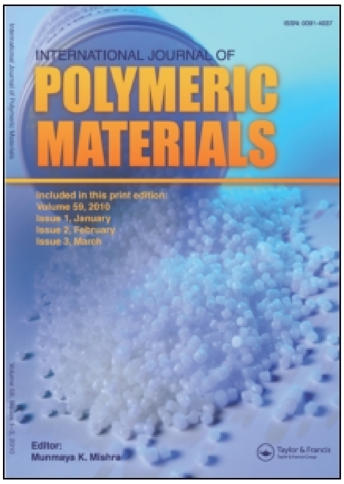

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Origin of Impact Strength in Polycarbonate: II. Effect of Thermal Treatments

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Origin of Impact Strength in Polycarbonate: II. Effect of Thermal Treatments

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The effect of thermal treatments on free volume, molecular motion and morphology of glassy polycarbonate has been studied in order to understand how these variables might be related to impact strength. Results indicate that quenching or annealing below T_g produce only slight changes in specific volume or the low temperature beta transition. Significant changes in morphology are observed in polycarbonate after annealing.

The previously suggested correlations between impact strength and free volume or the beta transition are difficult to understand in view of the slight changes in these variables after extensive annealing below T_g. It appears that a better correlation may exist between impact strength and the intermediate transition (between alpha and beta) and the size of the nodular structure in the glass.

INTRODUCTION

High impact strength in glassy polymers has been suggested to be related to a large excess volume[1] and pronounced low temperature transitions ($T < T_g$).[2] To test these suggested correlations and also to examine the role of morphology, high impact polycarbonate has been studied after subjecting the polymer to material treatments which are known to affect its impact strength.

Previously we have shown that blending either plasticizer or antiplasticizer with polycarbonate results in a similar suppression of the low temperature beta transition and equivalent volume losses.[3] However, these blends exhibit different mechanical properties. In Part I of this series we attributed the embrittling effect of crystallization to the restriction crystallites have on

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longer chain segments; the local segmental motion causing the beta transition was not restricted by crystallization, though its intensity was reduced.[4]

Thermal treatments are also known to affect the impact strength of glassy polycarbonate[5] and therefore it is of interest to know how these treatments affect specific volume, molecular motion and morphology of the polymer. Previous investigators have attributed the embrittling effect of annealing below T_g to specific volume decreases or changes in dynamic mechanical properties and/or morphology.[6,7,8] The degree to which these properties are interrelated is not fully understood. Also, at the outset of this research, data were not available to indicate the effect of annealing on the low temperature beta transition, which has been suggested to be related to high impact strength in polycarbonate. Recently Neki and Geil[9] reported their studies of polycarbonate showing that slight changes do occur in the shape of the beta loss peak with annealing.

The purpose of this paper is to present additional data on glassy polycarbonate showing how thermal treatments affect specific volume, dynamic mechanical properties and morphology to show how these variables may be related to impact strength.

EXPERIMENTAL PROCEDURE

Sample preparation

The same polycarbonate resin (Merlon M-50) used in Part I[4] of this series was used for this study. Amorphous films 0.003 to 0.006 cm thick were prepared by compression molding and solvent casting. Molded films were pressed at 250°C and either quenched in liquid nitrogen, slowly cooled by turning off the press heaters overnight, or cooled with cold water in the press. Cast films were prepared from a 16% by weight solution in methylene chloride. Solvent was removed by air drying 24 hours and then heating 1.5 hours at 160°C in a vacuum oven.

Specific volume measurements

Changes in specific volume were measured using a sodium bromide gradient column at 25°C. Values reported are averages of 3 samples with a sample to sample variation of less than 0.0003 cc/g.

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

Surface textures were examined by Pt-C replication using a JEM 6-A electron microscope. In some cases samples were etched with sodium hydroxide before replicating following the technique of Neki and Geil.[9]

Annealing

Annealing was performed in an air oven at temperatures of 100°C, 120°C, or 140°C. In addition, samples were also annealed in dry nitrogen at 110°C.

