linear polycarbonate; (b) branched polycarbonate; (c) polycarbonate blend, linear polycarbonate : branched polycarbonate (wt %) = 50 : 50.

tons of clamping force). We set the mold temperature at 80°C and nozzle temperature at 290°C for the operation of the injection-molding machine.

Observations of Phase Separation

Differential Scanning Calorimetry

The thermal characteristics were tested with differential scanning calorimetry (DSC) equipment (Perkin–Elmer DSC 7RSe). The weights of samples were 7.4 mg and the heating rate was 10°C/min. The peaks were measured as the increasing temperature.

Scanning Electron Microscope

The cross sections of injection-molded sample bars were observed by SEM to analyze the morphological features of the blends. The SEM equipment that we used was a Stereoscan 360 (Cambridge Instruments). The cross sections of the samples were prepared by breaking the sample bars after quenching them in liquid nitrogen for 30 min.
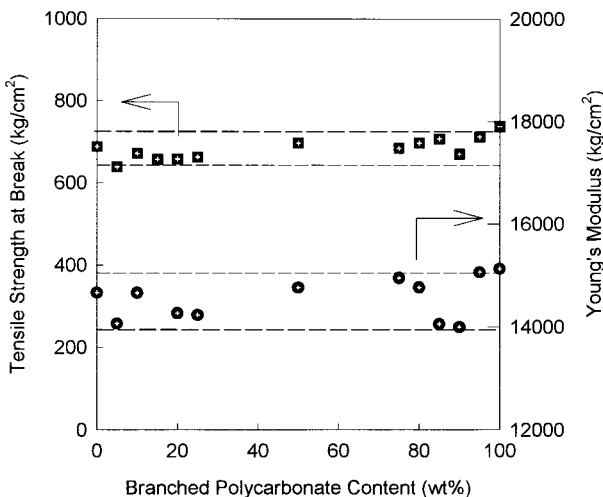
Figure 5 Tensile strength and Young's modulus according to the content of the branched polycarbonate in the blends of linear and branched polycarbonates.

Measurement of Mechanical Properties

Tensile Test

Tensile tests were performed on dumbbell-shaped specimens by an Instron 4204. The specimens had a 165-mm total length, 50-mm gauge length, 13-mm width, and 3.2-mm thickness. The Instron machine was operated at a 2.8 mm/min crosshead speed. Through the tensile tests, the Young's modulus and stress at break were obtained. Our tensile tests were performed under the ASTM D638 regulation at room temperature.

Flexural Test

Flexural tests were performed by an Instron 4204, which was the same machine that we used
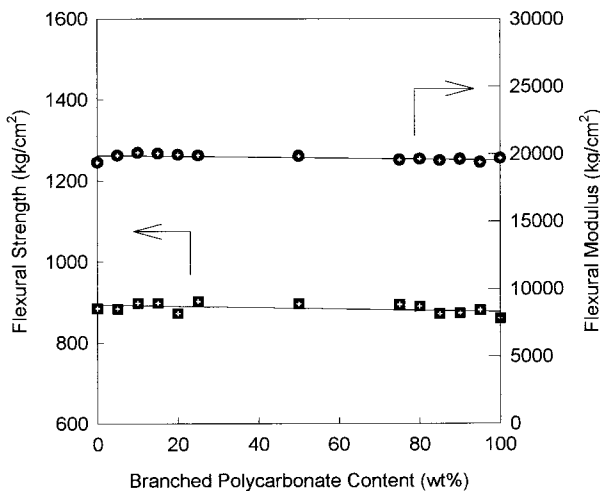
Figure 6 Flexural strength and flexural modulus according to the content of the branched polycarbonate in the blends of linear and branched polycarbonates.
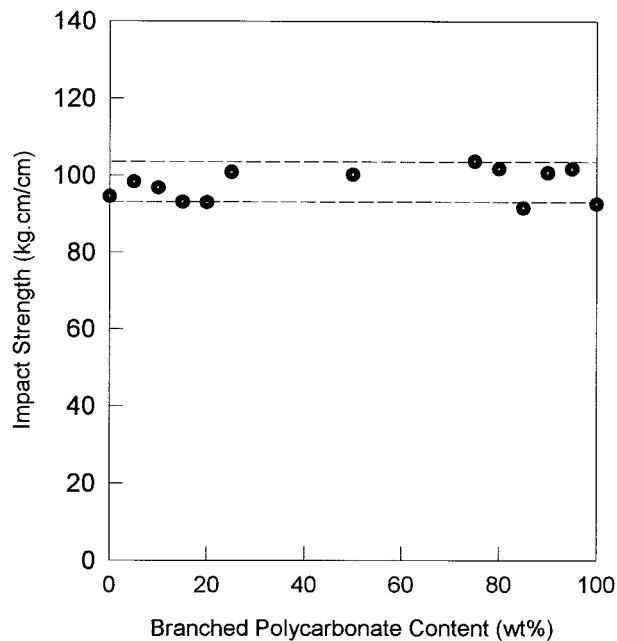
Figure 7 Impact strength according to the content of the branched polycarbonate in the blends of linear and branched polycarbonates.

