

The Effects of Annealing and Aging in Water on the Properties of an Amorphous Copolyester

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Synopsis

The influence of annealing in a dry oven and aging in water bath at 98°C on the thermal and mechanical properties of an amorphous poly(1,4-cyclohexanedimethylene/ethylene terephthalate) was studied up to 21 days. Oven annealing brought about crystallization, an increase in the tensile modulus and yield strength, and a decrease in elongation and Izod impact strength. The intrinsic viscosity, however, did not change. The samples that were immersed in water embrittled at a faster rate as a result of the combined adverse effects of hydrolysis and crystallization. The intrinsic viscosity decreased from 0.71 to 0.53 after 21 days. Within the limits of this study, the hydrolysis was found to be a zero-order process with respect to molecular weight. A transition from ductile (> 8% elongation) to brittle failure in tension was observed between 3 and 5 days.

INTRODUCTION

When amorphous polyesters are exposed to an environment of high humidity and above T_g temperatures, they undergo physical and chemical changes. Among the more notable physical changes is the development of crystallinity which is accompanied by density increase. In the absence of nucleating agents and external stress fields, the rate and degree of crystallinity depend primarily on the molecular structure of the polyester, temperature, and time. Substantial crystallinity can be achieved in a matter of minutes to a few hours depending on crystallization conditions and type of polymer. Taking poly(ethylene terephthalate) (PET) as an example, Lin and Koenig¹ reported that the exothermic crystallization peak (cold crystallization), which is observed in differential scanning calorimetry (DSC) of amorphous PET, disappears after annealing PET films for about 30 min at 110°C. The activation energy of PET crystallization was found to be about 40 kcal/mol. A sudden rise in density was also noted at the 30-min mark. In a humid atmosphere, or when the polymer is immersed in water, diffusion of water which usually follows Fickian behavior also occurs. The activation energy for water diffusion is of the order of 10 kcal/mol and equilibrium is achieved in several days.^{2,3}

The predominant chemical process when water is present is hydrolysis of ester linkages. The decrease in molecular weight is accompanied by a substantial loss of ductility,³⁻⁵ and, therefore, the process is sometimes referred to as hydrolytic embrittlement. Several studies on the hydrolysis of polyarylate,⁴ polycarbonate,⁵ and poly(butylene terephthalate)⁶ show that initially the hydrolysis is a zero-order process with respect to molecular weight having an activation energy of the order of 20 kcal/mol. The process is slower than crystallization or diffusion: the time to embrittlement in boiling water, for example, is usually 2-3 weeks.²⁻⁵

A polyester with an exceptionally good hydrolytic stability is an amorphous copolyester comprised of 1,4-cyclohexanedimethanol and a mixture of isophthalic and terephthalic acids (Eastman Chemicals, Kodar A-150). Joseph et al.⁷ reported only a 2% decrease in the intrinsic viscosity of Kodar A-150 after 12 days immersion in boiling water, the duration of the experiment. They observed, however, a substantial loss in ductility which was probably due to crystallization.

A polymer similar to Kodar A-150 is Kodar PCTG 5445 (Eastman Chemicals). It is an amorphous copolyester which is made of terephthalic acid and a mixture of 1,4-cyclohexanedimethanol with ethylene glycol. In the amorphous state it is a clear and tough material with T_g around 85°C. This paper describes the changes in some of the thermal and mechanical properties of PCTG 5445 due to annealing in a dry oven and aging in water at 98°C.

EXPERIMENTAL

PCTG 5445 is a reaction product of terephthalic acid and a mixture of 1,4-cyclohexanedimethanol (66 mol %) and ethylene glycol (34%). The intrinsic viscosity of the copolyester (prior to molding) is about 0.78. Injection-molded specimens of PCTG 5445 were received from Eastman Chemicals (Kingsport, TN). They included tensile and Izod bars 0.32 cm (0.125 in.) thick and 1.27 cm (0.5 in.) wide. They were amorphous and water clear. One group of specimens was placed in a 98°C oven, and another group was immersed in a 98°C water bath. The bath was made of stainless steel. The temperature was regulated to $\pm 1^\circ\text{C}$. The Izod bars were notched prior to testing. Periodically, five or more specimens were taken out and allowed to cool to room temperature for at least 24 h before testing. The tensile and Izod testing were done according to standard ASTM procedures.

