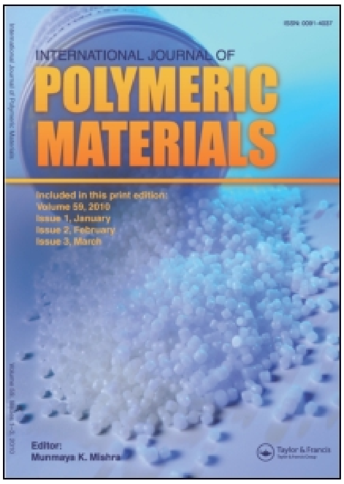

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Origin of Impact Strength in Polycarbonate:
I. Effect of Crystallization and Residual Solvent

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The high impact strength of glassy polycarbonate has been suggested to be related to an excess free volume, a large low temperature beta transition, or a unique morphology. To determine how crystallization affects free volume, molecular motion and morphology, samples of amorphous and partially crystalline polycarbonate have been studied by means of specific volume and dynamic mechanical measurements, electron microscopy and x-ray diffraction techniques.

Previous studies have given conflicting results concerning the effect of crystallization on the low temperature beta transition below T_g. Our results clarify this matter by showing that crystallization and residual solvent give different effects on the beta transition. Crystallization is shown to decrease the intensity of the beta loss peak suggesting that the beta motion occurs in the "non-crystalline" regions of the polymer. Solvent not only decreases the beta peak intensity, but also shifts the peak maximum to lower temperatures and causes an additional loss peak to occur at higher temperatures but still below T_g.

The embrittling effect of crystallization can be attributed to a lowering of the beta transition intensity or to a loss of free volume as judged by decreases in specific volume. However, more convincing evidence of the restricting effect crystallites have on amorphous chain segments is given by the observed changes in the alpha transition (T_g) and sample morphology with crystallization.

INTRODUCTION

The origin of high impact strength in a glassy polymer is not clear. Previous investigators have noted empirical correlations between high impact strength

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and excess free volume,[1] or the existence of pronounced low temperature ($T < T_g$) transitions.[2] Other possibilities include small crystal structures,[3] or a unique molecular packing arrangement.[4]

Exceptions to these empirical correlations have been observed[5] and, moreover, the theoretical basis for relating high impact strength to transitions or free volume is not clear. It is known that a nominally brittle glass such as polystyrene (which has low excess volume and no pronounced transitions below T_g) can exhibit high impact strength if the material is first oriented above T_g.[6] Conversely, a nominally ductile glass, such as polycarbonate, can be embrittled by annealing below T_g.[7] If impact strength is related to either free volume, transitions due to molecular motion, or morphological structure, then changes in these parameters should occur after orientation, annealing, or other treatments which are observed to affect impact strength.

Based upon this premise research was undertaken to study molecular motion, free volume, and morphology of a given polymer. Polycarbonate was selected for study because it exhibits unusually high impact strength. Also, it is a model material for the various empirical correlations since the high impact polycarbonate has both a large excess volume and a pronounced low temperature beta ($< T_g$) transition.

Material treatments which we have investigated include crystallization, blending with low molecular weight liquids, annealing, and orientation. All of these treatments are known to affect the impact strength of polycarbonate; however, in most cases their effects on the low temperature beta transition, free volume, and morphology of the polymer are not well established.

A previous report by us has shown how the low temperature beta transition and free volume in polycarbonate are affected by plasticizers and antiplasticizers.[8] This study presents data showing how the beta transition and free volume are affected by a change in morphology brought about by crystallization.

The effect of crystallization on the dynamic mechanical properties of polycarbonate has been reported by Neilsen[6] and more recently by Roe and Baer.[9] Neilsen's results included both the low temperature beta transition at −110°C (also referred to as the gamma transition by some authors) and the alpha or glass transition, T_g, at 145°C, whereas the results of Roe and Baer included only the beta transition temperature region. Conflicting results were reported by Neilsen, and Roe and Baer on the effect of crystallization on the low temperature beta transition.

Neilsen reported that the mechanical loss peak at 1 Hz shifted from −110°C to −30°C on going from an amorphous to a partially crystalline sample. (The percent crystallinity and sample preparation were not reported; however, the ease of crystallizing polycarbonate by exposure to solvent vapors was mentioned in the text.) No explanation for this large shift was given and some authors[10] have noted that such a large shift is difficult to understand if the beta molecular motion is due to local motions of the carbonate group.

