

Characterization of Petroleum Pitch Precursor Carbon Fibers Using Fourier Transform Infrared Photoacoustic Spectroscopy

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Introduction

The production of carbon fiber from petroleum pitch proceeds in several stages: the formation of a precursor carbon fiber; stabilization of the precursor carbon fiber; and carbonization of the stabilized precursor carbon fiber (1-2). The stabilization process is the most important stage, at which thermal oxidation takes place in the precursor carbon fiber. Only a properly stabilized precursor carbon fiber can assure satisfactory performance of the final carbon fiber product.

The main interest of this research is to study the nature of the chemical changes in a pitch based precursor carbon fiber during the stabilization and carbonization processes using Fourier transform infrared photoacoustic spectroscopy (FT-IR/PAS). Gas chromatography has been widely used to investigate the volatile oxidation products of petroleum pitch and pitch based precursor carbon fibers (3-7). The applications of infrared spectroscopy, however, was focused on the oxidation of coal (8-12). The infrared spectroscopy studies of carbon fibers were carried out using transmission techniques (13,14). To obtain a transmission infrared spectrum, a carbon fiber must be either ground into a powder to make a potassium bromide (KBr) pellet or dissolved in an organic solvent to be deposited onto a window. One problem for both methods is the destruction of sample integrity. Another problem associated with the KBr pellet method is the high light scattering of carbon powders and the consequent opaqueness of the KBr pellet, which results in poor signal-to-noise ratio. It is also very difficult to find an organic solvent, in which a carbon fiber will totally dissolve.

Photoacoustic detection was used in this research to collect infrared spectra of carbon fiber samples. When a photoacoustic cell is used as a detector in a FT-IR spectrometer, the absorbed infrared radiation is first converted to photoacoustic signals, which are detected by a microphone and Fourier transformed to yield a single beam spectrum. With photoacoustic detection, it is not the transmitted or reflected IR radiation, but the photoacoustic signals converted from the absorbed radiation which are detected by a detector. Samples are not altered during the analysis. Opaque sample can be examined without experiencing difficulties with the detection of transmitted radiation. FT-IR/PAS can also be used as a near surface analysis technique (15-17).

Experimental

Instrumentation. A Nicolet 20DXB FT-IR spectrometer with a MTEC Model 100 photoacoustic cell was used to collect the infrared spectra. Resolution for all the spectra was 8 cm^{-1} . A 6-mm sample cup was used for PAS data collection. Carbon black was used as a reference material, and helium was used to purge the photoacoustic cell prior to data collection. The mirror velocity used was 0.139 cm/s for PAS and 0.556 cm/s for transmission experiments. No smoothing function or base-line correction was used.

Materials. (1) *Raw materials*—Both the enriched petroleum pitch and the green fiber produced by a melt blown process were provided by Ashland Carbon Fiber Division, Ashland Oil Company, Ashland, Kentucky. The pitch has a softening point of 260°C . The diameter of the precursor carbon fiber is 14 microns.

(2) *The stabilized precursor carbon fibers*—The precursor carbon fiber stabilized by a programmed thermal oxidation process was provided by Ashland Carbon Fiber Division. The stabilization process began at 157°C and ended at 341°C for a total heating period of 80 min. Air was used as the oxidizing

medium. The precursor carbon fiber was removed from the heating apparatus at 10-min intervals.

(3) *The carbonized carbon fibers*—The precursor carbon fibers at different stages of the carbonization process were also provided by Ashland Carbon Fiber Division. The carbonization process started at 300°C at a 15°C/min temperature ramp to the final temperature (500, 700, 900 and 1100°C, respectively). The carbonization was carried in a nitrogen atmosphere. Immediately after reaching the designated temperature, the samples were cooled to below 300°C under nitrogen before being removed. Samples were ground to a powder prior to analysis.

(4) *Solvent extraction*—A Soxhlet extractor was used to extract 1 g of a carbon fiber sample by 65 ml of a solvent for 4 hr. The solvents used included: methylene chloride, hexane, benzene and tetrahydrofuran. The extraction mixture was finally filtered to remove solid particles from the solution.

