

Thermal Regeneration of the Tensile Properties of Hydrolytically Degraded Polyimide Film

R. DEIASI, *Research Department, Grumman Aerospace Corporation, Bethpage, New York 11714*

Synopsis

Heat treatment at temperatures of 224° to 310°C of hydrolytically degraded polyimide film has been shown to regenerate the ultimate tensile strength from 15.1 ksi to 24.3 ksi after 80 hr at 224°C and to 25.8 ksi after 2 hr at 310°C, whereas the elongation to failure is simultaneously increased from 6.3% to 38.3% at 224°C and to 50.7% at 310°C. Prior to degradation, the film had an ultimate tensile strength of 26.6 ksi and an elongation to failure of 62.0%. The kinetics of this regeneration indicate that the reaction corresponds to the two-step recombination of the hydrolytically attacked amide linkages that were initially present in the "as received" polyimide film. The regenerated polyimide exhibits a much improved hydrolytic stability over the untreated material and specimens heat treated directly without prior aqueous degradation.

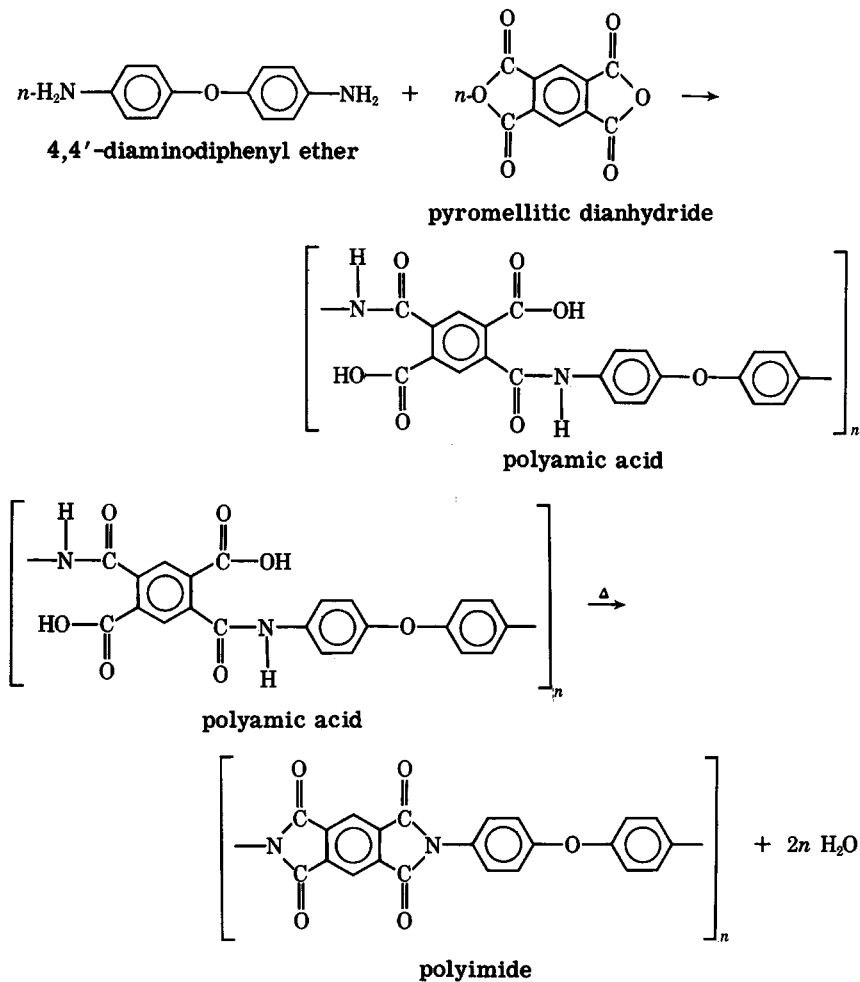
INTRODUCTION

Results of a recent study on the effect of an aqueous environment on the tensile properties of Kapton polyimide film suggest that the observed decrease in ultimate tensile strength and elongation to failure associated with treatment in distilled water at 25° to 100°C is the result of selective hydrolysis of either uncyclized amic acid or diamide linkages present in the polyimide.¹ It has been suggested that heat treatment of Kapton at 400°C in air for 10 to 15 min would decrease its susceptibility to hydrolytic degradation.² Preliminary experiments in our laboratory showed considerable blackening of the specimens under these conditions, possibly due to oxidative degradation. In view of the deleterious side effect of this heat treatment, hydrolytic stability tests were not run. However, this did serve as the starting point for an investigation of the effect of temperature on the tensile properties of hydrolytically degraded Kapton. This paper presents data for the thermal regeneration of the tensile properties of Kapton as well as the kinetics corresponding to this regeneration. In addition, comparison of the hydrolytic stability of the regenerated and "as received" polyimide is made.

EXPERIMENTAL

The polyimide used in this investigation was du Pont's Kapton film, the product of a two-step condensation polymerization of pyromellitic dian-

hydride and 4,4'-diaminodiphenyl ether with a polyamic acid intermediate, as shown:



