

Formation of a Metastable Phase of Bisphenol-A Polycarbonate Induced by Mechanical Stress

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ABSTRACT: Samples of bisphenol-A polycarbonate (BPA-PC) mechanically crushed in a ballmill were prepared and their physical properties were analyzed in order to elucidate the mechanism of the high impact resistivity of polycarbonates, which makes polycarbonates to be widely used engineering plastics. In this article, BPA-PC samples were prepared with different surface conditions to probe their molecular mobility. While BPA-PC films prepared by melt pressing showed a single glass transition at 150°C, the samples crushed in a ballmill, ground in a mortar with added alumina powder, or cast from solution in tetrahydrofuran showed glass transitions at approximately room temperature. The existence of glass transition behavior at room temperature was confirmed for the mechanically

crushed samples by differential scanning calorimetry, dielectric relaxation measurements, and friction measurements. The independence of the glass transition of mechanically crushed BPA-PC on molecular weight indicated that the chain ends do not play an important role in the glass transition behavior. The molecular structures of the films were also investigated by infrared spectroscopy. The relationship between this unique glass transition behavior and the high impact resistivity of BPA-PC is discussed based on the experimental results. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: surfaces; polycarbonates; differential scanning calorimetry; fracture; mechanical stress; impact resistance

INTRODUCTION

Polycarbonates (PC) are widely used engineering plastics because of their high impact resistivity, but the origin of their impact resistivity is still under discussion. It is often thought that the high impact resistivity of PC is related to the β - or γ -relaxation modes of PC, which are attributed to the local motions of PC.^{1–10}

Varadarajan and Boyer⁵ measured the dielectric spectra of bisphenol-A polycarbonate (BPA-PC) samples molded at 200°C and exposed to methylene chloride for different lengths of times. They detected the α -relaxation mode at 150°C, the β -relaxation mode at 70°C, a broad γ -relaxation mode around –100°C, and the δ -relaxation mode around –220°C. The broad γ -relaxation mode was divided into γ_1 , γ_2 , and γ_3 -relaxation modes attributed to phenylene motion, combined carbonate and phenylene motion, and carbonate motion, respectively. Exposure to methylene chloride simultaneously decreased the

intensity of the γ_3 -relaxation mode and the mechanical strength. Varadarajan and Boyer suggested a relationship between the γ -relaxation mode and the high impact resistivity of BPA-PC, but the exact nature of this relation was not fully clarified.

Matsuoka and Ishida⁶ also measured the dielectric spectra of BPA-PC as a representative amorphous polymer with multiple transitions. They detected two transition modes in the dielectric spectra of BPA-PC at –120 and 150°C. The secondary transition was attributed to the relaxation of local motions of polymer chains, which persisted in a highly restricted framework of glassy polymer chains.

Xie et al.⁸ synthesized oligomers of (BPA) carbonate and amorphous silica on which oligomers of BPA were grafted. High resolution solid state NMR was carried out, and the proton spin-lattice relaxation spectra also showed α , β , and γ -relaxation modes.

There are some polymer materials for which local motions (β or γ modes) can be detected below the glass transition temperature (T_g), and they often have high impact resistivity. However, there are also some polymer materials for which β or γ modes can be detected below the T_g , but do not have high impact resistivity.

Wu^{9,11} analyzed the secondary relaxation modes of 25 polymers, including BPA-PC. He plotted the temperature of the primary relaxation divided by

