

Aqueous Degradation of Polyimides

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Synopsis

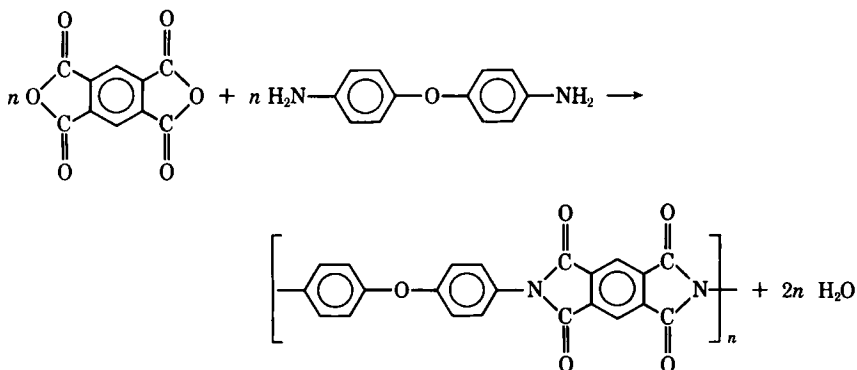
The effect of an aqueous environment on the tensile properties of Kapton polyimide film has been investigated. Immersion of specimens in distilled water at 25° to 100°C for time periods ranging from one hour to several hundred hours resulted in a decrease in the ultimate tensile strength of the polymer from 23 ksi to approximately 14 ksi, and a corresponding decrease in elongation to failure from 38% to approximately 5%. The kinetics of this decrease in mechanical properties are second order and yield an activation energy of approximately 15.6 kcal/mole. The reaction is slightly dependent on pH in the range 2.0 to 12.0, but is highly dependent on the pH in the range 0.4 to 2.0. The decrease in mechanical properties at pH 2.0 to 6.0 appears to be due to hydrolysis of either uncyclized amic acid linkages or diamide functional groups present in the polyimide, whereas that at pH below 2.0 is probably the result of hydrolysis of both imide and amide bonds. Prolonged reflux of the polyimide in water resulted in the extraction of a water-soluble, amide-containing material.

INTRODUCTION

Resins such as polyesters, epoxies, and polyimides are used as organic matrices in high-strength composite structures that are subjected to varying environmental conditions. Environmental effects such as stress cracking, plasticization, and crazing are well known in nylons, hydrocarbon polymers, and epoxies. Very little information is available concerning the environmental degradation of polyimides. Several workers¹⁻³ have superficially studied the effect of water on the tensile properties of polyimides, but no detailed work has been presented showing the effect of such parameters as time and temperature of treatment or the pH of the solution. This investigation deals with a systematic variation of these parameters and the derivation of the kinetics for the aqueous degradation of the mechanical properties of polyimide film. A specific effort has been made to differentiate between chemical effects, such as hydrolytic chain scission, and purely physical effects, such as plasticization. The environmental effects of organic solvents and other solutions were also investigated and are the subject of a separate paper.⁴

EXPERIMENTAL

The polyimide used in this investigation was du Pont's Kapton film, which is a condensation product of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether:



Dumbbell tensile specimens, with neck dimensions 1.50 in. \times 0.250 in. \times 0.005 in. were punched from 0.005 in. thick Kapton film rolls and are shown in Figure 1. The tensile properties of the film in its as-received condition showed a slight orientation effect that correlated with fabrication striations along the length of the roll. All specimens investigated were punched so that these striations were parallel to the length of the dumbbell.

Samples were immersed in water at temperatures ranging from 25° to 100°C for time intervals ranging from one hour to several hundred hours. The pH of the solution was monitored before and after each experiment. After treatment, the samples were removed from the solution, dried of any adhering water on filter paper, and permitted to come to room temperature.

