Equilibrium Acid Concentrations in Hydrolyzed Polyesters and Polyester–Polyurethane Elastomers*

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Synopsis

Equilibrium acid concentrations, $[A_e]$, were determined in butylene adipate and caprolactone polyesters, of low molecular weight, and in thermoplastic polyurethane elastomers based on these polyesters. Values of $[A_e]$ of the polyesters at 85°C were 0.7, 1.3, and 3–4 × 10^{-3} mol/g at relative humidities (RH) of 25%, 50%, and 93%, respectively. $[A_e]$ of the thermoplastic elastomers at 85°C were about 3 and 7 × 10^{-4} mol/g at 10% and 25% RH, respectively. Values of $[A_e]$ were not very dependent on temperature at constant RH. Equilibrated thermoplastic elastomers had low molecular weights and poor physical properties. Consequently, equilibration does not set a practical limit on hydrolytic degradation, even at low RH. Equations were developed that described the variation in acid content with time. Rate constants for hydrolysis and esterification increased as RH decreased. Reesterification in the elastomers in the absence of water is too slow to be a useful method of decreasing hydrolytic damage.

INTRODUCTION

Cuddihy[2] aged magnetic tapes at various temperatures and relative humidities (RH) in order to study the polyester–polyurethane binder that holds the magnetic particles on the tape base. The binder was highly crosslinked, so Cuddihy measured the fraction soluble in acetone. This fraction increased if tapes were aged at 100% and 30% RH but decreased if tapes were aged at 11% and 0% RH. Increases in the soluble fraction were attributed to hydrolytic scission of ester groups, thus changing some gel to soluble material. Decreases in the soluble fraction were attributed to esterification reactions between acid and alcohol groups, which incorporated soluble molecules into the gel. Cuddihy concluded that the binder on his tapes should appear stable to hydrolysis at about 24% RH at 20°C because of the dynamic equilibrium between hydrolysis and esterification. Very recently, Bertram and Cuddihy[3] applied another kinetic analysis to Cuddihy's data[2] and now suggest that tapes stored at 18°C and 40% RH should appear stable to hydrolysis because of this equilibrium.

Equilibrations of ester and water with acid and alcohol have been studied before,[4] but specific information is lacking at the lower water contents associated with environmental aging. The equilibration should occur in any polyester, whether it is crosslinked, not crosslinked, or incorporated into a polyurethane. Studies described herein used soluble polyesters of low molecular weight and polyester–polyurethane elastomers at several RH to find out if equilibration

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limits degradation to acceptable values and if it is practical to diminish hydrolytic damage that has occurred by aging polyesters at low RH.

KINETIC CONSIDERATIONS

Here we give preliminary kinetic considerations and derive equations consistent with them. The equilibrium between hydrolysis and esterification is described by the reactions.

$$E + W \underset{k'}{\overset{k}{\rightleftarrows}} A + H \tag{1}$$

where E, W, A, and H represent ester, water, acid, and alcohol, respectively. It is convenient to follow the equilibration by measuring the acid concentration at various times. Concentration units will be mol/g.

Hydrolysis is acid catalyzed[5] and at low [A] obeys the equations[6]

$$(d[A]/dt) = k[E_0][W_0][A] \tag{2}$$

$$\ln([A]/[A_0]) = k[E_0][W_0]t \tag{3}$$

where t is time and the 0 subscripts indicate use of initial concentrations. Plots of $\ln([A]/[A_0])$ vs. t are linear between $[A_0]$, about 10^{-5} mol/g, and [A], equal to about 5×10^{-4} mol/g. Such linearity appears reasonable over this range of [A], because [E] decreases only about 5% from its initial value of about 10^{-2} mol/g, and [W], which was measured in polyester polyurethanes, does not change significantly with hydrolysis.[6] Slopes of the $\ln([A]/[A_0])$ vs t plots are equal to $k[E_0][W_0]$. The values of this product are approximately proportional to RH.[6] $[E_0]$ (mol/g) is just the reciprocal of the molecular weight of the repeating ester unit multiplied by the weight fraction of ester. Hence $k[W_0]$ can be calculated.

Eventually the back reaction becomes important. Then one expects that

$$(d[A]/dt) = k[W][E][A] - k'[A]^2[H] \tag{4}$$

Here the term for the rate of the back reaction includes an $[A]^2$, because the acid catalyst for the forward reaction ought to catalyze the back reaction also. The 1:1 stoichiometry in reaction (1) indicates that $[E] = [E_0] - [A]$ and $[H] = [H_0] + [A]$. The polyesters used were initially diols so that $[H_0]$ for each is twice the reciprocal of its number average molecular weight M_n.

