CHARACTERISTICS OF KMnO₄-MODIFIED PAN FIBRES—ITS INFLUENCE ON THE RESULTING CARBON FIBRES’ PROPERTIES

R. B. Mathur, J. Mittal, and O. P. Bahl
Carbon Technology Unit, National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi-110012, India

and

N. K. Sandle
Chemistry Department, I.I.T., Delhi, India

(Received 27 April 1993; accepted in revised form 28 June 1993)

Abstract—Polyacrylonitrile precursor has been chemically impregnated with aqueous solution of KMnO₄ under varying conditions of temperature and time. FTIR of the as-modified PAN fibres shows a clear peak at 2340 cm⁻¹ corresponding to MnO₄⁻—C=N conjugation. Such conjugation helps not only as catalyst for cyclization reaction, but also as plasticizer. Calorimetric studies show that activation energy for cyclization reaction for KMnO₄-treated fibres is reduced from 119 KJ/mole to 90 KJ/mole. Experimental results show that the tensile strength of carbon fibres prepared from chemically modified samples goes up to 4.2 GPa, compared to 2 GPa obtained from unmodified samples. More importantly, elongation to break for such carbon fibres is pushed up to 1.82%, compared to 0.9% achieved with unmodified samples. Surface morphology of the treated and carbonized samples has also been investigated using SEM.

Key Words—PAN fibre, KMnO₄, cyclization, catalyst, plasticizer, tensile strength, Young’s modulus, carbon fibre.

1. INTRODUCTION

Polyacrylonitrile (PAN) fibres have been successfully converted into carbon fibres over the last three decades[1–6]. The vast potential of the raw material—its composition and structure, for example—is amply demonstrated by the fact that the carbon fibres developed from it have shown remarkable improvement in the tensile strength (T.S) over the years. It has, for example, gone up from 3 GPa (Modomer) in early 1980 to 7 GPa (Toray T-1000) in 1990. More importantly, the strain to failure of the so-called new generation of carbon fibres has gone up to 2.4 GPa[7]. This has been possible partly through better understanding of the low-temperature thermal stabilization process of PAN, as evident from the published literature[8–11] and specifically, in authors’ opinion, due to improvement in the characteristics of the raw material. A linear correlation between the precursor primary Young’s modulus and that of the resulting carbon fibres has been demonstrated already in the work reported earlier[12] from this laboratory.

The majority of the studies on the thermal stabilization aspect have been carried out on the special variety of “Courtex” PAN fibres obtained from M/S Courtaulds; U.K.[13–16]. Using this precursor, in our laboratory it has been possible to obtain carbon fibres with T.S equal to 3 GPa (carbonization temperature 1000°C). In the published literature, the maximum value of T.S quoted for Courtex-based carbon fibres is also about 3.5 (carbonization temperature approx. 1400°C)[17]. Is it therefore the maximum limit to which this precursor can be exploited? In order to ascertain this we have in the past tried several post-spinning modification techniques on the as-received Courtex precursor[18–21]. Although we have been successful in improving the structure and the reaction kinetics of the modified precursor, the resulting carbon fibre properties could not be pushed up beyond 3 GPa (HTT 1000°C).

In the study that follows, we have been successful in improving the strength of Courtex-based carbon fibres by carrying out its post-spinning modification with KMnO₄ solution. A few studies carried out previously on the KMnO₄ pretreatment of PAN[14,22–23] have already confirmed its role as a catalyst for cyclization reaction.

A systematic approach of pretreatment of PAN with KMnO₄ has been undertaken to arrive at the optimum pretreatment conditions. Emphasis has been laid to understand the structure and reaction kinetics of such modified precursor during stabilization, and to convert them into superior grades of carbon fibres.

*To whom correspondence should be addressed.
Table 1. Change in colour and solubility behaviour of PAN fibres during treatment with K\text{MnO}_4

<table>
<thead>
<tr>
<th>Time of treatment (min)</th>
<th>Colour</th>
<th>Solubility in DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>white</td>
<td>soluble</td>
</tr>
<tr>
<td>3</td>
<td>light brown</td>
<td>soluble</td>
</tr>
<tr>
<td>5</td>
<td>mod. brown</td>
<td>soluble</td>
</tr>
<tr>
<td>10</td>
<td>dark brown</td>
<td>soluble</td>
</tr>
<tr>
<td>20</td>
<td>light black</td>
<td>insoluble</td>
</tr>
<tr>
<td>30</td>
<td>black</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

2. EXPERIMENTAL

A special grade of acrylic fibre, namely, courtelle procured from M/S courtaulds, U.K., has been used in the present study. A single tow containing 12,000 monofilaments of 1.2 d'tex each was treated with 5% potassium permanganate solution at 85°C, 90°C, and 95°C for different times (i.e., 3, 5, 10, 20, and 30 min, respectively). The samples were washed thoroughly with distilled water and then dried. However, it was found that the reaction is so severe that at temperatures higher than 85°C the fibre gets destroyed within a few seconds. The studies were therefore confined to fibres treated at 85°C only for the times mentioned above, and samples were designated as K-3, K-5, K-10, K-20, and K-30, respectively. The changes in the physical characteristics of the precursor with time are given in Table 1.