in the tensile test. The machine was operated at a 2.8 mm/min crosshead speed. The test bar had a 130-mm length, 13-mm width, and 6.4-mm thickness. We used three-point bending as a test method and the distance between two supports was 100 mm. These tests were performed under the ASTM D 790 regulation at room temperature.

Impact Test

Izod impact tests were performed by an Izod impact test machine of CEAST. The notched specimen had a 63-mm length, 12.7-mm width, and 3.175-mm thickness. Our impact tests were performed under the ASTM D256 regulation at room temperature.

Measurement of Rheological Properties

Melt Viscosity, Storage, and Loss Moduli

The melt viscosities and storage and loss moduli (G' and G'') of linear and branched polycarbonate blends were measured by ARES (Advanced Rheometric Expansion System, parallel-plate mode). The shape of the specimen used in ARES had a 25-mm diameter and 2-mm thickness. The rheological data from ARES were plotted with respect to the frequency. We measured the viscosities, G', and G'' for three different temperatures: 260, 280, and 300°C.

(a) Temperature at 260°C

(b) Temperature at 280°C
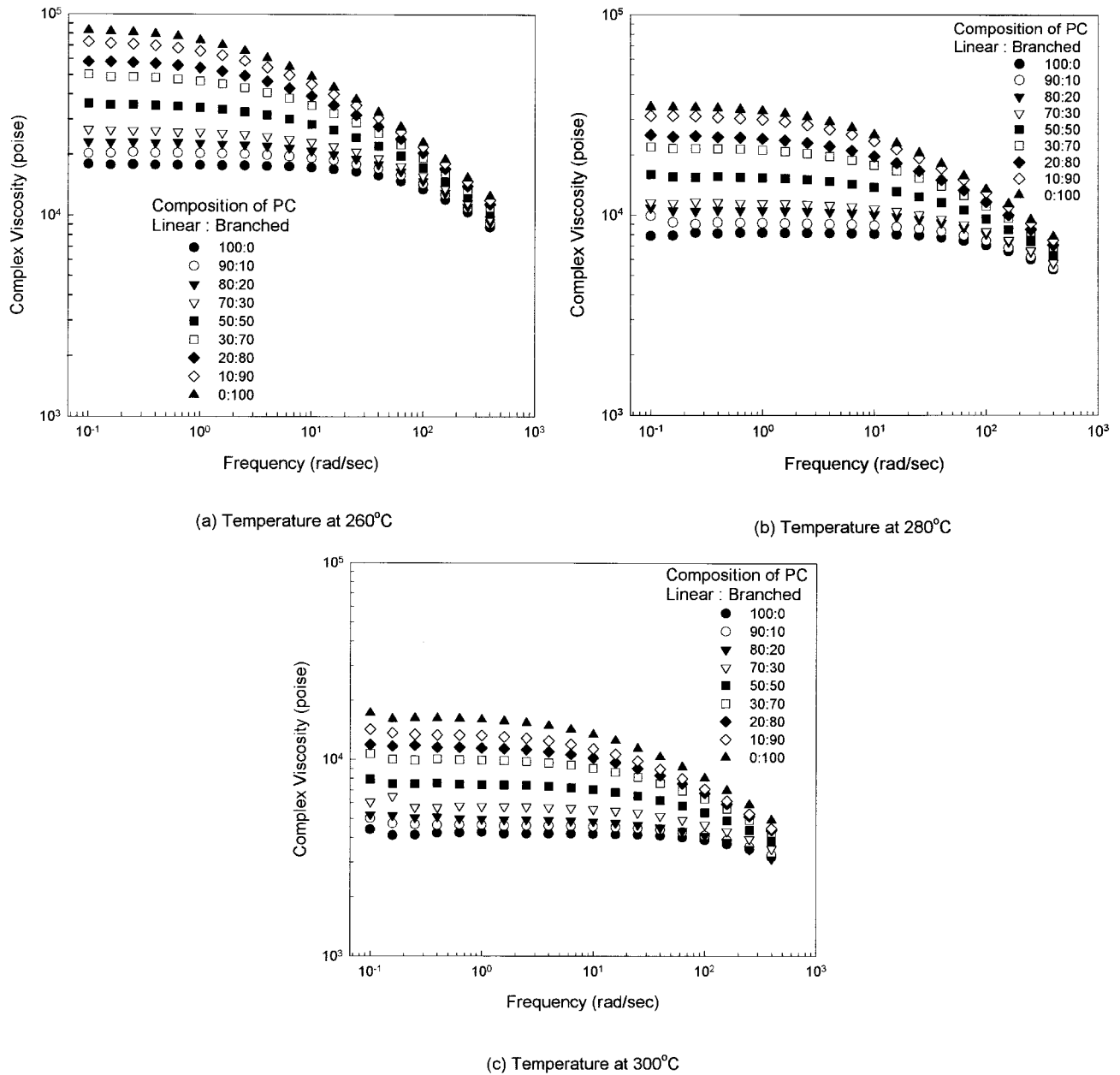
(c) Temperature at 300°C

