Effect of Heat Pretreatment and Strain Rate on Tensile Properties of Polycarbonate Sheet

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Synopsis

The effects of heat pretreatment and ambient gas (air and vacuum) on selected properties of the polycarbonate sheet have been studied. Changes in tensile properties as functions of heat pretreatment temperature (up to 160°C) and strain rate (wide range of $1.7 \times 10^{-4} - 13.1$ m/sec $= 0.29 - 2.3 \times 10^4$ %/sec) were determined and these are discussed in relation to changes in differential scanning calorimetry (DSC) and gel permeation chromatography (GPC) data. The performance characteristics of the present tensile testing are obtained over a wide range of extension rates without changing the mode of deformation and the shape of the test pieces. It was suggested from the experimental results that heat pretreatment below the glass transition temperature (T_g) causes ordered molecular domains to grow on the free surfaces of the sheet, consisting of thermally deteriorated macromolecules and possessing lower crazing stresses (exhibiting more brittle mechanical responses, leading to the decrease in breaking strain and energy). The effect of annealing above T_g on the tensile properties, and on the results of DSC and GPC, could not be precisely understood.

INTRODUCTION

For bisphenol-A polycarbonate (PC), embrittlement occurs for exposure to temperatures between 80 and 130°C, below the glass transition temperature. This transition in bulk properties from the ductile to a relatively brittle form was first noted by Peilstocker,[1] and diverse studies on influencing factors have been reported. Approaches thus far may be classified in the following two ways: (a) effect of deformation modes and failure of mechanical response in detail, and (b) physical arrangement and mobility of macromolecules in the bulk. As to (a), there have been many studies reporting the effects of (1) thermal history below and above T_g, (2) sample preparation, (3) test temperature, (4) strain rate, and so on.[2-15] On the other hand, as to (b), it has often been suggested that the toughness of a polymeric solid is in some way connected with the motion of chain segments in the glassy state. Many workers have tried to compare the dielectric and mechanical relaxation behavior of unannealed and annealed PC in the glassy state and to establish whether or not the difference in bulk properties of these two forms is reflected in their secondary molecular relaxation processes involving the main chain.[16-21] These have been reviewed by Heijboer who concluded that a change in impact properties is only likely when a corresponding loss peak originates from movement within the main chain.[22] However, there has been a view in which a satisfactory quantitative correlation between loss peaks and the ultimate properties of the polymer was not completely worked out; and the large decrease in impact strength of annealed PC is difficult to understand in view of the slight changes in either density or β transition.[19]

At present, a basic requirement is to provide detailed and systematic infor-

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mation on the effect of thermal history on the tensile mechanical properties of PC over a wide range of strain rates (containing impact test), relating to the molecular relaxation processes. Here, some points should be noted. (a) For materials like PC, in which there is significant plastic deformation, a thickness effect is apparent. (b) The effect of heat treatment is exerted homogeneously over the whole specimen. (c) Tensile breaking tests are performed over a wide range of extension rates without changing the mode of deformation and the shape of the test pieces. Generally, for high (impact) speeds, most of the experimental work has been carried out under cantilever impact conditions (Izod and Charpy impact tests). This is not appropriate because finding correlations between low-speed tensile and high-speed flexural properties is troublesome owing to the differences in the test piece shape and the mode of deformation (tension and flexure).

In the present article, therefore, taking into consideration these points, consistent tensile studies of PC sheet are reported in detail, where thermal history (up to 160°C) and strain rate ($1.7 \times 10^{-4} - 13.1$ m/sec $= 0.29 - 2.3 \times 10^4$ %/sec) were systematically varied, and further, the characterization of heat-treated PC sheets were performed using DSC (differential scanning calorimetry) and GPC (gel permeation chromatography).

