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Article

Thermal Expansion Behavior of Antiplasticized Polycarbonate

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Thermal expansion behavior and viscoelastic properties of antiplasticized polycarbonate (PC) are studied employing *p*-terphenyl (*p*-tPh) as an antiplasticizer. The rheological characterization reveals that the free volume fraction at the glass transition temperature and thermal expansion coefficient of the free volume in the rubbery region are unchanged by the *p*-tPh addition. However, the linear coefficient of thermal expansion in the glassy region is found to be reduced, which can be attributed to the reduction of free volume in the glassy state. Since the antiplasticized PC exhibits high modulus with a low thermal expansion coefficient, its suitability as a replacement for inorganic glasses will be considered.
Key Words: Polycarbonate / Antiplasticization / Mechanical properties / Viscoelastic properties / Thermal expansion

1. INTRODUCTION

Because of its excellent transparency, mechanical toughness and high heat-distortion temperature, polycarbonate (PC) is widely employed in optical applications such as plastic glasses, optical disks, and optical films.1-3) A lightweight replacement for an inorganic glass is being developed due to strong demand in the automobile industry to reduce the weight of electric vehicles. In order to serve as a replacement for an inorganic glass, however, rigidity and the dimensional stability under temperature change need to be improved.

The role of a conventional plasticizer is, in general, to increase the flexibility in the solid state and flowability in the molten state.4-12) A plasticizer weakens the intermolecular topological interaction between neighbor polymer chains, leading to low viscosity in the flow region. Furthermore, the glass-to-rubber transition occurs at low temperature because the relaxation time of the segmental motion is shortened. Even in the glassy state, a plasticizer usually enlarges the free volume fraction, which has been revealed by the positron annihilation lifetime spectroscopy,4,5,8) proton spin-lattice relaxation at nuclear magnetic resonance13,14) and pressure-volume-temperature diagram.15) Because of the enlarged free volume, the modulus decreases and the thermal expansion increases.11)

To counter this normal behavior of plasticization, additives known to enhance the modulus are used, which is called antiplasticization. According to previous studies,3,15-27) the decrease in the free volume is believed to be the origin of the modulus enhancement. Therefore, β-relaxation of an amorphous polymer, *i.e.*, local relaxation mode, is strongly affected by an antiplasticizer, because the mobility in a local mode is suppressed by loss of the free volume. This anomalous but well-known behavior has been reported for various polymers including poly(vinyl chloride),17-19) poly(methyl methacrylate),15,18,24) and cellulose esters.18,26,27) PC is also known to show antiplasticization when combined with various materials.3,16-18,20,22) The addition of an antiplasticizer enhances the modulus and reduces the β-relaxation mode located around at –100 ºC, which is attributed to mechanisms such as ring-flip process of phenyl groups28,29) and rotation of the phenylene rings.30)

Although numerous researches have been carried out on antiplasticization, to the best of our knowledge, the thermal expansion behavior of an antiplasticized glass has not yet been reported; this phenomenon should be clarified to improve our understanding of antiplasticization. Considering the mechanism of antiplasticization, it can be predicted that

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thermal expansion will be reduced because of the decrease in the free volume.

In this paper, thermal expansion behavior and viscoelastic properties of PC are investigated using several blends of PC with *para*-terphenyl (*p*-tPh). Since large thermal expansion is a serious problem for glassy polymers used in various applications instead of an inorganic glass, the results will have important implications for industrial applications.

2. EXPERIMENTAL

2.1 Materials

The polymeric material used in this study was a commercially available bisphenol A polycarbonate (PC) (Teijin Chemicals, Panlite L-1225Y). The number and weight-average molecular weights, which were characterized by a gel permeation chromatography (Tosoh, HLC-8020) with TSK-GEL/GMHXL, were 19,000 and 97,000, respectively, as a polystyrene standard.

Para-terphenyl (*p*-tPh), purchased from Tokyo Chemical Industry, was employed as an antiplasticizer in this study without further purification.