On the other hand, Roe and Baer reported that crystallization lowers the intensity of the low temperature beta loss peak while the temperature of maximum loss remained the same at a given frequency. They interpreted this as evidence that the beta molecular motion occurs in the noncrystalline regions of the polymer. They studied only one crystalline sample that was prepared by exposure to acetone and had a 38% crystallinity as determined by x-ray diffraction.

Mikhailov and Eidelnant[11] reported that the dielectric beta loss peak decreased in intensity and shifted to higher temperatures for a partially crystalline sample, but the extent of shift (from −60°C to −50°C at 1000 Hz) was much smaller than that observed by Neilsen. The degree of crystallinity and preparation of their sample were not reported.

Based upon the data in the literature it is not clear what effect crystallization has on the low temperature beta transition. Therefore, it is also not clear whether one should assign the beta molecular motion to the crystalline or the noncrystalline region. It is also apparent that most crystalline polycarbonates in reported studies are most likely prepared by exposure to solvent and yet data are not available to indicate what effect the residual solvent has on dynamic mechanical measurements of either amorphous or crystalline samples. These questions together with the question of the effect of crystallization on free volume, the low temperature beta transition, and morphology are hopefully to be answered in this study.

EXPERIMENTAL

Preparation of amorphous polycarbonate (PC) films

A commercially available PC resin, Mobay Merlon M-50, having a weight average molecular weight of 35,000 with no additives was used for this study and subsequent studies in this series. Amorphous samples were prepared by casting films, 0.003–0.005 cm thick, from a 16% by weight solution of PC in methylene chloride. Methylene chloride was selected because it is highly volatile (boiling point = 40°C) and its high rate of evaporation reduces the chance of crystallization occurring and of having residual solvent in the film. The films were allowed to air dry 24 hours at room temperature, followed by heating in a vacuum oven at 160°C for 1½ hours to remove residual methylene chloride. This temperature was selected because it is above the glass transition temperature of PC ($T_g = 145°C$); and, therefore, the diffusion of solvent molecules out of the films is enhanced. The use of higher temperatures for solvent removal would cause the films to soften excessively and lose their shape. After heating, no detectable methylene chloride was found by infrared; the specific volume and T_g of the dried film were found to be almost the same as that of the compression molded films.

Preparation of crystalline PC films

Crystalline films were prepared by decreasing the rate of methylene chloride evaporation from the polymer sample. Two different procedures were employed which were found to give different degrees of crystallinity.

In one case, films 0.003–0.006 cm thick were cast from the 16% methylene chloride solution and placed in a saturated methylene chloride atmosphere for one hour. During this time the films became opaque, suggesting that crystallization had occurred. After the one hour period the films were allowed to air dry 24 hours and then were heated in a vacuum oven 1½ hours at 160°C to remove residual solvent. An alternative technique was to allow the 16% methylene chloride solution to evaporate at 23°C from a shallow dish. This resulted in a 1 cm thick crystalline residue. After one month the residue sample was cut and polished to a uniform thickness of 0.010 cm and heated in vacuum at 160°C for 1½ hours to remove residual solvent.

Specific volume measurements

Specific volume measurements were used to calculate the percent crystallinity and were made using a sodium bromide gradient column at 25°C.

Dynamic mechanical measurements

Dynamic mechanical properties were measured using a Rheovibron Model DDV-II Dynamic Viscoelastometer in which samples were subjected to an oscillating tensile strain (0 to 1% in magnitude) at a fixed frequency of 110 Hz.

Morphological characterization

Platinum carbon surface replicas of amorphous and crystalline films were examined in a JEM 6-A electron microscope. Wide-angle and small-angle x-ray patterns were also obtained of film samples to demonstrate changes in crystallinity.

RESULTS

Specific volume measurements

Table I lists the specific volumes of amorphous and partially crystalline films used in this study. Except where noted the values represent the average of three samples with a sample to sample variation of less than 0.0002 cc/g.