If $k[W] = k[W_0]$ throughout, the only unknown is k'. This can be calculated from the equilibrium acid concentration $[A_e]$ since then $(d[A]/dt) = 0$ and

$$k' = \frac{k[W_0]([E_0] - [A_e])}{[A_e]([H_0] + [A_e])} \tag{5}$$

If similar substitutions are made for [E], [H], and [W] in eq. (4) and the variables are separated, one obtains

$$dt = \frac{d[A]}{[A](-k'[A]^2 - (k[W_0] + k'[H_0])[A] + k[W_0][E_0])} \tag{6}$$

This has the reduced form (dx/xX), where $x = [A]$ and $X = ax^2 + bx + c$. Here $a = -k'$, $b = -(k[W_0] + k'[H_0])$, and $c = k[W_0][E_0]$. After integration

$$t = \left[\frac{1}{2c} \ln \left|\frac{x^2}{X}\right| - \frac{b}{2ac(p-q)} \ln \left|\frac{x-p}{x-q}\right|\right]_{x_0}^{x} \tag{7}$$

Here, p and q are roots of $X = 0$.

Thus, from measurements of $[A_e]$ and the initial rate of acid formation, one can calculate times required to reach definite acid concentrations. It will be seen that calculated and observed times usually agree well at 95%, 50%, and 25% RH in polyesters but that k' increases markedly as RH decreases.

It was found that $[W]$ did depend on $[A]$ in polyesters, particularly at high RH. Some of the apparent variation in k' was eliminated by treating $[W]$ as a variable. Modifications to the equations that accomplish this are developed later.

$[H]$ in polyester polyurethanes is different from values in polyester diols because the isocyanate used to form the urethane does so by reacting with alcohol groups. We calculated $[H_0]$ as follows. M_n of the polyurethanes before any aging was about 20,000,[6] giving about 10^{-4} mol chain ends/g. The initial acid content was about 10^{-5} mol/g. Therefore, initially 10% of the chain ends were acid groups and so presumably the rest were alcohol groups. Consequently, $[H_0]$ for polyester polyurethanes will be taken as equal to 10^{-4} mol/g. Equations (6) and (7) should describe the equilibration of these polymers except at 0% RH. Under that condition there is no forward reaction and the applicable equation is

$$-(d[A]/dt) = k'[A]^2([H_0] + [A]) \tag{8}$$

After integration

$$t = \frac{1}{k'}\left[\frac{1}{[H_0][A]} - \frac{1}{[H_0]^2} \ln\left(\frac{[H_0]+[A]}{[A]}\right)\right]_{[A_0]}^{[A]} \tag{9}$$

EXPERIMENTAL

The materials studied and their $[E_0]$, $[H_0]$, and $[A_0]$ are listed in Table I. Additional data on these materials have been published.[6,7] 63 PBA is designated 63 PTMA in Ref. 6. No catalyst was used in preparing PBA 930. A tin ester catalyst was used to make PBA 1090. The high $[A_0]$ of 71 PCL and 63 PBA were brought about by preaging at high RH.

The polyester diols were aged in vessels sketched in Figure 1. These were of glass, except for a Teflon-glass valve at the top. About 10 g of polyester diol were placed in the inner dish. Preliminary experiments had shown that 2–10 g in the inner dish gave the same rates of acid formation, indicating that reaction was

TABLE I
Materials Studied and Their Initial Properties

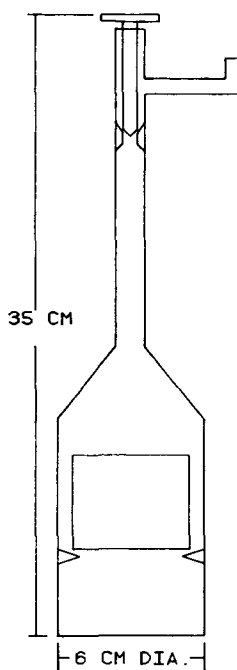| Material	Designation	Concentration (mol/g)		
		$10^3[E_0]$	$10^3[H_0]$	$10^5[A_0]$
Polycaprolactone diol, $M_n = 2000$	PCL 2000	8.77	1.00	0.74
Polyurethane with 71 wt % PCL	71 PCL	6.2	0.1	25.5
Poly(butylene adipate) diol, $M_n = 930$	PBA 930	10	2.15	8.4
Poly(butylene adipate) diol, $M_n = 1090$	PBA 1090	10	1.83	0.42
Polyurethane with 63 wt % PBA	63 PBA	6.3	0.1	35.4

Fig. 1. Equilibration vessel.

not diffusion-controlled. Beneath the inner dish were 50 cm^3 of an aqueous solution of LiCl. Concentrations were used that gave about 95%, 50%, 25% RH. Published data were used to calculate RH.[8] After a brief evacuation to eliminate oxygen, tubes were filled with argon and immersed in an oil bath at 85°C to a level above the bottom of the valve stem. The stem was removed at intervals, and samples of polyester were withdrawn using a preheated pipette.