RESULTS

Specific volume

The effect of thermal treatments on the specific volume of polycarbonate is shown in Table I. The specific volumes of samples from the same film before and after annealing are shown along with the percent change. The results in Table I indicate very slight decreases in specific volume occur upon annealing at 100°C and 120°C. However, some of these results are within the estimated uncertainty of 0.0003 cc/g in measuring relative changes in specific volume. The maximum observed decrease in specific volume (0.07%) occurs after annealing at 140°C. Specific volume changes due to cooling rate are as large as those obtained by annealing. Quenching increases the specific volume whereas slow cooling decreases it.

TABLE I

Specific volume measurements of polycarbonate at 25°C

Sample	Treatment	Specific volume		
Molded PC	Slowly cooled		0.8368	
	liquid N_2 quench		0.8376	
	Annealed	Before	After	% Change
Molded PC	100°C for 7 days	0.8371	0.8370	0.01
	120°C for 7 days	0.8371	0.8366	0.05
Cast PC	100°C for 7 days	0.8371	0.8368	0.03
	120°C for 7 days	0.8371	0.8368	0.03
	140°C for 2 hours	0.8373	0.8368	0.05
	140°C for 6 hours	0.8373	0.8367	0.07
	140°C for 10 hours	0.8373	0.8368	0.05

Dynamic mechanical properties

The effect of cooling rate on the low temperature beta transition is shown in Figure 1. Data are plotted for a slowly cooled sample and for a sample quenched in liquid nitrogen. The results indicate that the beta tan δ peak is slightly higher and broader for the quenched sample. The stored modulus, E', is also decreased by quenching and the relaxation in modulus occurs over a broader temperature interval.

Figure 2 shows the effect on the beta transition of annealing cast films of polycarbonate 7 days at 100°C and 120°C. The beta peak is decreased in intensity (a lower tan δ maximum) and is more irregular in shape. Slight increases in modulus are also apparent for the annealed films. Similar results are observed for annealed compression molded films as shown in Figure 3.

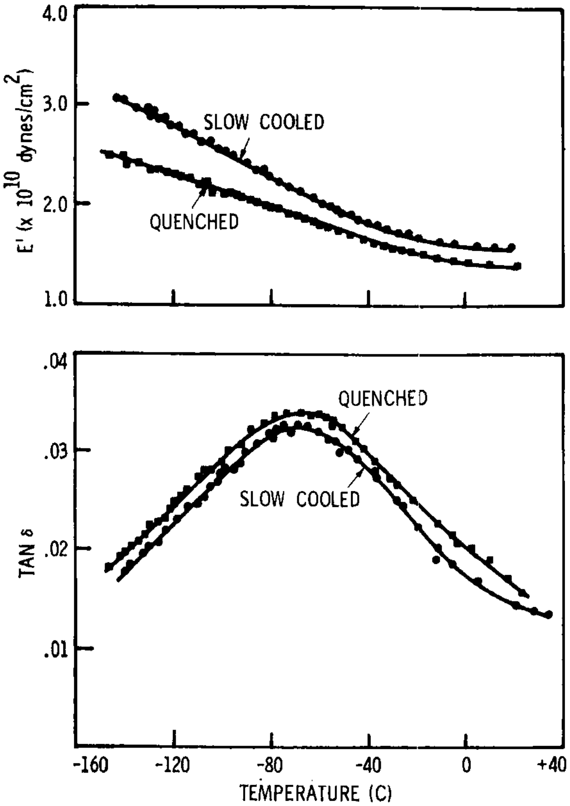

FIGURE 1 Effect of cooling rate on the beta transition of polycarbonate. Top: Stored modulus, E', vs temperature. Bottom: Loss factor, tan δ, vs temperature.