The percent crystallinity was calculated using the relation:

$$\% \text{ crystallinity} = \frac{V_a - V}{V_a - V_c} \times 100$$

where V_a = amorphous specific volume (inverse of the density), V_c = crystalline specific volume, and V = observed specific volume of the sample. Values of $V_a = 0.837$ and $V_c = 0.760$ were used for these calculations. The latter is obtained from the x-ray unit cell density of 1.315 g/cc reported by Bonart.[4]

TABLE I

Specific volume measurements of polycarbonate at 25°C

Sample/Treatment	Specific Volume	% Crystallinity
Molded Film/None	0.8371	0
Cast Film/1½ hours at 160°C	0.8371	0
Cast Film/8 months at 23°C	0.8368	0
Cast Film/8 months at 23°C 1½ hours at 160°C	0.8371	0
Cast Film/1 hour in $MeCl_2$ vapor 1½ hours at 160°C	0.8230	18
Residue from slow evaporation of $MeCl_2$/1½ hours at 160°C	0.8157[a]	27

[a] Average value of three samples: 0.8178, 0.8162, 0.8131.

The specific volumes of amorphous samples with residual methylene chloride are shown after extended periods of air drying. Since slight amounts of residual solvent could influence these measurements (methylene chloride has a specific volume of 0.760 cc/g), specific volumes were also measured after annealing 1½ hours in vacuum at 160°C. This treatment removes solvent but would not destroy any crystalline structure (if such existed) since polycarbonate melts at 220°C. The results indicate that the films with residual solvent did not crystallize even after 8 months at 23°C.

Dynamic mechanical measurements

The results of dynamic mechanical measurements on amorphous and partially crystalline films of polycarbonate are shown in Figure 1. Both the loss factor tan δ, and stored modulus, E', are plotted as functions of temperature from

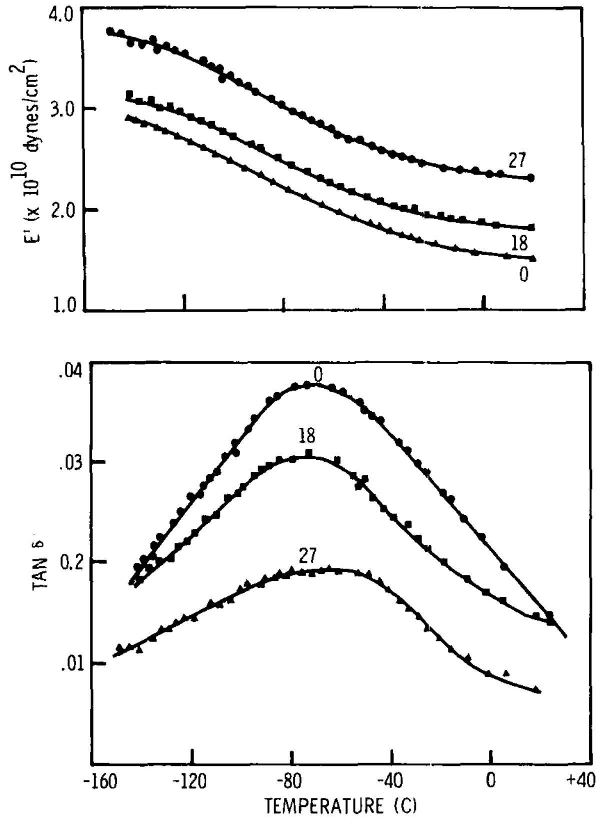

FIGURE 1 Effect of crystallinity on the beta transition. Top: E' vs. temperature; Bottom: tan δ vs. temperature. Numbers on curves indicate percent crystallinity by density.

−150°C to +23°C. The numbers on each curve represent the percent crystallinity which was determined from the measured specific volume as reported in Table 1.

The large transition in this temperature region shown by the peak in tan δ and the relaxation in E' is identified as the "beta" transition in polycarbonate.[2] The data show that the intensity of the beta loss peak decreases as the percent crystallinity increases while the temperature location of maximum loss remains unchanged. The stored modulus, E', is observed to increase as the percent crystallinity increases. Although crystallization increases E', and decreases tan δ, the loss modulus E'' ($= E'$ tan δ) decreases as the percent crystallization increases. Thus both the E'' and tan δ peaks are affected in a similar manner by increasing the percent crystallization.

Figure 2 shows the effect of crystallization on both the beta and alpha (T_g) transitions for the samples of different percent crystallinity. Data could not be taken above 160°C for the soft amorphous sample. However, the crystalline films are more rigid and can therefore support a stress required for the measurements.

The effect of crystallinity is to shift the alpha loss peak to a higher temperature. Also, some indication of peak broadening is observed and the intensity (tan δ maximum) of the loss peak is decreased. The origin of the broad shoulder in tan δ from 20°C to 160°C in the 27% sample is not known. It is possibly caused by residual solvent since the annealing treatment to remove solvent may have been less effective due to the higher alpha transition temperature and/or to the use of a thicker specimen.

