The Influence of Relative Humidity on Polyarylate Hydrolysis

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Synopsis

The influence of relative humidity (RH), between 55 and 100%, on the rate of hydrolytic degradation of polyarylate was investigated at 100°C. The equilibrium water sorption in weight percent, C_∞, was determined to be $C_\infty = 0.0043 \times (\text{RH})^{1.2}$. For specimens 0.32 cm thick, it takes about 24 h to reach $0.9 C_\infty$ at 100°C. The decrease in molecular weight ($\overline{M}_w$) due to the hydrolytic attack of water was linear with time, suggesting a zero-order process with respect to $\overline{M}_w$. The rate of decrease was found to be proportional to C_∞. A 30% decrease in $\overline{M}_w$ was observed after 21 days at 55% RH and 100°C and, at that point, the material has become brittle.

INTRODUCTION

When polymeric materials are used outdoors, they experience a hostile environment which causes changes in the materials' chemical composition. In the case of polyesters, a crucial change is the reduction in molecular weight due to hydrolysis of the ester linkages by water. This change is accompanied by loss of physical and mechanical properties and, after a certain exposure period, the material is unable to meet its design criteria and failure occurs. A number of studies have shown that when polyesters or polycarbonates are placed in a high humidity environment, the initial molecular weight decrease due to hydrolysis is linear with time, at least up to about 50% change.[1-4] That degree of change (one cleavage per chain, on average) is usually sufficient to result in embrittlement and failure of the polymers.[3-6]

That the hydrolytic process initially is zero-order with respect to molecular weight is probably due to an abundance of both ester linkages and water and to the fact that hydrolysis is slower than water diffusion.[4,6,7] The activation energy for the hydrolytic process is of the order of 20 kcal/mol: A value as low as 18 kcal/mol was reported by Pryde et al.[8] for polycarbonate in 96% relative humidity and as high as 25 kcal/mol was reported for poly(butylene terephthalate) by Kelleher et al.[2] Interestingly, when a blend of these polymers was aged in water, a value of 22 kcal/mol was observed for the embrittlement process.[7]

Recently, we have investigated the influence of water on polyarylate.[3,6] Polyarylate—an amorphous polyester— is the reaction product of Bisphenol-A and a mixture of isophthalic/terephthalic acids. When the polymer is immersed in water the activation energy of hydrolysis was calculated to be 19.8 kcal/mol, and the rate constant for the linear decrease in $\overline{M}_w$ was found to be about 1500 day^{-1} at 100°C.[3] Under these test conditions, the equilibrium water concentration was about 1.1 wt %. The glass transition tempera-

TABLE I
Relative Humidity vs. Saturated Salt Solutions at 100°C
(From *International Critical Tables*)[a]

Salt	RH (%)	Solubility (g/100 g H_2O)
KI	56	208
NaCl	73	39.2
$CuSO_4$	87	73.6 as $CuSO_4 \cdot 5H_2O$
K_2SO_4	95	24.1

[a] Ref. 9.

ture of polyarylate is 185°C and the mobility of ester linkages in the polymer chain is rather restricted at, or below, 100°C. Thus, the rate of hydrolysis of the polymer in the solid state would depend principally on water concentration and temperature.

The influence of temperature on water diffusion and hydrolysis rate of polyarylate was reported previously.[3,6] In the study described here, the dependence of hydrolysis rate at 100°C on relative humidity, i.e., water concentration, was investigated.

EXPERIMENTAL

Injection molded bars of polyarylate (Amoco's Ardel D-100) were received from Amoco. The bars were 1.2 cm wide and 0.32 cm thick. They were cut into small coupons, approximately 2 cm long, for placing in humidity chambers and measuring the change in molecular weight. For measuring equilibrium water sorption at various relative humidities, flat sections (6 × 6 × 0.32 cm) were used. All the tests were conducted at 100°C. Saturated salt solutions were placed at the bottom of desiccators which served as humidity chambers. The saturated salt solutions used in this study are listed in Table I along with the corresponding relative humidity and solubility at 100°C.[9] The coupons were placed on a perforated ceramic disk, about 8 cm above the saturated salt solutions. Chromel-alumel thermocouples were located about 1 cm above the ceramic disc for monitoring the temperature. The desiccators were placed in an air circulating oven in order to maintain 100°C. The temperature fluctuation in the oven was within ±2°C, but inside the desiccator it was not more than 1°C around the nominal value.

