

Bimodification of Polyacrylonitrile (PAN) Fibers

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SYNOPSIS

A new technique for the modification of PAN fibers has evolved, in which the starting precursor material is impregnated with an aliphatic carboxylic acid, as well as KMnO_4 . The bimodification of PAN, attempted by us for the first time, is aimed at achieving dual advantages in plasticization effect, as well as in a catalytic effect in a single treatment. The unmodified, unimodified, and bimodified precursors have been characterized for their mechanical, thermal, and physical behavior during various stages of processing to carbon fibers. These results are discussed in detail. The study further shows an 18% improvement in the mechanical properties of carbon fibers, prepared from bimodified precursor, as compared to that of unmodified precursor. One of the reasons for such improvement is the lowering in diameter of PAN fibers and in the resulting carbon fibers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Certain limitations during spinning prevent us from introducing the desired characteristics in a PAN precursor,¹ especially limiting the production of high performance carbon fibers therefrom. It has already been shown that such deficiencies may be partially overcome by postspinning modifications of the precursor.²⁻⁹ The majority of these studies, however, have been carried out with a view to improve the rate of cyclization by incorporating certain catalysts, namely CuCl ,⁷ KMnO_4 ,⁸ aminosiloxanes,⁹ and others, in the fiber structure. Additionally, the trend has been towards thinning of the precursor fiber to obtain low diameter carbon fibers, with diameters of 4–5 μ , as compared to 7–8 μ that is usually encountered. Such carbon fibers contain fewer defects per unit volume and hence should possess superior mechanical properties in conformity to the Weibull “weakest link” principle.¹⁰ Another advantage of low diameter PAN fibers should be the uniformity of thermal stabilization in a short amount of time. Authors have already reported studies in this direction by stretching the original PAN fibers, that is, the

as received “Courtelle” precursor, in the presence of certain plasticizers before the thermal stabilization step.^{11,12} Although these modification techniques help in decreasing the diameter of the precursor fibers and that of the resulting carbon fibers by about 20%, they do not help, however, in improving the mechanical properties of carbon fibers to the desired extent. This has led us to investigate the reasons for such behavior and to develop a new approach to overcome the shortcomings in the previous studies. The failure of a previous technique, wherein PAN fibers have been modified by using benzoic acid as plasticizer,¹³ could be attributed to:

1. The large size of the benzoic acid molecule, which could not diffuse to the core of the fiber. Therefore, during stretching, the molecular chains on the surface and those inside the core suffered a differential degree of stretch, leaving behind residual stresses in the fiber structure.
2. In addition, stretching of the precursor also causes an increase in crystallinity and improvement in the orientation of molecular chains along the fiber axis. This results in an increase in the density of the precursor fiber.¹³ This may inhibit diffusion of oxygen inside the body of the fiber, thereby reducing the rate of cyclization.

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Table I Treatment Conditions of Pan Precursor

| Composition | Condition | % of AcOH in Fiber |
|----------------------|------------|--------------------|
| 20% Aq AcOH | Room Temp. | None |
| 30% Aq AcOH | Room Temp. | None |
| Pure AcOH | Room Temp. | None |
| 30% AcOH in Methanol | Room Temp. | None |
| Pure AcOH | 70–80°C | 4.8% |
| Pure AcOH | 92–95°C | 5.8% |
| 50% Aq AcOH | 92–95°C | 3.7% |

In order to overcome the above problems, we have, in the present study, chosen an aliphatic acid (acetic acid AcOH) as plasticizer, because of the smaller size of its molecule, as compared to that of benzoic acid. It is believed that the acetic acid molecule should be able to diffuse to the core and should help in overcoming the problems faced with benzoic acid. In addition, the acetic acid modified precursor has been reimpregnated with an aqueous solution of KMnO_4 , having additional catalytic centers, to effect an enhanced rate of cyclization in the absence of oxygen.⁸ This study is, therefore, the first such attempt toward this end, wherein the postspinning modification of PAN has been done by using two different chemical species to achieve two different objectives simultaneously and may be termed bi-modification of PAN fibers. A systematic study has been undertaken to compare the various physical, mechanical, and thermal properties of unmodified, modified, and bimodified precursors. The behavior of these precursors has been followed, up to the carbonization stage, via a low temperature thermal stabilization step.

