

Nondestructive Evaluation of Carbon Fiber by Mirage–FTIR Spectroscopy

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Received 13 March 1996; accepted 11 September 1996

ABSTRACT: Carbon fiber, being black (high absorptivity) material, is difficult to analyze by the conventional infrared (IR) techniques. Probably due to this fact, most of the studies reported in literature have been restricted to the thermal degradation of polyacrylonitrile-based fibers only. In the present work, we have used a recently developed mirage–FTIR technique for recording the IR spectra of carbon fibre at different stages of production, right from the precursor to final product. A study of microstructural/chemical changes occurring not only provides the information on structure but also demonstrates an unusual and highly technical industrial application. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1785-1791, 1997

Key words: microstructural changes; stabilization; carbonization; carbon fiber; mirage–FTIR

INTRODUCTION

The use of carbon fibres in production of light-weight and tough materials is now well established. Major applications include high tech areas like aviation, defence, or space¹ and therefore demand high quality materials that should meet stringent specifications. Besides these high tech applications, other areas of applications have also been explored, such as the consumer product market, where the quality standards/requirements are not so specific and stringent, possibly to provide an outlet of the low-grade (and/or waste) materials. Such low-grade materials could also be produced for specific applications more economically (for instance, the use of cheaper textile-grade acrylic fibre as a precursor, or relatively lower carbonization temperatures in the oven, etc.). However, irrespective of applications, quality norms for each grade need to be established,

depending upon the end use. For any production process, quality (on-line or off-line) monitoring of the material/product is an essential requirement, as any deviation during production stage may lead to a variation in the ultimate quality of the product.

As is evident from the production line of carbon fibre processing shown in Figure 1, the specified quality norms at each stage need to be monitored, and deviations, if any, are used to correct the processing conditions. Chemical and structural changes in carbon fibre at each stage of, specially, thermal treatment are well known to play a major role in achieving the ultimate product quality.² Thus, this, makes it imperative to set up stage-wise quick quality check methods. In other words, evaluation of fibres at each stage requires a fast, nondestructive (NDE), preferably online monitoring, technique. The conventional methods for the quality assurance, on the other hand, are quite cumbersome and time-consuming. Except starting raw material (precursor fibre), all the intermediates and the final product are black

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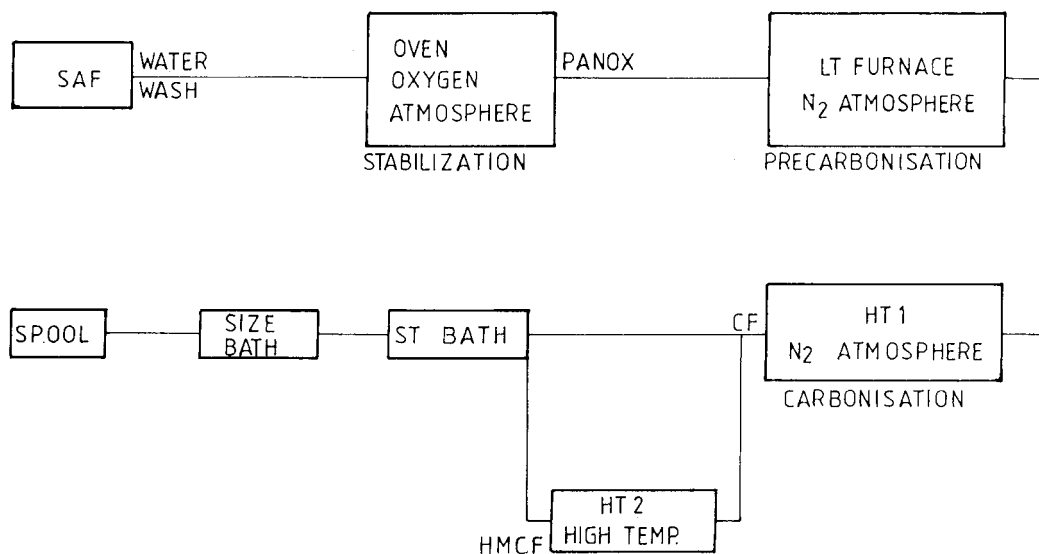


Figure 1 Production line diagram of carbon fibre.

