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Hydrolytic degradation mechanism of Kevlar 49 fibers when dissolved in sulfuric acid*

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Dedicated to Professor Dragutin Fleš on the occasion of his 70th birthday

SUMMARY

The hydrolytic degradation of Kevlar 49 fibers when dissolved in H_2SO_4 is characterized from (i) Fourier transform infrared (FTIR), CNH analyses and optical microscopy studies of insoluble crystals formed in the PPTA-H_2SO_4 dope and (ii) the rates of H_2SO_4-catalyzed hydrolysis of model compound aromatic amides. After hydrolysis of a PPTA amide linkage, the amide linkage adjacent to the freshly formed -COOH macromolecular end group rapidly hydrolyses resulting in the formation of terephthalic acid which then forms insoluble crystals in the PPTA-H_2SO_4 dope.

INTRODUCTION

Kevlar 49 fibers, E.I. duPont, [poly(p-phenylene terephthalamide) PPTA], have found considerable use as high performance fibers in polymer matrix composites. Future utilization of high performance fibrous polymer matrix composites will require exposure to increasingly severe thermo-mechanical-moisture environments. As such, there is a need to characterize the fiber degradation mechanisms in these extreme environments. The physical, chemical and mechanical degradation mechanisms in service environment conditions have been extensively studied and have been recently reviewed [MORGAN et al. (1984); MORGAN and ALLRED (1990)]. In many service environments moisture-induced chemical and physical degradation of Kevlar 49 fibers needs to be thoroughly characterized. We have previously reported (i) the hydrolytic degradation of Kevlar 49 fibers and the principal parameters that control this degradation [MORGAN et al. (1984); MORGAN and ALLRED (1990)] and (ii) the moisture-induced physical degradation of the fiber structure (KEINATH and MORGAN). In part of this ongoing study we report in this paper the hydrolytic degradation mechanisms of Kevlar 49 fibers upon dissolution in 100% H_2SO_4.

Kevlar (PPTA) fibers are extruded at about 80°C in the form of liquid-crystalline PPTA-H_2SO_4 dopes (~20 wt% PPTA) from a spinneret at 0.1-6 m/s. Previous studies [MORGAN et al. (1983)] while attempting to redissolve Kevlar 49 fibers in 100% H_2SO_4 resulted in the observation of insoluble crystals suspended in the PPTA-H_2SO_4 dopes. Previous investigators [ARPIN et al. (1977a) and ONOGI et al.] have studied the behavior of PPTA in 100% H_2SO_4 by optical microscopy, light scattering, U.V. spectroscopy and both wide angle and small angle X-ray diffraction. ARPIN and STRAZIELLE (1977b) have reported the dilute-solution properties of PPTA in 96% H_2SO_4 by intrinsic viscosity, light scattering and gel-permeation chromatography.

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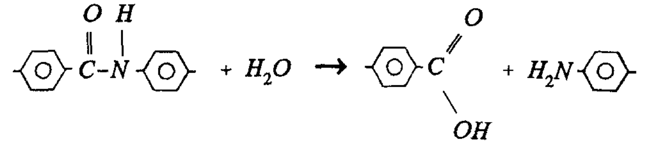
Acid catalyzed hydrolysis occurs at the amide linkage in PPTA.



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The acid hydrolysis of amides has been studied by several investigators (SMITH and YATES; RYSMAN DE LOCKERENTE et al.; NECHAEV et al.; MODRO et al.). The acid hydrolysis of amides has been shown to take place at temperatures of between 25-85°C and in sulfuric acid concentrations of 5-75%. RYSMAN DE LOCKERENTE et al. have examined the kinetics of the acid hydrolysis of $MeCONHC_6H_4R$, $ClCH_2CONHC_6H_4CONH_2$, $RC_6H_4CONHC_6H_4R'$, (R,R' = MeO, Me, H, Cl, NO_2) at 60 and 80°C in 10-75% H_2SO_4. They found that in concentrated sulfuric acid the reaction rate was affected by the substituent on the benzene ring but that this effect was negligible in dilute acid.

The H_2SO_4 hydrolysis of PPTA in PPTA-H_2SO_4 dopes is investigated in this study by (i) direct chemical and physical characterization of insoluble crystals formed in the PPTA-H_2SO_4 dope and (ii) monitoring the rates of H_2SO_4-catalyzed hydrolysis of model compound aromatic amides.