Untreated (U) and treated PAN fibres (K-3, K-5, K-10, K-20, and K-30) were then heat treated up to 270°C in a purified air atmosphere under constant load per tow. The oxidized fibres were carbonized at 1000°C in ultrapure nitrogen atmosphere at a heating rate of 25°C/min.

Mechanical properties of the as-treated PAN fibres and carbon fibres were measured on an Instron 1122 universal testing machine with a crosshead speed of 0.5 mm/min and a filament gauge length of 2 cm. An average of at least 25 single filament results for each sample is reported. The diameter of the fibres was measured on a metallurgical Leitz microscope using a Vicker's image shear eye piece to the accuracy of ±0.01. An average of 20 single filament diameters for each sample has been used for calculation.

Thermal analysis of the samples (e.g., DSC, TGA, and TMA) has been carried out on a Mettler TA 3000 Thermal analyzer.

FTIR has been recorded on NICOLET DX FTIR using KBr pellet method covering the range of 400-4000 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1 Physical changes in the precursor during treatment

3.1.1 Colouration. Table 1 presents the comparison of the colouration reaction of PAN precursor during treatment in K\text{MnO}_4 solution with time. It has been observed that the colour of fibres changes with the time of treatment in K\text{MnO}_4 from white to pale yellow in about three minutes, and becomes dark brown in 10 minutes. After treatment for 30 minutes it becomes completely black. The color change indicated in the table could be either due to settling of potassium permanganate at the dyeing centers of the fibre or due to changes in structure. It has been shown by earlier workers[23] that the \text{MnO}_4⁻ catalyzes the cyclization reaction (Fig. 1), which is reflected in the change in color of the precursor; but it is true at higher temperatures (i.e., beyond 180°C only). That is, for obtaining tan-colour fibre it must be heated to at least 200°C. On the other hand, the PAN fibres become tan-coloured after treatment for 10 minutes (K-10) in K\text{MnO}_4 solution at only 85°C. The fibre sample treated for 30 minutes at 85°C is not only completely black, but flame proof also; however, it loses all its strength, and is so brittle that it becomes difficult to handle. The observation confirms that at 85°C under the presence of K\text{MnO}_4 solution the PAN fibres undergo cyclization. The degradation causes it to become insoluble in DMF, as shown in Table 1 for K-30.

3.1.2 Weight gain of the fibre with treatment. As discussed above, if the permanganate gets incorporated inside the fibre structure it should result in weight gain. Figure 2 shows that the weight gain is about 30% for the 20-minute treated sample as against only 2% for the 3-minute treated sample. This weight gain is due to diffusion of \text{MnO}_4⁻ ions in the fibre structure. In order to have quantitative

Fig. 2. Weight gain in PAN fibres during treatment with K\text{MnO}_4.

Fig. 1. Proposed reaction mechanism of K\text{MnO}_4 treatment of PAN fibres.
estimates of the MnO$_2$ inside the fibre. TGA studies were carried out. It was found that whereas the untreated PAN fibre is completely lost up to 800°C when heated in the presence of air, the treated fibre sample does not show 100% weight loss. The remainder in the crucible is 2% for sample K-3, whereas it is as high as 30% for sample K-30. The remainder material should be MnO$_2$.

Figure 3 shows the amount of shrinkage occurring in the precursor, which increases with the treatment time (e.g., it is as high as 14% for K-20 against only 2% for K-3). This shrinkage therefore cannot be due to molecular stress relaxations or physical shrinkage, but to cyclization reaction only[24].

3.1.3 Solubility in DMF. Table 1 shows that the change in colour and solubility of the modified precursor fibre depends on the treatment time (e.g., fibres K-20 and K-30 are black and insoluble in DMF, whereas fibres K-3 to K-10 are brown and soluble). Since the thermally stabilized samples are also black and not soluble in DMF, it confirms that with KMnO$_4$ treatment the fibre structure does undergo degradation to form units of step ladder polymer.

