JOURNAL OF MATERIALS SCIENCE 27 (1992) 2429–2436

Preparation of high-performance carbon fibres from PAN fibres modified with cobaltous chloride

TSE-HAO KO, LI-CHUAN HUANG*
Department of Materials Science, College of Science, Feng Chia University, Taichung, Taiwan

Preparations of high-performance carbon fibres have been tested and the results are reported in this article. Polyacrylonitrile (PAN) fibres modified with cobaltous chloride have increased the crystal size, the crystallinity and the orientation, and also improved the tensile strength by about 15–40% and the modulus by about 10–20% of the resulting carbon fibres, which were carbonized at 1300 °C. The oxygen content, the *AI* value and the density for the modified PAN fibres are smaller than those for unmodified PAN fibres. Because the formation of the ladder polymer in the modified PAN fibres is slow and gradual during the stabilization process, the resulting carbon fibres have a better modulus than carbon fibres developed from unmodified PAN fibres. The activation energy of cyclization, E_a, is increased to 180.0 from 156.6 kJ mol^{-1} after the modification process. The modified PAN fibres do not reduce the time required for stabilization. The carbon fibres developed from the modified PAN fibres have a greater stacking size, L_c, than those developed from unmodified PAN fibres. A higher stacking size, and therefore a higher number of crystalline carbon basal planes, is one of the reasons for the improved modulus of the carbon fibres.

1. Introduction

Polyacrylonitrile (PAN) fibres have been found to be the most suitable precursors for making high-performance carbon fibre [1–3]. An important step, the stabilization process, in preparing carbon fibre from the PAN fibre is to heat the precursor at 200 to 300 °C in air (or in an oxygen-containing atmosphere). This process leads to the formation of a ladder polymer in stabilized fibre. Subsequently, carbonization is carried out at a temperature of up to 800–3000 °C in an inert atmosphere. The maximum temperature depends upon the type of carbon fibres ultimately required [4–6].

Carbon fibres are now important industrially and have gained a wide range of application, from game and sports articles to the aerospace industry. Because of their various technological applications in the industrial and engineering fields, the development of high-strain and high-modulus carbon fibres has been necessary. It has been established that the heat treatment of a PAN fibre under a tension load can improve the fibre quality [4, 7]. Bahl and co-workers [8, 9] pretreated precursors with CuCl to make high-performance carbon fibres. Cagliostro [10] has modified precursors with benzoic acid to improve the tensile strength of carbon fibre.

Five previous studies [11–15] presented the results of our process for the modification of PAN fibres with potassium permanganate to produce high-performance carbon fibres. We also discussed the reasons why a PAN fibre modified with potassium permanganate can reduce the stabilization time and improve the tensile strength of carbon fibre. In the present study, the effect of modification of the precursor with cobaltous chloride on the properties of the resulting stabilized fibres and on the properties of the final carbon fibres will be discussed. Before this study, we assumed that if the modification process for the precursor was adopted, it would decrease the required stabilization time and improve the properties and productivity of the carbon fibres more than any conventional process.

2. Experimental procedure

A special grade of acrylic fibre, Courtelle fibre (Courtaulds Ltd, UK), containing 6% methyl acrylate and 1% (itaconic) acid copolymer was used in this work. A single tow of Courtelle fibre contains 6000 strands of 1.1 denier monofilament. A fibre-wound frame was pretreated by immersing it in a 5% cobaltous chloride solution at 90 °C for 5 min, then washed with distilled water and dried to a constant weight in an oven. The cobalt content in the resulting carbon fibres was determined by atomic emission spectrometer analysis. The content of cobalt in the fibre had increased about 40 times over its original content after the modification process.

---

* *Present address*: Union Chemical Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan.

0022–2461

Stabilization of the precursor was carried out in a constant-temperature zone furnace with a fixed length method at 270 °C from 1 to 10 h, in a purified air atmosphere. The stabilized fibres were carbonized to 1300 °C at a rate of 240 °C h^{-1}, from 25 to 1300 °C, in a ceramic reaction tube and an oxygen-free nitrogen atmosphere. The specimens were cooled down immediately.

The mechanical properties of the stabilized fibres and the carbon fibres were measured by an Instron 1122 tensile testing machine at a crosshead speed of 0.5 mm min^{-1} and a load cell of 10 g, with a testing length of 2 and 2.5 cm for stabilized and carbon fibres, respectively. In each sample at least 25 filaments were tested, and the average value was reported. The diameters of all fibres were measured under an Olympus BHT microscope with a closed-circuit television camera which magnified the image of the fibre in order to measure the diameter of the fibre. 30 fibre diameters were measured in each experiment and the average measurement of these 30 fibres was calculated.