EXPERIMENTAL

“Courtelle” PAN precursor, 12 K, 1.2 *d*'tex, has been initially treated with acetic acid (AcOH) under different conditions, as specified in Table I. It is seen from the Table I that, at room temperature with various concentrations of aqueous AcOH solutions, there is no weight uptake of acetic acid in the fiber. This situation is not helped by the use of a solvent, for example, methanol. However, at higher temperatures, a maximum of 5.8% weight uptake is shown by the fiber in presence of pure AcOH. Even 50% aqueous AcOH solution shows 3.7% weight uptake at higher temperatures. This result shows that the interaction of nitrile groups with an acetic acid mol-

ecule is possible only at higher temperatures. A portion of this sample, termed “*M*,” which had the maximum uptake of acetic acid (5.8%), was chosen for further studies. The treated samples were rinsed thoroughly with water to ensure that no remaining acid adhered to the fiber surface. Untreated (*U*), as well as acetic acid treated fiber samples (*M*), were then subjected to further treatment with a 5% aqueous solution of potassium permanganate for three minutes at 85°C, were washed and dried, and were designated as samples *K* and *MK*, respectively. All four samples, that is, *U*, *M*, *K*, and *MK*, were oxidized one by one to 235°C and then were carbonized to 1000°C under identical conditions. A Siemens D-500 X-ray diffractometer, with $\text{CuK}\alpha$ radiation as a source, has been used to record diffractograms of the oxidized samples. Intensities of the peaks, and their corresponding *d*-values, have been evaluated automatically using computer software. Mechanical properties of the fibers have been measured on an Instron 1122 universal testing machine, as described previously.¹⁴ DSC and TGA of the samples have been carried out on a Mettler T-3000 thermal analyzer. The data, represented in Tables III and IV, is an average of at least three separate runs in each case. FTIR studies of the samples have been carried out on a Nicolet 5DX FTIR spectrometer.

RESULTS AND DISCUSSION:

Plasticizing Effect of Acetic Acid

Figure 1 shows the elongation behavior of the modified precursor *K*, *M*, *MK*, and that of the unmodified precursor *U*, stretched under identical conditions of load, with a constant rate of increase in temperature. The sample *M* shows overall stretching of 23%, which is 2.5 times that possible for sample *U*. As shown in Figure 1, not only the total elongation, but also the rate of elongation in different temperature ranges is steeper with all the modified samples as compared to unmodified samples. A closer look at the curves shows that, whereas the plasticizing effect of KMnO_4 is confined up to 120°C only, for ACOH treated fibers, it continues to higher temperatures, with a maximum at 205°C.

The plasticizing effect of both acetic acid and KMnO_4 can be explained as follows. The acetic acid molecules are linked through interaction with the —CN groups, forming conjugated double bonds. Due to the highly polar nature of the nitrile groups, there is initially a partial positive charge at the car-

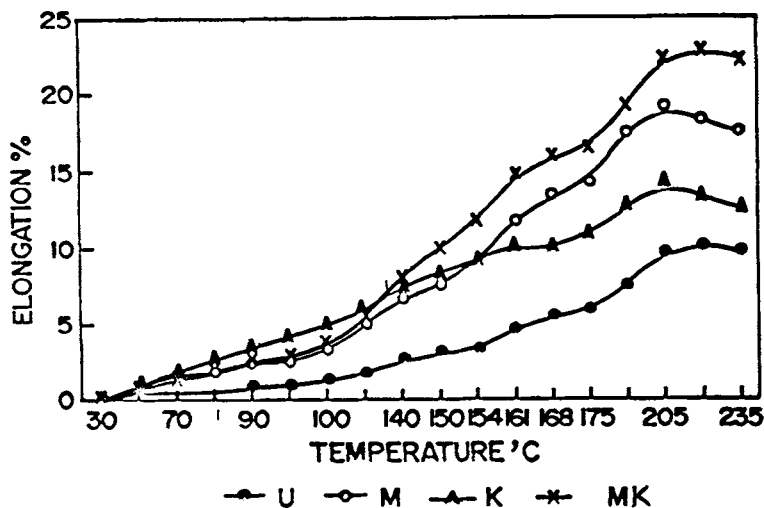


Figure 1 Elongation behavior of the different fibers during oxidation.

