

Estimation, using infrared spectroscopy, of the cyclization of poly(acrylonitrile) during the stabilization stage of carbon fibre production

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This paper describes an FTIR method for quantifying the extent of conversion from PAN to oxidized (stabilized) PAN fibre in a series of partially-treated commercial samples. The conversion is quantified in terms of a "conversion index". The results are considered in comparison with estimates obtained using WAXD and DSC measurements, and also with respect to changes in tensile strength of the samples. It is concluded that WAXD underestimates the degree of conversion in the initial stages of oxidation, and that DSC overestimates it near the end of the process. In contrast, the FTIR method is capable of giving a good indication of the conversion throughout the entire treatment period. The strength decreases monotonically through the series of samples, and correlates well with values of the conversion index as determined from FTIR.

1. Introduction

One of the most important commercial processes for the manufacture of high performance carbon fibre is based on poly(acrylonitrile) (PAN) as a raw material. The conversion to carbon fibre occurs in several stages: stabilization (or oxidation), carbonization, and graphitization.

In the stabilization stage, PAN fibre is heat-treated in an oxidizing atmosphere, normally air, at a temperature in the region of 200–300 °C. During this process it undergoes a number of chemical and physical changes. The detailed chemistry of the conversion is reported elsewhere [1–3], but the salient feature is the cyclization of nitrile groups to form an aromatized structure known as a "ladder polymer". The ladder polymer forms the skeleton upon which the structure of the high performance product will ultimately be based.

The extent of cyclization in the stabilized material has a strong bearing on the mechanical properties of the resulting carbon fibre product [4]. Watt [5] and others [6] have reported that optimal performance requires the conversion to be approximately 50% complete. This level may be achieved by initially carrying out saturation conversion, and subsequently reducing the concentration of cyclized material by treatment with pyrogallol [7].

It is important that the initial conversion should proceed as fully as possible to 100%. On the other hand, high temperature processes are expensive to

operate, and redundant treatment is clearly undesirable.

Stabilization is carried out commercially by either a step-wise or a continuous process. In the continuous process, the monofilament PAN fibre takes a tortuous path within the oxidation oven in order to provide sufficient residence time for complete conversion to take place at the required throughput. By means of halting the production process and sampling from different locations within the oven, it is possible to map the progression from PAN to ladder polymer. Various methods have been shown to be useful in quantifying the conversion. Bahl and Manocha [8], for example, used shrinkage measurements to determine the degree of conversion, while Uchida *et al.* [9] employed a method based on wide-angle X-ray diffraction (WAXD). They defined an "aromatization index", AI, as

$$AI = I_A / (I_A + I_P) \quad (1)$$

where I_A is the intensity of a diffraction peak associated with the aromatized structure at a 2θ value of 26.5°, and I_P is that of the equatorial (100) reflection at $2\theta = 17^\circ$ due to virgin PAN.

Tsai [10] also reports a method based on WAXD, but making use of variations in orientation occurring during stabilization.

Tsai and Hsu [11] reported a differential scanning calorimetry (DSC) technique for determining the aromatization index. The conversion from PAN to the

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ladder polymer is essentially an exothermic process and, by measuring the magnitude of the exotherm, an estimate can be made of the initial concentration of unreacted nitrile groups in the sample. Their definition of AI was

$$AI = (H_V - H_O)/H_V \quad (2)$$

where H_V is the intensity of the exotherm measured in virginal PAN fibre, and H_O is the intensity determined in the partially-oxidized material.

Whilst both methods have been moderately successful, both in practice suffer from certain drawbacks, which will be discussed. The present paper presents some initial data obtained using Fourier transform infrared (FTIR) absorption spectroscopy to estimate the conversion to ladder polymer. The data derived from FTIR are compared with those obtained using the WAXD and DSC methods on the same set of samples. The results are also considered in the light of differences in the measured tensile strengths of the samples.

2. Basis of infrared method

The estimation of conversion using FTIR will be quantified in terms of a parameter similar to those described already, but based on the relative intensities of vibrational bands associated with the PAN and ladder structures, respectively.