Melt-mixing of PC with *p*-tPh was performed using a 60 cm^3 batch-type internal mixer (Toyoseiki, Labo-plastmill) at 240 ºC. The rotational speed of the blades was 30 rpm, and the mixing time was 3 min. The mixture obtained was compressed into a flat sheet with a thickness of 300 μm or 3 mm by a compression-molding machine (Tester Sangyo, Table-type-test press SA-303-I-S) for 3 min at 240 ºC under 10 MPa, and subsequently quenched at room temperature. The films obtained were annealed for 20 min at T_α + 15 ºC, where T_α is the peak temperature of tensile loss modulus E'' at 10 Hz ascribed to α-relaxation, to remove the residual strain.

2.2 Measurements

The temperature dependence of oscillatory tensile moduli in the solid state, such as storage modulus E' and loss modulus E'', was measured from –150 ºC to 180 ºC using a dynamic mechanical analyzer (UBM, Rheogel-E4000). The frequency and heating rate were 10 Hz and 2 ºC/min, respectively. The rectangular specimen, in which the width is 5.0 mm, the length is 10 mm, and the thickness is 300 μm, was employed.

The angular frequency dependence of E' and E'' was also measured at various temperatures using the dynamic mechanical analyzer.

Thermal analysis was conducted by a differential scanning calorimeter (DSC) (Mettler, DSC820) under a nitrogen atmosphere. The samples were heated from room temperature to 160 ºC at a heating rate of 10 ºC/min. The sample amount in an aluminum pan was approximately 10 mg in weight.

The thermal expansion behavior was evaluated by a thermo mechanical analyzer (Bruker AXS, TMA4000SA) in a compression mode under a constant stress of 3.2 kPa. The initial length of the specimen was 3 mm and the cross-sectional area was 25 mm^2. Measurements were carried out from 20 ºC to 100 ºC at a heating rate of 2 ºC/min under a nitrogen atmosphere. The linear coefficient of thermal expansion β was calculated using eq.1.

$$\beta = \frac{1}{L_0}\frac{dL}{dT} \tag{1}$$

where L_0 is the initial length.

3. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of oscillatory tensile modulus for PC containing 0-20 wt% of *p*-tPh at 10 Hz. As seen in the figure, the storage modulus E' decreases slightly around at –100 ºC. Correspondingly, the loss modulus E'' shows a broad peak at this temperature. This is known as β-relaxation and can be ascribed to the local motion of the main chain.[28-30] In the temperature region beyond the β-relaxation, E' keeps almost a constant value until the glass-to-rubber transition, although there is a weak peak around at 75 ºC. Then, it falls off sharply at 160 ºC. This is a typical dynamic mechanical spectrum for a glassy polymer. The samples containing *p*-tPh show a weak β-relaxation peak as compared with the pure PC. As similar to other antiplasiticized systems, *p*-tPh only reduces the mobility of local chains by filling the free volume of PC, which has been reported by a number of researchers using various antiplasticizers.[3,16-18,20-22] In fact, there is no peak shift in the infra-red spectra (but not present here) by the *p*-tPh addition.

Moreover, the shoulder peak around at 75 ºC is found to be pronounced in the blend. This shoulder peak, called β'-relaxation, is often observed in blends with a diluent. According to Belfiore *et al.*,[20] this is attributed to the local motion of an entire PC repeat unit by chain co-operativity with diluent molecules. Furthermore, E' around at room temperature is enhanced by the addition of *p*-tPh, demonstrating that *p*-tPh acts as an antiplasticizer. Finally, the peak temperatures of α-relaxation T_α's of the blends are lower than that of the pure PC. The height and half-width of the E'' peak for the blend are almost the same as those for PC. The result suggests that the distribution of relaxation time is not changed greatly by *p*-tPh, although the blends demonstrate shorter relaxation time. Considering that most plasticizers broaden the relaxation peak owing to the broad distribution of relaxation time, p-tPh shows good miscibility with PC. However, the blend with 20 wt% of p-tPh is not transparent but opaque, whereas the blends with less than 15 wt% of p-tPh are transparent, as shown in Figure 2. Even for the blend with 20 wt% of p-tPh, the compressed film, prior to exposure to annealing procedure at $T_\alpha + 15$ ºC, is transparent. The results indicate that the maximum amount of p-tPh to show the miscibility with PC is approximately 15 wt% at the annealing temperature.