bon atom and a partial negative charge at the nitrogen atom, as shown in Figure 2. The oxygen in the acid group is attracted to the carbon, whereas hydrogen is attracted towards the nitrogen, resulting in hydrogen bonding between nitrogen and hydrogen. This should cause a decrease in the interactions among the nitrile groups or, in other words, a decrease in the cohesive forces among the molecules. This could then facilitate easy stretching during heating of PAN fibers without bond breakage. The slight, plasticizing effect for KMnO_4 treated fibers, *K*, is also evident in Figure 1, and has been explained as being due to the $\text{MnO}_4-\text{C}\equiv\text{N}$ conjugation, as shown in Figure 2.

In order further to ascertain the presence of such conjugation, IR spectra of the unmodified, as well as the modified samples, were recorded and are compared in Figure 3. In the treated precursor, a new peak is observed at 2340 cm^{-1} , due to the conjugation of $\text{C}\equiv\text{N}$ groups,⁸ indicating that both acetic acid and KMnO_4 attack the carbon atom linked to the nitrile group. In the KMnO_4 treated samples (*K*) the peak at 1600 cm^{-1} is strong, which indicates that a significant number of $-\text{C}=\text{N}$ groups are generated, due to the attack of KMnO_4 . In the sample that was treated with acetic acid, the peak at 1750 cm^{-1} is stronger, comparatively, due to increased concentration of $-\text{C}=\text{O}$ groups

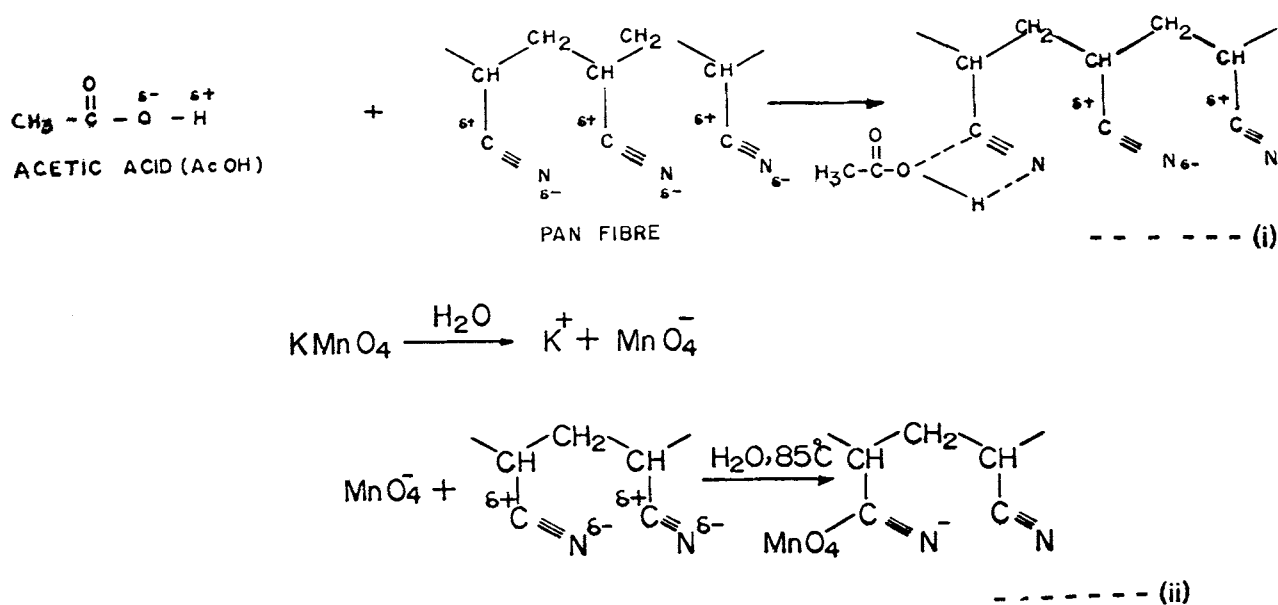


Figure 2 Conjugation reaction of PAN Fiber with (i) acetic acid, (ii) KMnO_4 .

