

# Water Absorption and Its Effect on Polyarylate

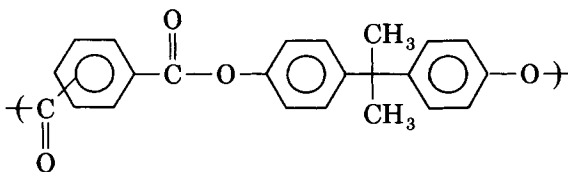
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## Synopsis

Water absorption and its effect on the tensile and impact properties of polyarylate was studied by immersing polyarylate specimens in water baths, between 23 and 98°C. The diffusivity was calculated to be  $11 \times 10^{-9}$  cm<sup>2</sup>/s at 23°C with an activation energy of 9.8 kcal/mole. The aromatic ester in polyarylate is hydrolyzed by water, which was found to cause a decrease in molecular weight and in mechanical properties. In the early stage, the reaction is zero-order and the activation energy of the hydrolytic embrittlement is 22 kcal/mole.

## INTRODUCTION

Polyarylates are amorphous polymers with excellent thermal and flammability properties and inherent ultraviolet (UV) stability.<sup>1</sup> They are aromatic polyesters derived from diphenols and aromatic dicarboxylic acids. Commercial polyarylates, such as AMOCO's Ardel D-100, are usually the reaction product of bisphenol-A with a mixture of isophthalic and terephthalic acids with repeat unit:



Like polyesters and polycarbonate, polyarylate is expected to be sensitive to water, which can attack the aromatic ester groups. The chemistry and kinetics of the hydrolysis of polyesters and polycarbonate are well documented and it is likely that those of polyarylate would be similar. Bier,<sup>2</sup> and Freitag and Reinking<sup>3</sup> commented briefly on it, but did not present supporting evidence. Specific data of polyarylate hydrolysis have not been reported in the literature.

In this paper water absorption and the effects of hydrolysis on some of the physical and mechanical properties of polyarylate are presented.

## EXPERIMENTAL

Injection-molded specimens of polyarylate (Ardel D-100) were received from AMOCO. The specimens included ASTM tensile and Izod bars, as well as discs, 7.5 cm (3 in.) in diameter. The specimens' thickness was 0.32 cm (0.125"). Before the beginning of the study, the specimens were conditioned for 12 h in

an air-circulating oven at 115°C resulting in bone dry samples as determined by thermogravimetric analysis (TGA). The Izod bars were notched before water immersion. The specimens were immersed in water baths at 23, 55, 70, 85, and 98°C. Periodically, 3–5 specimens were taken out, cooled to room temperature, then tested. The baths were made of stainless steel. Glass baths were reported to influence the hydrolysis of polycarbonate.<sup>4</sup>

Water absorption data were collected using the disc specimens. Edge effects were corrected according to Shen and Springer<sup>5</sup>. Tensile and Izod tests were conducted according to ASTM procedures. The falling dart test was done on a Dynatup instrumented impact testing machine using 1.25 cm (0.5") diameter dart and 6.3 cm (2.5") diameter support fixture. The impact velocity was 3.3 m/s (11 ft/s).

Molecular weight was determined by gel permeation chromatography (Water Associates, model 150-C ALC/GPC). Column arrangement consisted of five  $\mu$ -Styragel columns in series, with permeability limits of 10, 1, 0.1, 0.05, and 0.01  $\mu$ m. Narrow molecular weight distribution polystyrene was used for calibration.

## RESULTS AND DISCUSSION

### Water Absorption

The percent weight gain of the discs vs.  $(\text{time})^{0.5}$  is shown in Figure 1. The absorption follows Fick's law of diffusion, except for the deviation noted at 85 and 98°C beyond about 100 h, which may be due to the formation of microcracks. A similar observation was reported for a polycarbonate blend<sup>6</sup> and for epoxy composites,<sup>7</sup> and was attributed to surface cracks and sub-surface microvoids.<sup>7</sup>

The diffusivity,  $D$ , can be determined from the initial slope of the absorption curves. For small time, an approximate solution to Fick's law in one