The thermal analysis, i.e., differential scanning calorimetry (DSC), was done with a Mettler model TA3000 with DSC30 measuring cell. The DSC heating rate was 5°C/min. Each sample was scanned twice from room temperature to 280°C. The specimens that were immersed in water were dried over night under vacuum at about 60°C before the thermal analysis. Intrinsic viscosity (IV) measurements were done by Eastman Chemical personnel using phenol/tetrachloroethane solvent mixture.

RESULTS AND DISCUSSION

Oven Annealing

DSC thermograms of a PCTG pellet and an injection molded bar, both in the amorphous state, are shown in Figure 1. The thermograms exhibit the characteristic features of cold crystallization and melting that occur during DSC scanning. There are some differences between the two thermograms. First, the T_g of the injection-molded material is 83°C vs. 85°C for the pellet. Second, the cold crystallization peak temperatures are 157°C vs. 170°C. For the pellet the cold crystallization peak is broader and the end of cold crystallization and the onset of melting appear to coincide; it is, therefore, difficult to determine the exact values for the heats of crystallization and fusion. The melt temperature of both is about 242°C with a wide melt peak

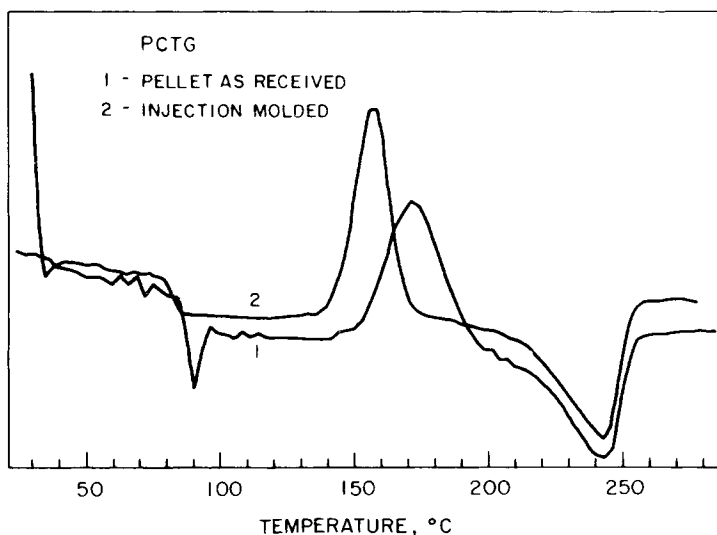


Fig. 1. DSC plots (first scan) of PCTG pellet as received (1) and injection-molded bar (2).

which begins at around 200°C. For the molded material the heats of crystallization and of fusion were determined by integration to have similar values of about 20 J/g, which indicate that the molded bars are totally amorphous. The difference in T_c and T_g between the pellet and the molded material may be due to a decrease in molecular weight. The intrinsic viscosity (IV) of the pellet is about 0.78 and that of the molded PCTG about 0.71 [Eastman Chemicals data]. The IV is known to be proportional to $(M_w)^a$, where the value of the exponent a is specific to the particular polymer-solvent system considered. That value is not known for the system studied here, but is between 0.5 and 0.7 for many systems. For a similar copolyester, which is based on 1,4-cyclohexanedimethanol condensed with a mixture of isophthalic and terephthalic acids, Joseph et al. suggested the value of 0.5 as a good approximation.⁷ If we use the values of 0.5 and 0.7, the above change in IV would indicate about a 12–17% decrease in the weight average molecular weight during molding.

