

# Effect of Heat Treatment on the Structure and Mechanical Properties of Polyacrylonitrile Fibers

A. K. GUPTA and A. K. MAITI, *Centre for Materials Science and Technology, Indian Institute of Technology, New Delhi-110016, India*

## Synopsis

Structure and mechanical properties of untreated and thermally treated (at 110°C and 150°C) drawn polyacrylonitrile (PAN) fiber have been studied through IR spectroscopy, wide angle X-ray diffraction, and tensile and dynamic mechanical properties measurements. The results are interpreted in terms of the change in the degree of bound nitrile group pairs on heat treatment. The heat treatment at both the temperatures resulted in higher degree of bound nitrile groups (through their dipolar interactions) in the heat-treated PAN than that of the untreated PAN, as evidenced by IR spectroscopy, X-ray diffraction, and the mechanical properties. The difference between the results for the two heat-treatment temperatures are not sufficiently large, although the changes produced by heat treatment at 110°C seems somewhat more prominent than those produced by heat treatment at 150°C.

## INTRODUCTION

The presence of strong dipolar nitrile groups in the polyacrylonitrile (PAN) molecule imparts special character to this polymer.<sup>1</sup> Segmental mobility in the glass transition region is greatly influenced by the dipole-dipole interaction between the nitrile groups.<sup>2</sup> Some structural changes produced by heat treatment on PAN are suspected from the dielectric relaxation study of heat-treated PAN.<sup>3,4</sup> This generates a curiosity about how the other properties change with the heat treatment. We have, therefore, carried out further investigations on PAN fibers which include IR spectroscopy, X-ray diffraction, and tensile and dynamic mechanical properties on heat-treated and untreated PAN fibers. In the previous studies a lowering of dielectric constant and dissipation factor as well as an increase in the relaxation temperature (loss peak temperature) as a result of a heat treatment at 120°C for 24 h on PAN has been observed.<sup>3</sup> Heat treatment at a temperature (160°C) much higher than the  $T_g$  produced changes in these dielectric relaxation parameters considerably lower than those observed for the case of heat treatment at 120°C.<sup>4</sup> The dielectric studies<sup>3,4</sup> suggested a higher degree of bound nitrile group pairs (through dipolar interactions) for PAN heat treated at 120°C than at 160°C.

The present work may be useful in ascertaining by the other techniques the conclusion drawn from the dielectric measurements.

The two heat-treatment temperatures (110°C and 150°C) were chosen such that one was slightly above and the other was much above the  $T_g$  of PAN. The duration for heat treatment was chosen 24 h for the reason already stated elsewhere.<sup>4</sup>

## EXPERIMENTAL

The drawn PAN fibers (1.5 deniers) used in this work were supplied by the Carbon Fibers Groups of the National Physical Laboratory, New Delhi.

Heat treatment at 110°C and 150°C for 24 h were done in a constant temperature oven, keeping the fibers in a closed container. For brevity in the subsequent discussion, the two heat-treated samples were denoted as PAN (110) and PAN (150), where the numbers in the bracket denote the heat treatment temperature. The untreated sample is denoted as PAN (U).

The IR spectra have been taken in KBr pellets on the spectrophotometer (spectromaster, U.K.) in the range 600–3000  $\text{cm}^{-1}$ .

X-ray diffraction patterns (intensity vs. diffraction angle plots) were obtained on a Philips X-ray diffractometer equipped with a scintillation counter and a chart recorder, with identical setting for all samples.  $\text{CuK}_\alpha$  radiation was used. The sample was in the disc form prepared by compressing the randomly aligned short fibers.

The tensile strength was measured on an Instron 1112 at a pulling rate of 5 cm/min. For each sample more than 30 tests on single fibers were carried out, and results represent averages of 30 tests.

The dynamic mechanical measurements were made on a Rheovibron Viscoelastometer (DDV-II) over a temperature range of 20–180°C at a frequency of 11 Hz. The temperature was controlled within  $\pm 0.1^\circ\text{C}$  and measured with a thermocouple kept in close vicinity of the specimen.

