Benzoic Acid Degradation of Polyacrylonitrile Fibers

Dharmendra S. Varma* and Howard L. Needles
University of California, Davis, California 95616

Domenick E. Cagliostro
Ames Research Center, NASA, Moffett Field, California 94035

Presented at The Second Chemical Congress of the North American Continent
Las Vegas, Nevada, August 25-29, 1980

Send proofs to:
D. S. Varma, M/S 223-6
Chemical Research Projects Office
NASA-Ames Research Center
Moffett Field, CA 94035

*Visiting Professor, 1979-81, from Indian Institute of Technology, Delhi, India.

The reactions of polyacrylonitrile (PAN) fibers in the presence of benzoic acid have been studied. Polyacrylonitrile fibers oxidize more readily in the presence of benzoic acid than in air at temperatures in the range of 170°C. The product decreased in solubility with extent of reaction. Gel permeation chromatography of the soluble fraction showed change in polydispersity. The insoluble product exhibited differences in weight loss as a function of decomposition temperature compared to PAN fibers. Infrared analyses of the fiber product showed absorption peaks similar to air-oxidized PAN. High-energy photoelectron spectral analysis showed a carbon-rich surface which contained oxygen and nitrogen. An air oxidized sample of fiber contained more oxygen at the surface than a fiber treated first with benzoic acid and then air oxidized.

Introduction

Carbon fibers, which are used extensively in advanced composite materials, can be manufactured from polyacrylonitrile (PAN) fibers. The manufacturing processes used are first preoxidation at 200-300°C and subsequent carbonization in an inert atmosphere at 1100-1600°C or at temperatures greater than 2000°C (Jenkins and Kawamura, 1976). The initial low-temperature treatment of PAN is important in determining the yields and ultimate properties of carbon fibers and has been the subject of investigation and review (Jenkins and Kawamura, 1976; Peebles, 1976). The type of atmosphere the initial treatment is executed in has a great influence on the ultimate carbon fiber. When the PAN is pyrolyzed at temperatures over 260°C in an inert atmosphere, chain fragmentation occurs which can result in a final carbon fiber with reduced properties (Grassie, 1977). This type of decomposition is delayed by preoxidation in air (Grassie and McGuchan, 1971; Grassie, 1977). The initial reaction of PAN can also be influenced by additives. PAN fibers have been heated in the presence of various additives present as copolymer or in physical mixture (Grassie and Hay, 1961; Overhoff et al., 1973; Grassie, 1977; Cagliostro, 1980). Benzoic acid is one of the more effective additives. Previous investigations of the degradation of PAN and PAN copolymers in the presence of benzoic acid have been limited and did not extend their significance to carbon fiber technology (Grassie and Hay, 1961; Grassie, 1977). Benzoic acid has been used, however, in conjunction with oxidation and carbonization to make carbon fibers (Overhoff et al., 1973; Cagliostro, 1980). In one special process the pretreated fibers are carbonized in an active carbon containing gas at lower temperatures 500-1000 °C (Cagliostro, 1980). The benzoic acid treatment here results in a carbon fiber with a higher char yield and improved mechanical properties (Cagliostro, 1980). It is this particular application that is of interest because the fiber properties are strongly influenced by the benzoic acid treatment. Therefore, further study was undertaken to characterize the process and product obtained. In this paper some preliminary results of this study are reported for reaction of a PAN fiber with a molten benzoic acid at 170-175 °C.

Experimental Section

Samples of PAN fibers used as precursors for a commercial carbon fiber process were used. The fibers were a homopolymer and dogbone in cross section. A summary of nominal properties is shown in Table I. The fibers were used directly or washed with acetone or methanol and dried to constant weight.

Reaction was carried out both in batch and continuous fiber reactors. In the batch reactors fibers were heated in a glass tube or Erlenmeyer flask with air or benzoic acid to the reaction temperature for a specific time interval, then cooled. In the continuous reactor a fiber tow was pulled through a molten benzoic acid bath at a constant speed under tension so that less than 10% shrinkage or stretching occurred.

The products from both reactors were washed with acetone or methanol and dried to constant weight.

Analytical Methods

Solubility of the fibers was evaluated by heating the samples in dimethyl sulfoxide (DMSO) or dimethy formamide (DMF) at 100°C for 60min. The insoluble fraction was collected by filtration and washed with acetone. The filtrate was collected separately. Solubility was calculated as follows:

$$\% \text{ Solubility} = \frac{W - W_1 \times 100}{W}$$

where W is the original fiber weight and W_1 is the weight of the fiber after extraction and drying. Soluble fractions were also analyzed for molecular weight distributions (MWD) by gel permeation chromatography using four styragel columns. Electronic spectra of the soluble fractions in DMSO were recorded on a Carey spectrophotometer.

Infrared (IR) spectra of the various fiber samples and extracts in KBr pellets were recorded on a Perkin Elmer 180 spectrometer.

Surface analysis was determined using high-energy photoelectron spectral techniques (ESCA) with a Hewlett-Packard instrument for surface areas of 5 mm^2 $A\ell K_\alpha$ radiation was used and the binding energies were measured with a precision of 0.5 eV. The reference binding energy was C(1s) at 284.6 eV.