(i) PPTA-H_2SO_4 DOPE DEGRADATION STUDIES

EXPERIMENT

A Leitz optical microscope was used to obtain micrographs of the PPTA-H_2SO_4 dope solution; FTIR analysis of crystals formed in the PPTA-H_2SO_4 dope was obtained using a Nicolet spectrometer. Samples were prepared in KBr pellets for FTIR.

A Kevlar 49-H_2SO_4 dope was prepared by adding Kevlar fiber to 100 ml of 100% sulfuric acid in a 500-ml resin kettle fitted with a thermometer, mechanical stirrer, argon inlet and gas outlet. Kevlar was charged into the kettle in 1-3 g increments over a period of four days with stirring and at a temperature near 60°C. At this point the dope was 11.2% Kevlar. 100 ml of oleum was added which made the dope solution 6% Kevlar. The dope was allowed to cool to room temperature. A sample of the dope was smeared onto a microscope slide and covered with a glass cover for optical microscopy studies. An aliquot of the Kevlar 49/H_2SO_4 dope was transferred to a 25-ml Erlenmeyer flask, heated at 90°C for 3.5 hours, then allowed to cool to room temperature. The white solid which formed was filtered on a fritted-glass funnel and washed with water, then placed in a vacuum oven to dry. The elemental analysis was found to be C, 52.38; H, 3.46; N, 0.48 (wt%).

Powdered Kevlar was obtained by pulverizing Kevlar fiber in a stainless steel capsule containing stainless steel beads at liquid nitrogen temperature. The elemental analysis calculated from the foregoing structure was: C, 70.58; H, 4.20; N, 11.76; in contrast we found C, 68.15; H, 4.65; N, 11.12. CNH studies have indicated that the low C value is a result of rapid moisture absorption of the PPTA fiber upon transfer from the dessicator to the CNH analyzer (MORGAN et al. d).

RESULTS AND DISCUSSION

When a sample of the PPTA-H_2SO_4 dope was smeared onto a microscope slide and covered with a cover glass, lozenge-shaped particles were observed under the microscope with polarized light. These lozenge-shaped particles were observable for several hours after slide preparation if a cover glass was used. When no cover glass was used the lozenge-shaped particles disappeared after a few minutes exposure to air. Exposing the prepared slide to temperatures of 125-150°C for as little as 10 minutes yielded insoluble crystals of the type that we had previously observed [MORGAN et al (1983)].

The Kevlar 49-H_2SO_4 dope was a dark-golden-colored, highly viscous solution; it maintained this appearance over a period of more than three months. Aliquots which were heated under the conditions which produced the insoluble crystals turned very dark brown, almost black, which indicated decomposition.

An aliquot of the dope was transferred to a 25-ml Erlenmeyer flask and placed in the vacuum oven at 126°C for 30 minutes. The flask was removed from the oven and allowed to cool to room temperature. The solid which formed was collected on a fritted-glass funnel and washed with water, then dried under vacuum. This white solid was examined by FTIR spectroscopy and the spectrum of the material (Fig. 1) was compared with those of powdered Kevlar (Fig. 2) and with terephthalic acid (Fig. 3). As can be

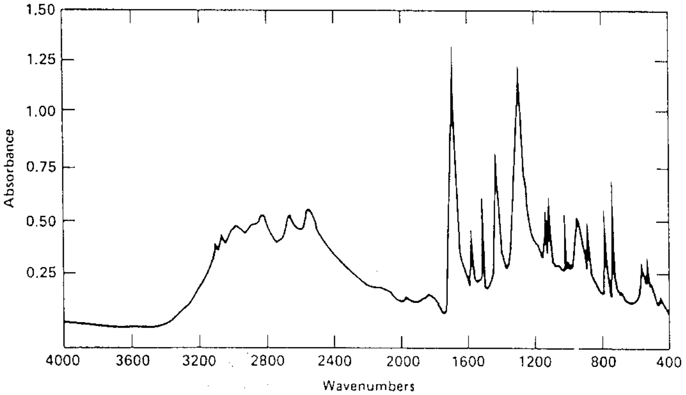


Figure 1. FTIR Spectra of Powder Recovered from Kevlar Sulfuric Acid Dope After Heating at 125°C for 30 min.