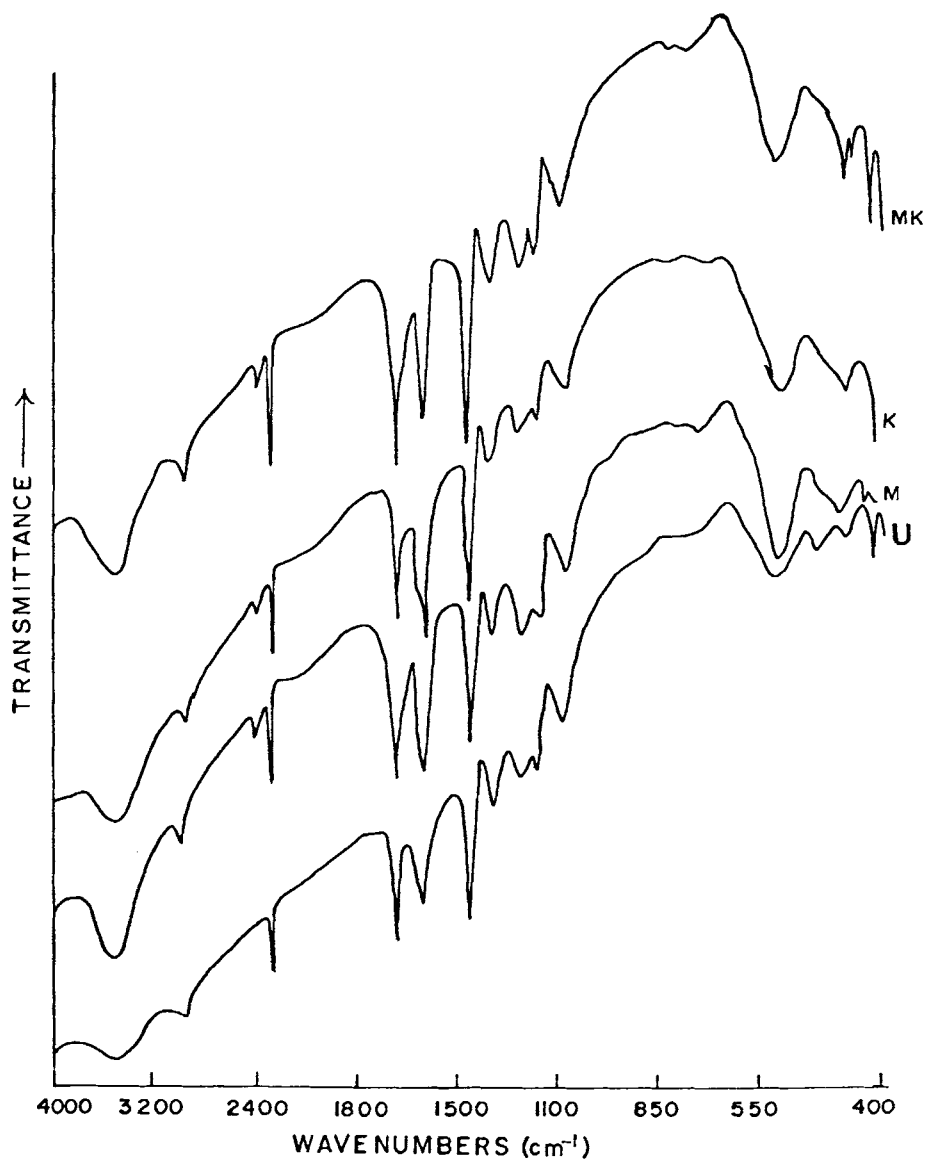


Figure 3 IR spectra of modified samples.

present in the acetic acid itself. The IR spectra of the bimodified samples clearly indicate the conjugation of nitrile groups, which is responsible for increased plasticity of molecular chains in modified PAN fibers.

