Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Degradation Studies of Polyethylene Terephthalate

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The rates of hydrolysis, oxidation, and thermal degradation of polyethylene terephthalate were studied as functions of temperature, relative humidity, and film thickness. The rate of hydrolysis was found to be very much faster than the rates of the other two reactions. A relation between extent of chemical degradation and physical degradation has been established, and the effect of both on electrical properties is shown. Using these data, the time required for the polymer to reach a given degree of degradation at any chosen temperature and relative humidity can be estimated.

The relation between extent of chemical degradation and time was established through the use of chemical reaction rate equations. This information was then applied with the aid of the Arrhenius equation to relate extent of degradation to both time and temperature. The effect of chemical degradation on physical properties such as tensile strength, elongation, and fold endurance was then determined. The effect on electrical properties such as dielectric breakdown strength, insulation resistance, and dielectric constant and dielectric loss was also studied. Having completed these tests, the physical and electrical durability of the material was estimated by using the chemical durability as the time parameter.

Polyethylene terephthalate is a synthetic polymer which in recent years was introduced in the electrical industry as insulating film or sheet and in the textile industry as fiber. It is made in this country by the Du Pont Co. and marketed in film form under the trade name Mylar and in fiber form as Dacron.

As there is relatively little information available on the service life of these materials because of their newness, this study was made to observe the chemical reactions likely to occur during service which would make them degrade. Accelerated tests of durability under conditions comparable to actual service temperatures and humidities were made. Changes in physical and electrical properties under these same conditions were measured and related to the extent of degradation. Using these data, reliable estimates of the life of the material in actual use can be made.

The most prevalent agents of degradation of this polymer are moisture, oxygen, heat, and light. The effects of the first three on the deterioration of polyethylene terephthalate are discussed here, but the effects of light have been omitted. Polyethylene terephthalate is an ester, hence water can react with it by breaking the ester links in the chain.

Various authors have stated (*2*, *9*, *12*) that this polymer is unusually resistant to hydrolysis, but no measurements of the rate of the reaction are presented which indicate the durability of polymer exposed to moisture. There are, however, several good papers on oxidation and thermal degradation. The mechanism of thermal degradation of polyethylene terephthalate was studied by Pohl (*7*), and a detailed study of both oxidation and thermal degradation is reported by Marshall and Todd (*6*). They studied the behavior of the polymer at temperatures above its melting point but obtained sufficient kinetic data to enable the rates for these reactions to be calculated at temperatures which might be encountered in service. These authors find that thermal and oxidation reactions seem to be initiated at the ester links. However, the rates of these reactions (*6*) are very much smaller than the rate of hydrolysis determined in this study. Consequently, hydrolysis may be expected to be a much larger factor in the deterioration of the polymer than the other two.

The early stages of degradation are of prime importance in determining useful life. Because the molecular weight of the polymer changes rapidly in the early stages of hydrolytic degradation, it was used to determine the extent of degradation. This method is admirably suited to a study of degradation by hydrolysis, because in this reaction only scission at ester links can occur. Therefore, a direct quantitative relation between number average molecular weight and extent of hydrolysis can be derived and used to measure the rate of reaction. Once the reaction rates are established, the activation energy of the process can be determined and the rate at which the reaction will proceed at any chosen temperature can be calculated. Thermal and oxidative degradation of polyethylene terephthalate have also been followed through change in molecular weight (*6*).

To determine the relation between changes in physical and electrical properties of the polymer and changes in molecular weight caused by degradation, test specimens were exposed to several conditions of temperature and humidity for various periods of time. Tensile strength and modulus were measured, and some tests of fold endurance were made. In addition, the density of degraded samples was measured, and information on water vapor transmission was obtained. The dielectric breakdown strength of exposed

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0.5-mil film samples and the insulation resistance, dielectric constant, and dielectric loss of 10-mil sheet samples were also determined.

Several other experiments performed involved hydrolysis under conditions which, though unusual, might be encountered occasionally in service: measurements of rate of hydrolysis at pH 2.0, rate of hydrolysis of stretched film, and rate of alcoholysis in butyl alcohol. The latter is believed similar in mechanism to hydrolysis and provides some comparison of the reactivity of the polymer with organic hydroxyl compounds and with water.

MATERIALS AND EXPERIMENTAL METHODS

Materials tested were:

Mylar film, grade C, 0.5 mil thick. This is representative of the film produced for capacitor insulation at the Circleville, Ohio, plant of the Du Pont Co.

Mylar sheet, grade A, 10.0 mils thick, also produced at Circleville. It is a general-purpose grade.

Dacron yarn, Type 5100. This is a high tenacity, brignt grade of yarn of 1100 denier manufactured at Du Pont's Kinston, N. C., plant. Finishing compounds on the yarn were removed by thorough extraction with petroleum ether and distilled water.

Strips of the films and sheets and skeins of yarn were exposed to air in ovens at 99°, 90°, 82°, 71°, 60°, and 50° C. Other samples were immersed in water at those temperatures, corresponding to 100% relative humidity (RH). At most of these temperatures, samples were also exposed to relative humidities of 95, 75, 50, and 20%. These were maintained in closed glass vessels containing a saturated solution of potassium sulfate for 95% RH, saturated sodium chloride solution for 75% RH, a solution of about 46% sulfuric acid for 50% RH, and a solution of about 62% sulfuric acid for 20% RH. The samples of polymer were suspended above these solutions.

Samples of each of the various materials were removed from test periodically, and their relative viscosity was measured. Briefly, a weighed sample is dissolved in a volume of solvent (60% phenol and 40% tetrachloroethane) to yield a concentration of 0.62 gram per 100 ml. The efflux time of the solution is determined in a capillary-type viscometer, and this is divided by the efflux time of the solvent to obtain the relative viscosity, η_r. The change in molecular weight of a sample exposed to hydrolysis can be calculated by using the relative viscosity of the polymer before and after exposure.

Relative viscosity is related to the intrinsic viscosity, $[\eta]$, in the following way (*1*):

$$\frac{\eta_{r-1}}{C} = [\eta] + k'[\eta]^2 C \qquad (1)$$

and

$$\frac{\ln \eta_r}{C} = [\eta] - \beta [\eta]^2 C \qquad (2)$$

where C is the concentration of the polymer in solution expressed as grams per 100 ml., k' and β are constants, and $k' + \beta = 0.5$.

Subtracting Equation 2 from 1 and solving for $[\eta]$

$$[\eta] = \left(\frac{\eta_{r-1} - \ln \eta_r}{(k' + \beta)C^2}\right)^{1/2} \qquad (3)$$

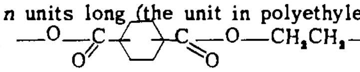
The concentration used in all these viscosity determinations is 0.62 gram per 100 ml., so

$$[\eta] = \left(\frac{\eta_{r-1} - \ln \eta_r}{0.192}\right)^{1/2} \qquad (3a)$$

The intrinsic viscosity of a polymer is related to its molecular weight, *M*, by

$$[\eta] = K M^a \qquad (4)$$

where *K* and *a* are constants which must be determined experimentally for each polymer-solvent system. One method commonly employed is to determine by osmometry the molecular weights of several samples of the same type polymer having different chain lengths. The intrinsic viscosity of the samples is also determined, and *K* and *a* are obtained by plotting log $[\eta]$ against log *M*. Molecular weight determined in this manner is the number average molecular weight—the molecule of average length in the whole distribution of chain lengths in the sample.

The extent of hydrolysis of the polymer is related to change in the number average molecular weight as follows. A polymer chain *n* units long (the unit in polyethylene terephthalate being ) reacts with one molecule of water. This divides the chain into two sections with an average length of $n/2$. If it reacts with two molecules of water, it will divide into three chains having an average length of $n/3$. The general case may be stated thus: After hydrolysis the length of the average molecular chain will be n/No. of H_2O molecules reacted + 1. The molecular weight of one unit is 192. Hence if the average molecular weight of polymer before hydrolysis M_0 equals $192n$, and the average after hydrolysis M_t equals $192n$/No. of moles of H_2O reacted + 1, then

$$\frac{M_0}{M_t} = \frac{192n\ (\text{moles } H_2O + 1)}{192n}$$

From Equation 4

$$\frac{M_0}{M_t} = \left(\frac{[\eta_0]}{[\eta_t]}\right)^{\frac{1}{a}}$$

and it follows

$$\left(\frac{[\eta_0]}{[\eta_t]}\right)^{\frac{1}{a}} - 1 = x \qquad (5)$$

where *x* is the number of moles of water which have reacted with one mole of polymer. Because one ester link is broken by each reacting water molecule, *x* is also the number of moles of ester links destroyed per mole of polymer. There are two ester links in each unit except for the terminal groups, so that in a chain *n* units long there are $2(n-1)$ ester links. If *n* is the average chain length of a sample of polymer, the initial concentration of ester links may be expressed as $2(n-1)$ and the concentration after hydrolysis as $2(n-1) - x$. This assumes that scission of ester links is random, and that the proper distribution of molecular sizes to keep Equation 4 valid is maintained.

The rate of hydrolysis at some constant temperature is obtained from

$$\frac{dx}{dt} = k(A - x)(B - x)$$

in which *k* is the reaction rate coefficient for that temperature, *A* and *B* are the initial molar concentrations of the two reactants, ester links and water, respectively, and *x* is the number of moles of each reactant which has reacted in time *t*. In these experiments the concentration of water remained essentially undiminished throughout the entire period of the reaction. When polymer was exposed to liquid water, the amount of the latter greatly exceeded the amount of polymer; and when exposed to humid atmosphere, the water vapor as it reacted was replenished from the reservoir of salt solution. Consequently there was a reaction of the first order with the water term constant, and it can be written

$$\frac{dx}{dt} = k_1(A - x)$$

where

$$k_1 = kB$$

When integrated this yields

$$\log \frac{A}{A-x} = k_1 t \qquad (6)$$

Though the water term is constant, the concentration of water which is different for the different humidities appears in k_1.

It is now necessary to obtain values for the exponent a in Equation 4 and for A in Equation 6. The values of exponent a found in the literature differed widely. Marshall and Todd (*6*) report $a = 0.73$; Keller, Lester, and Morgan (*3*) give data from which a can be calculated as $a = 1.09$; and Kitson (*4*) gave data which yielded $a = 0.48$. All of these values were obtained from plots of log $[\eta]$ vs. log M where M was determined by osmometry. In this study the correct values for the molecular weight and exponent a were determined by hydrolysis of 10-gram samples of 0.5-mil film at 130° C. The extent of hydrolysis was limited, so that a negligible amount of water-soluble products formed. The samples were weighed before and after hydrolysis, and the gain in weight represented the addition of the elements of water to the polymer through hydrolysis. Their intrinsic viscosities were also measured. The gain in weight is related to the molecular weight of the polymer in this way:

$$x = \frac{\text{moles water reacted}}{\text{mole polymer}} = \frac{W}{18} \times \frac{M_o}{100}$$

where W is per cent of gain in weight and M_o the initial molecular weight of the polymer.

From Equation 5

$$x = \left(\frac{[\eta_o]}{[\eta_t]}\right)^{\frac{1}{a}} - 1 = \frac{W M_o}{1800}$$

This equation contains two unknowns, a and M_o, and as such cannot be solved. However, the three different values of a given in the literature were substituted and x was plotted against W as shown in Figure 1. These data and calculated values of M_o are:

No. Hours Hydrolyzed at 130°C.	Weight Gain, %	$[\eta]$
0		0.581
24	0.156	0.306
36	0.318	0.229
48	0.426	0.188

when	$a = 0.48$	$M_o = 35{,}400$
	0.73	15,400
	1.09	8,200

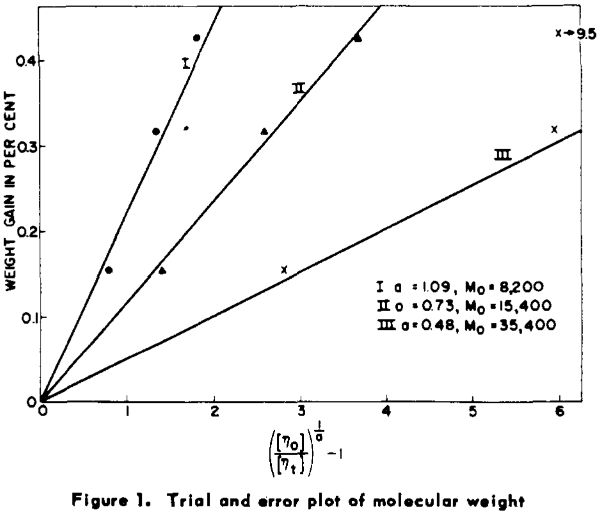


Figure 1. Trial and error plot of molecular weight

The value of M_o of 15,400 is close to the molecular weight reported by Du Pont and (*3,6*) for $[\eta] = 0.58$. For these calculations the values were rounded off to 15,000 for 0.5-mil film and $1/a = 1.35$ was used. The good straight-line fit of the points to curve 2 in Figure 1 supports the assumption of maintenance of proper distribution of molecular sizes during hydrolysis.

A chain of 15,000 molecular weight contains 154 ester links. This is the value of A in Equation 6 which has been used for the film. The intrinsic viscosity of the 10-mil sheet indicates that its molecular weight is about 16,000, and $A = 164$. Similarly, the molecular weight of Dacron is found to be 15,600, and $A = 160$.

The change in molecular weight measures the extent of the reaction, and this together with the time of exposure gives the rate of reaction. From the rate of reaction at several different temperatures, the energy of activation of the process and the reaction rate at any given temperature can be determined.