3.1.4 Plasticizing effect of KMnO$_4$. Figure 4 shows elongation behaviour of the modified precursors w.r.t. that of the unmodified sample U, stretched under identical conditions of load and with increasing temperature at the rate of 2°C/min. K-10 shows an elongation of about 15%, compared to about 10% shown by U. In addition, the slope is much sharper for modified samples around the glass transition temperature of PAN (i.e., 80°C). The plasticizing effect can be explained as due to MnO$_2$–C≡N conjugation as shown in Fig. 1. Such conjugation not only results in the weakening of polar forces among the molecular chains, but also helps in promoting the cyclization reaction explained elsewhere[14]. This is further confirmed by IR studies described below.

3.1.5 Infrared analysis of the samples. The influence of KMnO$_4$ treatment on the structure of precursor PAN is clearly seen from the IR spectra of samples presented in Fig. 5. The peak at 2240 cm$^{-1}$ is due to C≡N, and at 2940 cm$^{-1}$ is due to –CH$_2$; the one at 1730 cm$^{-1}$ is due to C=O groups in the as-received PAN precursor. It can be seen from the subsequent IR spectra of K-3, K-10, and K-20 that a new peak at 2340 cm$^{-1}$ close to 2240 cm$^{-1}$ starts appearing, which increases in intensity with treatment time. This is due to conjugation of MnO$_2$–C≡N group[14]. The peak at 1590 cm$^{-1}$, which may be due to either C≡C or C≡N group, also increases in intensity, showing the formation of ladder polymer during treatment itself, as also revealed by the colour change of the precursor discussed above.
The spectra of K-10 and K-20 reveal that the peak at 1590 cm\(^{-1}\) becomes very strong compared to the bands at 1430 cm\(^{-1}\) and at 1740 cm\(^{-1}\), and a pronounced shoulder is generated at 1640 cm\(^{-1}\). Both these observations suggest the formation of \(\beta\)-diketone groups during the treatment. Although it is very small at this stage, it indicates the possible oxidation of the PAN fibre. Strong absorbance at 650 cm\(^{-1}\) is due to the marked change suffered by the structure of PAN during prolonged permanganate treatment.

3.1.6 Effect of treatment on the mechanical properties. As shown in Fig. 6, the diameter of the untreated fibres does not change much initially up to 10 minutes treatment time. However, for 20-minute treated samples it increases to 15 microns, compared to 12.57 microns for untreated samples. The increase in diameter of treated fibres is due to diffusion of a sufficient quantity of MnO\(_4^\text{-}\) ion in the fibre structure, as evidenced by the weight gain shown in Fig. 2.

Figures 7 and 8 show the variation in tensile strength and primary Young's modulus, respectively, of fibres. The decrease in tensile strength with treatment time may be caused by the conjugation between the MnO\(_4^\text{-}\) and nitrile bonds. With the increase in the treatment time, more and more cyclization takes place, causing a further decrease in the tensile strength. With higher uptake of MnO\(_4^\text{-}\), chain breakage may also take place, and as a result samples K-20 and K-30 show a sharp fall in T.S.

Unlike T.S., the primary Young's modulus of the fibres increases initially with treatment time up to 10 minutes, and thereafter it starts falling. The improvement is almost 100% for K-20, in comparison to the untreated precursor. This increase in the modulus is due to better alignment of the molecular chains[15]. However, beyond this, the decrease in Y.M. is due to damage caused to the fibre structure.

3.1.7 Surface morphology of modified fibres. Figure 9 shows SEM micrographs of some of the samples. It has been observed that the fibre surface remains smooth and without any defect up to 10 minutes of treatment time. A typical example is given in Fig. 9a for sample K-5. However, with an increase in treatment time, fine cracks are found on the fibre surface, as shown in Fig. 9b for sample K-20. These fibres therefore show poor strength and are more brittle comparatively. The surface of the resulting carbon fibres from K-5 does not show any defect (Fig. 9c).

