Humid Aging of Plastics: Effect of Molecular Weight on Mechanical Properties and Fracture Morphology of Polycarbonate*

ROBERT J. GARDNER and JOHN R. MARTIN, *The Foxboro Company, Foxboro, Massachusetts 02035*

Synopsis

Polycarbonate tensile bars were aged up to 18 months at 0%, 75%, and 100% relative humidity and temperatures of 65–93°C. In the humid aged samples hydrolysis caused progressive reductions in molecular weight. Below a critical molecular weight ($\overline{M}_w = 33,800$, $\overline{M}_n = 14,300$) tensile strength dropped off rapidly. A transition from ductile to brittle failure was also observed at that point. Extrapolations indicate that the ductile–brittle transition at 38°C will be reached after 5 years at 100% relative humidity for the polycarbonate studied. Elongation was affected even in the early stages of hydrolysis. This suggests that whenever the degradation mechanism is a molecular weight reduction, toughness will be affected before the strength properties are lost. Mechanical properties are affected by annealing and antiplasticization which reduce localized stresses and increase short-range order. The brittle fracture surfaces of polycarbonate consist of four distinct regions. The size of the regions and the prominence of the features changed as the molecular weight decreased.

INTRODUCTION

The mechanical properties of some polymers are degraded after long-term exposure to warm, humid environments.[1] In polycarbonates, this degradation is primarily due to molecular weight reductions which are caused by hydrolysis at the carbonate linkages. However, changes in internal stresses and morphology also occur.

Design of engineering components often requires that long-term performance be predicted on the basis of accelerated short-term tests. Such tests are quite satisfactory as long as the accelerating variable does not introduce irrelevant failure modes. To quantify the factors that affect the mechanical performance of polycarbonate in humid environments, we have evaluated the significance of molecular weight changes as a function of time, temperature, and relative humidity. The fracture surfaces of the tensile specimens used in these tests showed a marked variation in morphology. Decreasing molecular weight resulted in a change from ductile to brittle failure. Normally, brittle fractures in polycarbonate are observed only at high strain rates or low temperatures. In the results reported here, brittle fractures were observed under standard tensile test conditions (ASTM D638) because humid aging caused a reduction in molecular weight.

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EXPERIMENTAL

As described in reference 1, injection-molded tensile bars of Lexan 141 were aged at 65, 82, and 93°C (150, 180, and 200°F) for up to 18 months at both 0% and 100% relative humidity (R.H.). Tests at 75% R.H. were conducted at 82 and 93°C (180 and 200°F) by suspending the samples over a saturated sodium chloride solution in sealed Pyrex jars.

All tensile tests were run according to ASTM D638 using the standard test speed of 0.5 cm/min (0.2 in./min). The molecular weight determinations were made in THF using a Waters Associates Model 244 high-speed gel permeation chromatograph. Numerical values cited are "apparent" molecular weights, based on polystyrene standards.

The fracture surfaces were examined with an ETEC Autoscan Model U-1 scanning electron microscope. Fracture surfaces were sputtered with gold to avoid charging.