The tensile tests were run on an Instron tensile tester with an initial grip separation of 2.07 in. and a cross-head speed of 0.1 in./min. Infrared analysis was performed using a Perkin-Elmer 521 spectrophotometer. The spectra of the films were recorded directly while that of the water-soluble extract was run in a KBr disk. X-Ray diffraction was done using a Picker theta-theta x-ray diffractometer and a General Electric XRD-5 diffraction unit for the flat plate studies.

DISCUSSION AND RESULTS

Figures 2 and 3 show the decrease in elongation to failure and ultimate tensile strength of Kapton film specimens as a function of treatment time in distilled water (pH 6.0) at 25°, 45°, 62°, 80°, and 100°C. It is

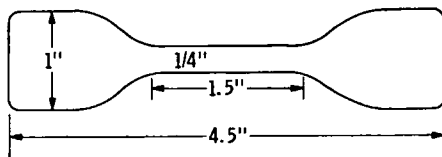


Fig. 1. Geometry of tensile specimen.

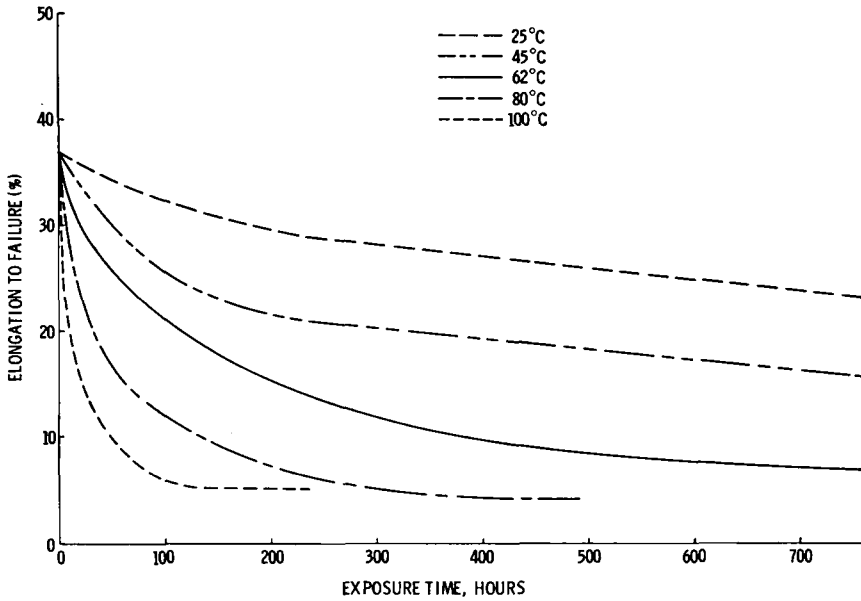


Fig. 2. Decrease in elongation to failure for samples immersed in distilled water.

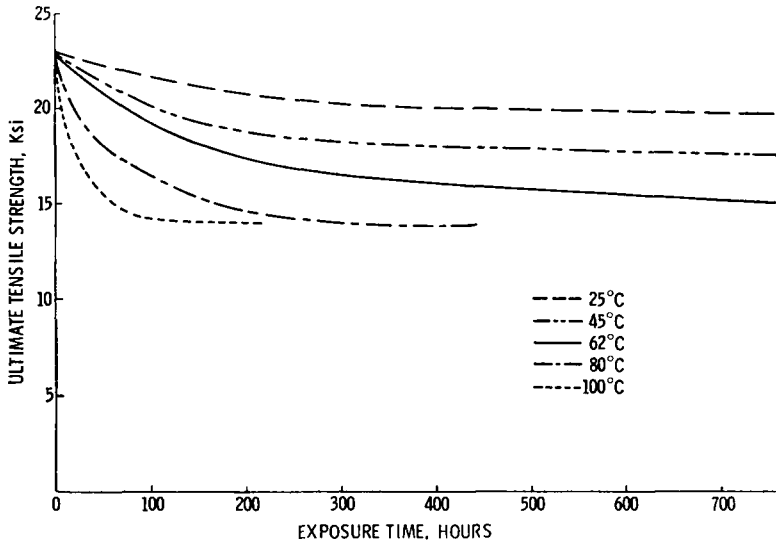


Fig. 3. Decrease in ultimate tensile strength for samples immersed in distilled water.