A Rigaku X-ray diffractometer providing Ni-filtered CuK_α radiation was used to measure the crystalline-related properties of the sample. The step-scan method was used to determine the d spacing and stacking size (L_c, stacking height of layer planes); the step-interval was set at 0.02°. The preferred orientation of the PAN fibres (0 0 1) and the carbon fibres $O(0\,0\,2)$ was determined by an X-ray diffractometer with a fibre specimen attachment. The precursors were located at around 17° (2θ) and the carbon fibres were set at around 25° (2θ) (the (0 0 2) plane of carbon fibres is thought to have a hexagonal structure). The 360° azimuthal circle was used to allow the fibre axis to be rotated 360° about the vertical. The d spacing, L_c, and $O(0\,0\,2)$ were calculated by using Equations 1 (the Bragg equation), 2 (the Scherrer equation), and 3, respectively [16]

$$n\lambda = 2d\sin\theta \qquad (1)$$

$$L(h\,k\,l) = K\lambda/B\cos\theta \qquad (2)$$

$$O(h\,k\,l)\,(\%) = [(360 - H)/360]100 \qquad (3)$$

in which $\lambda = 0.154$ nm, K is the apparatus constant (= 1.0) and B is the half-value width (in radians) of the X-ray diffraction intensity (I) versus 2θ curve. H is the half-value width in degrees of the curve of I versus azimuthal angle [17]. The preferred orientation, $O(0\,0\,2)$, has a value of 0% if the specimen is completely unoriented. If the crystallites are all arranged perfectly parallel to one another, it has a value of 100%.

A Mettler TA 3000 thermal analyser with a differential scanning calorimeter (model 20) and a Rigaku instrument for thermogravimetric analysis (TGA) were used to study the reaction of the PAN precursor. The sample weight was 3.5 mg and the heating rate was 10 °C min^{-1}, heated to 450 °C under an air atmosphere.

Density was measured at 25 °C according to the density gradient column method. The density column was prepared with a mixture of n-heptane and carbon tetrachloride, so that a density gradient of about 1.2 to 1.6 g cm^{-3} extended from top to bottom. For the measurement of densities from 1.6 to 2.0 g cm^{-3}, a density gradient column prepared with a mixture of carbon tetrachloride and 1,3-dibromopropane was adopted.

A Perkin–Elmer model 240C elemental analyser was used to carry out elemental analysis. Samples from the carbonization process were analysed for carbon, hydrogen and nitrogen. The oxygen content was determined by difference.

3. Results and discussion

3.1. Effect of modification on the structure of precursors

During the last few years, X-ray diffractometry has been used to examine the structure of acrylic polymers and fibres [17–22]. Flat-plate X-ray diffraction photographs of two samples are shown in Fig. 1. The inner diffraction arc (at 2θ = 17°) corresponds to (1 0 0) planes of the pseudo-hexagonal cell or (2 0 0) reflections of the orthorhomic cell [20]. The outer diffraction arc (at 2θ = 29°) could be attributed to the (1 0 1) of the pseudo-hexagonal cell or to the (2 0 1) reflection of the orthorhombic structure.

X-ray diffraction photographs of the original and modified precursors are shown in Fig. 1. The equatorial arc length and the line broadening of the inner diffraction arc both decreased when the precursor was modified with cobaltous chloride, as shown in Fig. 1b. The decrease in the equatorial arc lengths for this sample indicates a better distribution in molecular orientation along the fibre axis. The decreased line broadening of the reflections for the inner diffraction arc indicate an increase in crystal size. The inner and outer reflections for two fibres connect in a foggy arc to form a ring. The foggy arcs show the existence of a disordered phase in the fibre.

Warner *et al.* [22] proposed a model for the microstructure of PAN fibre and indicated that the existence of the ordered regions was due to the formation of lamellar-like structures. They calculated the length of the rods of lamellae (the crystal size) to be 8 nm. In the modified precursor of Bahl *et al.* [23] the value was about 10.7 nm. In the study of Jain and Abhiraman [24] it was about 4.7 nm. In this study, the precursor was found to have a similar structure; the value was 3.5 nm. When the precursor was modified with cobaltous chloride it was approximately 3.9 nm, an increase of about 10%.

The variations in the structural parameters of the precursor during modification are shown in Table I. Because of the increase in crystal size and the length of rods, the modified precursor shows about 4% improvement in its crystalline content. The improvements in crystal size and crystallinity were due to some molecular chains packing into molecular rods from the amorphous phase during modification. This process also improved the alignment of the molecular chains along the fibre axis. As a result, the orientation of the modified precursor was higher than that of the original fibre.