3.2 Thermal stabilization of modified PAN fibres

3.2.1 Dilitometry of fibres during stabilization. In situ shrinkage behaviour of the precursor during stabilization has been recorded on a Mettler thermal analyzer as described earlier[25]. Figure 10 shows the comparative dilitometry curves of the precursor and that of treated samples under the constant probe force. As seen in the figure, the shrinkage pattern of the fibres changes with treatment time, although the ultimate shrinkage up to 230°C is same (e.g., in untreated precursor the rate of shrinkage is much higher initially, as compared to treated samples, and up to 230°C, 13.8% shrinkage is observed). However, shrinkage for K-10 up to 130°C is only 0.2%, as against 4.9% for precursor U. The difference may be due to shrinkage suffered by K-10 during treatment itself. A similar trend is observed for K-20. Interestingly, for both these samples there is slight elongation in the beginning. This could be due to the plasticizing effect of MnO\(_4^\text{-}\) ions. The trend is entirely different for K-20, showing that for longer treatment times, total shrinkage up to 230°C is only 5%. A large quantity of MnO\(_4^\text{-}\) in the fibre, which may not necessarily be attached to pendant nitrile groups, acts as an inhibitor for
3.2.2 TGA studies of the modified samples. Figure 11 shows TGA curves of the samples during heating to 400°C in the presence of air. The difference in weight loss for each sample increases gradually with treatment time. However, the curves show two regions of weight loss (i.e., before and after heating to 300°C, with degree of steepness increasing with treatment time). The total weight loss in K-20 is 60%, compared to only 18% for the precursor U. The weight loss is 42% for the sample K-20 in the temperature range 300–400°C, compared to only 10.6% for U and 12% for K-5. Up to 300°C the weight loss also increases with treatment time (i.e.,
21% in K-30 as compared to 8% in U). There is, however, very small difference in the weight loss up to 300°C in the U, K-3, K-5, and K-10. It shows that in K-20 and K-30 there is complete breakdown of the polymer chains due to permanganate attack, which facilitates the formation of CO and CO₂ during heating; this results in the sharp weight loss observed in Fig. 11 for these samples.

3.2.3 DSC studies of the modified samples. DSC of PAN fibres in the presence of air shows a characteristic exothermic peak due to cyclization reaction at 270°C. Table 2 describes the results obtained from DSC curves of the modified and unmodified samples. It shows that with increase in treatment time, not only is the cyclization initiation temperature lowered (195°C for samples U and 180°C for K-10), but also the activation energy is reduced from 120 KJ/mole (U) to 90 KJ/mole for K-10. However, beyond K-10 the trend is reversed because of the fibre damage, as discussed earlier. Further, calculations show that the total time required for 100% completion of cyclization reaction at 220°C and 240°C for sample U is >100 minutes and 50 minutes, respectively, whereas it is only 85 minutes and 35 minutes, respectively, for K-10. This confirms a definite catalytic role of permanganate in cyclization reaction. The peak exotherm temperature which is 268°C, however, remains the same for U and K-10. It implies, therefore, that the exotherm for modified samples is spread over a broader temperature range (180–268°C) for K-10 compared to U (195–268°C). A broader exothermic range should be preferable from the carbon-fibre point of view.

3.3 Carbon fibres

As shown in Table 3, the value of tensile strength of resulting carbon fibres shows significant improvement with treatment time of the precursor. The value goes up to 4.2 GPa for CK-10, compared to only 2.1 GPa for the carbon fibres developed from U (cu), an improvement of 100%. Additionally, the strain to failure of these carbon fibres goes up to 3.8%, which assumes special significance in terms of engineering applications of such carbon fibres. Slight improvement in the value of Y.M. of carbon fibres is expected because of the higher amount of elongation received by the fibres during the thermal stabilization step. As discussed in section 3.1.4, the elongation received by K-10 is 15%, compared to only 10% for sample U. This will obviously cause better alignment of the molecular chains[6].

The reason for the improvement in the carbon fibre properties can thus be explained as follows:

1. The plasticizing effect during oxidation imparts better orientation of molecular chains.
2. Its catalytic effect converts PAN into a ladder polymer structure in short duration without over-oxidizing the backbone.
3. Diffusion of MnO₄⁻ in the fibre also promotes cyclization from within the core, thus avoiding the core sheath formation during the stabilization process[26].

The Uniformity of stabilization across the fibre cross section is essential to avoid stress concentration in the resulting carbon fibre structure.

4. CONCLUSIONS

KMnO₄ acts as catalyst for cyclization of nitrile groups in PAN, which improves the economics of the stabilization process. It also shows a plasticizing effect during thermal treatment.

Treatment of PAN for only 10 minutes with KMnO₄ pushes the tensile strength of the resulting carbon fibres to 4.2 GPa, which is generally not possible at 1000°C.

Strain to failure of the resulting carbon fibres also goes up from 0.9% in untreated fibre to 1.8%, which is very useful for new-generation engineering application of carbon fibres.

Acknowledgement—The authors wish to thank Prof. E. S. Rajgopal, Director, NPL, for his constant encouragement during the course of this work and his permission to publish it. One author (J. Mittal) is thankful to CSIR for awarding a Research Associateship.

REFERENCES

10. E. Fitzer and D. J. Muller, Carbon 13, 63 (1965).
17. J. D. H. Hughes, Carbon 24, 551 (1986).