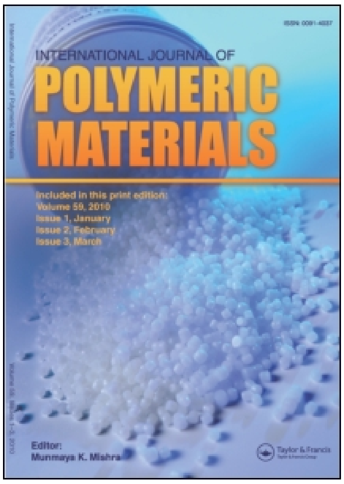

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Effects of Solvent-induced Crystallization on the Amorphous Phase of Poly(carbonate of bisphenol A)

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By the combined use of DSC, WAXD and pycnometry techniques, it was demonstrated that the increase in free volume and reduction in T_g observed in semi-crystalline poly(carbonate of bisphenol A) (PC), whose crystallization was solvent-induced, are due to the creation of many microvoids, microcavities and crazes in the amorphous fraction of the polymer during the crystallization. Accordingly, the polymer chains and chain-segments present right at the polymer-air interfaces, forming the walls of these micro-cavities, are more mobile than the chains and segments in the bulk amorphous phase, resulting in a commensurate reduction in T_g. Upon annealing at elevated temperatures the microvoids, *etc.*, heal, the polymer-air interfacial specific surface area decreases, and T_g increases toward the T_g of the bulk amorphous PC containing no microvoids, crazes and internal polymer-air interfaces.

Keywords: Polycarbonate; amorphous; crystallization; WAXD glass transition; density

INTRODUCTION

Unlike the relatively rapid crystallization of polymers such as poly(ethylene terephthalate) (PET) and polycaprolactam (Nylon-6), the crystallization of poly(carbonate of bisphenol A) (PC) is rather slow and is usually induced by the effects of certain plasticizing substances. A common method to crystallize PC is by exposing it to

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vapors of acetone [1]. In a recent article describing the partial crystallization of PC by such method and the effects of crystallinity on its behavior and glass transition temperature, T_g, [2], it was stated that "a T_g decrease was observed... as a function of percentage crystallinity, X_c, and has been related to the possible confinement of the mobile amorphous phase in regions whose sizes are smaller than the correlation lengths of the cooperative movements that characterize the motions occurring at T_g". Since the notion that arrested mobility of polymer chains and chain-segments leads to a reduction (!) in T_g appears to be inconsistent with a large body of experimental results recently reviewed by one of us [3], since it is well established that cavitation and crazing of amorphous polymers caused by exposure to solvents reduces the T_g of these polymers [4–7], and since it has recently been shown that the T_g of polymers at the polymer-air interfacial layer is lower than that of the bulk polymer even in the absence of any residual solvent [8, 9], we have decided to perform crystallization and crystallization/annealing experiments on PC in order to determine whether T_g indeed decreases upon crystallization and if so what gives rise to this unexpected phenomenon.

EXPERIMENTAL

Clear PC sheet was obtained from Emco Industrial in thickness of about 1.5 mm and was cut into strips of 10 × 100 mm in size. The strips were exposed at 19°C to an atmosphere saturated with acetone vapors in a manner similar to the crystallization procedure of Mercier and associates [1]. The strips turned translucent after about 6 hrs exposure and opaque after about 12 hrs. After 48 hrs exposure the strips were retrieved and dried at 20°C under dynamic vacuum of less than 1 mm mercury pressure for 6 hrs after reaching constant weight. Since no weight loss of the samples occurred upon subsequent thermal treatments, we believe the studied samples contained no absorbed or entrained acetone. Several of the crystallized samples were then annealed under vacuum for 24 hrs at 120°C while others were annealed under vacuum for 18 hrs at 200°C. Uncrystallized PC strips were subjected to the same thermal treatments such that crystallized and uncrystallized