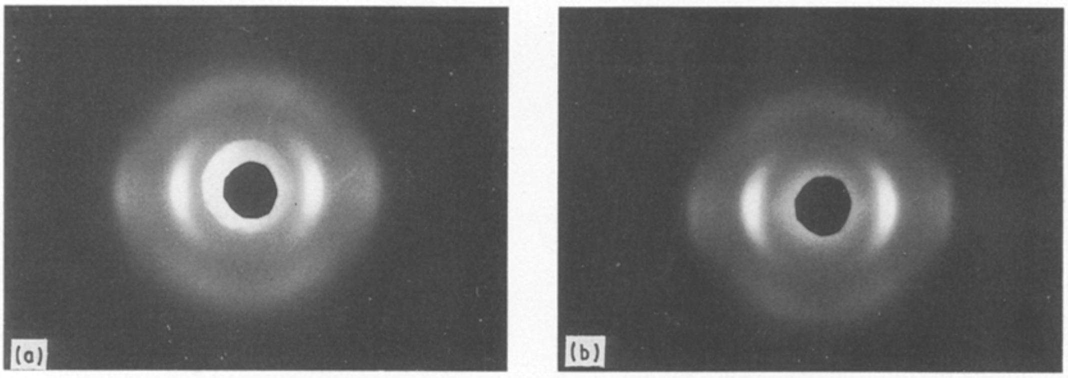


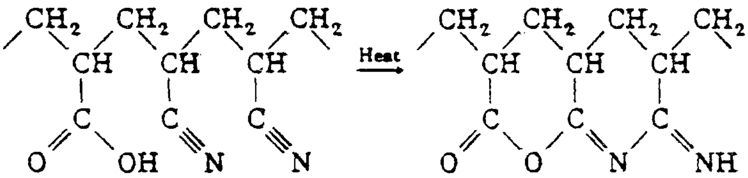
Figure 1 Wide-angle X-ray diffraction photographs of (a) original PAN fibres, (b) modified PAN fibres.

TABLE I Structural parameters of PAN fibres

	Original precursor	Modified precursor
Crystal size (nm)	3.5	3.9
Crystallinity (%)	50.5	54.2
Orientation (%)	80.0	82.2

3.2. Thermal studies

When PAN fibre is heated in an inert or oxidizing atmosphere, C≡N bonds will be converted into C = N bonds. These reactions result in the formation of ladder polymers in stabilized fibres. The acid constituent in PAN fibres acts as an initiator for ladder polymer by the following mechanism as shown by Grassie and Hay [25]:



The cyclization of PAN fibre during stabilization is always associated with a large exotherm. The exothermic behaviour and the activation energy, E_a, of cyclization of PAN fibres have been studied by differential thermal analysis (DTA) and differential scanning calorimetry (DSC) [23, 26, 27]. The amount of energy required to raise the molecules to the activated state is called the activation energy, E_a. A smaller value of E_a suggests that the cyclization reaction can be initiated at a lower temperature. This finding was proved by our previous studies [11, 13]. In this study, the complete test procedure was done by using the DSC unit connected to a TC-10 microprocessor which printed out the E_a values on the attached printer–plotter. The activation energy of cyclization was 180.0 kJ mol^{-1} for the modified precursor and was larger than 156.6 kJ mol^{-1} for the original precursor. This finding indicated that the required time of stabilization of the modified PAN fibre may not be reduced.

TGA curves for both samples are shown in Fig. 2. The weight loss for both fibres begins at about 180 °C. The weight loss for both samples increases slowly below 275 °C, and then rises rapidly for the original precursor. However, the weight loss of the modified precursor increases slowly below 400 °C, indicating that the formation of ladder polymers is slow and constant during stabilization. The effect of the formation of ladder polymers on the mechanical properties of the final carbon fibres will be discussed in the next section.

3.3. Density and other properties of stabilized fibres

X-ray diffractometer studies on PAN fibres showed two equatorial diffraction peaks at Bragg angles of $2\theta = 17$ and 29°. When the thermal treatment temperature is above 180 °C, the X-ray intensity at $2\theta = 17°$ decreases slowly and a new peak appears at $2\theta = 25°$, corresponding to the sheet-like structure of the ladder polymer. Uchida *et al.* [28] attributed the new reflection to the sheet-like structure of aromatized ladder polymer, introduced an "aromatization