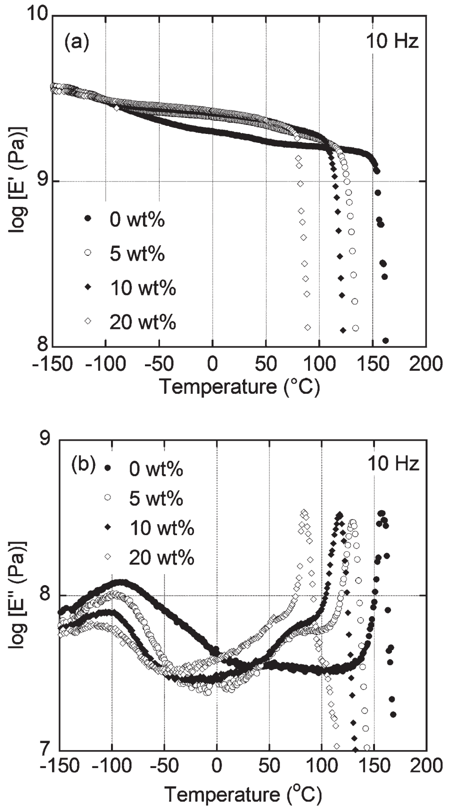

Fig. 1. Temperature dependence of (a) tensile storage modulus E' and (b) loss modulus E'' at 10 Hz for (closed circles) PC, (open circles) PC/p-tPh (5 wt%), (closed diamonds) PC/p-tPh (10 wt%), and (open diamonds) PC/p-tPh (20 wt%).

Fig. 2. Sample specimens with 300 μm thickness; (top) 10 wt% and (bottom) 20 wt% of p-tPh.

That the antiplasticizing effect is observable when the chain mobility in a local mode is reduced by loss of the free volume is well known.[22,31] Therefore, the modulus enhancement has a close relationship with the intensity of β-relaxation mode.

Figure 3 shows E' at room temperature of the blends as a function of p-tPh content. The modulus increases monotonically with increasing p-tPh and seems to reach a plateau value beyond 10 wt%. The result indicates that the filling effect of free volume is saturated around 10 wt% of p-tPh. This is expected because the free volume fraction in the glassy state is believed to be around 2.5 vol%. The excess amount of p-tPh, which does not fill the free volume, will act as a conventional plasticizer, leading to the decrease in T_α, as shown in Figure 4.

In Figure 4, the calculated values following the Gordon-Taylor equation[32] (eq.2) are represented by the solid line, assuming that T_α of p-tPh is –28 ºC, which is similar to that of *ortho*-terphenyl (–30 ºC).[33]

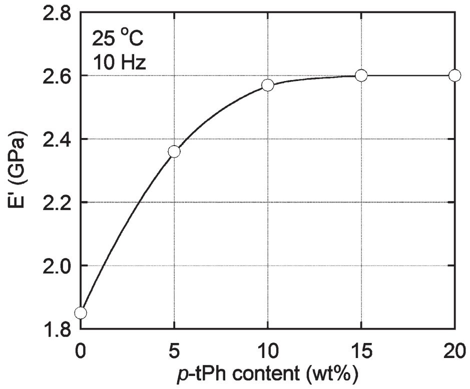

Fig. 3. Tensile storage modulus at 25 ºC for PC/p-tPh.