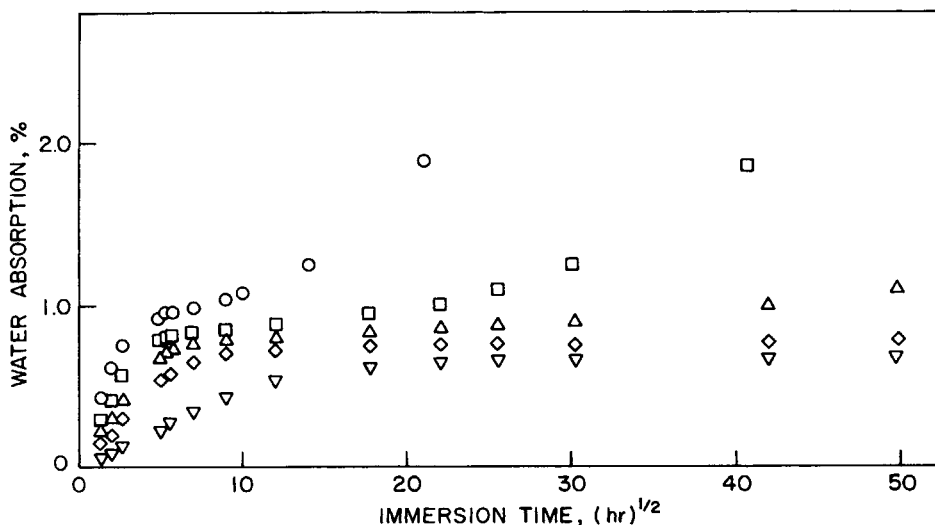


Fig. 1. Water absorption vs.  $(\text{time})^{0.5}$ : (○) 98°C; (□) 85°C; (Δ) 70°C; (◇) 55°C; (▽) 23°C.

TABLE I  
Water Diffusivity in Polyarylate  
(disc specimens, diameter = 7.6 cm, thickness = 0.32 cm)

Temperature		Diffusivity <sup>a</sup> cm <sup>2</sup> /s × 10 <sup>-9</sup>
°C	K	
23	296	11
55	328	56
70	343	103
85	358	209
98	371	320

<sup>a</sup> Corrected for edge effects after Ref. 5.

dimension is:<sup>7</sup>

$$\frac{W_t - W_o}{W_\infty - W_o} = 4 \left( \frac{Dt}{\pi d^2} \right)^{1/2} \quad (1)$$

$W_t$  is the weight gain, due to water absorption, at time  $t$ .  $W_o$  is the initial water content (essentially zero in the dried samples) and  $W_\infty$  is the equilibrium absorption, which was reported to be temperature independent.<sup>7</sup> It is rather difficult to ascertain the exact value of  $W_\infty$  because of the sudden rise in water absorption at the high temperatures on the one hand, and the

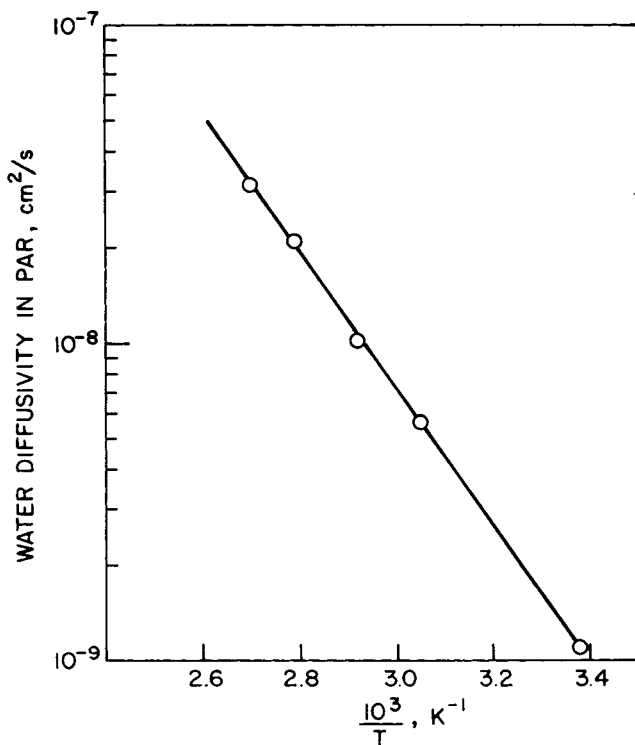


Fig. 2. Arrhenius plot of diffusivity.  $\epsilon_d = 9.8$  kcal/mole.

apparently very long period to reach equilibrium at low temperatures, on the other. In calculating  $D$ , the equilibrium value was estimated to be 1.1%. This estimation is based on the data shown in Figure 1 for 70, 85, and 98°C. From that data it appears that equilibrium absorption of about 1.1% water is approached before the sudden rise in the rate of absorption.