RESULTS

Figure 1 is a plot of molecular weight versus time at various aging conditions. The samples aged in humidity showed a rapid initial drop in weight-average
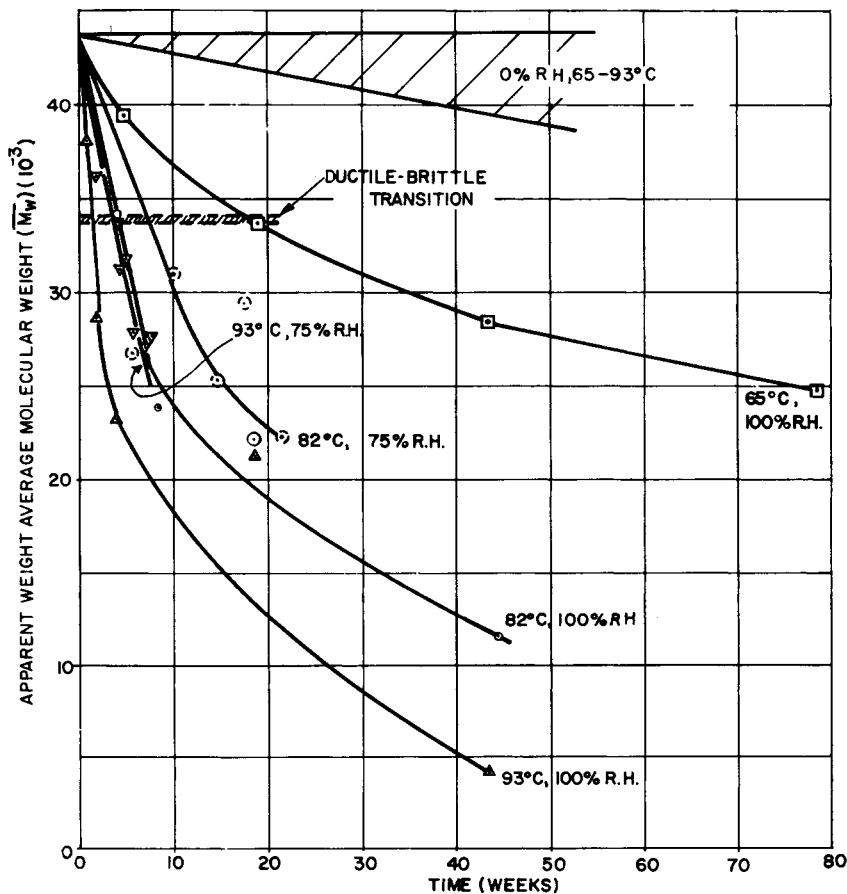

Fig. 1. Change in $\overline{M}_w$ as function of time at 0%, 75%, and 100% R.H.

molecular weight ($\overline{M}_w$). These reductions clearly affect mechanical properties as illustrated in Figures 3 and 4. Number-average molecular weight ($\overline{M}_n$) plots give similar results since the ratio of weight average to number-average molecular weight remained close to the initial value of 2.25.

DISCUSSION

Hydrolytic Degradation

Chemical reaction rates depend on the temperature and the concentration of reactants. Initially, the concentration of carbonate linkages is essentially the same in all samples. It changes only slightly during the course of the hydrolytic degradation reaction being considered here. Therefore, the hydrolysis rate will only be a function of temperature and concentration of water in the polycarbonate. Water concentration at 65°C and 100% R.H. was 0.416%. This level increased to 0.470% at 93°C. At 75% R.H., the corresponding values were 0.337% and 0.365%, respectively. Hence, the increased degradation rate at 93°C is the result of both higher temperature and increased water concentration. The effect of water concentration alone is illustrated by the curves for 75% and 100% R.H. at 82 and 93°C in Figure 1. At constant temperature, the degradation rate over most of the range is cut in half when the relative humidity is reduced from 100% to 75%.

In theory, the hydrolysis reaction is complicated by a gradual increase in water concentration. Hydrolysis of polycarbonate results in the formation of hydrophilic OH endgroups which should increase water content as hydrolytic degradation progresses. There have also been studies which report that amorphous polymers absorb water up to an "equilibrium" concentration and then, after a time lag, absorb additional water.[2] This behavior is attributed to clustering effects. Neither of these complications appears to have affected this study because water absorption remained at constant levels until after the ductile–brittle transition was reached. Even if clustering occurred, it is unlikely that water molecules held in separate cluster regions would be as active in hydrolytic degradation as water molecules dispersed through the polymer structure.

One can postulate a test to see whether high-temperature tests at 100% R.H. truly represent long-term degradation at lower temperatures. If valid, the molecular weight distribution (MWD) in samples degraded in humidity at low temperatures should match that of samples degraded in the accelerated tests at higher temperatures. The excellent match between the MWD of specimens aged for 18 months at 65°C and two weeks at 93°C (Fig. 2) suggests that the degradation mechanism is unchanged over this temperature range.