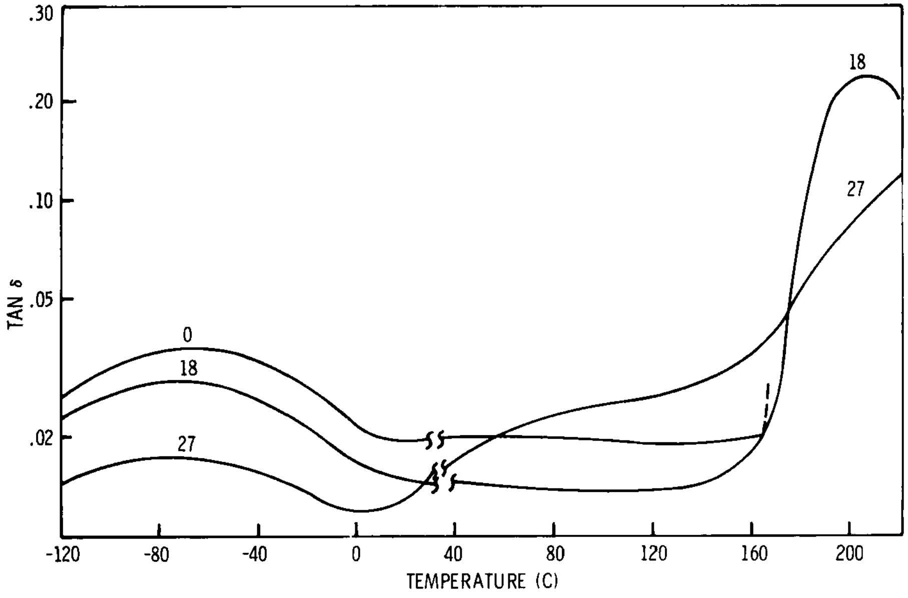

FIGURE 2 Effect of crystallinity on alpha and beta transitions. The breaks in the curves are due to resetting the samples upon changing from a cold stage to a heating stage.

Since the crystalline and amorphous samples were prepared by casting from methylene chloride it was desirable to know how residual solvent influences the dynamic mechanical properties of polycarbonate. To determine this a film was cast from a polycarbonate methylene chloride solution and was not heated to remove solvent. Dynamic mechanical measurements were taken after various periods of time while solvent evaporated from the film at room temperature. Independent weighing experiments were performed on solvent cast films to estimate the amount of residual solvent as a function of time at 23°C. This was done by weighing samples before and after heating the films in a vacuum oven at 160°C for $1\frac{1}{2}$ hours.

Results for polycarbonate with residual methylene chloride are shown in Figure 3. The period of elapsed time since casting the film is indicated on each curve. The weight percent of residual methylene chloride estimated from weighing is shown in parentheses.

The data show that the presence of large amounts of solvent (5 wt %) shifts what appears to be the beta tan δ peak to a higher temperature. However, as solvent evaporates from the film ($\leqslant$2 wt %), this peak shifts to higher temperatures and decreases in intensity. Therefore, this peak should be

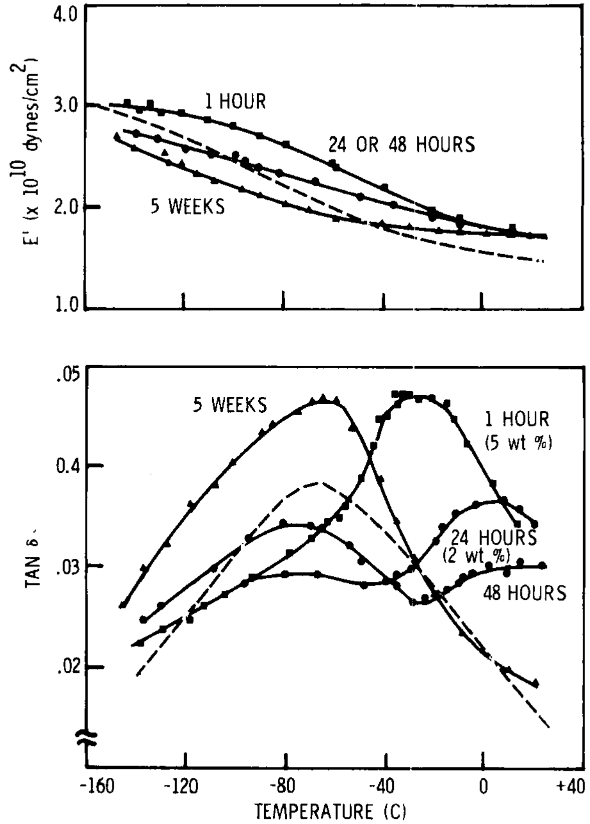

FIGURE 3 Effect of residual methylene chloride on the beta transition. Data are shown for the same sample after various periods of air drying. (The dashed line represents unmodified polycarbonate.) The amount of methylene chloride is shown in parentheses.