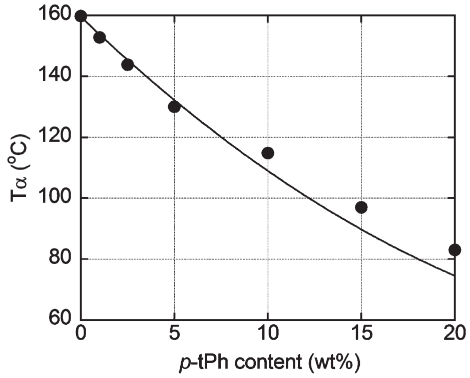

Fig. 4. Peak temperature of E'' ascribed to α-relaxation, T_α, for PC/p-tPh.

$$T_\alpha = \frac{w_{PC}T_{\alpha-PC} + kw_{tPh}T_{\alpha-tPh}}{w_{PC} + kw_{tPh}} \quad (2)$$

where w_i and $T_{\alpha i}$ are the weight fraction and T_α of i component, respectively, and k is a constant evaluated from the experimental data.

The experimental data track the solid line with a slight upward deviation for the blends containing more than 15 wt% of *p*-tPh. Since T_α decreases monotonically with increasing *p*-tPh in the experimental range with a small deviation from the solid line, it is suggested that only a small amount of *p*-tPh is segregated from the matrix for the blend with 20 wt% of *p*-tPh.

In order to investigate the glass-to-rubber transition in detail, the master curves of the frequency dependence of oscillatory tensile moduli are obtained as exemplified in Figure 5. The glass transition temperature T_g evaluated by the DSC measurement is employed as the reference temperature; 150 ºC for PC and 105 ºC for the blend containing 10 wt% of *p*-tPh.

As is well known, the shift factor a_T follows the WLF (Williams-Landel-Ferry) equation as follows;

$$\log a_T = \frac{-c_1(T-T_r)}{c_2 + (T-T_r)} \quad (3)$$

where c_1 and c_2 are the constants, and T_r is the reference temperature ($T_r = T_g$ in Figure 5).

Further, the constants c_1 and c_2 are expressed by the free volume fraction at T_g, *i.e.*, f_g and the thermal expansion coefficient of the free volume in the rubbery region α_f as follows;

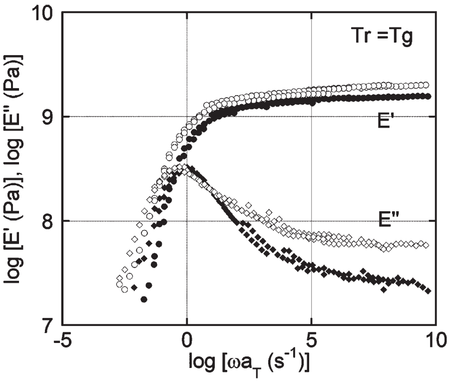

Fig. 5. Master curves of (circles) tensile storage modulus E' and (diamonds) loss modulus E'' for (closed symbols) PC and (open symbols) PC/*p*-tPh (10 wt%). The reference temperature is T_g determined by DSC measurements.

$$c_1 = \frac{B}{2.303 f_g}, \quad c_2 = \frac{f_g}{\alpha_f} \quad (4)$$

where B is a constant and generally considered to be unity.

The values of f_g and α_f are summarized in Table I. It is found that neither parameter, *i.e.*, α_f or f_g, was affected by the *p*-tPh addition considering the experimental error, which suggests that the glass-to-rubber transition occurs when the free volume fraction reaches a constant value even for antiplasticized systems. Moreover, the thermal expansion beyond T_g is expected to be independent of the *p*-tPh content.