EFFECT OF STRETCHING ON THE PHYSICAL CHARACTERISTICS OF THE MODIFIED FIBERS

Table II shows data on various characteristics of unmodified, modified, and of the resulting carbonized samples. As shown in Table II, sample *M* behaves in a way opposite to samples *K* and *MK*.

Whereas there is an increase in the diameter of *M* (as compared to sample *U*), samples *K* and *MK* show a reduction in diameter. On the contrary, tensile strength and Young's modulus for sample *M* decrease, whereas both show improvement for samples *K* and *MK*.

Reduction in the strength of sample *M* can be explained as being due to a decrease in the cohesive or dipolar forces between molecules of PAN, which is a result of the formation of conjugated bonds, as depicted in Figure 2. Heating of PAN up to 100°C during impregnation may cause further disorientation of molecular chains due to relaxation, thus resulting in an increase in diameter and a lowering of Young's modulus. A decrease in the diameter and

Table II Mechanical Properties of Fiber Samples

| Treatment | Fiber Type | Dia. (Microns) | T.S. (MPa) | Y.M. (GPa) | % Elongation at Break |
|--|------------|-------------------|---------------|---------------|--------------------------|
| Untreated (<i>U</i>) | Precursor | 12.57 | 522 | 6.5 | 15.6 |
| | Carbonized | 7.23 | 1961 | 214 | 0.9 |
| Modified with AcOH (<i>M</i>) | As Treated | 13.02 | 426 | 5.4 | 19.5 |
| | Carbonized | 6.96 | 2317 | 210 | 1.1 |
| Modified with KMnO ₄ (<i>K</i>) | As Treated | 12.40 | 587 | 6.8 | 21.1 |
| | Carbonized | 7.11 | 2231 | 230 | 0.9 |
| Modified with KMnO ₄ + AcOH (<i>MK</i>) | As Treated | 11.80 | 559 | 7.1 | 23.8 |
| | Carbonized | 6.88 | 2449 | 200 | 1.2 |

an increase in tensile strength and Young's modulus of fibers *K* and *MK* could possibly be due to the role that KMnO₄ plays on the intermolecular crosslinking agent. It will not allow the molecular chains to disorient during relaxation at 100°C, as in the case of sample *M*. Improvement in the orientation of molecular chains of PAN by chemical treatment with Hydrazine hydrate and hydrogen peroxide has also been shown by Popovska et al.⁴

Interestingly, the elongation due to break for the modified samples is increased by 50% (*MK*). The reason for this could be the lowering of cohesive forces between the molecules because of the conjugation of acetic acid and permanganate with nitrile groups. This is also reflected in the elongational behavior of modified samples at higher temperatures (Fig. 1).

CALORIMETRY

Table III summarizes the results of DSC studies on the samples. A general view of Table III gives an indication that the reaction kinetics for all the samples are different, for example, there is a 17% decrease in activation energy for the cyclization re-

Table III DSC Studies of the Samples

| | <i>ST</i> ^a (°C) | <i>EA</i> ^b (KJ/Mol) | Heat Flow (J/g) | <i>PT</i> ^c (°C) |
|-----------|--------------------------------|------------------------------------|--------------------|--------------------------------|
| <i>U</i> | 195 | 119.32 | 1229 | 268 |
| <i>M</i> | 200 | 99.68 | 1389 | 278 |
| <i>K</i> | 185 | 111.45 | 1262 | 263 |
| <i>MK</i> | 190 | 108.12 | 1342 | 271 |

^a *ST*, Cyclization start temperature.

^b *EA*, Activation energy.

^c *PT*, Exotherm peak temperature.

action for sample *M*, while it is only 8% for *K* and *MK*, respectively. Samples *M* and *MK* show larger degrees of cyclization, as revealed by the total heat flow, which is 150 J/g more than that of the sample *U*. However, a comparatively smaller change for sample *K* is not explicable, although the reaction initiation temperature and peak exotherm show a shift of reaction kinetics to a lower temperature range. On the other hand, the reaction kinetics for sample *M* shifts to higher temperatures, so much so that the exothermic peak registers a shift of 10°C.