labelled a "solvent" peak and is distinct from the beta loss peak. The actual beta peak is initially suppressed by the methylene chloride but reappears at lower temperatures as the solvent evaporates.

The stored modulus *E*′ is initially increased by the suppression of the beta transition. In other words, not only is the loss peak suppressed, but also the relaxation in modulus associated with the beta transition is suppressed. Thus the modulus remains more nearly constant and has a higher value over this temperature region. As solvent evaporates, the relaxation of the stored modulus is observed to recover. Similar results were obtained for polycarbonate with absorbed acetone indicating the generality of the effect observed.

Figure 4 shows the effect of residual methylene chloride on the beta transition for a sample partially crystallized by exposure to methylene chloride

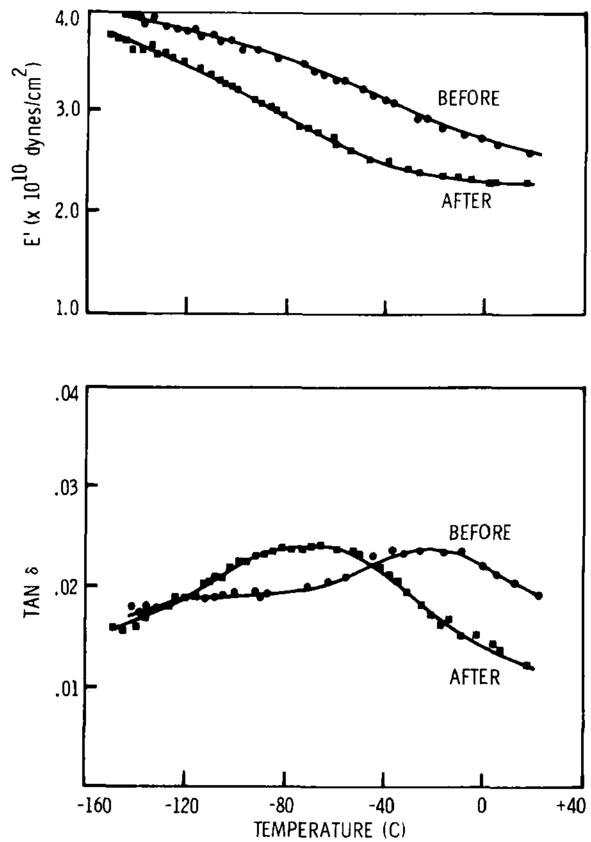

FIGURE 4 27% crystalline polycarbonate before and after annealing 1.5 hours at 160°C to remove methylene chloride.

vapor. Before annealing to remove solvent the beta peak appears to be shifted to higher temperatures. After annealing 1½ hours at 160°C in vacuum the location of the peak is the same as for dry amorphous polycarbonate although the intensity is less. The presence of solvent in the crystalline sample also increases the stored modulus, E', which again recovers upon removal of solvent.

X-ray

Figure 5 shows wide-angle and small-angle x-ray diffraction patterns for an amorphous and a 27% crystalline sample. The wide-angle patterns demonstrate that the diffuse halos for the amorphous sample are replaced by more discrete reflections for the solvent-induced crystalline sample. The small-angle pattern shows a broad peak occurring at a Bragg spacing of about 150 Å for the 27% crystalline film. A similar result was observed for an 18% crystalline film. No discrete reflections were observed for the amorphous sample at small angles. A wide-angle X-ray pattern for an amorphous sample with 1–2% residual methylene chloride was the same as that of a dry amorphous sample with no observable change in location of diffuse halos.