RESULTS AND DISCUSSION

Reaction rate data for 0.5-mil Mylar film undergoing hydrolysis are given in Tables I through V and Figures 2 through 6. Many of the rate curves in the figures show an abrupt change in slope. At first sight this suggests that the reaction may be autocatalytic and that the curves may be exponential in form. However, careful consideration of all of the data indicates that it is more likely that the curves comprise two different and distinct slopes or rates. Within experimental error, two straight lines can be fitted, and for a given type sample, the change in slope occurs at about the same level of degradation. Also at this point, the samples undergo marked changes in physical properties, becoming brittle and opaque. As degradation proceeds, the density of the polymer increases as shown in Table VI. This indicates that the crystalline content increases (*5*). It also has been shown by Thompson and Woods (*11*) that as the crystallinity of polyethylene terephthalate increases, voids appear, and at about 60% crystallinity there is an

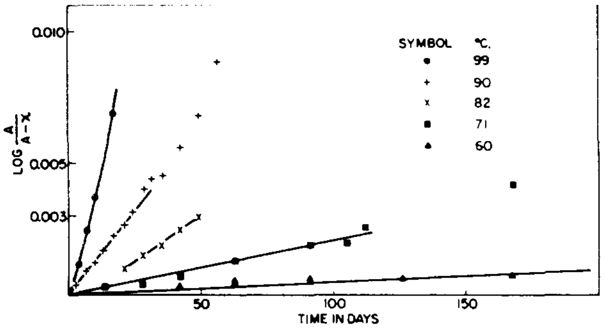


Figure 2. Rate of hydrolysis of 0.5-mil Mylar film at 100% relative humidity

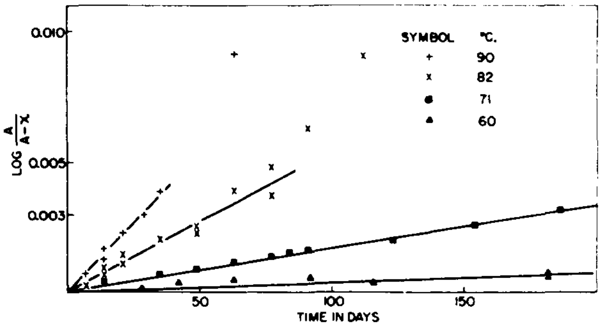


Figure 3. Rate of hydrolysis of 0.5-mil Mylar film at 95% relative humidity

Table I. Rate of Degradation of 0.5-Mil Mylar Film

(100% relative humidity)

T, °C.	Slope	Time, Days t	Viscosity		Moles H_2O Reacted, x	$\text{Log}\,\frac{A}{A-x}$
			Relative, ηr	Intrinsic, $[\eta]$		
130	3.906×10^{-3}	0.0	1.406			
		0.5	1.269	0.3995	0.6600	0.0018652
		1.0	1.201	0.3045	1.394	0.0039493
		1.5	1.148	0.2276	2.546	0.0072398
		2.0	1.121	0.1876	3.462	0.0098745
99	3.528×10^{-4}	0	1.406			
		4	1.307	0.4512	0.4035	0.0011394
		7	1.245	0.3663	0.8607	0.0024340
		10	1.208	0.3137	1.2927	0.0036609
		17	1.148	0.2329	2.4273	0.0068997
90	1.291×10^{-4}	0	1.406			
		3	1.365	0.5280	0.1352	0.0003812
		7	1.323	0.4726	0.3186	0.0008994
		10	1.304	0.4472	0.4205	0.0011874
		13	1.278	0.4116	0.5889	0.0016636
		17	1.253	0.3775	0.7855	0.0022209
		21	1.237	0.3548	0.9416	0.0026635
		24	1.221	0.3323	1.1211	0.0031730
		28	1.199	0.3012	1.4220	0.0040289
		31	1.190	0.2879	1.5743	0.0044624
		35	1.188	0.2851	1.6082	0.0045591
		42	1.169	0.2585	1.9772	0.0056118
		49	1.153	0.2343	2.3996	0.0068202
		56	1.132	0.2037	3.1067	0.0088509
82	6.982×10^{-5}[a]	21	1.316	0.4632	0.3588	0.0010129
		28	1.287	0.4239	0.5316	0.0015018
		35	1.269	0.3993	0.6603	0.0018661
		42	1.243	0.3633	0.8862	0.0025065
		49	1.228	0.3423	0.0441	0.0029544
71	2.075×10^{-5}	0	1.406			
		14	1.371	0.5363	0.1117	0.0003152
		28	1.361	0.5331	0.1496	0.0004219
		42	1.338	0.4924	0.2474	0.0006982
		63	1.296	0.4361	0.4696	0.0013264
		63	1.298	0.4390	0.4565	0.0012892
		91	1.266	0.3950	0.6797	0.0019201
		105	1.264	0.3923	0.6953	0.0019650
		112	1.239	0.3578	0.9195	0.0026010
		168	1.196	0.2968	1.4706	0.0041669
60	4.549×10^{-6}	0	1.406			
		42	1.370	0.5348	0.1158	0.0003265
		63	1.350	0.5084	0.1957	0.0005520
		63	1.356	0.5165	0.1694	0.0004790
		91	1.344	0.5003	0.2209	0.0006232
		126	1.342	0.4976	0.2300	0.0006493
		168	1.333	0.4861	0.2693	0.0007603
		300	1.309	0.4537	0.3967	0.0012874
		300	1.312	0.4578	0.3800	0.0012334

[a] Samples exposed to 80°C. for first 3 weeks and then to 82°C. thereafter. Slope is rate during 82° exposure only.

abrupt decrease in the density of the amorphous part of the polymer. This is attributed to the formation of voids which suggests that cohesive forces within the amorphous region may be great enough to inhibit void formation until a considerable amount of internal stress builds up through crystal formation, whereupon voids and cracks suddenly appear and surface area is increased. This could explain an abrupt rather than a gradual change in the rate of hydrolysis. Moreover, the change in slope is more pronounced in 10-mil sheet than in 0.5-mil film. This difference would be expected, because at the outset their surface-volume ratio is 1 to 20, and increasing the surface area in the manner described could be expected to reduce this ratio.

The first part of the rate curves, that of lower slope, is the region of greatest practical interest in this study. Beyond this, the tensile and flexural strength of the specimens have almost vanished. Accordingly, to determine rates for this purpose, only those points up to this critical degree of degradation were used. This point of degradation for 0.5-mil film was taken as $[\eta] = 0.3042$. The dash line in the tables is the line of demarcation. A best fit of the data was determined by the method of least squares with the curve made to pass through the origin. The slopes of these lines are given by the expression

$$\frac{\Sigma\, t \log \dfrac{A}{A - x}}{\Sigma\, t^2}$$

These slopes were used in the Arrhenius equation to determine the activation energy of the process.

In this equation

$$k_1 = C\, e^{-E/RT}$$

where k_1 is the coefficient from Equation 6,-the slope of the rate curve.

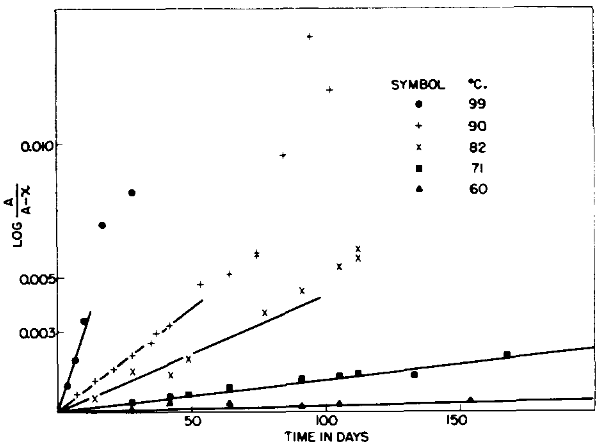


Figure 4. Rate of hydrolysis of 0.5-mil Mylar film at 75% relative humidity

C is a constant which includes a variety of physical factors whose values are peculiar to each reaction.

E is the activation energy. This is the minimum energy which a pair of colliding molecules must possess in order for reaction to take place. It is usually expressed on a molar basis,–i.e., kilocalories per mole.

R is the gas constant. Its value is nearly 2.0 calories per °C. per mole.

T is the absolute temperature.

The activation energy is most easily extracted from the equation in the form

$$\log k_1 = \log C - \frac{E}{2.303R} \times \frac{1}{T}$$

The activation energy of the hydrolysis of 0.5-mil film was determined for each humidity by plotting log k_1 against $1/T$. The slope of this line, $E/2.303R$, was obtained by the method of least squares. The curves for different relative humidities are shown in Figure 7. The activation energy is very nearly the same for all conditions, and a

Table II. Rate of Degradation of 0.5-Mil Mylar Film

(95% relative humidity)

T, °C.	Slope	Time, Days, t	Viscosity Relative, ηr	Viscosity Intrinsic, $[\eta]$	Moles H_2O Reacted, x	Log $\frac{A}{A-x}$
90	1.079×10^{-4}	0	1.406			
		7	1.338	0.4924	0.2473	0.0006978
		14	1.277	0.4098	0.5948	0.0016805
		14	1.299	0.4402	0.4512	0.0012741
		21	1.251	0.3742	0.8081	0.0022849
		29	1.226	0.3391	1.0639	0.0030094
		35	1.202	0.3055	1.3762	0.0038985
		63	1.129	0.1998	3.2153	0.0091635
82	5.521×10^{-5}	0	1.406			
		7	1.354	0.5135	0.1787	0.0002219
		14	1.325	0.4748	0.3103	0.0008759
		14	1.343	0.4987	0.2261	0.0006380
		21	1.293	0.4316	0.4903	0.0013849
		21	1.310	0.4546	0.3895	0.0011000
		35	1.263	0.3909	0.7036	0.0019888
		49	1.243	0.3628	0.8841	0.0025005
		49	1.236	0.3534	0.9520	0.0022611
		63	1.202	0.3055	1.3844	0.0039217
		77	1.183	0.2779	1.7087	0.0048457
		77	1.205	0.3113	1.3234	0.0037483
		91	1.159	0.2432	2.2328	0.0063428
		112	1.129	0.1998	3.2153	0.0091635
		112	1.130	0.2010	3.1813	0.0090657
71	1.739×10^{-5}	0	1.406			
		14	1.362	0.5240	0.1505	0.0004246
		35	1.336	0.4898	0.2606	0.0007355
		35	1.337	0.4908	0.2559	0.0007221
		49	1.324	0.4737	0.3177	0.0008967
		63	1.306	0.4496	0.4145	0.0011706
		77	1.291	0.4287	0.5059	0.0014291
		84	1.284	0.4198	0.5528	0.0015620
		91	1.279	0.4129	0.5880	0.0016611
		123	1.262	0.3896	0.7186	0.0020312
		154	1.237	0.3548	0.9416	0.0026635
		154	1.241	0.3606	0.9052	0.0025604
		186	1.221	0.3320	1.1305	0.0031997
		212	1.196	0.2976	1.4710	0.0041682
60	4.173×10^{-6}	0	1.406			
		28	1.389	0.5595	0.0543	0.0001533
		42	1.365	0.5280	0.1352	0.0003816
		63	1.357	0.5176	0.1700	0.0004797
		92	1.348	0.5054	0.2070	0.0005842
		126	1.360	0.5215	0.1579	0.0004454
		182	1.335	0.4885	0.2652	0.0007485
		182	1.341	0.4964	0.2376	0.0006805
		210	1.335	0.4885	0.2652	0.0007485
		300	1.307	0.4511		0.0013261
		300	1.313	0.4593		0.0012160

Table III. Rate of Degradation of 0.5-Mil Mylar Film

(75% relative humidity)

T, °C.	Slope	Time, Days, t	Viscosity: Relative, ηr	Viscosity: Intrinsic, $[\eta]$	Moles H_2O Reacted, x	Log $\frac{A}{A-x}$
99	$3.111 \times 10^{-4\,a}$	0	1.406			
		4	1.317	0.4647	0.3533	0.0009973
		7	1.267	0.3962	0.6770	0.0019136
		10	1.215	0.3236	1.1988	0.0033943
		17	1.151	0.2322	2.4680	0.0070163
		28	1.138	0.2124	2.8930	0.0082360
		39	1.080	0.1245	7.0070	0.0202241
		39	1.081	0.1269	6.8850	0.0198637
		55	1.071	0.1114	8.3030	0.0240701
90	7.731×10^{-5}	0	1.406			
		7	1.341	0.4966	0.2376	0.0006805
		14	1.306	0.4496	0.4142	0.0011697
		21	1.282	0.4172	0.5667	0.0016009
		28	1.257	0.3829	0.7574	0.0021409
		35	1.240	0.3592	0.9152	0.0025885
		37	1.228	0.3422	1.0451	0.0029576
		42	1.220	0.3306	1.1425	0.0032338
		53	1.184	0.2796	1.6790	0.0047611
		64	1.178	0.2714	1.7950	0.0050917
		74	1.167	0.2551	2.0410	0.0057942
		74	1.165	0.2522	2.0840	0.0059171
		84	1.126	0.1945	3.3800	0.0096382
		94	1.100	0.1562	4.8950	0.0140284
		102	1.110	0.1711	4.2130	0.0120464
82	4.457×10^{-5}	0	1.406			
		14	1.352	0.5110	0.1902	0.0005369
		28	1.286	0.4229	0.5391	0.0015320
		42	1.294	0.4337	0.4867	0.0013745
		49	1.262	0.3896	0.7187	0.0020316
		77	1.206	0.3113	1.3122	0.0037164
		91	1.190	0.2879	1.5820	0.0044844
		105	1.173	0.2634	1.9000	0.0053916
		112	1.168	0.2565	2.0160	0.0057231
		112	1.163	0.2494	2.1330	0.0060573
71	1.2125×10^{-5}	0	1.406			
		28	1.363	0.5254	0.1468	0.0004141
		42	1.350	0.5084	0.1983	0.0005594
		49	1.346	0.5031	0.2158	0.0006089
		64	1.320	0.4687	0.3373	0.0009522
		64	1.320	0.4687	0.3373	0.0009522
		91	1.300	0.4414	0.4502	0.0012715
		105	1.294	0.4335	0.4867	0.0013745
		112	1.288	0.4258	0.5257	0.0014849
		133	1.293	0.4322	0.4931	0.0013927
		168	1.259	0.3855	0.7408	0.0020943
60	2.881×10^{-6}	0	1.406			
		28	1.394	0.5658	0.0379	0.0001069
		42	1.372	0.5372	0.1134	0.0003200
		64	1.373	0.5385	0.1097	0.0003095
		64	1.375	0.5412	0.1023	0.0002887
		91	1.380	0.5477	0.0838	0.0002362
		105	1.368	0.5320	0.1283	0.0003621
		154	1.362	0.5241	0.1505	0.0004246
		300	1.341	0.4965	0.2376	0.0007708
		300	1.334	0.4871	0.2699	0.0008754

[a] Considerable condensation of moisture on these samples because of temperature fluctuations. Hence this slope is probably too high.