For the diffusion of water through the disc surface, the diffusivity at different temperatures is listed in Table I and plotted in Figure 2. The diffusivity values have been corrected for edge effects.<sup>5</sup> From Figure 2 (Arrhenius plot), the activation energy of water diffusion in PAR was calculated to be 9.8 kcal/mole. Comparable values were reported for epoxy resins<sup>8</sup> and a blend of polycarbonate/polybutylene terephthalate.<sup>6</sup>

### Molecular Weight

The diffusion of water is the first step in the overall hydrolysis of polyarylate. The chemical reaction itself is a heterogeneous reaction which results in a decrease in molecular weight. Gel permeation chromatography (GPC) data of polyarylate that was placed in 85°C water bath are shown in Figure 3. There is a shift in the elution time which indicates a change in the molecular weight. But the change in the breadth of the curves, which shows the molecular weight distribution, is quite small. The weight and number average molecular weight are listed in Table II and plotted in Figure 4. The decrease in molecular weight with time appears to be linear, but the molecular weight distribution remains relatively constant. After 69 days in 85°C water, the decrease in  $M_w$  is about 60%, which corresponds to slightly over one scission per chain. Thus, in terms of the chemistry of hydrolysis, this represents the early stage of the reaction. Assuming no water extraction of low molecular weight hydrolysis products, the virtually constant  $M_w/M_n$  suggests that the hydrolytic attack occurs randomly along the polymer chain, rather than proceeding from chain ends.

The linear decrease of  $M_w$  and  $M_n$  with time means that, initially, the hydrolysis of polyarylate is a zero-order process. A linear decrease in molecular weight was reported also for polycarbonate in the initial period of hydrolysis.<sup>9</sup> Zero-order reactions are usually encountered in heterogeneous reactions

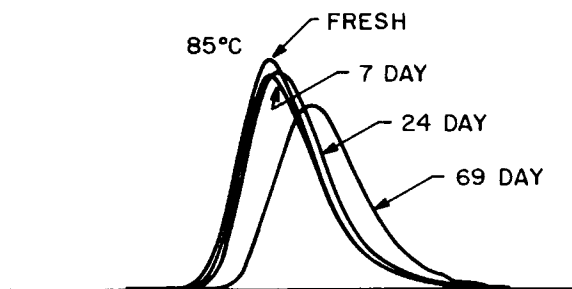


Fig. 3. Superposed GPC curves of polyarylate aged at 85°C water.

TABLE II  
Molecular Weight of Polyarylate Immersed in Water (85°C)

Immersion time (day)	$M_w$	$M_n$	$M_w/M_n$
0	49,670	18,690	2.7
5	45,920	15,080	3.0
7	45,900	16,180	2.8
14	42,450	16,850	2.5
24	39,060	13,760	2.8
35	34,010	12,720	2.7
69	20,030	7,160	2.8

involving several successive steps. The bottleneck in the process, namely, the step that determines the rate, is thought of as an equilibrium-type surface reaction which is relatively slow. In the present process the two major steps are water diffusion and the hydrolysis of the aromatic ester groups. From Figure 1 it is seen that water diffusion, especially in the first few days, is relatively fast and is not likely to be the rate-controlling step. Fast diffusion would occur when the samples are immersed in water or when the relative humidity is high. It is possible that at some lower relative humidity level diffusion would become the rate-limiting step.