Acid contents of these samples were measured by titration, as described earlier.[6] Water contents [W] were measured by diluting samples 10-fold with dry tetrahydrofuran and injecting 10-mL portions into a gas chromatograph having a Poropak column kept at 140°C. The height of the water peak was used to determine the water content, by comparison with a calibration which was constructed by injecting water–tetrahydrofuran mixtures of known concentration. This method is not very precise, since deviations between replicate injections averaged about 15%. The dependence of [W] on [A] can be strong so the data were adequate for our purpose.

Equilibration was assumed to have occurred when the acid content became nearly constant. Then the vessel usually was transferred to a 55°C oil bath and additional samples were taken. When equilibration had occurred, the solution of LiCl was removed. Its density was measured to check the concentration, which was changed slightly from the initial value because water is sorbed by the ester and consumed by hydrolysis. Back reactions were studied at 85°C by adding more concentrated LiCl solutions to tubes that had been equilibrated at 95% or 50% RH. Thus equilibrium was approached from both sides at 50% and 25% RH.

Erratic values of [A$_e$] were obtained at 100% RH. Under this condition an

aqueous phase eventually collected in the inner dish, probably because of thermal gradients in the bath. To explore this effect, diols and water in equal weights were stirred together at 60°C and then separated. Evaporation of the water from the aqueous layer left a residue of low molecular weight polyester. About 5% and 1% water soluble materials were found in polycaprolactone diols of M_n 540 and 2000, respectively. The soluble material from the former polyester was redissolved in water and aged at 85°C. It formed acid with a rate constant about three times that found initially for the bulk diol exposed to water vapor only. Therefore, we suspect that if an aqueous liquid phase contacts these polyesters, low molecular weight organic components dissolve in the water, and form acid rapidly. This diffuses into the organic phase, augmenting the acid content there. Gel permeation chromatograms confirmed that it is the low molecular weight components from the polyester diols that are water-soluble. Only a single phase in the inner dish was observed at 95%, 50%, and 25% RH, and so these are the RH for which we report equilibrium data.

Polyester–polyurethanes were aged in sealed glass tubes containing aqueous LiCl solutions giving about 25% and 10% RH. Our interest in the polymers was primarily in their behavior at low RH so equilibration was not attempted at high RH. Reaction at zero RH was studied by pumping on thermostatted samples. Volatiles evolved for several days, as evidence by condensation outside the baths. [A_0] was taken as the value after volatilization appeared to have ended. Molecular weights of some polyester–polyurethanes were determined by gel chromatography, as described before.[6]

RESULTS

Polyesters

The equilibrium acid contents of the polyesters at 85°C are listed in Table II along with the final RH and an indication of whether the results came from a

TABLE II
Equilibration of Polyesters at 85°C

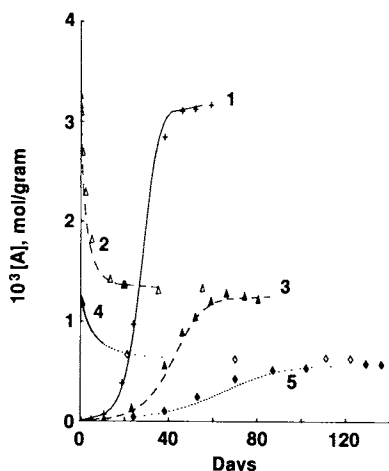| Polyester (Fig.)	RH (%)	F/B	$10^3[A_e]$ (mol/g)	Line	$k[W_0]$ (g/mol·day)	$10^{-4}k'$ (g²/mol²·day)
PCL 2000 (2)	93	F	3.16	1	23.7	1.01
	53	B	1.33	2	13.3	3.19
	50	F	1.25	3	13.0	3.50
	25	B	0.62	4	6.8	5.52
	25	F	0.57	5	6.8	6.23
PBA 930 (3)	93	F	3.95	1	21.8	0.55
	53	B	1.52	2	13.2	2.01
	50	F	1.24	3	12.3	2.57
	25	B	0.62	4	6.0	3.29
	25	F	0.76	5	6.0	2.56
PBA 1090 (4)	93	F	3.98	1	27.0	0.70
	53	B	1.54	2	15.2	2.48
	50	F	1.38	3	14.5	2.82
	25	B	0.67	4	10.5	5.85
	25	F	0.75	5	10.5	5.02