PC samples were obtained for all 3 conditions: dried at 20°C, annealed at 120°C, and annealed at 200°C. Wide-angle X-ray diffraction (WAXD) scans were obtained on a Philips diffractometer (PW 3710) from 5° to 55° 2θ in the parafocus geometry using copper K_α radiation and a diffracted beam monochromator. The scans were analyzed by profile fitting the data using a modified version of the program SHADOW. Modified Lorentzian peak shapes were used for both the amorphous and the crystalline peaks. Best fit for the data from amorphous samples was obtained by using two amorphous peaks, at 17° and 19°, for the first major peak, a small peak at 25° and two additional amorphous peaks at 27° and 44°. The positions of these amorphous peaks, especially the two low-angle peaks, are expected to have significant contribution from interchain distances, and hence may be used as a measure of the density of the amorphous fraction of the semi-crystalline samples [10]. The data from the semi-crystalline samples were fitted to two crystalline peaks at 17° and 25° in addition to the amorphous peaks mentioned above. The crystallinity was evaluated by normalizing the area under the crystalline peaks relative to the area under the entire scans after subtracting the background, according to the procedure of Hermans and Weidinger [11]. Typical WAXD scans of amorphous and semicrystalline samples are shown in Figures 1a and b, respectively. The peaks shown in Figure 1a for the amorphous sample are arbitrary, and may not be interpreted as corresponding to interchain distances. The peaks are used only as an analytical convenience to describe the data, and used as a *template* in calculation of the crystallinity of the semicrystalline sample from the scan in Figure 1b. The bulk density of all the samples was measured by pycnometry, using as the immersion medium solutions of $ZnCl_2$ in water containing a few drops of non-ionic surfactant to minimize the appearance of minute air bubbles in the pycnometry flasks. Differential scanning calorimetry (DSC) scans were conducted at a heating rate of 20 K/min in a duPont DSC Model 9900 instrument, with samples of around 10 mg each under nitrogen atmosphere. In all instances, the samples were first ramped up to 250°C, kept there for 5 minutes, rapidly quenched to below 0°C, and then reheated again to 250°C. The results of the first scan were used for the determination of the glass transition and melting temperatures of the PC samples, and those of the second scan were used to verify that the polymer did not

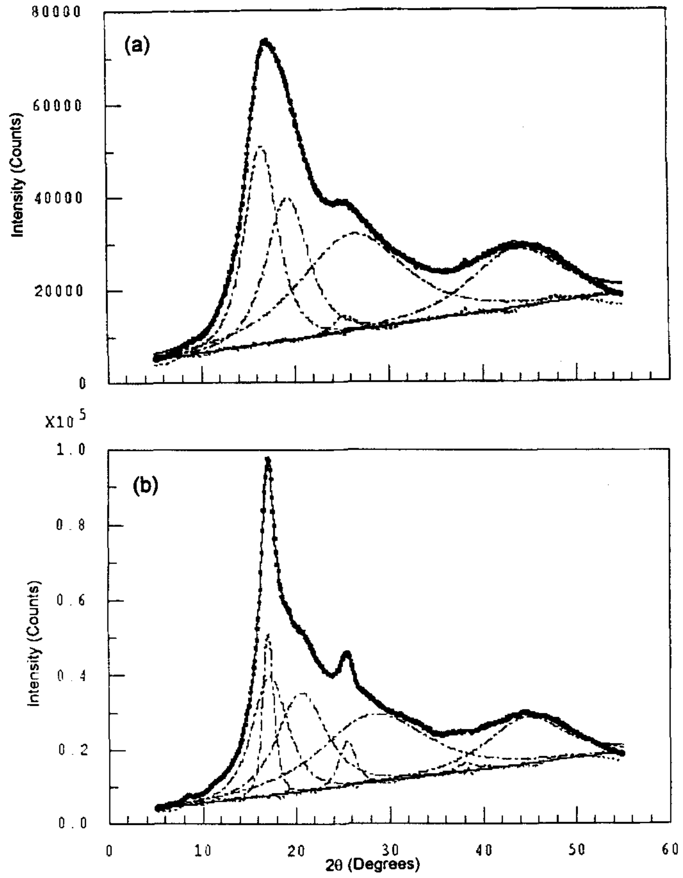

FIGURE 1 Profile fitted WAXD scans of two typical samples. (a) Amorphous sample 97A. (b) Semicrystalline sample 97B. In this figure, the circles are the observed data, the line through the circles is the fitted curve, which is the sum of the components shown by dotted lines. The difference between the observed and the calculated intensities is shown as a dotted line oscillating about the solid base line.

degrade during the DSC studies and that its crystallinity and thermal history were erased upon annealing at 250°C and quick quenching. Because the amorphous samples were subjected to different annealing conditions, both their T_g's and specific gravities (densities), ρ, were not identical to one another. This necessitated that each crystallized sample will be compared to its uncrystallized analogue subjected to the same thermal treatment.