EXPERIMENTAL

Specimens

A bisphenol-A polycarbonate sheet (trade name Panlite, Teijin Co., Ltd.) was used as a starting material throughout this study (100 μm thickness). Before being subjected to the annealing treatment, the sheet was cut out in the form of a grid as shown in Figure 1 (each was used as a test piece for high- and low-speed tensile testings as described later). For the sheet, this may be a convenient method to satisfy the requirement for uniformity of many test pieces and prevent the occurrence of cracks at the cut plane in the preparation of test pieces from the annealed embrittled sheet. Heat treatments were performed in a circulating-air oven at temperatures between 40 and 160°C (with interval of 20°) for 48 hr, followed by natural cooling back to room temperature. In order to clarify the effects of traces of absorbed water in the starting material and ambient
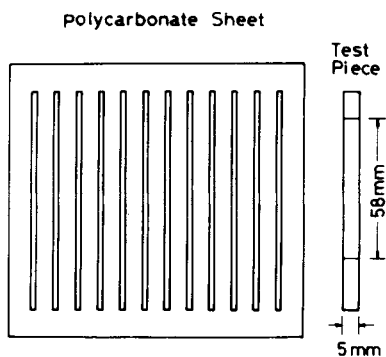

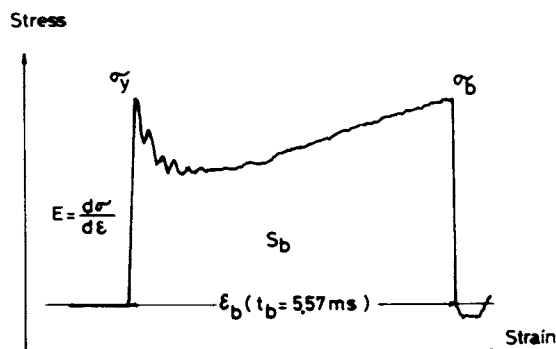Fig. 1. Uniform preparation of test pieces from sheet for low- and high-speed lensile testings.

Fig. 2. Typical stress–strain impact curve of as-given PC sheet at deformation speed of 13.1 m/sec = 2.26 × 10⁴ %/sec; definition of five mechanical properties: initial Young's modulus E; yield stress σ_y; breaking stress σ_b; breaking strain ε_b; breaking energy S_b. $E = d\sigma/d\varepsilon$. $\dot{\varepsilon} = 226$ sec⁻¹.

oxygen, further annealing was also tried for the dried PC sheet at 140°C in a vacuum oven (48 hr).

Tensile Breaking Tests

From the annealed sheet in the form of a grid, 15 to 18 test pieces were obtained (the practical dimensions were 5 × 58 mm).   For the lower speed tensile testing, a conventional tensile tester was utilized, which covered the rate of deformation from 1.7×10^{-4} to 2.8×10^{-2} m/sec.   For the higher speeds, a flywheel-type tensile impact tester was used.   This apparatus has already been described and will therefore not be discussed here.[23]   The tensile speeds could be easily con-
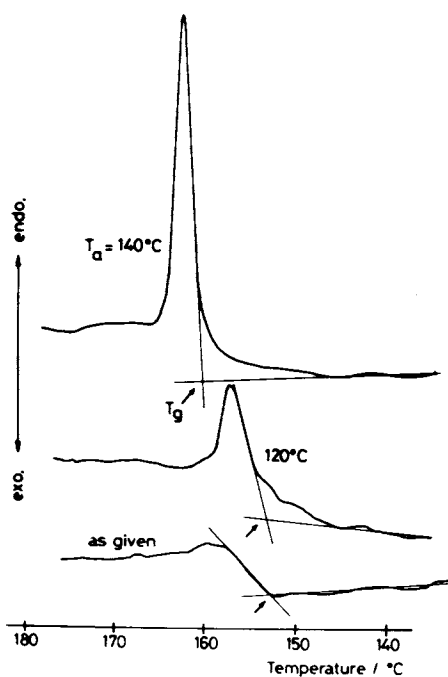

