

Analytical Characterization of Weather-Degraded Polyacrylonitrile Fiber

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SYNOPSIS

Polyacrylonitrile (PAN) fiber was analytically characterized to identify the structural changes that occur due to atmospheric degradation. Degradation structures comprised of C=C, C=N, and C=O species were identified using infrared spectroscopy. A significant decrease in the molecular weight was measured using size exclusion chromatography. PAN-acrylate copolymer fibers were analyzed and found to exhibit the same type of structures and changes in properties upon atmospheric degradation.

INTRODUCTION

Weather-induced degradation of polyacrylonitrile (PAN) fibers leads to an undesirable color change in some fiber products. For uncolored fibers atmospheric degradation results in an increased yellowing. For colored fibers the perceived color change varies depending on the base color of the fiber. Color changes caused by atmospheric degradation usually require several years of direct exposure to sunlight in geographic areas prone to high temperatures ($> 35^{\circ}\text{C}$). In order to study the effect of manufacturing conditions and composition variables in a timely manner, we utilized a simulated atmospheric chamber with accelerated conditions to produce samples visibly comparable to those degraded by the atmosphere.

The thermal degradation mechanisms of PAN homopolymer have been thoroughly studied and reviewed.¹⁻¹² There are (at least) five well-established degradation mechanisms for PAN¹ that produce chromophores consisting of structures such as $-\text{C}=\text{N}-$, $-\text{C}=\text{O}$, and $-\text{C}=\text{C}-$. PAN degradation has been characterized by infrared, NMR, and UV-visible spectroscopic techniques.²⁻¹² The present study was carried out to determine if the weather-induced discoloration of PAN fibers results in

chemical structural changes that correspond to the known thermal degradation mechanisms of PAN.

EXPERIMENTAL

Infrared spectra were recorded on a Bio-Rad (Digilab) FTS-50 FTIR spectrometer at 4 cm^{-1} resolution. FTIR-ATR spectra were obtained using a Spectra-Tech Model 221 ATR accessory and a KRS-5 crystal. FTIR transmission spectra were obtained from solvent-cast films on NaCl plates prepared from a 0.02 mg/mL dimethylsulfoxide (DMSO) solution. For samples containing TEA (triethylamine), the TEA was added to the PAN-DMSO solution at 0.002 mg/mL.

Size exclusion chromatography was performed at Jordi Associates, Inc., with a $10 \times 500\text{ mm}$ mixed-bed styrene divinylbenzene column (Jordi No. 15005) using mobile phase of 0.1 M lithium bromide in dimethylformamide. Number-average (M_n) and weight-average (M_w) molecular weights and polydispersity (D) were calculated based on calibration with narrow distribution polyethylene glycol.

Weatherometer-degraded samples were prepared in an Atlas Weatherometer using Society of Automotive Engineers Material Practice SAE J1885. L - a - b color measurements were performed using an Applied Color System Spectro Sensor II spectrophotometer. C, H, N, and O analyses were performed by Galbraith Laboratories (Knoxville, TN).

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Table I Weatherometer-Degraded Unfinished, Uncolored PAN Fiber^a

kJ Exposure	Δb^b	ΔE^c
70	2.6	3.1
140	4.3	4.8
280	8.9	9.7
560	18.3	20.1
1120	32.4	37.3

^a *L-a-b* color measurements versus control (Unexposed).

^b Δb corresponds to yellowness.

^c ΔE corresponds to total reflectivity.

RESULTS AND DISCUSSION

Weatherometer-Degraded Greige Fiber

Unfinished, uncolored (greige) PAN in the form of an awning fabric was subjected to various lengths of exposure in an Atlas Weatherometer: 70, 140, 280, 560, and 1120 kJ. This sample was chosen in order to observe changes in color and structure without interference from added colors and finishes. A color change, from beige to orange, occurred and increased with increased exposure length. The amount of color change was measured quantitatively using *L-a-b* color values as shown in Table I. In *L-a-b* color measurement, the ΔE corresponds to the total reflectivity and Δb corresponds to yellow-blue reflectivity.¹³

For these samples, the yellowness and darkness increase with increased weatherometer exposure.