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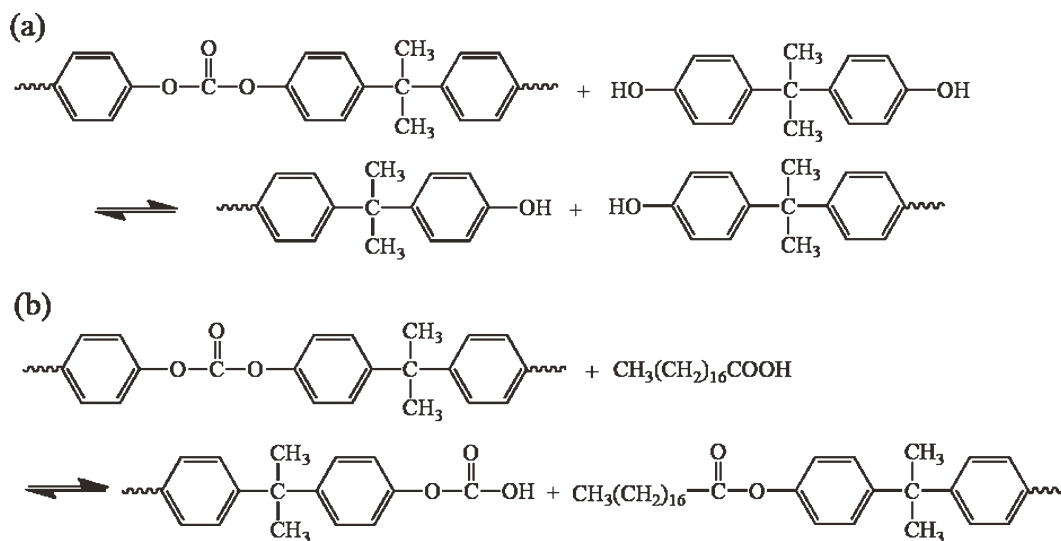


Figure 1 Schemes of the degradation reactions to prepare BPA-PC samples with different molecular weight by reacting with (a) BPA and (b) SA.

that of the secondary relaxation against Flory's characteristic ratio. He also argued that the secondary relaxation temperature of polymers, including BPA-PC, corresponded to the temperature at which the polymer changed from brittle to ductile. He maintained that the brittle-to-ductile transition temperature of polymers can be predicted from their characteristic ratio.

Because the β or γ modes of PC cannot explain the origin of their high impact resistivity completely, many experimental approaches have been attempted on PC samples prepared by different annealing, and mechanical treatments. Mechanical tests to investigate the mechanical properties directly, calorimetry to estimate their crystalline behavior¹² and glass behavior, and dielectric measurements to detect the mobility of polymer chains were also carried out.¹⁻⁹

This study focuses on the properties of mechanically crushed BPA-PC prepared by fracturing in a ballmill or grinding in a mortar with alumina powder. Although a glass transition was detected at 150°C in the film prepared by melt pressing, the mechanically crushed samples showed glass transitions around room temperature. Because the phases with lower T_g at crazes made by mechanical crushing can contribute to high impact resistibility by preventing further fracture, the physical properties of these phases were estimated in this study. The physical properties of surface phases of BPA-PC were also investigated, because it is possible that the lower glass transition is caused by the surface phase at crazes made by mechanical crushing. The molecular mobility of BPA-PC chains in the films prepared by casting from tetrahydrofuran (THF) solution was investigated, because thin films have a large surface area ratio. There have been many reports on the

change of T_g in thin films of polymers, since Keddie reported the decrease of T_g in thin films of polystyrene,¹³ and the increase in thin films of poly(methyl methacrylate).¹⁴ The mechanism of this change has been reported by Kajiyama,¹⁵⁻¹⁷ Kanaya,^{18,19} de Genes,²⁰ and many other researchers.

To estimate the influence of polymer chain ends on the properties of BPA-PC, samples with different molecular weights and chain ends were prepared by two different degradation reactions.

Glass transition behavior was measured by differential scanning calorimetry (DSC) and dielectric measurements. The temperature dependence of the mechanical properties was investigated by friction measurements. Structural differences among the samples prepared by different methods were analyzed by infrared spectroscopy.

EXPERIMENTAL

Sample preparation

BPA-PC used in this study was Lupilon[®] purchased in the form of pellets from Mitsubishi Engineering-Plastics. The samples with different molecular weights and chain ends were prepared by adding different amounts of BPA or stearic acid (SA) and heating for 5 min at 350°C. As shown in Figure 1, polymer chains obtained from the reactions with BPA and SA have different chain ends.

The molecular weight and molecular weight distribution of the samples were estimated by gel permeation chromatography (GPC). The measurements were carried out with a Tosoh HPLC-8020 system using THF as eluent. The molecular weights of the samples, calibrated with standard polystyrene, are

TABLE I
Molecular Weight and Molecular Weight Distribution
of BPA-PC Samples Degraded with BPA or SA

Degraded with SA		Degraded with BPA		Not degraded	
$M_w/10^3$	M_w/M_n	$M_w/10^3$	M_w/M_n	$M_w/10^3$	M_w/M_n
2.53	1.31	3.50	2.32	33.2	1.96
3.80	1.74	5.00	1.18		
6.71	1.93	6.94	1.89		
9.52	2.02	9.44	2.02		
11.0	2.09	10.5	2.03		
11.5	1.69	11.3	1.82		
14.7	2.21	14.1	1.92		
18.3	2.17	16.7	1.92		
19.9	1.97	18.0	2.25		
23.3	1.97	19.8	2.13		
23.6	2.23	25.4	2.28		

The molecular weight was determined by GPC calibrated with standard polystyrene.

summarized in Table I. M_w and M_n stand for weight and number average molecular weight, respectively.