## RESULTS

### Infrared Spectroscopy

The IR spectra of these samples in the range relevant to our present discussion are presented in Figure 1. In these IR spectra the band around 2240  $\text{cm}^{-1}$  attributed<sup>1,5-7</sup> to  $-\text{C}\equiv\text{N}$  stretching is clearly apparent. The other band apparent around the frequency 2900  $\text{cm}^{-1}$  is due to the CH stretching.<sup>5</sup> It is observed in

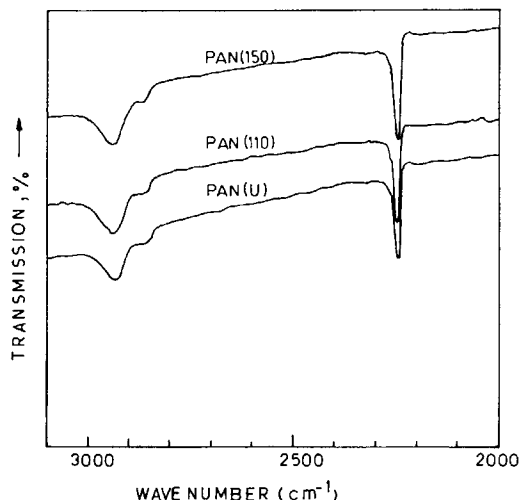


Fig. 1. Infrared spectra of PAN (U), PAN (110) and PAN (150).

these results that the intensity of  $C\equiv N$  stretching band, as represented by the relative heights of the  $C\equiv N$  and  $CH$  stretching bands, is lower for the heat-treated samples than the untreated sample. The ratio of the heights of  $C\equiv N$  stretching band to  $CH$  stretching band is 2.75, 2.63, and 2.45 for PAN (U), PAN (150), and PAN (110), respectively. This lowering of the intensity of  $C\equiv N$  stretching band implies a lower degree of the free nitrile groups in the system. Formation of bound nitrile group pairs due to dipolar interactions may lower the degree of free nitrile groups. Thus these results indicate a higher degree of bound nitrile groups in PAN (110) and somewhat lower in PAN (150) and lowest in PAN (U).

### X-Ray Diffraction

The wide-angle X-ray diffractograms showing the radial scans as the intensity ( $I$ ) vs. angle of diffraction ( $2\theta$ ) for these samples are shown in Figure 2. An intense sharp reflection at  $2\theta \approx 16.5^\circ$  (peak 1) and another sharp peak at  $2\theta \approx 29.5^\circ$  (peak 2) and a broad diffuse reflection in the region in between these two sharp peaks is a characteristic feature of the X-ray diffraction pattern of PAN reported by various authors.<sup>8-10</sup> The intense diffraction corresponds to a lateral repeat distance  $5.4 \text{ \AA}$  and has been represented as the (100) diffraction of a hexagonal lattice.<sup>10</sup> The reflection at  $2\theta \approx 29.5^\circ$  conforms to the second-order reflection of peak 1.<sup>11</sup> Furthermore, there is a general diffuse scattering covering an extensive portion of the pattern which seems to indicate that the disordered

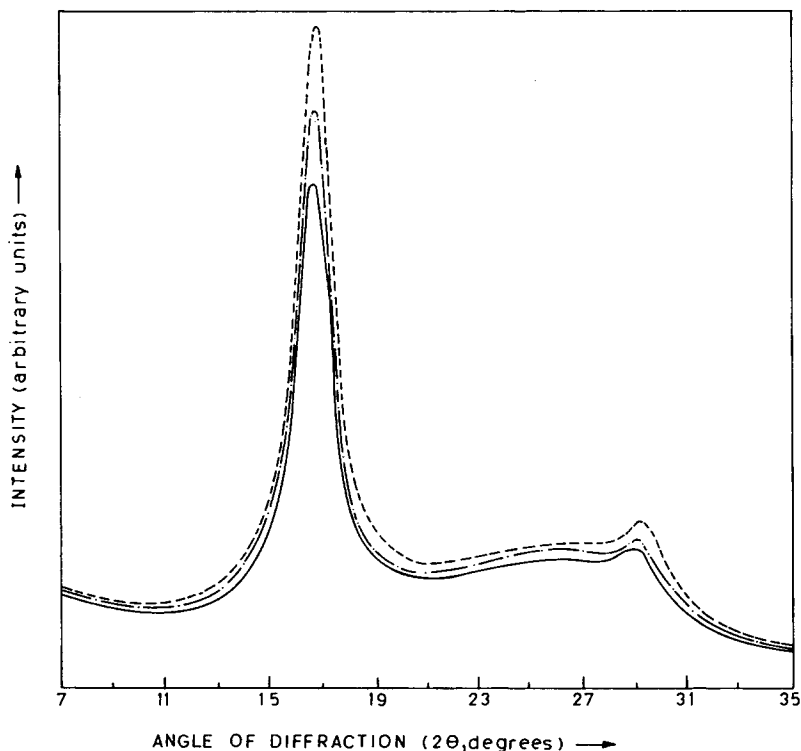


Fig. 2. X-ray diffractograms of PAN (U) (—), PAN (110) (---), and PAN (150) (- · - ·).