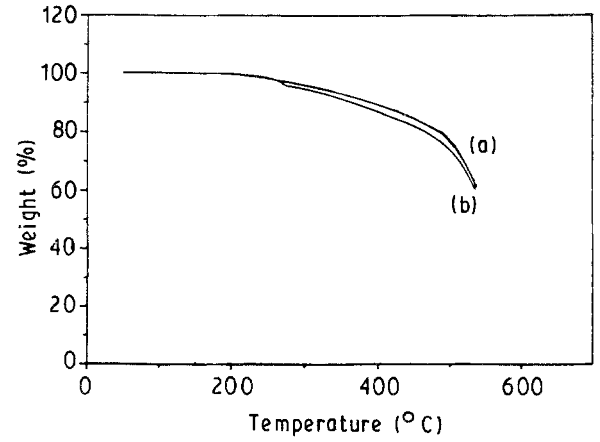


Figure 2 TGA curves for (a) modified PAN fibres, (b) original PAN fibres.

index", AI, given by

$$AI(\%) = 100\frac{I_a}{I_a + I_p}$$

in which I_a is the diffraction intensity given by the aromatic structure (ladder polymer) at around $2\theta = 25°$, and I_p is the diffraction by the PAN crystal at around $2\theta = 17°$. It was found that the AI value increases as the temperature or the heat-treatment time increases during the stabilization process [3, 11, 13, 28]. Ko *et al.* [11] improved the testing method and recommended that the AI value should be a criterion for checking the stabilization process and as a method to estimate the amount of ladder polymer. The greater the AI value, the more the formation of ladder polymer in the fibre.

Fig. 3 presents plots of the aromatization index versus the stabilization time. The AI values of the stabilized fibres increase when the stabilization temperature is raised. Up to a stabilization time of 7 h, the amount of ladder polymer increases rapidly, and after 7 h it increases slowly with rising thermal treatment time. Before the stabilization time 7 h, the AI values of the stabilized fibres developed from the modified precursor are lower than those of the stabilized fibres developed from the original precursor. After 7 h of heat treatment, the AI values of the former are higher than those of the latter.

Fig. 4 shows the variation of density with stabilization time. The density of stabilized fibres increases as the thermal treatment time is raised, and the AI values increase at the same rate. In the early stage of thermal treatment (before 7 h), the density of both fibres increases rapidly, and after the stabilization time of 7 h it increases less rapidly with rising thermal time. These findings indicate that there is a less amount of ladder polymer in the modified fibre than in the original fibre before the heat-treatment time of 7 h.

In our previous study [13], we found that the transformation of ladder polymers from acrylonitrile (AN) units is initiated in the disordered phase, and then proceeds in the boundaries of the ordered phase. When the heat-treatment temperature is high enough to collapse the intermolecular and intramolecular dipolar interactions among the nitrile groups in the ordered phase, ladder polymers are formed in the ordered phase. Because the modified precursor has a higher crystal size, higher crystallinity and greater orientation than the original precursor, the AI value and density of this fibre are lower than that of the original precursor during the early stage of stabilization.

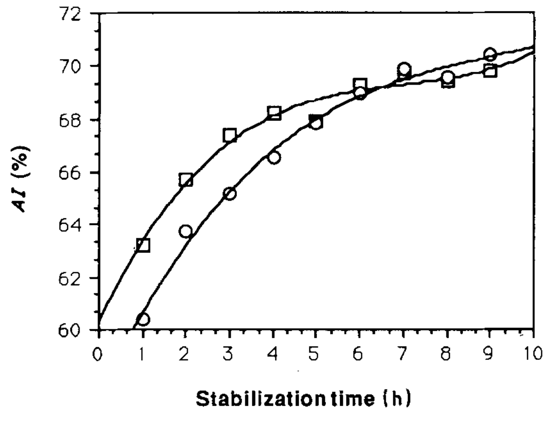


Figure 3 AI values of PAN fibres as a function of stabilization time: (□) original PAN fibres, (○) modified PAN fibres.

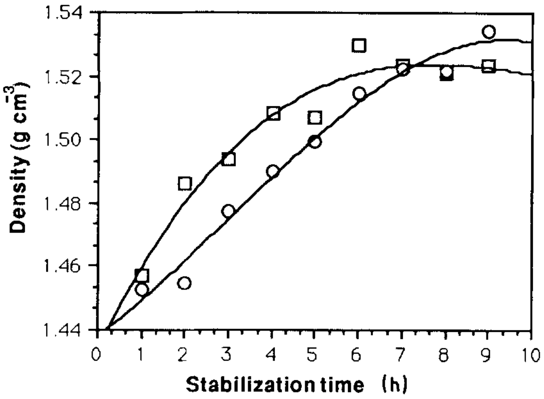


Figure 4 Density of PAN fibres as a function of stabilization time: (□) original PAN fibres, (○) modified PAN fibres.