Results and discussion

The Raw Materials. The photoacoustic infrared spectra of the enriched petroleum pitch precursor and the green fiber made from the petroleum pitch are presented in Figures 1A and 1B, respectively. The bands at 2968 and 2921 cm^{-1} in Figure 1 are due to the asymmetric stretching of CH_2 - and $-\text{CH}_2$ -, respectively. Both the bands at 2968 and 2864 cm^{-1} increased their intensities relative to the band at 2921 cm^{-1} in the infrared spectrum of the tetrahydrofuran extract of the green fiber. Therefore, the band at 2864 cm^{-1} in Figure 1 can be assigned to the symmetric stretching mode of CH_2 -. The symmetric stretching mode of $-\text{CH}_2$ -, usually at 2850 cm^{-1} (18), is probably overlapped by the band at 2864 cm^{-1} in Figure 1.

The broad band at 3045 cm^{-1} in figure 1 is due to the unsaturated hydrocarbon stretching mode. In order to determine the nature of the unsaturated hydrocarbons contained in the raw materials, the green fiber was treated in a 5% solution of bromine in carbon tetrachloride for 5 min at room temperature, then analyzed by FT-IR/PAS. The intensity of the band at 3045 cm^{-1} was reduced in the spectrum of the bromine-treated green fiber. The reduction in the intensity of the band at 3045 cm^{-1} was due to the saturation of the aliphatic unsaturated hydrocarbons by bromine. Therefore, it can be concluded that the unsaturated hydrocarbons in the green fiber have both aliphatic and aromatic components.

The green fiber was extracted by benzene and hexane. It was found that both the aromatic hydrocarbon stretching band around 3045 cm^{-1} and the $-\text{CH}_2$ - asymmetric stretching band at 2918 cm^{-1} were significantly enhanced in the spectrum of the benzene extract compared with the spectrum of the green fiber (Figure 1B). This probably indicates that the $-\text{CH}_2$ - in the green fiber has a major contribution from the methylene bridges linking aromatic rings. It was also found that the CH_2 - asymmetric stretching band at 2960 cm^{-1} was much stronger while the band at 3045 cm^{-1} was weaker in the infrared spectrum of the hexane extract than in the spectrum of the green fiber (Figure 1B). Probably this can be explained by the fact that the methyl groups in the green fiber has a major contribution of methyl substitutes on the aromatic rings which have few hydrogens.

Three strong and distinct bands at 880, 834 and 750 cm^{-1} , respectively, due to aromatic out-of-plane C-H bending can be clearly identified in the spectra of the pitch precursor and the green fiber (Figures 1A and 1B). The assignment of the three aromatic out-of-plane C-H bending modes are listed in Table I. The strong band at 1600 cm^{-1} in Figure 1 is due to the aromatic ring stretching mode. The intensity of the aromatic ring stretching mode is enhanced by the presence of phenolic groups or methylene bridges linking the aromatic rings (19). It is very likely that some other aromatic C-H bending modes are superimposed by the three strong bands at 880, 834 and 750 cm^{-1} in Figure 1 as reported in the IR study of coal samples (18).

The two weak bands at 3550 and 3450 cm^{-1} shown in both the spectrum of the pitch precursor (Figure 1A) and the spectrum of the green fiber (Figure 1B) are probably associated with the stretching mode of free hydroxyl and hydrogen-bonded hydroxyl. A weak carbonyl band at 1697 cm^{-1} , which is not visible in the spectrum of the pitch precursor (figure 1A), is present in the spectrum of the green fiber (Figure 1B). The carbonyl was the oxidation product formed during

the melt blown process, by which the green fiber was produced. The functional groups present in the green fiber and the corresponding IR vibrational band frequencies are summarized in Table I.

Table I. The functional groups and the corresponding IR vibrational frequencies of green fiber.