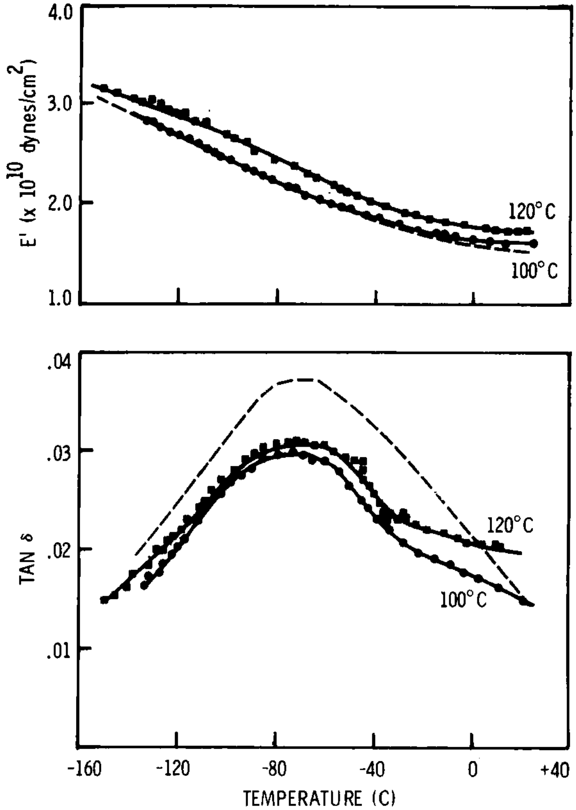

FIGURE 2 Effect on the beta transition of annealing cast films of polycarbonate 7 days at 100°C and 120°C. (The dashed line represents unannealed polycarbonate in this and subsequent figures.)

These results are similar to the results found by Neki and Geil. They did not report a loss of peak intensity and the peak shape they reported appeared less irregular than those reported here. These slight differences may be due to different methods of sample preparation.

The effect of annealing cast films at 140°C for 2, 6, and 10 hours is shown in Figure 4. Annealing for 2 hours develops a shoulder on the high temperature side of the beta loss peak; however, the tan δ maximum appears unchanged. Further annealing at 140°C produced a less irregular peak shape with an apparent increase in peak intensity.

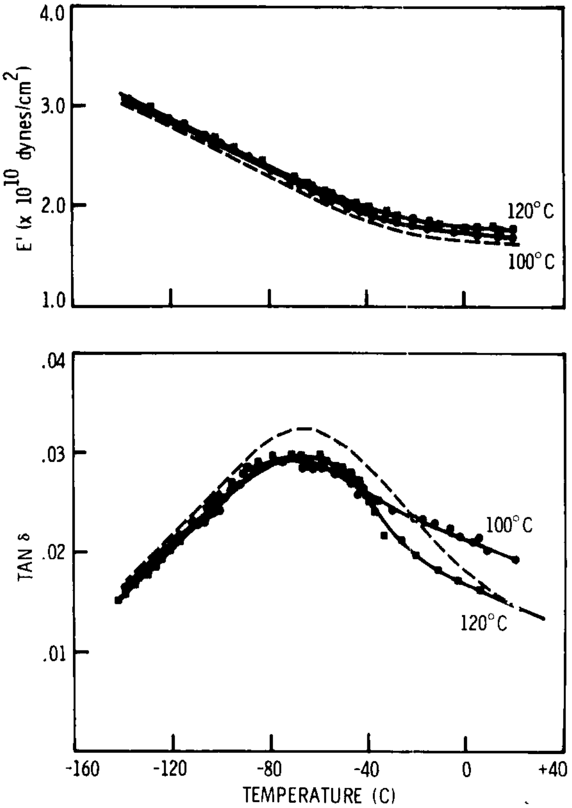

FIGURE 3 Effect on the beta transition of annealing molded films of polycarbonate 7 days at 100°C and 120°C.

Electron microscopy

A Pt-C replica of compression molded polycarbonate is shown in Figure 5. A nodular texture 50–150 Å in size is observed. Polishing the molded film using standard metallographic techniques to remove any possible impressions from the mold surface revealed a similar texture as shown in Figure 6. A somewhat smaller (70 Å) nodular structure was observed in rapidly quenched films.