Figure 8 Complex viscosity curves of linear and branched polycarbonates blends: (a) temperature at 260°C; (b) temperature at 280°C; (c) temperature at 300°C.

Melt Tension

Melt tensions of the blends were measured by a caprograph of (Toyoseiki Company). The diameters of the reservoir and die were 9.55 and 1.00 mm, respectively, and the L/D of the die was 10. The molten polymer was pushed from the reservoir to the die by a plunger with a 10-mm/min speed. The molten strand from the die was drawn by two rolls with speeds of 10, 20, and 30 m/min and measured tensions at temperatures of 260, 280, and 300°C.

RESULTS AND DISCUSSION

Phase Separation

A differential scanning calorimeter (DSC) was used to evaluate the component miscibility using a T_g treatment. It is a well-known fact that a single T_g is a necessary but not sufficient condition for the miscibility of polymer blends. Figure 3 shows DSC traces of the polycarbonate blends. If we accept measuring errors of about
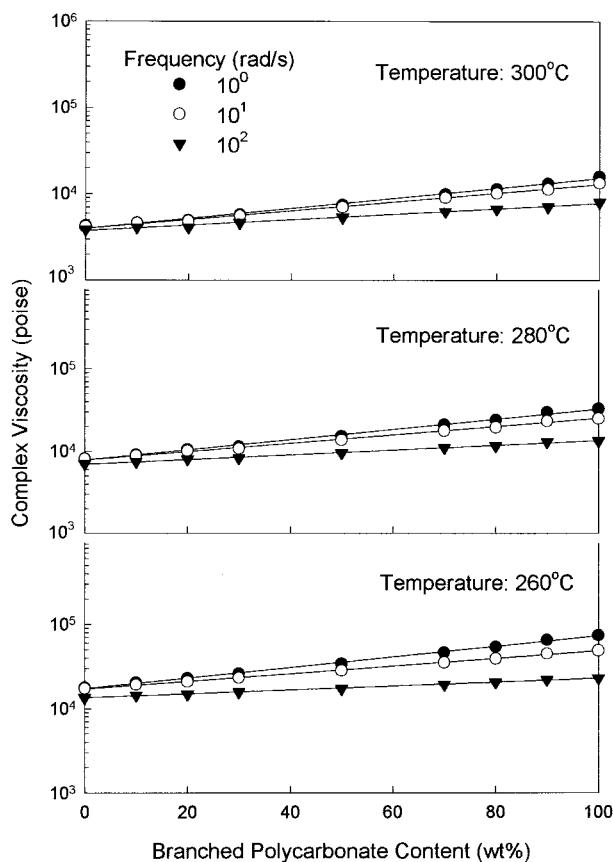
Figure 9 Complex viscosities according to the content of the branched polycarbonate in the blends of linear and branched polycarbonates for various frequencies.