apparent, from these curves, that this decrease approaches an asymptote after approximately 100 and 350 hr for samples heated at 100° and 80°C, respectively. The asymptote corresponds to an ultimate elongation of about 5% and a tensile strength of about 14 ksi. Although the asymptote for samples treated at 62°C is not apparent in Figures 2 and 3, the

mechanical properties at this treatment temperature approached the above values after approximately 950 hr.

The kinetics corresponding to the percentage decrease of tensile strength and elongation to failure have been investigated in order to achieve a better understanding of the nature of the degradation process. The decrease in each tensile property was found to be second order with respect to that property, by obtaining good agreement for the rate constants k calculated from the integrated form of the simple second order rate expression,⁵ i.e.,

$$k = \frac{1}{t} \frac{\lambda - \lambda_0}{(\lambda_\infty - \lambda_0)(\lambda_\infty - \lambda)}$$

where t = treatment time, λ = (tensile property at time t /tensile property of untreated sample) $\times 100\%$, λ_0 = value of λ for untreated sample and λ_∞ = value of λ at the asymptote.

These calculated rate constants, as well as the treatment temperature, are listed in Table I, where k_E and k_{TS} are the rate constants for the decrease in elongation to failure and ultimate tensile strength, respectively. Based on the rate constants calculated for the decrease in elongation to failure for samples heated for times up to 1500 hr at 25° and 45°C, approach of the tensile properties to within 0.5% of the asymptote at the higher temperature treatment was calculated to occur after 22,000 and 4000 hr, respectively, at these temperatures.

Figure 4 shows the envelope of stress-strain curves obtained for 50 untreated samples. The values of tensile properties at failure for samples treated in water at the designated temperatures are plotted on the same graph. Clearly, the treated samples have the same tensile deformation mechanism as the untreated specimens but fail at a lower value of elongation and lower tensile strength. The modulus was found to be unaffected by the time and temperature of immersion, suggesting that the observed decrease in mechanical properties is not simply due to a plasticization phenomenon. This hypothesis is confirmed by the reversibility test data given in Table II. The high standard deviations were attributed to the very high notch sensitivity of the samples and to the 10% difference in sample thickness as reported by du Pont.⁶

Cooper⁷ had observed that extreme brittleness for heat-treated specimens of Westinghouse AI-8 (pyromellitic dianhydride plus 3,4'-diamino-

TABLE I
Kinetics of Aqueous Degradation of Kapton Film

T , °C	k_E , % ⁻¹ hr ⁻¹	k_{TS} , % ⁻¹ hr ⁻¹
25	1.9×10^{-5}	—
45	1.1×10^{-4}	—
62	4.7×10^{-4}	1.5×10^{-4}
80	1.3×10^{-3}	5.4×10^{-4}
100	3.8×10^{-3}	2.0×10^{-3}

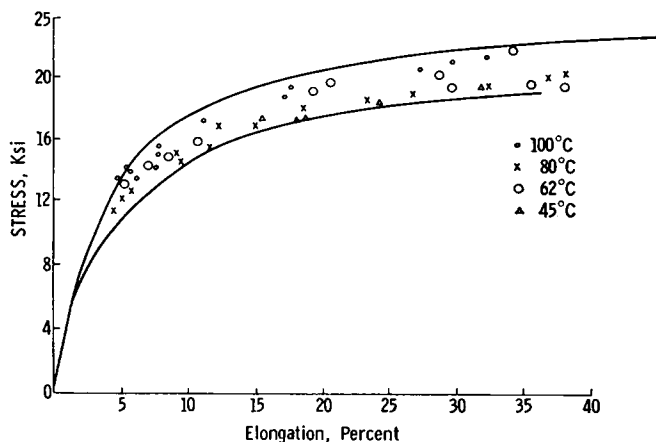


Fig. 4. Average failure points of treated Kapton samples superimposed on the envelope of stress strain curves of 50 untreated samples.