Tensile Strength

The change in tensile strength with apparent molecular weight (Fig. 3) is similar to what has been observed previously in other amorphous polymers[3] and specifically in polycarbonate.[4] Above a minimum molecular weight ($\overline{M}_{min}$), the tensile strength is insensitive to further increases. Below this molecular weight, the tensile strength drops off rapidly with decreasing molecular weight. For $\overline{M}_w$, the minimum molecular weight is 33,800; and for $\overline{M}_n$, it is 14,300. Our data show
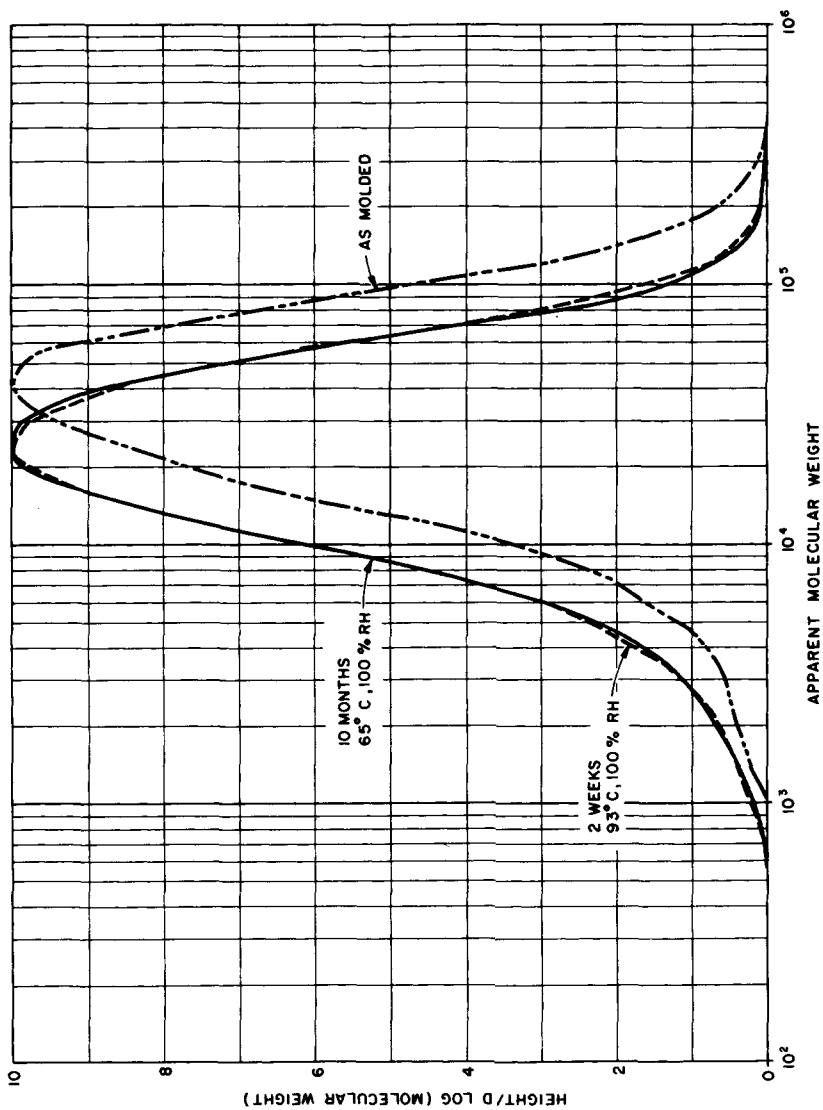
Fig. 2. Comparative molecular weight distributions of samples aged for 18 months at 65°C (150°F) and two weeks at 93°C (200°F).
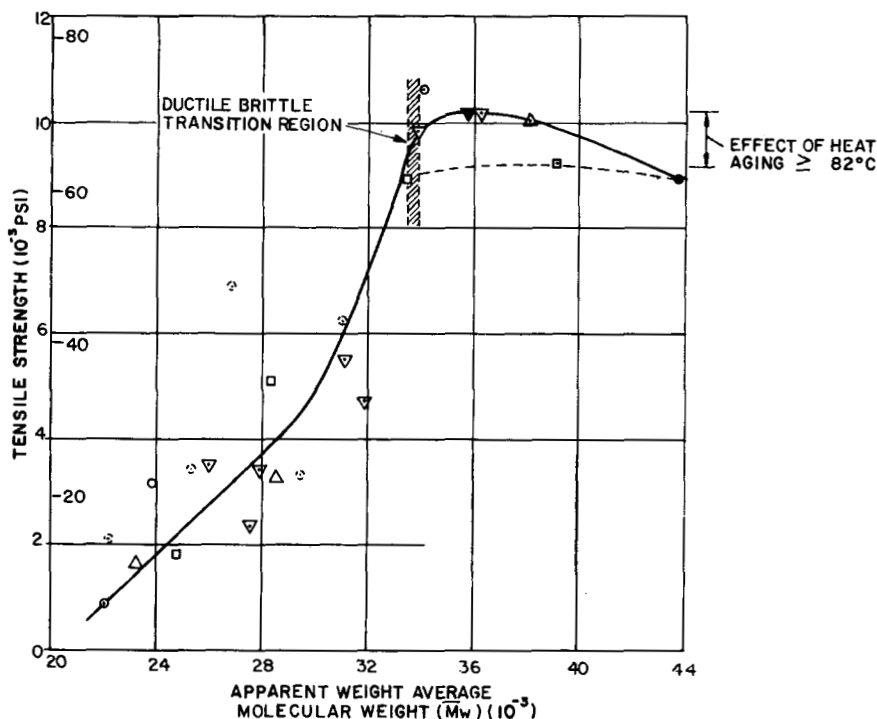
Fig. 3. Tensile strength vs. $\overline{M}_w$ at 75% and 100% R.H: (△) 93°C, 100% R.H.; (○) 82°C, 100% R.H.; (□) 65°C, 100% R.H.; (▽) 93°C, 75% R.H.; (◌) 82°C 75 R.H.