Higher values of heat flow (ΔH) should be associated with a larger degree of cyclization,¹⁵ and hence should cause shrinkage of the molecular chains if left unconstrained. Shrinkage behavior of these samples was therefore studied, using the TMA techniques described earlier.¹⁶ The probe force was set such that the fibers experienced free shrinkage when heated.

As shown in Figure 4, the modified samples show only 3–4% shrinkage up to 190°C, whereas it is 7–8% for sample *U*. Up to this temperature, the shrinkage is mainly physical in nature.¹⁶ In modified samples, this shrinkage is partially compensated for by the simultaneous elongation in the fiber, due to the plasticizing effect of AcOH and KMnO₄. This is further evident from the behavior of the curves around 100°C, at which a net elongation of 2% is registered by the samples *M* and *MK*. However, the shrinkage picks up beyond 190°C, because of the onset of the cyclization reaction. Interestingly, the amount of shrinkage between 190–230°C is 9% for samples *K* and *MK*, as opposed to only 5% for samples *U* and *M*. The higher degree of cyclization shows the catalytic effect of KMnO₄ during thermal stabilization of PAN fibers.

Table IV shows the weight loss behavior of the samples as the oxidation progresses. One finds that the weight loss in sample *U* is only 1.6% up to 200°C, whereas for sample *M*, it is 5%, which confirms that

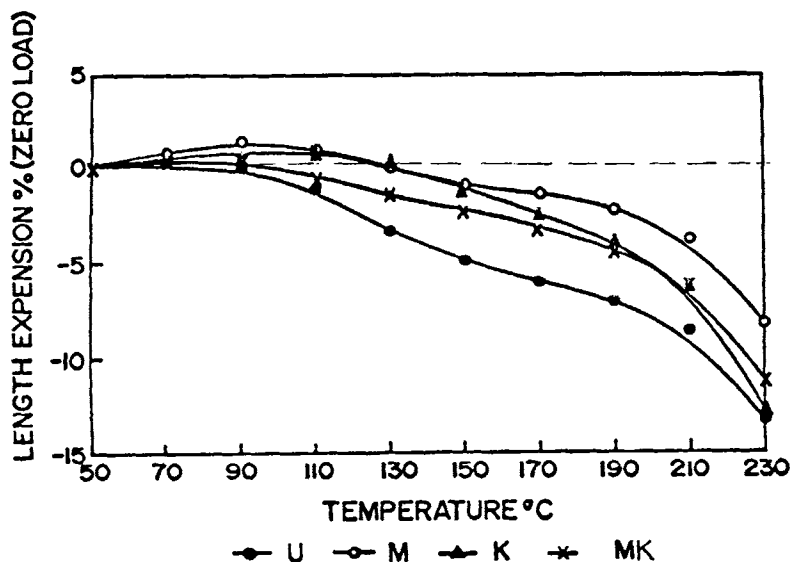


Figure 4 TMA behavior of the different fibers.

almost all the impregnated acetic acid (5.8%) evaporates during heating up to 200°C. Since there is no chemical reaction in the PAN at this temperature, the weight loss can be easily attributed to removal of acetic acid alone. The exact temperature of evolution of acetic acid has been determined by differential TGA curves, as shown in Figure 5 for samples *M* and *U*. A sharp weight loss of 4% between 120°C and 130°C is observed for sample *M*, whereas there is negligible weight loss for sample *U*. This suggests that the acid does not form strong chemical bonds with the PAN structure and remains under conjugation alone, as shown in Figure 2. On the contrary, as shown in Table IV, there is no loss of KMnO_4 in this temperature range, which shows the same weight loss as that of sample *U*. Interestingly, the weight loss is only 3.2% for sample *MK*, which means that the presence of KMnO_4 inhibits the removal of acetic acid in the lower temperature range. The weight loss in the temperature range of 200–300°C is the same for all the samples, except *MK*. This is the region where most of the cyclization re-

actions are completed with the evolution HCN , NH_3 , and H_2O , and others. However, the higher weight loss for *MK* in this range can be explained by removal of the 3% balance of AcOH , the release of which was partly inhibited by the presence KMnO_4 up to 200°C. The last column of Table IV shows the total weight loss of samples up to 400°C.