DSC thermograms of some annealed bars are shown in Figure 2. The DSC data of all annealed bars are summarized in Table I. These data are for the first DSC scan, thus showing the effect of annealing on the state of crystallinity. The most obvious effect of annealing is the gradual decrease and disappearance of the cold crystallization peak. From Table I it is seen that the heat of crystallization, ΔH_c , diminishes within a few hours. Also, the peak temperature, T_c , decreases from 157 to 132°C. The decrease of ΔH_c is an indication of the extent of crystallization. It can be shown that a plot of ΔH_c vs. time has a sigmoidal shape which is characteristic of the Avrami crystallization model⁸ and is common to many polymers.

Some time between 8 and 12 h of annealing at 98°C, a transition from cold crystallization peak to an endothermic low melting peak takes place. Such transition has been observed in other polyesters.^{1,9} It occurs after the primary crystallization is well advanced or completed, and is known as secondary crystallization (SC). The work of Yagpharov⁹ suggests that the properties of

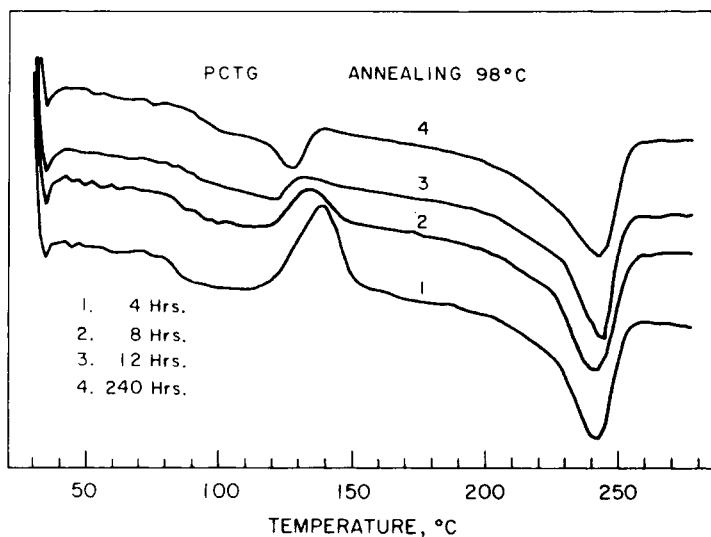


Fig. 2. DSC plots (first scan) of PCTG bars annealed in 98°C oven: (1) 4 h; (2) 8 h; (3) 12 h; (4) 240 h.

the secondary crystals, described as "fringed micelle" type, differ significantly from those of the primary crystals. A sharp rise in the density coinciding with SC transition was observed in PET.¹ The melting temperature of SC crystallites is known to depend on annealing temperature and is, usually, about 15°C above the latter. The SC melt temperature, T_{m2} , of PCTG was found to be around 125°C. It appears to be independent of annealing time, with the exception of the 12 h mark when SC was first detected and T_{m2} was 121°C. For comparison, when PET was annealed at or above 120°C, its T_{m2} was observed to increase with annealing time, and the rate of increase was temperature-dependent.^{1,9} The rate exhibited a maximum at 180–200°C which coincided with the temperature region of maximum crystallization of PET. Below and above that region the rate decreased sharply. Extrapolation to

TABLE I
DSC Data (First Scan) of PCTG Annealed at 98°C Oven

Time (h)	T_g (°C)	T_c (°C)	T_{m2} (°C)	T_{m1} (°C)	ΔH_c (J/g)	ΔH_{m2} (J/g)	ΔH_{m1} (J/g)
0	83	157	—	242	22	—	20
1	83	148	—	242	22	—	19
2	84	147	—	242	21	—	20
4	85	138	—	242	13	—	19
8	87	132	—	241	4	—	22
12	85	—	121	243	—	2	21
19	90	—	126	242	—	2	19
28	86	—	128	243	—	3	19
72	89	—	125	243	—	3	20
144	92	—	126	241	—	3	20
240	92	—	127	242	—	3	20

temperatures below 120°C shows that the rate would diminish at 80–100°C. Thus, the observation that T_{m2} of PCTG appears to be independent of annealing time is true for annealing at about 98°C, and, based on PET behavior, it is reasonable to expect that at higher temperatures PCTG would behave likewise. The SC endothermic energy, ΔH_{m2} , was found to be 2–3 J/g. There appears to be a slow and small increase in ΔH_{m2} with annealing time as a result of formation of the “fringed micelle” type crystallites. Again, the annealing temperature may be too low to show this more convincingly, but such trend was observed in other polymers.⁹