Some indication of enlargement of the surface texture by annealing was observed by examining the molded polycarbonate film used for dynamic mechanical measurements after annealing 7 days at 120°C. Figure 7 shows the surface of this film was characterized by poorly defined 250–300 Å regions. Other thin films also evidenced poorly defined surface structure after annealing. The surface of a thick (1 mm) molded polycarbonate sample which was

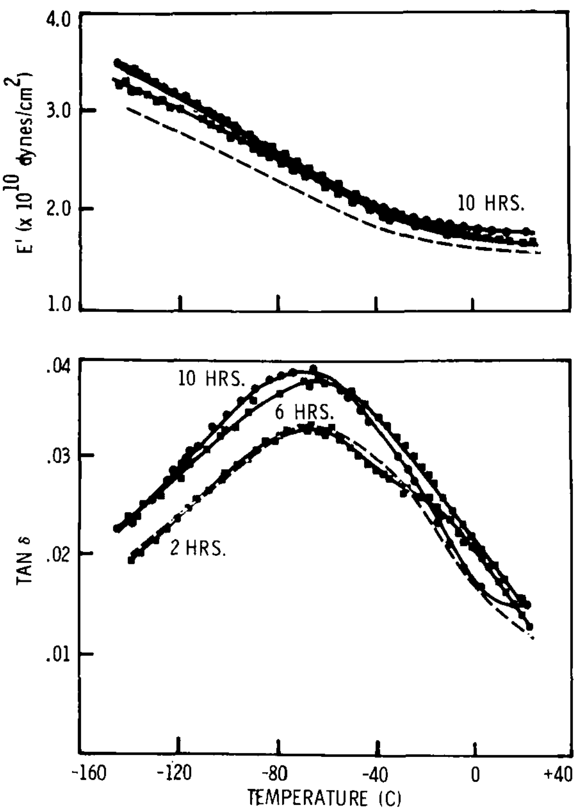

FIGURE 4 Effect on the beta transition of annealing cast films of polycarbonate 2, 6, 10 hr at 140°C.

annealed in a dry nitrogen atmosphere for 7 days at 110°C is ahown in Figure 8. This sample evidenced both nodular enlargement to about 300 Å and also alignment of these units to form rod-like features 1200 Å long. Although this result was reproducible it is not clear why similar structures were not observed at other temperatures using the thinner films. Further study is required to fully understand this surface structure.

To reveal more clearly the effect of annealing on the morphology of the thin films, samples of polycarbonate were etched with sodium hydroxide. Figure 9 is a micrograph of etched solvent cast polycarbonate which was not annealed below T_g. Etching reveals 200–400 Å plateau-like structures within the amorphous film. Although this large structure is not observed by Pt shadowing before etching, a texture similar in size was observed before etching

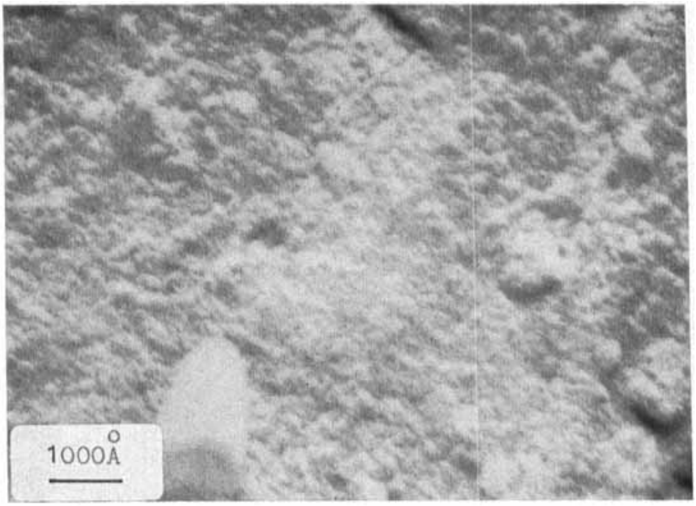

FIGURE 5 Pt-C replica of compression molded polycarbonate.