an increase in tensile strength with decreasing molecular weight above $\overline{M}_{min}$. This is caused by annealing effects, which reduce localized stresses and increase short-range order.

Annealing and Antiplasticization

The increase in local order caused by annealing is small, but real, as indicated by the tensile modulus data. At 0% R.H., the initial modulus of 2400 MPa (348,000 psi) was increased by 4% to 5% during the heat aging. The change occurred within a month at 82°C (180°F) and 93°C (200°F), and in the 1 to 4 month time period, at 65°C (150°F). When aged in humidity at 65°C (150°F), the modulus increased by 9% in less than 1 month. If the 9% change were solely related to hydrolysis, one would expect still further increases as hydrolysis continued in the 18-month test. These increases were not observed, so the additional moisture effect is apparently attributable to antiplasticization. This phenomenon occurs when a small amount of a plasticizer (water) enhances the rate at which molecular reordering occurs.

Elongation

Elongation decreases dramatically as molecular weight is reduced (Fig. 4). There is no indication in the data that elongation levels off at high molecular weights. However, the material used in this study was a standard injection molding grade of moderate molecular weight. Higher molecular weight com-
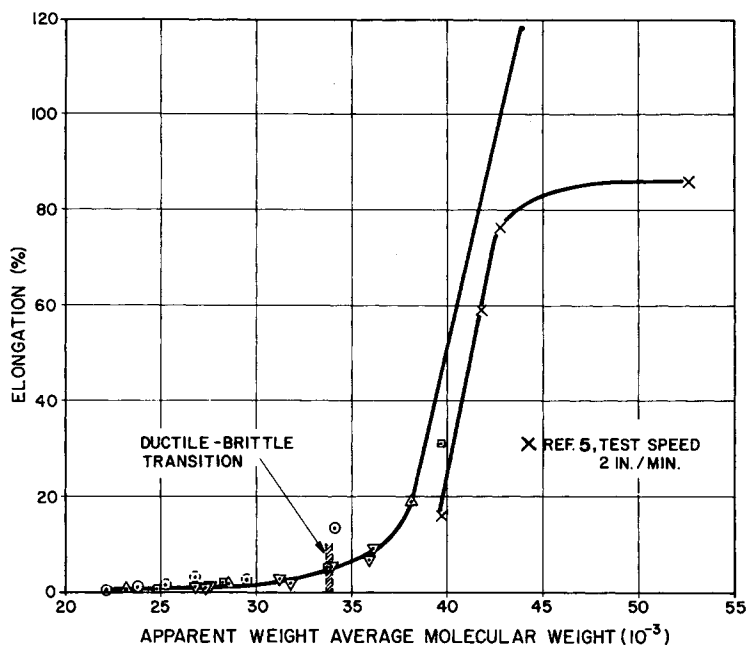
Fig. 4. Elongation vs $\overline{M}_w$ at 75% and 100% R.H. See Fig. 3 for symbol key.

mercial grades of polycarbonate exhibit only slightly higher elongation, so the starting material used in this study is probably at or near the molecular weight insensitive region. This belief is reinforced by crossplotting data presented in reference 5 as shown in Figure 4. The differences in elongation values between these two studies can be attributed to differences in the strain rates and injection molding conditions. Strain rate in reference 5 was an order of magnitude higher than that used in the present study. From a comparison of Figures 3 and 4, it is obvious that much higher molecular weights are required in order to reach the plateau region when one uses elongation as the criteria rather than tensile strength. A few of the studies cited in reference 3 made similar observations. This conclusion implies that whenever the degradation mechanism is a molecular weight reduction, toughness will be lost before strength properties are affected.

Ductile–Brittle Transition

The location of the ductile–brittle transition of polycarbonate in relation to the factors affecting toughness is of particular interest. Observations from this study indicate that polycarbonate ductile failures occur through a shear yielding mechanism. Brittle failures result from craze formation which leads to crack nucleation and propagation. Crazing and shear yielding are distinct processes. The stress needed to produce them changes with temperature, strain rate, and stress state.[6,7] The crazing stress is also a function of molecular weight.[8] The transition from ductile to brittle failure occurs when the craze initiation stress falls below the shear yield stress.[9] Thus, the combination of decreasing molecular weight (decreasing craze stress) and annealing effects (increasing yield stress) causes the transition from ductile to brittle failure for the polycarbonate samples examined here.

The transition from ductile to brittle failure occurred at $\overline{M}_w$ = 33,800 and $\overline{M}_n$ = 14,300. These represent significant molecular weight reductions ($\sim$ 25%). However, at low temperature or at strain rates characteristic of impact conditions, the transition would presumably shift to a higher molecular weight. Long and Sokol[5] ran their tests at a strain rate ten times greater than that used in this study. Although they did not extend their tests to the ductile–brittle transition, their data, when combined with the present work, suggested that the ductile–brittle transition occurs at higher molecular weights when strain rate is increased. It is noteworthy that the ductile–brittle transition in the present study occurs at the minimum molecular weights as defined in the tensile strength tests.