Fig. 2. Equilibration of PCL 2000 at 85°C (+, 1), 93% RH; (▲, 3; △, 2) F and B reactions, 50% and 53% RH; (♦, 5; ◊, 4) F and B reactions, 25% RH. Lines by eq. (7) with the $k[W_0]$ and k' in Table II.

forward (F) or back (B) reaction. Kinetic data are shown in figures whose numbers appear under the listed polyesters. Also listed are line numbers and values of $k[W_0]$ and k' used in calculating each line in these figures by eq. (7). $[E_0]$, $[H_0]$, and $[A_0]$ for forward reactions, are the values in Table I. $[A_0]$ for each back reaction is $[A_e]$ for the previous forward reaction. $k[W_0]$ in back reactions are those in corresponding forward reactions, scaled proportional to RH if RH was slightly different.

The largest $[A_e]$, about 4×10^{-3} mol/g is about 40% of $[E_0]$, so it is worthwhile to use eq. (7), which allows for the change in $[E]$. Each ester group hydrolyzed also represents a chain scission, so that M_n of the polyester can be as low as 250 at equilibrium. $[A_e]$ changes about 4×10^{-5} mol/g for each percent change in RH. $[A_e]$ at 55°C[1] are not very different from those at 85°C, and so the former are not shown here.
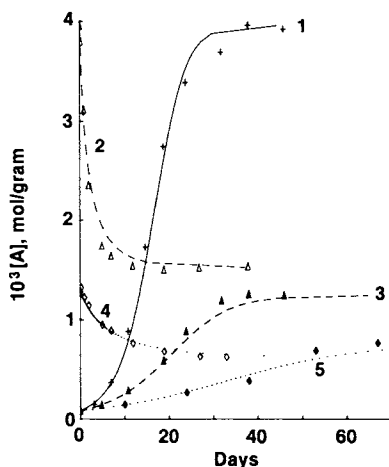

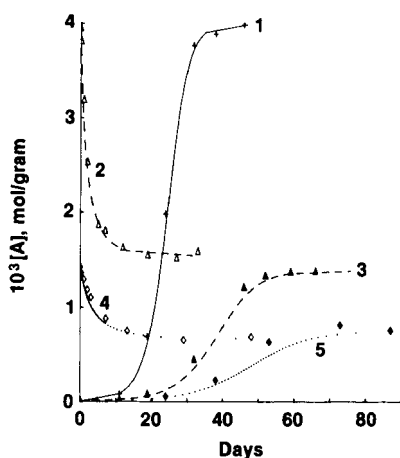Fig. 3. Equilibration of PBA 930 at 85°C. Symbols and lines as in Figure 2.

Fig. 4. Equilibration of PBA 1090 at 85°C. Symbols and lines as in Figure 2.

The titration is such that $[A_e]$ ought to be good to ~1–2% of itself. RH at equilibrium should be known to about 1%. Differences between $[A_e]$ in forward and back reactions, after correction for the small differences in RH, exceed these uncertainties in PBA 930 and PBA 1090 at 50% RH, and in all three polyesters at 25% RH. Causes of these unexpectedly large discrepancies are not known.

Each line in Figures 2–4 is a computer-driven plot of t, $[A]$ that was obtained by using eq. (7) to calculate t at 50 values of $[A]$ between $[A_0]$ and $[A_e]$. The lines are composed of straight segments joining the t, $[A]$. This segmental construction accounts for occasional abrupt changes in slope.

Values of $k\,[W_0]$ are larger in PBA 1090 than in PBA 930, particularly at 25% RH. The esterification catalyst in PBA 1090 may account for the differences. Possible such catalysts are themselves subject to hydrolysis, which would complicate the situation.
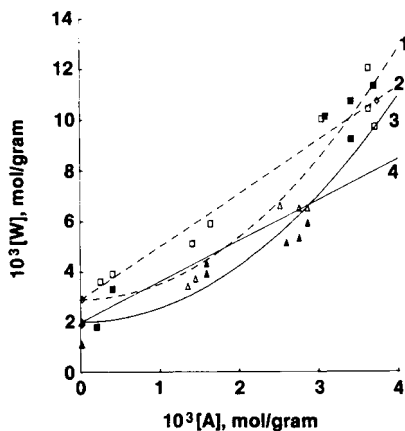