phase is distributed throughout the structure in a nondiscrete manner.<sup>10</sup> The position of the sharp reflection peaks on the  $2\theta$  axis remains unchanged for all the samples and no new reflection seems to occur in heat-treated samples. This suggests that the ordered structure (crystalline lattice) remains unaffected by the heat treatment. Furthermore, like the results of Bohn et al.,<sup>10</sup> the present results also negate the formation of orthorombic lateral order as a result of heat treatment as suggested by Stefani et al.,<sup>12</sup> since there are no additional reflections in the diffraction pattern for heat-treated samples. The height (i.e., the intensity) of the peak (peak 1) changes with heat treatment which implies a change in the degree of order (crystallinity). The peak height  $h$  of peak 1 follows the order:

$$h_{\text{PAN (U)}} < h_{\text{PAN (150)}} < h_{\text{PAN (110)}}$$

Calculation of crystallinity index (CI) according to the extrapolation of crystalline and amorphous parts of the diffraction pattern by the method used by Bell and Dumbleton<sup>13</sup> leads to the value of CI shown in Table I.

### Tensile Properties

The plots of specific stress versus extension for these samples are shown in Figure 3, and the values of some parameters for quantitative comparison are summarized in Table II. These results suggest that:

(i) The slope of the initial part (which is a measure of the initial modulus) is higher for the heat-treated samples than for the untreated samples.

(ii) The extension at break is 38% for the untreated sample and 33 and 35% for PAN (150) and PAN (110), respectively.

(iii) The breaking load (which is a measure of the tensile strength) also increases for the heat-treated sample. It is highest for PAN (110) and somewhat lower for PAN (150).

(iv) The area under the specific stress-extension curve (which is a measure of the work of rupture) is higher for the heat-treated samples than the untreated sample. It is highest for PAN (110) and slightly lower for PAN (150).

### Dynamic Mechanical Properties

Variations of dissipation factor ( $\tan\delta$ ) with temperature for these samples are shown in Figure 4. The loss peak occurring around 110–130°C in the three samples has been attributed to the segmental mobility.<sup>8,14–16</sup> These results show that the loss peak height ( $\tan\delta_{\text{max}}$ ) decreases and the peak is shifted to lower temperature for the heat-treated samples. The difference between  $\tan\delta_{\text{max}}$  for the two heat-treated samples is not large, although  $\tan\delta_{\text{max}}$  seems slightly larger