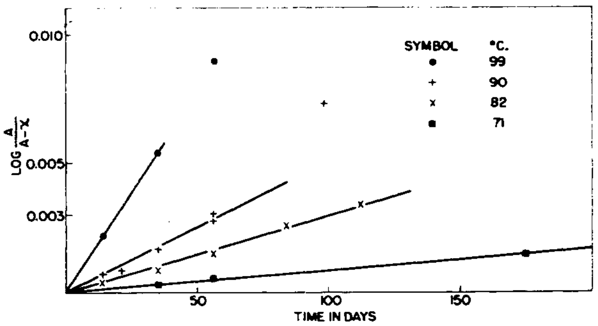


Figure 5. Rate of hydrolysis of 0.5-mil Mylar film at 50% relative humidity

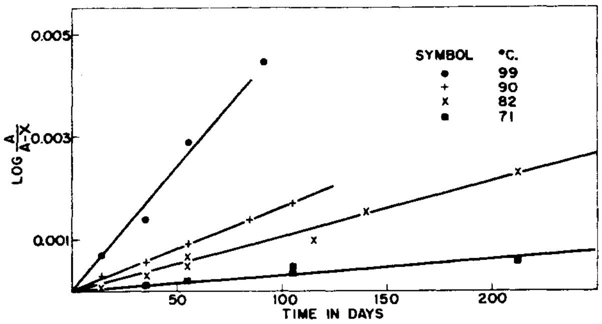


Figure 6. Rate of hydrolysis of 0.5-mil Mylar film at 20% relative humidity

Table IV. Rate of Degradation of 0.5-Mil Mylar Film

(50% relative humidity)

T, °C.	Slope	Time, Days t	Viscosity		Moles H_2O Reacted, x	$\log \frac{A}{A-x}$
			Relative, ηr	Intrinsic, $[\eta]$		
99	1.560×10^{-4}	0	1.406			
		14	1.253	0.3775	0.7840	0.0022166
		35	1.173	0.2643	1.9000	0.0053911
		56	1.131	0.2023	3.1590	0.0090015
		91	1.090	0.1404	5.808	0.0166958
90	5.129×10^{-5}	0	1.406			
		14	1.337	0.4911	0.2559	0.0007221
		21	1.325	0.4753	0.3129	0.0008832
		35	1.276	0.4085	0.6098	0.0017204
		56	1.225	0.3376	1.0826	0.0030640
		56	1.233	0.3493	0.9894	0.0027990
		98	1.147	0.2257	2.588	0.0073603
82	3.005×10^{-5}	0	1.406			
		14	1.364	0.5267	0.1431	0.0004037
		35	1.326	0.4766	0.3080	0.0008694
		56	1.286	0.4224	0.5391	0.0015230
		84	1.239	0.3577	0.9260	0.0026191
		112	1.214	0.3228	1.2125	0.0034329
		212	1.119	0.1846	3.7070	0.0105820
71	9.000×10^{-6}	0	1.406			
		35	1.373	0.5385	0.1096	0.0003091
		56	1.352	0.5110	0.1902	0.0005369
		56	1.348	0.5057	0.2070	0.0005842
		175	1.287	0.4238	0.5324	0.0015040
		212	1.266	0.3950	0.6866	0.0019378

statistical test of the data shows that they may be considered equal within experimental error. Table VII contains the experimental values and Table VIII the mean value of activation energy of the process together with the statistical expressions for log k_1 at any temperature.

Similar data were obtained with 10-mil Mylar sheet. In Tables IX through XIII it may be seen that the reaction rates for this material are decidedly slower than those for 0.5-mil film. The change in slope of the rate curves shown in Figures 8 through 12 occurs at a somewhat lower level of degradation than that for the 0.5-mil film. Hence the critical intrinsic viscosity selected for 10-mil sheet is 0.3310, and rate of reaction is calculated using samples degraded to this level. This means that though the 10-mil sheet hydrolyzes less rapidly than 0.5-mil film, it loses its tensile and flexural strength at an earlier stage of degradation.

The activation energy of hydrolysis of 10-mil sheet at

Table V. Rate of Degradation of 0.5-Mil Mylar Film

(20% relative humidity)

T, °C.	Slope	Time, Days t	Viscosity		Moles H_2O Reacted, x	$\log \frac{A}{A-x}$
			Relative, ηr	Intrinsic, $[\eta]$		
99	4.837×10^{-5}	0	1.406			
		14	1.339	0.4938	0.2466	0.0006960
		35	1.293	0.4317	0.4931	0.0013927
		56	1.234	0.3400	0.9792	0.0028997
		91	1.190	0.2879	1.582	0.0044844
		212	1.096	0.1507	5.192	0.0148946
90	1.631×10^{-5}	0	1.406			
		14	1.376	0.5415	0.0986	0.0002783
		35	1.349	0.5071	0.2027	0.0005720
		56	1.323	0.4726	0.3226	0.0009107
		84	1.294	0.4331	0.4867	0.0013745
		105	1.277	0.4100	0.6025	0.0017026
82	1.128×10^{-5}	0	1.406			
		14	1.396	0.5684	0.0313	0.0000882
		35	1.372	0.5372	0.1134	0.0003200
		56	1.354	0.5136	0.1821	0.0005140
		56	1.342	0.4978	0.2333	0.0006684
		115	1.318	0.4659	0.3480	0.0009825
		140	1.286	0.4224	0.5391	0.0015230
		212	1.251	0.3744	0.8065	0.0022805
		274	1.216	0.3254	1.1886	0.0033652
71	3.182×10^{-6}	0	1.406			
		35	1.393	0.5645	0.0412	0.0001164
		56	1.384	0.5529	0.0707	0.0001993
		105	1.357	0.5175	0.1700	0.0004797
		105	1.366	0.5353	0.1357	0.0003829
		212	1.349	0.5071	0.2027	0.0005720

different humidities is given in Table XIV and Figure 13, and the mean value of activation energy is given in Table XV. This is about 5 kcal. per mole higher than that for 0.5-mil film. The difference in the rate of hydrolysis of the two types of samples may be due to the large difference in their thickness. The rate of diffusion of moisture into the 10-mil sheet can exert considerable influence on the rate of reaction, whereas its role in 0.5-mil film may be negligible. For the same reason the activation energy of diffusion, which for many organic polymers is of the order of 5 kcal. per mole, may appear in the over-all energy of the process for the one and not for the other.

A further indication of the effect of diffusion on the rate of reaction of the 10-mil material is the shape of the curve obtained by plotting reaction rate against relative humidity. Figure 14 is such a plot of 0.5-mil film and of 10-mil sheet. The points for the thin material form a reasonably good straight line, whereas those of the thick sheets show pronounced curvature. Taylor, Herrmann, and Kemp (*10*) have shown that the so-called diffusion constant for water in rubber is dependent upon the concentration of water in the rubber. When this is low the constant is low, but at high concentrations the value of the diffusion constant rises

Table VI. Density of Polyethylene Terephthalate Samples

Samples	Density at Room Temp.
Dacron	1.373
0.5-mil film	1.389
10-mil sheet	1.395

(Hydrolyzed 10-mil sheet)

Conditions		Time,	$\text{Log}\ \dfrac{A}{A-x}$	Density
°C.	%RH	Days		at 25°
99	75	8	0.00112	1.3985
		23	0.00383	1.4046
		49	0.01635	1.4217
90	75	8	0.00025	1.3972
		23	0.00072	1.3974
		50	0.00157	1.3980
82	75	8	0.00012	1.3960
		91	0.00145	1.3982

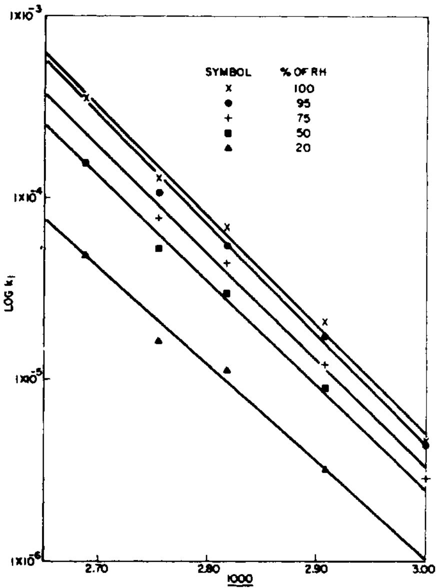


Figure 7. Activitation energy of hydrolysis of 0.5-mil Mylar film hydrolyzed to $\eta_r = 1.200$

Table VII. Activation Energy for Hydrolysis of 0.5-Mil Mylar Film

		Log *K* Relative Humidity, %				
Temp., °C.	1/*T*	100	95	75	50	20
130	0.002481	−2.40827				
99	0.002688	−3.45247			−3.75771	−4.31453
90	0.002755	−3.88907	−3.96698	−4.11176	−4.28997	−4.78755
82	0.002817	−4.21875	−4.25798	−4.35096	−4.52216	−4.98338
71	0.002907	−4.68298	−4.75970	−4.91632	−5.04576	−5.49730
60	0.003003	−5.34208	−5.37955	−5,54046		
Slope		5578	5711	5878	5716	5239
Activation energy, kcal./mole		25.7	26.3	27.1	26.3	24.1

Table VIII. Rate of Hydrolysis (k_1) 0.5-Mil Mylar Film

(mean value of E = 25.72 kcal./mole. Most probable value of $\log_{10}k_1$. Confidence limit 0.95)

%RH

100 $\text{Log}\ k_1 = -3.998936 + (-5583.93)\left(\frac{1}{T} - 0.0027752\right) \pm (0.113236)\sqrt{0.166667 + \frac{(1/T - 0.0027752)^2}{2.7291 \times 10^{-7}}}$

95 $\text{Log}\ k_1 = -4.5932075 + (-5583.93)\left(\frac{1}{T} - 0.0028704\right) \pm (0.113236)\sqrt{0.25 + \frac{(1/T - 0.0028704)^2}{2.7291 \times 10^{-7}}}$

75 $\text{Log}\ k_1 = -4.7252725 + (-5583.93)\left(\frac{1}{T} - 0.0028704\right) \pm (0.113236)\sqrt{0.25 + \frac{(1/T - 0.0028704)^2}{2.7291 \times 10^{-7}}}$

50 $\text{Log}\ k_1 = -4.619297 + (-5583.93)\left(\frac{1}{T} - 0.0028262\right) \pm (0.113236)\sqrt{0.333333 + \frac{(1/T - 0.0028262)^2}{2.7291 \times 10^{-7}}}$

20 $\text{Log}\ k_1 = -4.895690 + (-5563.93)\left(\frac{1}{T} - 0.0027917\right) \pm (0.113236)\sqrt{0.25 + \frac{(1/T - 0.0027917)^2}{2.7291 \times 10^{-7}}}$

T is absolute temperature.

Table IX. Rate of Degradation of 10-Mil Mylar Sheet

(100% relative humidity)

T, °C.	Slope	Time, Days t	Viscosity: Relative, ηr	Viscosity: Intrinsic, $[\eta]$	Moles H_2O Reacted, x	$\text{Log} \frac{A}{A-x}$
130	2.648×10^{-3}	0	1.425			
		0.833	1.266	0.3952	0.7692	0.0020418
		1.250	1.217	0.3268	1.2865	0.0034201
		1.875	1.150	0.2303	2.6668	0.0071201
		2.50	1.119	0.1844	3.9496	0.0105870
99	1.834×10^{-4}	0	1.425			
		4	1.352	0.5110	0.2502	0.0006629
		7	1.313	0.4591	0.4448	0.0011795
		10	1.268	0.3979	0.7527	0.0019979
		17	1.227	0.3409	1.1597	0.0030821
		21	1.158	0.2318	2.6355	0.0064813
		24	1.141	0.2171	2.9718	0.0079420
		28	1.117	0.1814	4.0600	0.0108867
		59	1.055	0.0870	12.6583	0.0348854
90	6.922×10^{-5}	0	1.425			
		3	1.410	0.5866	0.0379	0.0001005
		8	1.379	0.5465	0.1421	0.0003763
		13	1.333	0.4859	0.3384	0.0008971
		17	1.331	0.4832	0.3484	0.0009235
		27	1.293	0.4321	0.5682	0.0015072
		31	1.263	0.3910	0.7945	0.0021091
		36	1.243	0.3633	0.9819	0.0026081
		42	1.223	0.3353	1.2088	0.0032130
		49	1.196	0.2969	1.6021	0.0042635
		56	1.176	0.2682	1.9857	0.0052905
		65	1.148	0.2274	2.7308	0.0072926
		78	1.129	0.1993	3.4569	0.0092522
82	2.583×10^{-5}	0	1.425			
		7[a]	1.410	0.5866	0.0379	0.0001005
		14[a]	1.377	0.5439	0.1494	0.0003959
		21[a]	1.365	0.5282	0.1958	0.0005188
		28	1.361	0.5229	0.2120	0.0005619
		35	1.340	0.4952	0.3046	0.0008073
		42	1.319	0.4672	0.4113	0.0010905
		49	1.308	0.4524	0.4739	0.0012568
		63	1.267	0.3965	0.7609	0.0020198
		63	1.274	0.4062	0.7049	0.0018706
		137	1.212	0.3197	1.3556	0.0036033
		137	1.218	0.3282	1.2732	0.0033847
71	7.504×10^{-6}	0	1.425			
		14	1.412	0.5892	0.0318	0.0000843
		28	1.396	0.5686	0.0826	0.0002189
		42	1.372	0.5374	0.1683	0.0004460
		63	1.372	0.5374	0.1683	0.0004460
		63	1.376	0.5426	0.1532	0.0004058
		91	1.357	0.5177	0.2287	0.0006060
		105	1.341	0.4965	0.2999	0.0007948
		164	1.309	0.4537	0.4680	0.0012411
		168	1.298	0.4389	0.5355	0.0014205
		210	1.295	0.4348	0.5550	0.0014721
60	1.245×10^{-6}	0	1.425			
		42	1.412	0.5892	0.0318	0.0000843
		63	1.403	0.5776	0.0599	0.0001585
		63	1.402	0.5763	0.0630	0.0001670
		91	1.406	0.5815	0.0504	0.0001333
		126	1.406	0.5815	0.0504	0.0001333
		168	1.394	0.5660	0.0893	0.0002366
		300	1.379	0.5465	0.1421	0.0003763
		300	1.385	0.5543	0.1204	0.0003189

[a] Specimens started at 80° C. and transferred to 82° C. after 21 days.

rapidly. This, they say, is typical of polymers which sorb water. In that event, one could expect Mylar which adsorbs about 0.5% of water at saturation to behave similarly, and this could give rise to the nonlinear increase in rate at high humidities.