Functional Groups	IR Vibrational Frequency (cm^{-1})	
-CH ₃	ν_{CH}	2968, 2866
	δ_{CH}	1444, 1377
-CH ₂	ν_{CH}	2918, 2850*
	δ_{CH}	1444*
Unsaturated Aliphatic Hydrocarbon	$\nu_{\text{C-H}}$	3045
Aromatic Hydrocarbons	$\nu_{\text{C-H}}$	3075-3035
1,2-bisubstituted Aromatic Hydrocarbons	$\gamma_{\text{C-H}}$	750
Trisubstituted Aromatic Hydrocarbons	$\gamma_{\text{C-H}}$	834
Aromatic Hydrocarbons with Isolated Hydrogens	$\gamma_{\text{C-H}}$	880
Aromatic Ring	$\nu_{\text{C=C}}$	1600
C=O	ν	1697
-OH	ν	3450, 3550

* Overlapped bands.

The Stabilization of the Fitch Precursor carbon Fiber. The petroleum pitch based precursor carbon fiber at different stages of the stabilization process were analyzed by FT-IR/PAS (Figures 2 and 3). It can be seen in the infrared spectra of the partially stabilized carbon fiber (Figures 2A-2D) that the band at 3550 cm^{-1} associated with the stretching mode of the free hydroxyl and band at 1697 cm^{-1} associated with the carbonyl stretching mode increased their intensities during the first 40 min of the programmed thermal stabilization process. This indicates that free hydroxyl and carbonyl were formed as the oxidation products at the early stages of the stabilization process. No changes are visible in the bands due to the C-H stretching and bending modes in Figure 2.

When the carbon fiber was oxidized for 50 min, the amount of the free hydroxyl was increased to such an extent that the hydroxyls form hydrogen bonding to each other as demonstrated by a broad band at 3400 cm^{-1} with an increased intensity in Figure 3A. The intensity of the carbonyl band at 1697 cm^{-1} is increased significantly, while the C-H stretching bands in the 3045-2864 cm^{-1} region, the aliphatic C-H bending bands at 1444 and 1377 cm^{-1} , and the aromatic out-of-plane bending bands in the 880-750 cm^{-1} region were reduced in Figure 3A. All the infrared spectroscopy data demonstrated that an accelerated oxidation occurred during the 40-50 min time period. A broad band around 1250 cm^{-1} was formed in Figure 3A. This is mainly due to the C-O stretching mode, since large amount of -OH were formed during the same period. There is more reduction in the 880 cm^{-1} band intensity than the bands at 835 and 750 cm^{-1} so that the relative intensity of the 880 cm^{-1} band is lower than those of the other two bands in the Figure 3A. This reveals that the isolated hydrogens in the aromatic rings were easier to be oxidized than the other types of hydrogens in the aromatic structures in the carbon fiber.

When the stabilization time was increased to 70 min, the hydroxyl

stretching band at 3400 cm^{-1} and the carbonyl stretching band at 1697 cm^{-1} continue to increase their intensities and to broaden, while bands due to both the aliphatic and aromatic C-H continue to reduce their intensities (Figure 3b and 3c). The broad band around 1250 cm^{-1} also increases its intensity. The band at 1600 cm^{-1} due to the aromatic ring stretching mode appears to have changed little in Figures 3b and 3c. Oxygen attacked both the aromatic and the aliphatic hydrocarbons while the aromatic ring remained intact during this stage of oxidation.