Tensile specimens, the geometry of which has been previously described,¹ were punched from 5-mil-thick Kapton film. Specimens were immersed in boiling distilled water for 12 days to ensure complete hydrolytic degradation¹ and maximum brittleness. After degradation, the samples were removed from the aqueous environment, dried of any adhering water, and permitted to come to room temperature.

Regeneration of the tensile properties of the degraded polyimide was achieved by heat treatment of the specimens (usually in groups of 5) in a vertical-tube furnace in a flowing nitrogen atmosphere at temperatures above 220°C. The temperature was controlled to within $\pm 2^\circ\text{C}$. The samples were tested in tension to failure on a table-model Instron tensile tester at a cross-head speed of 0.1 in./min.

Inherent viscosities ($C = 0.5\%$ polyimide at 25°C) were measured in concentrated sulfuric acid. Dissolution times ranged from 100 to 300 min. Viscosity measurements were taken at 25°C in a No. 200 Cannon Fenske viscometer (solvent flow time of 112 sec).

Calorimetric measurements were made, using a du Pont 900 thermoanalyzer with the differential scanning calorimeter (DSC) plug-in module. Runs were made at a heating rate of $10^\circ\text{C}/\text{min}$ with dried nitrogen (0.1 lpm) flowing through the calorimeter to prevent oxidation and to remove any reaction products. The temperature was calibrated using the melting points of pure indium and tin powders.

RESULTS AND DISCUSSION

Regeneration of Tensile Properties

The hydrolytic degradation of 5-mil Kapton polyimide film in distilled water at 100°C , as manifested by the change in ultimate tensile strength (UTS) and elongation to failure (ETF), has been shown to approach completion after approximately five days.¹ To ensure a completely degraded, uniform starting material, the as-received polyimide film having UTS and ETF of 26.6 ± 0.8 ksi and $62.0 \pm 5.9\%$, respectively, was heated for 12 days in distilled water at 100°C . The UTS and ETF for the degraded polyimide are 15.1 ± 0.8 ksi and $6.3 \pm 1.2\%$, respectively. The specimens in this condition served as the starting material for the regenerative heat treatment.

The UTS and ETF for the as-received material used throughout this investigation are higher than the corresponding values of 23 ksi and 38% reported for the material tested previously.¹ The material used in the previous investigation was taken from a much older lot, and it is quite possible that the difference is due to a slight hydrolytic attack of the polyimide from water vapor at room temperature since it has been shown that samples immersed in water at room temperature show slight aqueous deg-