(high absorptivity); therefore, it is difficult to record a good quality infrared (IR) spectrum with conventionally available techniques³⁻⁶ (which detects mainly transmitted or reflected radiation). This problem has been overcome to some extent using photothermal-based techniques,⁷⁻⁸ which work on the principle of measurement of absorbed energy, making it more suitable for the present work. Photoacoustic-Fourier transform infrared (FTIR) spectroscopy is one such commercially available accessory that has been used.⁹ Though this combination provides a good alternative, it has limitations in terms of sample handling and sensitivity.^{5,6} Another extension of this family of techniques, which works on the principle of photothermal beam deflection, has been reported to be a good alternative.^{10,11} In the present work, we have used a recently developed combination technique, Mirage-FTIR, for recording good quality IR spectrum of such samples for the NDE of structural changes during different stages of carbon fibre production.

EXPERIMENTAL

The working principle of Mirage-FTIR spectroscopy has been described elsewhere.¹² The line diagram and experimental setup showing the location of the Mirage cell in the FTIR (Bruker IFS-113V) spectrometer are shown in Figure 2. The probe beam alignment with respect to the sample surface is done with the help of an oscilloscope or

lock in amplifier. The optimally aligned system is then used to record the IR spectrum of the sample. A resolution of 8 cm^{-1} and mirror velocity of 0.059 cm/s were used for the measurement. The setup also requires noise filtering beyond the spectral range of measurement, i.e., $400\text{--}4000\text{ cm}^{-1}$ and signal amplification, which was done using a Stanford Research SR 560 very low noise voltage preamplifier. The absorbance spectrum was obtained by ratioing sample spectrum with that of reference. Diffuse reflectance infrared Fourier transform (DRIFT) spectrum of carbon fibre was recorded under vacuum using a praying mantis model diffuse reflectance attachment with a Bruker IFS-113V FTIR spectrometer.

RESULTS AND DISCUSSION

Carbon fibres are essentially prepared by thermo-oxidative treatment of polyacrylonitrile (PAN) fibres or its copolymers of methyl acrylate (MA $\approx 5\text{--}6\%$) or its equivalent containing a minor third constituent commonly known as special acrylic fibre (SAF) to distinguish it from textile-grade acrylic fibres.^{2,13,14} Though rayon and pitch fibres had also been used earlier as precursors, they were found unsuitable due to high carbon loss (as CO/CO_2) in case of former and poor tensile properties, in the case of pitch, unless extremely purified and very costly mesophase pitch was used.^{2,15} The literature survey revealed that high molecular orientation in stretched special

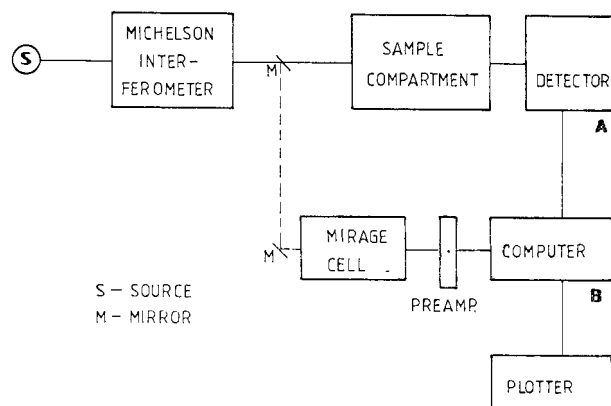


Figure 2 Block diagram of experimental setup for the (A) FTIR and (B) Mirage-FTIR measurement.

acrylic fibre through out the pyrolysis process leads to uniform, high tensile strength, and modulus of the final product (carbon fibre) and could be one of the major factors for its popularity.^{1,2}

In order to understand the mechanism of the structural changes during carbon fibre formation, knowledge of changes occurring at each stage of thermal treatment and the likely changes is essential. The various stages of carbon fibre production line are shown in Figure 1. The sample at each stage of production right from precursor SAF needs to be analyzed. The IR spectrum of the samples at each stage of the production using the novel combination Mirage-FTIR technique were recorded non-destructively and analysed to understand the mechanism of structural changes at each stage as discussed below.