Solvent-cast (DMSO) films of greige PAN fibers that were subjected to varying amounts of weatherometer degradation were examined by IR transmission spectroscopy. Relatively small changes in spectra were observed in the 1500–1800 cm^{-1} region. The same degraded samples were examined by FTIR-ATR spectroscopy. The relative intensities of the bands in the 1500–1800 cm^{-1} were much larger than those obtained using the transmission technique. This result indicates that more degradation is occurring near the fiber surface. The FTIR-ATR spectra of PAN fibers with varying levels of degradation are shown in Figure 1. The spectra are normalized with respect to the C≡N and CH₂ bands of the PAN. A dramatic increase, which is correlated with the exposure length, is observed in the 1500–1800 cm^{-1} region. FTIR-ATR spectra of the control (unexposed) sample, the 1120-kJ exposed sample, and the subtraction (1120 kJ minus control) are shown in Figure 2. The increase in the area of the 1500–1800 cm^{-1} region correlates well with the increase of the ΔE and Δb color values (Table I). These results show that the degradation is a surface phenomenon and that the color change is correlated with the increase of the spectral bands in the 1500–1800 cm^{-1} region. IR bands in the 1500–1800 cm^{-1} region are characteristic of double bond structures, such as C=O, C=C, and C=N, which have been

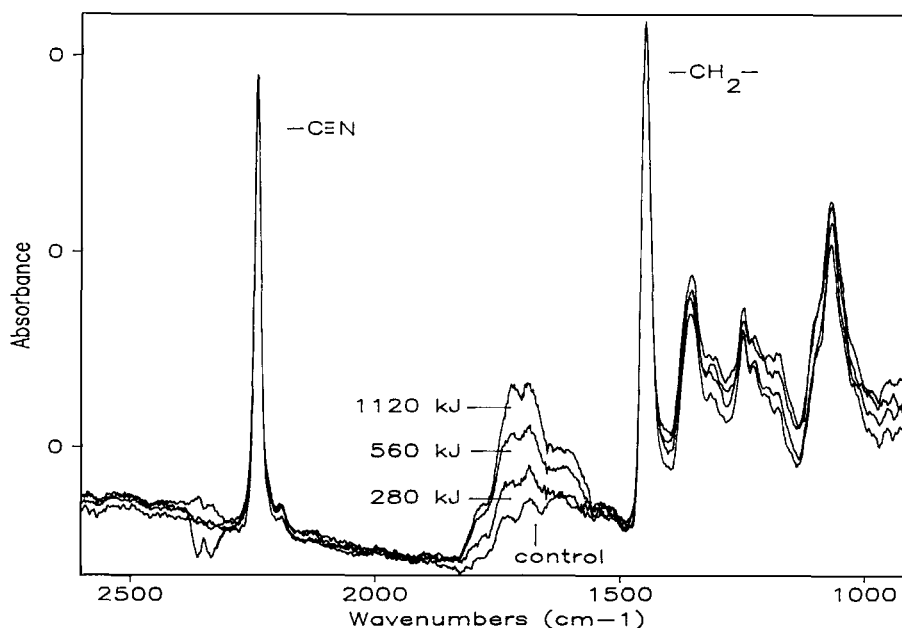


Figure 1 An overlay of FTIR-ATR spectra of weatherometer-degraded greige PAN fibers with increasing amounts of degradative exposure.