Two types of mechanical crushing were applied to the samples. One sample was crushed in a ballmill (Retsch MM200) at a frequency of 30 Hz. The other was ground in a mortar by adding an equivalent weight of Al_2O_3 powder with a diameter of 1 μm at room temperature. No significant decrease of molecular weight was observed from the results of GPC measurements for the mechanically crushed samples. Thick films were prepared by putting BPA-PC pellets on a glass plate heated at 250°C, and pressed to form a film with thickness of $\sim 30 \mu m$.

BPA-PC pellets were dissolved in THF to make a solution with a concentration of 0.02 g cm^{-3} , and this solution was cast into thin films with a thickness of $\sim 1-10 \mu m$. The films were dried in a vacuum oven (Yamato Scientific, DP22) equipped with a vacuum pump (Ulvac, DA-30P) at room temperature for more than one day. The absence of the solvent was confirmed by their infrared spectra.

The samples were prepared for dielectric measurements as follows. First, BPA-PC films were either melt pressed or solvent cast onto glass plates on which Al had been evaporated *in vacuo*. Al was evaporated again on the BPA-PC film to form Al films on both sides of the BPA-PC film. Al electrodes were attached to the Al films. The effective area of the electrodes was $\sim 0.4 cm^2$. The process of Al evaporation induced further removal of THF from the films, because they were exposed to high vacuum (below 10^{-3} Pa) and heat ($\sim 70^\circ C$). The dielectric constant and loss tangent were measured with an LCR meter (Hewlett Packard HP4284) between -70 and $200^\circ C$ at frequencies of 1, 3, 10, and 30 kHz. The samples were heated at $3^\circ C/min$ under vacuum with the pressure below 0.01 Pa.

Measurements

A Mac Science DSC-3100 and a Mettler Toledo DSC-30 were used to analyze thermal properties. The scan rates were $10^\circ C/min$ for the DSC-3100, and $20^\circ C/min$ for the DSC-30.

The surface T_g of BPA-PC was investigated with a home-made instrument to measure the surface friction of films as shown in Figure 2. The details of this instrument were described in our previous articles.^{21,22} Surface T_g can be determined by measuring the temperature dependence of the friction force, because the transition from glassy state to sticky rubbery state increases the friction force. We have measured friction forces of films of polystyrene with different molecular weights with the same instrument.²¹ The friction force and stick slip width of the polystyrene films increased steeply below the T_g of the bulk phase of polystyrene. The temperature at which the friction force increased steeply agreed well with the surface T_g determined by DSC.

Fourier transform infrared (FTIR) spectra of the films prepared by melt pressing and solvent casting were obtained with a Shimadzu FTIR 8900 spectrometer at room temperature using a resolution of $4 cm^{-1}$.

The dielectric constant and loss tangent were measured with an LCR meter (Hewlett Packard HP4284) between -70 and $200^\circ C$ at frequencies of 1, 3, 10, and 30 kHz. The samples were heated at $3^\circ C/min$ under vacuum with the pressure below 0.01 Pa.

RESULTS

Figure 3(a) shows DSC curves for nondegraded samples, which were crushed in a ballmill for different times. Although the samples with milling times less than 15 s have a single glass transition at $150^\circ C$, a baseline change similar to a glass transition appears at approximately room temperature in the curve of the sample with a milling time of 20 s. This baseline change became clearer as the milling time of sample increased. The DSC curves were essentially independent of the milling time longer than 30 s.