When PAN fibre is heated in the stabilization process, C≡N bonds will be converted into C=N bonds, and the cohesive energy between the relative chains will drop appreciably [29]. This accounts for the decrease in strength of the stabilized fibres. The extent of the decrease in strength will depend on the percentage conversion of C≡N to C=N [3]. Therefore, the percentage conversion, the amount of ladder polymer, the AI value and the density will be greater at long times of heat-treatment than at the initial stage of stabilization, and will be greater for the PAN fibre than for the modified PAN fibre. This explains why the decrease in the tensile strength of stabilized fibre shows similar results, as in Fig. 5. The tensile strength of stabilized fibres decreases rapidly at initiation and then decreases gradually with stabilization time. Because of a higher AI value and greater density for the original precursor, this fibre has a lower tensile strength than the modified precursors during stabilization.

Watt and Johnson [30] indicated that the AN units of Courtelle fibre would be converted into ladder polymers above 180 °C, and that oxygen would attack the backbone of the ladder polymers. The oxygen content of both stabilized fibres as a function of stabilization time is shown in Fig. 6. Because of the increase in the formation of ladder polymers during stabilization, the oxygen content of both stabilized fibres increased as the thermal treatment time increased. The oxygen content of the modified fibre was less than that of the original precursor. For the modified fibre the oxygen content was less and the AI value and density were smaller than for the original precursor, indicating that the formation of the ladder polymers was slow and steady. This action could minimize the chances of both excessive rupture and chain scission of the precursor during stabilization. This is possibly one of the reasons that carbon fibre developed from the modified PAN fibre can improve the mechanical properties of carbon fibres.

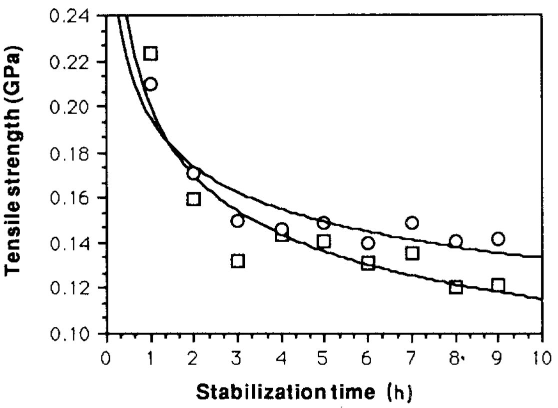


Figure 5 Tensile strength of PAN fibres as a function of stabilization time: (□) original PAN fibres, (○) modified PAN fibres.

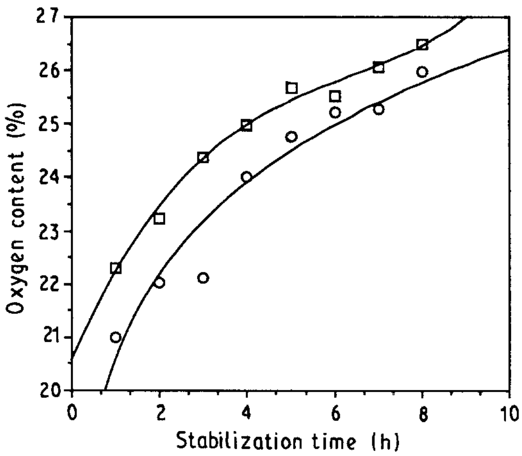


Figure 6 Oxygen content of both stabilized fibres as a function of stabilization time: (□) original PAN fibres, (○) modified PAN fibres.

An LKB ultramicrotome was used in preparing the samples for fibre cross-section investigation. The stabilized fibres were mounted in thermosetting polyester, and then sectioned to 1 μm thick. The cross-sections of stabilized fibres were observed under an Olympus BHT microscope. Examination of the fibre cross-sections showed that when thermally treated in air up to 5 h at 270 °C, original and modified precursors were characterized by a two-zone morphology, a dark outer ring and a cream-coloured core. The outer ring had been identified as an oxygen-rich zone, with the cream-coloured core containing less oxygen [25, 30]. The core area would gradually decrease with the stabilization time and finally disappear [11]. In that case, no sheath–core structure was visible in the cross-section of the stabilized fibres, so these could be identified as fully stabilized PAN fibres [31].

Johnson [32] indicated that the type I and II carbon fibres developed from fully stabilized PAN fibres have better mechanical properties than those developed from partially stabilized PAN fibres. In this study, at the 6th hour of heat-treatment, the fibre was brown throughout the cross-section. No two-zone structure was visible in either of the stabilized fibres, indicating that their composition was similar to that of fully stabilized PAN fibres.

According to all the evidence above, the modified precursor had a higher activation energy, a lower *AI* value, a smaller density, a lower oxygen content, and a greater tensile strength than the original precursor during the stabilization process. Direct evidence from the investigation of cross-sections of both fibres indicated that they were the same colour in cross-section at the same stabilization time. These findings indicated that the precursor modified with cobaltous chloride would not reduce the required time for stabilization.

