

Hydrolytic Stability of a Polyalkane Imide

INTRODUCTION

In the present series of papers,^{1,2} the effects of an aqueous environment on the tensile properties of Kapton polyimide film have been investigated. This environment has been shown to cause a marked decrease in the ultimate tensile strength (UTS) and elongation to failure (ETF), which has been attributed to hydrolysis of uncyclized amic acid or diamide linkages along the chain. Thermal treatment of the hydrolytically degraded film has been found to regenerate up to 97% of the UTS and 81% of the ETF, and the hydrolytic stability of this material is greatly improved. As part of this general study, this note contains the results of the effect of an aqueous environment on the tensile properties of Poly-X, a polyalkane imide. The kinetics of aqueous degradation are derived, and a comparison is made between this material and Kapton polyimide film.

EXPERIMENTAL

The film used throughout this study was 5-mil developmental Poly-X polyimide film supplied by Raychem Corporation. It is derived from pyromellitic dianhydride and a long chain aliphatic diamine.³ Environmental treatment was carried out by immersion of the specimens in distilled water at temperatures ranging from 68° to 100°C. The temperature was controlled to within $\pm 1^\circ\text{C}$. Total water pickup was 0.4%.

Tensile specimens, the geometry of which has been described previously,¹ were punched from the 5-mil film. Tensile testing was performed on groups of five specimens at room temperature on an Instron table-model tensile tester at an extension rate of 7%/min.

RESULTS AND DISCUSSION

The results of the tensile tests on Poly-X treated in distilled water show that the UTS and, to a much greater extent, the ETF decrease significantly as a function of time and temperature. This effect is similar to that observed for Kapton polyimide film,¹ which was found to be due to hydrolytic chain scission. However, since the water pickup by Kapton is approximately 10 times greater than that of Poly-X, and Kapton is completely amorphous whereas Poly-X is approximately 35% crystalline, it was not immediately apparent that the mode of aqueous degradation would be identical in both cases. Figure 1 shows the stress-strain curve for untreated Poly-X as well as points designating the observed ultimate tensile properties for some specimens treated in water. The yield stress and the yield strain of 6.86 ± 0.32 Ksi and $13.6 \pm 0.5\%$ for untreated film do not show any appreciable change as a function of aqueous treatment, but the ultimate properties show a time-temperature-dependent decrease and occur along the curve for untreated Poly-X. This behavior is similar to that observed for Kapton film in an aqueous environment, suggesting the possibility of hydrolysis as the mode of aqueous attack.

To investigate the kinetics of this attack, the ETF was used as the monitoring parameter because of the large changes observed as a function of treatment time. As shown in part in Figure 2, the ETF does not approach zero after long treatment times, but rather approaches a temperature-dependent asymptotic value (ϵ_∞), which was taken as the point at which the reaction had gone to completion.

These values as well as the time at which ϵ_∞ was determined are listed in Table I. The time-dependent values for ETF were substituted into the integrated forms of the reaction rate equation, and the order of the reaction was calculated to be second order by obtaining good agreement for the reaction rate constant k . The values of the rate constants obtained for the four temperatures studied are also listed in Table I.

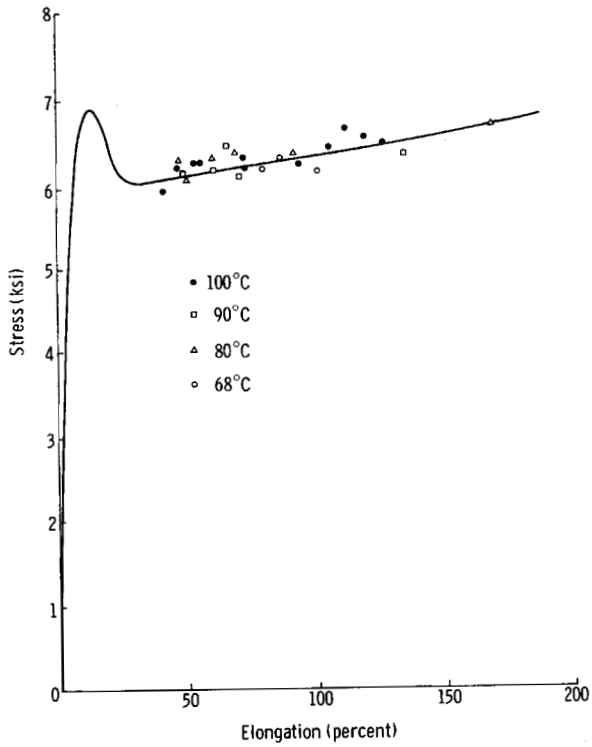


Fig. 1. Ultimate tensile properties of water-treated Poly-X superimposed on the stress-strain curve of untreated Poly-X.