TABLE I  
Crystallinity Index (CI) calculated from X-Ray Diffraction Pattern

Sample	CI (%)
PAN (U)	56.8
PAN (110)	59.8
PAN (150)	54.8

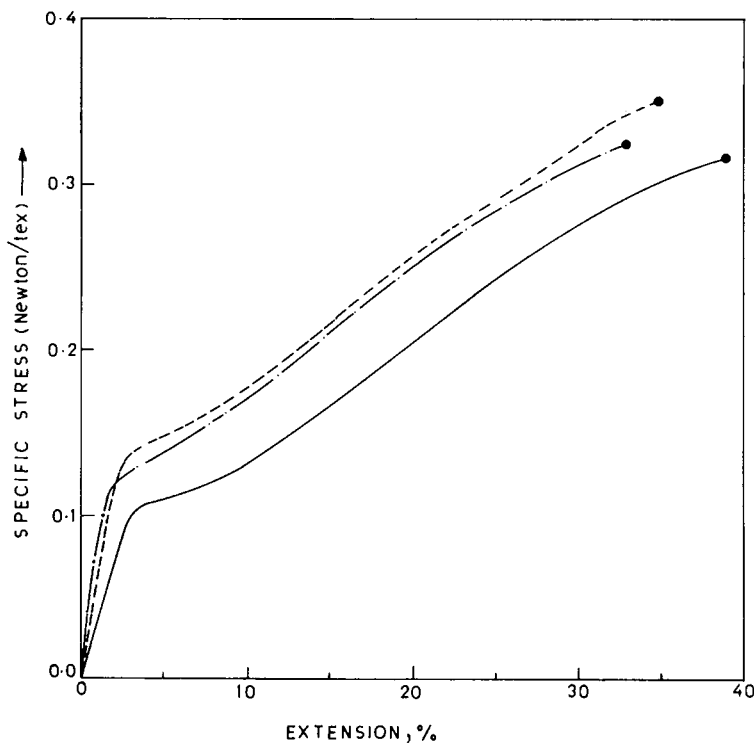


Fig. 3. Specific stress-extension curves of PAN (U) (—), PAN (110) (- - -), and PAN (150) (- · - ·).

for the sample treated at 150°C. The peaks appear slightly broader for the heat-treated samples than the untreated one.

## DISCUSSION

The IR spectra seem to support the fact that there is some increase in the number of bound nitrile group pairs due to their dipolar interactions. The degree of bound nitrile group pairs is higher in PAN (110) than in PAN (150). Since the heat-treatment temperature for PAN (110) was only slightly above the  $T_g$  of PAN whereas that for PAN (150) was much above  $T_g$ , the thermal energy of segment mobility during heat treatment might account for the observed difference in the degree of bound nitrile groups. Due to the segment mobility the probability of nitrile groups of neighboring chains coming in close vicinity

TABLE II  
Breaking Stress, Extension at Break, and Area under Stress-Strain Curve for Various Heat-Treated and Untreated PAN Fiber Samples

Sample	Extension at break (%)	Specific stress at breaking load N/tex $\times 10^2$	Area under curve (arbitrary unit)
PAN (U)	38	33.50	90.95
PAN (110)	35	40.00	96.53
PAN (150)	33	35.00	92.92

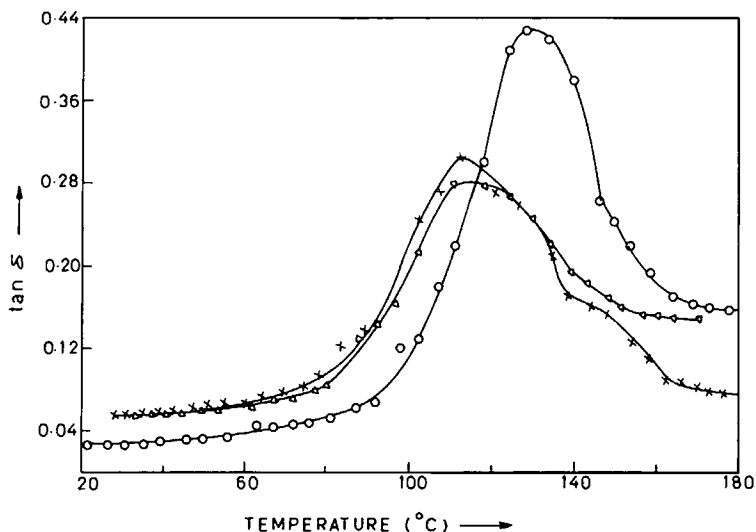


Fig. 4. Variation of  $\tan \delta$  with temperature for PAN (U) (—o—o), PAN (110) (— $\Delta$ — $\Delta$ ), and PAN (150) (—x—x).

increases, and this might result in the formation of bound nitrile group pairs by virtue of their dipolar interaction. At higher temperature the thermal energy of segment mobility will be higher, which might produce a greater effect in opposing the dipolar interaction forces of nitrile groups. Thus the heat treatment at higher temperature may result in a lower degree of bound nitrile group pairs.

The increased degree of bound nitrile group pairs would affect the structure. The structure of PAN may be visualized as follows: The two types of structures are generally believed for PAN, viz., (i) a single-phase paracrystalline which is an ordered phase with disorder distributed indiscretely in the structure<sup>10</sup> and (ii) the two-phase structure implying distinct ordered (crystalline and disordered (amorphous) phases.<sup>8,9</sup> In the single-phase model the ordered structure is a lateral order involving parallel alignment of molecular chains with bound nitrile groups and the disordered structure is the one with unbound nitrile groups. The two-phase model does not seem to be greatly different except that in this the disordered (amorphous) phase is sufficiently prominent and shows its characteristic phenomena such as glass transition<sup>2</sup> and also there are evidences of preparing completely amorphous PAN.<sup>8</sup> The X-ray diffraction pattern for PAN reported by most authors<sup>8-10</sup> has similar characteristic reflections. The sharp reflection at  $2\theta = 16.5^\circ$  has been attributed to the ordered phase by the protagonists of both the single- as well as two-phase models.