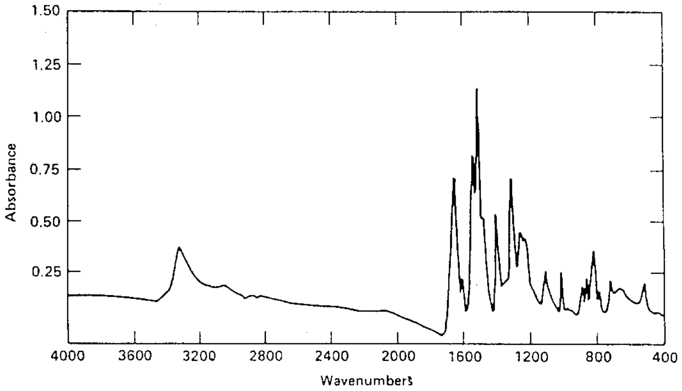


Figure 2. FTIR Spectra of Powder Kevlar.

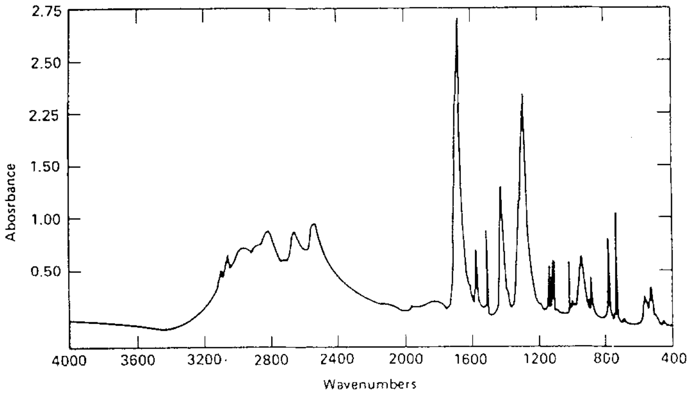


Figure 3. FTIR Spectra of Terephthalic Acid.

seen from the spectra, the material which was recovered from the Kevlar dope after heat treatment is indeed terephthalic acid. The spectrum of this material is identical to that of pure terephthalic acid except for some slight variations in peak intensities. The Kevlar spectrum (Fig. 2) shows absorbances that are typical of amides, namely the N-H absorbance at ~3400 cm^{-1} and the C=O at 1649 cm^{-1}. In contrast, in the terephthalic acid and the powder recovered from the dope, the C=O peak occurs at 1671 cm^{-1}. This difference in frequency of the carbonyl absorbance is in keeping with what would be expected since carbonyls of carboxylic acids generally absorb at higher frequencies than amide carbonyls.

The elemental analysis of the material obtained from decomposition of the Kevlar contained 0.48% nitrogen, whereas Kevlar should contain 11.76% nitrogen.

Optical microscopy of terephthalic acid in 100% H_2SO_4 reveals insoluble platelets similar to those observed in Kevlar 49-H_2SO_4 dopes illustrated in Fig. 4.

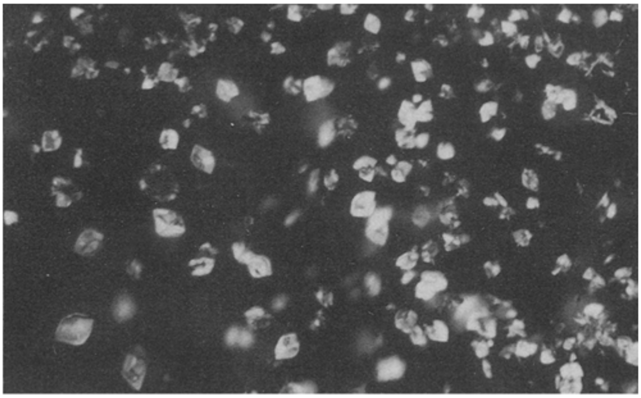


Figure 4. Terephthalic Acid Crystals in Kevlar 49-100% Sulfuric Acid Dope [90-140°C 1.5 hours].

The disappearance of the terephthalic acid crystals upon exposure of the PPTA-H_2SO_4 dope to the atmosphere is most likely a result of rapid moisture absorption into the dope which causes the terephthalic acid crystals to redissolve in the dope.