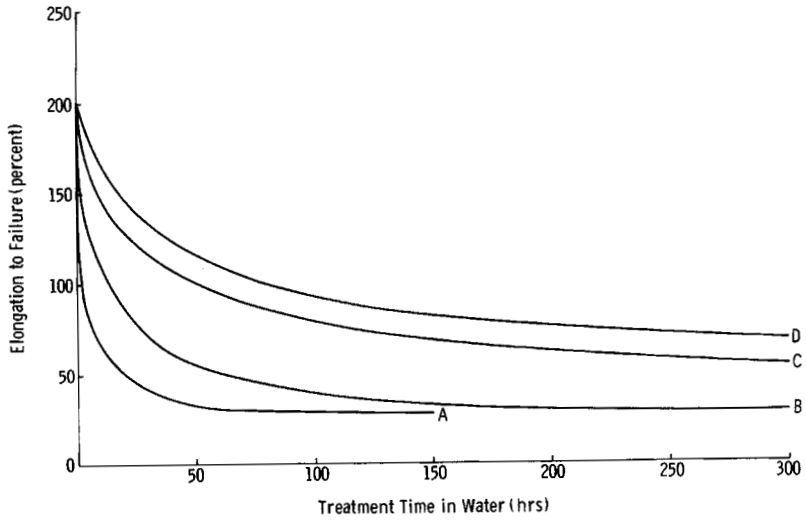


Fig. 2. Decrease in elongation to failure for Poly-X specimens treated in water at (A) 100°C, (B) 90°C, (C) 80°C, and (D) 68°C.

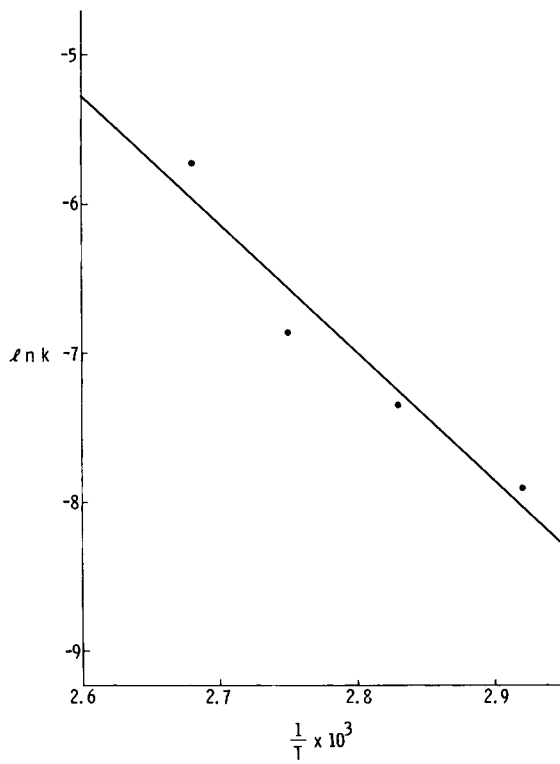


Fig. 3. Arrhenius plot for the aqueous degradation of Poly-X.

TABLE I
Kinetics of Aqueous Degradation of Poly-X

Treatment temp., °C	ϵ_{∞} , %	$t_{\epsilon_{\infty}}$, hr	Second-order rate constant k , % ⁻¹ hr ⁻¹
68	45	700	3.8×10^{-4}
80	35	600	6.7×10^{-4}
90	21	300	1.1×10^{-3}
100	21	100	3.5×10^{-3}

An Arrhenius plot of the rate constants for the degradation of Poly-X is shown in Figure 3. A least-squares fit of the Poly-X data yields an activation energy and activation entropy of 17.5 kcal/mole and 38 e.u., which are in excellent agreement with the calculated values of 15.6 kcal/mole and 36.0 e.u. for the hydrolytic degradation of Kapton.¹ On the basis of this agreement, it is not unreasonable to assume that Poly-X polyimide film undergoes selective hydrolysis on exposure to water above 65°C.

References

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3. E. C. Stivers (to Raychem Corp.) U.S. Pat. 3,551,200 **16**, 2909.

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