The absorption spectrum of virginal PAN features a strong absorption band at 2240 cm^{-1} , assigned to nitrile $\text{C}\equiv\text{N}$ stretching. The fully-cyclized ladder polymer yields a spectrum containing a moderately intense band at 1600 cm^{-1} , due to a vibration of the conjugated $\text{C}=\text{C}/\text{C}=\text{N}$ bonds [1, 12].

For a partially-stabilized sample, an FTIR conversion index may be defined in terms of the intensities of these peaks, as

$$A_I = I_O/(I_V + I_O) \quad (3)$$

where I_O is the measured intensity of the conjugated band at 1600 cm^{-1} , associated with the developing structure, and I_V is that of the nitrile band at 2240 cm^{-1} , belonging to the unmodified PAN molecule.

In order to distinguish between the conversion parameters derived from the different techniques, the following notation will be employed for the remainder of this paper[†]:

1. A_I : conversion index from FTIR measurements;
2. A_X : aromatization index from WAXD measurements;
3. A_D : aromatization index from DSC measurements.

3. Experimental details

3.1. Materials studied

The samples used in the study were obtained from the continuous stabilization stage of the PANOTEX

process for high performance carbon fibre, by means of halting the run and removal from the oven. The designations P1–P6 are given to the samples, the digit indicating the relative residence time in the oxidation chamber.

Although the detailed history of the samples was not revealed to us by the supplier, we understand the temperature to have been in the range $200\text{--}250^\circ\text{C}$. The maximum residence time in the stabilization oven would have been ca. 100 min, and it may be assumed that the treatment period increases in equal intervals through the series, since the samples had been extracted from equidistant locations. Sample P1, originating near the beginning of the process, would have received little treatment while P6, from the end of the process, is expected to be the most fully-stabilized sample.

3.2. Instrumentation and methods

3.2.1. X-ray diffraction

Equatorial WAXD profiles of the fibre samples were obtained using a SCINTAG diffractometer equipped with a Ni-filtered CuK_α source. Specimens were prepared in the form of fibre bundles, positioned with the fibre axis normal to the X-ray beam.

3.2.2. DSC

The thermograms were recorded using a Perkin Elmer DSC-4 instrument. The specimens were contained within standard sample pans, and the analysis was carried out at a heating rate of $10^\circ\text{C min}^{-1}$.

3.2.3. FTIR

The spectroscopy was performed using a Spectra-Tech IR-PLANTM infrared microscope attached to a Philips PU9800 FTIR spectrometer. This combination allowed the analysis of single fibre specimens. The recorded spectra were obtained by averaging over 64 scans per sample.

3.2.4. Tensile testing

Tensile testing of single fibre samples was carried out using a Model 1122 Instron tensile testing machine, with a gauge length of 25 mm and a nominal strain rate of 0.02 min^{-1} . Fifteen replicates were carried out for each sample.

3.3. Procedure for obtaining FTIR intensities

Because the two bands of interest lie in regions of the spectra occupied by several other features, it was not immediately apparent what would be the most appropriate procedure for subtraction of the background absorption. In consequence, three different methods

[†]The notation "A" is used for consistency with that employed by others for estimating the progress of the oxidation process. However, it should be realized that none of the methods directly measures the extent of ring formation, so that the term "aromatization" ought, strictly speaking, to be avoided.