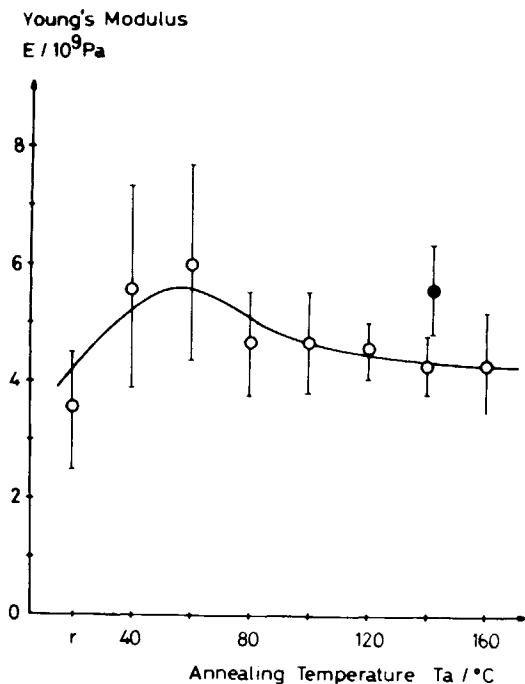Fig. 3. Typical DSC thermograms of PC sheets annealed for 48 hr.

Young's Modulus
$E / 10^9 Pa$

Fig. 4. Dependence of Young's modulus of PC sheets on annealing temperature for 48 hr at 13.1 m/sec = 2.26×10^4 %/sec impacting speed at 23°C. PC($\dot{\varepsilon}/226$ sec^{-1}): O, annealed in air; ●, annealed in vacuum.

trolled by changing the revolutions of the flywheel, and in the present study were adopted for the range of 1.3–13.1 m/sec. These enabled us to test over five decades of strain rate ($1.7 \times 10^{-4} - 13.1$ m/sec = $0.29 - 2.3 \times 10^4$ %/sec). The experiments were conducted at an almost constant temperature, 23 ± 1°C, and below a relative humidity of 50%. Nine specimens were tested per each strain rate for higher speeds and five for lower speeds (owing to the small scattering of data points), and the arithmetic mean and estimated standard deviation were calculated from the set observations. Figure 2 shows the schematic stress–strain curve of the as-received PC sheet at the deformation speed of 13.1 m/sec = 2.3×10^4 %/sec, and the definitions of five mechanical quantities: (1) modulus of elasticity E; (2) tensile stress at yield σ_y; (3) tensile stress at breaking σ_b; (4) extension until failure ε_b; and (5) breaking energy indicated by the area under the curve S_b.

DSC and GPC Measurements

Differential scanning calorimetry analysis was performed with a Perkin–Elmer DSC, type 1B, at a scanning rate of 16°/min in nitrogen gas. Glass transition temperature data were obtained as the extrapolated onset points, and the area of the endothermic peak at T_g was calibrated with benzoic acid. Typical thermograms are shown in Figure 3.

Molecular weight distributions of the annealed PC samples were obtained by gel permeation chromatography (Japan Waters, Ltd., ALC/GPC-244 with a column μ-Styragel), using methylene chloride as a solvent. The molecular weight was calibrated with the standard mono-dispersed polystyrenes.
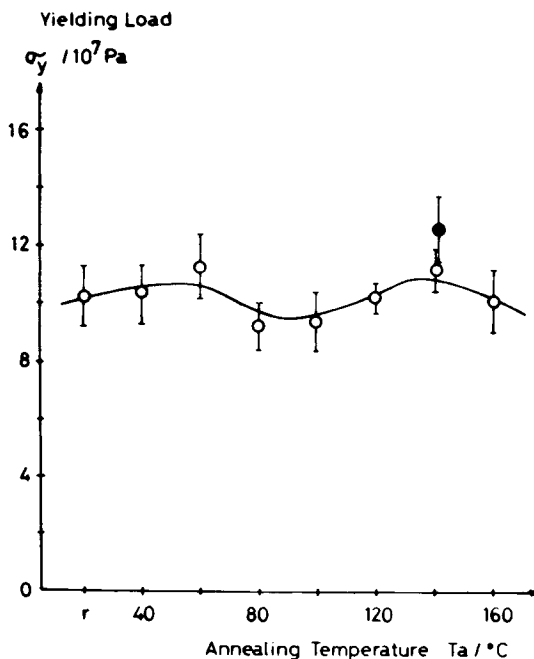
Fig. 5. Dependence of yielding load of PC sheets on annealing temperature for 48 hr at 13.1 m/sec = 2.26×10^4 %/sec impacting speed at 23°C. PC($\dot{\varepsilon}$/226 sec^{-1}): O, annealed in air, ●, annealed in vacuum.