3.4. Stacking size of carbon fibres

To observe the influence of the modification of precursor and stabilization on the mechanical properties of carbon fibres, both stabilized fibres were carbonized to 1300 °C under similar conditions. There is a large weight loss during the carbonization process, producing a large volume of volatile gases and some tarry substances. Volatile compounds such as HCN, NH_3, H_2, CO, CO_2, CH_4 and H_2O are formed [33, 34]. The evolution of these gases leads to the formation of the carbon basal planes in fibres during the carbonization process.

Watt *et al.* [35] indicated that the number of carbon basal planes parallel to the fibre axis increased as the temperature increased from 320 to 800 °C. Stacking sizes, L_c, of incipient layer planes from 1.2 nm at 410 °C to about 1.7 nm at 800 °C were measured under transmission electron microscopy (TEM). Oberlin and Oberlin [36] measured the thickness and diameter of the basic structural unit (BSU) of carbon fibre by TEM.

In our case, the microstructure parameters of carbon fibres developed from two different precursors were studied by X-ray diffraction techniques. The Scherrer equation was used to calculate the values of L_c (stacking height of graphene planes, stacking size) from the width of the 002 reflection. The Bragg equation was used to calculate the d spacing (the distance between the layer planes) from the 0 0 2 reflection. Therefore, the mean number of layer planes of single-crystalline carbon fibres could be obtained from L_c/d.

The stacking height of graphene planes, L_c, of carbon fibres as a function of the stabilization time is shown in Fig. 7. Carbon fibres developed from modified PAN fibres have a larger L_c than those developed from the original PAN fibres. The stacking height of graphene planes, L_c, in the carbon fibres developed from both PAN fibres increased rapidly up to a stabilization time of 7 h. After this heat-treatment time, there was a significant decrease.

From Section 3.3, we know that the formation of ladder polymers, density, *AI* values and oxygen contents increased as the stabilization time increased. It is known that there is a considerable evolution of H_2O in the early stage of the carbonization process, 300–500 °C. This reaction promoted cross-linking between adjacent chains and led to a marked increase in fibre modulus [33]. Because the oxygen will be

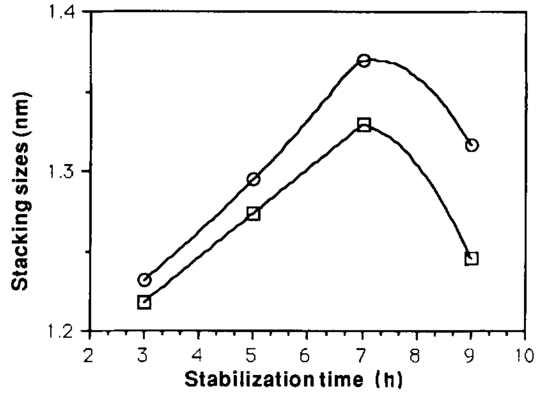


Figure 7 Stacking size of carbon fibres as a function of stabilization time: carbon fibres developed from (□) original PAN fibres, (○) modified PAN fibres.

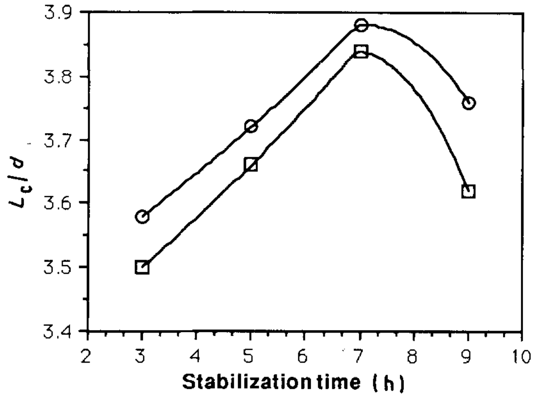


Figure 8 The mean number of layer planes of carbon fibres as a function of stabilization time: carbon fibres developed from (□) original PAN fibres, (○) modified PAN fibres.

bonded or absorbed in the stabilized fibre, this reaction leads to more oriented ladder polymers during the stabilization process and promotes an early crosslinking reaction during the carbonization process. Therefore, the stacking height of graphene planes in the final carbon fibres increases with an increase in the stabilization time.

However, after the stabilization time of 7 h, a sharp drop appears in L_c for both fibres. This finding is due to some of the molecular chains in the stabilized fibres being broken down during a long heat-treatment time. Therefore, this reaction limited the crystalline packing of carbon basal planes in carbon fibres during the carbonization process. The variation of the mean number of layer planes for carbon fibres during carbonization exhibits a similar phenomenon, as shown in Fig. 8.