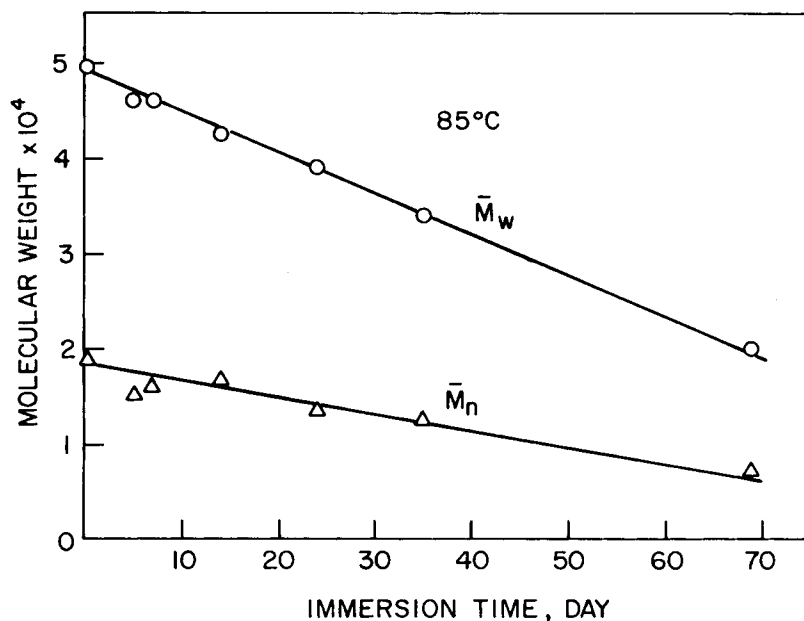


Fig. 4. Change in molecular weight due to hydrolysis at 85°C: (○)  $\bar{M}_w$ ; (Δ)  $\bar{M}_n$ .

### Tensile and Impact Properties

Freshly molded polyarylate has tensile strength of about 70 MPa and elongation to break of 50–60%. The yield strength is around 69 MPa and occurs at about 8.5% strain. When the aged specimens were tested in tension, the most immediate obvious effect of water was seen in the elongation to break. The elongation was observed to decrease with time at a rate which increased with temperature. The dependence of the elongation to break on immersion time at various water temperatures is shown in Figure 5. Note that the time axis is in a logarithmic scale. The solid straight lines at 70°C and above are designed to show the trend, not to suggest any functional dependency. In fact, there may be a dormant period before the effect of hydrolysis becomes noticeable, as suggested by the data at 55°C.

The effect of hydrolysis on the tensile yield strength was not as immediate as its effect on the elongation to break. It was observed that as long as the specimens were capable of yielding in tension, which remained fairly constant at around 8.5% strain, there was no appreciable change in the yield strength. In some cases a mild increase in the yield strength was noted. The tensile yield strength vs. immersion time is plotted in Figure 6. The solid data point at the beginning of the test is for the fresh material. From Figure 6 it is seen that the yield strength remained relatively constant over a period of time. As the hydrolysis proceeded, however, the specimens became brittle at some point. That is, the specimens failed before yielding. The data showing the sudden decline in strength at 70, 85, and 98°C are after the specimens became

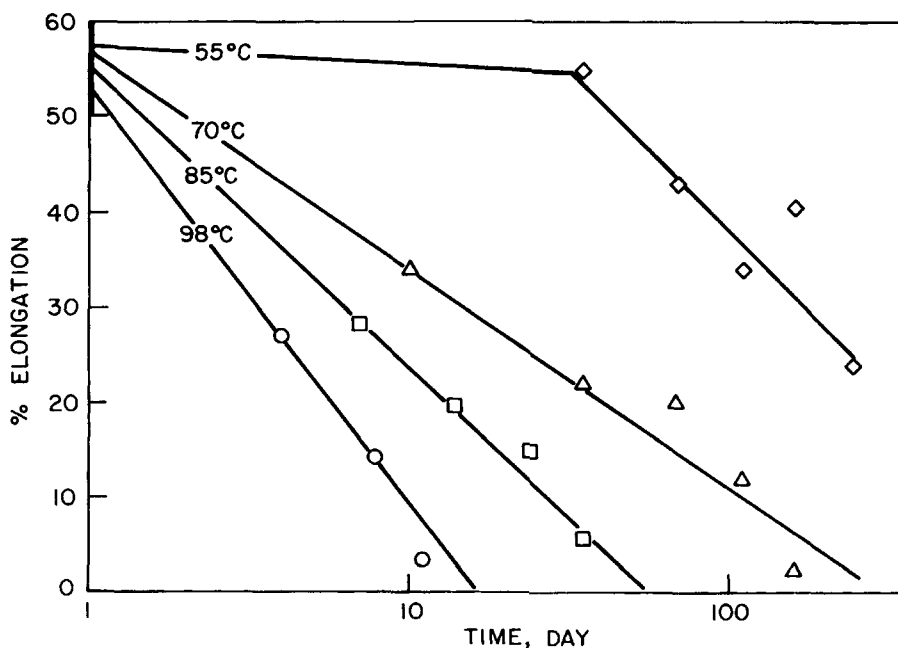


Fig. 5. Plots of elongation to break vs. time: (○) 98°C; (□) 85°C; (Δ) 70°C; (◇) 55°C.