As evidenced by our X-ray diffraction results, the heat treatment produces some change in the degree of order but no change in the lattice spacing. The degree of order increases with heat treatment, which indicates that a portion of the bound nitrile groups occurs at the boundaries of the ordered region, which in turn causes an increase in the degree of order. The degree of order is higher in PAN (110) than in PAN (150).

Furthermore, although these X-ray diffraction data suggest the formation of some bound nitrile groups at the boundary of the ordered regions, they do not

rule out the possibility of bound groups in the interior of the disordered phase. Studies on dielectric relaxation in the glass transition region of heat-treated PAN indicate an influence of bound nitrile group pairs on the segment mobility in the amorphous phase.<sup>3</sup>

These tensile properties data also imply a higher degree of bound nitrile groups in the noncrystalline phase of the heat-treated samples. Since the noncrystalline phase is the weakest phase and hence responsible for the breaking phenomenon, the higher degree of molecular interlinking through bound nitrile groups should result in higher values of breaking stress, work of rupture, yield point, and initial modulus. Due to the interlinking of the segments through the bound nitrile groups, the energy needed to produce a given deformation will be higher in the case of higher degree of bound nitrile groups. In the present data (Fig. 3) the PAN (110) sample shows a higher yield point, higher breaking strength, and a higher work of rupture than the PAN (150) sample (Table II). However, the extension at break is higher for PAN (110) than for PAN (150), which either seems due to some lack of experimental precision or needs further investigation.

The results of dynamic mechanical relaxation may be explained as follows. Owing to the interlinking of molecular chains through the bound nitrile groups, the relaxing segments will be of smaller size, as their size will now be limited by the bound nitrile groups at the two ends. Thus the higher the degree of bound nitrile groups, the smaller will be the size of the relaxing segments. The lower segment size may involve lower thermal energy for relaxation; hence the relaxation must occur at lower temperature for the samples which have higher degree of bound nitrile groups. Experimental data of dynamic mechanical relaxation (Fig. 4) shows lower relaxation temperatures for the heat treated samples compared to the PAN (U).

Furthermore, the magnitude of the  $\tan\delta_{\max}$ , which is a measure of the energy dissipated in segmental mobility, is much lower for the heat-treated samples than the untreated PAN. The smaller size and/or lower number of the relaxing segments might be the cause for lower values of loss parameter in heat-treated samples. In these results it is apparent that loss peak temperature as well as the loss peak height for PAN (110) is lower than those for PAN (150) (Fig. 4), which is the trend as expected on the basis of the degree of bound nitrile groups. However, these differences between the data for the two heat-treated samples are not sufficiently large to stress this point.

It may be worthwhile mentioning that these dynamic mechanical loss curves show some difference in behavior with the dielectric relaxation curves.<sup>3</sup> In dielectric relaxation the loss peak temperature for the heat-treated sample was found higher than that for the untreated sample. The peak height, however, showed a similar trend of variation for both dynamic mechanical and dielectric relaxation. These differences may be due to the different states of the sample. The samples used for dielectric study<sup>3</sup> was PAN powder and those for mechanical relaxation are drawn PAN fibers, whose orientation may change during heat treatment and might affect the observed relaxation; further investigations would be required to ascertain this point.

## CONCLUSION

This work shows that the effect of variation of degree of bound nitrile groups, as observed earlier<sup>4</sup> in the case of PAN powder, is operative in PAN fibers as well. The heat treatment on PAN fibers causes an increase in the degree of bound nitrile groups which produces changes in IR spectra and degree of order determined by X-ray diffraction. Improvements in the mechanical properties on heat treatment are observed on PAN fibers. However, the difference between the heat treatment at the two temperatures studied (i.e., 110°C and 150°C) is rather marginal, though the effects produced by the lower temperature are somewhat greater in magnitude than those by the higher temperature. This is in contrast with the considerable differences observed in PAN powder.<sup>4</sup> It seems that, unlike the powder sample, the fibers had considerable orientation of molecules, which might change on heat treatment and thus provide additional constraints on the structural changes during the heat treatment.

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