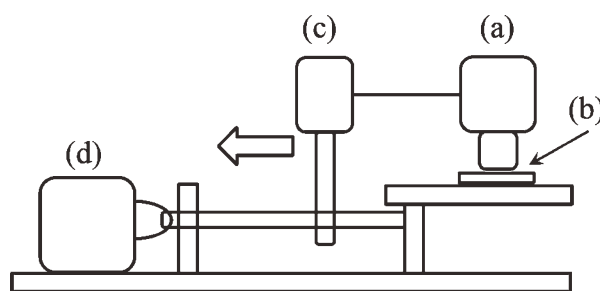


Figure 2 A schematic image of an instrument for friction measurements. (a) Weight, (b) glass plate, (c) force gauge and (d) motor to move the force gauge. The surfaces both of the weight and glass plate contacting with each other were coated with BPA-PC.

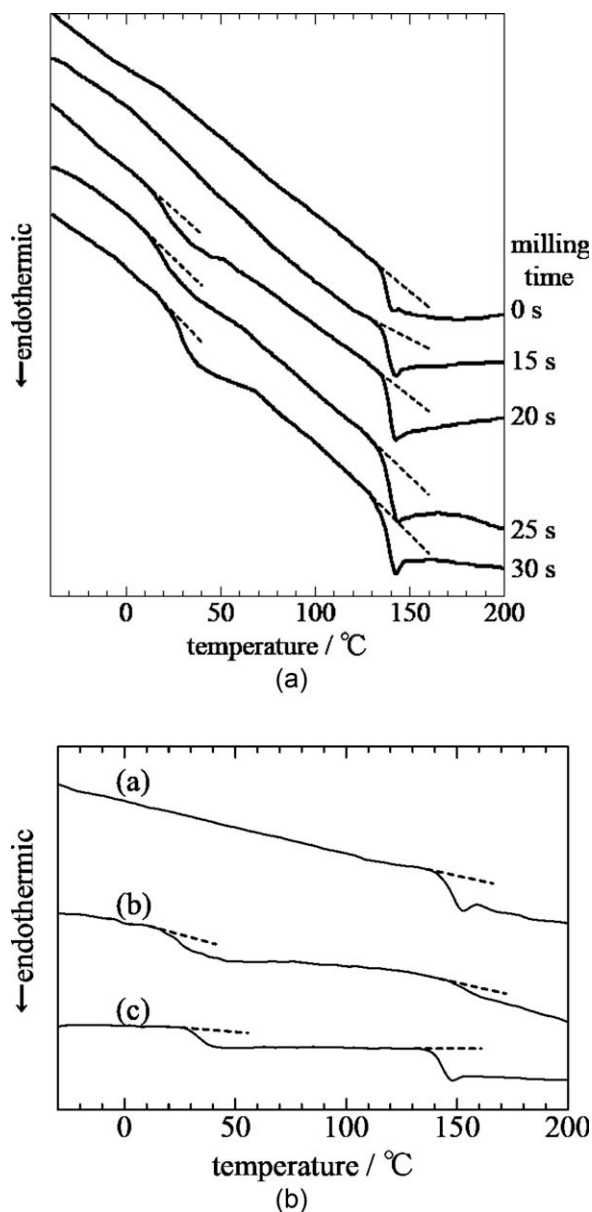


Figure 3 (a) DSC curves of BPA-PC samples crashed in a ballmill at frequency of 30 Hz for different milling times. (b) DSC curves of BPA-PC samples prepared by different methods: (a) melt pressed, (b) ground in a mortar with alumina, and (c) cast from THF.

Figure 3(b) illustrates the DSC curves of the films prepared by different methods. Although the melt pressed film has a single glass transition at 150°C, the films prepared by grinding with alumina and casting from THF solutions showed thermal changes similar to a glass transition around room temperature in addition to the glass transition at 150°C. This thermal change suggests the formation of a phase composed of polymer chains with higher mobility. In the following, this temperature will be designated as “sub- T_g ”.

DSC measurements at different heating rates were also carried out. The sub- T_g can be detected in all

the DSC curves for the samples ground with alumina and cast from THF measured at the rate between 3 and 40°C/min, although some broadening of the baseline changes of sub- T_g was detected at higher heating rates. The sub- T_g determined by 3°C/min was only 5°C lower than that determined by 20°C/min. These results suggest that the heating rate gives no significant influence to the sub- T_g , and the details of the influences are not discussed in this manuscript.