Stabilization

The conversion process during this stage involves treatment of stretched SAF in a low-temperature furnace that had a temperature $\approx 225\text{--}230^\circ\text{C}$ in the presence of atmospheric oxygen. During this stage, the precursor is converted into a nonflammable and infusible fibre. This is probably the most important stage during which major chemical/structural changes occur and decide the ultimate properties of final product.^{16,17} It may be worth mentioning here that, of the scant literature available,¹⁷⁻²⁴ results have mostly been reported on the PAN fibre or its film around this low-temperature treatment in excess or limited supply of oxygen. The former being complicated, the majority of the results have been restricted to low-temperature treatment ($\sim 200^\circ\text{C}$) in limited supply of oxygen (i.e., under reduced pressure).

The main reason for this restricted study could possibly be the problem of getting any meaningful information from the IR spectra of samples treated at high temperature since the minute changes may not be observable in the IR spectrum (recorded by conventionally available techniques like ATR or DRIFT) due to poor resolution as shown in Figure 3, whereas certain significant changes at low-temperature treatment of SAF precursor could be seen in their IR spectrum (due to partial blackening of sample at this stage). We present the analysis of IR spectrum at this stage in the light of available information. The stabilization step of fibre involves slow and controlled oligomerization of nitrile groups, leading to highly conjugated cross-linked oxidized structure due to following processes:

1. Cyclization via cyanide group, leading to a ladder type structure;
2. dehydrogenation, leading to formation of conjugated double bonds; and
3. oxidation, leading to removal of carboxylic acid group or loosely bonded hydrogen.

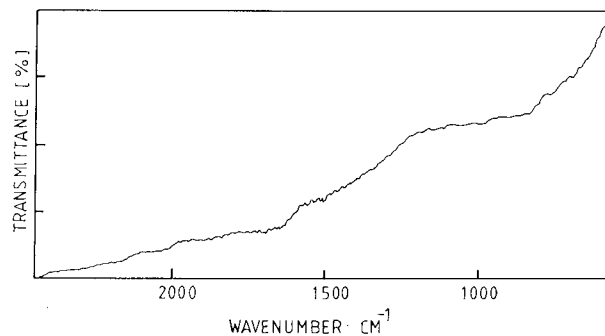
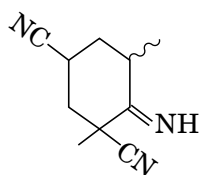


Figure 3 DRIFT spectrum of carbon fibre.

In other words, this process is the result of cyclization of linear cyanide through N bridges, followed by dehydrogenation, leading to the formation of crosslinked conjugated double bonds and aromatic rings, which undergo further oxidation and form a ladder structure, as shown in Figure 4.^{1,2,15}

The IR spectra of SAF and stabilized fibre (S-fibre) are shown in Figures 5(a) and (b), respectively. IR analysis of SAF has been given in our earlier work.²⁵ A comparative observation of these spectra in the light of possible chemical/structural changes reveals the following.

1. The bands $\approx 2900 \text{ cm}^{-1}$ (triplet $\nu_{\text{C-H}}$ -methylene stretching) show a marked decrease (to an almost insignificant level) in intensity, indicating a dominating dehydrogenation process. Similar observations have also been reported by other workers.¹⁷
2. Significant reduction in sharp and intense peak $\approx 2240 \text{ cm}^{-1}$ ($\nu_{\text{C=N}}$) and also of skeleton vibration $\approx 1070 \text{ cm}^{-1}$ is a very clear indication of loss of linear pendent cyanide in the structure. The appearance of medium to weak band $\approx 2195 \text{ cm}^{-1}$ assigned to the nitrile group attached to the olefinic chain clearly indicates a major structural change as a result of cyclization. Colemann and coworkers^{21,22} and McGuchan^{23,24} have also reported a similar observation and suggested that structural changes in S-fibre are the result of formation of amino-substituted unsaturated nitrile and iminonitriles, which also have characteristic bands in this region, for instance, formation of β -imino-nitrile^{21,23}.