Though diffusion seems to offer the most plausible explanation of the difference in reaction rate and activation energy between film and sheet, there are other known chemical and physical differences which should be considered. The initial density of the 10-mil sheet is greater than that of the 0.5-mil film indicating that it is more crystalline, and the molecular weight of the 10-mil sheet is somewhat higher. Another feature of the two which is significantly different is molecular orientation. The film is more highly oriented than the sheet, and is probably more highly stressed internally. This could make the film appear more reactive than the sheet. However, an experiment with stretched film, which is described later, indicates that increased orientation does not cause an increase in rate of hydrolysis. The behavior of Dacron also supports this contention.

Dacron yarn is highly oriented uniaxially, yet its rate of

(text continued p. 69)

Table X. Rate of Degradation of 10-Mil Mylar Sheet

(95% relative humidity)

T, °C.	Slope	Time, Days t	Viscosity Relative, ηr	Viscosity Intrinsic, $[\eta]$	Moles H_2O Reacted, x	$\text{Log}\ \frac{A}{A-x}$
90	6.490×10^{-5}	0	1.425			
		7	1.390	0.5608	0.1029	0.0002727
		14	1.352	0.5111	0.2501	0.0006629
		14	1.353	0.5124	0.2458	0.0006514
		21	1.311	0.4564	0.4563	0.0012101
		35	1.257	0.3827	0.8472	0.0022493
		42	1.229	0.3437	1.1359	0.0030186
		56	1.168	0.2566	2.1692	0.0057827
		63	1.151	0.2318	2.6355	0.0070359
		63	1.152	0.2333	2.6047	0.0069529
		77	1.122	0.1889	3.7919	0.0101592
82	2.381×10^{-5}	0	1.425			
		14	1.392	0.5634	0.0961	0.0002545
		14	1.395	0.5673	0.0860	0.0002277
		21	1.372	0.5361	0.1722	0.0004562
		28	1.360	0.5216	0.2162	0.0005728
		42	1.327	0.4779	0.3688	0.0009776
		49	1.317	0.4645	0.4223	0.0011197
		49	1.311	0.4563	0.4563	0.0012101
		63	1.287	0.4239	0.6091	0.0016159
		98	1.215	0.3240	1.3134	0.0034922
		98	1.217	0.3268	1.2865	0.0034201
		133	1.135	0.2082	3.2018	0.0085627
71	7.053×10^{-6}	0	1.425			
		14	1.407	0.5827	0.0472	0.0001251
		35	1.394	0.5660	0.0893	0.0002366
		35	1.394	0.5660	0.0893	0.0002366
		49	1.389	0.5595	0.1064	0.0002818
		49	1.383	0.5517	0.1275	0.0003378
		63	1.378	0.5452	0.1457	0.0003861
		91	1.363	0.5256	0.2039	0.0005402
		126	1.332	0.4846	0.3434	0.0009103
		133	1.329	0.4806	0.3585	0.0009504
		140	1.328	0.4792	0.3636	0.0009639
		166	1.314	0.4605	0.4391	0.0011644
		281	1.266	0.3952	0.7692	0.0020418
60	1.203×10^{-6}	0	1.425			
		14	1.407	0.5827	0.0472	0.0001251
		28	1.407	0.5827	0.0472	0.0001251
		42	1.406	0.5815	0.0504	0.0001334
		63	1.414	0.5917	0.0258	0.0000683
		91	1.412	0.5892	0.0318	0.0000843
		182	1.394	0.5660	0.0893	0.0002366
		300	1.385	0.5543	0.1204	0.0003189
		300	1.379	0.5465	0.1421	0.0003763

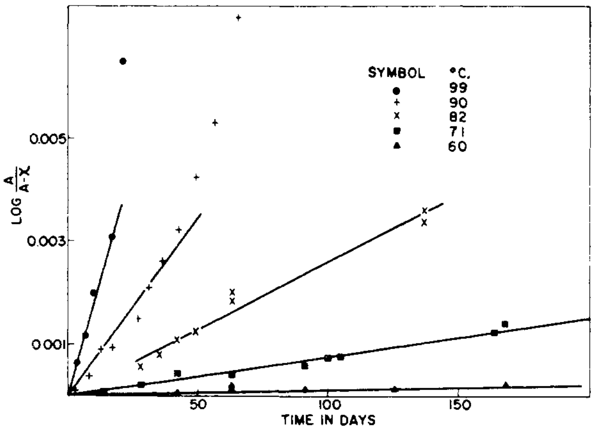


Figure 8. Rate of hydrolysis of 10-mil Mylar sheet at 100% relative humidity

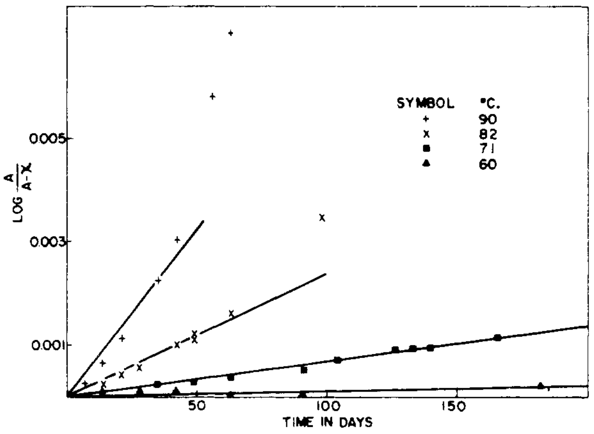


Figure 9. Rate of hydrolysis of 10-mil Mylar sheet at 95% relative humidity

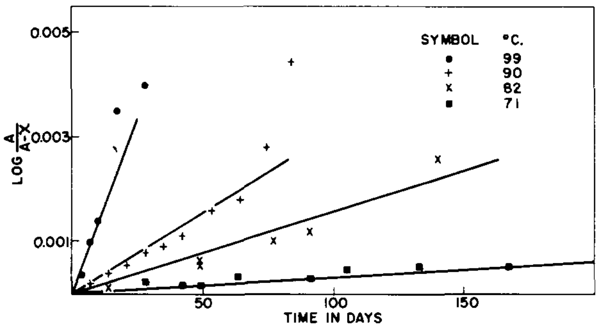


Figure 10. Rate of hydrolysis of 10-mil Mylar sheet at 75% relative humidity

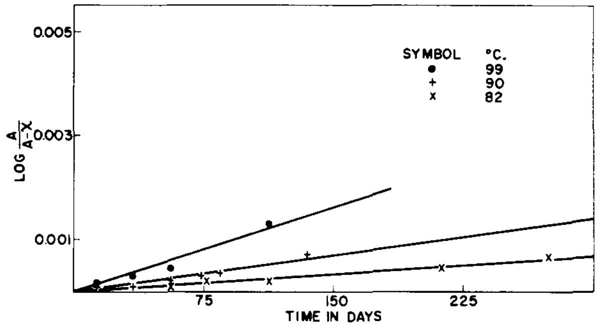


Figure 12. Rate of hydrolysis of 10-mil Mylar sheet at 20% relative humidity

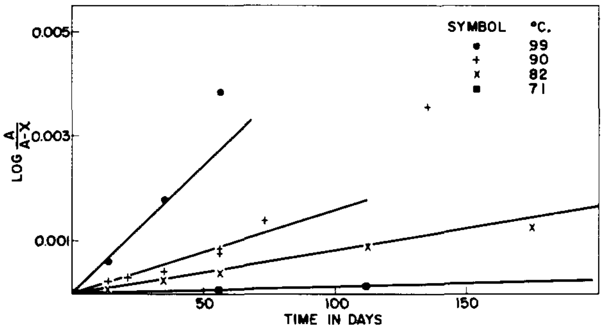


Figure 11. Rate of hydrolysis of 10-mil Mylar sheet at 50% relative humidity

Table XI. Rate of Degradation of 10-Mil Mylar Sheet

(75% relative humidity)

T, °C.	Slope	Time, Days t	Viscosity Relative, ηr	Viscosity Intrinsic, $[\eta]$	Moles H_2O Reacted, x	$\log \frac{A}{A-x}$
99	1.342×10^{-4}	0	1.425			
		4	1.381	0.5491	0.1347	0.0003570
		7	1.327	0.4780	0.3688	0.0009776
		10	1.300	0.4416	0.5228	0.0013867
		17	1.214	0.3225	1.327	0.0035288
		28	1.199	0.3012	1.552	0.0041302
		39	1.107	0.1664	4.6852	0.0125877
		39	1.108	0.1629	4.6165	0.0124006
		52	1.087	0.1362	6.4549	0.0174390
		66	1.069	0.1086	9.1168	0.0248396
90	3.131×10^{-5}	0	1.425			
		7	1.400	0.5737	0.0695	0.0001841
		14	1.377	0.5439	0.1494	0.0003959
		21	1.362	0.5243	0.2079	0.0005510
		28	1.341	0.4965	0.2999	0.0007948
		35	1.331	0.4832	0.3484	0.0009235
		42	1.318	0.4659	0.4168	0.0011050
		53	1.287	0.4239	0.6091	0.0016159
		64	1.278	0.4116	0.6743	0.0017893
		74	1.236	0.3535	1.056	0.0028062
		84	1.192	0.2912	1.671	0.0044489
		102	1.136	0.2097	3.162	0.0084547
82	1.587×10^{-5}	0	1.425			
		14	1.408	0.5840	0.0441	0.0001168
		49	1.354	0.5137	0.2415	0.0006399
		49	1.358	0.5190	0.2245	0.0005949
		77	1.323	0.4726	0.3897	0.0010332
		91	1.309	0.4537	0.4680	0.0012411
		140	1.244	0.3647	0.9717	0.0025809
71	3.392×10^{-6}	0	1.425			
		28	1.395	0.5673	0.0860	0.0002277
		42	1.401	0.5750	0.0663	0.0001755
		49	1.400	0.5737	0.0695	0.0001841
		49	1.403	0.5776	0.0599	0.0001585
		63	1.387	0.5569	0.1133	0.0003003
		63	1.384	0.5530	0.1240	0.0003284
		91	1.385	0.5543	0.1204	0.0003189
		105	1.370	0.5347	0.1761	0.0004665
		133	1.367	0.5308	0.1878	0.0004977
		168	1.364	0.5269	0.1998	0.0005295
		309	1.329	0.4806	0.3585	0.0009504

Table XII. Rate of Degradation of 10-Mil Mylar Sheet

(50% relative humidity)

T, °C.	Slope	Time, Days t	Viscosity		Moles H_2O Reacted, x	$\log \frac{A}{A-x}$
			Relative, ηr	Intrinsic $[\eta]$		
99	4.966×10^{-5}	0	1.425			
		14	1.356	0.5164	0.2329	0.0006172
		35	1.279	0.4130	0.6668	0.0017694
		56	1.206	0.3112	1.4425	0.0038368
		91	1.131	0.2023	3.3688	0.0090141
		112	1.096	0.1498	5.5518	0.0149566
90	1.619×10^{-5}	0	1.425			
		14	1.394	0.5660	0.0932	0.0002366
		21	1.385	0.5543	0.1204	0.0003189
		35	1.372	0.5374	0.1683	0.0004460
		56	1.342	0.4979	0.2952	0.0007824
		56	1.337	0.4912	0.3189	0.0008452
		73	1.300	0.4416	0.5228	0.0013867
		135	1.213	0.3211	0.1341	0.0035658
82	9.459×10^{-6}	0	1.425			
		14	1.414	0.5917	0.0258	0.0000683
		35	1.393	0.5647	0.0927	0.0002455
		56	1.379	0.5465	0.1421	0.0003763
		56	1.377	0.5439	0.1494	0.0003959
		112	1.333	0.4859	0.3384	0.0008971
		175	1.309	0.4537	0.4680	0.0012411
		212	1.246	0.3675	0.9516	0.0025272
		274	1.218	0.3282	1.273	0.0033847
71	1.583×10^{-6}	0	1.425			
		56	1.411	0.5879	0.0349	0.0000924
		112	1.403	0.5776	0.0599	0.0001585
		212	1.383	0.5517	0.1275	0.0003378
		274	1.372	0.5374	0.1683	0.0004460

Table XIII. Rate of Degradation of 10-Mil Mylar Sheet

(20% relative humidity)

T, °C.	Slope	Time, Days t	Viscosity		Moles H_2O Reacted, x	$\log \frac{A}{A-x}$
			Relative, ηr	Intrinsic, $[\eta]$		
99	1.085×10^{-5}	0	1.425			
		14	1.401	0.5750	0.0663	0.0001755
		35	1.388	0.5582	0.1099	0.0002910
		56	1.372	0.5374	0.1683	0.0004460
		112	1.304	0.4470	0.4980	0.0013207
		212	1.172	0.2624	2.075	0.0055299
90	4.722×10^{-6}	0	1.425			
		14	1.409	0.5853	0.0410	0.0001086
		35	1.412	0.5892	0.0318	0.0000843
		56	1.396	0.5686	0.0826	0.0002189
		73	1.387	0.5569	0.1133	0.0003003
		84	1.381	0.5491	0.1347	0.0003570
		135	1.347	0.5045	0.2723	0.0007216
82	2.207×10^{-6}	0	1.425			
		56	1.411	0.5879	0.0349	0.0000924
		77	1.396	0.5686	0.0826	0.0002189
		112	1.400	0.5737	0.0695	0.0001841
		212	1.372	0.5374	0.1683	0.0004460
		274	1.354	0.5137	0.2415	0.0006399

Table XIV. Activation Energy for Hydrolysis of 10-Mil Mylar Sheet

Temp., °C.	$1/T$	Log K Relative Humidity, %				
		100	95	75	50	20
99	0.002688	−3.73660			−4.30399	−4.96457
90	0.002755	−4.18323	−4.18776	−4.50432	−4.78968	−5.32587
82	0.002817	−4.58788	−4.62324	−4.79942	−5.02415	−5.65620
71	0.002907	−5.12471	−5.15163	−5.46954	−5.80052	
60	0.003003	−5.90483	−5.91973			
Slope		6784	6892	6464	6664	5407
Activation energy, kcal./mole		31.2	31.7	29.8	30.7	24.9

Table XV. Rate of Hydrolysis (k_1) of 10-Mil Mylar Sheet

(Mean value of activation energy = 29.73 kcal./mole. Most probable value of $\log_{10}k_1$. Confidence limit 0.95.)