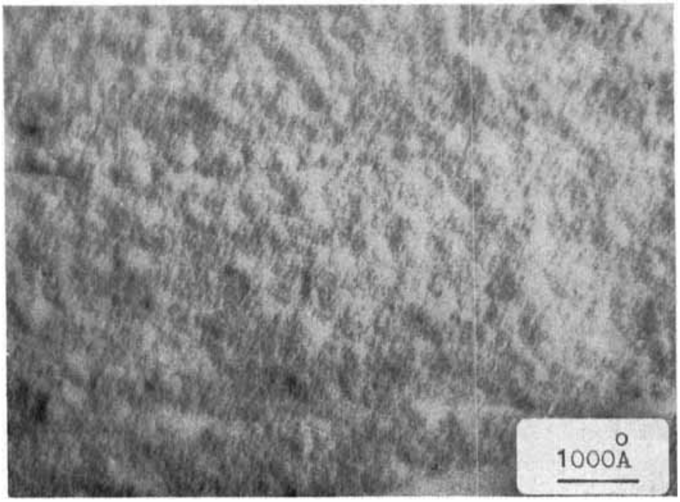

FIGURE 6 Pt-C replica of polished surface of compression molded polycarbonate film.

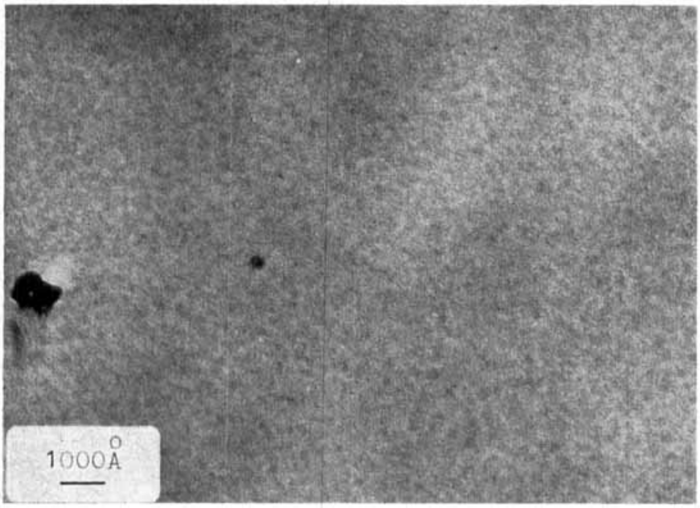

FIGURE 7 Pt-C replica of molded polycarbonate annealed 7 days at 120°C.

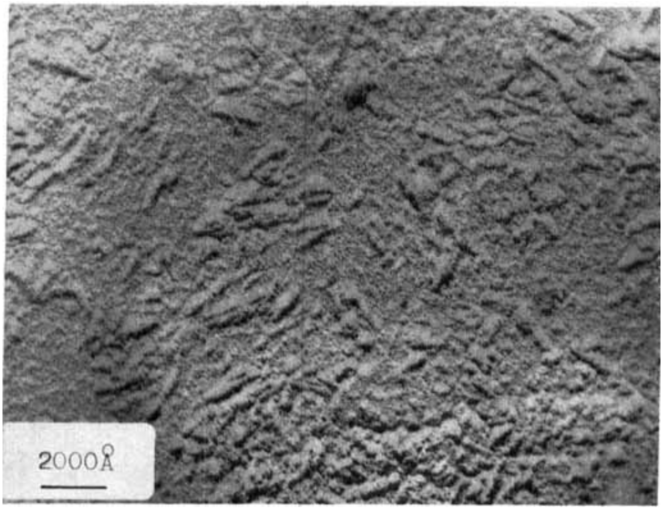

FIGURE 8 Pt-C replica of molded polycarbonate annealed 7 days at 110°C in dry nitrogen.