To determine the nature of the carbonyl-containing oxidation products formed during the stabilization process, the carbon fiber stabilized for 70 min was treated with an 0.1M NaOH solution at room temperature for 5 min. The spectrum of the carbon fiber thus treated showed a reduction in the intensity of the carbonyl band at 1697 cm^{-1} and the formation of a new band at 1380 cm^{-1} , which was due to the symmetric stretching of carboxylate carbonyl. The symmetric stretching band of the carboxylate was obviously overlapped by the strong band at 1600 cm^{-1} . Formation of carboxylate upon the treatment of the carbon fiber by a NaOH solution reveals that the carbonyl band at 1697 cm^{-1} in Figure 3c has a contribution of carboxyl. The carbonyl band at 1697 cm^{-1} was further reduced after the carbon fiber had been treated in a NaOH solution for 140 hr. Because an extended treatment of the carbon fiber in a NaOH solution allows saponification to take place, the further reduction of the intensity of the carbonyl band at 1697 cm^{-1} demonstrated that ester was also formed in carbon fiber during the stabilization process. The carbonyl band, which remained in the spectrum of the carbon fiber treated in the NaOH solution for 140 hr, was probably due to aldehyde and ketone.

The photoacoustic spectrum of the fully stabilized carbon fiber is shown in Figure 3d. The broad, intense band at 3400 cm^{-1} is due to the hydrogen-bonded -OH groups of alcohol and phenol. The carbonyl band appears to broaden toward the high frequency region so the peak is around 1735-1697 cm^{-1} region. When the fully stabilized carbon fiber was extracted in methylene chloride, the infrared spectrum showed two distinct carbonyl bands at 1841 and 1771 cm^{-1} , respectively, and a band at 896 cm^{-1} . When the methylene extract was exposed to moisture, the intensities of the two carbonyl bands at 1841 and 1771 cm^{-1} as well as the band at 896 cm^{-1} were reduced substantially while a strong and broad band at 1715 cm^{-1} due to carboxyl carbonyl was formed. Therefore, it can be concluded that anhydride was formed as an oxidation product in the carbon fiber. The anhydride formed in the carbon fiber is probably cyclic aromatic anhydride, the dehydration product of a 1,2-dicarboxylic acid which is in turn the oxidation product of two CH_2 - groups bonded to the adjacent carbons in an aromatic ring. The band at 896 cm^{-1} in the extract of the methylene chloride extract was due to the C-O stretching of five-member cyclic anhydride. The oxidation products in the stabilized carbon fiber is listed in Table II.

Table II. The oxidation products of the pitch precursor carbon fiber.

Oxidation Products	IR band Frequency (cm^{-1})
Carbonyls of ketone and aldehyde	1697
Carbonyls of carboxylic acid and ester*	1697-1735
Carbonyl of aromatic cyclic anhydride	1841, 1771
Isolated hydroxyl	~3550
H-bonded hydroxyl	~3450

* Overlapped bands.

The Carbonization Process. The photoacoustic infrared spectra of the pitch precursor carbon fibers at different stages of the carbonization process are presented in Figures 4B-4E. After the stabilized carbon fiber was heated from 300°C to 500°C, the amount of hydroxyl and carbonyl in the carbon fiber was decreased as demonstrated by the significant reduction in the intensities of the

two bands at 3400 cm^{-1} and 1697 cm^{-1} in Figure 4B. It is also found that most of the aliphatic hydrocarbons were eliminated during this period, because the aliphatic hydrocarbon bands in the 2968-2864 cm^{-1} region (the C-H stretching modes) and in the 1444-1377 cm^{-1} region (the C-H bending modes) decreased drastically in the infrared spectrum of the carbon fiber heated to 500°C (Figure 4B). The aromatic hydrocarbon bands at 3050 cm^{-1} (the C-H stretching modes) and in the 880-750 cm^{-1} region (the aromatic C-H out-of-plane bending), as well as the aromatic ring stretching band at 1600 cm^{-1} appears to be unchanged in Figure 4B compared with the spectrum of the stabilized carbon fiber (Figure 4A). The infrared spectrum of the carbon fiber heated to 700°C (Figure 4C) reveals that all the hydroxyl and most of the carbonyl groups were eliminated in the carbon fiber. Only a very weak carbonyl band at 1697 cm^{-1} is seen in Figure 4C. The intensities of the aromatic hydrocarbon stretching band at 3050 cm^{-1} as well as the out-of-plane bending of the 1,2-bisubstituted aromatic C-H band at 750 cm^{-1} were drastically reduced in Figure 4C. The intensity of the aromatic ring stretching band at 1600 cm^{-1} was also reduced significantly in Figure 4C. The infrared spectroscopy data indicated that the aromatic rings were condensing and the hydrogens in the aromatic rings were being eliminated when the carbon fiber was heated from 500 °C to 700 °C.