RESULTS AND DISCUSSION

WAXD studies of all studied PC samples indicated that a crystallinity level of 14% was attained in the crystallized samples and that this crystallinity level remained unchanged by subsequent anneals at elevated temperatures. The uncrystallized samples showed zero crystallinity whether annealed or not. From a crystal density, ρ_c, of 1.315 g/cm^3 [12] and the relationship

$$X_c = (\rho_c/\rho)(\rho - \rho_A)/(\rho_c - \rho_A)$$

where ρ is the density determined by pycnometry, the amorphous density, ρ_A, of the amorphous phase in the semi-crystalline samples was calculated and is presented in Table I below. In this table are also given the % crystallinities of the samples, their anneal temperatures, their ρ values in g/cm^3, and the T_g in °C as measured in the first heat-up of each sample. In the first heat-up, the semi-crystalline samples showed a melting point, T_m, at around 208°C which was wiped out prior to the second heat-up. In all cases, a T_g of about 150°C was observed in the second heat-up. A T_m of only 208°C is significantly lower than the usually reported T_m of 220 – 230°C for PC [13], reflecting, we believe, the very small crystallite sizes obtained by us during the solvent-induced crystallization.

The data in Table I indicate that a substantial reduction in the density of the sample coded 97B occurred upon crystallization, and that annealing at elevated temperatures tends to increase the density of the semi-crystalline as well as the fully amorphous samples.

Table II are shown the *d*-spacings of the crystal and the amorphous peaks as obtained from WAXD analysis. Also shown are the apparent crystal sizes associated with the crystal peaks. In all instances the

TABLE I Properties of amorphous and semi-crystalline PC samples

Sample code	*Anneal temp.*, °C	X_c	ρ	ρ_A	T_g, °C
97A	20	0	1.1924	1.1924	152.4
97B	20	14	1.1797	1.16027	93.6
97C	120	0	1.1947	1.1947	153.6
97D	120	14	1.2093	1.19368	152.6
97E	200	0	1.1968	1.1968	152.5
97F	200	14	1.2080	1.1922	148.8

TABLE II WAXD results of PC samples, in nm

Sample	*Anneal temp.,°C*	X_c	*Peak d-spacings and crystal sizes*							
			Crystalline				*Amorphous*			
97A	20	0	–	–	–	–	0.534	0.458	0.339	0.207
97B	20	14	0.518	5.8	0.349	4.4	0.513	0.431	0.315	0.203
97C	120	0	–	–	–	–	0.534	0.458	0.340	0.208
97D	120	14	0.521	6.5	0.352	4.8	0.522	0.435	0.321	0.204
97E	200	0	–	–	–	–	0.531	0.458	0.333	0.207
97F	200	14	0.520	7.1	0.353	5.2	0.534	0.451	0.326	0.205

crystalline WAXD reflections were relatively sharp while the amorphous peaks were broad and shallow. The apparent increase in crystal size with annealing may be explained as a possible artifact of the technique whereby an increase in crystal internal perfection may be interpreted as an apparent increase in crystal size. The reasons for the apparent slight increase with anneal in crystal unit cell dimensions are not understood by us at present. The exact *d*-spacings of the first three amorphous peaks of the semi-crystalline samples are hard to locate exactly due to interferences by the crystalline peak in the WAXD scans. The trend is, nonetheless, that changes in the anneal temperature of the fully amorphous samples appear not to affect the *d*-spacings of the amorphous peaks and that a small decrease in average interchain distance takes place upon crystallization in the amorphous phase of the semi-crystalline samples. Comparison of Tables I and II indicates that the small decrease in interchain distance (increased local amorphous density) observable by X-ray techniques is reflected neither in a commensurate increase in the bulk density of the amorphous component of the samples nor in an increase of their T_g. The changes in ρ_A and T_g, especially of sample 97B treated at 20°C, are, then, most likely associated with the appearance of microcavities, crazes, and similar microvoids, and not with alterations in interchain spacings and densification of the "bulk" amorphous phase of the semi-crystalline PC samples.