Annealing was found to influence also the glass transition temperature. From Table I it is seen that T_g increases gradually from 83 to 92°C after 240 h of annealing. That annealing and crystallization brings about a rise in T_g has been observed before for many polymers.^{7,9,10} Interestingly, for PET Lin and Koenig¹ reported diminishing intensity of the transition as seen in DSC scan, but no increase in the transition temperature.

The primary melting point T_{m1} and the heat of fusion, ΔH_{m1} , seem to be unaffected by annealing at 98°C for up to 10 days, the duration of the test. This is usually the case when the annealing temperature is close to the polymer's T_g , but, when it is much higher, the degree of crystallinity generally increases with time. For example, for PET with a T_g of about 80°C, it was reported¹ that when the annealing temperature was above 140°C, ΔH_{m1} increased with time, and the rate of increase showed positive linear temperature dependence. Extrapolation of the PET data suggests that for PET a zero growth rate would occur at, or below, about 100°C. It is likely that the behavior of PCTG during annealing is similar to PET's, and that at higher temperature the polymer would crystallize further.

The PCTG samples were generally scanned twice in the DSC. The reason for the second scan was to see if any degradation took place during annealing. At the start of the second scan the samples were at the same amorphous state after quenching from 280°C. Since T_g and some of the thermogram features are influenced by material changes, e.g., a decrease in molecular weight or formation of new molecular structures as a result of transesterification, it is sometimes possible to detect such changes using DSC. The data listed in Table II show that there were no changes in the major characteristics of the thermograms, which suggest that the PCTG did not change during the 10 days of annealing at 98°C. This is further supported by the intrinsic viscosity data (Table III), which show the IV to remain constant.

TABLE II
DSC Data (Second Scan) of PCTG Annealed at 98°C Oven

Time (h)	T_g (°C)	T_c (°)	T_{m1} (°)	ΔH_c (J/g)	ΔH_{m1} (J/g)
0	80	153	239	23	25
12	83	152	242	25	26
72	82	152	241	24	25
144	83	154	241	24	25
240	81	158	240	24	23

TABLE III
Intrinsic Viscosity (IV) of PCTG Aged at 98°C

Time (days)	Intrinsic viscosity ^a		(IV/IV ₀) ²
	Water	Oven	
0	0.71	—	1
1	0.69	—	0.94
3	0.68	—	0.92
6	—	0.70	—
7	0.64	—	0.81
10	—	0.71	—
13	0.60	—	0.71
21	0.53	—	0.56

^a IV measured by K. Romance, Eastman Chemicals, Kingsport, TN.

TABLE IV
Tensile and Impact Data of PCTG Annealed in 98°C Oven

Time (h)	Yield Strength (MPa)	Modulus (GPa)	Elongation (%)	Izod (J/m)
0	44	1.2	> 200	1700
1	46	1.3	> 200	700
3	45	1.3	> 200	430
5	47	1.5	> 200	20
72	62	1.4	20	24
144	64	1.5	20	17
240	64	1.7	15	20

The tensile and impact data are shown in Table IV. Since, as was shown above, annealing did not cause molecular degradation, the changes in properties are mostly the result of crystallization. As is well known, crystallization results in stiffening and loss of ductility. This is quite evident from the results in Table II. It is worth noting, though, that the tensile properties remained fairly constant during the first 5 h of annealing, even though crystallinity has already developed. The most sensitive property to crystallization was notched Izod impact strength which dropped from 1700 to 20 J/m in the first few hours of annealing. It is interesting to mention that in that period the Izod values of any group of annealed specimens (usually 5–10) scattered widely, with some specimens in the group showing high impact values, some medium, and some very low values, which is reminiscent of ductile–brittle transition region. The Izod values in Table IV are the average for each group and are shown merely to illustrate the critical effect of crystallization.