Figure 6 shows the temperature dependence of the linear coefficients of thermal expansion β for PC and the blend with 5 wt% of *p*-tPh in the glassy state. The value of PC at room temperature is approximately 70 × 10^{-6} ºC^{-1}, which is in harmony with the data reported previously.[34,35] It is demonstrated by the figure that *p*-tPh effectively reduces the thermal expansion of PC in the glassy state. Moreover, the blend shows a steep slope. Consequently, the reduction of the thermal expansion is not obvious at high temperatures. This is predictable because the free volume fraction at T_g that shifts to a lower temperature is not changed by the antiplasticizer.

Figure 7 shows the linear coefficients of thermal expansion at various temperatures as a function of *p*-tPh content. It is

Table I. Thermal expansion coefficients of free volume in the rubbery region and free volume fractions at T_g for PC and PC/*p*-tPh.

p-tPh content (wt%)	α_f (×10^{-4} ºC^{-1})	f_g
0	1.9±1.0	0.017±0.005
5	1.6±0.8	0.016±0.004
10	1.6±0.8	0.015±0.004

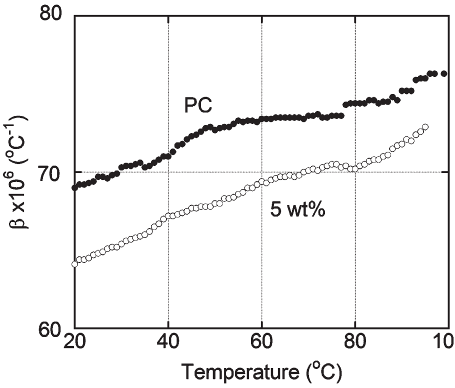

Fig. 6. Temperature dependence of linear coefficients of thermal expansion β for (closed) PC and (open) PC/*p*-tPh (5 wt%).

interesting to note that the values of the blend with 10 wt% of *p*-tPh are almost identical to those of PC/*p*-tPh (5 wt%), a similar trend to the modulus at room temperature.

It has been reported that conventional plasticizers enhance thermal expansion due to the increased anharmonicity of the potential function with low modulus.[11)] In this study, however, the opposite phenomenon is observed, which is presumably attributed to the reduction of free volume. Because marked thermal expansion is a severe problem for transparent plastics, the phenomenon should be noted. In fact, the thermal expansion coefficient is still higher than that of a typical inorganic glass (*ca.* 7×10^{-6} ºC^{-1}). However, the result should have an impact on the industrial applications, because it is close to the value of aluminum (*ca.* 40×10^{-6} ºC^{-1}); a material that is often used for frames.

4. CONCLUSION

A small addition of *p*-tPh enhances the modulus in the glassy state, demonstrating that it acts as an antiplasticizer for PC. The β-relaxation mode of PC, attributed to the local motion of the main chain, is reduced due to the decrease in the free volume of PC. The free volume fraction at T_g is, on the contrary, unchanged by the addition of *p*-tPh.

Furthermore, thermal expansion in the glassy state is found to be reduced by the *p*-tPh addition without loss of excellent transparency when the content is lower than 15 wt%. This result is attributed to the low level of free volume fraction. Reduced thermal expansion will be a great benefit as it will allow a glassy polymer to be employed instead of an inorganic glass, thus potentially leading to the development of a new material design of a plastic glass.

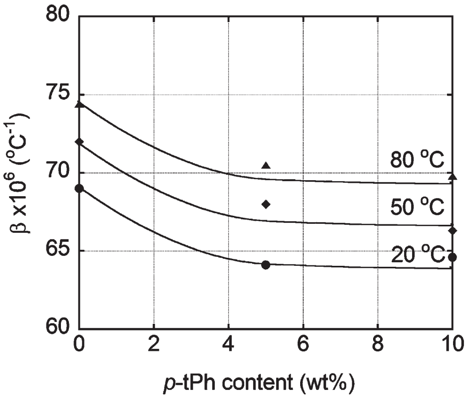

Fig. 7. Linear coefficients of thermal expansion β at various temperatures for PC/*p*-tPh; (circles) 20 ºC, (diamonds) 50 ºC, and (triangles) 80 ºC.

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