Fig. 5. Water content of polyesters at 55°C and 85°C, as a function of acid content: ($\blacktriangle$, $\blacksquare$) 55°C; ($\triangle$, $\square$) 85°C; ($\blacktriangle$, $\triangle$) PCL 2000; ($\blacksquare$, $\square$) PBA 930 and PBA 1090; (1) $[W] = 614\,[A]^2 + 0.0029$; (2) $[W] = 2.09\,[A] + 0.0029$; (3) $[W] = 555\,[A]^2 + 0.002$; (4) $[W] = 1.61\,[A] + 0.002$.
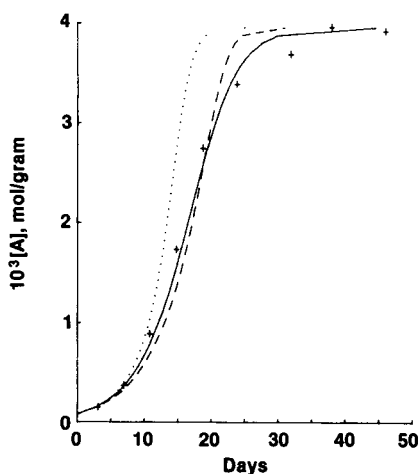
Fig. 6. Equilibration of PBA 930 at 85°C, 93% RH: (+) experimental data; (——) eq. (7), [W] = [W_0]; (·····) eq. (7′), [W] = 2.09 [A] + 0.0029; (- - -) integral of eq. (6″), [W] = 614 [A]^2 + 0.0029.

k' increases by factors of 6–8 for these polyesters as RH decreases from 93% to 25%. This was surprising since [W] is not an explicit factor in the back reaction. Consequently, [W] was determined at various [A] because the observed variation in k' might be caused by changes in k[W] with [A]. Figure 5 is a plot of [W] vs. [A] for results at the 85°C, 93% RH and 55°C, 89% RH. There is about a fourfold increase in water content between [A_0] and [A_e], so that k[W] presumably increases by the same factor. It is convenient to represent the solubility by analytical functions in order to modify eqs. (4)–(7). Quadratic and linear variations are shown in Figure 5, one of each for PCL 2000 and one each for the PBA polyesters.

The water content is almost 20 wt % when [A] = 4 × 10^{-3} mol/g. Therefore, in addition to substituting functions for [W] in eq. (4), one ought to allow for the dilution of ester and hydroxyl by water. This can be done by multiplying E_0 and H_0 by (1–18[W]) because 18[W] represents the weight of water in each gram of polyester and dissolved water. [A] need not be multiplied by this factor because any dissolved water was included in the weight of samples used in the titrations by which [A] was determined.

Let constants in the equations relating [W] and [A] be k'' and [W_0], i.e.: linear variation, [W] = k''[A] + [W_0]; quadratic variation, [W] = k''[A]^2 + [W_0]. If linear variation is correct,

$$k' = \frac{k(k''[A_e] + [W_0])([E_0] - 18[E_0]k''[A_e] - 18[E_0][W_0] - [A_e])}{[A_e]([H_0] - 18[H_0]k''[A_e] - 18[H_0][W_0] + [A_e])} \quad (5')$$

Equations for dt, (6′), and t, (7′), will not be written out because they have the same reduced forms as eqs. (6) and (7), respectively, but with

$$a = -18[E_0]k(k'')^2 - kk'' - k' + 18k'k''[H_0]$$

$$b = kk''[E_0] - 36kk''[E_0][W_0] - k[W_0] - k'[H_0] + 18k'[H_0][W_0]$$
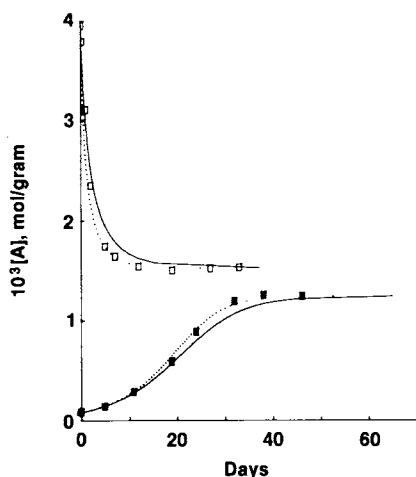
$$c = k[E_0]([W_0] - 18[W_0]^2)$$

Fig. 7. Equilibration of PBA 930 at 85°C, 53% and 50% RH: (■, □) experimental data for F and B reactions; (——) eq. (7), [W] = [W_0]; (·····) eq. (7'), [W] = 0.55 [A] + 6.4 × 10^{-4}.