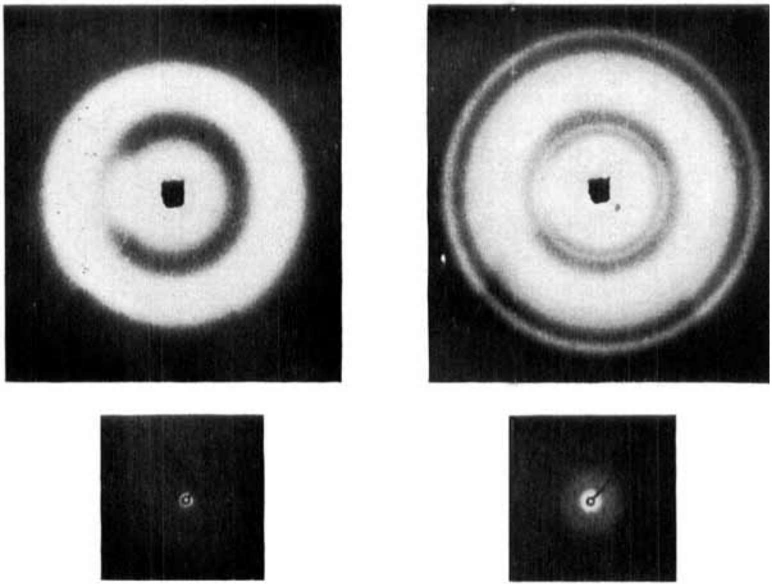

FIGURE 5 Wide-angle (top) and small-angle (bottom) x-ray patterns of polycarbonate having crystalline contents based on density of (left) 0%, (right) 27%. Portions of the patterns are affected by the reflections from the sample holder.

Electron microscopy

A platinum carbon (Pt-C) replica of an amorphous cast film of PC is shown in Figure 6. The surface is observed to have a characteristic roughness which consists of 75-125 Å "nodular" regions. No larger structures were observed.

Figures 7 and 8 are Pt-C replicas of a cast film of PC which was exposed to methylene chloride vapor for 5 minutes immediately after casting. These micrographs demonstrate that the initial phase of crystallization involves the formation of lamellar structures which appear to be composed of 200 Å nodular units.

Figure 9 is a Pt-C replica of a cast PC film exposed to saturated methylene chloride vapor for one hour. This film is 18% crystalline as determined by density. A randomly oriented lamellar structure is observed over the entire surface. The observed lamellar center-to-center distances range from 100 to 200 Å and are similar to the periodicity measured by x-ray diffraction. The 27% crystalline sample was not replicated because the surface texture had been distorted by polishing.

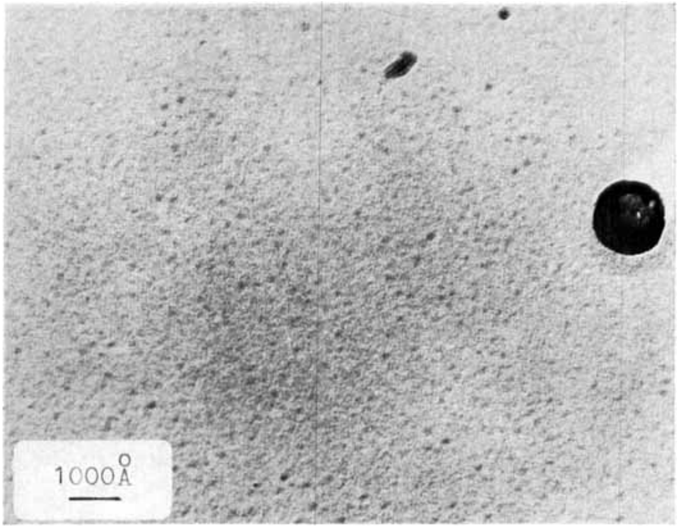

FIGURE 6 Pt-C replica of amorphous polycarbonate film cast from a methylene chloride solution.

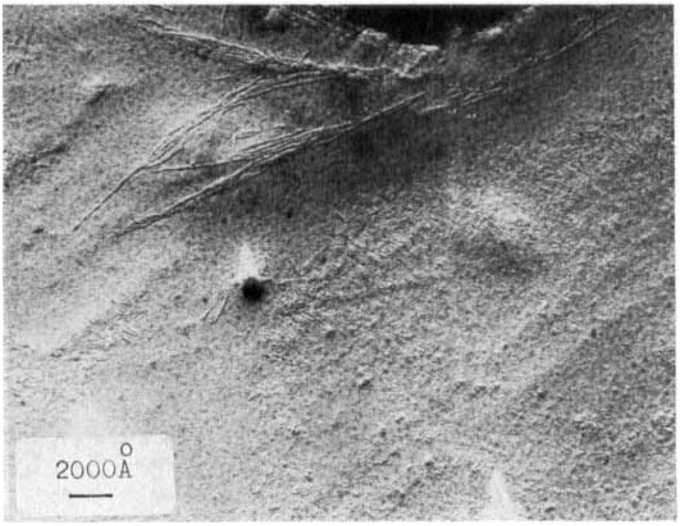

FIGURE 7 Pt-C replica of polycarbonate cast film exposed to saturated methylene chloride vapor for 5 min.