RESULTS

Figures 4–6 show the correlations between the heat pretreatment temperatures (T_a, 48 hr) and the tensile impact properties of PC (E, σ_y, and ε_b) at the deformation speed of 13.1 m/sec = 2.3×10^4 %/sec. It was found that as far as tensile impact testing is concerned, Young's modulus and yielding load (Figs. 4 and 5) are hardly affected by the annealing temperature. As to the breaking strain (Fig. 6), however, different behavior was observed. With impact strain, PC sheets, which were treated to $T_a = 100°C$, deformed predominantly by macroscopic shearband deformation, and all specimens exhibited necking and cold drawing prior to fracture. At T_a higher than 120°C, PC sheet ceased thorough cold-drawing and the value of ε_b started to decrease steeply. This means the beginning of formation of the structure which induces the brittle behavior, bordering at about $T_a = 100$–120°C. The breaking energy S_b, in the present study, represents the work necessary to rupture the specimen. In the approximation of this value to the product of yield strength and elongation, the pattern of changes (from about 7 to 0.5 MJm^{-2}) is easily understood to be very similar to that of ε_b and therefore is not shown here.

It was assumed that these tensile impact properties would correlate with changes of morphology and molecular weight distribution owing to the supplied thermal energy. As shown in Figure 3, it is clear that the DSC thermograms are altered significantly by the annealing temperature. The results are summarized in Figure 7. Although the thermal history of the as-given PC sheet has not been revealed, the glass transition temperature (T_g) and its enthalpy (ΔH) certainly began to increase from about 100°C. This indicates the formation of a more

Breaking Strain
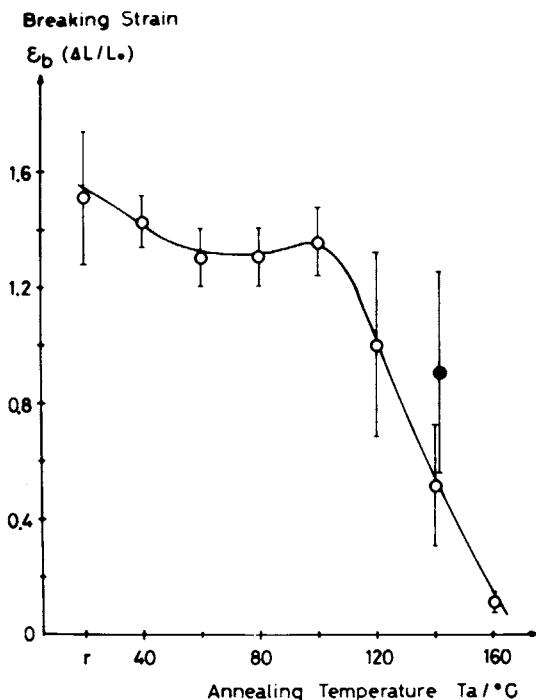
ε_b ($\Delta L / L_o$)

Fig. 6. Dependence of breaking strain of PC sheets on annealing temperature for 48 hr at 13.1 m/sec = 2.26 × 10⁴ %/sec impacting speed at 23°C. PC($\dot{\varepsilon}$/226 sec⁻¹): O, annealed in air; ●, annealed in vacuum.