% RH	
100	$\text{Log } k_1 = -4.34742 + (-6456.11)\left(\frac{1}{T} - 0.00277521\right) \pm 0.15951 \sqrt{0.166667 + \frac{(1/T - 0.00277521)^2}{2.45925 \times 10^{-7}}}$
95	$\text{Log } k_1 = -4.97059 + (-6456.11)\left(\frac{1}{T} - 0.00287042\right) \pm 0.15951 \sqrt{0.2500 + \frac{(1/T - 0.00287042)^2}{2.45925 \times 10^{-7}}}$
75	$\text{Log } k_1 = -4.92443 + (-6456.11)\left(\frac{1}{T} - 0.00282889\right) \pm 0.15951 \sqrt{0.333333 + \frac{(1/T - 0.00282889)^2}{2.45925 \times 10^{-7}}}$
50	$\text{Log } k_1 = -4.97023 + (-6456.11)\left(\frac{1}{T} - 0.00279172\right) \pm 0.15951 \sqrt{0.2500 + \frac{(1/T - 0.00279172)^2}{2.45925 \times 10^{-7}}}$
20	$\text{Log } k_1 = -5.33451 + (-6456.11)\left(\frac{1}{T} - 0.00275330\right) \pm 0.15951 \sqrt{0.333333 + \frac{(1/T - 0.00275330)^2}{2.45925 \times 10^{-7}}}$

T is absolute temperature.

hydrolysis is decidedly slower than that of either the film or sheet. This is reflected in its retention of physical properties. Some rate data for this material are given in Tables XVI through XVIII. It is claimed by Whinfield (*12*) that in alkaline hydrolysis, drawn fibers of polyethylene terephthalate are attacked at the surface and their diameters are progressively decreased, but the remainder of the fiber is unaffected. This is not the case with sheet and film samples, which appear to degrade uniformly throughout.

Hydrolysis of Mylar at pH 2.0. Samples of film and sheet were immersed in a hydrochloric acid solution of pH 2.0 and heated at 130° C. The relative viscosity of the degraded samples compared with those hydrolyzed at neutral pH 7.0 is shown below:

Sample	No. Hours Heated at 130° C.	Relative Viscosity	
		pH 2.0	pH 7.0
0.5-mil Mylar film	12	1.261	1.269
	24	1.202	1.201
10-mil sheet	20	1.266	1.266
	30	1.214	1.217

It is apparent that there is no difference in the rates at these pH values. This indicates that the hydrolysis of polyethylene terephthalate is not catalyzed by hydrogen ions, as many simple monomeric esters are.

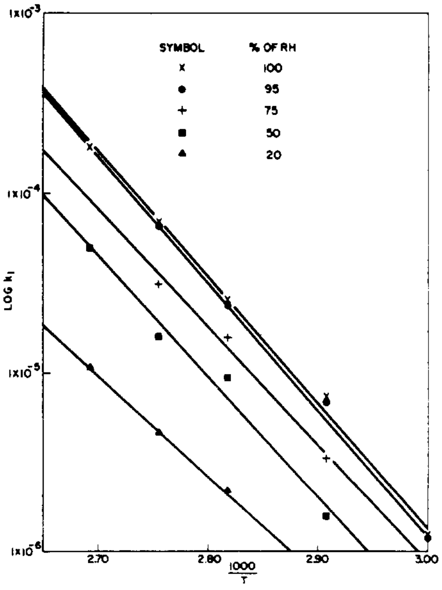


Figure 13. Activation energy of hydrolysis—10-mil Mylar sheet hydrolyzed to $\eta_r = 1.220$

Alcoholysis. A sample of 10-mil Mylar sheet was heated for 80 hours at 130° C. in *n*-butyl alcohol. This drastic treatment did not greatly affect the sample. It was still flexible and strong. Tensile strength was reduced about 20% while elongation at break more than doubled. Its intrinsic viscosity decreased to 0.4939 from an initial value Of 0.6050. At this temperature, water degrades the polymer to the same extent in about 8 hours. In this experiment, the gain in weight of the sample was measured after exposure to alcohol and found to be several times greater than the weight gain calculated from change in molecular weight. Assuming the latter to be a reliable indicator of chain scission by the alcohol, it would appear that the alcohol might also react with the polymer in some other way. For example, it might esterify carboxyl end groups.

Hydrolysis of Stretched Film. To see what effect stressing the polymer might have on rate of hydrolysis, samples of 0.5-mil film were stretched in the Instron tensile tester until a section between bench marks elongated 90%. Some samples were then exposed to 90° C. in dry air and others to 90° C., 95% relative humidity. After exposure, their tensile strength and elongation were measured. The stretched portions of the samples were separated from the unstretched, and the intrinsic viscosity of the various parts was determined. All of these data are given in Table XIX. The stretched samples retained much more of their tensile strength than the unstretched when both were subjected to

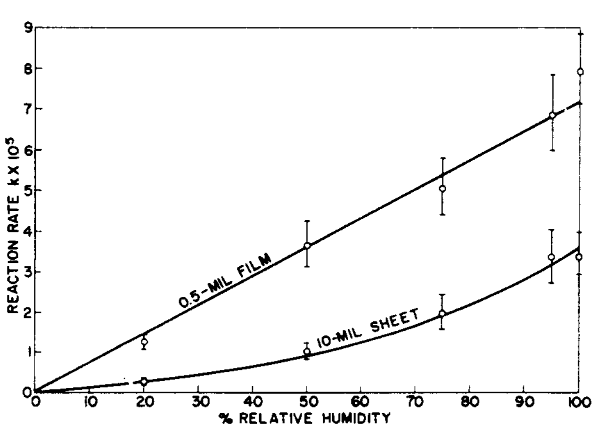


Figure 14. Rate of hydrolysis versus relative humidity at 85° C. [Confidence limit, 0.95]

Table XVI. Rate of Degradation of Dacron Yarn

(95% relative humidity)

		Time, Days	Viscosity		Moles H_2O Reacted,	$\log \frac{A}{A-x}$
T, °C.	Slope	t	Relative, ηr	Intrinsic, $[\eta]$	x	
90	1.454×10^{-6}	0	1.418			
		14	1.408	0.5870	0.0224	0.00006087
		28	1.378	0.5480	0.1219	0.00033111
		77	1.310	0.4575	0.4318	0.0011735
		133	1.219	0.3313	1.2131	0.0033053
		133	1.221	0.3341	1.1878	0.0032360
82	0.9167×10^{-5}	0	1.418			
		14	1.414	0.5948	0.0045	0.00001216
		77	1.352	0.5138	0.2242	0.0006089
		175	1.293	0.4343	0.5356	0.0014562
		223	1.257	0.3847	0.8088	0.0022010
		291	1.193	0.2942	1.5987	0.0043612
		291	1.192	0.2927	1.6159	0.0044086
71	2.179×10^{-6}	0	1.418			
		77	1.390	0.5637	0.0800	0.0002173
		210	1.370	0.5375	0.1516	0.0004118
		291	1.347	0.5071	0.2458	0.0006678
		291	1.351	0.5124	0.2284	0.0006205

Table XVII. Rate of Degradation of Dacron Yarn

(75% relative humidity)

		Time, Days	Viscosity		Moles H_2O Reacted	$\log \frac{A}{A-x}$
T, °C.	Slope	t	Relative, ηr	Intrinsic $[\eta]$	x	
90	1.381×10^{-5}	0	1.418			
		14	1.399	0.5754	0.0505	0.0001370
		77	1.328	0.4817	0.3353	0.0009110
		133	1.269	0.4014	0.7083	0.0019269
		133	1.273	0.4069	0.6771	0.0018418
82	8.077×10^{-6}	0	1.418			
		105	1.362	0.5270	0.1828	0.0004966
		175	1.319	0.4696	0.3819	0.0010380
		223	1.291	0.4316	0.5487	0.0014920
		291	1.242	0.3638	0.9509	0.0025887
		291	1.238	0.3582	0.9923	0.0027017
71	1.111×10^{-6}	0	1.418			
		105	1.404	0.5819	0.0347	0.0000942
		175	1.394	0.5689	0.0667	0.00018110
		291	1.380	0.5507	0.1147	0.0003116
		291	1.376	0.5454	0.1292	0.0003509

hydrolysis. The stretched samples were still flexible, while the unstretched had become brittle. The molecular weight of the unstretched film appears to have been reduced more than that of the stretched samples as indicated by their intrinsic viscosities.

Infrared Spectrometry. Wood and Dodd (*13*) have observed the absorption of Mylar film, 5 mils thick, before and after it was degraded by hydrolysis at 130° C. for various periods of time. They found that hydrolysis does not seem to cause band disappearance nor new band appearance. However, it does cause an increase in the absorbance in a band around 3425 $cm.^{-1}$, which is the general region of absorbance by various types of OH groups. The amount of absorbance by the various samples was measured, and was plotted against the extent of reaction which had occurred calculated from change in relative viscosity of the polymer. The relation is shown in Figure 15. This offers another possible way of following the degradation of this polymer.

Thermal Degradation and Oxidation. Samples heated in air are of course subjected to both thermal degradation and oxidation. The two are not separated, because under most service conditions the polymer would be subjected to both simultaneously, and furthermore, no deleterious effects due to the combination were observed during the time of exposure at the temperatures employed in this study. The reason for this will become clear when the reaction rates of these processes are considered. It is shown (*6*) that the rate of thermal degradation of polyethylene terephthalate under nitrogen at 300° C. is 0.130 per day. The activation energy of the process is 32 kcal. per mole. The calculated rate at 100° C. is 4.1×10^{-8} per day. The rate of reaction of polyethylene terephthalate in a nitrogen-oxygen mixture of the same composition as air is approximately double that in nitrogen, and it is reasonable to assume that the activation energy is also about 32 kcal. per mole. The rate of hydrolysis of 0.5-mil film at 100° C. and 100% RH was found to be 4×10^{-4} per day or 10,000 times faster than thermal degradation and 5000 times faster than oxidation in air. None of the samples heated in air showed a significant change in viscosity nor any real impairment of physical or electrical properties. Wooley, Kohman, and McMahon (*14*) showed that Mylar can endure long exposure to high temperature in air and still retain high dielectric strength.

Chemical degradation can also be correlated with electrical and physical properties of the polymer such as dielectric breakdown strength, dielectric constant, dielectric loss, resistivity, tensile strength and elongation, fold endurance, water vapor transmission, and density.

Dielectric Breakdown Strength. This characteristic was investigated in detail, because it is often the most sensitive of the electrical properties to degradation of insulating materials, and a feature of prime importance in most insulation applications. For these measurements 0.5-mil film was tested in the jig shown in Figure 16.

The jig assembly consists of a shallow brass box containing a strip of blotting paper. A strip of aluminum foil is laid over the paper and in contact with the brass box. Next a strip of Mylar film is placed on the aluminum foil, and a half-inch-thick Lucite block, which fits in the box, is placed on the Mylar. This block contains 20 holes 0.5 inch in diameter, into each of which a brass cylinder 0.5 inch in diameter and 3 inches long is inserted. The bottom of each cylinder is capped with aluminum foil. The reason for this arrangement of blotting paper, aluminum foil, etc., is to assure good contact between electrodes and dielectric while minimizing the likelihood of puncturing the insulating film. A direct current potential is applied between the aluminum foil under the Mylar and one brass cylinder at a time. Voltage is increased at the rate of 8 kv. per minute until breakdown occurs. This is repeated with each of the 20 brass cylinders.