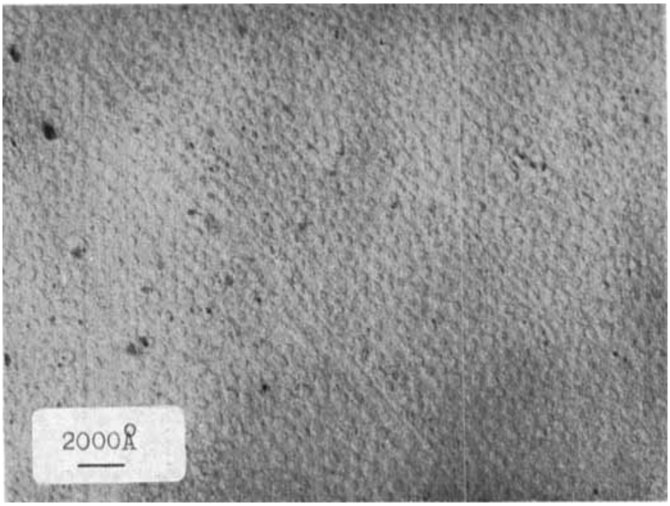

FIGURE 9 Pt-C replica of polycarbonate cast film after etching with sodium hydroxide.

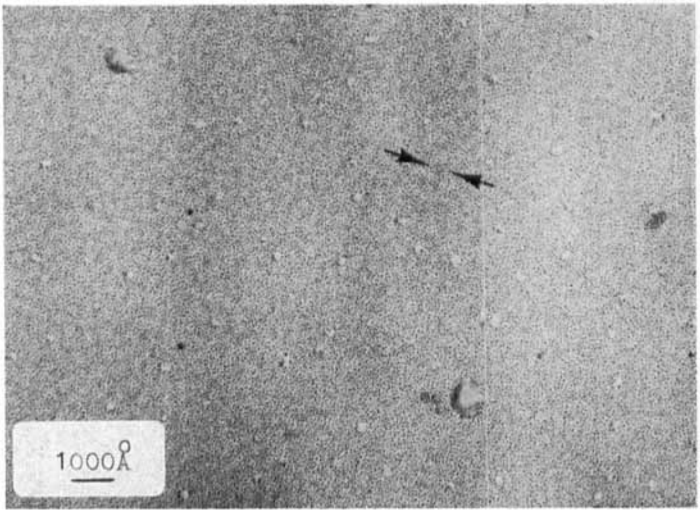

FIGURE 10 Au-C replica of polycarbonate cast film showing a surface texture with regions 300 Å in diameter.

by Au decoration. This is shown in Figure 10. Etching a cast film after annealing 7 days at 100°C revealed a structure as shown in Figure 11. In this case the plateau-like features are 900 Å in size and appear to be surrounded by 200 Å nodular units. Similar results were obtained at 120°C. Also, a similar structure is observed using a molded film annealed 7 days at 100°C as seen in Figure 12. These results are similar to those of Neki and Geil[9] and Frank *et al.*[8] in showing that annealing increases the size of the nodular structure in polycarbonate. However, Kramer[10] has recently reported that a 165 Å structure measured by analysis of small angle x-ray scattering from amorphous polycarbonate did not significantly change in size after annealing. In view of this report it is possible the larger structures observed by electron microscopy reflect *aggregation* of smaller structures rather than their growth.

Annealing at 140°C for 6 hours (which produced the largest specific volume decrease) did not result in an increase in the size of the etched structure. This is shown in Figure 13 where the structure is similar to the unannealed structure shown in Figure 9.