A 990 DuPont thermal analyzer was used for thermogravimetric analysis (TGA). A 10-mg sample was pyrolyzed in a N_2 atmosphere at a 10°C/min heating rate.

Results and Discussion

Discoloration of PAN fibers in benzoic acid was observed on heating at temperatures of 130-200°C. Discoloration of PAN on heating has been reported in the literature and various chromophores have been suggested to account for it (Burlant and Parsons, 1956; Grassie and McNeill, 1959; Schurz, 1958; Grassie and Hay, 1961; Skoda et al., 1959; Grassie, 1977). Discoloration depends on additive, temperature, time, and atmosphere, as well as whether the reactor is opened or closed. The color varies from white to yellow, orange, red, brown, and black (see Table II). Generally, in an air or nitrogen swept reactor, the red is absent and the brown and black products are obtained at temperatures above 200°C in about 180 min. The benzoic acid product, however, deepens to brown and black in 120-180 min at 175°C. Similar chromophores are apparently produced both in benzoic acid reaction, as well as in air, but at accelerated rates.

Table III reports the elemental analysis for various reaction products. A comparison of elemental composition for a sample of PAN oxidized in air at 260°C, compared to PAN treated with benzoic acid at 175°C, shows approximately the same carbon, oxygen, and nitrogen contents. The sample treated with benzoic acid, however, contained more hydrogen than the air-treated sample. After oxidizing the benzoic-acid-treated fiber in air at 260°C, the carbon, nitrogen, and oxygen contents remained nearly the same, but the hydrogen content was reduced. Thus, in benzoic acid at the lower temperature (175°C) the oxidation reaction involving loss of nitrogen was accelerated to a greater extent than loss of hydrogen (see Table III).

Solubility as a function of reaction time at 170°C is shown in Figure 1. The solubility curve is sigmoidal. Solubility decreased markedly after treatment with benzoic acid for 60 min, while PAN heated in air at 170°C for 100 min remained completely soluble. The visible spectra of soluble fraction of the treated fiber shows a shift in λ_{max} to lower wavelengths as reaction time increases. This shift in λ_{max} may indicate variations in conjugation associated with darker coloration of the fiber.

The IR spectra of various PAN samples heated to various time periods at 170°C also changed progressively. Even before treatment the original spectra showed an absorption at 1665 cm^{-1}, probably due to amide from hydrolysis of the sample. Heating the PAN fibers for 15 min did not change the principal absorption bands, but some new weak intensity bands were also observed (Figure 2). These included a medium intensity band at 1710 cm^{-1} with a shoulder at 1685 cm^{-1}, and small peaks at 1600, 1580, 770, 715, and 640 cm^{-1}. Similar features were present in the spectrum of sample heated for 30 min, with the exception of an additional band at 3500-3200 cm^{-1}. The sample heated for 45 min showed increased absorption in this region, and peaks at 3460, 3240, and 3080 cm^{-1} became more distinguishable (Figure 2). With more time, the relative intensity of the peak at 1650 cm^{-1} to that at 1710 cm^{-1} increased along with the peak at 720 cm^{-1} (Figure 2). After 90 min, the spectrum was no longer clearly resolved but became diffuse. The nitrile absorption was significantly reduced when heating time was 150 min or more. Infrared spectra of fibers after extraction with DMSO were similar to spectra of fibers before extraction, except that the peak at 720 cm^{-1} was absent.

ESCA, a surface analysis technique, showed a different elemental distribution at the fiber surface than in bulk (Table V). Even the reference sample of PAN powder, obtained from the Aldrich Company, as well as the untreated fiber, showed some surface hydrolysis or oxidation. This may be due to fiber processing or aging and has been reported in ESCA analyses of PAN (Dwight et al., 1978).

In all samples the surface contained less nitrogen than the bulk analysis and was richer in carbon and oxygen. The chemically treated samples, however, contained more surface nitrogen than the untreated fibers, possibly because the original surface layer reacted or dissolved during treatment and exposed underlying material.

The ESCA high-resolution spectra had only limited use to determine functionality. Deconvolution of the complex curves (Figure 3) showed the binding energies listed in Table IV using the C(1s) line set to 284.6 eV.

In Table V are shown the results for atomic ratios obtained after estimating a correction for the contribution to the C(1s) and oxygen values due to contamination of the samples by dimethyl silicone oil. Here twice the atomic silicon was subtracted from the carbon C(1s) found and the same values as the silicon was subtracted from the oxygen.