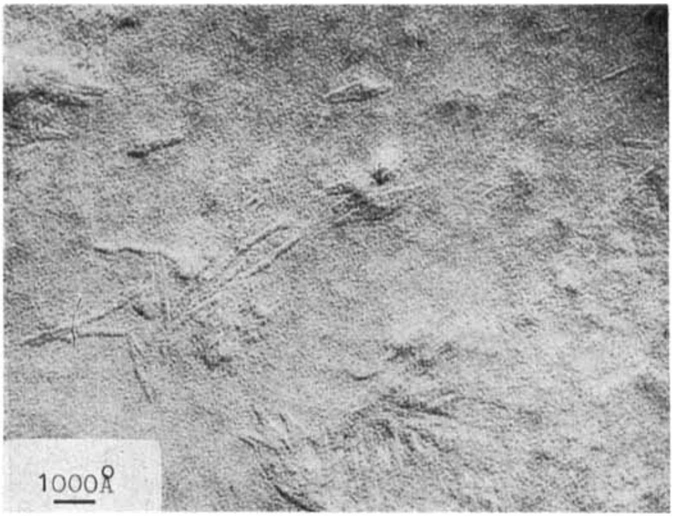

FIGURE 8 Pt-C replica of polycarbonate cast film exposed to saturated methylene chloride vapor for 5 min. (Another view of the same specimen.)

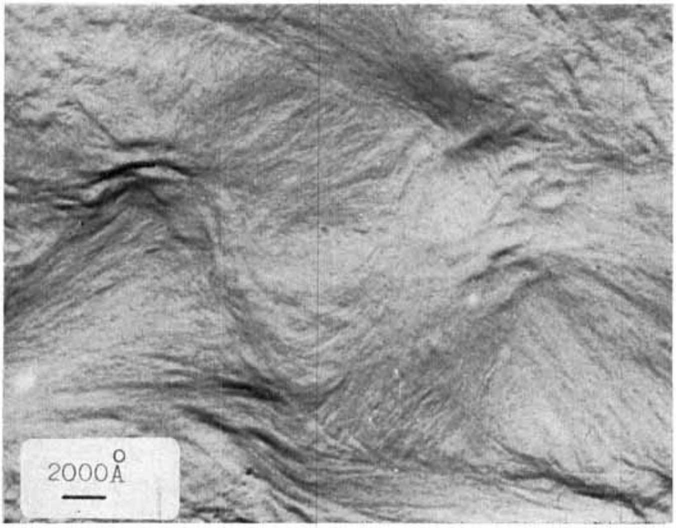

FIGURE 9 Pt-C replica of polycarbonate cast film exposed to saturated methylene chloride vapor for 60 min.

DISCUSSION

Crystallization and molecular motion

As indicated earlier, previous publications on the effect of crystallization on the low temperature beta transition appeared to give conflicting results. The data presented here offer a possible explanation for this apparent conflict. It was shown that the presence of residual solvent molecules in polycarbonate results in the occurrence of a "solvent" peak near 0°C which may be mistaken as a shift in the beta loss peak. Furthermore, the presence of lesser amounts of solvent will cause a shift of the temperature of maximum loss of the true beta loss peak to a lower temperature.

Since this strong effect of residual solvent occurs in crystalline as well as amorphous samples, it is clear that spurious results can be obtained in studying transitions in "solvent-crystallized" polycarbonate if samples are not treated first to remove residual solvent.

The results presented here on the effect of crystallization on the beta transition agree with the data reported by Roe and Baer[9] who compared one amorphous and one crystalline sample. The progressive decrease in intensity of the beta loss peak (either tan δ or E'') with increasing crystallinity reported here indicates that the beta motion occurs in the non-crystalline phase.