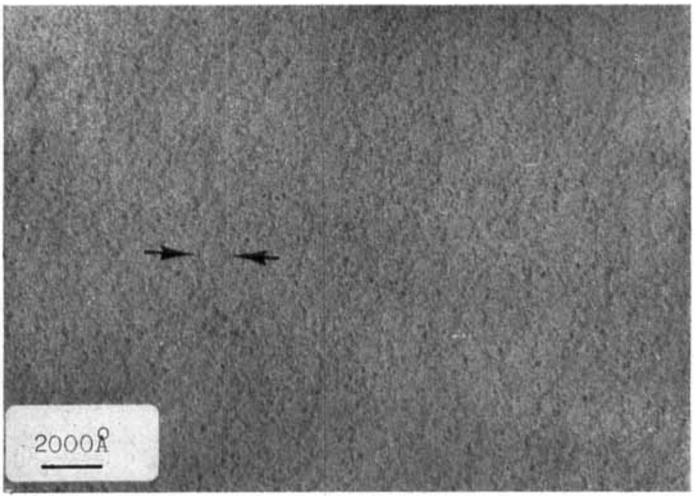

FIGURE 11 Pt-C replica of polycarbonate cast film etched with sodium hydroxide after annealing 7 days at 100°C.

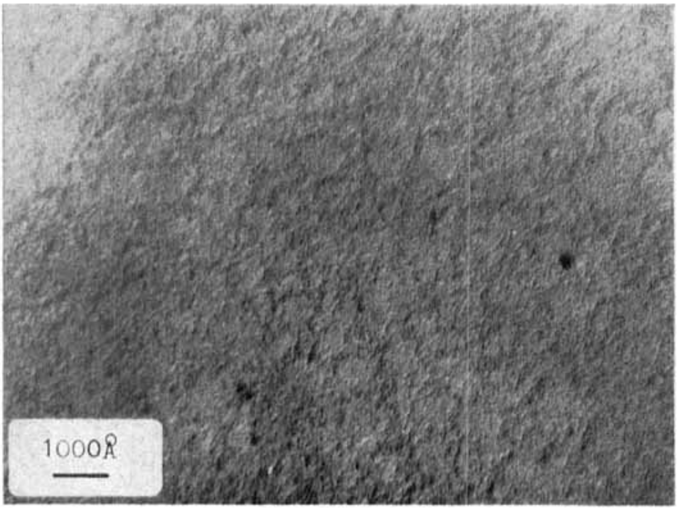

FIGURE 12 Pt-C replica of molded polycarbonate film etched with sodium hydroxide after annealing 7 days at 100°C.

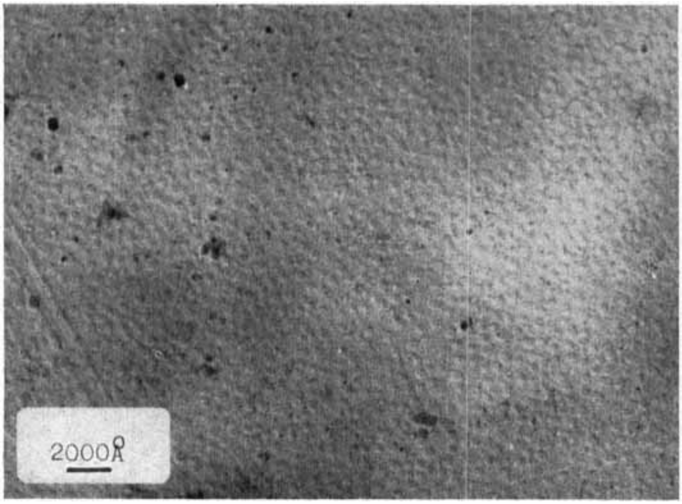

FIGURE 13 Pt-C replica of polycarbonate cast film etched in sodium hydroxide solution after annealing 6 hours at 140°C.

