

## Free Volume and the Annealing and Antiplasticizing of Bisphenol A Polycarbonate

RICHARD E. ROBERTSON\* and CATHERINE W. JOYNSON,  
*General Electric Research and Development Center,  
Schenectady, New York 12301*

### Synopsis

Annealing below the glass transition temperature and the addition of an antiplasticizer are each known to increase the yield stress and the density of glassy bisphenol A polycarbonate. We have studied the combined effects of annealing and antiplasticizing to see if the individual effects would interfere with one another, as might be expected if the same free volume were involved in each. We find that the effects, even when they individually approach saturation, remain additive. This suggests that the free volume in the glass has at least two parts, one of which is affected by annealing and the other by antiplasticization. The available data indicate that the rate at which the yield stress changes with measured volume is different for the two parts.

### INTRODUCTION

The addition of an antiplasticizer and the annealing of the glass below the glass transition temperature are both known to increase yield stress by, it is believed, decreasing the free volume.<sup>1-6</sup> We wish to report our results from combining the two effects. Our purpose was to see whether the effects were related or would interfere with one another, which might be expected if antiplasticizing and annealing affected the same free volume.

The increase in yield stress from antiplasticizing has been studied by Jackson and Caldwell.<sup>1-3</sup> They found that the addition to bisphenol A polycarbonate of the biphenyl with an average of 5 chlorines per molecule, Aroclor 1254, can increase the room-temperature tensile modulus 42% from that of the pure polymer, and the addition of the triphenyl with an average of 4.5 chlorines per molecule, Aroclor 5442, can increase the modulus 39%. Because these substances increase the room-temperature modulus, rather than decrease it as occurs with a plasticizer, they are called antiplasticizers. The tensile yield stress, which remains roughly proportional to the modulus, increased correspondingly. Concomitant with the increase in modulus and yield stress is a shrinkage in volume. Jackson and Caldwell<sup>1</sup> report that the volume of the antiplasticized polycarbonate is about 2% to 2.5% less than the sum of the corresponding volumes of the separated polymer and

\* Present address: Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121.

antiplasticizer. We might also mention the similar finding for polystyrene. Litt and Tobolsky<sup>4</sup> report that the addition of 6% benzophenone to polystyrene results in a 5% increase in tensile modulus and a 0.6% decrease in volume from the sum of the corresponding volumes of the separated components, even using the crystalline volume for the benzophenone.

Increases in tensile yield stress due to the annealing of bisphenol A polycarbonate at various temperatures below the glass transition temperature have been reported by Golden, Hammant, and Hazell.<sup>5</sup> Compared to the value for a rapidly cooled specimen, the tensile yield stress was found to increase at least 12% when the specimens were annealed at 129°C before testing and 15% when annealed at 118°C. These annealing temperatures are approximately 21° and 32° below the glass transition temperature, and for both, the ultimate increase in yield stress suggested by the curves of Golden et al. is about 18%. These increases in yield stress from annealing also seem to be accompanied by a decrease in volume. Golden et al. report increases in density of approximately 0.22% and 0.17% after 2 hr of annealing at 120°C and 129°C, respectively, and LeGrand<sup>6</sup> reports increases in density around 0.07% from annealing bisphenol A polycarbonate at 110°, 120°, 122°, and 125°C for 3 hr.

## EXPERIMENTAL

The bisphenol A polycarbonate used had a viscosity-average molecular weight of 30,000 and contained no additives. The two antiplasticizers used were those previously used by Jackson and Caldwell,<sup>1</sup> Aroclor 1254 and Aroclor 5442, both manufactured by Monsanto Co. Aroclor 1254 is a liquid at room temperature, with a pour point of 10°C, and Aroclor 5442 is just barely a brittle glass at room temperature, with a pour point of 46°C. Only the single concentration of 10% by weight of antiplasticizer was studied.

For the unplasticized specimens, an extruded sheet 0.005 in. thick was used. For the antiplasticized specimens, films were cast from methylene chloride solutions containing 16% polymer by weight. The cast films were dried under vacuum at a temperature of 60°C for 24 hr and had a final thickness between 0.0022 and 0.0028 in.

Both the extruded and cast films after drying were annealed at 15°C above their glass transition temperatures for approximately 7 hr and then quenched into ice water. The next step, whether a tensile test, annealing below the glass transition temperature, or a differential scanning calorimeter measurement, was completed within 3 hr of quenching.

For the annealing, the specimens were heated to either 15° or 25°C (approximately) below their glass transition temperatures and held there for exactly 2 hr. Only the single annealing time of 2 hr was studied. From these temperatures the specimens were again quenched into ice water and tested within 8 hr.