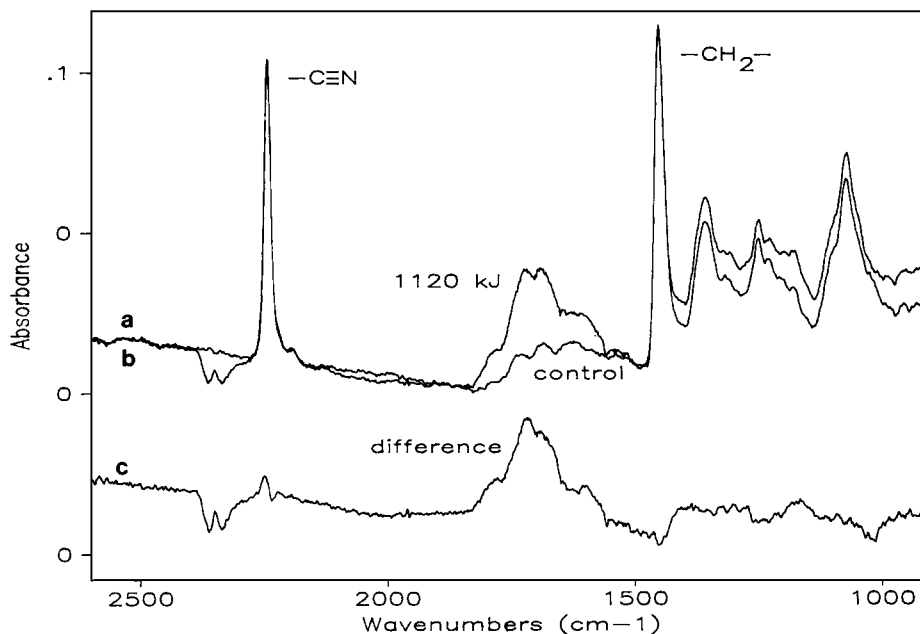


Figure 2 FTIR-ATR spectra of (a) weatherometer-degraded greige PAN fiber, (b) the corresponding control greige fiber, and (c) (a) minus (b).

reported in the literature in studies dealing with PAN degradation.²⁻¹²

The C, H, N, and O composition of the control (unexposed), 560-kJ exposed, and 1120-kJ exposed greige fiber are shown in Table II. The only significant elemental change occurring with increased weatherometer exposure is the increase in the %O, which would be expected from the formation of C=O species. Although these results confirm formation of C=O species, they do not discriminate between carboxylic acid, amide, or ketone structures. The small changes in C, H, and N would not be detected because they are much smaller than the precision of the respective analyses.

In previous internal work on degradation of acrylics, bands in the 1500–1800 cm^{-1} region were assigned to carboxylic acid and amide structures. A weak base, triethanolamine, was added to the DMSO

solutions of a degraded fiber sample and solvent-cast films were prepared and examined by IR spectroscopy. If a carboxylic acid structure were present, a reduction in the C=O stretch of the carboxylic acid band around 1700 cm^{-1} and the appearance of a C=O stretch band for a carboxylate anion around 1570 cm^{-1} would be expected. The IR spectrum of the degraded PAN showed no evidence of a carboxylate anion upon addition of the weak base. Thus, it appears that a carboxylic acid structure is not present in the degraded samples examined in this study. Based on the reported mechanisms of PAN degradation,¹ literature reports dealing with IR studies of degraded PAN,²⁻¹⁰ conventional IR band assignments, and the lack of evidence of a carboxylic acid band, the assignments for the degradation structures in the greige PAN are shown in Table III.

The control sample and the 1120-kJ degraded sample were analyzed by ¹³C-NMR and ESCA. No differences could be detected between the two samples due to the low-level concentration of the degradation structure.

Table II Weatherometer-Degraded Unfinished, Uncolored PAN Fiber^a

	%C	%H	%N	%O, Average (Replicate Values)
Control	68	6.1	25	0.50 (0.59, 0.41, 0.51)
560 kJ	68	6.1	26	0.66 (0.67, 0.65)
1120 kJ	67	6.1	26	0.76 (0.77, 0.75)

^a C, H, N, and O analysis.

Weatherometer-Degraded Finished Fiber

Four shades of colored and finished PAN were degraded in a Weatherometer and analyzed by FTIR-ATR. Spectra of the control (unexposed), weath-

Table III Weatherometer-Degraded Unfinished, Uncolored PAN Fiber^a

IR Band (cm ⁻¹)	Functional Group	Degradation Pathway ^b
1780	C=O adjacent to O or C=C	A
1690	C=O (ketone)	C
1620-1580	C=C, C=N	A, E

^a Infrared band assignments and degradation structures.

^b Reference 1, p. 3.

erometer-exposed, and the subtraction (exposed minus control) for one of the colored fibers is shown in Figure 3. Changes observed in the 1500-1800 cm⁻¹ region are very similar to those observed for the degraded greige fiber. New bands appear that are due to PAN and finish degradation, and bands corresponding to the finish are reduced. Overall, the spectra of these four degraded fibers are similar. Thus, it appears that finish and color (pigment type) do not greatly affect the chemical structures formed upon degradation.