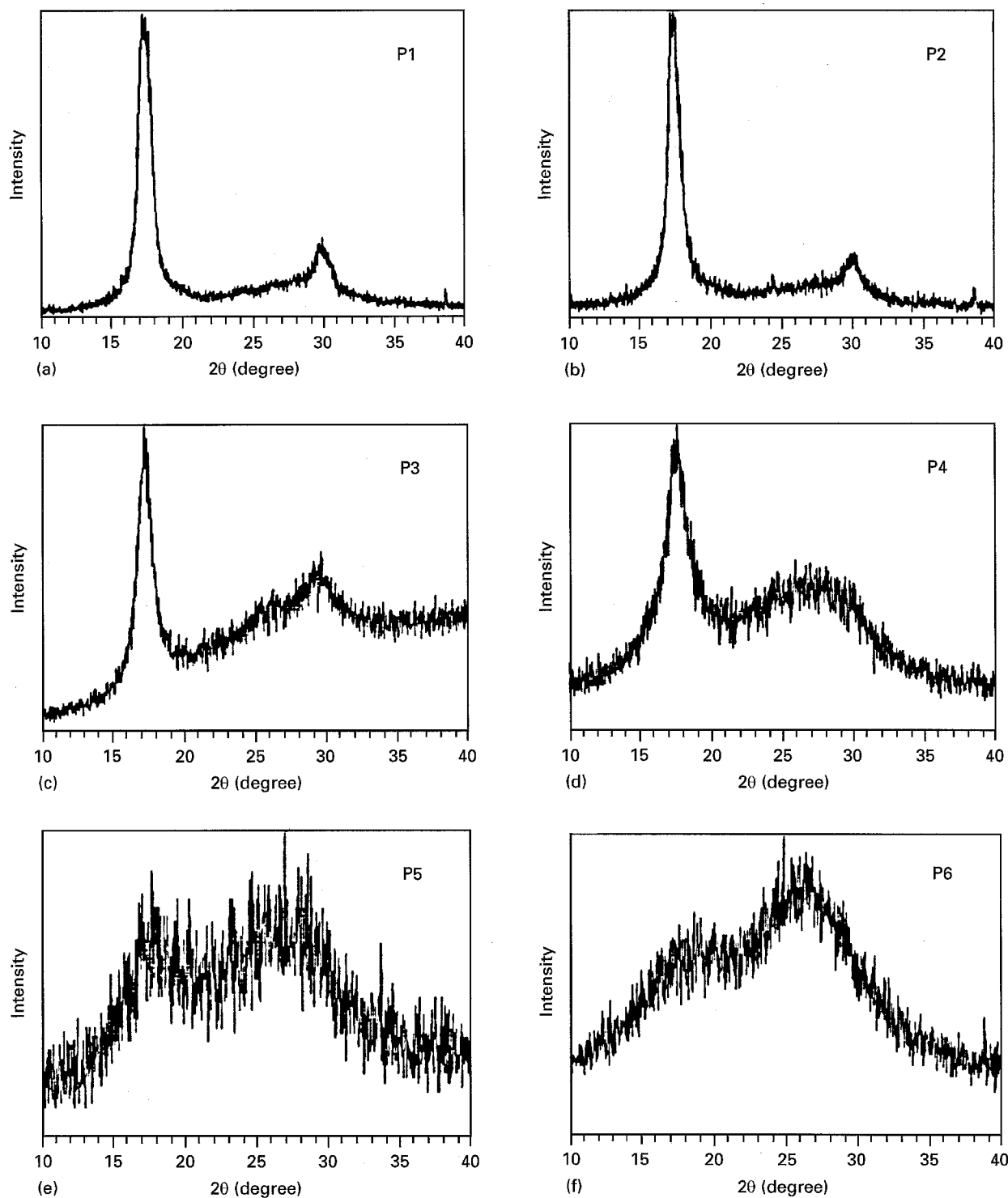


Figure 1 Wide-angle X-ray diffraction profiles of the samples.

were used, in which:

- (a) the maximum transmission level was taken as the baseline;
- (b) a linear baseline was estimated visually, and drawn locally to each peak;
- (c) a linear baseline was drawn between points lying at fixed frequencies on either side of each peak.

The results of all three methods of baseline subtraction will be presented; no attempt is made to justify any one method in preference to the remaining two.

4. Results

4.1. WAXD

Fig. 1 shows the WAXD profiles recorded for each sample. Sample P1 displays the diffraction pattern characteristic of the original PAN structure, with the prominent (100) peak featured at a Bragg angle of approximately 17° , and one of lesser intensity appearing at ca. 29° .

As stabilization proceeds it is evident, from the worsening signal:noise ratio, that the intensity of the main peak declines (samples P2–P6). The secondary peak at 29° becomes swamped by a much broader feature centred approximately at 26.5° .