In Figs 7 and 8, the carbon fibres developed from the modified PAN fibres have a greater stacking size and a higher mean number of layer-planes than those developed from the original PAN fibres. These findings are due to catalysis by Co which promoted the growth and close packing of the oriented layer planes. Therefore, the carbon fibres have greater L_c and L_c/d values than those developed from the original PAN fibres during similar stabilization and carbonization.

3.5. Mechanical properties of carbon fibres

Cooper and Mayer [37] indicated that boron doping and neutron irradiation of PAN-based carbon fibres would increase the stiffness and improve the modulus of carbon fibres. Our previous studies [11, 38] presented the results of the modification of PAN fibres with potassium permanganate to produce high-performance carbon fibres. The carbon fibres developed from the modified PAN fibres showed an improvement in tensile strength of 20 to 40% [38].

In this study, the result of the influence of the modification process on the modulus of the resulting carbon fibres is plotted in Fig. 9. For both carbon fibres, a sharp increase in modulus before the stabilization time of 7 h is observed. When the stabilization time is longer than 7 h, a much slower asymptotic decrease in modulus for the carbon fibres developed from original PAN fibres and a considerable decrease for those fibres developed from the modified PAN fibres occurs with time. However, the carbon fibres developed from the modified PAN fibres have a greater modulus by about 10–20% than those developed from the original PAN fibres.

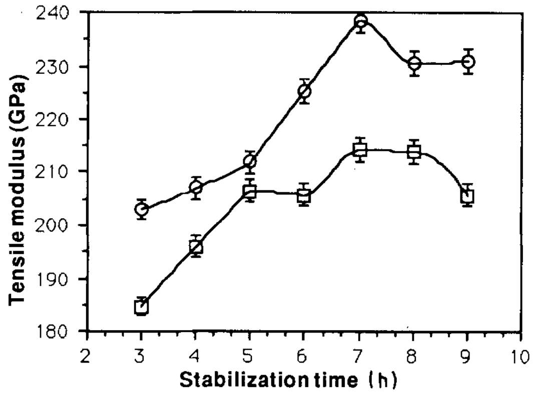


Figure 9 Modulus of carbon fibres as a function of stabilization time: carbon fibres developed from (□) original PAN fibres, (○) modified PAN fibres.

It is known that the determination of modulus is dependent on the preferred orientation in the carbon-based planes and the degree of graphitic crystallinity. Ko *et al.* [39] indicated that the average amount of the preferred alignment of carbon basal layers in the fibrils along the fibre axis would affect the mechanical properties of carbon fibres. In this article, each stabilized sample was carbonized under the same heat-treatment conditions. In Section 3.3, we found that the formation of the ladder polymers was slow and steady when the modified PAN fibres were heat-treated during stabilization. This reaction would improve the mechanical properties of the resulting carbon fibres. Another finding, as shown in Fig. 8, is that fibres developed from the modified carbon fibres have a greater mean number of layer planes (L_c/d) than those developed from the original PAN fibres during the same stabilization and carbonization processes. We would like to point out that a higher mean number of layer planes (L_c/d), i.e. a higher number of crystalline carbon basal planes, will improve the modulus.

The progression of tensile strength changes of carbon fibres is plotted as a function of the stabilization time in Fig. 10. For both samples, a sharp increase in tensile strength during the stabilization time from 1 to 6 h can be observed. After 6 h, a slower decrease in tensile strength occurs with the stabilization time (from 6 to 8 h). The tensile strength of carbon fibre developed from the original PAN fibre, which was stabilized for 9 h, decreased sharply. However, there was a significant improvement in tensile strength of 15 to 40% for the carbon fibres developed from the modified PAN fibres.

During stabilization, oxygen will be bonded or absorbed to the backbone of the ladder polymers in stabilized fibres [30]. During carbonization most of the oxygen of C=O groups on the backbone of ladder polymers is released as water vapour, as a result of which cross-linking between adjacent chains takes place [33]. Bahl and Manocha [3] indicated that the oxygen may form excessive C=O bonds when PAN is over-stabilized. During carbonization this may be released as CO or CO_2, thus leaving defects in the fibres. In this study, the intake of oxygen was very rapid with time during stabilization, as shown in Fig. 6. We believe that the decrease in the tensile strength of the resulting carbon fibres after the stabilization time of 6 h is due to the same reason.

Why do the carbon fibres developed from the modified PAN fibres not only increase in stacking size and in the mean number of layer planes but also improve in tensile strength and modulus, more than do the carbon fibres developed from the original PAN fibres? Co metal has been found to catalyse the formation of graphitic and turbostratic carbons during the heat-treatment stage in experiments conducted by several authors [40, 41]. Therefore, the carbon fibres have a higher stacking size and mean number of layer planes, which leads to the improvement in modulus. Because Co metal has a d shell unoccupied by electrons, the energy level of such configurations is scarcely changed by accepting additional electrons from carbon [41]. We propose that the Co atoms perform as a solid-solution hardener, which increases both the tensile strength and modulus of the resulting carbon fibres.