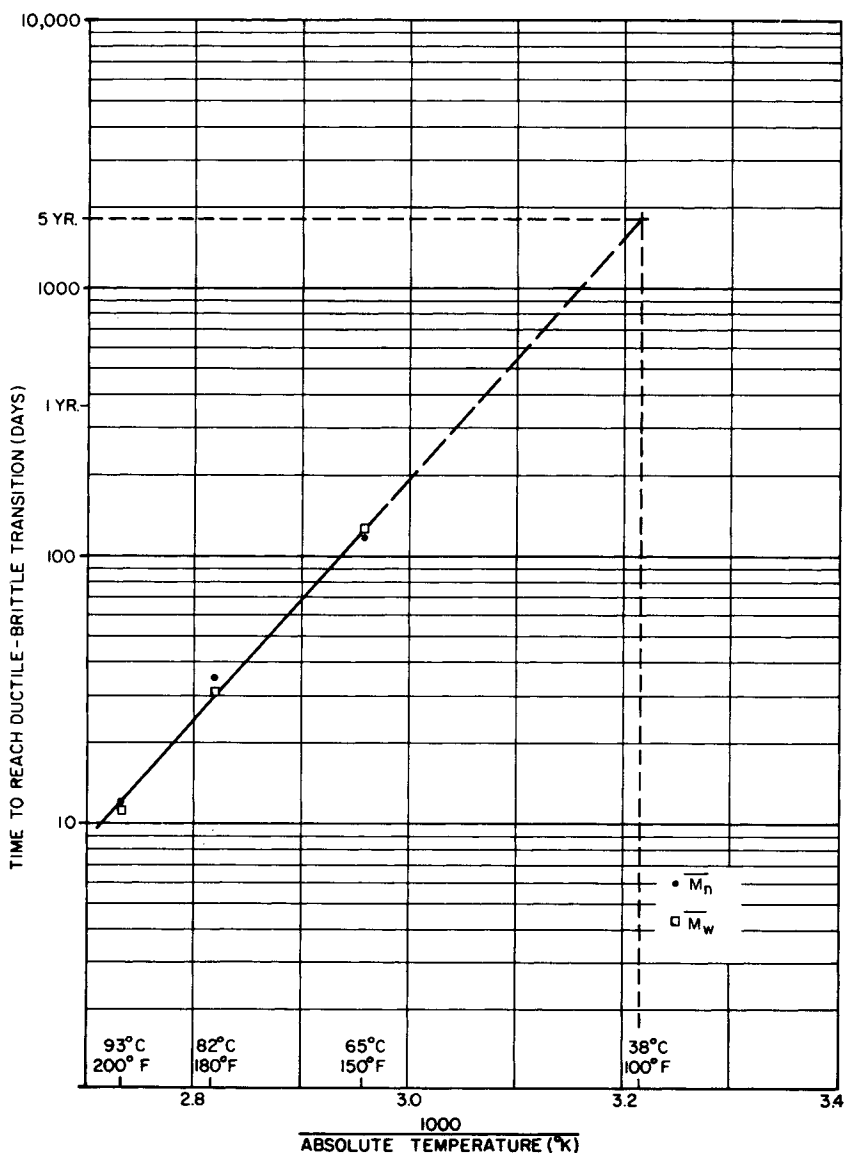Figure 5 is an Arrhenius plot of the time it takes for polycarbonate to reach

Fig. 5. Ductile lifetime of polycarbonate at 100% R.H.

the ductile–brittle transition at 100% R.H.:   at 93°C (200°F) it takes 12 days; the projected time at 38°C (100°F) is 5 years.   This illustrates the severe effect that humidity can have on polycarbonate when it is combined with moderate temperatures.

Fracture Surface Analysis

Ductile failure is a high-energy process with failure occurring by massive tearing.   This results in the fracture surfaces being distorted and irregular. Striations run along the surface following the direction of failure.   Figure 6 illustrates the lamellar structure which is evident in some of the ductile fracture surfaces.   This lamellar feature was accentuated by extended annealing.   There is also a suppression of local ductility with extended annealing, as shown in Figure 7.   These features may be caused by an increase in the short-range molecular order.   In general, the ductile fracture surfaces were remarkably similar.


Fig. 6. Lamellar structure evident on many of the ductile fracture surfaces.

Fig. 7. Suppression of local ductility on ductile fracture surface after extended annealing.