Further examination of the spectrum indicates that a pair of new bands ≈ 1610 and 1575 cm^{-1} appear on stabilization, which cannot be assigned to any single mode vibrations due to strong overlapping and, instead, may represent mix mode vibrations like conjugated $\left(\text{C}=\text{C}\right)$ and/or $\left(\text{C}=\text{N}\right)$ (1610 cm^{-1}) and $\delta_{\text{NH}} + \nu_{\text{C}=\text{C}}$ (1575 cm^{-1}). These absorptions could also be due to linear polymerization of nitrile group, giving rise to

heterocyclic systems similar to one suggested by, for example, Colemann and Painter.²¹

Strong bands ≈ 1451 , 1350 , and 1250 cm^{-1} in the precursor spectrum [Fig. 5(a)] are known to be due to various nonstretching vibrational modes and mix modes of δ_{CH_2} , δ_{CH} , + δ_{NH} in plane bending and twisting, $\gamma_t(\text{CH}_2)$, etc. Considerable reduction or disappearance of these bands associated with appearance and/or shift of several weak bands (as a part of very broad band between 1700 – 1000 cm^{-1}) around 1385 , 1325 , and 1260 cm^{-1} (heterocyclic $\gamma_{\text{C-O}}$) also support the cyclization/dehydrogenation process during thermo-oxidative conversion. It may be interesting to note that the upshift of a doublet at 785 cm^{-1} (due to C—H out-of-plane deformation) to 792 and the appearance of medium band $\approx 630 \text{ cm}^{-1}$ in the stabilized fibre could be explained on the basis of steric hindrance associated with the cyclization (i.e., multiple heterocyclic ring structure) and later possibly due to overtone of C—O. Such a possibility cannot be ruled out because nitrogen is known to be present even in the stabilized fibre (supported by the elemental analysis), and the oxidation step is expected to create at least a few C—O bonds in the complicated matrix structure.

Carbon Fiber

Not much structural information is available in literature on the carbon fibre due mainly to the inability to record a good quality spectrum owing to the highly absorbing (black) nature of samples. The stabilized fibre thus obtained is subjected to heat treatment at higher temperature [this involves one low-temperature (LT) furnace at a temperature ≈ 630 – 900°C (precarbonization) and a HT1 furnace at ≈ 1000 – 1200°C (carbonization), as shown in Fig. 1] in the absence of oxygen (i.e., N_2 and/or Ar),^{2,26} which tends to remove most of the noncarbon atoms of stabilized fibre structure (intermolecular cross-linking takes place to remove the noncarbon elements like H_2O , N_2 , etc.) leading to a very close carbon-based graphitic structure. The possible structural rearrangement at each step of conversion process is shown in Figure 4.^{1,2,15,27,28} At this stage, conventionally recorded IR spectra²⁹ may not show any significant features because relatively poor resolution or the quality of spectrum (Fig. 3) do not reveal minor structural changes arising out of heteroatomic vibrations still present in the carbon fibre. The IR spectra of fibre, which is precarbon-