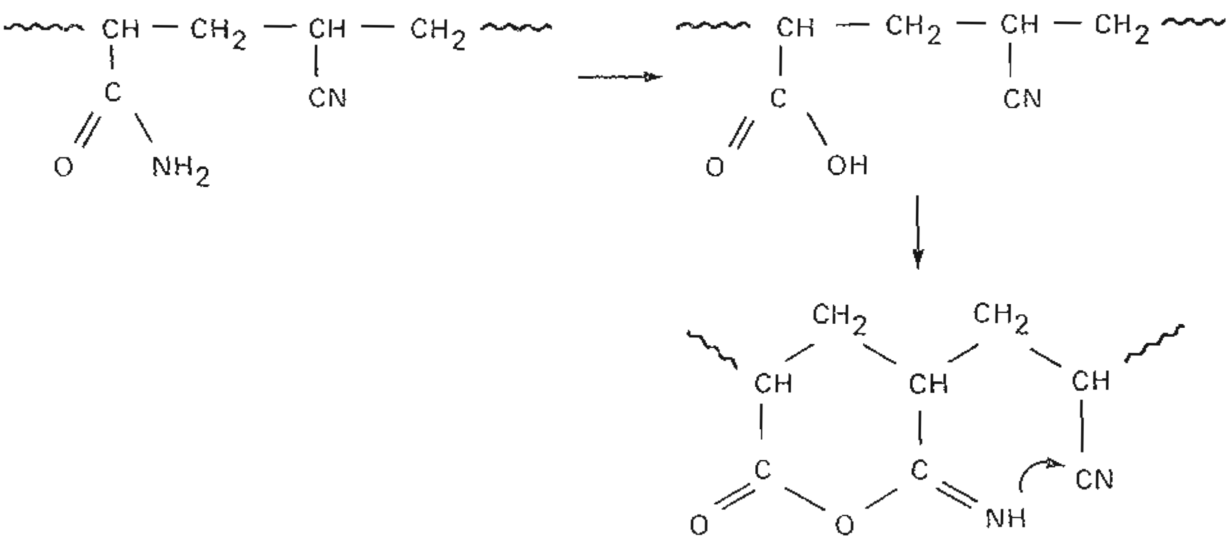
Although tentative assignments could be made for carbon, oxygen and nitrogen functional groups in these samples, the spectra were considered too complex and some of the reference binding energies in the literature considered in question, therefore none are presented. The conclusion still can be drawn however that the sample which was only air oxidized contains nearly twice the oxygen content at the surface than any of the other samples, and the comparison of bulk and surface elemental analysis are different. This shows that the samples are heterogeneous in composition. These facts could impact on carbonization processes in the active carbon containing gas.

The TGA's of untreated and treated PAN fiber in N_2 are shown in Figure 4. The benzoic-acid-treated product resulted in higher char yield at 800°C if treated for longer than 60 min at 175°C.

Table VI gives results of molecular weight distribution of DMF soluble fractions. No changes in the MWD of PAN heated up to 45 min in benzoic acid at 170°C was observed. This suggests that during the initial stage of reaction (30-min treatment time), chain scission or crosslinking does not occur. Solubility data also support this observation (PAN treated with benzoic acid for 30 min is 100% soluble).

The reaction mechanism present might be explained by two potential paths:

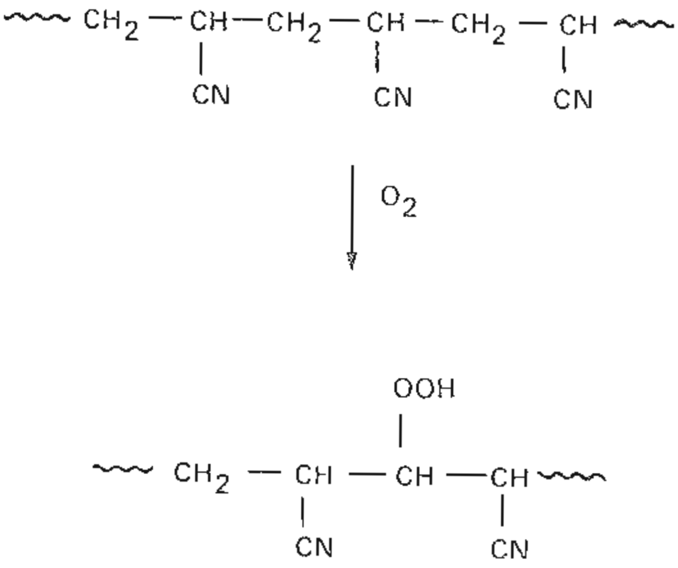
(a) The i.r. results may be accounted for on the basis of hydrolysis of amide groups to acid and then formation of a heterocyclic structure which includes oxygen. A similar reaction mechanism has been reported in the literature for PAN copolymers containing carboxyl groups (Grassie and McNeill, 1959).



Absorption in the IR in the range of 1600-1710 and 3000-3500 cm^{-1} supports the presence of the amide structures. The presence of the carboxyl group of the acid is supported by the presence of absorption in the region of 1700-1725 cm^{-1} (-C=O) and a shoulder at 1310 cm^{-1} (OH). The presence of cyclic oxygen is supported by this absorption also (-C-O). The conjugated sequence which contains the -C=N-C=N- groups could also account for the chromophore and the λ_{max} shift. Very few conjugated double bonds can shift the λ_{max} in the visible range from shorter wavelengths. No change in molecular weight is observed for reaction time up to 45 min. Therefore, little crosslinking or chain scission occurs based on this result. However, the elemental analysis of benzoic acid treated fibers indicates an increase in oxygen content which is more than the corresponding decrease in nitrogen content of PAN fibers and can not be accounted for by just the hydrolytic and cyclization mechanisms cited above. Additional oxidation involving hydrogen loss, crosslinking and/or other reactions appear to occur. The improved thermal stability (TGA data) BZ treated PAN may be attributed to the cyclized structures. Good char yields have been reported in literature in the case of polymers having fused structures (van Krevelen, 1975). The mechanism presented agrees with this result.