ordered glass structure by molecular rearrangement and/or thermal deterioration during annealing, which is dominated by the highest exposed temperature. On the other hand, at $T_a = 160°C$, which is higher than T_g, the values of T_g and ΔH did not fall on the extrapolated lower temperature range. This implies, qualitatively, the occurrence of a different structural change above T_g, after thoroughly breaking the structure formed before. A similar phenomenon was also observed in the change of the molecular weight distribution. Figure 8 clearly indicates the beginning of thermal degradation from $T_a = 100°C$, leading to lower molecular weights. Moreover, molecular weight dispersion was also enlarged from the same temperature, which means the inhomogeneous deterioration at the surface and inner bulk part, even though 100 μm sheets were used.

Compared with heat treatment at 140°C in air and vacuum, the latter case revealed a similar annealing effect on ε_b and S_b in the first case of $T_a = 120°C$ (a temperature lag of 20°C). This difference is clearly due to the promotion of thermal degradation and/or molecular rearrangement from catalyzation by ambient oxygen and water, and by traces of water already absorbed in the PC sheet (0.15 wt % at 50% RH).[24]

Next, it was interesting to clarify how the transition from ductile to brittlelike behavior in the tensile impact testing changes with the different deformation speeds, and how oxygen and traces of water affect this embrittlement. Then, the dependence of the tensile properties on the strain rates (1.7 × 10⁻⁴ − 13.1 m/sec = 0.29 − 2.3 × 10⁴ %/sec) were investigated for the three following cases: (a) as-given, (b) annealed for 48 hr at 140°C in air, and (c) annealed for 48 hr at
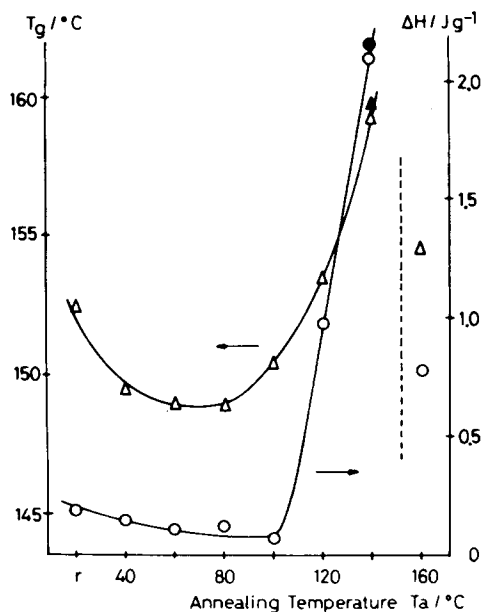
Fig. 7. Changes in glass transition temperature (T_g) and its enthalpy (ΔH) of PC sheets annealed for 48 hr from DSC measurements: △, ○, annealed in air; ▲, ●, annealed in vacuum.

140°C in vacuum. The results are shown in Figures 9–11. Generally, it was found that Young's modulus and the yield strength increased roughly semi-logarithmically with the tensile speed (Figs. 9 and 10). In the lower speed region, their values were observed to follow the order (b) > (c) > (a), while in the higher
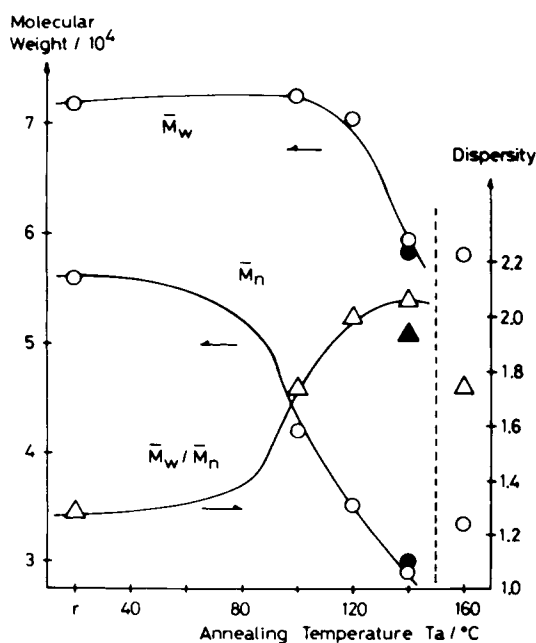

Fig. 8. Changes in molecular weight and dispersity of PC sheets annealed for 48 hr from the GPC measurements: △, ○, annealed in air; ▲, ●, annealed in vacuum.