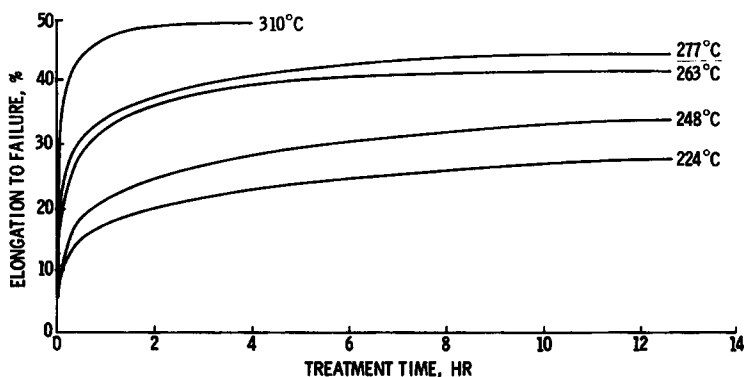


Fig. 1. Effect of regenerative heat treatment on the elongation to failure of hydrolytically degraded Kapton polyimide film.

TABLE I
Maximum Amount of Observed Regeneration of Tensile Properties

Temp., °C	Time, hr	Ultimate tensile strength, ksi	Elongation to failure, %
224	80	24.3	38.3
248	50	24.4	40.0
263	15	24.4	43.6
277	12	24.8	45.7
310	2	25.8	50.7

TABLE II
Inherent Viscosities in Concentrated Sulfuric Acid

Treatment	$(\eta_{inh})_{25^\circ\text{C}}$, dl/g
As received	1.23
Degraded 12 days in H ₂ O at 100°C	1.03
Degraded 12 days in water at 100°C plus regeneration in N ₂ at 310°C for 3 hr	1.23

radation. The UTS and ETF for the degraded specimens, however, are in good agreement for both materials (14.0 ksi versus 15.1 ksi and 5.0% versus 6.3%).

Figure 1 depicts the regeneration of hydrolytically degraded Kapton as measured by the elongation to failure, as a function of heat treatment time at elevated temperatures. The maximum attainable regeneration of both the UTS and ETF, as well as the treatment time required for maximum regeneration at the temperatures investigated, are listed in Table I. Additional heat treatment for times approximately twice those for maximum regeneration caused neither further regeneration nor a decrease in the properties due to oxidative degradation.

Table II contains the inherent viscosity for as-received Kapton as well as specimens subjected to hydrolytic degradation and hydrolytic degradation plus regenerative heat treatment. These data confirm the hypothesis of a molecular weight decrease resulting from hydrolytic chain scission on exposure to boiling water and a corresponding increase in molecular weight to a value that approximates the as-received polymer after heat treatment at 310°C for 3 hr.

Kinetics of Regeneration

Attempts to substitute the time-dependent values of ETF, ϵ , into the integrated form of the first- and second-order rate expression did not give a constant value for the reaction rate constant. A plot of $\ln(d\epsilon/dt)$ versus $\ln(\epsilon_\infty - \epsilon)$, an example of which is shown in Figure 2, indicates that the order of the reaction initially approximates second order for $0 < t < 0.2 t_{\max}$ (where t_{\max} = time to regenerate maximum tensile properties at a particular temperature). For $t > 0.2 t_{\max}$, the reaction follows first-order

TABLE III
Rate Constants Associated with the Kinetics of Regeneration

Temp., °C	Second-order step k , % ⁻¹ min ⁻¹	First-order step k , min ⁻¹
224	1.08×10^{-4}	7.37×10^{-4}
248	2.63×10^{-4}	1.60×10^{-3}
263	1.33×10^{-3}	2.77×10^{-3}
277	1.68×10^{-3}	6.43×10^{-3}
310	6.01×10^{-3}	2.98×10^{-2}