sile strength and the Young's modulus obtained from tensile tests for different compositions of the blends. Tensile strengths are in the range of 650–710 kg_f/cm^2 regardless of the branched polycarbonate contents in the blends. The Young's moduli of the blends for all compositions are distributed at 14,000–15,000 kg_f/cm^2. Figure 6 shows the flexural strengths and flexural moduli that remain the same values for all the compositions. Impact strengths are in the range of 95–105 kg cm/cm for various branched polycarbonate contents as shown in Figure 7. As we observed in Figures 5–7, we concluded that the mechanical properties that we tested are independent of the compositions of the linear and branched polycarbonate blends.
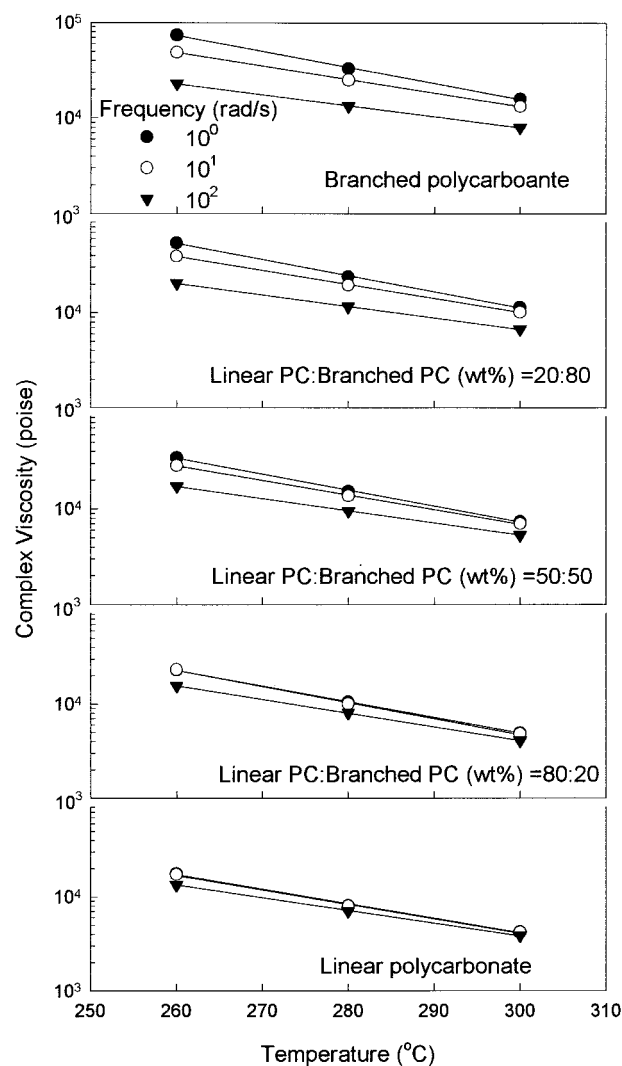

Figure 10 Complex viscosities according to the temperature for various compositions of linear and branched polycarbonates.

2°C, the T_g's of all the compositions of linear and branched polycarbonate blends are same for 153°C.

The morphologies were observed using SEM to investigate the phase separation of the polycarbonate blends. Figure 4 shows SEM photographs of cross sections of the polycarbonate blends. Figure 4(a,b) shows the linear and branched polycarbonates, respectively, and Figure 4(c) shows the blend of linear and branched polycarbonates. Phase separation was not observed in the polycarbonate blend through the SEM photographs. As we observed in the DSC traces and SEM photographs, the blends of linear and branched polycarbonates show a homogeneous single phase.

Mechanical Property

We performed tensile, flexural, and impact tests to analyze the mechanical properties of the blends. Figure 5 shows the variations of the ten-
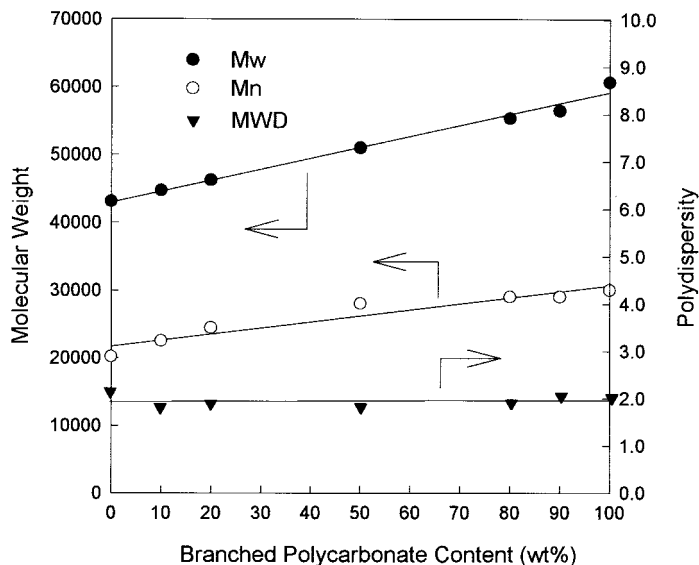
Figure 11   Molecular weight of linear and branched polycarbonates blends.