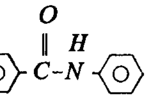
Despite using 100% H_2SO_4, small quantities of moisture that will hydrolyze PPTA are most likely present in the PPTA-H_2SO_4 dope as a result of rapid moisture absorption into Kevlar 49 fibers even during extremely short periods of transfer from the dessicator into the H_2SO_4 [MORGAN et al. (1983)].

(ii) H_2SO_4-CATALYZED HYDROLYSIS OF MODEL COMPOUND AROMATIC AMIDES

EXPERIMENTAL

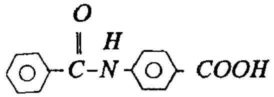
The acid-catalyzed hydrolysis of the following aromatic amides which are similar in structure to Kevlar, was investigated.

Compounds I, III, and IV were obtained commercially and used without further purification. Compound II was synthesized in the laboratory by reaction of aminobenzoic acid with benzoyl chloride in aqueous alkaline solution. The elemental analyses of II was consistent with the proposed structure; calculated for $C_{14}H_{11}O_3N$ was C, 69.71; H, 4.60; N, 5.81; found was C, 69.89; H, 4.74; N, 5.79. Solutions of I, II, III, and VI were prepared at concentrations of 7.1 x 10^{-5}M, 8.2 x 10^{-6}M, 1.4 x 10^{-4}M and 4.4 x 10^{-5}M respectively. The hydrolysis was carried out at 90°C in concentrated (97%) sulfuric acid. The reaction was monitored by observing the disappearance of the amide absorbance in the UV spectrum using a Cary 17D spectrophotometer.



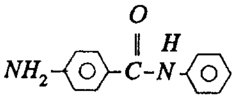
I

benzanilide



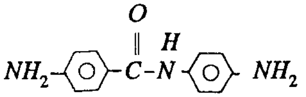
II

p-benzamidobenzoic acid



II

p-aminobenzanilide



III

p,p'-diamino benzanilide

RESULTS AND DISCUSSION

The hydrolysis reaction was first order due to the large excess of water. The UV data was fitted to a first-order curve by,

$$\ln(A_t - A_\infty) = -kt + \ln(A_0 - A_\infty)$$

where A_0 is the initial absorbance, A_t is absorbance at time t. A_∞ values were determined by choosing a value below the last observed value and then using a linerized least squares fit. The fitting gave a slope equal to A_0-A_∞ from which A_∞ could be determined and compared with the assumed value. The process is iterated until the two values agree. Experimental data for the acid hydrolysis of I, II, and III are illustrated in the UV spectra in Figures 5, 6, and 7, respectively. The rate constants, k, determined for I, II, and III where 3.10 x $10^{-4}S^{1}$, 1.08 x $10^{-3}S^{-1}$ and 2.01 x $10^{-5}S^{-1}$ respectively, so that the order of reactivity was II>I>III. In the case of IV no observable amount of hydrolysis

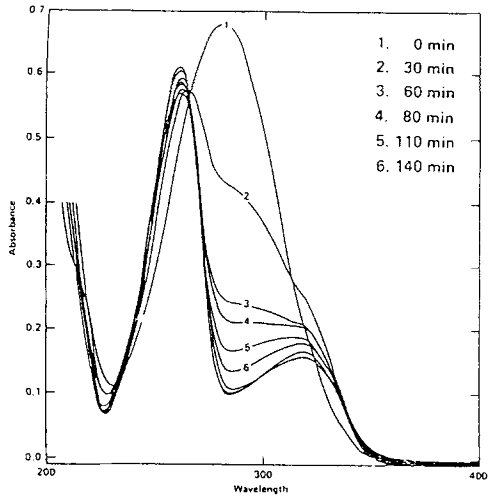


Figure 5. UV Spectra of Acid Catalyzed Hydrolysis of Benzanilide.