Young's Modulus

E / 10^9 Pa
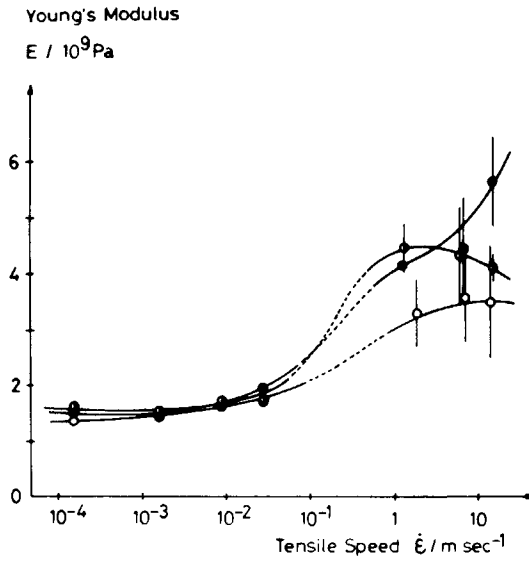

Fig. 9. Strain rate dependencies of Young's modulus of PC sheets: (1) as-given, O, (2) annealed at 140°C for 48 hr in air, ◑, (3) annealed, at 140°C for 48 hr in vacuum, ●.

speed region, (c) > (b) > (a).   Since the degradation could be avoided (relatively) in the case of vacuum, the PC sheet for (c) still retains its original tenacity and this reflects an inversion in the order, i.e., (c) > (b), in the impact speed range. As to breaking strain as well as energy, the effect of heat pretreatment in air and vacuum is different (Fig. 10).   During all the strain rates up to impact speed, the nature of deformation of the as-received PC sheet did not change, i.e., cold drawing, the sheet exhibiting excellent tenacious properties.   When annealed in air, the transition from ductile to brittlelike behavior was observed in the rather low strain rate range (2×10^{-3} m/sec = 3.5 %/sec).   On the other hand, it was