Rheological Property

Viscosity, Storage, and Loss Moduli

Figure 8 shows the viscosities of linear and branched polycarbonate blends at temperatures of 260, 280, and 300°C. The viscosities increase as the content of the branched polycarbonate increases in the blends at each measured temperature. As the temperature increases from 260 to 300°C, the viscosities decrease and the range of the shear rate for Newtonian regions increases. Figure 9 shows increasing viscosities linearly according to the increment of the branched polycarbonate content in blends at 10^0, 10^1, and 10^2 rad/s of frequency and at three different temperatures. The differences of the viscosities between the frequencies for each composition become smaller and smaller as the temperature increases, indicating that the shear-thinning effect decreases as the temperature increases.

Figure 10 shows the viscosity decrease of the blends at high temperatures. As the content of branched polycarbonate increases from 0 to 100 wt % in the blends, the differences of the viscosities between the frequencies for each temperature become larger and larger. This behavior indicates that the shear-thinning effect increases as the content of branched polycarbonate increases. 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 or diffusion speed. High molecular weight or branched molecules have less relaxation or diffusion speed compared with low molecular weight or linear molecules, and this gives a high shear-thinning behavior.[8,35,36]

Generally, viscosities increase as the molecular weight (M_w) increases. Figure 11 shows variations of the molecular weight according to the compositions of linear and branched polycarbonate blends. Figure 12 indicates how viscosities vary with the molecular weight in the blends. The molecular weights (M_w) in Figure 12 are based on Figure 11. The general relationship between the molecular weight and zero shear viscosity is given by[5-8]

$$\eta_0 = k'M \qquad (M < M_c) \qquad (1a)$$

$$\eta_0 = k''M^{3.4} \qquad (M > M_c) \qquad (1b)$$

where η_0 is the zero-shear viscosity; k' and k'', proportional constants; and M_c, a critical molecular weight for the formation of effective entanglement couples. It was found for polydisperse systems that the molecular weight (M) should be used is a weight-average molecular weight: M_w.[8] The dependence of the viscosity on the molecular weight (M_w) in Figure 12 is about 4.14–4.47 power for low frequency (Newtonian region): 10^0 rad/s. As the frequency increases to 10^2 rad/s, the dependency of the viscosity on the molecular weight (M_w) decreases to about 1.65–2.28 power. If we compare our blend system with eq. (1), our blend system