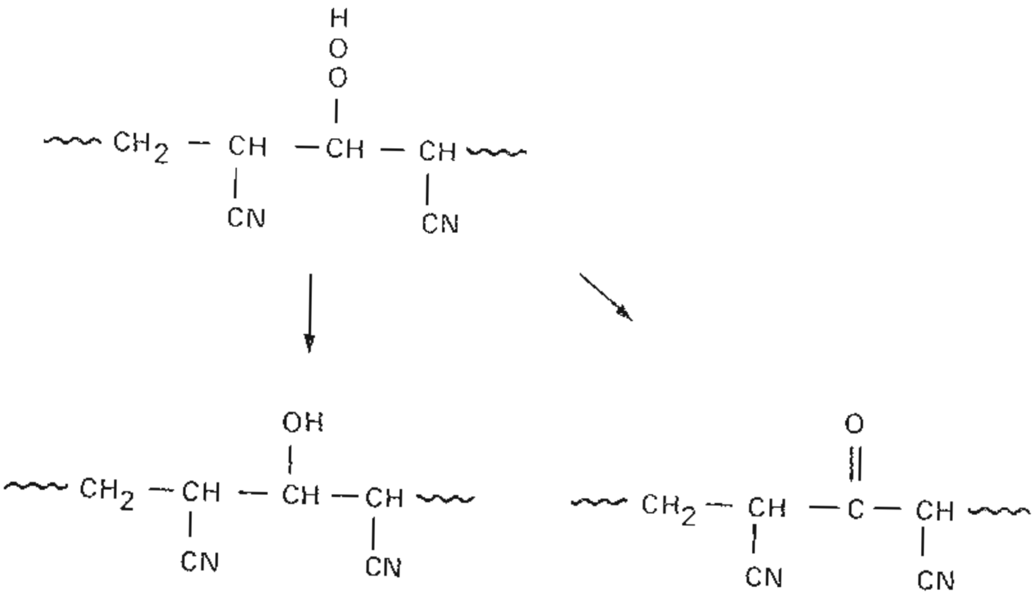
(b) Another potential mechanism to explain some of these results is a radical initiated oxidation. The PAN may contain hydroperoxides which decompose and initiate the chain reaction (Reich et al., 1969; Brandrup and Peebles, 1968). In this mechanism the benzoic acid would act as a catalyst to decompose the hydroperoxides to free radicals and thus accelerate the chain reaction (Reich and Stivala, 1969). The following free radical mechanisms could ensue and also result in the ketonic groups found by IR (1705-1725 cm^{-1}).

Initiation:



$$\sim CH_2-\underset{CN}{\underset{|}{CH}}-CH_2-\underset{CN}{\underset{|}{CH}}-CH_2-\underset{CN}{\underset{|}{CH}}\sim \xrightarrow{O_2} \sim CH_2-\underset{CN}{\underset{|}{CH}}-\overset{OOH}{\overset{|}{CH}}-\underset{CN}{\underset{|}{CH}}\sim$$

Decomposition of hydroperoxides:



Termination: Radicals inert products (may be crosslinked products not formed in the intial stages).

Thus it is difficult to pinpoint one type of mechanism during PAN degradation in presence of benzoic acid. Observed increase in oxygen content and loss of hydrogen of degraded fibers, as well as appearance of C=0 peaks (1705-1725 cm^{-1}) give support to oxidation reaction (mechanism b). Improvement in the char yield, discoloration and appearance of new absorption bands in i.r. spectra lend support to mechanism (a). Both of these mechanisms might be contributing towards the benzoic acid initiated degradation of PAN fibers.

Acknowledgments

We wish to express our appreciation to Dr. A. E. Pavlath of the Department of Agriculture at the Western Regional Research Laboratory, Albany, California, and to Pat Zajicek of Surface Science, Inc., Palo Alto, California, for running and discussing the ESCA spectra.

References

Brandrup, J., Peebles, L. H., Jr., Macromolecules, 1, 64. (1968)

Burlant, W. J., Parsons, J. L., J. Polym. Sci., 22, 349 (1956).

Cagliostro, D. E., Textile Res. J., 50, 632 (1980).

Dwight, D. W., McGrath, J. E., Wightman, J. P., J. Appl. Polym. Sci., Applied Polymer Symposium 34, 1978, pp. 35-47.

Grassie, N., "Developments in Polymer Degradation," Applied Science Publishers, London, 1977, pp. 137-169.

Grassie, N., Hay, J. N., "Thermal Discoloration of Nitrile Polymers," SCI Monograph, 13, 1961, pp. 184-199.