Yielding Load

σ_y / 10^7 Pa
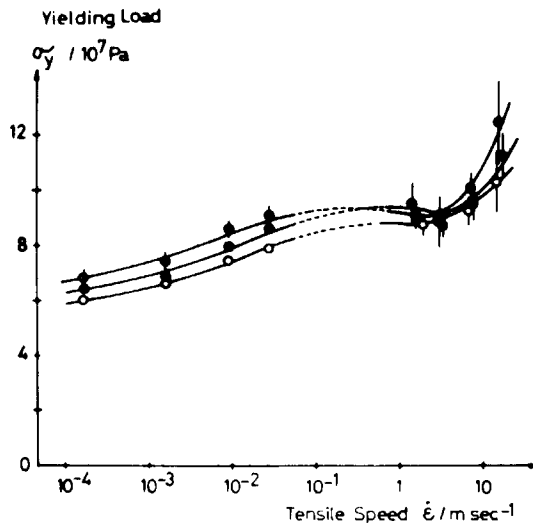

Fig. 10. Strain rate dependencies of yielding load of PC sheets: (1) as-given, O; (2) annealed at 140°C for 48 hr in air, ◑; (3) annealed at 140°C for 48 hr in vacuum, ●.
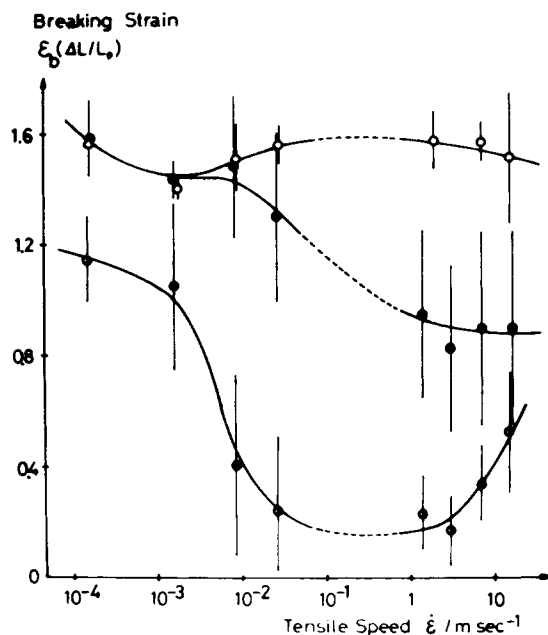
Fig. 11. Strain rate dependencies of breaking strain of PC sheets: (1) as-given, O; (2) annealed at 140°C for 48 hr in air, ◑, (3) annealed at 140°C for 48 hr in vacuum, ●.

found that this transition occurs at about 0.1 m/sec = 1.7×10^2 %/sec for annealing in vacuum. In spite of such a remarkable effect of water and oxygen at $T_a = 140°C$ on ε_b and S_b, there were scarcely appreciable changes in the structural properties; T_g, ΔH, M_w, M_n, M_w/M_n as shown in Figures 7 and 8.

DISCUSSION

From these experimental results through a wide range of tensile testing, DSC, and GPC, we consider the effect of heat pretreatment on the structural changes in the following way. Annealing PC below T_g produces ordered molecular domains which grow on the free surfaces of the sheet, where mobility restrictions are less severe than in the inner bulk.[12,19,25–27] These surface morphological entities can be further promoted by higher thermal energy, ambient oxygen, and water, which preferentially sever the molecular chains interrupting thermal motions at the surface. Since below T_g all molecular chains have insufficient mobility, deteriorated macromolecules remain near the surface in the process of cooling and aggregate, resulting in the formation of ordered structure. Despite such structural changes on the surface, the data of DSC and GPC indicate the total bulk properties and reflect the average of affected and unaffected structures, the latter being predominant (the same things may be likely in the dielectric and mechanical relaxation measurements). Therefore, such a difference in the annealing effect in air and vacuum (Figs. 7 and 8) might be buried in the unaffected bulk portion (i.e., remain undetected). In that sense, it is reasonable to consider that Young's modulus and the yield stress, which are hardly influenced by heat pretreatment, respond to the initial bulk-flow process which originates mainly from the unchanged portion of the PC sheet. On the other hand, although the

surface aggregate entities do not play a direct role in the bulk flow process, such structures can affect the fracture initiation process which generally occurs at surfaces, serving as sites for craze initiation and growth. It has been suggested that lower-molecular-weight PC possesses lower crazing stresses and, therefore, exhibits more brittle mechanical responses, leading to decreases in ε_b and S_b.[2,4,14,15,28,29] Figures 6 and 11 support this suggestion and indicate that this surface crazing is enhanced by environmental factors (heat treatment temperature and ambient gas), and dependent on the strain rate. If thicker test pieces (e.g., 3–5 mm) are used, the volume fraction of the unaffected portion should be larger and the surface aggregate entities may not play a role, relatively, in craze initiation. This suggests that the annealing temperature which induces the transition from ductile to brittlelike behavior might be higher than that in the present study (100–120°C at 100 μm thickness).

We have not been able to understand precisely the effect of annealing above T_g on the tensile properties, and further, the results for DSC and GPC measurements. At present, we suspect that the ordered domains, consisting of lower-molecular-weight polymer chains at the surface, creep in the inner bulk portions because all molecules have received sufficient mobility above T_g, and the homogeneously mixed structures formed in the cooling process are different from the maldistributed structure formed during annealment below T_g.

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