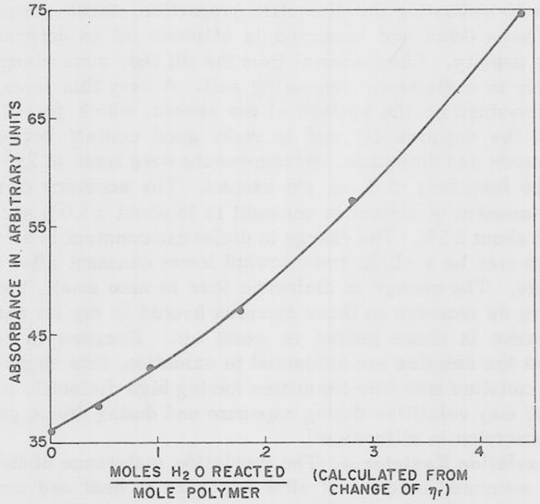


Figure 15. Absorbance at 3425 cm. Related to degradation by hydrolysis

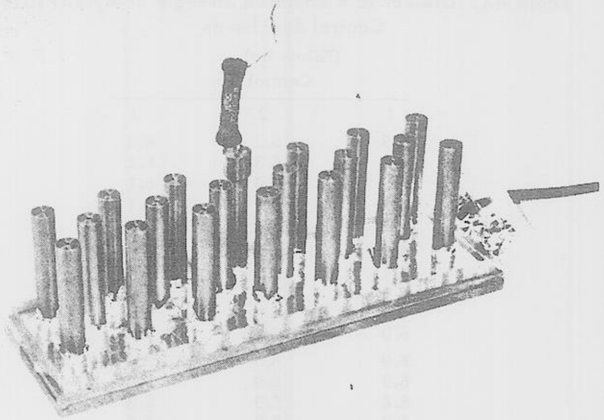


Figure 16. Apparatus for dielectric strength test

The dielectric breakdown strength of 0.5-mil film tested

Table XVIII. Rate of Degradation of Dacron Yarn

(50% relative humidity)

T, °C.	Slope	Time, Days t	Viscosity: Relative, ηr	Viscosity: Intrinsic, $[\eta]$	Moles H_2O Reacted, x	$\text{Log}\ \frac{A}{A-x}$
99	2.352×10^{-5}	0	1.418			
		14	1.408	0.5871	0.0224	0.00006087
		35	1.356	0.5191	0.2073	0.0005631
		56	1.319	0.4696	0.3819	0.0010380
		91	1.247	0.3708	0.9013	0.0024533
		115	1.185	0.2826	1.7429	0.0047570
		212	1.073	0.1153	8.1966	0.0228384
90	5.034×10^{-6}	0	1.418			
		14	1.405	0.5832	0.0316	0.0000858
		21	1.404	0.5819	0.0347	0.0000942
		35	1.401	0.5780	0.0441	0.0001200
		56	1.387	0.5598	0.0902	0.0002449
		77	1.347	0.5071	0.2458	0.0006678
		84	1.386	0.5585	0.0937	0.0002543
		105	1.362	0.5270	0.1828	0.0004966
		151	1.197	0.2999	1.5316	0.0041774
		151	1.196	0.2985	1.5481	0.0042225
82	4.249×10^{-6}	0	1.418			
		35	1.406	0.5845	0.0285	0.0000775
		56	1.390	0.5637	0.0800	0.0002173
		115	1.366	0.5323	0.1670	0.0004536
		175	1.354	0.5164	0.2157	0.0005858
		212	1.317	0.4669	0.3927	0.0010674

Table XIX. Change in Physical Properties of 0.5-Mil Mylar Film

Exposure Conditions			Unstretched			Stretched		
°C.	%RH	Time, Days	Breaking strength, lb.	Elongation, %	Intrinsic viscosity	Breaking strength, lb.	Elongation, %	Intrinsic viscosity
90	95	35	1.8	1.3	0.2985	3.4	17.71	0.3370
90	Air	35	4.6	60.0	0.5813	5.4	44.0	0.3171
Unheated			5.3	99.4	0.5572	5.4	24.0	0.5767

this way at 25° C. and 40 to 50% RH is shown in Tables XX through XXIV. Test results for two samples taken from each condition of exposure are given. One is the sample that was exposed for the longest period which was still flexible enough to test, and the other was exposed for next to the longest period. Two averages are given: the average of all breakdown values of a given sample, to show any general effect of chemical degradation; and the average of the lower half which might reveal localized attack. Surprisingly little change in breakdown strength was found by either measure.

Table XX. Dielectric Breakdown Strength of Mylar Films Control Specimens

(Kilovolts)

	Control No. 1	Control No. 2	Control No. 3	
	6.3	6.3	6.3	
	6.2	6.3	6.1	
	6.2	6.3	6.1	
	6.2	6.2	6.1	
	6.2	6.2	6.1	
	6.2	6.1	6.0	
	6.1	6.1	6.0	
	6.0	6.1	6.0	
	6.0	6.0	6.0	
	6.0	6.0	5.9	
	5.9	6.0	5.8	
	5.9	6.0	5.8	
	5.8	5.9	5.8	
	5.8	5.9	5.6	
	5.4	5.9	5.6	
	5.3	5.9	5.6	
	5.0	5.9	5.5	
	5.0	5.8	4.5	
	4.0	5.8	4.2	
	3.6	1.0	0	
Average	5.65	5.78	5.45	
Grand av.				5.63
Av. of lower half values	5.17	5.41	4.84	
Grand av.				5.14

The data indicate that hydrolyzed film does not lose its dielectric strength until it has degraded to the point where it is brittle and physically weak. Samples heated in air have shown no deterioration thus far and may have improved slightly.

Dielectric Constant and Dielectric Loss. These characteristics of 10-mil Mylar sheet were also measured (Table XXV). The original ,material, hydrolyzed samples, and samples heated in air were included in these measurements. Prior to measuring the dielectric properties, these samples had been dried and immersed in silicone oil to determine their density. After removal from the oil they were clamped tightly in a dielectric measuring cell. A very thin layer of oil remained on the surface of the sheets, which served to keep the samples dry and to make good contact between electrode and dielectric. Measurements were made at 25° C. at the frequency of 1 kc. per second. The accuracy of the measurement of dielectric constant is to about ±1.0% and of tan δ about ±5%. The change in dielectric constant is small. There may be a slight trend toward lower constant after exposure. The change in dielectric loss is also small, but it shows an increase in those samples heated in dry air and a decrease in those heated in moist air. Because in both cases the samples are subjected to oxidation, this suggests that moisture may free impurities having high dielectric loss which may volatilize during exposure and during drying prior to immersion in silicone oil.

Insulation Resistance. The insulation resistance of Mylar was measured before and after exposure to heat and moisture (Table XXVI). Resistance was measured in accordance with ASTM method D 1202-52T after conditioning the samples at 50% RH, 75° F.; and at 90% RH, 95° F. At the lower humidity and temperature, the resistance of all samples was above the range of the galvanometer.

Mylar sheet heated in either dry or moist air showed a decrease in resistance of three to four orders when conditioned at 90% RH and 95° F. However, when the surface of the samples was cleaned, their resistance increased to that of the unexposed material. The reason for the decrease in surface resistivity is indicated in the photomicrographs

Table XXI. Dielectric Breakdown Strength of 0.5-Mil Mylar Film in Water

(Kilovolts. To convert to kv./mil, multiply by 2.04)

Temp., ° C.	99	99	90	90	82	82	71	71	60	60	50	50
Time, Days	7	10	14	21	42	49	91	105	91	126	63	126
	6.3	6.0	6.9	6.0	6.2	5.8	6.2	6.0	5.9	5.9	6.5	6.6
	6.1	5.8	6.3	5.9	6.2	5.7	6.2	5.9	5.9	5.6	6.4	6.3
	6.1	5.8	6.3	5.9	5.9	5.7	6.2	5.7	5.8	5.5	6.4	6.3
	6.0	5.7	6.3	5.9	5.9	5.7	6.0	5.6	5.7	5.5	6.3	6.3
	6.0	5.6	6.2	5.8	5.7	5.6	6.0	5.6	5.6	5.4	6.3	6.3
	6.0	5.6	6.0	5.7	5.6	5.6	6.0	5.6	5.5	5.4	6.2	6.3
	5.9	5.5	5.5	5.7	5.4	5.6	5.9	5.6	5.3	5.3	6.2	6.2
	5.9	5.4	5.4	5.7	5.4	5.5	5.7	5.5	5.2	5.3	6.1	6.2
	5.9	5.3	5.3	5.6	5.3	5.2	5.6	5.5	5.0	5.1	6.1	6.2
	5.8	5.3	5.2	5.6	5.3	5.1	5.4	5.3	4.9	5.0	6.0	6.0
	5.8	5.2	4.9	5.6	5.2	5.1	5.4	5.1	4.9	5.0	6.0	5.9
	5.6	4.2	4.6	5.6	5.1	5.1	5.2	5.1	4.9	4.9	6.0	5.8
	5.5	4.2	4.1	5.4	5.1	5.0	5.1	5.0	4.9	4.9	6.0	5.8
	5.5	< 0.4	3.6	5.4	5.0	5.0	5.0	5.0	4.8	4.9	6.0	5.7
	5.4		1.9	5.4	5.0	5.0	5.0	4.9	4.7	4.5	6.0	5.7
	5.4	Brittle		5.3	4.6	4.7	4.7	4.8	4.6	4.5	5.9	5.6
	5.3			5.3	4.4	4.2	4.6	4.6	4.4	4.3	5.7	5.4
	5.3			5.3	4.1	4.0	4.4	4.2	4.3	4.1	5.3	5.4
	4.9			5.2	3.3	3.8	3.8	3.9	3.9	3.9	4.0	4.9
	4.8			5.2	3.0	2.4 Brittle		0.8	3.8	3.8	2.8	4.5
Av.	5.67	5.0	5.24	5.57	5.11	4.99	5.39	4.98	5.00	4.94	5.81	5.87
% of original	101	89	93	99	91	89	96	89	89	88	103	105
Av. of lower half	5.35	4.29	4.37	5.37	4.53	4.43	4.80	4.34	4.52	4.48	5.37	5.47
% of original	104	84	85	105	88	85	94	85	88	87	105	107

Table XXII. Dielectric Breakdown Strength, 0.5-Mil Film in Air

(Kilovolts. To convert to kv./mil, multiply by 2.04)

Temp., ° C.	99		90		82		71		60		50	
Time, Days	39	67	63	161	63	315	63	105	42	63	14	63
	7.5	7.4	6.6	7.1	6.8	6.8	6.8	6.9	6.2	6.6	6.7	6.4
	7.4	7.1	6.6	7.0	6.7	6.8	6.5	6.8	6.2	6.5	6.6	6.3
	7.2	7.1	6.5	6.9	6.7	6.7	6.5	6.8	6.0	6.4	6.5	6.3
	7.1	7.0	6.4	6.9	6.7	6.7	6.5	6.7	6.0	6.3	6.5	6.3
	7.1	6.9	6.4	6.9	6.6	6.5	6.5	6.7	6.0	6.3	6.5	6.2
	7.1	6.8	6.4	6.9	6.6	6.5	6.5	6.7	6.0	6.3	6.4	6.2
	7.0	6.8	6.4	6.9	6.6	6.5	6.4	6.6	5.9	6.3	6.3	6.0
	7.0	6.7	6.4	6.9	6.5	6.4	6.4	6.6	5.9	6.3	6.2	6.0
	6.9	6.7	6.1	6.8	6.5	6.4	6.3	6.6	5.9	6.3	6.2	6.0
	6.9	6.5	6.0	6.8	6.3	6.4	6.2	6.5	5.8	6.2	6.1	6.0
	6.9	6.4	6.0	6.8	6.3	6.3	6.2	6.5	5.8	6.2	6.1	6.0
	6.8	6.4	5.9	6.7	6.2	6.3	6.2	6.5	5.8	6.1	6.0	5.9
	6.6	6.3	5.5	6.6	6.2	6.3	6.2	6.5	5.7	6.1	6.0	5.8
	6.4	6.2	5.3	6.6	5.9	6.2	6.1	6.4	5.7	6.0	6.0	5.6
	5.2	6.0	5.2	6.6	5.8	6.2	5.9	6.3	5.6	6.0	6.0	5.6
	5.1	5.8	4.9	6.5	5.8	5.9	5.7	6.3	5.5	6.0	5.9	5.6
	4.8	5.4	4.8	6.5	5.7	5.1	5.7	6.2	5.5	5.9	5.9	5.5
	3.9	5.4	4.4	6.4	5.3	4.1	5.6	6.1	5.3	5.9	5.8	5.5
	3.7	4.1	3.4	6.3	5.2	3.9	5.3	6.1	5.2	5.4	5.7	5.3
	2.0	1.6	3.3	6.3	1.0	3.8	2.9	5.9	4.6	5.3	5.6	4.7
Av.	6.13	6.13	5.62	6.72	5.97	5.99	6.02	6.48	5.73	6.12	6.15	5.86
% of original	109	109	100	119	106	107	107	115	102	109	110	104
Av. of lower half	5.14	5.36	4.87	6.53	5.34	5.41	5.58	6.28	5.47	5.89	5.90	5.55
% of original	100	104	95	127	104	105	108	122	107	115	115	108

in Figure 17. These show the progressive accumulation of particles on the surface of Mylar heated at 130° C. in 100% RH. This is not all due to degradation, because similar deposits have been observed on the surface of Mylar heated in dry air. At least some of this surface contamination is low molecular weight polymer which is present in the film at the outset and is brought to the surface by heat. This substance is apparently nonconducting when dry, but sufficiently hygroscopic or ionic to be conductive in high humidity.

Density. The density of polyethylene terephthalate as shown by Kolb and Izard (*5*) is related to the degree of crystallinity of the polymer. The amount of crystallinity, or more particularly the change in amount of crystallinity, in the polymer is intimately connected with its modulus and flexibility. It also has some influence on the dielectric properties (*8*), but this is so small that for most purposes the important effects are mechanical. The density of amorphous polymer is 1.330 to 1.335 at room temperature, while density of a pure crystal as estimated from x-ray diffraction

Table XXIII. Dielectric Breakdown Strength, 0.5-Mil Film in 95% Relative Humidity

(Kilovolts. To convert to kv./mil, multiply by 2.04)

Temp., ° C.	90		82		71		60		50	
Time, Days	14	21	35	49	77	91	91	126	91	126
	7.2	7.0	5.9	6.7	6.2	5.6	6.2	5.9	6.6	7.1
	7.0	6.9	5.7	6.3	6.0	5.6	6.1	5.9	6.3	6.8
	7.0	6.9	5.7	6.2	6.0	5.5	6.0	5.7	6.2	6.7
	7.0	6.8	5.6	6.2	5.9	5.5	5.9	5.7	6.2	6.7
	6.9	6.8	5.5	6.2	5.8	5.4	5.9	5.7	6.1	6.6
	6.8	6.7	5.4	6.2	5.7	5.4	5.7	5.6	6.0	6.6
	6.4	6.5	5.4	6.2	5.7	5.3	5.7	5.6	6.0	6.5
	6.4	6.5	5.4	6.2	5.6	5.3	5.7	5.6	6.0	6.5
	6.3	6.4	5.4	6.1	5.6	5.2	5.6	5.6	5.9	6.5
	6.3	6.3	5.4	6.1	5.5	5.2	5.6	5.6	5.9	6.5
	6.3	6.2	5.3	6.1	5.5	5.2	5.6	5.6	5.7	6.4
	6.2	6.2	5.2	6.0	5.4	5.1	5.5	5.6	5.7	6.3
	6.2	6.1	5.2	6.0	5.3	5.1	5.5	5.5	5.7	6.3
	6.1	6.0	5.2	5.6	5.3	5.0	5.4	5.4	5.7	6.2
	5.8	6.0	5.1	5.4	5.2	4.9	5.3	5.4	5.6	6.2
	4.0	5.3	5.0	5.2	5.1	4.8	5.2	5.4	5.6	6.0
	3.7	4.4	5.0	5.1	5.0	4.8	5.0	5.4	5.6	6.0
	3.6	3.7	5.0	5.0	5.0	4.7	4.9	5.3	5.6	6.0
	2.3	2.7	5.0	3.8	4.2	4.2	4.7	5.2	5.3	5.9
	1.2	2.6	5.0	1.0	2.0	3.6	4.6	5.2	5.2	5.7
Av.	5.63	5.80	5.32	5.58	5.30	5.07	5.50	5.54	5.84	6.37
% of original	100	103	95	99	94	90	98	99	104	113
Av. of lower half	4.54	4.92	5.10	4.92	4.80	4.74	5.17	5.40	5.57	6.10
% of original	89	96	99	96	93	92	101	105	108	119