Aging in Water

PCTG test bars were immersed in 98°C water up to 21 days. The IV data are listed in Table III. The IV is proportional to $(M_w)^a$, where the exponent a is in the range of 0.5–0.7 for many polymer–solvent systems. As discussed in the previous section, the exact value of the exponent is not known. To illustrate the relative change in molecular weight a value of 0.5 was chosen

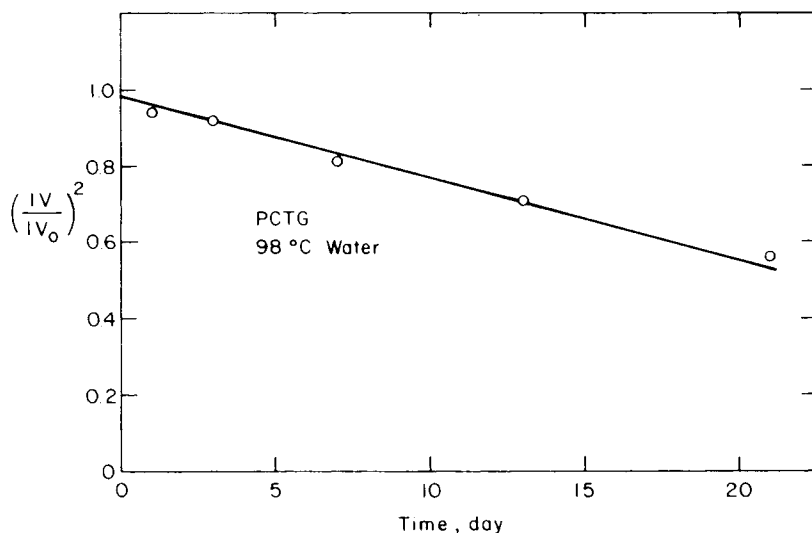


Fig. 3. Relative change in molecular weight of PCTG aged in 98°C water.

and the calculated values of $(IV/IV_0)^2$ are listed. These values are also plotted as a function of time in Figure 3. As can be seen, the molecular weight decreases linearly with time. It can be shown that if the exponent a were taken to be 0.6 or 0.7, the relative change in M_w would also be linear. This indicates that the hydrolysis of PCTG, up to at least 21 days, is a zero-order process with respect to molecular weight. As mentioned earlier, this was observed in the initial hydrolysis of many other polymers as well.²⁻⁶ What this means is that the rate of hydrolysis is independent of water or ester linkages concentration. This is not surprising since water diffusion is relatively fast and, hence, there is an abundance of both water and ester linkages. It should be noted that the change in molecular weight is less than 50%, representing an average of less than one scission per polymer chain, which is the early stage of the chemical reaction. While the hydrolysis rate of PCTG is less than polyarylate's and some other polymers,⁴ it is not comparable to Kodar A-150 which is known for its good hydrolytic stability. After 13 days, PCTG shows a 15% decrease in IV compared to about 2% for Kodar A-150 as reported by Joseph et al.⁷ The difference in the chemical structure of the two copolyesters may account for the different hydrolytic stability. As stated before, PCTG is based on ethylene glycol and 1,4-cyclohexanedimethanol which are reacted with terephthalic acid. Kodar A-150 is based on 1,4-cyclohexanedimethanol which is reacted with a 20/80 mixture of isophthalic/terephthalic acids. Thus, the PCTG copolyester contains PET segments which are known to hydrolyze readily. However, additional research is necessary to show if the PET segments are, indeed, the "weak link" in the copolyester.