TABLE I Sample codes and measured parameters

Sample	% X_c	D_{100} (nm)	% A_X (± 1)	% A_D (± 1)	% A_I (± 1)				Strength (± 0.02 GPa)
					(i)	(ii)	(iii)	Mean	
P1	80	8.7	0	0	23	23	23	23	0.39
P2	80	9.2	0	10	50	54	54	53	0.29
P3	41	7.8	0	28	68	67	58	64	0.25
P4	36	6.2	31	80	74	83	79	79	0.2
P5	28	3.4	55	100	78	81	68	76	0.18
P6	28	—	71	100	78	89	85	84	0.16

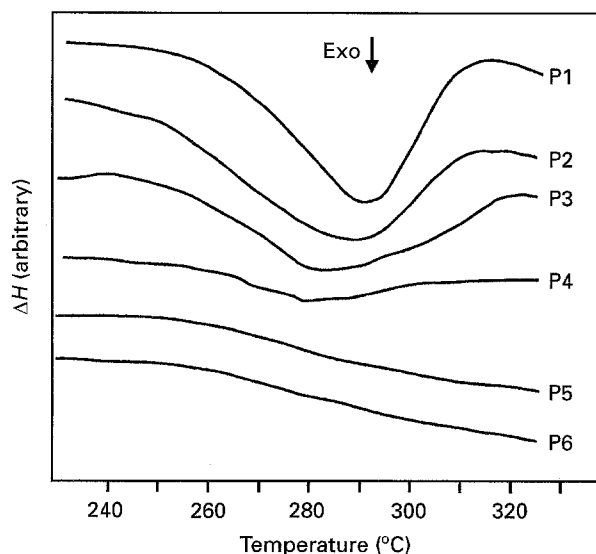


Figure 2 DSC thermograms of the samples.

This new peak is associated with the developing structure.

Calculated values of A_X of the samples, based on Equation 1, appear in Table I, along with estimates of their crystallinity and lateral crystal size, determined from the breadth of the (100) reflection.

4.2. DSC

Fig. 2 shows the thermograms obtained for the six samples. The exothermic peak near 290°C is associated with the conversion from PAN to ladder polymer, its integrated intensity being a measure of the amount of unmodified material initially present in the sample. It can be seen that there is a progressive decrease in the intensity of the peak with increasing residence time, as might be anticipated. The peak also gradually shifts to lower temperatures.

A_D values were calculated according to Equation 2, and appear in Table I.

4.3. FTIR

Fig. 3 shows the relevant spectral features for the six samples, in the wavenumber range 1000–3000 cm^{-1} . For clarity, the regions containing the two peaks of interest have been separated and shifted relative to one another.