Grassie, N., McGuchan, R. M., Europ. Polym. J., 7, 1357 (1971).

Grassie, N., McNeill, I. C., J. Polym. Sci., 39, 211 (1959).

Jenkins, G. M., Kawamura, K., "Polymeric Carbons - Carbon Fiber, Glass and Char," Cambridge Univ. Press, 1976, pp. 86-106.

Overhoff, D., Winkler, E., Mueller, D.; "Process for Manufacture of Carbon or Graphite Fibers,", German Patent 2 220 614 (Nov. 1973).

Peebles, L. H., Jr., "Degradation of Acrylonitrile Polymers," Encyclopedia of Polymer Science and Technology, H. Mark, N. Gaylord, Ed., Supplement V. I, 1976, pp. 1-25.

Reich, L., Stivala, S. S., "Autooxidation of Hydrocarbon and Polyolefinics," Marcel and Dekker, Inc., New York, 1969, pp. 53-59.

Schurz, J., J. Polym. Sci., 28, 438 (1958).

Skoda, W., Schurz, J., and Bayzer, H.; Z. Phys. Chem., 210, 35 (1959).

van Krevelen, D. W.; Polymer, 16, 615 (1975).

Table I. Polyacrylonitrile Fiber Properties

Denier	2.31
Cross-sectional area	205 μ^2/filament
Filaments/tow	96
Carbon	66.93 wt %
Hydrogen	5.93 wt %
Nitrogen	25.41 wt %
Oxygen	1.07 wt %
Anatase (TiO_2)	Present, but not determined quantitatively. Usually, TiO_2 is used as a delustrant as ~1-2% by weight.

Table II. Discoloration of PAN

Time min	Temperature °C	Atmosphere	Moles Benzoic acid/ moles per merunit	Final Color	Reference
			Open Systems		
190.2	175	Air	None	Light yellow	(authors)
30.0	170	Air	∿5/1 molar ratio	Yellow	(authors)
45.0	170	Air	∿5/1 molar ratio	Light brown	(authors)
60.0	170	Air	∿5/1 molar ratio	Brown	(authors)
135.0	175	N_2	∿5/1 molar ratio	Brown/Black	(authors)
135.0	170	Air	∿5/1 molar ratio	Dark brown	(authors)
180.0	170	Air	None	Dark brown	(Skoda, 1959)
360.0	170	Air	∿5/1 molar ratio	Black	(authors)
			Closed Systems		
3900.0	180-190	Vacuum	None	Tan	(Grassie, 1977)
372.6	175	Vacuum	∿1/1	Orange	(authors)
382.2	175	Vacuum	∿52/1	Orange	(authors)
300.0	175	N_2	∿5/1	Orange	(authors)
361.8	175	N_2	∿5/1	Red, some black areas near gas/ liquid interface	(authors)

Table III. Effect of Precarbonization Processes on Elemental Analyses

Sample Treatment	wt %*				Atomic Ratio
	C	H	O	N	
1 None, theoretical PAN	67.9	5.66	--	26.4	C_3H_3N
2 PAN fiber received (dried to const. wt. at 50°C)	66.93	5.93	1.07	25.40	$C_3H_{3.19}N_{0.97}O_{0.04}$
3 PAN fiber reacted with Benzoic acid at 175°C in continuous feed reactor:					
21.2 min	66.81	5.80	2.11	25.08	$C_3H_{3.13}N_{0.97}O_{0.07}$
47.7 min	66.71	5.60	n.a.	24.32	$C_3H_{3.03}N_{0.92}O_X$
63.6 min	66.25	5.59	n.a.	22.76	$C_3H_{3.05}N_{0.88}O_Y$
169.5 min	62.06	4.29	9.78	20.38	$C_3H_{2.49}N_{0.85}O_{0.42}$
339 min	58.81	4.21	11.62	18.25	$C_3H_{2.58}N_{0.80}O_{0.44}$
720 min	59.29	3.77	12.77	19.01	$C_3H_{2.29}N_{0.82}O_{0.48}$
4 PAN fiber oxidized at 260°C for 192.0 min	59.63	3.16	9.75	20.54	$C_3H_{1.91}N_{0.89}O_{0.37}$
5 PAN fiber reacted with Benzoic acid at 175°C for 169.5 min in continuous feed reactor than oxidized at 260°C for 192.0 min	57.69	2.60	11.64	18.89	$C_3H_{1.62}N_{0.84}O_{0.45}$

* Accuracy of analyses for duplicates better than 3%

Table IV. Deconvolution Analysis of ESCA spectra

	Binding Energies (eV)					
Sample	C1	C2	C3	O	N	Si
Untreated Fiber	284.6	286.4	288.7	532.2	399.1	–
Air oxidized fiber ∿180 min, 260°C, continuous reactor	284.6	286.5	288.7	531.7	399.2	101.7
Benzoic Acid treated fiber ∿180 min, 175°C, continuous reactor	284.6	286.4	288.8	531.9	399.1	101.8
Benzoic Acid treated fiber ∿180 min, 175°C further air oxidized ∿180 min, 260°C continuous reactor	284.6	n.a.	n.a.	n.a.	398.6	n.a.