(a) Temperature at 260°C
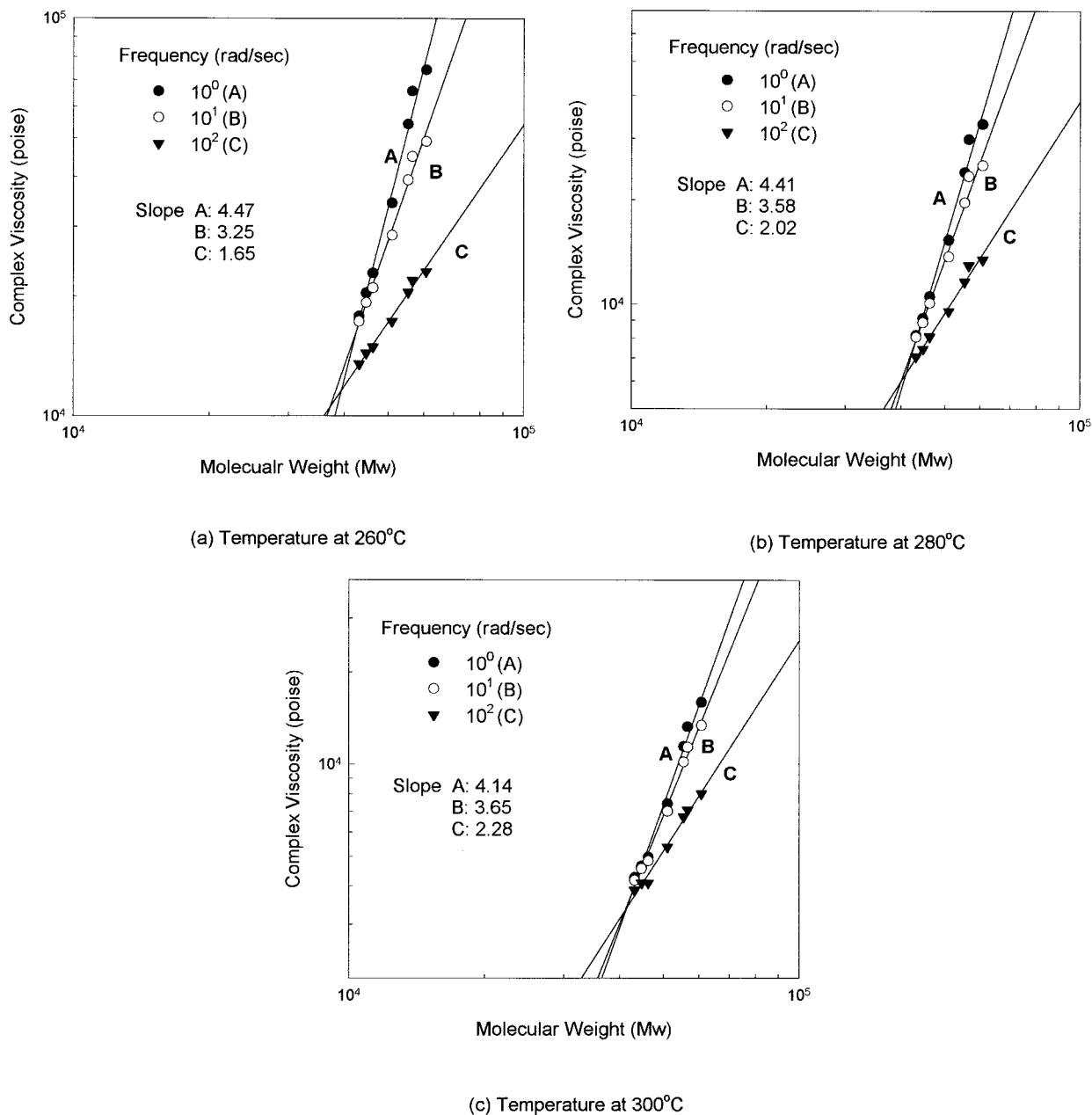
(b) Temperature at 280°C

(c) Temperature at 300°C

Figure 12 Complex viscosities according to the molecular weight of blends of linear and branched polycarbonates for various frequencies: (a) temperature at 260°C; (b) temperature at 280°C; (c) temperature at 300°C.

is more dependent on the molecular weight (M_w) than is eq. (1). This discrepancy comes from that our blend system contains branched polycarbonate. According to the reptation model, the branching points of the branched polymer act as an anchor and this hinders movement of the polymer molecules. Therefore, the dependence of the zero–shear viscosity on the molecular weight increases as the content of the branched polymer increases.[36] As temperature increases, the dependence of the viscosity on the mo-

lecular weight (M_w) increases at high frequency: 10^2 rad/s. However, at low frequency, 10^0 rad/s, the dependence of the viscosity on the molecular weight (M_w) decreases as the temperature increases.