After a predetermined exposure period, the coupons were removed from the humidity chambers and dried under vacuum at room temperature for 1 week. The dried coupons were then dissolved in methylene chloride and their average molecular weights were determined by size exclusion chromatography, as described previously.[3]

RESULTS AND DISCUSSION

Water Sorption

The sorption of water by polyarylate as a function of time is given in Table II. The water sorption C_t is defined here as the percent weight gains of polyarylate coupons exposed for the period of t h, to 55–100% RH, at 100°C. The C_t at any given relative humidity, approaches the equilibrium value C_∞

TABLE II
Water Sorption Data of Polyarylate at Various RH and 100°C

Time (h)	Percent weight gain at				
	56%	73%	87%	95%	100%[a]
2	0.30	0.41	0.45	0.46	0.45
4	0.35	0.50	0.56	0.59	0.61
7	0.40	0.60	0.63	0.73	0.76
24	0.50	0.66	0.82	0.92	0.95
31	0.49	0.68	0.81	0.95	0.97
53	0.51	0.69	0.86	0.98	1.02
120	0.53	0.73	0.91	1.00	1.08
200	0.54	0.74	0.91	1.01	—

[a] Data from Ref. 6.

in just a few days, as is seen in Figure 1. The shape of the plot in Figure 1 is typical to Fickian diffusion, which has been also seen by immersing polyarylate in water.[6] The tests conducted here were designed to obtain C_∞, and the results are not considered suitable for determining the diffusion kinetic parameters. At best, the data suggest that the influence of RH on C_t/C_∞ at any given time is generally small, and is nil when $C_t/C_\infty > 0.9$. For some engineering resins, especially hydrophobic polymers, the permeability is relatively independent of the partial pressure of water; however, its dependency on the partial pressure of water is generally more pronounced for hydrophilic polymers, e.g., nylon.[10] The water permeability is a function of temperature with an activation energy of the order of 10 kcal/mol for many polymers.[10] For polyarylate it was found to be 9.8 kcal/mol.[6] It is worth noting that it only takes about 24 h to reach ca. 90% of the C_∞ at 100°C. Thus, when a polyarylate component is used outdoors, equilibrium with environmental conditions is likely to be achieved relatively fast.
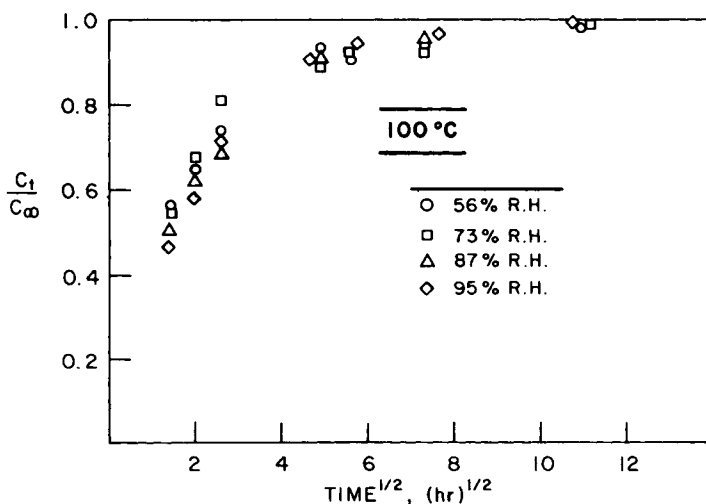