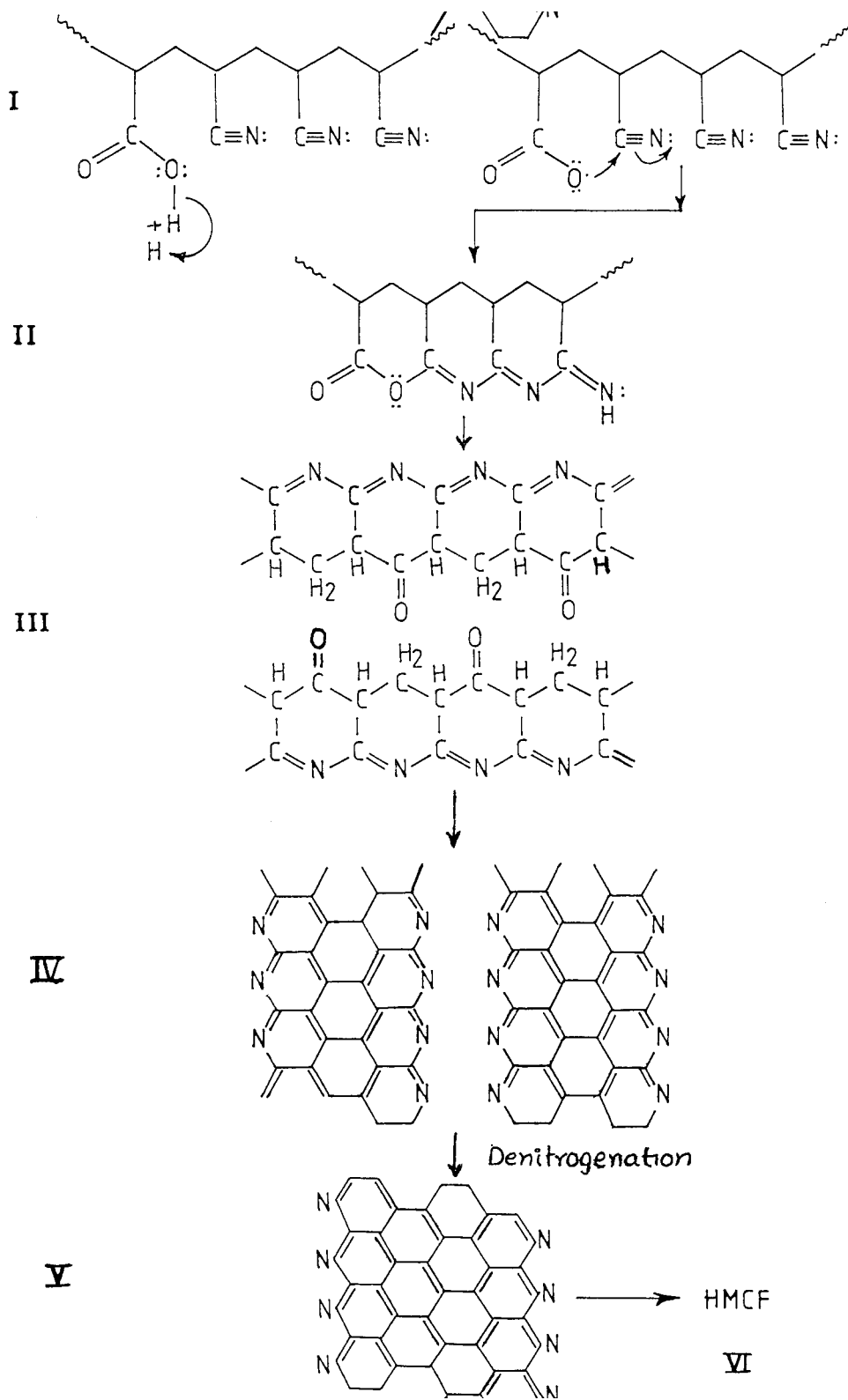


Figure 4 Structural rearrangement during conversion of SAF into CF (I), SAF (II), cyclized fibre (III), stabilized fibre (IV), evolution of nitrogen (V), CF, and (VI) HMCF.^{1,2,15,27,28}