The storage (G') and loss moduli (G'') of the blends are shown in Figure 13. As the content of the branched polycarbonate increases, G' increases rapidly compared with G''. Through these phenomena, we could realize that the branched
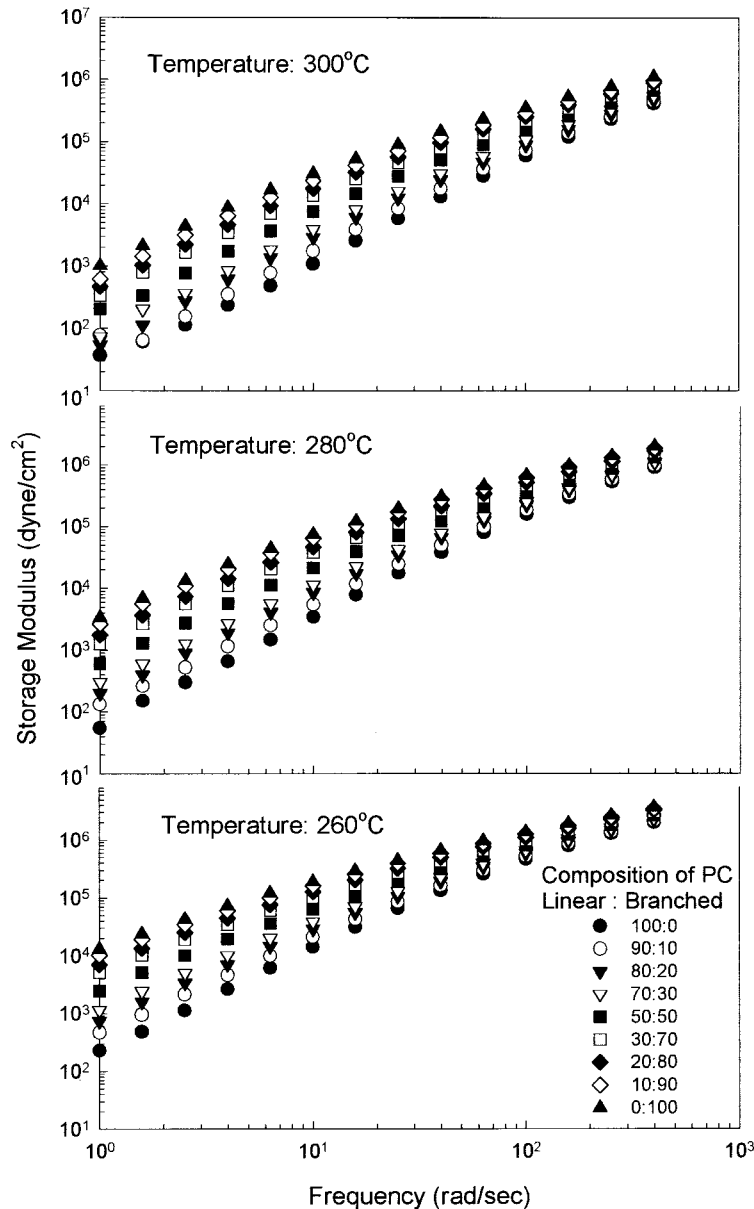
(a) Storage modulus

Figure 13 Storage and loss moduli of linear and branched polycarbonates blends for various temperatures: (a) storage modulus; (b) loss modulus.

polycarbonate has a higher melt elasticity than that of linear polycarbonate.

Melt Tension

Melt tensions of blends are shown in Figure 14. The melt tension increases as the content of the branched polycarbonate increases. The increments are remarkable at over 50 wt % of the branched polycarbonate. When an extensional force is exerted to the polymer molecules, molecules tend to arrange parallel to the direction of force during stretching. In this stretching and arranging process, branched polymer molecules require a higher force than do linear polymer molecules since branched chains act as a hindrance of movement. The melt tension increases slightly as the extensional velocity increases from 10 to 30 m/min and it decreases as the temperature increases.
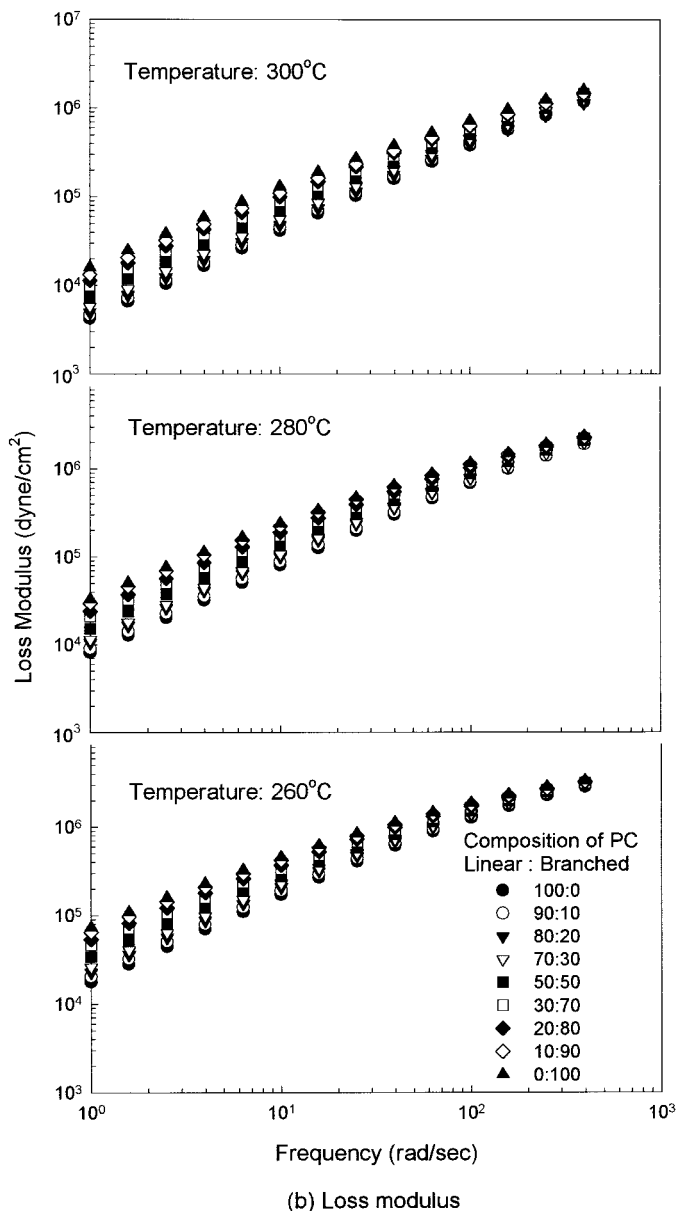
(b) Loss modulus