Fig. 1. Water sorption data for polyarylate (0.32 cm thick samples) at 100°C.
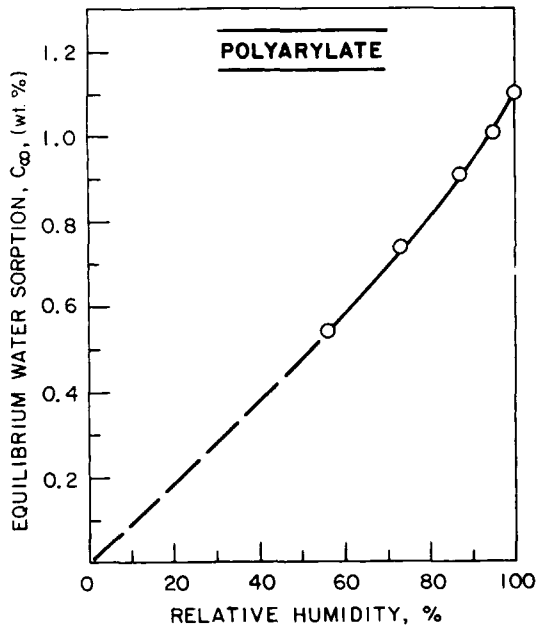
Fig. 2.   Water sorption isotherm of polyarylate at 100°C.

The equilibrium water sorption depends on relative humidity as is shown in Figure 2. The values used correspond to an exposure time of 200 h. The sorption isotherm is not linear but has the following empirical relationship:

$$C_\infty = 0.0043 \times (RH)^{1.2} \tag{1}$$

The above correlation describes the isotherm at 100°C. The dependence of C_∞ on temperature is only partially known from our previous study.[6] In that study polyarylate specimens were completely immersed in water (100% RH) and C_∞ was found to be around 1.1%, apparently independent of temperature between 70 and 100°C. At lower temperatures water sorption did not reach that value, possibly due to the short duration of the test. It appears that there is no general rule for the temperature dependence of C_∞. For example, Robeson and Crisafulli reported that the equilibrium percent values of water sorption at 23° and 96°C were practically the same for polysulfone, poly(ether sulfone), and polyetherimide.[11] On the other hand, C_∞ of polycarbonate is known to be temperature dependent.[11,12] At this point, it is not certain that the equilibrium water sorption in polyarylate is independent of temperature, though limited data suggest such a possibility.[6]