The results of this study are similar to reported results for other crystallizable amorphous polymers. McCrum *et al.*[10] had reported the observation of Baccaredda *et al.* that the "delta" transition at −110°C in amorphous isotactic polystyrene was reduced in intensity by crystallization but that the temperature of maximum loss was unchanged. The beta transition (at −80°C) in polyethylene terephthalate is also reduced in intensity (though to a lesser degree than observed here for polycarbonate) and the temperature of maximum loss is unchanged.[10]

The observed changes in the alpha transition of polycarbonate with crystallization are similar to the findings of both Neilsen[6] and Mikhailov and Eidelnant[11] which showed that crystallization shifts the alpha transition to higher temperatures and decreases its intensity. The decrease in intensity is expected based on the fact that the alpha transition is associated with the amorphous chains, their volume fraction being decreased by crystallization. The shift to higher temperature suggests that the presence of crystallites restricts the movement of the amorphous chains. Matsuoka and Ishida[12] have explained the peak shift to higher temperatures by considering that crystallites impose a tension on the amorphous chain segments. The fact that the alpha motion is restricted, whereas the beta motion is not, can possibly be attributed to the difference in size of the chain segments involved in these respective motions. That is, motion of perhaps 20–30 monomer units (alpha) may be restricted by lamellar crystals whereas local motion of perhaps one or more monomer units (beta) may not necessarily be.

Effects of solvents

Although the study of crystalline samples indicates that the beta motion is occurring in the amorphous regions, available evidence (from this study and that of previous investigators)[13,14] indicates that the non-crystalline region itself may be composed of ordered domains within the nodules and less ordered internodular and irregularly folded regions associated with the nodules. Thus, the question arises as to whether the beta motion occurs in the less ordered regions (as might be expected) and whether there is any experimental evidence for this. The effect of solvents on polycarbonate's beta transition indicates that small amounts of solvent tend to suppress the beta loss peak suggesting that the beta molecular motion may be impeded by solvent similar to the effects of plasticizer and antiplasticizer.[8]

It may seem contradictory that solvent molecules restrict the beta motion and yet allow increased mobility of chain segments so that crystallization can occur. Solvents induce crystallization by lowering the glass transition to below room temperature.[15] This requires a certain critical amount of solvent to penetrate the glass and mobilize the polymer chains. If less than this amount of solvent is absorbed, however, the solvent is simply incorporated into the glass structure. It is suggested here that this small amount of solvent would penetrate initially into the less ordered (internodular or folded) regions and restrict local segmental motions such as beta. Apparently these small amounts of residual solvent do not permit crystallization to occur since cast films allowed to air dry several months do not evidence any density increase. The observation that extended exposure to solvent vapor causes crystallization and results in an alignment of the nodular surface structures may indicate that larger amounts of solvent are required to penetrate and mobilize the ordered chain segments inside the nodules, allowing crystalline chain packing to occur. The penetration of solvent initially into less ordered (and presumably less dense) regions is compatible with the loss of volume previously reported for polycarbonate when mixed with low molecular weight liquids.[8]

Thus the effects of solvents on specific volume, the beta loss peak and morphology are compatible with associating the beta molecular motion with the less ordered regions. The decrease in intensity of the beta loss peak with crystallization is consistent with a decrease in the volume fraction of such regions. However, it is not clear whether to attribute the beta motion to a particular site such as a loose fold or tie molecule. Either of these sites may be decreased in number by crystallization.

Crystallization and ductility

The correlation of high impact strength with the low temperature beta transition appears to be supported by the observation that crystallization embrittles polycarbonate and lowers the intensity of the beta loss peak. However, most solvents also lower the intensity of the beta loss peak but do *not* embrittle polycarbonate.[16] This indicates that the beta motion can be restricted without restricting ductile yielding and tends to negate the suggested correlation between high impact strength and the beta transition peak intensity.

It was noted that crystallization shifts the alpha loss peak to higher temperature. This is a direct indication that the presence of crystallites does restrict movement of large non-crystalline chain segments and it is anticipated that the ductility of the amorphous phase may be similarly affected. This argument only applies if ductility is related to movement of large chain segments which are believed responsible for the alpha loss peak in amorphous polymers. The beta peak does not evidence the same restriction since its temperature remains unchanged.

The changes in density by crystallization are difficult to relate directly to "free volume" since the structure and/or occupied volume may also be changed by crystallization. However, the shift of the alpha transition to higher temperatures is consistent with a free volume decrease for the amorphous region and the loss of ductility may be due in part to a loss of free volume.

In summary, the embrittling effect of crystallization appears to be most easily understood by considering the observed changes in morphology and the restricted mobility of the larger chain segments in the amorphous phase.

Acknowledgments

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