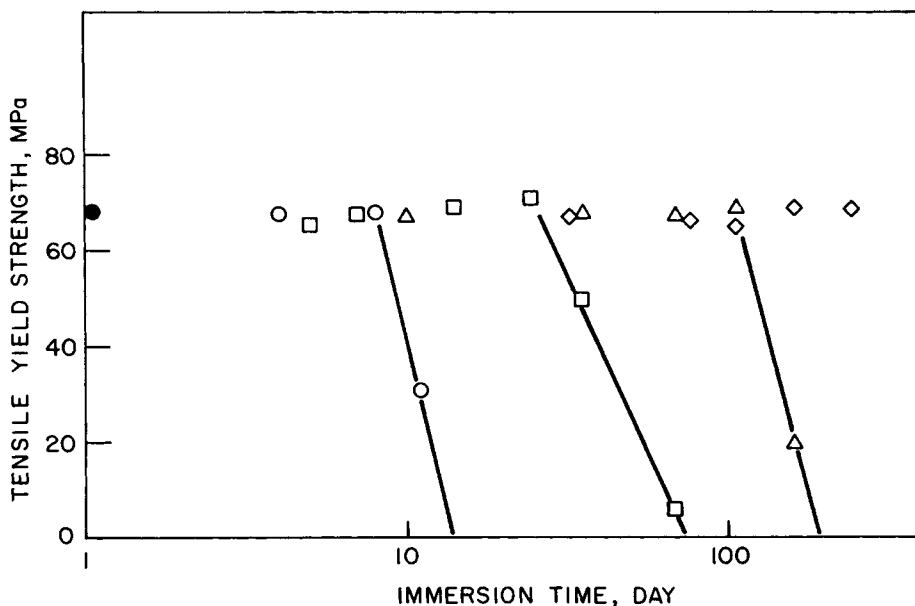


Fig. 6. Plots of tensile yield strength vs. time: (○) 98°C; (□) 85°C; (△) 70°C; (◇) 55°C.

brittle. Thus, these data points correspond to the tensile strength at break, not yield strength.

From Figure 6 it is seen that the transition from ductile to brittle failure depends on temperature and appears to take place over a relatively short time span. At 85°C, for example, the specimens exhibited ductile failure for 24 days and brittle failure when tested 10 days later. At 98°C the transition was between 8 and 11 days.

The influence of aging in water on the tensile strength to break was essentially similar to the effect on the yield strength. That is, as long as the specimens were capable of yielding, the tensile strength did not change significantly with immersion time. But once the material became brittle, the tensile strength decreased rapidly. This can be seen, for example, in Figure 6 at 85°C.

In an attempt to quantify the embrittlement process, we define the transition as the point where the elongation to break and the elongation at yield coincide. The latter is about 8.5%. So defined, the times to embrittlement at 55, 70, 85, and 98°C were obtained from Figure 5 and plotted (Arrhenius plot) in Figure 7. The time to embrittlement at 55°C was obtained by extrapolation. From Figure 7, the activation energy of the embrittlement process, due to hydrolysis, was found to be about 22 kcal/mole. In general, the activation energy for the hydrolysis of ester linkages in polymers lies between 18 and 25 kcal/mole.

At this point it would be of interest to compare the hydrolysis of polyarylate and polycarbonate. For the activation energy of polycarbonate hydrolysis a value of 18 kcal/mole was reported by Pryde et al.,<sup>10</sup> and a value of 22 kcal/mole was calculated by the authors from data presented by Gardner and Martin.<sup>9</sup> A rigorous comparison of the rate of hydrolysis is rather difficult, since the test conditions in the above references are somewhat different. As a