The glass transition temperatures were measured with a Perkin-Elmer differential scanning calorimeter at a scanning rate of 40°C/min.

The yield stresses were measured with dumbbell-shaped tensile specimens cut from the films and having a gauge length of approximately 1 in. These were drawn at room temperature and at the three elongation rates 0.01, 0.1, and 1.0 in./min. The specimens drew with the formation of a neck without crazing, though because of the increased yield stresses the specimens sometimes broke before necking or as the neck was developing. The yield stresses reported were obtained by dividing the load at the maximum by the initial cross-sectional area. The modulus was obtained from the maximum slope of the stress-strain curve with the assumption that the specimen was 1 in. long.

## RESULTS

As often happens with tensile measurements, the data were somewhat scattered. We therefore averaged the three or so measurements made at each rate and then averaged these averages by fitting them to equations with the following extension rate dependence:

$$\begin{aligned}\sigma_y &= a + b \log \dot{\epsilon} \\ E &= A + B \log \dot{\epsilon}\end{aligned}$$

where  $\sigma_y$  is the yield stress,  $E$  is the modulus, and  $\dot{\epsilon}$  is the extension rate. We found that within 95% confidence limits the same coefficients  $b$  and  $B$  could be used for all of the data. With  $\dot{\epsilon}$  expressed in in./min,  $b$  was  $0.32 \pm 0.05 \times 10^3$  dynes/cm<sup>2</sup> and  $B$  was  $0.057 \pm 0.023 \times 10^{10}$  dynes/cm<sup>2</sup>.

Table I gives the glass transition temperatures ( $T_g$ ) and the yield stresses and moduli at 25°C and at an extension rate of 0.1 in./min obtained from the least-squares fitting. This extension rate corresponds approximately to the strain rate of 0.1 min<sup>-1</sup>.

The 10% Aroclor 1254 is seen to have reduced the glass transition temperature of the mixture 43°C from that of the pure polymer and raised the room temperature yield stress approximately 32% and the tensile modulus 41%, a value that seems a little too large when compared with the other moduli in the table. The 10% Aroclor 5442 is seen to have reduced the glass transition temperature 29°C and raised the room temperature yield stress approximately 24% and the modulus 27%. The annealing for 2 hr in the vicinity of 17°C below the glass transition temperature has increased the room temperature yield stress by approximately 21%, but the modulus is much less affected. The annealing for 2 hr in the vicinity of 26°C below the glass transition temperature has increased the yield stress by approximately 16%, and again the modulus is less affected.

When antiplasticizing and annealing are combined in the same specimen, the increases in yield stress are essentially the sum of the individual effects, which suggests no interference between the two. The increase in the modulus, however, may be more than just additive, though this is not certain.

TABLE I  
Yield Stress and Tensile Modulus at 0.1 in./min and 25°C

Material	$T_g$ , °C	Tensile yield stress, $10^8$ dynes/cm <sup>2</sup>	Per Cent increase in yield stress, arising from		Tensile modulus, $10^{10}$ dynes/cm <sup>2</sup>
			Anti- plasti- cizing	Aging	
Bisphenol A polycarbonate quenched	150	5.49 ± 0.20	0	0	1.27 ± 0.11
aged at 17°C below $T_g$		6.65	0	21 ± 5	1.22
aged at 26°C below $T_g$		6.39	0	16 ± 5	1.29
Bisphenol A polycarbonate with 10% Aroclor 1254 quenched	106.7	7.22 ± 0.20	32 ± 5	0	1.79 ± 0.11
aged at 16°C below $T_g$		8.36	32 ± 5	16 ± 4	1.73
aged at 31°C below $T_g$		8.34	32 ± 5	16 ± 4	1.92
Bisphenol A polycarbonate with 10% Aroclor 5442 quenched	120.9	6.79 ± 0.20	24 ± 5	0	1.61 ± 0.11
aged at 17°C below $T_g$		8.26	24 ± 5	22 ± 4	1.77
aged at 25°C below $T_g$		7.97	24 ± 5	17 ± 4	1.76