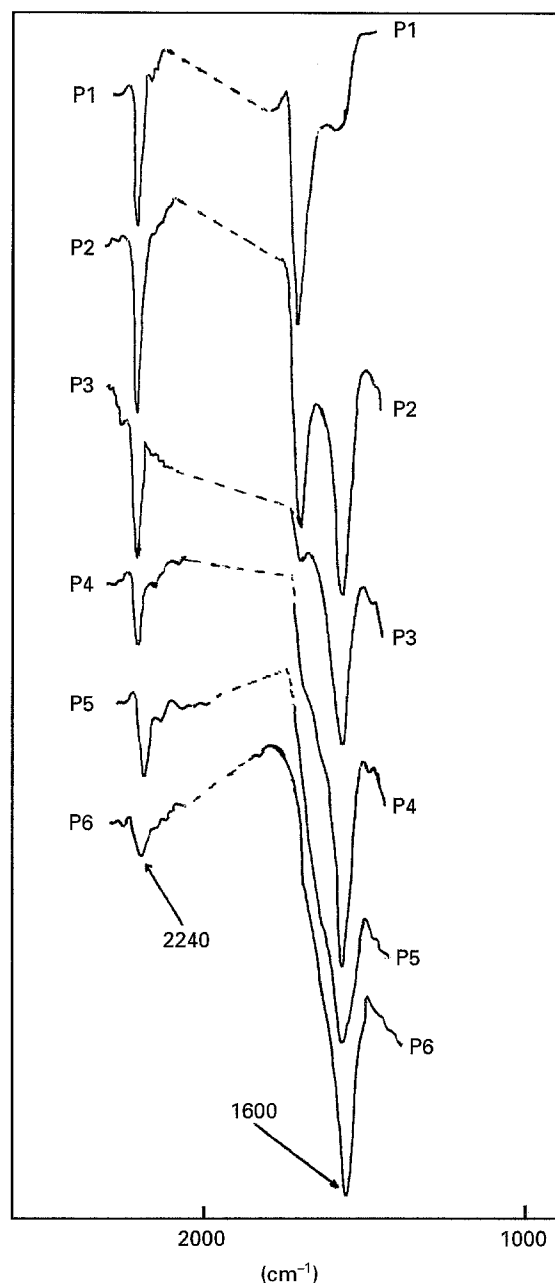


Figure 3 Parts of the FTIR absorption spectra of the samples: the intensity of the 1600 cm^{-1} peak relative to that at 2240 cm^{-1} increases steadily throughout the series.

There is a general trend, as stabilization proceeds, for the PAN peak at 2240 cm^{-1} to decrease in intensity, while that due to the aromatized structure, at 1600 cm^{-1} , strengthens.

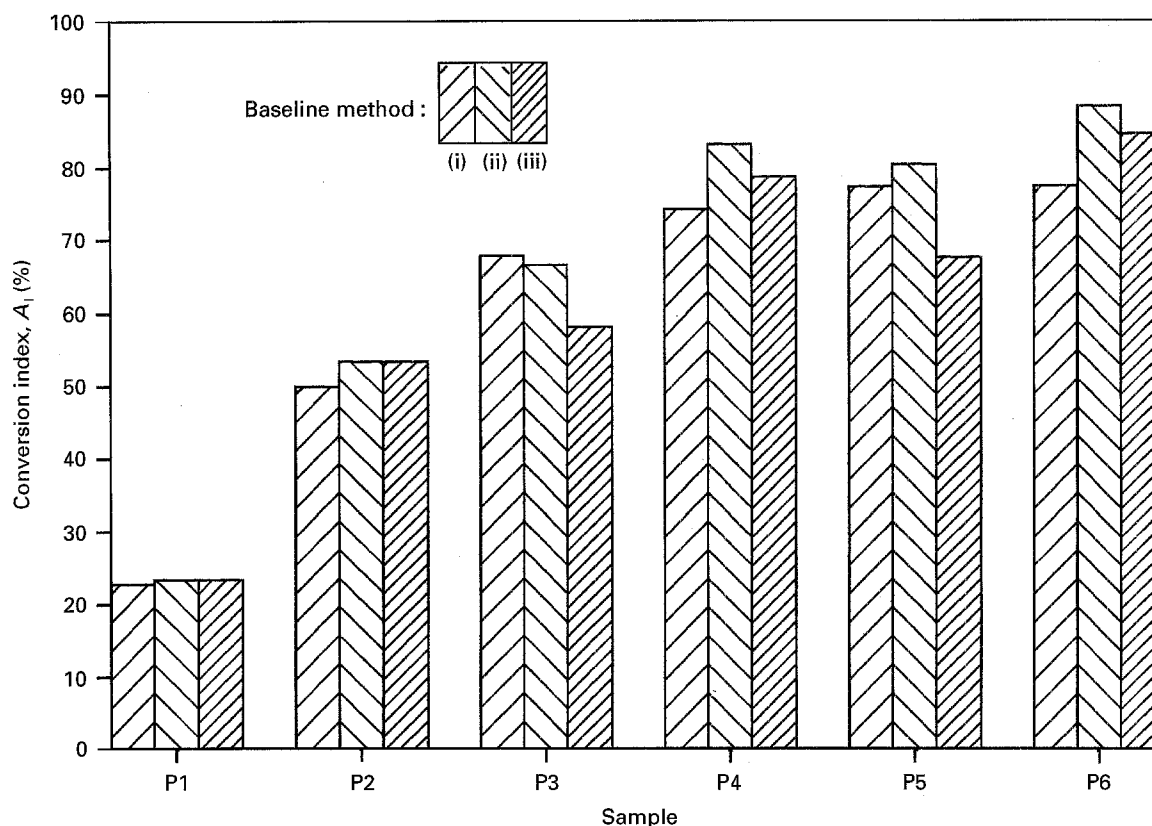


Figure 4 Measured A_1 values of the samples, obtained using different baseline correction methods.