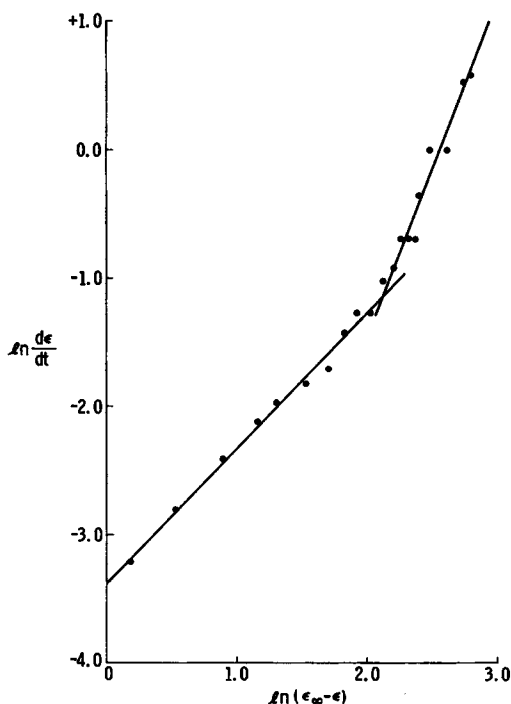


Fig. 2. Kinetics of regeneration of Kapton polyimide film at 224°C.

kinetics. The rate constants were determined for the second- and first-order reactions from the slope of a plot of $1/(\epsilon_{\infty} - \epsilon)$ versus t and $\ln [(\epsilon_{\infty} - \epsilon_0)/(\epsilon_{\infty} - \epsilon)]$ versus t , respectively, where ϵ_0 is the ETF of the fully degraded polyimide, ϵ is the ETF at time t , and ϵ_{∞} is the ETF of the fully regenerated polyimides, the value of which is temperature dependent, as shown in Table I. The calculated values of the rate constants are listed in Table III.

The activation energy and entropy for both reactions, listed in Table IV, were calculated from a least-squares fit of the slope and intercept of an Arrhenius plot of $\ln k$ versus $1/T$. Table IV also contains the experimental values obtained by two different investigators for the thermal cyclization of polyamic acid derived from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether. Both investigators started with polyamic acid films and

TABLE IV
Activation Energy and Activation Entropy Associated with the Regeneration

E_a , kcal/mole	Δs^\ddagger , e.u.	Reaction order	Reaction
27.6 ± 8.2	-24	2	this investigation—step 1
24.8 ± 5.4	-27	1	this investigation—step 2
26	-10	1	Kreuz et al. —step 1
23	-24	1	Kreuz et al. —step 2
24		1	Laius et al. —step 1 ($i = 0.3$)
30		1	Laius et al. —step 2 ($i = 0.7$)

followed the conversion to polyimide using IR spectroscopy. Kreuz et al.³ had observed a fast and a slow cyclization step depending on the degree of cyclization. Although the difference in activation energy for both steps is small, the entropy difference is quite significant ($\Delta s^\ddagger = -10$ e.u. and -24 e.u. for the first and second steps, respectively), indicating that control of the rates resides in the frequency factor. Laius et al.⁴ also observed a continuous change in both the frequency factor and the activation energy as a function of the degree of conversion, i . Both investigators suggest that the steric effects as well as the reduction of the polymer mobility and increased stiffness during the gradual saturation of the chain with rings may decrease the ability of the amide groups to arrange themselves for cyclization. Another possible explanation advanced by both is that the concentration of retained solvent accelerates the reaction through the generation of complexes with the free carboxyl, and that the amide $-\text{NH}$ group assists in favorable orientation for ring closure.

The good agreement of our activation data for the first-order reaction with that of both Laius and Kreuz indicates that our first-order reaction probably corresponds to a thermal cyclization of amic acid linkages. Factors such as solvent content and degree of cyclization have been shown to affect the rate of cyclization of polyamic acids,³⁻⁵ i.e., the higher the solvent content and the lower the degree of cyclization, the faster the reaction rate. These factors can readily explain why our rate constants for cyclization are lower than those previously reported,^{3,4} because first, the solvent content in our specimens is probably quite low as a result of its removal during the preliminary hydrolytic degradation process; and second, the degree of cyclization at the start of the regeneration procedure is already greater than 95% since only a few selective linkages along the chain have been hydrolyzed during the preliminary aqueous degradation procedure.