Brittle fracture specimens exhibited four distinct regions. Region I is mirror smooth and associated with craze formation and crack nucleation. The crack propagates through the center of the craze in this area at a low speed, producing a smooth featureless surface. At higher magnifications it can be seen that the surface is made up of a fine nodular structure which may be the ends of retracted craze fibrils. The size, shape, and location of this region varied with each sample, but there was a definite trend of increasing size with decreasing molecular weight. This indicates that crack propagation is more stable at lower molecular weights. Unlike ductile failure, which often initiates at the surface of the tensile bar, the brittle failures always start in the interior of the tensile bar. This could be due to the presence of compressive stresses in the surface which inhibit craze growth.[10]

Region II is the most complex area on the fracture surface. This region undergoes a substantial change in appearance with decreasing molecular weight.
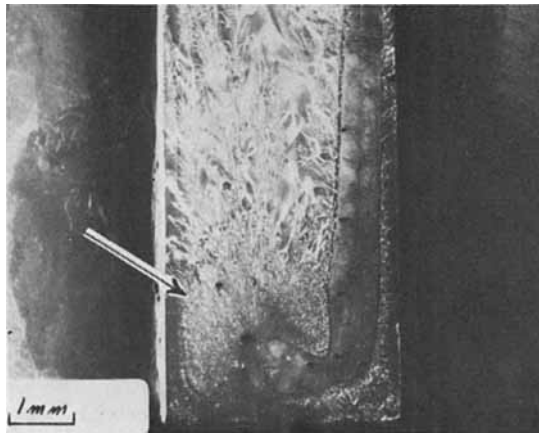
(a)

(b)

Fig. 8. (a) Region II, overall view, located in bottom portion of sample. (b) Region II, detail of banded feature.

When brittle fracture first appears ($\overline{M}_w$ = 34,000), the region is characterized by a rough grainy appearance with a banded structure superimposed perpendicular to the direction of crack propagation (see Fig. 8). Region II tends to spread out radially from region I. As molecular weight decreases, the grain becomes finer and the frequency of the banded structure increases. Further decreases ($\overline{M}_w \sim$ 25,000) result in a separation of the grain and banded features into separate domains (Fig. 9). At molecular weights down around $\overline{M}_w$ 22,000, the grain has taken on a more fibrous appearance, and the banded feature is no longer present. The grainy feature is similar to that reported by Hull and Owen[6] for the fracture surfaces of polycarbonate impact samples and resembles what Murray and Hull[11] called patch from their work with polystyrene. The two types of banded structures that occurred on the polycarbonate fracture surfaces are similar to the mackerel patterns in polstyrene reported by Murray and Hull.[12] One of the patterns was also observed in poly(methyl methacrylate).[13]

Region III forms a border along the edge of the fracture surface (Fig. 10). Initially, it is well defined in the vicinity of regions I and II, but it becomes obscure around region IV. As molecular weight decreases, its appearance around region IV becomes sharper. Unlike other areas, the size of region III is independent of molecular weight. Compressive stresses in the skin of the tensile bars, which result from the rapid cooling of the melt in the mold, probably play a key role in the formation of this border. These compressive stresses inhibit the growth of crazes which prevent crack nucleation in this region.

Region IV has no distinguishing characteristics. It is very rough and irregular, and there are usually banded structures present on many of the jagged surfaces. The banded features are always perpendicular to the direction of crack propagation. In this region, many of the banded areas do not follow the general direction of failure. This implies that crack growth becomes unstable, and random crack deviation occurs. Initially, region IV occupies about two thirds of the fracture surface. The size of this region decreases with decreasing molecular weight. For example, at a $\overline{M}_w$ of 22,000, there is slight evidence of the presence of region IV. This leads to the conclusion that as molecular weight decreases, crack propagation becomes more stable.
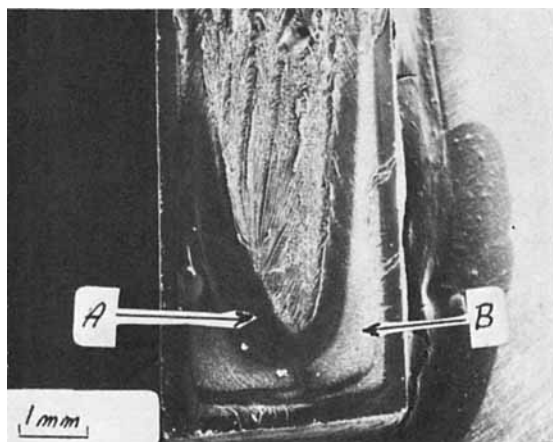