Table I presents values of the conversion factor, A_1 , calculated according to Equation 3, using each of the three methods of baseline correction referred to earlier, along with the mean value. The data is also shown graphically in Fig. 4.

4.4. Tensile strength

Measured values of strength of the samples appear in Table I, and in graphical form in Fig. 5. Fig. 6 compares the structural and tensile data. It is clear that the tensile parameter decreases uniformly throughout the series from P1 to P6.

5. Discussion

As shown in Table I, and as may be inferred from an inspection of Fig. 1, the aromatization index based on WAXD is virtually zero for both sample P1 and sample P2. While this result might be considered reasonable for P1, which would have received little heat treatment, it is certainly surprising for sample P2, where one would expect some conversion to have taken place, even if only slight. A shortcoming of the WAXD method is that it relies on the coherent scattering associated with an "ordered" molecular phase. PAN is believed [13] to exhibit a hexagonal "polymorph", in which, although there is lateral ordering, little or no longitudinal regularity exists. More importantly though, the aromatization is believed to occur initially in the totally *disordered* regions of the PAN structure [14]. Support for this view comes also from our own estimates of crystallinity and lateral crystal

size. It can be seen (Table I) that the crystallinity remains constant up to sample P2, and that the crystal thickness, if anything, increases slightly initially, presumably due to annealing of the structure. Subsequently, it appears that the oxidation process begins to involve the crystal surfaces, leading to progressive thinning of the fibrils. This is accompanied by a corresponding decline in crystallinity.

Thus, the initial stages of the oxidation reaction remain undetected by the WAXD technique. Furthermore, the breadth of the peak at 26° for samples P3–6 would actually suggest that the developing structure is far from highly ordered, which brings into question whether X-ray diffraction is in fact an appropriate technique to apply.

Considering the DSC data, it will be observed that the exotherm is virtually absent from the thermograms of samples P5 and P6, suggesting 100% conversion in these two cases. This does not accord with the X-ray data, which indicates the presence of residual PAN material, even in these samples (cf. samples P5 and P6 in Fig. 1).

The results from FTIR show A_1 progressively increasing throughout the series of samples (irrespective of which method of baseline determination is used). More significantly, its value is non-zero even for sample P1, which appears to contradict the results from WAXD, but which would agree qualitatively with the indications from the DSC analysis. On the other hand, A_1 has still not attained a plateau value, and is certainly below 100%, by sample P6, suggesting that the conversion is incomplete. This latter observation would support the interpretation of the WAXD