Analysis of the second-order reaction is not as straightforward. One possible interpretation of the rate-determining step would involve dehydration of the terminal α -dicarboxylic acid group produced during the chain scission since amines are not generally known to react with carboxylic acid groups but can react readily with acid anhydrides. However, differential

scanning calorimetry experiments performed on two model compounds, *o*-phthalic acid and pyromellitic acid, indicate that dehydration begins to occur in the vicinity of 175°C. The maximum rate of dehydration was observed at approximately 220°C for phthalic acid and 230°C for pyromellitic acid. These data suggest that additional substitution in the 4- and 5-positions of the aromatic ring does influence the rate of dehydration, a factor that cannot be accounted for directly in the case of a polyimide chain with a terminal dicarboxylic acid group. It also indicates that the rate of dehydration is occurring at a sufficiently rapid rate in the temperature range of interest (224°–310°C) to be ruled out as the determining step for the first reaction, since dehydration will probably occur during the first 2 min of heat treatment and the second-order reaction has been found to continue for approximately 0.4 hr at 310°C to 16 hr at 225°C. However, at lower temperatures, it appears that the rate of dehydration could become the rate-limiting step.

Another possible alternative for the second-order reaction would be an acylation reaction of the amino endgroup of one shortened chain by the terminal anhydride group of an adjacent chain. This reaction should be second order with respect to the number of chains, which is what the kinetics of regeneration show, and would require an appropriate reorientation of the two endgroups from two adjacent chains for acylation to take place. However, it has been postulated from a dynamic mechanical properties study, that torsional oscillation about the C—O—C diphenyl ether linkages occur at approximately 120°C in polyimides.⁶ Thus, it appears that once the rapid dehydration of the acid occurs, rotation about the C—O—C and C—N bonds can cause nucleophilic attack of the amine substituent on one of the carbonyl carbons of the anhydride group and result in amide formation.

Hydrolytic Stability

Hydrolytically degraded samples that were subsequently regenerated for 3 hr at 310°C in flowing nitrogen were retested for hydrolytic stability (using ETF and UTS as monitoring parameters) at 100°, 80°, 65°, and 50°C in distilled water. The behavior of regenerated polyimide is similar to that of as-received material, i.e., there is a time-temperature-dependent decrease in both UTS and ETF. However, as shown in Figure 3, the regenerated material at 100°C approaches asymptotic values for UTS and ETF of 23.0 ksi and 36.0% respectively, after approximately 300 hr, whereas the corresponding values for as-received polyimide are 15.1 ksi and 6.3% after approximately 120 hr. At 80°C, these values of UTS and ETF were approached after approximately 1400 hr, whereas at 65°C and 50°C, the calculated approach to the asymptotes was 2500 and 10,000 hr, respectively. These results show that the as-received polyimide is attacked much more rapidly than the regenerated material. This is also shown in the plot of the temperature dependence of the rate constant for decomposition (Fig. 4).

TABLE V
Kinetics of Aqueous Degradation

Temp., °C	k , % ⁻¹ hr ⁻¹ (as-received) ¹	k , % ⁻¹ hr ⁻¹ (degraded and regenerated)
100	3.8×10^{-3}	2.2×10^{-3}
80	1.3×10^{-3}	3.9×10^{-4}
65	—	2.2×10^{-4}
62	4.7×10^{-4}	—
50	—	5.3×10^{-5}
45	1.1×10^{-4}	—