Figure 13   (*Continued*)

CONCLUSIONS

The behaviors of mechanical and rheological properties were studied at various compositions of linear and branched polycarbonate blends. Phase separations of the blends were analyzed by using a DSC trace and SEM photographs. The blends are completely homogeneous and single phase.

Through these investigations, we observed that the mechanical properties were not changed regardless of the compositions of the linear and branched polycarbonate blends. However, the rheological properties such as viscosity, storage modulus (G'), and melt tension are quite various to the compositions of the blends, and those decreased with increasing temperature. At a high portion of linear polycarbonate, a high-flow property can be obtained, and at a high portion of branched polycarbonate, high melt elasticity and melt tension can be obtained. The rheological properties are much more dependent on the composition of linear and branched polycarbonates in their blends than are the mechanical properties.

Through the blending of linear and branched polycarbonates, various rheological properties are achieved without loss of any mechanical proper-
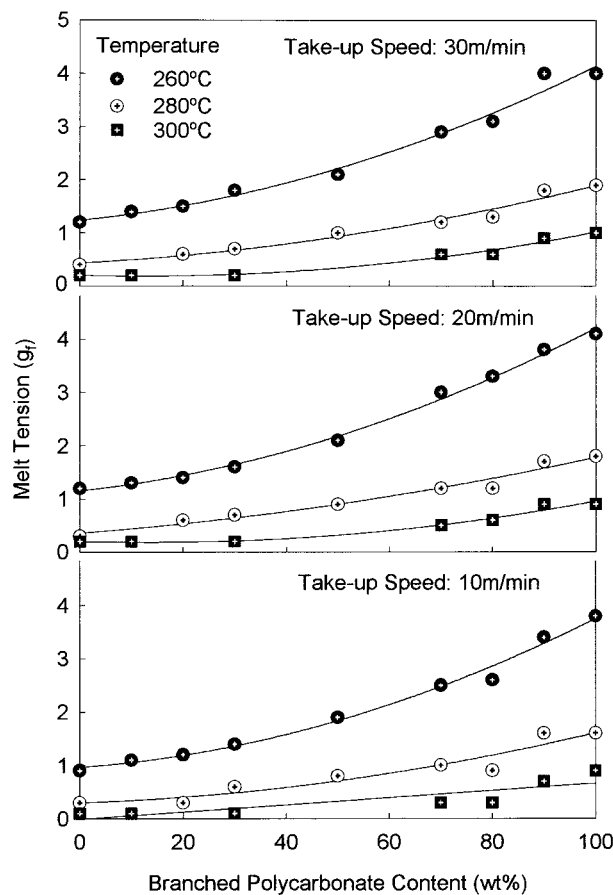
Figure 14 Melt tensions of linear and branched polycarbonates blends.

ties of the polycarbonate. Different rheological properties are needed according to the various polymer-shaping operations, that is, flowability in injection molding and melt tension in blow molding and die extrusion. These various rheological properties can be accomplished by the blending of linear and branched polycarbonates.

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