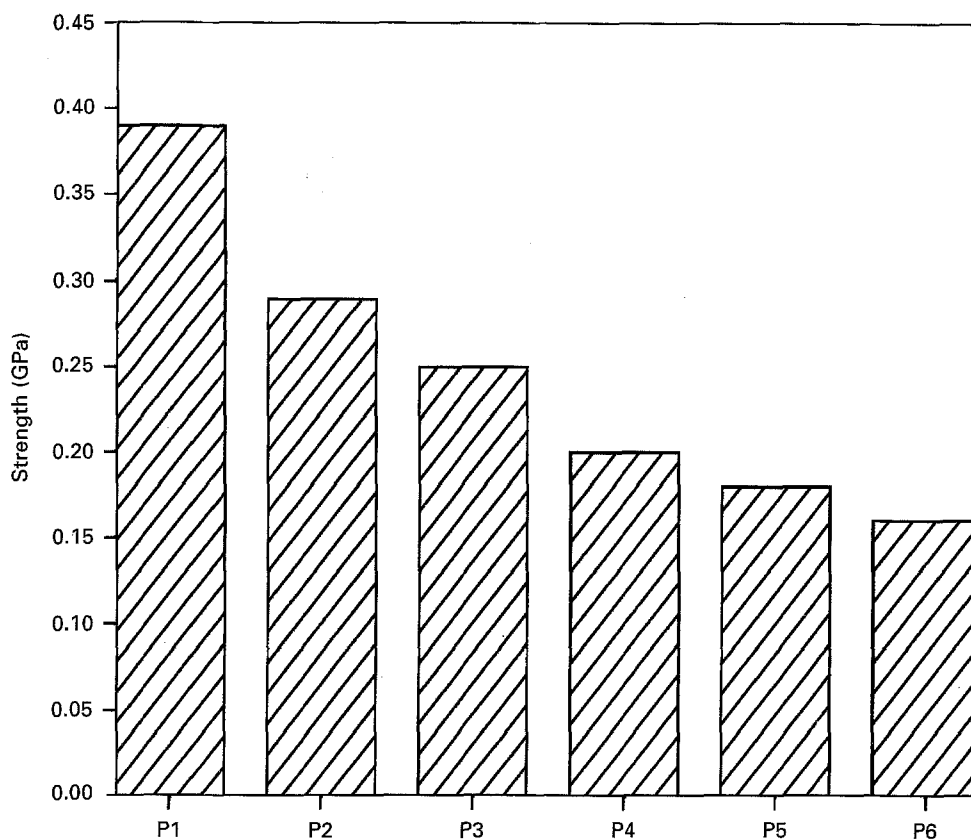


Figure 5 Measured strength values of the samples.

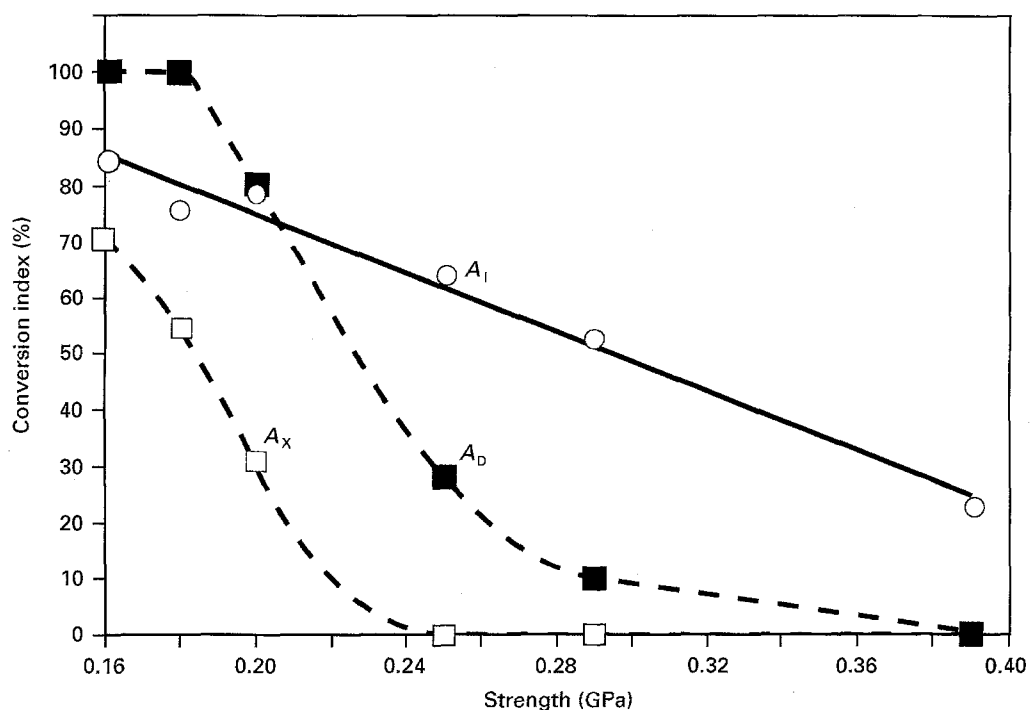


Figure 6 Conversion index obtained from WAXD (open squares), DSC (solid squares) and FTIR (open circles), as a function of measured strength. FTIR values shown are the means of those from using the three baseline correction methods.

results, but would be at odds with the conclusion suggested by the DSC method.