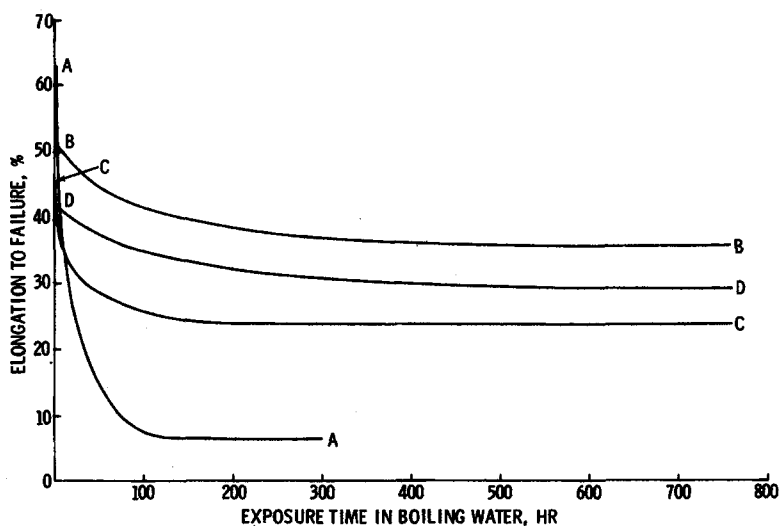


Fig. 3. Hydrolytic stability of Kapton polyimide film: (A) as-received, (B) degraded in water at 100°C for 12 days + 3 hr in N₂ at 310°C; (C) heat treated at 310°C in N₂ for 3 hr; (D) heat treated at 310°C in N₂ for 3 hr + hydrolytic degradation for 1000 hr at 100°C + 3 hr at 310°C in N₂.

To confirm the mode of hydrolytic attack, the kinetics of the degradation of the regenerated polyimide were studied. The decrease in ETF as a function of treatment time was found to follow second-order kinetics best by substitution into the integrated form of the rate expression and obtaining a constant value for the reaction rate constant, the values of which are listed in Table V together with the rate constants obtained previously¹ for the aqueous degradation of as-received Kapton polyimide film. An Arrhenius plot of $\ln k$ versus $1/T$ (Fig. 4) yields an activation energy of 16.9 ± 3.4 kcal/mole for the aqueous degradation of the regenerated polyimide and 15.6 kcal/mole for that of the untreated Kapton. This excellent agreement suggests that the reaction occurring in both materials is hydrolysis of amide linkages. The higher asymptotic values for the UTS and ETF obtained for the degradation of regenerated material indicate that fewer hydrolytically susceptible linkages remain after the regeneration process than were

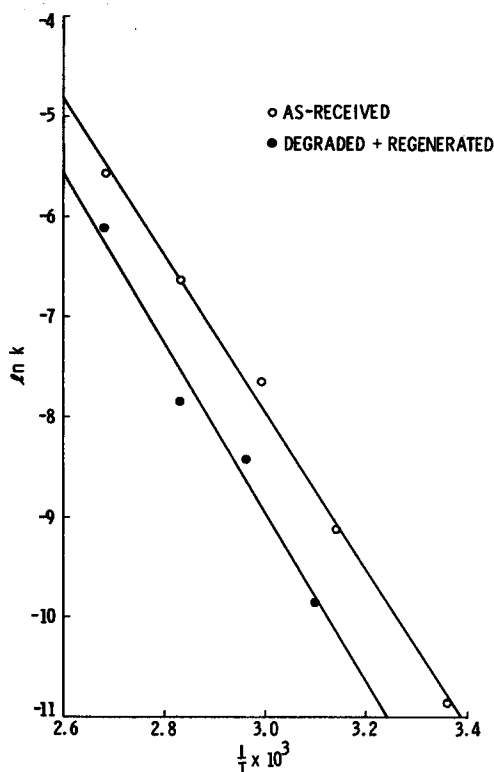


Fig. 4. Arrhenius plot for the aqueous degradation of (O) as-received and (●) degraded plus regenerated Kapton polyimide film.

originally present in the as-received film, suggesting that some of the susceptible amide linkages have been converted to nonsusceptible imide linkages as a result of the combined degradation and regeneration treatment, which has been confirmed by the regeneration kinetics.

Heat Treatment of As-Received Material

In an attempt to improve the hydrolytic stability without first undertaking the time-consuming aqueous degradation step, samples of Kapton were treated directly at 310°C for 3 hr in flowing nitrogen. The film darkened during this heat treatment, which was not observed for specimens given the prior aqueous degradation step, and exhibited a decrease in UTS and ETF to 24.6 ksi and 44.2% respectively. Measurement of the total transmittance of polychromatic light through these films yields a reduction in transmittance of approximately 25% for the heat-treated film. Although the heat treatment time employed is significantly less than that reported for a comparable decrease in ultimate tensile properties at 300°C in either air or an inert atmosphere,⁷ it appears that the observed darkening of the film is probably the result of the onset of slight oxidative degradation.