benzamide) was the result of an increase in the crystallinity of the polyimide. The x-ray diffraction pattern of the untreated film and samples treated to maximum brittleness (corresponding to ten days at 100°C in water) showed only diffuse rings for both samples. The average crystallite size was calculated using the Scherrer equation, i.e.,

$$L = \frac{K\lambda}{B_0 \cos \theta},$$

where L is the crystallite dimensions, B_0 is the breadth of the reflection occurring at an angle 2θ , and K is a constant equal to approximately unity. The average crystallite size, calculated from the most intense reflection at 7 degrees, 2θ , was 12 Å and 14 Å for the untreated and treated samples, respectively. This indicates that both samples are completely amorphous and that the brittleness of the treated specimen is not the result of increased crystallinity.

Another mechanism that might explain the degradation of this material is chain scission caused by hydrolysis. The elongation to failure and the

TABLE II
Reversibility Tests of Kapton Film Refluxed in Water

Treatment	Tensile strength, ksi	Elongation to failure, %
95 hr reflux	13.8 ± 0.9	5.9 ± 1.1
95 hr reflux + 24 hr in vacuo	15.6 ± 1.5	7.2 ± 1.4
117 hr reflux	15.4 ± 2.2	7.6 ± 2.4
117 hr reflux + 24 hr in vacuo	15.4 ± 1.2	6.6 ± 0.7

tensile strength can be related to the number-average molecular weight by an equation of the type⁸

$$P_m = P_\infty - \frac{A}{\bar{M}_n}$$

where P_m and P_∞ are the values of the mechanical property at molecular weight \bar{M}_n and at infinite molecular weight, respectively, and A is a constant that indicates how the mechanical property changes with the number-average molecular weight \bar{M}_n . Wallach⁹ has calculated the value of P_∞ and A for Kapton or polyimide film to be 25 ksi and 36×10^4 ksi-g/mole from a plot of tensile strength versus \bar{M}_n^{-1} of the uncyclized amic acid. These constants were used to calculate a molecular weight of 164,000 g/mole for the untreated samples and a value of 31,000 g/mole for the limiting molecular weight, corresponding to the asymptotic value of the tensile strength. The average number of bonds broken per chain at any time can be related to molecular weight before and after treatment by

$$n = \frac{\bar{M}_{n_1} - \bar{M}_{n_2}}{\bar{M}_{n_2}}$$

where n is the number of bonds broken, and \bar{M}_{n_1} and \bar{M}_{n_2} are the initial and final number-average molecular weights, respectively. This analysis indicates that the observed change in tensile strength corresponds to an average cleavage of 4.3 bonds/chain and a decrease in the degree of polymerization from 860 to 160. The asymptotic values of the mechanical properties at long treatment times indicate that the hydrolysis is clearly not occurring at the abundant imide linkages. This hypothesis agrees with literature maintaining the hydrolytic stability of simple imides at neutral pH. However, aromatic amide structures that contain another amide group or a carboxyl group substituted in the ortho position on the ring have been reported to exist in small quantities in polyimides^{10,11} and are known to be susceptible to hydrolysis as a result of an internal cooperative mechanism involving the ortho substituent.^{12,13} The structures have not been detected in the infrared spectrum of the polyimide (Fig. 5), but this is not unexpected, since the ratio of the hydrolyzable groups to imide groups is only about 0.6%.