Table XXIV. Dielectric Breakdown Strength, 0.5-Mil Film in 75% Relative Humidity

(Kilovolts to convert to kv./mil, multiply by 2.04)

Temp., °C.	99		90		82		71		60		50	
Time, Days	7	10	14	28	49	63	91	105	91	105	63	105
	6.8	6.4	7.2	6.1	6.8	6.0	6.5	7.0	7.0	6.8	6.7	6.4
	6.8	6.4	7.1	5.9	6.7	6.0	6.5	6.9	6.9	6.7	6.5	6.2
	6.6	6.3	7.0	5.8	6.7	6.0	6.4	6.8	6.8	6.7	6.5	6.2
	6.5	6.2	6.9	5.8	6.7	6.0	6.4	6.8	6.8	6.7	6.3	6.1
	6.4	6.2	6.9	5.8	6.7	5.8	6.3	6.7	6.7	6.7	6.3	6.1
	6.4	6.2	6.9	5.8	6.7	5.8	6.2	6.7	6.7	6.6	6.3	6.0
	6.4	6.1	6.9	5.7	6.6	5.8	6.2	6.7	6.6	6.5	6.3	6.0
	6.4	6.1	6.9	5.7	6.4	5.8	6.2	6.6	6.6	6.5	6.3	6.0
	6.4	6.0	6.8	5.7	6.4	5.7	6.2	6.6	6.4	6.4	6.3	5.9
	6.4	6.0	6.8	5.6	6.4	5.7	6.2	6.5	6.4	6.3	6.2	5.9
	6.3	5.9	6.7	5.4	6.4	5.6	6.2	6.5	6.4	6.3	6.2	5.8
	6.3	5.8	6.6	5.4	6.4	5.6	6.2	6.4	6.3	6.3	6.1	5.8
	6.3	5.8	6.6	5.2	6.3	5.6	6.1	6.3	6.2	6.2	6.0	5.7
	6.2	5.8	6.4	5.0	6.3	5.6	6.0	6.3	6.1	6.2	6.0	5.7
	6.2	5.7	6.3	4.6	6.3	5.5	6.0	6.2	6.0	6.0	6.0	5.6
	6.1	5.7	5.7	2.8	6.2	5.5	5.9	6.2	5.9	5.9	6.0	5.5
	6.0	5.5	5.4	1.5	6.2	5.4	5.7	6.2	5.6	5.9	5.9	5.5
	5.9	5.5	4.7		6.2	5.4	5.7	6.1	5.2	5.8	5.8	5.4
	5.9	5.4	2.2		5.9	5.3	5.7	6.0	4.6	5.8	5.8	5.3
	5.8	4.7	0.6		5.3	5.0	5.1	5.9	2.6	5.1	5.7	2.5
Av.	6.30	5.88	6.03	5.16	6.38	5.65	6.08	6.47	6.09	6.27	6.16	5.68
% of original	112	105	107	92	113	101	108	115	108	111	109	101
Av. of lower half	6.10	5.58	5.12	4.58	6.15	5.45	5.86	6.21	5.95	5.49	5.95	5.28
% of original	119	109	100	89	120	106	114	121	116	107	116	103

Table XXV. Dielectric Constant and Loss of 10-Mil Mylar Sheet Exposed to Heat and Moisture

(Samples measured at 1 kc. and 25 °C.)

Temp., °C.	Atmos., % RH	Time, Days	Dielec. Const.	Tan δ
100		8	3.33	0.00422
	Dry	49	3.29	0.00489
		8	3.30	0.00404
	75	23	3.27	0.00356
		49	3.30	0.00313
90		8	3.35	0.00415
	Dry	91	3.20	0.00575
		8	3.33	0.00451
	75	23	3.40	0.00410
		50	3.30	0.00398
	Before exposure		3.35	0.00422

would be 1.46. The latter never has been observed in bulk and probably could not be attained short of growing a single crystal of the material. The density of the materials used in this study (Table VI), indicates that a sizable fraction of their composition is crystalline. However, these materials have all been cold-drawn and oriented in the course of manufacture, and with this treatment the polymer remains flexible and transparent despite a high crystal content. Moreover, it appears to inhibit further crystallization by heat. For example, amorphous unoriented film will crystallize rapidly at 110° C. becoming brittle and opaque, while highly oriented film may be heated at 180° C. for days and still be flexible and transparent, and its density will show comparatively little increase.

The sheet, film, and yarn in these tests are all oriented to some degree, the film and yarn highly. Consequently, long heating in air has not reduced their flexibility nor increased their tensile modulus. This is brought out in the explanation of tensile strength and elongation. However, when hydrolyzed they become brittle and "short." Table VI shows also that chemical degradation by hydrolysis is accompanied by an increase in density,. or an increase in the fraction of crystalline polymer. As shown in Figure 18, the relation between degradation and density change is very nearly linear until the density approaches what is probably the maximum attainable in bulk.

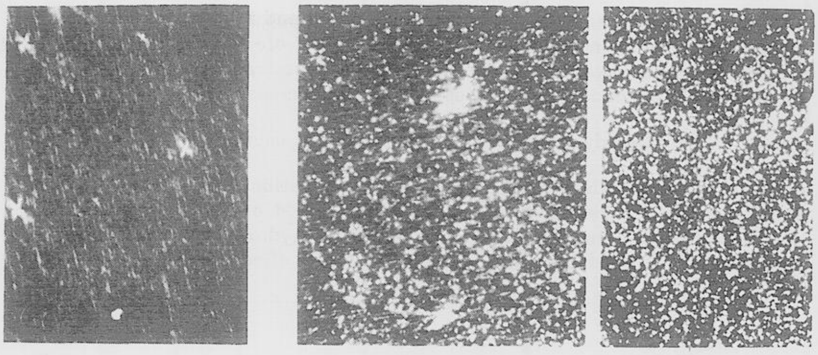
Rather early in this study the simultaneous occurrence of decomposition and crystallization during hydrolysis became obvious. The question then arose as to whether the relation between chemical degradation and physical degradation observed at higher temperatures would hold at lower ones. The evidence indicates that it will. Thus far, the lowest temperature at which the critical [η] of film—namely, 0.3042—has been reached is 71 °C.; and samples degraded to this level at 100, 95, and 75% RH are all brittle and essentially without tensile strength. This temperature is below the second-order transition of partly crystalline polyethylene terephthalate, so there is reason to expect the relation to hold at still lower temperatures.

Tensile Strength, Elongation at Break, and Fold Endurance. The tensile stength and elongation tests were made

Table XXVI. Insulation Resistance of 10-Mil Mylar

Sample No.	Aging		Time, Days	Ohms			
					2 Days at 90% RH, 95 °F.		
					IR		
	°C.	% RH		50% 75 °F.	Max.	Min.	Av.
Control		None		$>2 \times 10^{13}$	2×10^{12}	2×10^{12}	2×10^{12}
70S8	80	Air	245	$>2 \times 10^{13}$	6×10^{8}	3×10^{8}	4×10^{8}
87S9	90	Air	105	$>2 \times 10^{13}$	2×10^{8}	4×10^{7}	8×10^{7}
45S9	90	95	35	$>2 \times 10^{13}$	3×10^{8}	5×10^{7}	2×10^{8}
53S9	90	75	77	$>2 \times 10^{13}$	7×10^{8}	4×10^{8}	6×10^{8}
65S8	80	95	98	$>2 \times 10^{13}$	4×10^{9}	1×10^{9}	2×10^{9}
67S8	80	75	140	$>2 \times 10^{13}$	2×10^{10}	4×10^{8}	6×10^{9}
Values obtained after washing							
Control		None		$>2 \times 10^{13}$			$>2 \times 10^{12}$
87S9	90	Air		$>2 \times 10^{13}$			$>2 \times 10^{12}$
45S9	90	95		$>2 \times 10^{13}$			$>3 \times 10^{11}$

Figure 17. Comparison of unhydrolyzed and hydrolyzed Mylar films



Unhydrolyzed

24 hours

36 hours

Hydrolyzed at 130 °C.

on a Model TT-C Instron machine. The rate of separation of the grips was 5 inches per minute with the initial grip separation set at 3 inches. The folding endurance tests were made on an MIT folding endurance machine in accordance with Method B of ASTM Designation D 643 employing a tension of 1.5 kg. Specimens for the physical tests were conditioned and tested at 50% relative humidity and 73° F.

The results of the physical tests are given in Tables XXVII through XXXI. For the Mylar and Dacron samples, intrinsic viscosity data and the calculated values for the term $\log \frac{A}{A-x}$ are also included for purposes of comparison. The term $\log \frac{A}{A-x}$ is calculated from viscosity data and is a measure of the degree of degradation. Figures 19, 20, and 21 show the relation between tensile strength and $\log \frac{A}{A-x}$. The points used in plotting these figures represent the results obtained on Mylar and Dacron specimens hydrolytically degraded under a variety of conditions.

Figure 19 shows that there is an abrupt change in the slope of the curve at $\log \frac{A}{A-x} = 0.003$ for the 0.5-mil Mylar. A similar sharp change occurs in the curve for the 10-mil Mylar (Figure 20) at $\log \frac{A}{A-x} = 0.0023$. Where these breaks occur, both the 0.5-mil and the 10-mil Mylar materials have lost about one third of their original tensile strength. The Dacron curve in Figure 21, however, does not exhibit a similar break, although the point has been reached where only one half of its original strength remains.

Inspection of the results given in Tables XXVII through

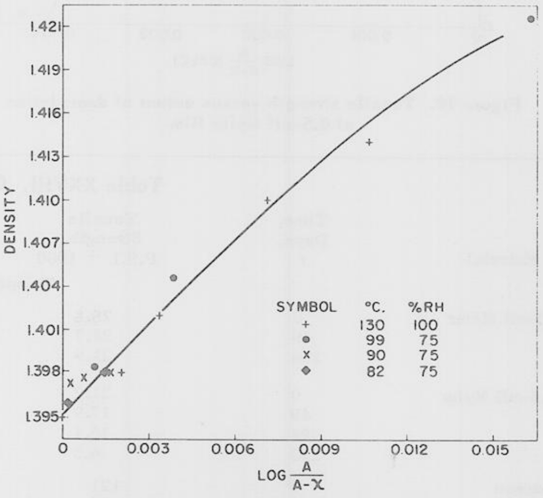


Figure 18. Change in density during degradation of 10-mil Mylar sheet

Table XXVII. Changes in Physical Properties

Material	Time, Days, t	Tensile Strength, P.S.I. ÷ 1000	Elongation, %	Fold.End Double Folds	$[\eta]$	$\log \frac{A}{A-x}$
			Temperature 82° Air			
10-mil Mylar	0	25.8	158	6072	0.603	0
	14	26.2	167	12772	0.588	0.00005
	49	25.9	222	9627	0.603	0
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	14	21.1	99.9		0.565	0.00011
	49	22.1	106		0.570	0.00008
Dacron	0	121	11.6		0.595	0
	14	122	18.3		0.595	0
	175	127	20.0		0.595	0
			Temperature 90° Air			
10-mil Mylar	0	25.8	158	6072	0.603	0
	14	23.9	141	21392	0.591	0.00007
	35	23.1	160	17216	0.603	0
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	14	19.7	84.3		0.551	0.00021
	35	18.2	69.3		0.582	0
	49	19.3	83.5		0.574	0.00005
Dacron	0	121	11.6		0.595	0
	14	120	19.0		0.595	0

XXXI reveals that percentage maximum elongation and folding endurance are sensitive criteria of changes in molecular weight. In some instances increases occur in these properties, although degradation as evidenced by an increase in $\log \frac{A}{A-x}$ has already commenced. This apparent improvement in the materials would result from a relaxation and shrinkage due to heating which in the early period of exposure outweighs and obscures the effect of hydrolytic degradation. Beyond this stage, the pronounced effect of hydrolytic degradation on these properties is well illustrated by the values obtained at the break point, where the Mylar has lost one third of its original tensile strength. At this point the 10-mil Mylar is so brittle that it has zero folding endurance, and its elongation has been reduced from 158 to about 6%. Similarly, the elongation of the 0.5-mil Mylar has been reduced from 99 to about 2% at the break point.