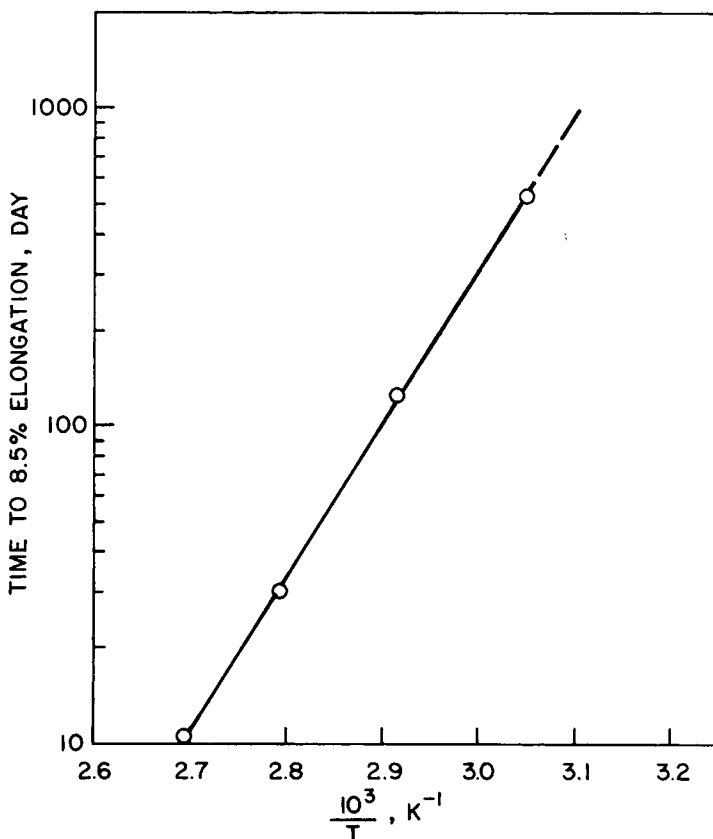


Fig. 7. Arrhenius plot of time to hydrolytic embrittlement:  $\epsilon_a = 22$  kcal/mole.

first approximation, however, the data of this study may be compared with the data of Gardner and Martin.<sup>9</sup> In both studies the testing conditions were similar. In Ref. 9 the initial  $M_w$  and  $M_n$  of the polycarbonate were 45,000 and 20,000, respectively. Comparing polycarbonate hydrolysis at 100% relative humidity (condensing humidity) with the data of polyarylate hydrolysis shows that, at a given temperature, polyarylate hydrolyzes at a slower rate. For example, from Figure 7 it can be seen that, at water temperature of 55°C, it would take over 500 days for the polyarylate to embrittle, assuming no other degrading processes. Under similar, but not exact, test conditions polycarbonate would embrittle in 320 days.<sup>9</sup> Whether the difference in the rate of embrittlement of the two polymers is due to the hydrolysis rate of the carbonate vs. the arylate groups, or some other factors is not clear at this point. As diffusion is not a rate-limiting step in either polymer, water concentration is not expected to be an influencing factor here.

From the hydrolysis data at 85°C it is possible to obtain a rough estimate of the molecular weight at which the tensile ductile-brittle transition occurs. From Figure 5 or Figure 7 it is seen that, at 85°C, the elongation to break would decrease to 8.5%, defined here as the ductile-brittle transition point, after 30 days. From Figure 4 (molecular weight vs. time at 85°C) it is seen that, after 30 days,  $M_w = 36,000$  and  $M_n = 13,000$ . Because of the limited



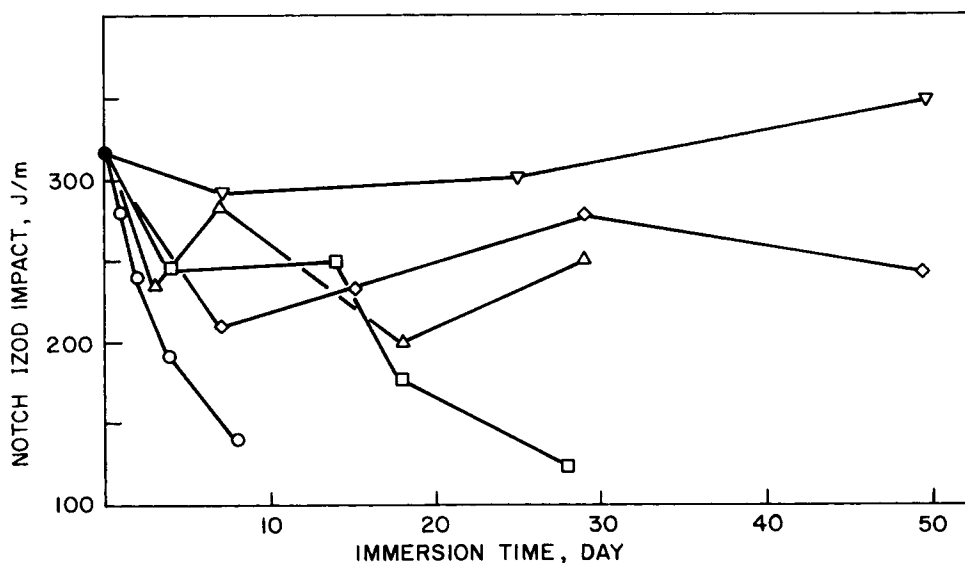


Fig. 8. Plots of notched Izod vs. time: (○) 98°C; (□) 85°C; (△) 70°C; (◇) 55°C; (▽) 23°C.

molecular weight data, these values should be taken as a first approximation only. Interestingly, the corresponding values reported for polycarbonate<sup>9</sup> are 33,800 and 14,300, respectively.