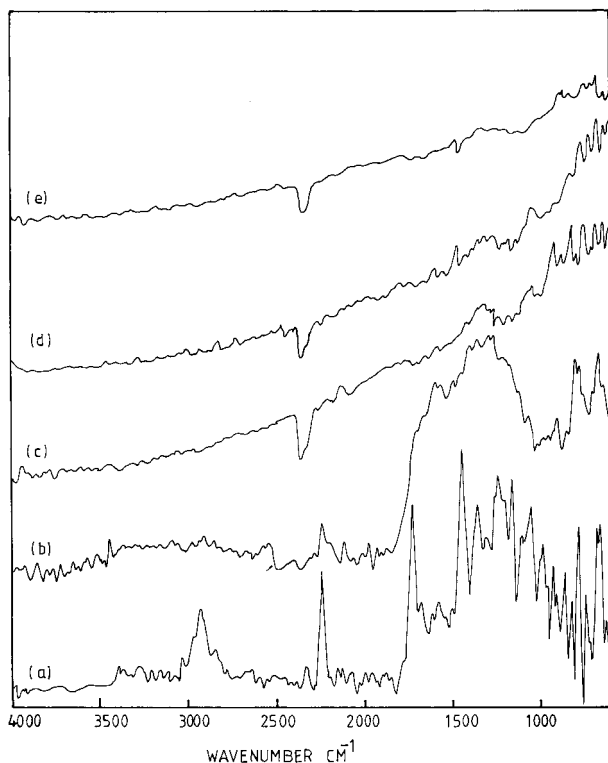


Figure 5 Mirage-FTIR spectra: (a) SAF, (b) stabilized fibre, (c) precarbonized fibre (LTI), (d) carbon fibre, and (e) high-modulus carbon fibre (HMCF).

ized in the LT furnace ($\approx 630\text{--}900^\circ\text{C}$) and that carbonized in the HT1 furnace ($1000\text{--}1200^\circ\text{C}$), are shown in Figure 5(c) and (d), respectively. An analysis of the structural features of the CF based on these IR spectra reveals the following.

1. Retention of the 2195 cm^{-1} (very low intensity) in Figure 5(c) shows that residual olefinic-nitrile bonding in the heterocyclic structure is still present. However, it is considerably reduced further when fibre is carbonised in the HT1, as shown in Figure 5(d).
2. Absence of any band $\approx 2900\text{ cm}^{-1}$ (ν_{CH_2}) confirms the absence of CH bonding in the structure [Fig. 5(c) (d)].
3. All the bands between 2000 and 1000 cm^{-1} are lost, except the band at $\approx 1360\text{ cm}^{-1}$ (broad and medium) and weak bands between $1150\text{--}950\text{ cm}^{-1}$. The band $\approx 1360\text{ cm}^{-1}$ could be assigned to a lactone structure;³⁰ whereas the band at $\approx 1150\text{ cm}^{-1}$ is due to mixed bending mode $\gamma_{\text{CN}} + \gamma_{\text{NH}}$. The intensity of these bands are further

reduced considerably in the case of HT1 treated fibre [Fig. 5(d)].

High-modulus Carbon Fibres (HM-CF)

It is known and also shown above that carbon fiber produced after 1200°C treatment is still not an absolute carbon skeletal. The carbon fibre, therefore, is given further high-temperature treatment in the absence of oxygen to obtain still better mechanical properties.^{26,31,32} During this treatment, nearly all the heteroatoms are expected to be lost in the carbon fiber matrix, leading to an exclusive carbon-based regular structure. This is also revealed by the comparative IR spectral analysis of the two fibres, namely, carbon fiber and HM-CF. It is evident from Figure 5(d) and (e), showing IR spectra of carbon fiber and HM-CF, that the small broad bands ≈ 1360 and $\approx 1150\text{ cm}^{-1}$ of carbon fiber [Fig. 5(d)] tend to decrease and change into a nearly flat plateau, indicating the loss of residual heteroatoms from the structure, making it almost a totally carbon matrix (graphitic structure).

CONCLUSIONS

Because carbon fibre is black (high absorptivity), is difficult to analyze it by conventional methods. An attempt has been made here using recently developed the Mirage-FTIR combination technique for NDE recording of IR spectra of fibre at each stage of the production line, right from the precursor to the final stage product to understand the mechanism of the structural/chemical changes occurring at different stages. This shows the utility/capability of the Mirage-FTIR technique as a characterization tool for highly absorbing materials.

This work was carried out as a part of project sponsored by IndoFrench Centre for promotion of advance research (IFCPAR).

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