If quadratic variation is correct,

$$k' = \frac{k(k''[A_e]^2 + [W_0])([E_0] - 18[E_0]k''[A_e]^2 - 18[E_0][W_0] - [A_e])}{([H_0] - 18[H_0]k''[A_e]^2 - 18[H_0][W_0] + [A_e])[A_e]} \quad (5'')$$

$$dt = \frac{d[A]}{Q_5[A]^5 + Q_4[A]^4 + Q_3[A]^3 + Q_2[A]^2 + Q_1[A]} \quad (6'')$$

where

$$Q_5 = -18k(k'')^2[E_0]$$
$$Q_4 = 18k'k''[H_0] - kk''$$
$$Q_3 = kk''[E_0] - 36kk''[E_0][W_0] - k'$$
$$Q_2 = 18k'[H_0][W_0] - k[W_0] - k'[H_0]$$
$$Q_1 = k[E_0][W_0] - 18k[E_0][W_0]^2$$

No attempt was made to integrate eq. (6″) to give an expression in closed form. Instead, a prepackaged trapezoidal integration program[9] was used to calculate t at 50 values of [A] between [A_0] and [A_e].

Figure 6 compares the three calculation methods with one another and with the experimental data for PBA 930 at 93% RH. Linear variation of [W] with [A] gives a more rapid rise of [A] with t than observed. There is about as good agreement between the experimental data and the line with [W] independent of [A] as there is with the line for quadratic variation of [W] with [A].

Water solubilities were also determined at 50% and 25% RH. Quadratic relationships between [W] and [A] did not give as good a fit to kinetics as linear relationships.[1] Therefore, we use only the latter here. Data for the three polyesters at 50% and 25% RH were represented by the equations [W] = 0.55 [A] + 6.4 × 10^{-4} and [W] = 0.17 [A] + 2.5 × 10^{-4}, respectively. Figures 7 and 8 compares the experimental [A], t data for PBA 930 at 50% and 25% RH with values calculated by eqs. (7) and (7'). There is very little difference between results calculated by these equations.
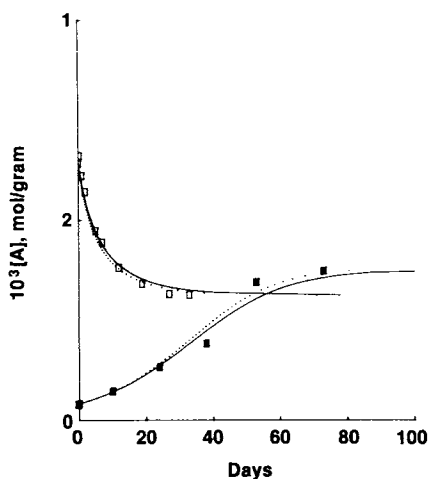
Fig. 8. Equilibration of PBA 930 at 85°C, 25% RH: (■, □) experimental data for F and B reactions; (——) eq. (7), $[W] = [W_0]$; (·····) eq. (7′), $[W] = 0.17 [A] + 2.5 \times 10^{-4}$.

Similar calculations were made for PBA 1090 and PCL 2000. Results are qualitatively similar to those in Figures 6–8.

Table III contains the k and k' that were used in these calculations. Both k and k' increase by factor of 3–4 as RH decreases. Thus allowance for the dependence of $[W]$ on $[A]$ reduces but does not eliminate changes in k' with RH

TABLE III
k and k' with $[W]$ Dependent on $[A]$[a]

Polyester	RH (%)	F/B	$10^{-4}k$	$10^{-4}k'$
			$(g^2/mol^2 \cdot day)$	
PCL 2000	93	F	1.19[b]	3.11[b]
	93	F	1.19	2.96
	53	B	2.08	6.72
	50	F	2.03	7.08
	25	B	2.72	7.82
	25	F	2.72	8.62
PBA 930	93	F	0.75[c]	1.61[c]
	93	F	0.75	1.61
	53	B	2.06	4.55
	50	F	1.92	5.22
	25	B	2.40	4.65
	25	F	2.40	4.65
PBA 1090	93	F	0.93[c]	2.05[c]
	93	F	0.93	1.93
	53	B	2.38	5.67
	50	F	2.27	6.09
	25	B	4.20	8.49
	25	F	4.20	7.56

[a] Except as indicated: $[W] = k''[A] + [W_0]$ where k'' in mol H_2O/mol acid and $[W_0]$ in mol/g are 2.1 and 2.9×10^{-3} at 93% RH, 0.55 and 0.64×10^{-3} at ~50% RH, and 0.17 and 0.25×10^{-3} at 25% RH.

[b] $[W] = k''[A]^2 + [W_0]$ where $k'' = 555$ (mol H_2O/mol acid)^2 and $[W_0] = 2 \times 10^{-3}$ mol/g.