Figure 4 illustrates the molecular weight dependence of the glass transition temperature of BPA-PC samples degraded with added BPA or SA. T_g and sub- T_g were determined from the DSC curves of samples melt-pressed and ground with Al_2O_3 , respectively. Although T_g of the samples degraded with both BPA and SA decreased with decreasing M_w , sub- T_g was almost independent of M_w above 10^4 . This result indicates that the polymer chain ends did not play an important role for the formation of the phase with higher molecular mobility (sub- T_g), at least for the BPA-PC with molecular weight higher than 10^4 .

Figure 5 indicate the temperature dependence of the friction force and stick slip measured for solvent cast film. Both friction force and stick slip abruptly increased around 0°C, which was much lower than the T_g of the film prepared by melt pressing, but comparable to the sub- T_g of the solvent cast film and the two mechanically crushed films. The abrupt increase of the friction force and stick slip can be attributed to the change of the polymer film from the glassy state to the rubbery state. The increase of

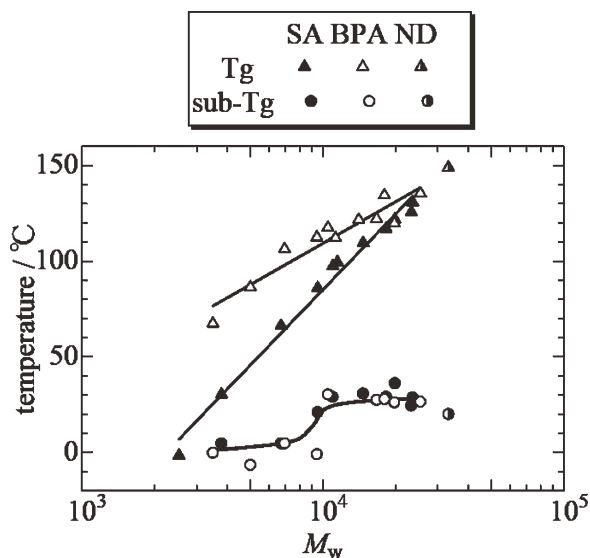


Figure 4 Molecular weight dependence of glass transition temperature (T_g) and sub- T_g (the temperature at which a thermal signal like glass transition was detected) of BPA-PC samples degraded with BPA or SA. ND in the figures means the data for the samples not degraded.

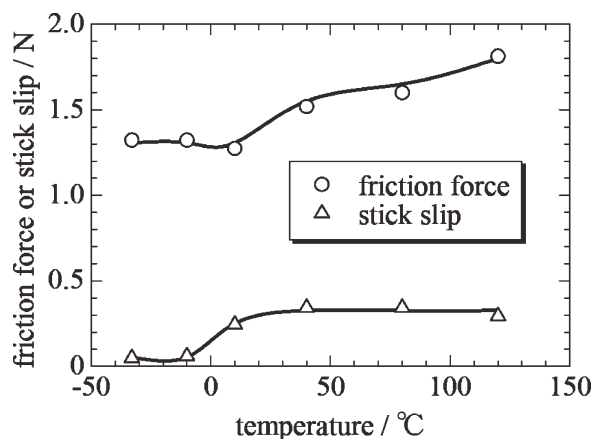


Figure 5 Temperature dependence of friction force and stick slip measured on the films prepared by solvent casting.

the friction force supports the existence of a glass transition around room temperature in the solvent cast film.

The dielectric relaxation spectra of BPA-PC are shown in Figure 6, where ϵ' and $\tan \delta$ indicate the real part of the dielectric constant and the loss tangent, respectively. There have been many reports on the dielectric behavior of BPA-PC; it has been reported that there are three relaxation modes in the dielectric spectra of BPA-PC: the α -relaxation mode at 150°C, the β -relaxation mode between -50 and 0°C, and the γ -relaxation mode at -100°C, which were attributed to the mode of micro-Brownian motion of polymer chains, that of local motion of polymer chains induced by the rotation at the bonds between phenylene groups and carbon atoms, and that of local motion in the monomer units, respectively.^{5,6,23} Comparing the α - and β -relaxation modes in Figure 6 (a,b), the relaxation temperatures of the film prepared by solvent casting (b) were lower than those of the film prepared by melt pressing (a). This difference agrees well with the DSC results, a glass transition was observed for the solvent cast film at a temperature lower than the T_g of the melt pressed film.