PAN-Acrylate Copolymers

Most commercial acrylic fiber is composed of mostly PAN and a small amount (< 15%) of polymethylmethacrylate or polymethylacrylate. Colored PAN-

acrylate fiber samples from three different manufacturers were analyzed. Figure 4 shows FTIR-ATR spectra of one of the copolymer fibers before and after weatherometer degradation, and the subtraction spectrum (degraded minus control). The subtraction spectra for all of the copolymer samples compare well with the subtraction spectra for the PAN homopolymer samples, such as the one in Figure 2. The degradation structures produced in the copolymers appear to be the same as produced in the PAN homopolymer. The slight differences between the subtraction spectra of the copolymer and homopolymer in the 1740-cm⁻¹ range correspond to the ester band of the copolymer. It cannot be determined whether the negative band is due to loss of ester or an artifact in the spectral subtraction.

The size exclusion chromatography results for some of the PAN homopolymer and PAN-acrylate copolymer fibers subjected to an average of 1680 kJ of weatherometer exposure are shown in Table IV. In every sample the M_w and M_n are significantly reduced. Since the FTIR-ATR results indicate a surface degradation, a significant amount of chain scission is apparently occurring to cause such a large change in the molecular weight values.

Atmosphere-Degraded Finished Fiber

Three samples of atmosphere-degraded finished and colored PAN homopolymer fibers were analyzed by

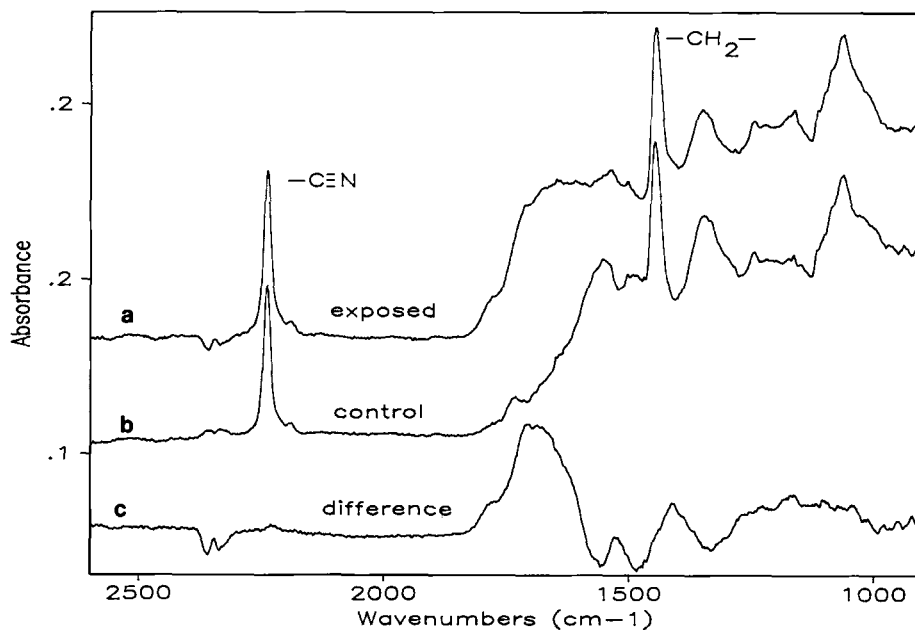


Figure 3 FTIR-ATR spectra of (a) weatherometer-degraded colored PAN fiber, (b) the corresponding unexposed fiber, and (c) (a) minus (b).