When the carbonization temperature reached 900 °C, all the vibrational bands in the infrared spectrum (Figure 4C) were diminished. As a result, the infrared spectrum (Figure 4D) appears to be a flat line. All the functional groups in the carbon fiber were totally eliminated at this stage of carbonization. The infrared spectrum of the carbon fiber heated to 1100°C (Figure 4E) is identical to Figure 4D.

Conclusions

1. The unoxidized pitch carbon fiber contains aromatic hydrocarbons, saturated and unsaturated aliphatic hydrocarbons, as well as small amount of carbonyl and hydroxyl.
2. Hydroxyls of alcohol and phenol, carbonyls of ketone/aldehyde, carboxylic acid, ester and anhydride are formed during the stabilization process of the pitch precursor carbon fiber.
3. All the carbonyls, hydroxyls and hydrocarbons in the stabilized carbon fiber were gradually eliminated during the carbonization process. The aromatic ring condensation started to take place when the temperature reached above 500°C. All the functional groups were eliminated at 900 °C.

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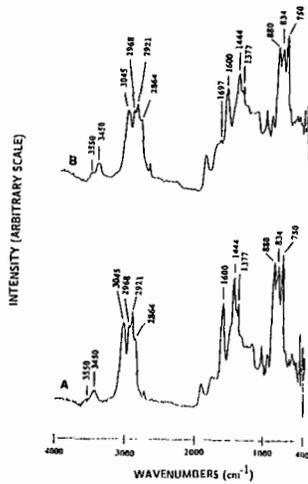


Figure 1 Photoacoustic infrared spectra of (A) the petroleum pitch; (B) the pitch precursor carbon fiber.

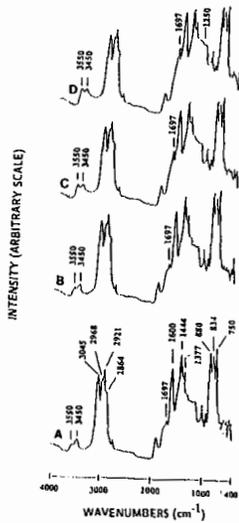


Figure 2 Photoacoustic infrared spectra of the pitch precursor carbon fiber stabilized for different times (min): (A) 10; (B) 20; (C) 30; (D) 40.

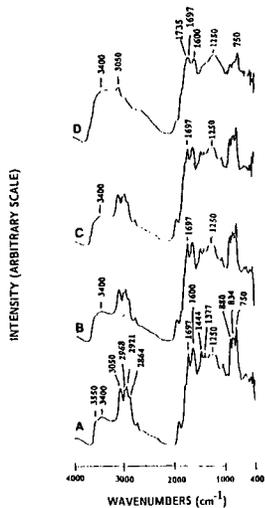


Figure 3 Photoacoustic infrared spectra of the pitch precursor carbon fiber stabilized for different times (min): (A) 50; (B) 60; (C) 70; (D) 80.

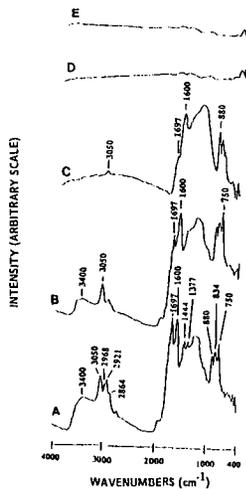


Figure 4 Photoacoustic infrared spectra of (A) the full stabilized carbon fiber. The photoacoustic infrared spectra of the carbon fiber heated to different temperatures during carbonization(°C): (B) 500; (C) 700; (D) 900; (E) 1100.