Specimens heat treated directly were tested for hydrolytic stability at 100°C. The decrease in UTS and ETF approach 20.5 ksi and 23.8% after approximately 160 hr, which is approximately half the time required for the degraded and regenerated material to approach the higher asymptotic values of 23.0 ksi and 36.0%. The observed decrease in ETF is shown in Figure 3. Clearly, the hydrolytic stability of the specimens given a direct heat treatment without prior aqueous attack is greatly improved over the as-received film, but the deleterious effect on the initial properties probably makes this treatment an undesirable one. In addition, this treatment does not improve the hydrolytic stability of the polyimide to the extent that the degradation plus regeneration treatment has been shown to do, and the latter treatment does not appear to cause any deleterious side reactions.

Specimens given the direct heat treatment at 310°C and degraded at 100°C in distilled water for 1000 hr were given a second heat treatment of 3 hr at 310°C, and the hydrolytic stability at 100°C was compared with that of the material given only one heat treatment. This second heat treatment did not even regenerate the ultimate tensile properties (24.3 ksi and 41.2%) to the already reduced values caused by the first heat treatment and only a slight improvement in the degree of hydrolysis was obtained (i.e., the UTS and ETF after aqueous attack were 22.0 ksi and 26.8%, respectively). However, as shown in Figure 3, the rate of aqueous attack after the second heat treatment is approximately five times slower (the reaction approaches completion after 900 hr) than that observed for samples given only one heat treatment; and in this sense hydrolytic stability has indeed been improved, but still not to the extent of the material that was first degraded and then regenerated.

CONCLUSIONS

1. Aqueous degradation of Kapton polyimide film has been confirmed to involve hydrolytic chain scission at amide linkages.
2. Heat treatment at 224° to 310°C has been shown to regenerate 91.5% to 97.0% of the ultimate tensile strength and 62% to 81% of the elongation to failure of the as-received film.
3. The kinetics of the regeneration correspond to the acylation of the terminal amino group from one shortened chain by the terminal acid anhydride group of a second adjacent shortened chain. The resulting amic acid linkage then undergoes internal cyclization.
4. Specimens heat treated at 310°C without prior aqueous degradation exhibited a decrease in the ultimate tensile strength and elongation to failure to 92% and 71% of their original values as well as a slight darkening of the film, which is probably due to the onset of slight oxidative degradation.
5. The regenerated polyimide shows much greater hydrolytic stability than either the as-received film or specimens heat treated at 310°C without prior aqueous degradation.

The author wishes to acknowledge the assistance of W. Poit, H. Behan, C. Lottermoser, and J. Klein for their assistance in sample preparation and performing the experiments, and that of Drs. G. Geschwind and P. Adler of the Materials Research Group and Dr. D. A. Labianca of the Chemicals and Plastics Division of the Union Carbide Corporation for their many helpful and stimulating discussions regarding this work.

References

1. R. DeIasi and J. Russell, *J. Appl. Polym. Sci.*, **15**, 2965 (1971).
2. M. Katz, Film Department, E. I. du Pont De Nemours and Co., private communication.
3. J. Kreuz, A. Endrey, F. Gay, and C. Sroog, *J. Polym. Sci. A-1*, **4**, 2607 (1966).
4. L. Laius, M. Bessonov, E. Kallistova, N. Adrova, and F. Florinskiy, *Vysokomol. Soedin. A*, **9**, 2185 (1967).
5. G. Kolesnikov, O. Fedotova, O. Paresishvili, and S. Belevskii, *Trans. Mosk. Khim-Tekhnol. Inst.* **61**, 217 (1969).
6. E. Butta, S. DePetris, and M. Pasquini, *J. Appl. Polym. Sci.*, **13**, 1073 (1969).
7. J. Heacock and C. Berr, *SPE Trans.* **5**, 105 (1965).

Received April 14, 1972

Revised June 6, 1972