Table IV Weight Loss (%) During Oxidation in Different Temperature Ranges

| | 100–200°C | 200–300°C | 300–400°C | 100–400°C |
|-----------|-----------|-----------|-----------|-----------|
| <i>U</i> | 1.61 | 5.28 | 10.65 | 17.54 |
| <i>M</i> | 5.01 | 5.36 | 10.74 | 21.11 |
| <i>K</i> | 1.59 | 5.24 | 10.80 | 17.43 |
| <i>MK</i> | 3.22 | 8.25 | 12.56 | 24.03 |

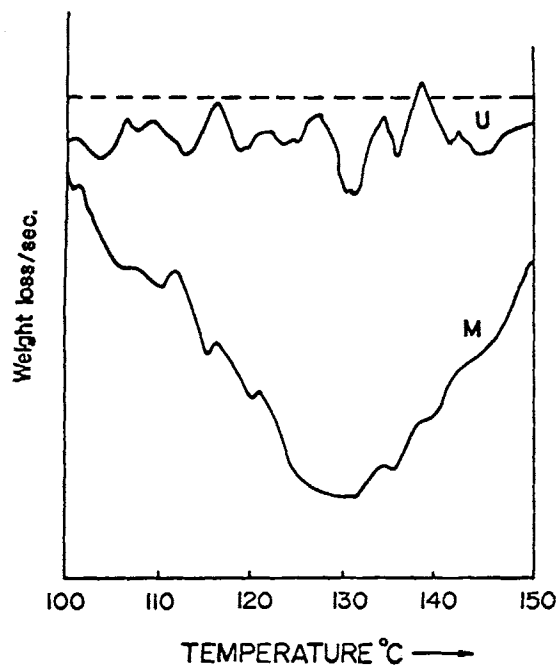


Figure 5 DTG of the treated and untreated PAN precursors.

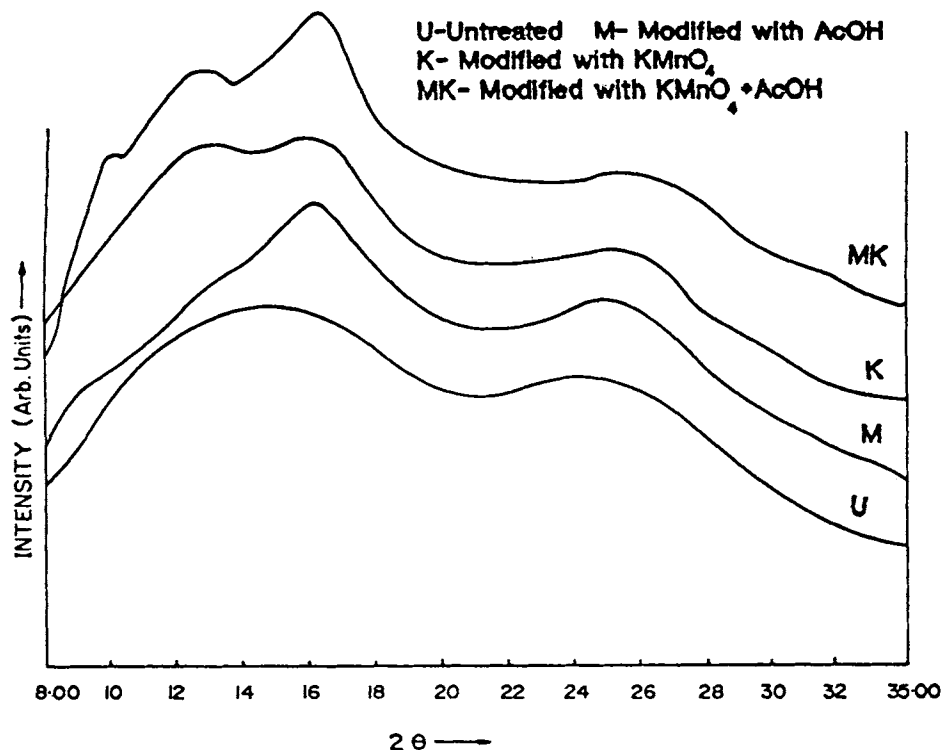


Figure 6 X-ray diffractograms of oxidised samples ($\text{CuK}\alpha$).