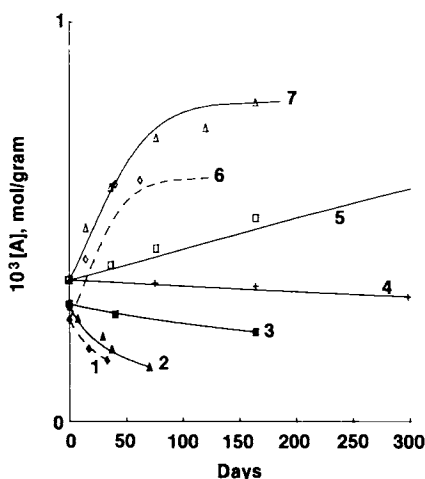[c] $[W] = k''[A]^2 + [W_0]$ where $k'' = 614$ (mol H_2O/mol acid)^2 and $[W_0] = 2.9 \times 10^{-3}$.

Fig. 9. Acid content vs. time in 63 PBA and 71 PCL. (1–4) by eq. (9); (5–7) by eq. (7). ($\blacklozenge$, $\blacktriangle$, $\blacksquare$, $\lozenge$, $\triangle$, $\square$, +) experimental data. ($\blacklozenge$, $\blacktriangle$, $\blacksquare$, +) 0% RH: ($\blacklozenge$) 71 PCL, 85°C; ($\blacktriangle$) 63 PBA, 85°C; ($\blacksquare$) 63 PBA, 55°C; (+) 63 PBA, 30°C. ($\lozenge$, $\triangle$, $\square$) 25% RH: ($\lozenge$) 71 PCL, 85°C; ($\triangle$) 63 PBA, 85°C; ($\square$) 63 PBA, 55°C.

and indicates that k depends on RH. Of course, it must really be the change in [W] with RH that affects k and k'. Later we speculate on how [W] can affect k and k'. Since [W] also depends on [A], k and k' presumably change during reaction, contrary, to all of our equations. Thus the generally good agreement between our kinetic approaches and the experimental data is rather surprising, especially since k is calculated from data at low [A] and k' is calculated from data at high [A].

Polyester–Polyurethanes

Figure 9 shows data obtained with polyester–polyurethanes. Most of the experiments involved 63 PBA because PBA elastomers are used in making tape binder. Lines 1–4 are plots of eq. (9) (0% RH) using k' calculated from the [A_0] found when the rate of weight loss had become negligible and the [A] at the longest time at each temperature. Lines 5–7 are plots of eq. (7) for results obtained at about 25% RH. k [W_0] was calculated by eq. (3) from [A_0] and t, [A] at the first analysis. Lines 5, 6, and 7 lie below these first points because the back reaction is appreciable. Values of the rate constants and [A_e] are listed in Table IV.

These [A_e] are really subjective estimates since [A] never became constant. A value of 8×10^{-4} mol/g for 63 PBA at 25% RH and 85°C seemed reasonable since the rate of increase in [A] had become much less than it was initially. [A_e] = 8×10^{-4} mol/g was also used for 63 PBA at 25% RH and 55°C because values of [A_e] of the polyesters were independent of temperature. Successive values of [A] in 71 PCL were nearly equal to 6×10^{-4} mol/g, and so we chose this value as [A_e]. The values of k [W_0] and k' for 63 PBA at 25% RH, 85°C are less than found for PBA 930 and PBA 1090 but [A_e] for the latter are kept lower by the larger value of [H_0]. Values of k' at 0% RH, 85°C much exceed the values at 25%

TABLE IV
63 PBA and 71 PCL, Constants Used in Calculations

Line	Polymer	Temp (°C)	RH (%)	$10^4[A_e]$ (mol/g)	$k[W_0]$ (g/mol·day)	$10^{-5}k'$ (g²/mol²·day)
1	71 PCL	85	0			2.71
2	63 PBA	85	0			1.93
3	63 PBA	55	0			0.185
4	63 PBA	30	0			0.030
5	63 PBA	55	25	~8	0.438	0.033
6	71 PCL	85	25	~6	5.33	0.688
7	63 PBA	85	25	~8	3.52	0.269

RH. Thus, k' appears to depend on humidity in polyurethanes as well as in polyesters.

M_n was determined for preaged 63 PBA and for samples aged at 0% RH at 85°C for 70 days and at 55°C for 164 days. Respective M_n are 2650, 5350, and 3750. Thus M_n is indeed increasing during aging at 0% RH, and the changes are larger the greater the change in [A]. None of the aged samples could be considered elastomeric since they broke on small extensions. The rate of change in [A] presumably decreases with [A] according to eq. (9) so that it does not seem practical to regenerate elastomers by reversing hydrolysis.