The notched Izod impact data of polyarylate as a function of immersion time are shown in Figure 8. In the first 3 to 7 days there is an initial sharp drop in Izod impact at all the test temperatures. Beyond that period, the time-temperature dependence becomes complex. At 98°C the Izod impact continues to decrease monotonically with time, but at lower temperatures, there appears to be a recovery. The extent and duration of that recovery seems to depend on temperature. At 23°C, the recovery is complete, and at long immersion times (50 days), the impact energy exceeds the initial value. The recovery at 55°C also appears to continue through most of the test period. A decrease with irregular pattern is seen at 70 and 85°C. At 70°C and also, possibly, at 55°C, the pattern appears to be cyclic. If this pattern has any significance, aside from normal scatter of the data, is not known.

In the falling dart impact test, an instrumented impact machine was used. A description of the machine and its capabilities is presented elsewhere.<sup>11</sup> A trace of an impact event, depicting the rise in the load imposed on the center of the disc along with the energy absorbed by the disc, is shown in Figure 9. The load rises gradually to a maximum value, whereupon a catastrophic failure occurs. Both fresh and aged polyarylate discs failed in this manner. By contrast, in polycarbonate the dart penetrates the disc, but does not break it.

Figure 10 shows the dependence of impact load, that is, load at break, on time. The impact energy absorbed by the discs is plotted in Figure 11. At water temperature of 55 and 70°C, there is virtually no change in the dart impact values within the limit of the test period. But at 85 and 98°C, the impact values decrease appreciably with time.

The Izod and dart impact results are surprising when compared to the tensile results. Because of the high strain rates in impact testing one would

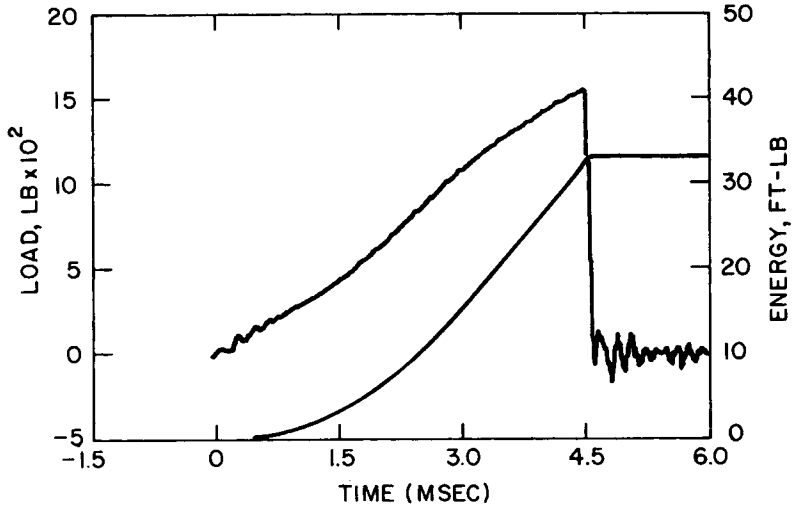


Fig. 9. A typical dart impact record of fresh polyarylate.

expect to observe a more rapid and more pronounced effect of hydrolysis. In dart testing, moreover, the extent of surface degradation is usually critical. Cracks initiated at the surface, assumed to be the first to hydrolyze, may readily propagate through the bulk. Yet the loss in tensile elongation, on percentage basis, is greater than the loss in dart impact energy. It is not clear why this is so. It does point, however, to the fact that water diffusion is substantially faster than the rate of hydrolysis. Therefore, when polyarylate is immersed in water the extent of hydrolysis would be about equal throughout the specimen. It must be said, though, that these observations were for