A further complication in determining sorption isotherms of polyarylate is the development of microcracks in the test specimens. In a previous study it was observed that after apparent equilibrium was achieved, there was an increase in water uptake, presumably due to the development of microcracks.[6] Figure 3 is a series of photographs of specimens exposed to 85 and 95% RH, showing large cracks in the samples. The large cracks, which are visible to the naked eye and probably originated from microcracks, have grown to that
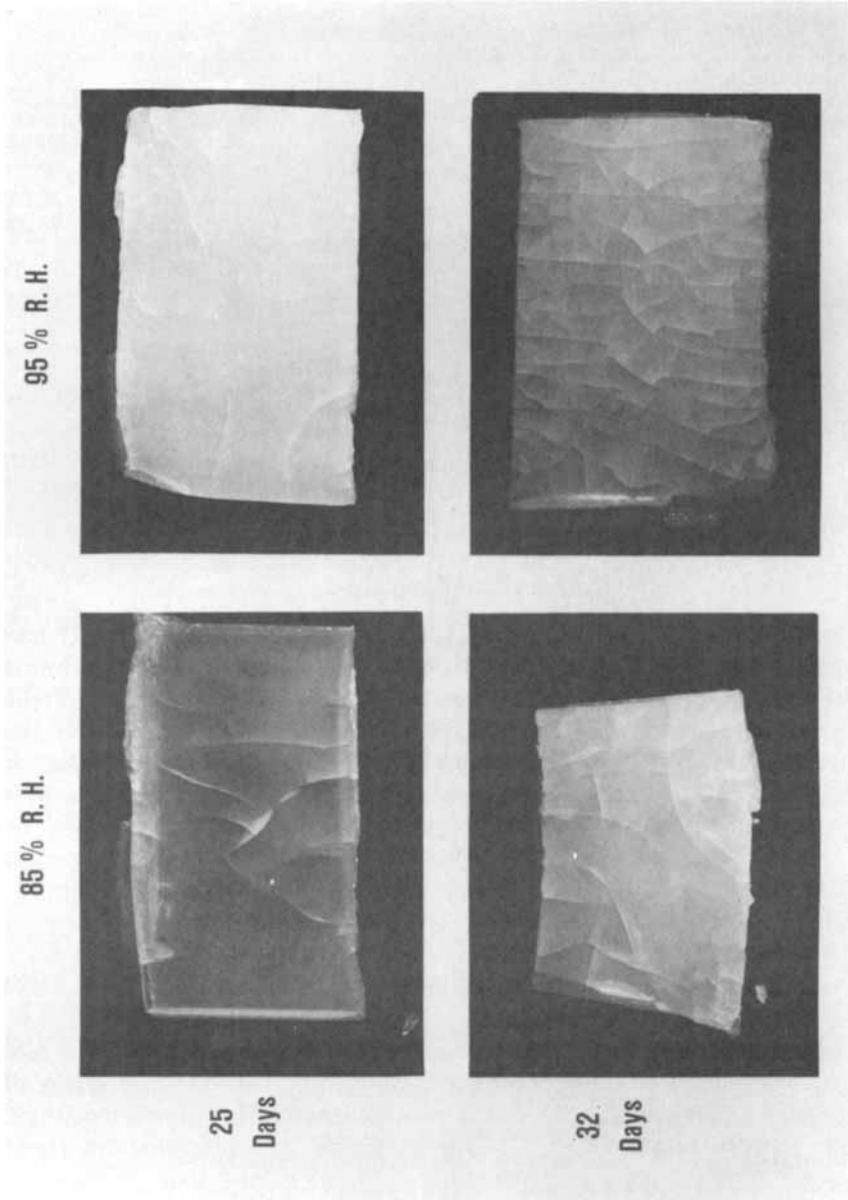
Fig. 3. Polyarylate specimens after 25 and 32 days exposure to 85 and 95% relative humidity showing development of cracks (magnification 5X).

TABLE III
Molecular Weight ($\overline{M}_w$) of Polyarylate Hydrolyzed at 100°C

Time (day)	Relative humidity (%)				
	56	73	87	95	100[a]
4	44,170	43,535	40,470	39,570	43,210
9	40,730	38,570	34,015	34,440	36,000
15	33,260	31,880	23,110	24,450	26,500
25	29,940	22,000	14,640	13,705	—
32	26,150	17,250	9185	5960	—

[a] Based on data from Ref. 3.

stage as a result of thermal shock when specimens were taken out of the desiccators. Similar cracks were also seen when polyarylate samples that were immersed in boiling water for about 20 days were taken out of the water bath a few times. No cracks were seen in the specimens that were exposed to 56 and 73% RH.

Polyarylate Hydrolysis

The molecular weight results for $\overline{M}_w$ and $\overline{M}_n$ are listed in Tables III and IV, respectively. Calculation of the polydispersity, i.e., $\overline{M}_w/\overline{M}_n$, shows that it is about 2.6 and is relatively stable, as was also seen before.[3] Because the polydispersity is high to begin with, it would take large changes in the molecular weight to observe the appreciable deviation from it. Also, if the hydrolytic attack occurs randomly along the polymer chain, as was proposed previously,[3,6] the polydispersity would remain constant. It can be shown that plots of average molecular weight vs. time yield reasonable straight lines, as was also seen in other studies.[1-4] Thus, the change of $\overline{M}_w$ with time may be written as

$$\overline{M}_w = \left(\overline{M}_w\right)_0 - kt \qquad (2)$$

where $(\overline{M}_w)_0$ is the initial weight-average molecular weight and k is a rate constant. The values of these parameters along with the standard errors of estimate (SE) are listed in Table V. The rate constant k is expected to depend on water concentration C_t or relative humidity, probably in the form:

TABLE IV
Molecular Weight ($\overline{M}_n$) of Polyarylate Hydrolyzed at 100°C

Time (day)	Relative humidity (%)				
	56	73	87	95	100[a]
4	15,820	15,325	15,850	13,790	16,063
9	15,590	14,440	13,155	12,880	13,500
15	11,580	12,310	8225	9065	10,000
25	11,080	8220	5610	5190	—
32	10,050	6800	3870	2680	—

[a] Based on data from Ref. 3.