Additional data obtained with 63 PBA and 71 PCL are in Table V. Most of these data are from experiments at about 10% RH. The acid content of 63 PBA increases at ~10%, RH, 85°C but appears to decrease very slightly at 55°C and 35°C. [A] increases slightly at 23% RH, 35°C. Therefore, $[A_e]$ is ~3.5 × 10^{-4} mol/g at ~18% RH, 35°C. The rates of change in [A] are so slow that very precisely determined [A] would be required to locate true equilibrium.

Results listed for 71 PC at ~10% RH, are more erratic but show qualitatively the same behavior as those for 63 PBA, an increase in [A] at 85°C and little change at 55°C and 35°C.

DISCUSSION

To us it appears unlikely that equilibrium limits hydrolysis in a practical sense in thermoplastic elastomers. Values of $[A_e]$ must approach 5 × 10^{-4} mol/g even at 25% RH and probably more than 10^{-3} mol/g at 50% RH. This is much more acid than present normally, indicating that enough scissions should have occurred by reaction 1 so that $M_n[A_e] \sim 1$ mol acid/polymer molecule. Thus $M_n \sim [A_e]^{-1}$ or ~2000 at 25% RH and less at higher RH. Materials of such molecular weights are not elastomeric.

The presence of crosslinks could change this conclusion. Random degradation generates a most probable distribution. Therefore, an M_n of 1000–2000 means that the weight average molecular weight M_w is 2000–4000. One crosslinked unit per weight average molecule represents the gel point so that a polymer with an initial crosslink density of 2.5–5 × 10^{-4} mol/g presumably would just have gel at $[A_e] = 5 \times 10^{-4}$ to 10^{-3} mol/g. Somewhat more crosslinks might be desirable, presumably, but a practical upper limit would be to crosslink all the urethane groups, giving about one crosslinked unit in 10 ester groups.

TABLE V
Aging of Preaged 63 PBA and 71 PCL at Low RH

days	10⁴[A] (mol/g)			
	12% RH, 85°C	10% RH, 55°C	12% RH, 35°C	23% RH, 35°C
		63 PBA		
0	3.54	3.54	3.54	3.54
14	3.84			
36	3.93	3.41		
76	4.40	3.43		3.57
120	4.86			
164	5.33	3.39	3.38	3.68
298			3.35	3.84
		71 PCL		
0	2.55	2.55	2.55	
14	3.21			
38	4.37	3.20	2.60	
58	3.51			
105		3.33		
123			2.81	
158		2.89		
176			2.67	
252		2.96	2.56	

The table's caption reads: $10^4[A]$ (mol/g).

There might also be a kinetic factor giving a lower $[A_e]$ in a gel than in an un-crosslinked polymer. Acid and hydroxyl groups must separate by diffusion for a hydrolytic scission to be effective. The separation is limited in a gel because the diffusing ends are ultimately attached to the network. Such ends can be considered as somewhat like geminate pairs and would be subject to more rapid recombination than in uncrosslinked elastomers. This would reduce $[A_e]$ by increasing the rate of the back reaction. An effect such as this ought to be more significant if the crosslinking density is high.

Hydrophobic gelling agents could reduce $[A_e]$ simply by reducing the solubility of water in polymers.

The decreases in k and k' as [W] increases are interesting. Esterification has been reviewed quite recently, but little mention was made of hydrolysis.[10] The esterification process in bulk media at low [A] and [H] is usually third order overall, first order in alcohol, and second order in acid.[10] The mechanism is thought to be dimerization of two acid groups to form an associated ion pair, which reacts slowly with the alcohol. The rate constant k' is the product of the equilibrium constant for formation of the ion pair and the rate constant for its slow reaction. Increases in [W] could decrease k' by decreasing either of these constants by solvating any of the participating species.

Another review contains much more material on hydrolysis but self-catalyzed hydrolysis is not mentioned.[11] Frequently the rate of mineral-acid-catalyzed hydrolysis is first order in H^+ and first order in ester. The order with respect to water is uncertain, with workers finding first order in some systems and second order in others. First or second order in [W] implies that our k should be independent of [W] or should increase with [W]. Instead k decreases as [W] increases. The mechanism of most mineral-acid-catalyzed hydrolyses is written as addition of water to a protonated ester which decomposes to alcohol and carboxylic acid.

In our system the concentration of protons is small so that other intermediates might be involved. Our finding seems to imply that additional water interfers with the formation or decomposition of whatever the intermediates are.

CONCLUSIONS

Equilibrium acid contents are similar in polyesters of low molecular weight and in polyester–polyurethane elastomers made with the same polyesters. Equilibration does not set a practical limit on hydrolysis in such polyurethanes but might do so in highly crosslinked systems. Reesterification at low relative humidity is too slow to be a useful means of regenerating polyester polyurethanes.

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