The decrease of ϵ' with an increase of temperature from 110 to 140°C in Figure 6(b) suggests the crystallization of BPA-PC in the solvent casting, because crystallization lowers the mobility of polymer chains. Murata et al.²⁴ also detected a similar decrease of ϵ' induced by crystallization in polyamides of *m*-xylylenediamine and aliphatic dicarboxylic acids.

The absence of THF in the film was confirmed by infrared spectroscopy, before the dielectric measurement was carried out. It should also be noted that the dielectric measurements were carried out under vacuum with pressure below 0.01 Pa. It has been reported that some solvents, including THF, can induce the crystallization of BPA-PC, and the crystalline structure remains even after evaporating the

solvents.^{5,25,26} The weaker signals of sub- T_g detected by the dielectric measurements than those by DSC were mainly caused by the slow heat rate of the dielectric measurements. The metastable phase with sub- T_g was annealed, and partially changed into the stable phase with T_g , while the samples were slowly heated during the dielectric measurements.

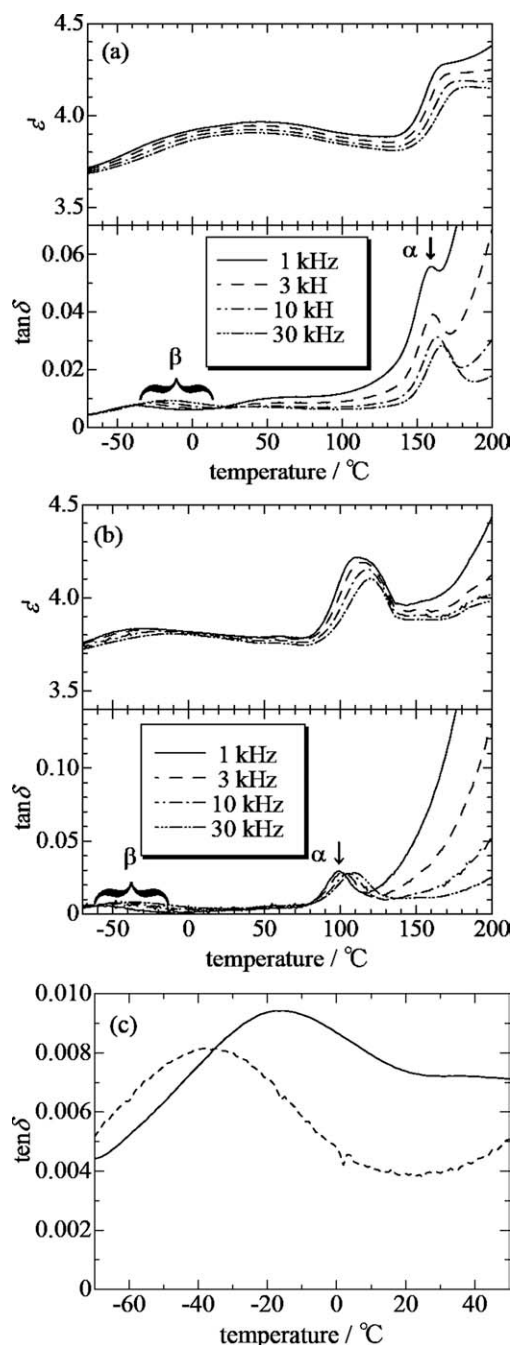


Figure 6 Dielectric relaxation spectra of BPA-PC films prepared by (a) melt pressing, and (b) solvent casting. The spectra were obtained at the frequencies of 1, 3, 10, and 30 kHz. α - and β -relaxations are indicated in the figures. The dielectric relaxation spectra for both films at the frequencies of 30 kHz are compared in (c).

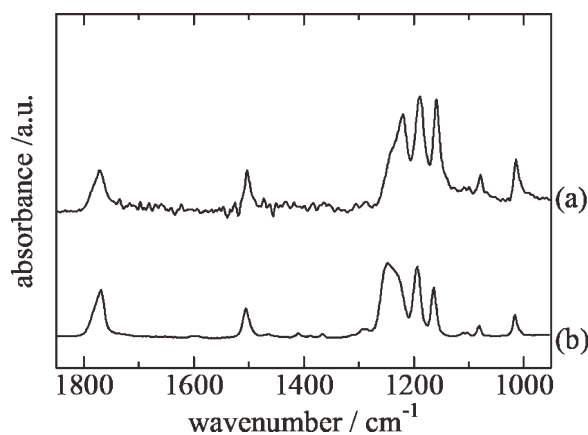


Figure 7 FTIR spectra of BPA-PC films prepared by (a) melt pressing and (b) solvent casting.