The DSC characteristics of samples that were immersed in water were found to change with time. The DSC data of the first and second scan are listed in Tables V and VI, respectively. Figure 4 shows second scan thermograms of some aged samples. Referring to Tables V and VI, it is seen that the

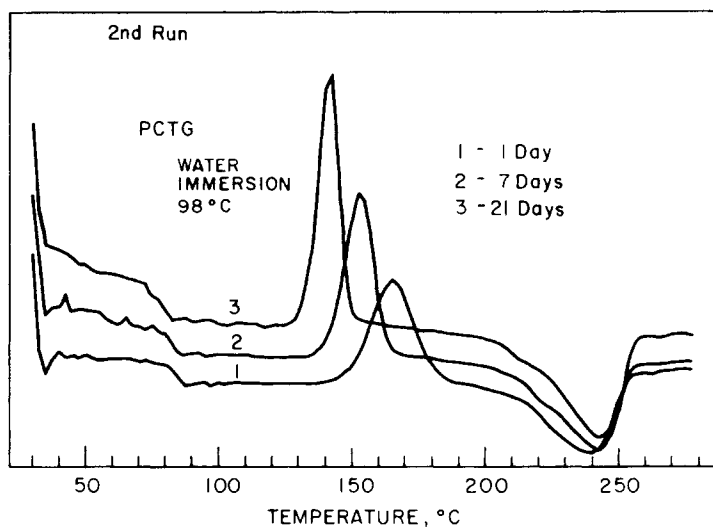


Fig. 4. DSC plots (second scan) of PCTG bars aged in 98°C water: (1) 1 day; (2) 7 days; (3) 21 days.

T_g decreases to 78°C after 21 days. This is probably due to the decrease in molecular weight. The T_g is related to molecular weight according to a relationship that was developed by Fox and Flory.¹¹ The initial rise in T_g , seen in Table V, is the result of crystallization, as discussed previously. It is interesting to note, though, that in water the T_g was found to increase to 97°C compared to 92°C in oven annealing (Table I).

TABLE V
DSC Data (First Scan) of PCTG Annealed at 98°C Water

Time (days)	T_g (°C)	T_{m2} (°C)	T_{m1} (°C)	ΔH_{m2} (J/g)	ΔH_{m1} (J/g)
1	97	131	241	3	21
3	96	133	243	3	21
5	96	134	246	3	22
7	93	135	244	3	23
13	84	135	243	3	23
21	78	137	246	3	28

TABLE VI
DSC Data (Second Scan) of PCTG Annealed at 98°C Water

Time (days)	T_g (°C)	T_c (°C)	T_{m1} (°C)	ΔH_c (J/g)	ΔH_{m1} (J/g)
1	84	165	241	24	25
3	84	162	242	24	24
5	84	156	241	24	25
7	83	153	241	25	27
13	83	155	241	24	26
21	78	142	241	26	31

The SC melting point, T_{m2} , was found to increase gradually from 131 to 137°C, but ΔH_{m2} did not change (Table V). When these data are compared to oven's data (Table I) it is seen that the SC melting points in the former are higher, but the extent of SC is roughly the same, judging from the ΔH_{m2} values. The primary melting peak characteristics appear to be unaffected up to 13 days. In the last measurement at 21 days, however, an increase in ΔH_{m1} was observed. This is probably due to the decrease in molecular weight and T_g , allowing the material to crystallize further. As mentioned before, when the temperature is sufficiently above the T_g , crystallization increases with time at a rate which depends on the temperatures difference.

Water immersion also has a significant effect on the cold crystallization temperature. This is illustrated in Figure 4 as well as summarized in Table VI. T_c was found to decrease from 165 to 142°C after 21 days. While the cold crystallization peaks become narrower, maybe indicating the formation of more uniform crystallites, the ΔH_c remains fairly the same at about 24 J/g. Also, the primary melting peak of the 21 days sample (curve 3, Fig. 4) appears to be not as broad as that of a 1-day sample. This change in the shape of the melting and the cold crystallization peaks suggests the possibility that the decrease in molecular weight, as a result of hydrolysis, brings about a more uniform crystallization.