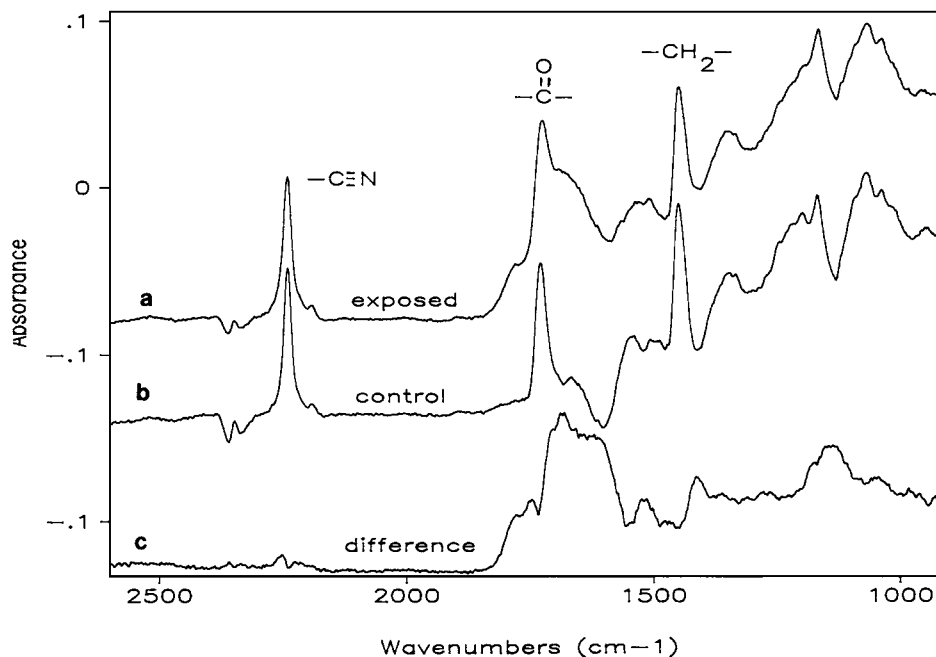


Figure 4 FTIR-ATR spectra of (a) weatherometer-degraded PAN-acrylate fiber, (b) the corresponding unexposed fiber, and (c) (a) minus (b).

IR spectroscopy. Solvent-cast (DMSO) films of the three atmosphere-degraded samples with direct sunlight exposure showed only weak additional bands in the 1500–1800 cm^{-1} region, similar to that which was observed for the weatherometer-degraded greige PAN fiber. The FTIR-ATR spectra of the three atmosphere-degraded direct-sunlight samples are shown in Figure 5. The spectra of these samples are very similar to each other and to that of the weatherometer-degraded greige sample (Fig. 1). All three samples have very similar spectra when normalized with respect to the $\text{C}\equiv\text{N}$ and CH_2 bands of the PAN. FTIR-ATR spectra of one of the atmosphere-degraded samples with and without exposure to direct sunlight is shown in Figure 6 and compared with the spectrum of the weatherometer-degraded greige sample (Fig. 1). The sample exposed to direct sunlight [Fig. 6(b)] exhibited discoloration, and its spectrum is very similar to that of the weatherometer-degraded sample [Fig. 6(c)]. The sample that was not exposed to direct sunlight [Fig. 6(a)] did not exhibit unacceptable discoloration, and its spectrum does not have the degradation bands observed in the sample exposed to direct sunlight [Fig. 6(b)]. The spectrum of the sample that was not exposed to direct sunlight compares well with the spectrum

of a control fiber with the same topical finish. The bands in the 1500–1800 cm^{-1} region are due to the topical finish components that are still present.

Table IV Weatherometer-Degraded PAN (1680 kJ) Homopolymer and Copolymer Fibers with Color and Finish^a

	M_n	M_w	D
Homopolymer A			
Control	33500	92400	2.77
Degraded	27800	82600	2.97
Homopolymer B			
Control	30600	86200	2.82
Degraded	19800	60900	3.09
Copolymer C			
Control	29400	99800	3.44
Degraded	21500	79900	3.73
Copolymer D			
Control	20700	76500	3.70
Degraded	19500	67300	3.45
Copolymer E			
Control	23400	73300	3.14
Degraded	12400	43100	3.49

^a Size exclusion chromatography results: number-average (M_n) and weight-average (M_w) molecular weights and polydispersity (D).