The values for tensile strength at 100°, 80°, and 62°C were converted to mole fraction of hydrolyzable bonds as described previously. These values were substituted into the differential form of the rate expression, i.e.,

$$\frac{-dx_h}{dt} = kx_h^n,$$

where x_h is the mole fraction of hydrolyzable bonds. A plot of $\log(-dx_h/dt)$ against $\log x_h$ yielded straight lines with slopes of approxi-

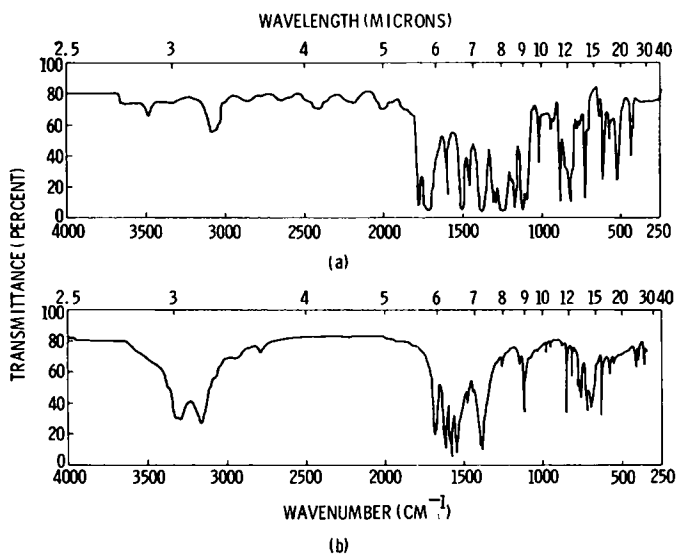


Fig. 5. Infrared spectrum of (a) untreated Kapton, (b) aqueous extract.

mately 2 for the three temperatures investigated. This indicates that the reaction is second order with respect to the concentration of hydrolyzable linkage and that following the change in tensile properties as a measure of the rate of the reaction is justifiable. On this basis, a least-squares Arrhenius plot of the rate constants listed in Table I versus $1/T$ is shown in Figure 6. The energy of activation was calculated, from the slopes of these lines, to be 16.0 kcal/mole and 15.1 kcal/mole for the decreases in elongation, and tensile strength, respectively. These values, which are within experimental error of each other, are in good agreement with reported values of the activation energy for the hydrolysis of amides¹⁴ and substantiate the hypothesis that the hydrolytic degradation is the result of amide hydrolysis.

pH Dependence

The effect of pH on the elongation to failure for samples refluxed in water for 24 hr is shown in Figure 7. A similar curve is obtained for a plot of tensile strength against pH. The dilute acid portion of the curve, pH 2.0 to 5.5, indicates that the rate of hydrolysis is slightly dependent on the hydrogen ion concentration. Additional work is being done in order to ascertain whether the mechanism for hydrolysis involving an ortho-substituted amide or carboxyl group suggested previously could occur throughout the dilute acid region and the effect of pH on the mechanism. A sharp decrease above pH 12 is the result of a base-catalyzed hydrolysis of imide linkages. Polyimide samples treated for longer time periods at these alkaline pH's exhibited a complete breakdown of the structural integrity, with tensile strength and elongation to failure