TABLE V
Linear Regression Analysis Parameters of $\overline{M}_w$ Data

	Relative humidity (%)				
	56(0.54)[a]	73(0.74)	87(0.91)	95(1.0)	100(1.1)[b]
k (day^{-1})	637	957	1120	1216	1520
SE	82	41	108	51	40
$(\overline{M}_w)_0$	45,670	46,920	43,338	44,303	49,435
SE	1885	937	2467	1176	314

[a] Number in parentheses = % equilibrium water sorption.
[b] Based on data from Ref. 3.

$k \propto (C_t)^n$. A logarithmic plot of k vs. C_∞ is shown in Figure 4. The use of C_∞ is reasonable because, as was shown earlier, the equilibrium is achieved very fast in comparison with the chemical reaction. From the slope of the plot in Figure 4 it is seen that the value of n is very close to unity. This means that the rate is simply proportional to water concentration. With regard to relative humidity, the relationship between C_∞ and RH is given in eq. (1) and substitution is straightforward. The relationship between k and RH is not linear over the entire range of relative humidity, but is reasonably so over a limited range. As can be seen from Figure 2, between about 55 and 95% RH the correlation between C_∞ and RH is fairly linear, and in that range k is proportional to RH for all practical purposes.

As mentioned above, some of the polyarylate specimens in the 87 and 95% RH developed cracks (Fig. 3). To see if the salts have any added influence on hydrolysis rate, samples were immersed in aqueous solution of K_2SO_4 and NaCl at 100°C. The molecular weight data after 24 days are listed in Table VI. The differences are not significant statistically and, hence, it appears that these salts have no effect, at least when the concentration is around 0.2%.
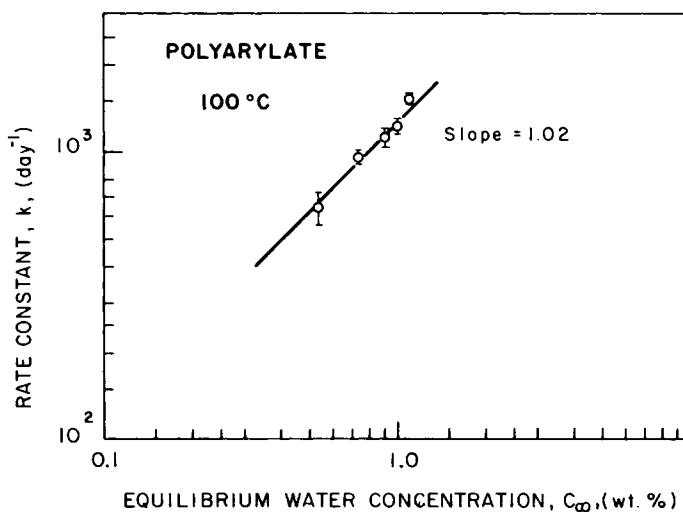

Fig. 4. A plot of the rate constant for polyarylate molecular weight degradation vs. C_∞.