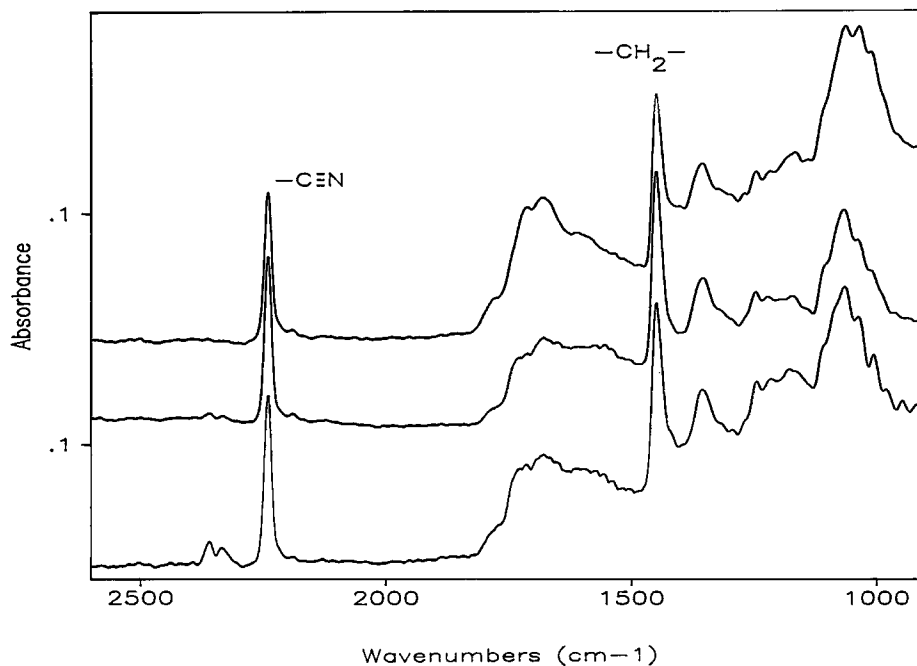


Figure 5 An overlay of FTIR-ATR spectra of three colored PAN fiber atmosphere-exposed and in direct sunlight.

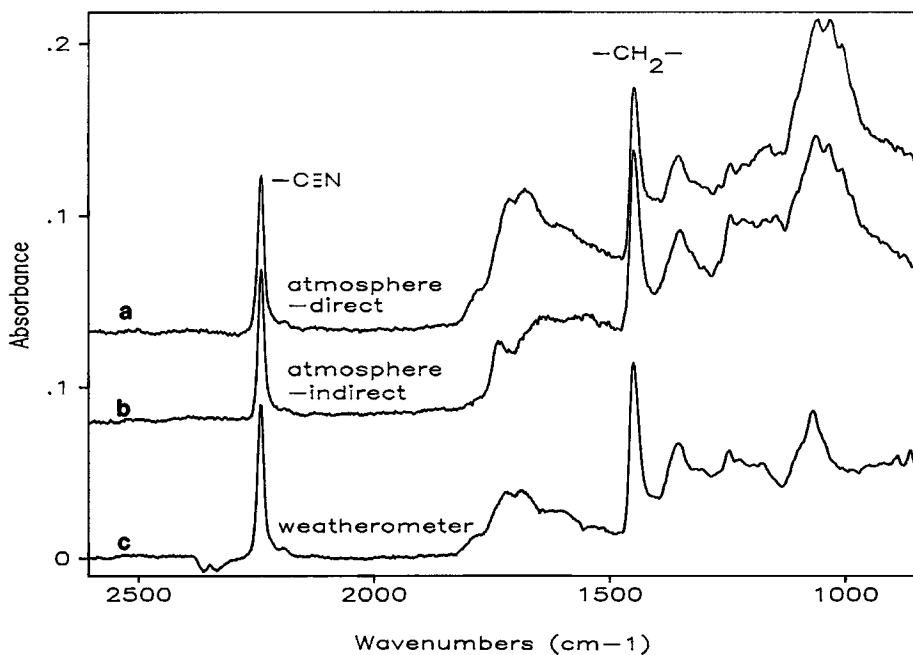


Figure 6 FTIR-ATR spectra of (a) colored PAN fiber, atmosphere-exposed but not in direct sunlight; (b) colored PAN fiber, atmosphere-exposed and in direct sunlight; and (c) weatherometer-degraded (1120 kJ) greige PAN fiber.

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