## DISCUSSION

The effects of antiplasticizing and annealing have remained additive even as the individual effects have approached saturation. According to Jackson and Caldwell,<sup>1</sup> Aroclor 1254 and 5442 are capable of increasing the tensile modulus 42% and 39%, respectively. At a concentration of 10%, we found the tensile moduli to be increased by these substances 41% and 27%, respectively, or 70% or more of the maximum effect. We found that 2 hr of annealing at approximately 17° and 26°C below the glass transition temperature resulted in 21% and 16% increases in yield stress, respectively. Our extrapolation of the data Golden et al.<sup>5</sup> suggests that the maximum increase in yield stress obtainable from annealing is 18%, which is about what we found, but their data suggest a slower approach to this maximum. At 129°C (21° below  $T_g$ ), their data suggest the 18% increase in yield stress is obtained only after 50 hr, with approximately one half of the increase being obtained after the first 2 hr; and, on annealing at 118°C (30° below  $T_g$ ), their data suggest the 18% increase is obtained only after 100 hr, with approximately 40% of the increase being obtained after 2 hr. On the other hand, LeGrand's data,<sup>6</sup> for the effect of annealing on density, shows that when annealed at 125°C (25° below  $T_g$ ), most of the change in density occurred within the first 2 hr. From Table I we see that the total increase in yield stress from both the 10% concentration of antiplasticizer and the 2 hr of annealing is in the range of 45% to 52%,

depending on the particular antiplasticizer and annealing temperature used.

That the additivity continues even as the individual effects approach saturation indicates that annealing and antiplasticizing do not affect the same free volume. Hence, there must be at least two parts to the free volume of glassy bisphenol A polycarbonate and perhaps of most other polymers as well.

The several parcels of free volume and the fact that annealing and antiplasticizing affect only certain of these parcels is suggested also by the different changes annealing and antiplasticizing induce in the mechanical loss spectrum. Robeson and Faucher<sup>7,8</sup> have shown that antiplasticizers affect low-temperature loss peaks, in particular, the loss peak at  $-120^{\circ}\text{C}$  in bisphenol A polycarbonate. With a concentration of 30% Aroclor 5460, which is a somewhat more highly chlorinated triphenyl than we used, they found<sup>7</sup> the  $-120^{\circ}\text{C}$  loss peak in polycarbonate to be almost completely suppressed. This also explains why the room temperature modulus is increased by antiplasticizers. The loss peak is accompanied by a reduction in the modulus, so the modulus is lower above the temperature of the loss peak than below it. With the suppression of the loss peak, the concomitant reduction in the modulus is suppressed as well. On the other hand, annealing below the glass transition seems to affect the shoulder just below the glass transition.<sup>5,9</sup> Because the loss peak and the concomitant change in modulus occur above room temperature, they have little effect on the room-temperature modulus, though the drop in modulus at the glass transition is sharpened. It also might be correct to think of the annealing as allowing the glass to assume a lower energy structure, a structure possibly approaching the equilibrium structure for the annealing temperature, and thus further removed from the liquid state.

Still, the present work was needed to confirm that the parts of the free volume affected by antiplasticizing and annealing are completely different. Because antiplasticizers lower the glass transition, and so shift the glass transition to lower temperatures, the shoulder that is suppressed by annealing is obscured by antiplasticizing. On the other hand, the loss spectra for the annealed polycarbonate specimens reported by Golden et al.<sup>5</sup> and Frank and Stuart<sup>9</sup> did not include the temperature region of the  $-120^{\circ}\text{C}$  loss peak to show that it was unaffected. Thus, it was not clear from these published loss data that antiplasticizing and annealing suppress exclusively a low-temperature peak and the shoulder of the glass transition peak, respectively.

As an indicator of free volume, we have assumed a one-to-one (inverse) correspondence with the yield stress, an assumption consistent, for example, with the earliest use of free volume by Lucretius as the "void" required for flow.<sup>10</sup> The measure of free volume most commonly used, however, is the difference between the glassy or liquid and crystal volumes, the "unoccupied" volume. These two measures of free volume seem not to be equivalent, however, because the rates at which the yield stress change

with change in total volume appear to differ for annealing and antiplasticizing. For the antiplasticized polycarbonate,<sup>1</sup> the modulus and presumably the yield stress were increased 42% at the rate of 21% or less per 1% decrease in total volume. For the antiplasticized polystyrene studied by Litt and Tobolsky,<sup>4</sup> the modulus and perhaps the yield stress were increased 5% at a rate of 8% per 1% decrease in volume. On the other hand, for the annealed polycarbonate studied here, the yield stress increased 21%, which, using even the largest change in density mentioned above, 0.22%, gives a rate of 100% per 1% decrease in total volume. Since the free-volume concept was invented to describe flow, the yield stress would seem to be a more direct indicator of it than unoccupied volume. To the extent that this is true, the above suggests that changes in free volume probably cannot be equated to changes in unoccupied volume.

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