DISCUSSION

Specific volume

Annealing decreased specific volume less than 0.1% similar to results reported by LeGrand[7] and also by Brady and Yeh.[11] However, the largest changes observed here occurred after annealing at 140°C whereas the largest changes in the beta loss peak, namely in shape and intensity, occurred after annealing at 100°C and 120°C. Similarly, annealing at 140°C did not change the appearance of the nodular surface texture. Therefore, a correlation between the specific volume changes and either the changes in the beta transition or the nodular structure is not apparent. Also, assuming the specific volume decreases represent "free volume" decreases, it is difficult to understand how such small changes can be responsible for the tremendous loss of impact strength reported for annealed polycarbonate.[6,7]

Molecular motion

The effect of liquid nitrogen quenching on the beta transition was to slightly increase the intensity of the loss peak and broaden the transition. The effect is consistent with the conclusion of our previous study which asserted that the beta molecular motion occurs in the less ordered regions of the glass structure,[4] which extent may be increased slightly because of the smaller nodular size.

Annealing at 100°C and 120°C was observed to cause a slight decrease in intensity of the loss peak and also a change in the peak shape. After annealing, the beta loss peak appears to be composed of a superposition of three peaks: one below −100°C, the central peak at −65°C, and one above −40°C. The three component peaks may originate from motion of different chemical groups,[12] chain conformations,[13] or structural features such as loose chain folds or tie molecules between the nodules. The fact that the temperature of maximum loss is relatively unchanged suggests that in general the beta molecular motion is not largely restricted in annealed polycarbonate. It is possible that the composite peak structure is related to the development, by annealing of a more ordered glass structure as shown by the growth or aggregation of the nodular structure after annealing at 100°C. Annealing at 140°C for 6 hours did not result in an irregular beta peak shape nor did we notice an increase in size of the nodular structure.

Although annealing produces some changes in the beta transition, it appears the major effect of annealing below T_g on molecular motion in polycarbonate is the suppression of the weak intermediate transition (between 25°C and T_g) reported by previous investigators.[6,8,14,15] Studies in this laboratory have also indicated that this intermediate loss peak is almost completely eliminated by annealing whereas it is largely enhanced by rapid quenching and orientation.[16]

Morphology

The morphology of annealed polycarbonate is clearly distinguishable from that of the unannealed polymer. An increase in size of the nodular structure occurs by annealing whereas quenching results in a decrease in nodular size.

It is interesting to note that annealing for 6 hours at 140°C did not produce a change in morphology and, according to the results of Golden *et al.*,[6] also does not produce a large change in fracture toughness or yield strength. On the other hand, large changes in impact strength occur by annealing polycarbonate at 100°C or 120°C which also produces a significant change in morphology according to our results. This apparent correlation between the size of the morphological structure and impact strength is currently being investigated and will be the subject of a future paper.[16]

Correlations with impact strength

The large decrease in impact strength reported for annealed polycarbonate is difficult to understand in view of the slight changes in either density or the beta transition. This tends to question the previously suggested correlations between impact strength and these parameters. Significant changes are observed in the morphology of amorphous polycarbonate after annealing and the loss of ductility can be understood in terms of these morphological changes.

Studies of drawn polycarbonate thin films by Carr *et al.*,[17] have suggested that a "break-up" (or relative movement) and alignment of nodular structures occur during the ductile response to drawing. In annealed films, which generally have larger morphological structures, there appears to be a restriction to this process. For the latter, a shearing of the nodular structures was observed by Carr *et al.*, with increased tendency for localized failure such as crazing. Similar results were obtained by us in studying polycarbonate thin films.[18] One might expect that any restriction to drawing should be apparent in studies of molecular motion, just as crystallization embrittles polycarbonate and is also observed to restrict the alpha motion.[4] The results of this study and previous studies by others,[8,9] do not indicate a large restriction on the beta motion after annealing; however, the molecular motion associated with the intermediate transition in polycarbonate is largely suppressed by annealing. Thus it appears that the aggregation or growth of larger morphological structures by annealing does not suppress the local beta motion but does suppress the larger chain motion which causes the intermediate transition. This suggests the possibility that high impact strength at 23°C may in some way be associated with transitions or loss processes at higher temperatures and not with the low temperature beta transition. This hypothesis will be further examined in Part III of this series.

Acknowledgments

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