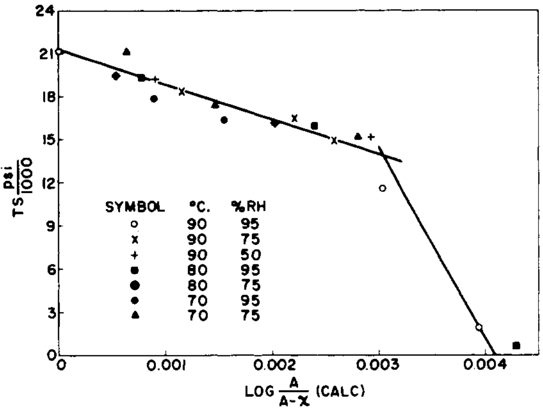


Figure 19. Tensile strength versus extent of degradation of 0.5-mil Mylar film

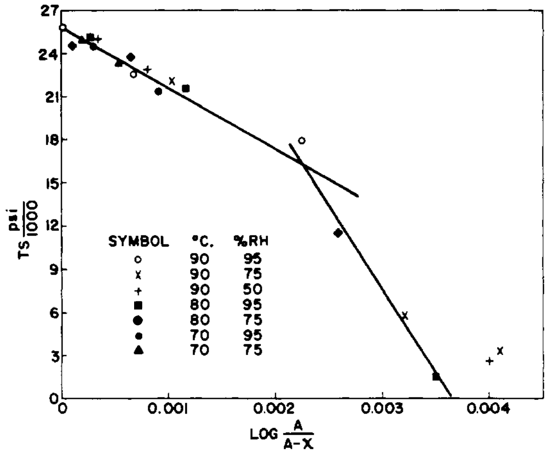


Figure 20. Tensile strength versus extent of degradation of 10-mil Mylar sheet

Table XXVIII. Changes in Physical Properties

Material	Time, Days, t	Tensile Strength, P.S.I. ÷ 1000	Elongation, %	Fold. End. Double Folds	$[\eta]$	$\log \frac{A}{A-x}$
			Temperature 71 °C. 95% RH			
10-mil Mylar	0	25.8	158	6,072	0.603	0
	49	24.7	211	8,919	0.5556	0.00030
	126	21.9	166		0.4846	0.00091
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	49	17.9	67.0		0.4737	0.00089
	84	16.4	55.9		0.4198	0.00156
	212	6.3	0.8		0.2976	0.00417
Dacron	0	121	11.6		0.600	0
	77	115	19.7		0.5608	0.00024
			Temperature 90 °C. 95% RH			
10-mil Mylar	0	25.8	158	6,072	0.603	0
	14	22.5	157	4,818	0.5124	0.00065
	35	17.9	5.9	0	0.3827	0.00225
	63	2.43	0.5	0	0.2318	0.00704
	77	1.02	0.3	0	0.1889	0.01016
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	14	17.3	60.4		0.4250	0.00148
	29	11.6	2.06		0.3395	0.00301
	35	2.12	3.67		0.3055	0.00390
Dacron	0	121	11.6		0.5950	0
	14	119	22.5		0.5840	0.00008
	29	115	22.3		0.5452	0.00035
	77	97	22.3		0.4416	0.00137
	133	59.2	16.8		0.3327	0.00327
			Temperature 82 °C. 95% RH			
10-mil Mylar	0	25.8	158	6,072	0.603	0
	14	25.1	160	10,015	0.5673	0.00023
	49	21.7	184	3,951	0.4605	0.00116
	98	1.47	0	0	0.3240	0.00345
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	14	19.3	94.8		0.4867	0.00076
	49	16.0	7.9		0.3581	0.00238
	77	0.84	0		0.2946	0.00430
Dacron 1100 den.	0	121	11.6		0.600	0
	14	120	31.6		0.5917	0.00003
	77	108	22.5		0.5111	0.00063
	175	103	20.3		0.4343	0.00146

Table XXIX. Changes in Physical Properties

Material	Time, Days, t	Tensile Strength, P.S.I. ÷ 1000	Elongation, %	Fold.End. Double Folds	$[\eta]$	$\log \frac{A}{A-x}$
		Temperature 71°C. 75% RH				
10-mil Mylar	0	25.8	158	6,072	0.603	0
	49	25.1	208	14,180	0.5757	0.00018
	175	23.2	167	6,773	0.525	0.00054
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	49	21.2	115		0.5032	0.00061
	112	17.5	65.7		0.4275	0.00145
	273	15.2	3.9		0.3497	0.00279
Dacron	0	121	11.6		0.600	0
	105	115	19.7		0.5819	0.00009
	175	118	19.8		0.5689	0.00018
		Temperature 82°C. 75% RH				
10-mil Mylar	0	25.8	158	6,072	0.603	0
	14	24.5	157	8,351	0.5840	0.00012
	49	23.9	210	5,428	0.5164	0.00062
	140	11.5	1.6	0	0.3647	0.00258
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	14	19.5	88.6		0.5111	0.00054
	49	16.2	23.1		0.3896	0.00202
	105	7.2	0.8		0.2634	0.00541
Dacron	0	121	11.6		0.600	0
	14	122	19.4		0.6007	0
	105	112	21.3		0.5283	0.00050
	175	113	21.3		0.4696	0.00104
	296	75.3	17.4		0.3568	0.00273
		Temperature 90°C. 75% RH				
10-mil Mylar	0	25.8	158	6,072	0.603	0
	14	24.4	167	7,119	0.5621	0.00026
	35	22.2	201	3,038	0.4699	0.00106
	77	5.78	0.7	0	0.3353	0.00321
	84	3.36	0.3	0	0.3027	0.00409
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	14	18.4	74.8		0.4496	0.00117
	29	16.4	9.2		0.3744	0.0022
	35	14.9	2.5		0.3451	0.00259
Dacron	0	121	11.6		0.600	0
	14	119	21.5		0.5724	0.00015
	77	106	22.0		0.4792	0.00094
	133	85.9	18.7		0.4041	0.00188

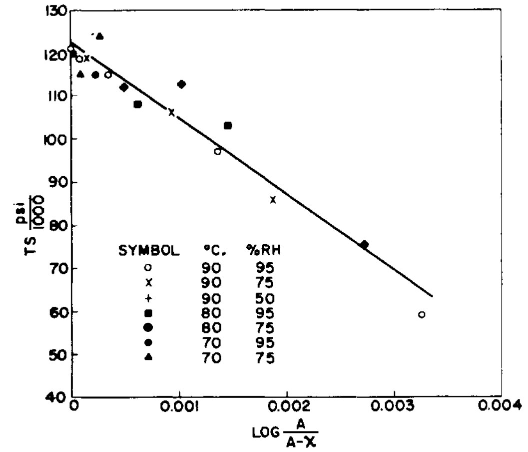


Figure 21. Tensile strength versus extent of degradation of Dacron yarn

Water Vapor Transmission. Water vapor transmission measurements were made on the 0.5-mil film before and after hydrolytic degradation. Specimens were exposed at 90° C. and 95% RH for periods up to 25 days and then mounted on aluminum cups containing saturated sodium chloride solution and placed in a desiccator over anhydrous calcium chloride at 73° F. The cups were weighed periodically until the weight loss became constant.

The results of the water vapor transmission tests are given in Table XXXII. No significant change in the rate of water vapor transmission occurred after the film had been exposed to 90° C. and 95% RH for up to 25 days. This exposure results in a degree of degradation somewhat less than that which exists at the break point as previously discussed. This extreme condition was purposely avoided because of the difficulty which could be experienced in handling and mounting highly embrittled specimens. This 25-day exposure is calculated to produce a strength loss of about 40% and a reduction in elongation from 99.4 to about 18%.

The results indicate that no substantial changes have occurred in the continuity of the film as a result of the hydrolytic degradation, and this is reflected in no abrupt change in the rate curve for degradation.

CONCLUSION

The rate of hydrolytic degradation of Mylar and Dacron is shown in Tables VIII, XV, XVI, XVII, and XVIII. The rate of hydrolysis of this polymer is several orders of magnitude greater than the rate of oxidation or of thermal decomposition. Chemical degradation is related to physical degradation as shown in Figures 19 and 20. A quasi-relationship between these and electrical degradation has also been established. With these data, reasonably accurate estimates can be made of the minimum time required for these materials to reach a given degree of degradation at any chosen temperature or humidity.

Figure 19 shows that when $\log \frac{A}{A-x}$ for 0.5-mil film

Table XXX. Changes in Physical Properties

Material	Time, Days, *t*	Tensile Strength, P.S.I. ÷ 1000	Elongation, %	Fold.End. Double Folds	$[\eta]$	$\log \frac{A}{A-x}$
		Temperature 71 °C. 50% RH				
10-mil Mylar	0	25.8	158	6,072	0.603	0
	126	23.8	158	10,932	0.5698	0.00021
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	56	18.8	76.3		0.509	0.00055
	175	18.5	76.6		0.4238	0.00152
Dacron	0	121	11.6		0.600	0
	140	117	19.3		0.5974	0.00001
		Temperature 82 °C. 50% RH				
10-mil Mylar	0	25.8	158	6,072	0.603	0
	56	23.9	206	8,165	0.545	0.00039
	140	20.2	147		0.4578	0.00119
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	56	16.8	62.5		0.4224	0.00153
	84	16.0	9.4		0.3577	0.00261
Dacron	0	121	11.6		0.800	0
	56	118	21.2		0.5637	0.00022
	175	116	20.6		0.5164	0.00059
		Temperature 90 °C. 50% RH				
10-mil Mylar	0	25.8	158	6,072	0.603	0
	21	25.1	170	9,745	0.5543	0.00032
	56	22.8	208	4,283	0.4979	0.00080
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	21	19.2	92.6		0.4753	0.0009
	56	15.1	2.5		0.3381	0.00305
	98	0	0		0.2257	0.00737
Dacron	0	121	11.6		0.600	0
	21	116	20.7		0.5789	0.00011
	77	112	21.7		0.5296	0.00047
	105	107	20.6		0.5270	0.00050

reaches 0.003, about one third of the tensile strength of the film has been lost, and from there on the rate of loss increases sharply. Up to this point the electrical properties of the polymer do not seem to be affected seriously. Hence this may be considered a safe limit for defining the useful life of the film. The corresponding value of $\log \frac{A}{A-x}$ for 10-mil sheet is 0.0022, as shown in Figure 20. Using these criteria, curves have been drawn showing the estimates of minimum time required to reach this point at various temperatures and humidities. These estimates are shown in Figures 22 and 23, and they effectively epitomize this study.

Polyethylene terephthalate compared with other organic esters is truly unusually resistant to hydrolysis. It is even more resistant to oxidation and thermal decomposition. At moderate temperatures and humidities these agents of degradation should not cause serious changes in Mylar or Dacron for many years. A possible exception is their effect on surface resistivity at very high humidities.

Low pH does not speed up hydrolysis, and the polymer is less reactive with hydroxyl compounds such as aliphatic

Table XXXI. Changes in Physical Properties

Material	Time, Days, *t*	Tensile Strength, P.S.I. ÷ 1000	Elongation, %	Fold.End. Double Folds	$[\eta]$	$\log \frac{A}{A-x}$
		Temperature 82 °C. 20% RH				
10-mil Mylar	0	25.8	158	6,072	0.603	0
	77	25.3	181	11,426	0.5686	0.00022
	283	21.7	181		0.5085	0.00069
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	56	18.7	74.0		0.505	0.00059
	140	16.5	66		0.4224	0.00153
	282	11.5	4.2		0.3185	0.00355
Dacron	0	121	11.6		0.595	0
	77	119	19.1		0.5780	0.00012
		Temperature 90 °C. 20% RH				
10-mil Mylar	0	25.8	158	6,072	0.603	0
	84	24.8	192	7,847	0.5491	0.00036
0.5-mil Mylar	0	21.2	99.4		0.5813	0
	56	17.8	60.1		0.4726	0.00091
	105	16.3	29.7		0.4100	0.00171
Dacron	0	121	11.6		0.595	0
	56	118	20.5		0.5884	0.00005

Table XXXII. Water Vapor Transmission Hydrolyzed 0.5-Mil Mylar Film

Treatment	Grams/Square Meter 24 Hours
Film as received	15.6 16.2 18.5
Film exposed to 95% RH st 90°C.	
12 days	16.4 17.4
18 days	16.3 17.9
25 days	15.4 16.3

alcohols than with water. When the polymer is cold-drawn and exposed to hydrolysis, it retains tensile properties longer than undrawn polymer under the same conditions. In the form of 10-mil thick sheets, Mylar hydrolyzes less rapidly than 0.5-mil thick films. However, Dacron filaments hydrolyze much more slowly than the sheet material, even though their diameter is only 0.5 mil. It is evident that the outward form of the polymer samples influences its resistance to hydrolysis, and also that the structure of the polymer on a molecular scale is equally important in this respect.

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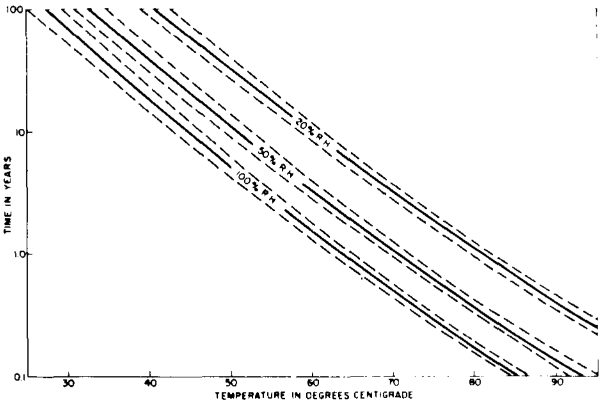

Figure 22. Degradation of 0.5-mil Mylar film

to log $\frac{A}{A-X}$ = 0.003 (confidence limit 0.95)

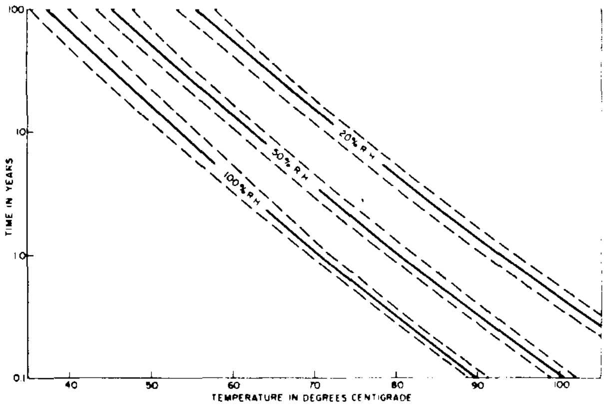

Figure 23. Degradation of 10-mil Mylar sheet

to log $\frac{A}{A-X}$ = 0.0022 (confidence limit 0.95)

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Some Anhydride Curing Agents for Epoxy Resins

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In his original patent, Castan (2) described the curing of polyolepichlorohydrin condensation products with dicarboxylic acid anhydrides, and in recent years the use of anhydrides in this application has continued to grow. Although they lack the high reactivity of polyamine curing agents and generally cannot be employed in room-temperature curing, anhydrides find use with the epoxy resins of low molecular weight because of their low exotherms, freedom from skin sensitization, and the good chemical and electrical properties which they usually impart.

The availability of itaconic and citric acids from fermentation sources affords an interesting opportunity to compare the effect of various modifications of a basic succinic anhydride structure on the properties of epoxy-resin curing agents. Itaconic (I), citraconic (II), and methylsuccinic (III) anhydrides may be derived from itaconic acid, while