Figure 7 shows the FTIR spectra of the films prepared by (a) melt pressing and (b) solvent casting. The spectrum of the film obtained by solvent casting has a peak at 1260 cm^{-1} , which was assigned to asymmetric stretching mode of carbonate bonds. Because it was reported that the crystallization of BPA-PC can be induced by some solvents, including THF, the difference at 1260 cm^{-1} may be caused by the structural change induced by crystallization.^{5,25,26}

DISCUSSION

The DSC curves shown in Figure 3 indicate that the increase of surface area caused by mechanical fracture or solvent casting induced phases with larger scale molecular mobility than that in thick films. The friction measurements in Figure 5 and the dielectric measurements in Figure 6 also support the existence of the phases with larger scale molecular mobility in the solvent cast films.

Large amplitude motions below the T_g of some polymers, such as polyethylene have been studied and summarized by Wunderlich and Grebowicz.²⁷ They attributed the large amplitude motions below the T_g to the local *trans-gauche* interchanges producing conformational disorder, and they called them "sub-glass transitions" based on the results of dynamic mechanical, dielectric, and solid state NMR measurements.

When mechanical force is applied to a glassy material, cracks, or crazes appear in the material before it fractures. Because of cracks or crazes, fractured materials have larger ratio of surface area to volume. Thin films prepared by solvent casting also have a large surface area, and it is proposed that surface properties of BPA-PC are related to the existence of sub- T_g .

As shown in Figure 4, the sub- T_g was independent of the molecular weight and the chemical species of the chain ends. This independence indicates that there is no relation between the glass transition behavior of the surface phase in the films prepared

by grinding with Al_2O_3 and the chain ends, at least for the samples with molecular weight above 10^4 .

Considering the results described earlier, the following mechanism of the high impact resistivity of BPA-PC may be possible. When a mechanical impact is applied to BPA-PC, cracks appear in it. Because the cracks increase the surface area and the molecular mobility, BPA-PC chains at the cracks change from the fragile glassy state to the ductile rubbery state. The rubbery state at the cracks prevents the growth of the cracks, and therefore the fracture of the whole material.

It is a quite general technique to disperse rubbery particles, such as polybutadiene, in glassy plastics to increase the impact resistivity. In the polymer blend or copolymer, the rubbery region absorbs the applied mechanical force, and prevents the growth of cracks. Mechanical impact applied to BPA-PC induces the formation of cracks. As shown in Figure 3, BPA-PC has a lower T_g at the surface, and behaves as if it is in the rubbery state at room temperature. The surface phase may absorb the mechanical impact, and give impact resistivity to BPA-PC.

The sub- T_g detected in this study is comparable to the β -relaxation temperature observed in the dielectric measurements by Varadarajan and Boyer⁵. They detected β -relaxation at 70°C for samples quenched below -200°C , but this relaxation was undetectable upon annealing at 190°C .

CONCLUSION

Pellets of bisphenol-A polycarbonate (BPA-PC) were mechanically crushed by fracturing in a ballmill or grinding in a mortar with Al_2O_3 . Although the results of DSC for the sample without mechanical treatments showed a single glass transition, the samples treated with mechanical crushing had an additional glass transition below the glass transition temperature (T_g) of the sample without mechanical crushing. Similar glass transitions (sub- T_g) were also observed in the results of DSC and dielectric measurements for the thin films prepared by casting from a solution in THF. These results suggest the existence of a surface phase of BPA-PC with larger scale molecular mobility.

The samples with lower molecular weight were prepared by decomposing BPA-PC with BPA or SA, and their thermal properties were investigated by DSC. Although the T_{gs} of BPA-PC decomposed with BPA and SA was lowered for their lower molecular weight, the sub- T_{gs} were essentially independent of the molecular weight for samples with a molecular weight above 10^4 . The chain ends of BPA-PC do not play an important role in the formation of the surface phase which caused the appearance of the sub- T_g .

Although details of the structure and formation mechanism of the surface phase with higher molecular mobility could not be elucidated in this study, this phase can contribute to the mechanical properties of BPA-PC, such as its high impact resistivity.

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