It is instructive to examine the strength data (Table I and Figs 5 and 6): changes in the tensile properties of the samples may be taken as a fourth, albeit indirect, indication of how far the oxidative treatment

has progressed. Two key observations can be made:

- (i) no initial plateau is evident with respect to the effective treatment time (relative to that of sample P1) but, rather, the strength falls significantly and immediately beyond sample P1;

- (ii) there is a monotonically decreasing trend of strength through the series, with the values appearing to approach a limit lying "below" that measured for sample P6.

The first observation suggests, perhaps tentatively, that sample P1 was not virginal PAN fibre, since the strength is already changing rapidly at this point. However, the results from WAXD taken at face value imply that P1 is indeed unreacted PAN. WAXD therefore appears to contradict the mechanical data in the early stages.

The implication of the second observation is that sample P6 does not represent a fully-oxidized fibre. Thus, the conversion index, by whichever method it is determined, ought to be measurably less than 100%. On this basis, it would appear that whereas the WAXD method omits to detect changes occurring during the early stages of oxidation, the DSC technique overestimates the extent of conversion towards the end of the process. The reason for this may be associated with the finite time the specimen spends at temperatures intermediate between that at which the commercial process takes place (ca. 200–250 °C) and that at which the exotherm appears (270–290 °C).

By contrast, the observations indicate a good degree of agreement between the FTIR and tensile data across the set of samples. In particular, linear regression analysis shows high correlation between the tensile and FTIR data, but little correlation between the tensile and WAXD or DSC results (calculated values of R^2 being 0.98, 0.67 and 0.85, respectively).

Unlike WAXD, which detects changes taking place exclusively within the crystalline material, the FTIR method is based on "molecular" characteristics, and is therefore much less sensitive to the distinction between ordered and disordered fractions. There will undoubtedly be spectral features associated with, for example, conformational differences occurring in the two phases, but these are likely to be quite subtle, and to contribute to the total measured band intensity (that is, the conditions used would not be expected to resolve such features).

6. Conclusions

Of the various methods available for monitoring the oxidative stabilization of PAN fibre, WAXD, DSC and FTIR all have some merits. However, WAXD appears to underestimate the true extent of conversion in the early stages, while DSC overestimates it in the later stages.

FTIR gives a realistic indication of the conversion factor throughout the process. Unlike WAXD, the FTIR method can monitor changes taking place in both amorphous and crystalline regions of the fibre. Additionally, the FTIR technique avoids the ambiguity encountered with DSC (arising from the finite

heating rate) when the conversion is at an advanced stage.

It is recognized that the deductions based on tensile observations need to be checked further. This is particularly the case with respect to the early stages of conversion, where a more definite conclusion could have been reached if the authors had had access to true virginal PAN fibre from the same batch as the samples supplied. (It may be of interest to note that on the basis of the regression analysis, the virginal PAN material would be predicted to have a strength of ca. 0.48 GPa, compared with 0.11 GPa for 100% stabilized fibre.) In order to better clarify this question, we intend to conduct a simulation of the commercial process by subjecting acrylic fibre of known history to controlled heat treatments.

It is further acknowledged that owing to uncertainties inherent in estimating the absorption baseline, the "absolute" values of the conversion index quoted here, and derived from FTIR, may be unreliable. Techniques are available which could be used to advantage: for example, second derivative spectroscopy, which would enable better band separation. In any event, there will be occasions where a qualitative indication of the trend is sufficient.

Thus, the authors are of the opinion that of the various methods reported for monitoring the stabilization of PAN fibres, FTIR offers the best prospects over the entire process. It is reasonable to conjecture that advances in instrument technology will enable this to be carried out on-line in the future.

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