Fig. 9. Segregation of grain and banded features in region II: (A) banded area; (B) grain area.
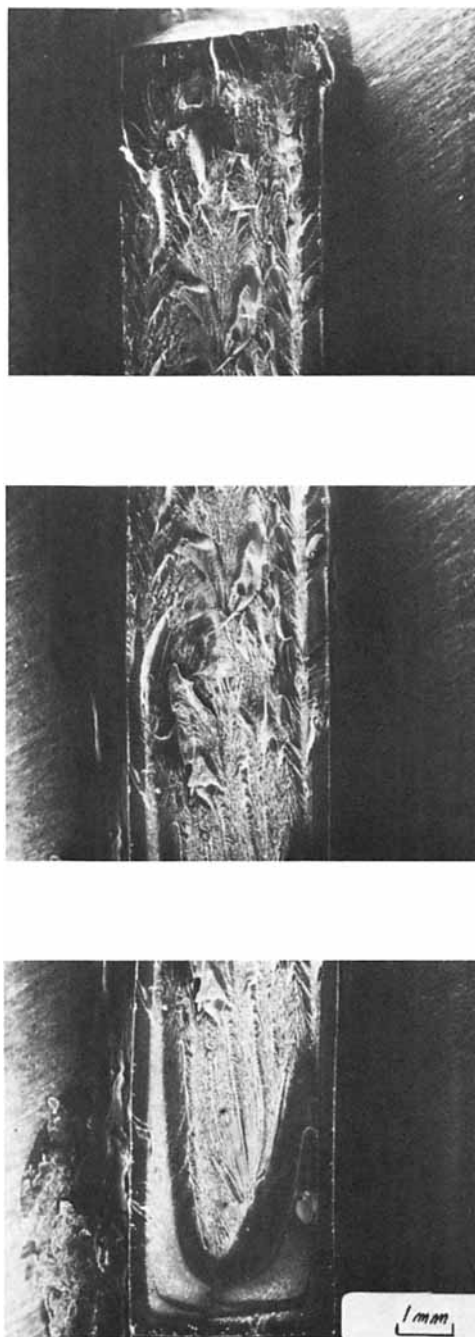
Fig. 10. Region III is the area which forms a border along the outer edge of the surface.

CONCLUSIONS

Brittle fracture occurred in low-speed tensile tests of an injection-molding grade of polycarbonate after the specimens have been exposed to 100% relative humidity for more than 12 days at 93°C (200°F). Extrapolations based on these 18-month tests indicate that the ductile–brittle transition at 38°C (100°F) will

be reached after 5 years at 100% R.H.   Reducing the relative humidity from 100% to 75% cuts the hydrolysis rate in half at 82°C (180°F) and 93°C (200°F).

Under standard tensile test conditions, the ductile–brittle transition is observed at $\overline{M}_w$ = 33,800 and $\overline{M}_n$ = 14,300.   Tensile strength is also reduced when the molecular weight drops below this level.   The transition is related to the ease of crazing relative to shear yielding.   As molecular weight decreases, the stress required for craze initiation decreases.   When this stress falls below the level needed to initiate shear yielding, brittle failure results.

Elongation increases with molecular weight over the entire range examined in this study.   Much higher molecular weights are required to reach the plateau region when one uses elongation as the criteria rather than tensile strength.   This implies that whenever the degradation mechanism is a molecular weight reduction, toughness will be lost before strength properties are affected.

The size and texture of the various brittle fracture features are strongly affected by molecular weight.

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