Table V. Atomic Ratios at Surface

Sample	Atomic Ratios
Untreated Fiber	$C_3O_{0.32}N_{0.12}$
Air oxidized fiber, 180 min, 260°C, continuous reactor	$C_3O_{0.61}N_{0.44}$
Benzoic Acid Treated Fiber, ∿180 min, 175°C continuous reactor	$C_3O_{0.34}N_{0.29}$
Benzoic Acid treated fiber, ∿180 min, 175°C air oxidized ∿180 min, 260°C	$C_3O_{0.31}N_{0.40}$

Table VI. GPC Data for PAN Treated with Benzoic Acid at 170 °C

Treatment time, min	Mw	Mn	Mw/Mn
0	335K	173K	1.93
15	276	129	2.13
30	309	128	2.41
45	343	142	2.42
60	232	104	2.23
150	91.6	55.2	1.66
360	2.5	2.3	1.09
PAN treated to 100 min without benzoic acid	316	142	2.23

Figure Captions

Figure 1. Solubility of PAN fiber in DMSO as a function of benzoic acid treatment time at 170°C.

Figure 2. IR spectra of original PAN and benzoic-acid-treated PAN fibers.

(a) Original PAN fiber

(b) 15-min treated fibers

(c) 30-min treated fibers

(d) 60-min treated fibers

(e) 90-min treated fibers

(f) 150- and 180-min treated fibers

Figure 3. ESCA carbon spectra.

(a) Reference PAN (Powder, Aldrich Co.)

(b) Original PAN fiber

(c) PAN fiber treated ∿180 min in benzoic acid at 175°C

(d) PAN fiber treated ∿180 min in benzoic acid air oxidized at 260°C for ∿180 min

(e) PAN fibers air oxidized for ∿180 min at 260°C

Figure 4. TGA thermograms of PAN fiber and DMF insoluble benzoic-acid-treated PAN: Original PAN fiber; 60-min treated PAN; 360-min treated PAN.