TABLE VI
Polyarylate Molecular Weights after 24 Days Immersion at 100°C

Medium	$\overline{M}_w$	$\overline{M}_n$	d
Deionized water	13,025	5545	2.35
0.2 wt % K_2SO_4/water	13,955	5945	2.35
0.2 wt % NaCl/water	13,200	4840	2.73

For polyarylate the transition from ductile to brittle failure in the standard ASTM tensile test occurs when $\overline{M}_w$ and $\overline{M}_n$ are about 34,500 and 12,700, respectively.[3] This represents roughly 30% decline in the molecular weight. At that point the elongation to break is 8%, down from an initial value of about 55%. The dependence of k on temperature is given by

$$k = k_0 e^{(-E_a/RT)} \tag{3}$$

where E_a is equal to 19.8 kcal/mol.[3] This value was obtained when polyarylate was immersed in water. It is reasonable to expect the activation energy to be independent of C_∞, or relative humidity; their effect would be seen in k_0 in eq. (3). Having established the hydrolysis rate as a function of temperature at 100% RH and as a function of RH at 100°C, it is possible to estimate the time to embrittlement in tensile testing (i.e., 8% elongation to break) at different environmental conditions, assuming, of course, steady state situation and neglecting other degradations. Table VII lists some calculated values of the time to reach 30% decrease in the molecular weight of polyarylate. It appears from Table VII that, in moderate environments, hydrolytic embrittlement is slow and the material may retain its properties for a long time. But continuous exposure to conditions of high humidity and temperature may cause quick failure.

CONCLUSIONS

The hydrolysis of polyarylate appears to be a zero-order process with respect to molecular weight between 56 and 100% relative humidity at 100°C. A zero order was also seen between 55 and 98°C at 100% RH.[3,6] The combined results suggest that polyarylate hydrolysis would be a zero-order process, with an activation energy of 19.8 kcal/mol, over a broad range of conditions which may be encountered in the environment. The rate of molecular degradation is proportional to water concentration which is proportional to $(RH)^{1.2}$ The temperature and humidity in the environment are variable, usually within a known range and known average conditions. Since thermal and water concen-

TABLE VII
Exposure time to 30% Decrease in $\overline{M}_w$ of Polyarylate

	100°C	50°C	30°C
55% RH	21 days	4.0 years	30 years
95% RH	11 days	2.1 years	15 years

tration equilibriums are achieved relatively fast in comparison with an expected service life of polyarylate articles, i.e., hours and days vs. years, it is possible to estimate the latter in a given climate by using the average conditions as a first approximation. Refinement is obviously possible if the environmental conditions are well defined. The approach described here is a practical tool for a rough, but quick estimate of the service life of polymers which degrade in a similar manner. Since sunlight, heat, humidity, atmospheric pollutants, and physical stresses all combine to produce molecular changes, the estimates are likely to be on the optimistic side.

References

1. F.C. Schilling, W. M. Ringo, N. J. A. Sloane, and F. A. Bovey, *Macromolecules*, **14**, 532 (1981).

2. P. G. Kelleher, R. P. Wentz, M. Y. Hellman, and E. H. Gilbert, *SPE 40th ANTEC*, **28**, 111 (1982).

3. A. Golovoy, M. F. Cheung, and M. Zinbo, *J. Appl. Polym. Sci.*, **35**, 2001 (1988).

4. A. Golovoy and M. F. Cheung, Polym. Eng. Sci., to appear.

5. R. J. Gardner and J. R. Martin, *SPE 36th ANTEC*, **24**, 328 (1978).

6. A. Golovoy and M. F. Cheung, *J. Appl. Polym. Sci.*, **35**, 1511 (1988).

7. A. Golovoy, M. F. Cheung, and H. van Oene, *Polym. Eng. Sci.*, **28**, 200 (1988).

8. C. A. Pryde, P. G. Kelleher, M. Y. Hellman, and R. P. Wentz, *SPE 39th ANTEC*, **27**, 98 (1981).

9. *International Critical Tables*, McGraw-Hill, New York, 1926, Vol. 1, p. 67.

10. J. A. Barrie, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic, London, 1968, Chap. 8.

11. L. M. Robeson and S. T. Crisafulli, *J. Appl. Polym. Sci.*, **28**, 2925 (1983).

12. M. Narkis, S. Sibony, L. Nicolais, A. Apicella, and J. P. Bell, *Polym. Commun.*, **26**, 339 (1985).