X-RAY DIFFRACTION

Wide angle X-ray diffraction is an important tool for determining the extent of cyclization¹⁷ in PAN fibers. X-ray diffractograms, of various samples after thermal stabilization, are shown in Figure 6. The figure shows the development of a broad peak at about $2\theta = 25.5^\circ$, corresponding to formation of pregraphitic (002) planes in the stabilized samples. The authors have already established, in their previous study,¹⁸ the appearance of another peak at about $2\theta = 13^\circ$, as the stabilization of PAN fibers progresses. The appearance of this peak has been explained as being due to the development of additional aroma-

tization and intermolecular crosslinks in the stabilized fiber structure. Intensities of these peaks are shown in Table V, relative to 100% normalization for the parent peak at 17° , and these intensities give an indication of the extent of stabilization. Intensity of the peak at 13° shows that KMnO_4 treated samples, that is, *K* and *MK*, are more stable and should possess a comparatively better aromatic structure. The peak at 13° for sample *U* is so weak that it could not be resolved from the parent peak at 17° .

Another parameter, which could give an indication of the extent of cyclization, is the d spacing, corresponding to the (002) pregraphitic structure developed in stabilized fibers. Ko et al.⁸ have re-

Table V Relative Intensities of X-Ray Diffraction Peaks

| Fiber Type | Intensity Ratio at 2θ | | | $d_{(002)}$ (Å) |
|---|------------------------------|-----------------|-----------------|--------------------|
| | $\sim 13^\circ$ | $\sim 17^\circ$ | $\sim 26^\circ$ | |
| Untreated | Unresolved | 100 | 80 | 3.57 |
| Modified with AcOH | 80 | 100 | 73 | 3.49 |
| Modified with KMnO_4 | 98 | 100 | 69 | 3.43 |
| Modified with KMnO_4 + AcOH | 83 | 100 | 62 | 3.40 |

ported a decrease in d value with the extent of stabilization. As shown in Table V, the d value for sample U is 3.57 Å and this value decreases to 3.40 Å with modification, showing that, with modification, a better ordered structure is formed in the oxidized PAN fibers. It must be mentioned here that the numerical values of d -spacings are indicative of the trend only, and should be taken to be accurate to ± 0.05 Å, in view of the broad diffraction peaks.

CARBON FIBERS

As evident from Table II, the mechanical properties of carbon fibers improve with modification and have direct correlation with the diameter, in the sense that the lower the carbon fiber diameter, the higher the carbon fiber tensile strength. Although the difference in diameter among various samples is not appreciable, it is yet significant, since the measurements, which have been performed using a Vicker's shear image eyepiece, are accurate to ± 0.01 μm . Further, the values quoted in Table II are an average of 20 independent filament measurements on each sample. One can thus unambiguously conclude that the modification helps in reducing the diameter of carbon fibers and, as a result, the tensile strength of the resulting carbon fibers improves.

This study demonstrates the suitability of AcOH as plasticizer, but does not necessarily exploit the full potential of such modification. For example, the PAN fibers have been stretched during oxidation to only 20%; these could be further stretched by applying more load on the fiber tow. However, because of the limitations of the present batch experimentation, wherein we take about 20 cm lengths of the fiber tow, the application of more load makes the tow break through the knot, because of the stress concentrations at the site. One can achieve a greater degree of stretch during continuous scale processing when the tow is passed through differential speed rollers. The reduction in diameter of precursor PAN, and that of the resulting carbon fiber diameter, will then be much greater. This should, in turn, lead to still better carbon fiber properties.

CONCLUSIONS

Acetic acid can be a useful plasticizer for improvement of the orientation of molecular chains, and at

the same time for decreasing the diameter of PAN fibers prior to normal stabilization and carbonization steps. The proposed technique of bimodification helps in improving the mechanical properties of the resulting carbon fibers, which are superior to that which is possible by individual treatments. Overall, the study points towards possible routes of modification of PAN fibers using various chemicals in combination.

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