Returning to the densities of the amorphous phase in Table I, we find that samples annealed at 200°C were the densest amongst both the fully amorphous and semi-crystalline series. When the fully amorphous samples are compared, we find that the free volume of each increase as the anneal temperature decreases. Setting sample 97E as the baseline, we find that the percent free volume in the samples progresses as shown in Table III. When the excess free volume of the amorphous phase in each of the semi-crystalline samples is compared with that of the corresponding amorphous sample subjected to the same thermal treatment, the results in Table IV are obtained.

Using the value of $\Delta\alpha = 3.1 \times 10^{-4}\,\mathrm{deg}^{-1}$ [14] for the difference between the coefficients of volume thermal expansion above and below T_g, one may calculate the amount by which T_g will be lowered as a function of increased free volume in the polymer. For our PC samples the calculated results are presented in Table V together with the corresponding experimental results from Table I. It is obvious from Table V that, although not identical, the calculated and observed T_g's are consistent with one another and move in the expected direction as function of the amount of extra free volume existing in the amorphous fraction of the semi-crystalline samples.

Optical microscopy studies of the semi-crystalline samples failed to reveal any cracks, fissures or other visible voids in the samples. On the other hand, the WAXD data in Table II indicate a slight decrease in the interchain spacings in the amorphous phase of the semi-crystalline samples. Considering both facts together, we conclude that the extra free volume in these samples is present in the form of minute voids

TABLE III Free volume of amorphous samples

Sample code	$\rho = \rho_A$, *g/cm*^{3}	*Extra free volume,* %
97A	1.1924	0.368
97C	1.1947	0.176
97E	1.1968	0.0

TABLE IV Extra free volume in amorphous phase of semi-crystalline samples

Compared samples		*Extra free volume,* %
97B/97A	(1.1924 − 1.16027)/1.16027	2.77
97D/97C	(1.1947 − 1.19368)/1.19368	0.85
97F/97E	(1.1968 − 1.1922)/1.1922	0.386

TABLE V Reduced T_g as function of extra free volume in amorphous phase

Sample	*Calculated* ΔT_g, *K*	*Calculated* T_g, °*C*	*Measured* T_g, °*C*
97B	−89.4	152.4 − 89.4 = 63	93.6
97D	−2.7	153.6 − 2.7 = 150.9	152.6
97F	−12.5	152.5 − 12.5 = 140	148.8

such as crazes, microcavities and microcracks. In order for a substantial extra free volume to be present in the semi-crystalline samples, the number of crazes and other microvoids must be very large. Their presence is associated, naturally, with very large specific surface area. The presence of polymer-air interfaces allows the chains and chain segments in the interfacial layer a larger motional freedom that in the "bulk" of the amorphous phase. The increased motional freedom is reflected in a reduction in T_g [3] and the presence of large specific surface area permits this increased motional freedom and reduced T_g to be measurable and, in fact, to be prominent in the T_g interval in the DSC scans of the semi-crystalline samples. The small motional confinement of chains in the amorphous phase which may be inferred from the WAXD results of the semi-crystalline samples, appears not to be reflected in the overall amorphous density and in the glass transition temperature of the PC samples in the present study.

CONCLUSIONS

The plasticizing effects of acetone molecules absorbed from the gas phase imparted to PC chains sufficient mobility to undergo partial crystallization. The volume shrinkage due to crystallization and the removal of all acetone by the application of vacuum combined to produce a miriad of microvoids, crazes and microcavities in a fashion not substantially different from the process of solvent-induced crazing in amorphous polymers [4–7]. These minute voids create a very large polymer-air interfacial specific surface area, and contribute to the generation of a large free volume in the amorphous phase of the semi-crystalline samples. The large polymer-air interfacial area causes a reduction in T_g below that usually found in the bulk polymer, brought about by the increased chain and chain-segment mobility at the polymer-air interfaces. The magnitude of the T_g reduction is expected to depend on the specific surface area thus created as well as on the local density and characteristics of the amorphous phase in the thin polymer-air interfacial layers. The extra free volume present in the amorphous portion of the semi-crystalline PC appears to be unrelated to the interchain spacings in this phase as determined by WAXD procedures.

Upon annealing at elevated temperatures, the number and possibly sizes of such microvoids decreases with the commensurate loss of free volume and increase in T_g of the amorphous fraction of the semi-crystalline PC samples. The loss of free volume is larger in samples annealed above T_g than in those annealed below it.

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