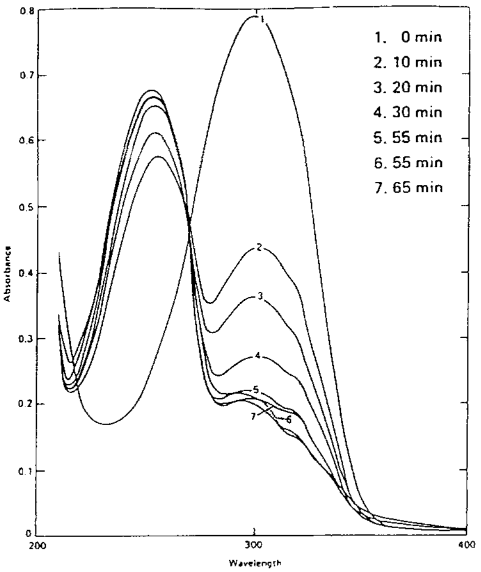


Figure 6. UV Spectra of the Acid Catalyzed Hydrolysis of p-Benzamidobenzoic Acid.

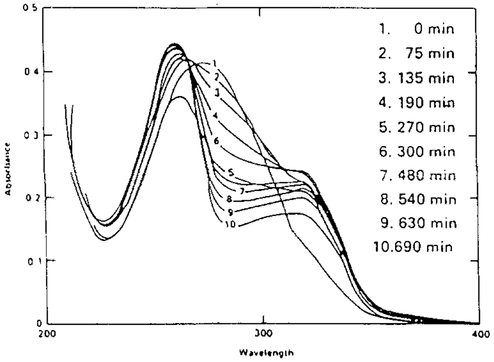
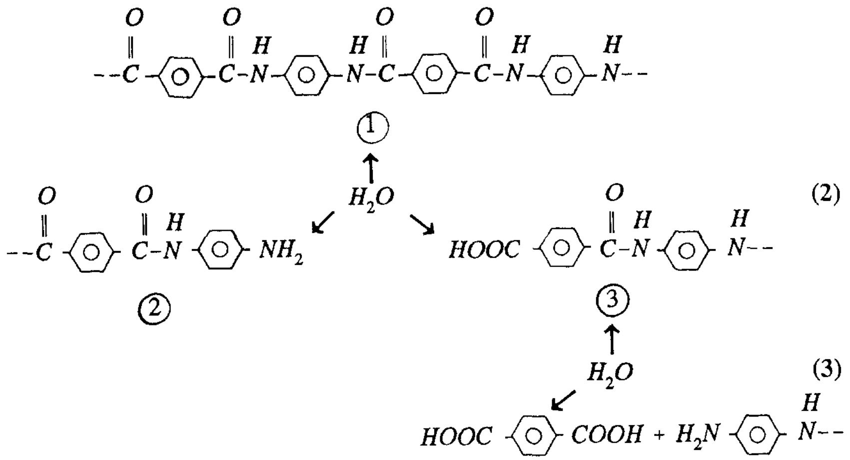


Figure 7. UV Spectra of Acid Catalyzed Hydrolysis of p-Aminobenzanilide.

occurred even after holding the sample at 110°C for two hours. The order of reactivity of the compounds I-IV can be explained in terms of the substituents' effects on the stabilization of the amide bond. The nitrogen of the -NH_2 group exerts a strong resonance effect on the aromatic ring. The lone pair of electrons on the nitrogen are partly delocalized into the ring and therefore would tend to make the amide linkage stronger by resonance stabilization. The carboxyl group, (-COOH) on the other hand contains two highly electronegative oxygen atoms which withdraw electrons from the carbonyl carbon, causing it to become more electronegative. The carbonyl carbon in turn withdraws electrons inductively from the ring thereby causing an electron deficiency at the amide bond and weakening it.

These studies indicate that after amide hydrolysis in PPTA [Eqn. (2); at amide linkage 1] that rapid hydrolysis will subsequently occur at the amide linkage adjacent to a -COOH macromolecular end group [Eqn. (3); at amide linkage 3] to produce terephthalic acid. Hydrolysis of the amide linkage adjacent to a -NH_2 macromolecular end group [Eqn. (3); at amide linkage 2] will be many orders of magnitude slower.



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(3)

CONCLUSIONS

From chemical and physical characterization of crystals formed in PPTA-H_2SO_4 dopes and the rates of H_2SO_4-catalyzed hydrolysis of model compound aromatic amides it is concluded that after hydrolysis of an amide linkage in PPTA rapid hydrolysis of the amide linkage adjacent to the freshly formed -COOH macromolecular end group occurs resulting in the formation of terephthalic acid, which forms insoluble crystals in the PPTA-H_2SO_4 dope.

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