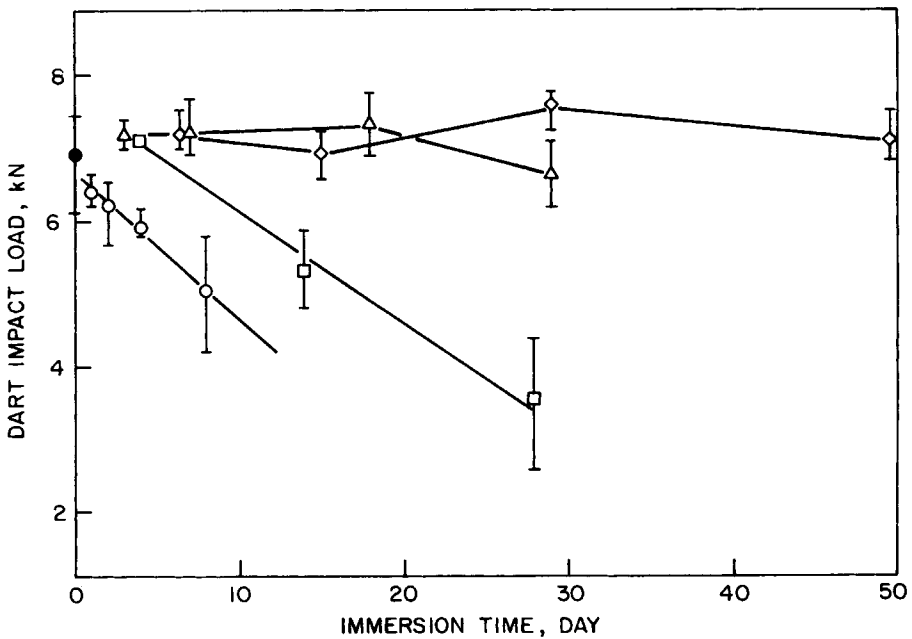


Fig. 10. Plots of dart impact load vs. time: (○) 98°C; (□) 85°C; (△) 70°C; (◇) 55°C.

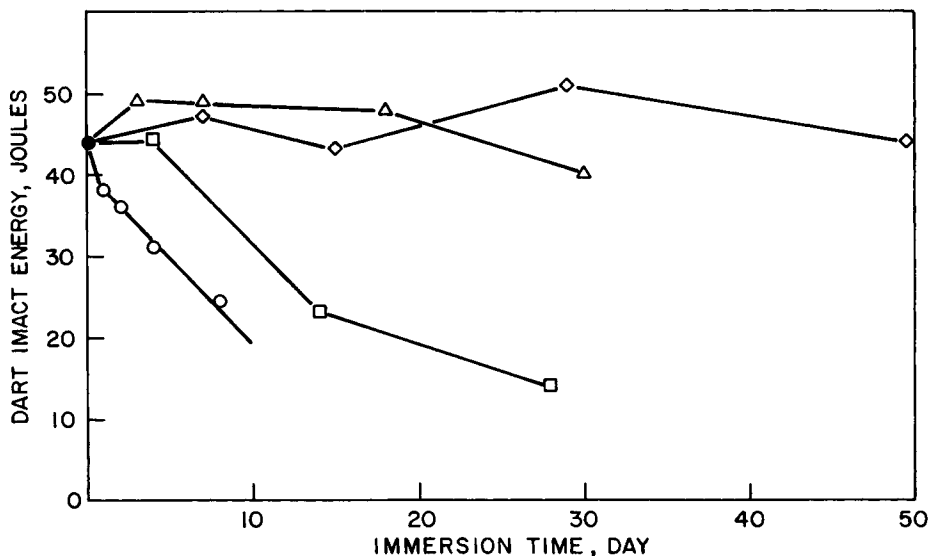


Fig. 11. Plots of dart impact energy vs. time: (○) 98°C; (□) 85°C; (△) 70°C; (◇) 55°C.

specimens with thickness of 0.32 cm and may not apply for substantially thicker specimens.

## CONCLUSIONS

Water absorption and the temperature dependence of the diffusivity in polyarylate is similar to other glassy polymers.

The aromatic ester in polyarylate is hydrolyzed by water which results in lower molecular weight and loss of ductility. The activation energy for the embrittlement process is about 22 kcal/mole and is similar to values reported for polyesters and polycarbonate. The rate of diffusion is larger than the rate of hydrolysis and, at the early stage, the hydrolysis appears to be a zero-order reaction.

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