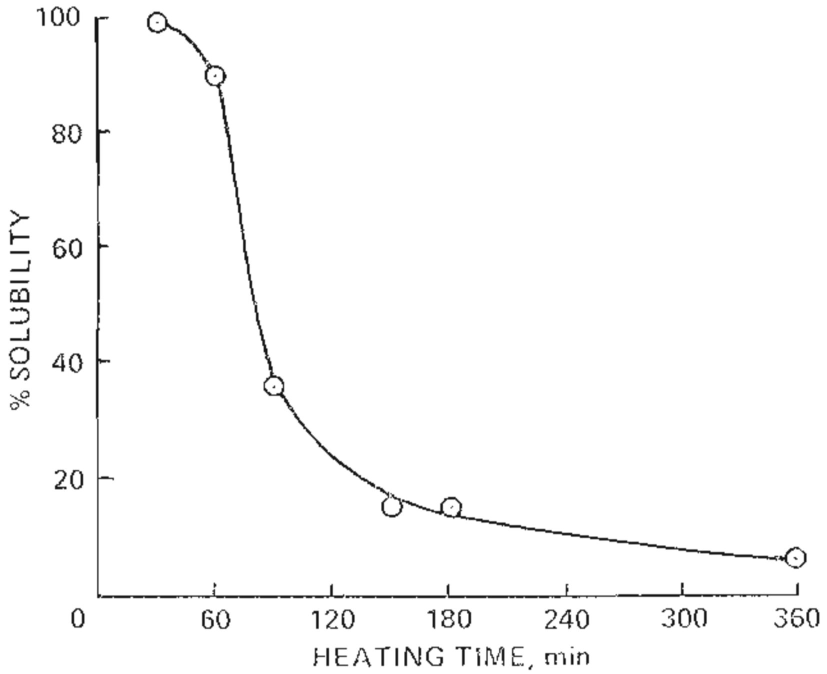

100
80
60
40
20
0
% SOLUBILITY
60
120
180
240
300
360
HEATING TIME, min

Fig. 1

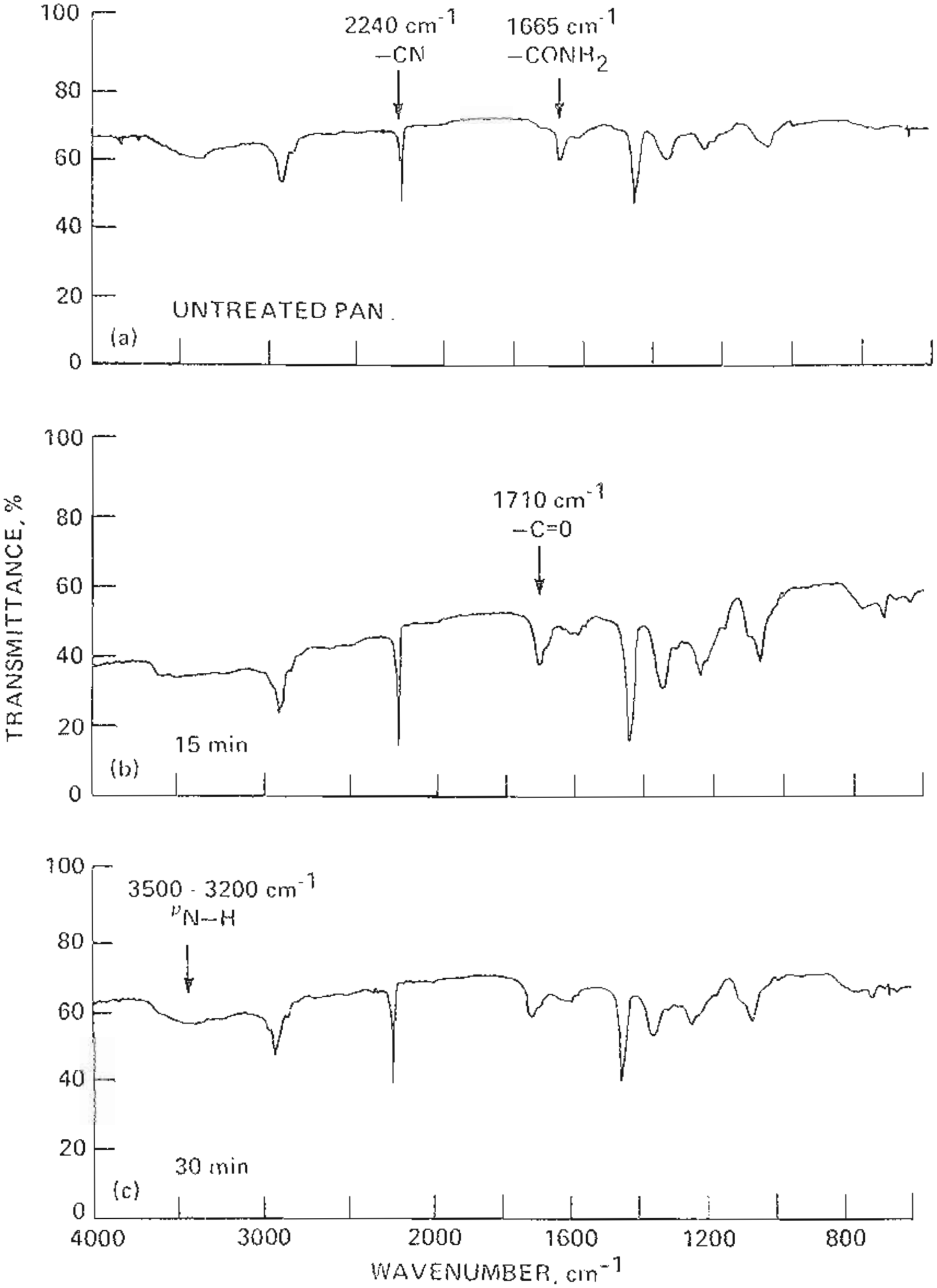


Fig. 2 (page 1 of 2)