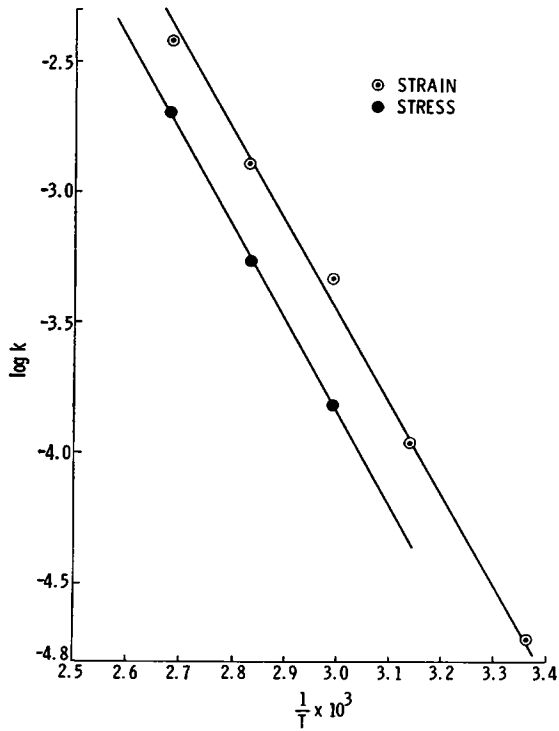


Fig. 6. Arrhenius plot for the aqueous degradation of Kapton.

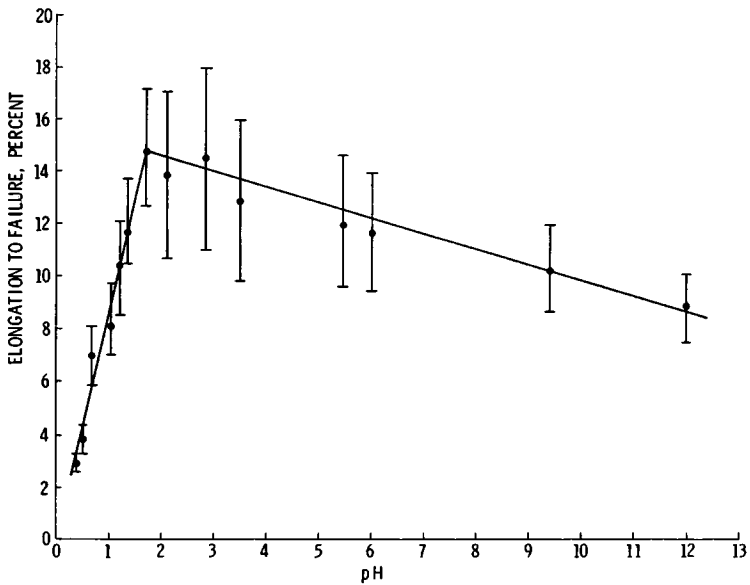


Fig. 7. pH Dependence of strain to failure for Kapton samples treated 24 hr in water at 100°C.

approaching zero rather than the asymptotes that were observed for the samples treated in dilute acid.

In the stronger acid region of the plot, below pH 2, the elongation to failure shows a linear dependence on the pH. At pH < 0.5, the elongation to failure is lower than the 5% reached after 100 hr of reflux in distilled water. This indicates that a second process, which is dependent upon the concentration of hydrogen ion, is occurring at low pH, i.e., the strong acid hydrolysis of amide and imide bonds,¹⁵ which is consistent with the mechanical properties dropping below the asymptote found in the neutral regions.

Aqueous Extract

After approximately 24 hr of aqueous reflux of the Kapton samples, a yellow coloration was observed in the distilled water. This color became intensified as a function of the time of treatment. In an effort to isolate the water-soluble material, an H₂O extraction was performed on a 50-g portion of shredded polyimide film in a Soxhlet apparatus. The distilled water turned orange brown after one week's extraction, but no precipitation was observed. After approximately 95% solvent evaporation, about 200 mg of a light-brown extract was precipitated by ethanol addition.

An infrared spectrum of this extract, as well as untreated Kapton film shown in Figure 5, indicates that these two materials were radically different. The absorption bands characteristic of cyclic imides at 1780 cm⁻¹ and 1720 cm⁻¹ are noticeably absent in the spectrum of the extract. Strong absorptions are present at 1618, 1548, 719, and 630 cm⁻¹, all indicative of amide linkages.

These data indicate that the extract is not low molecular weight polyimide. The lattice parameters, as obtained from x-ray diffraction, revealed that the extract was not a simple mixture of monomers. Further work, including purification and elemental analysis, is planned in order to elucidate the structure of the extract.

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