Table VII lists some of the mechanical properties of PCTG bars as a function of immersion time in 98°C water. The data reflect the compounded effects of crystallization and hydrolysis. Because at 98°C crystallization is much faster than hydrolysis, we observe an initial drop in the strain to break and Izod impact strength, and an increase in the tensile yield strength and modulus, similar to the results shown in Table IV for oven annealing. The adverse effects of hydrolysis become apparent at and beyond 5 days. It is seen that at 5 days the aged PCTG no longer yields in tension, but fails in a brittle mode at 6% strain. The strain at yield of amorphous PCTG was observed to be at around 8%. The tensile strength was also observed to decrease rapidly as a result of hydrolysis. If we define the transition from ductile to brittle failure as the point where the strain to break and strain at yield coincide, i.e., 8%, then the time to embrittlement of PCTG, immersed in 98°C water, is between 3 and 5 days. This is shorter than that of some amorphous polymers^{2,4} and is probably due to the added effect of crystallization.

TABLE VII
Tensile and Impact Data of PCTG Annealed in 98°C Water

Time (days)	Yield Strength (MPa)	Modulus (GPa)	Elongation (%)	Izod (J/m)
0	44	1.2	> 200	1700
1	60	1.3	16	23
3	61	1.8	16	15
5	51 ^a	1.5	6	18
7	47 ^a	1.5	3	18
13	19 ^a	1.6	0.7	13
21	8 ^a	1.6	0.3	10

^aTensile strength to break.

CONCLUSIONS

The results of this study show that the hydrolysis of the copolyester PCTG 5445 is a zero-order process with respect to molecular weight, at least up to a decrease of about 50%, corresponding to an average of one scission per molecule. Because a zero-order hydrolytic reaction was observed also in a number of other polymers a general conclusion seems to emerge: The hydrolysis of ester and carbonate linkages in solid polymeric materials exposed to a humid environment is initially a zero-order process, and since water diffusion is usually fast, the hydrolysis rate of a given polymer at a given relative humidity is primarily a function of temperature.

The hydrolysis of PCTG 5445 is accompanied by a loss in mechanical properties. When the hydrolysis is conducted above the polymer's T_g , as was the case in this study, embrittlement occurs fast because of the combined adverse effects of crystallization and hydrolysis. Particularly intriguing was the impact behavior (notch Izod) of PCTG. The impact strength data were rather sensitive to the slightest development of crystallinity (sometimes not visible), exhibiting wide scatter and suggesting the possible existence of a ductile-brittle transition region.

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References

1. S. B. Lin and J. L. Koenig, *J. Polym. Sci.: Polym. Symp.*, **71**, 121 (1984).
2. A. Golovoy, M. F. Cheung, and H. van Oene, *J. Polym. Eng. Sci.*, **28**, 200 (1988).
3. A. Golovoy and M. F. Cheung, *J. Appl. Polym. Sci.*, **35**, 1511 (1988).
4. A. Golovoy, M. F. Cheung, and M. Zinbo, *J. Appl. Polym. Sci.*, **35**, 2001 (1988).
5. R. J. Gardner and J. R. Martin, *SPE 36th ANTEC*, 328 (1978).
6. P. G. Kelleher, R. P. Wentz, and D. R. Falcone, *SPE 39th ANTEC*, 95 (1981).
7. E. A. Joseph, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **27**, 4807 (1982).
8. B. Wunderlich, *Macromolecular Physics*, Academic, New York, 1976, Vol. 2, Chap. 6.
9. M. Yagpharov, *J. Thermal Anal.*, **31**, 1073 (1986).
10. D. R. Paul and J. W. Barlow, *ACS, OPRL Prepr.*, **40**, 745 (1979).
11. T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

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