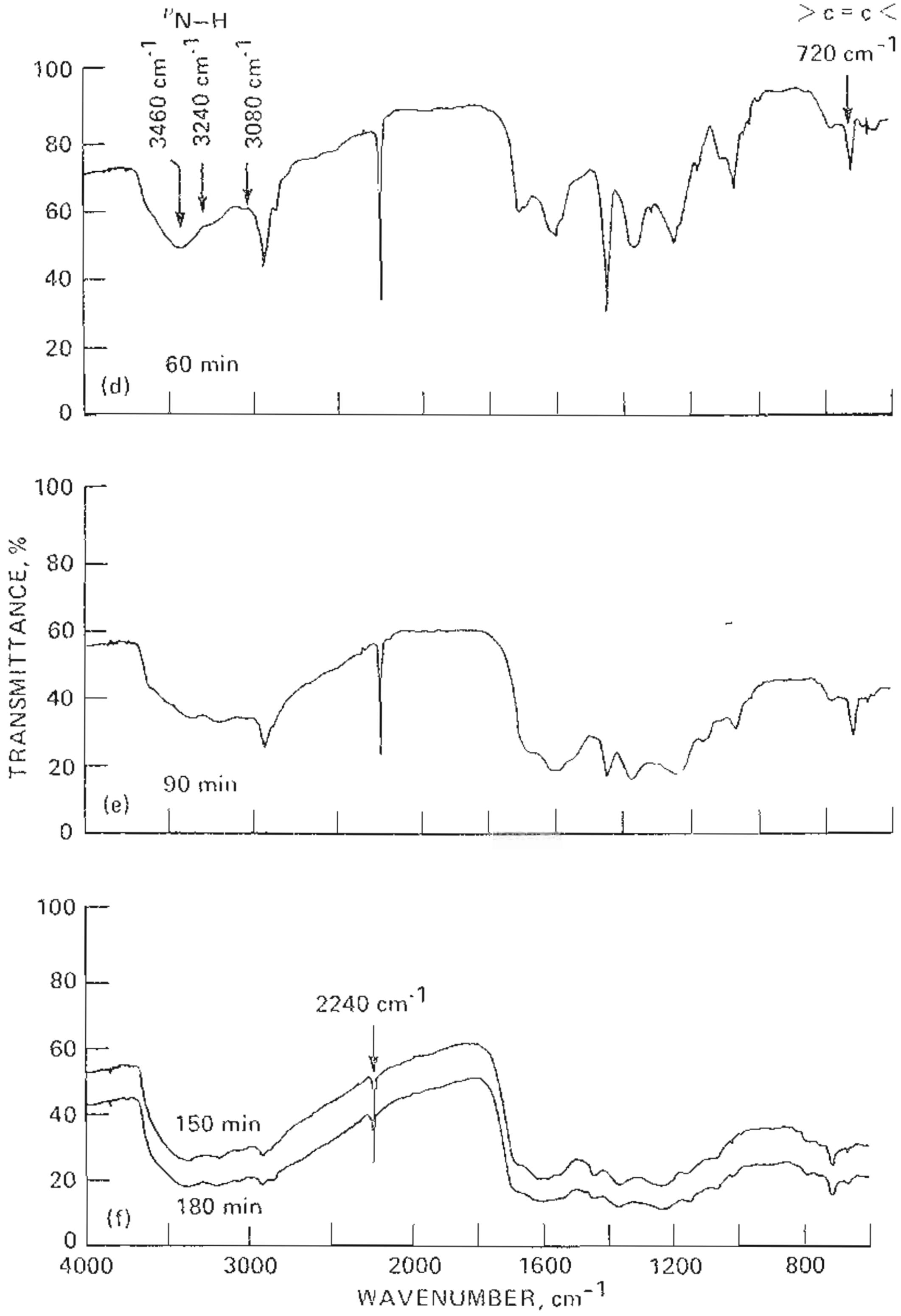


Fig. 2 (page 2 of 2)

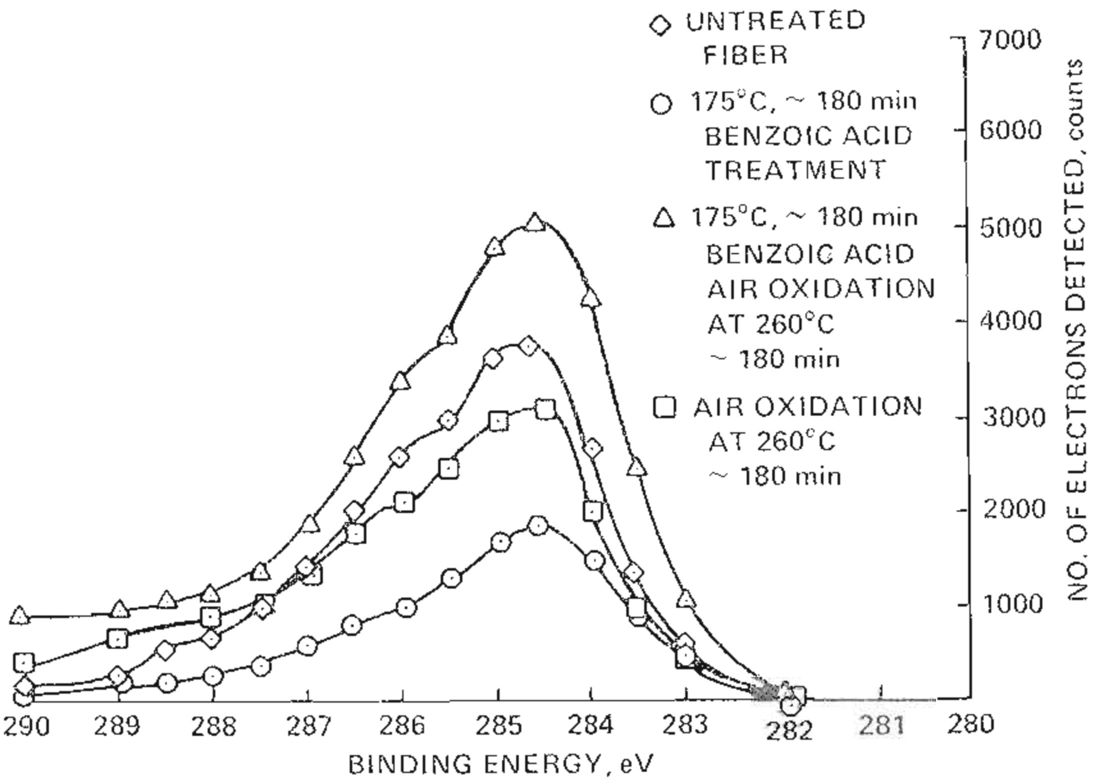

◇ UNTREATED FIBER
○ 175°C, ~ 180 min BENZOIC ACID TREATMENT
△ 175°C, ~ 180 min BENZOIC ACID AIR OXIDATION AT 260°C ~ 180 min
□ AIR OXIDATION AT 260°C ~ 180 min
7000
6000
5000
4000
3000
2000
1000
NO. OF ELECTRONS DETECTED, counts
290
289
288
287
286
285
284
283
282
281
280
BINDING ENERGY, eV

Fig. 3