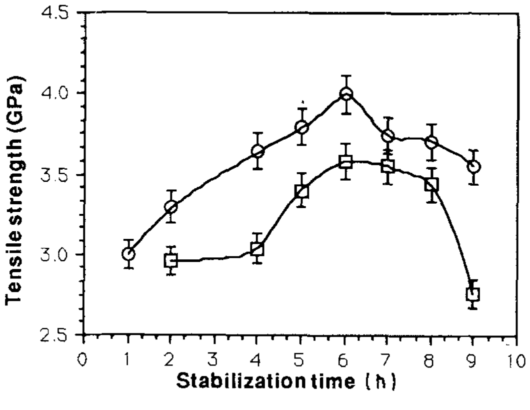


Figure 10 Tensile strength of carbon fibres as a function of stabilization time: carbon fibres developed from (□) original PAN fibres, (○) modified PAN fibres.

4. Conclusions

The effect of modification of PAN fibres with cobaltous chloride on the properties of the resulting PAN fibres and on the mechanical properties of the resulting final carbon fibres have been investigated. The main conclusions and advantages are as follows:

1. The modified PAN fibres have a greater crystal size, a higher crystallinity, and a better molecular orientation than the original PAN fibres.
2. The activation energy of cyclization for the modified PAN fibres was higher than that for the original PAN fibres. The formation of ladder polymers for the modified PAN fibres was slow and constant during stabilization.
3. The modified precursors had a lower *AI* value, a smaller density, a lesser oxygen content, and a greater tensile strength than the original precursors during stabilization. These findings showed that the precursor modified with cobaltous chloride would not reduce the required time for the stabilization process.
4. Cobalt atom acted as a catalyst, promoting the growth and close packing of the oriented layer planes. This reaction improved the modulus and tensile strength of the resulting carbon fibres developed from the modified carbon fibres.

Acknowledgement

The authors would like to thank Dr J. Magusar (MIT) and Professor C. H. Lin for his interest in this work and Mr P. Chiranairadul for his help in the laboratory. They also thank the National Science Council of the Republic of China for financial support in this study (Contract No. NSC79-0405-E-035-01).

References

1. A. SHINDO, *Rep. Govt. Ind. Inst., Osaka (Japan)* No. 317 (1961).
2. W. JOHNSON, L. N. PHILLIPS and W. WATT, UK Patent 1 110 791 (1968).
3. O. P. BAHL and L. M. MANOCHA, *Carbon* **13** (1974) 297.
4. J. W. JOHNSON, *Appl. Polym. Symp.* No. 9 (1969) 229.
5. G. A. COOPER and R. M. MAYER, *J. Mater. Sci.* **6** (1971) 60.
6. R. MORETON, W. WATT and W. JOHNSON, *Nature* **213** (1967) 690.
7. W. WATT, L. N. PHILIPS and W. JOHNSON, *The Engineer (London)* **221** (1966) 815.
8. R. B. MATHUR, D. GUPTA, O. P. BAHL and T. L. DHAMI, *Fibre Sci. Tech.* **20** (1984) 227.
9. O. P. BAHL, R. B. MATHUR and T. L. DHAMI, *Mater. Sci. Eng.* **73** (1985) 105.
10. D. E. CAGLIOSTRO, *Textile Res. J.* (October 1980) 632.
11. T. H. KO, H. Y. TING and C. H. LIN, *J. Appl. Polym. Sci.* **35** (1988) 631.
12. T. H. KO, P. CHIRANAIRADUL, H. Y. TING and C. H. LIN, *ibid.* **37** (1989) 541.
13. T. H. KO, C. H. LIN and H. Y. TING, *ibid.* **37** (1989) 553.
14. T. H. KO, H. Y. TING, C. H. LIN and J. C. CHEN, *ibid.* **35** (1988) 863.
15. T. H. KO and C. H. LIN, *J. Mater. Sci. Lett.* **7** (1988) 628.
16. B. D. CULLITY, "Element of X-ray Diffraction" (Addison-Wesley, Reading, Massachusetts, 1978).
17. L. G. WALLNER and K. RIGGERT, *J. Polym. Sci.* **B1** (1963) 111.
18. J. J. KLEMENT and P. H. GEIL, *ibid.* **A2** (1968) 1381.
19. B. G. GOLVIN and P. STORR, *Eur. Polym. J.* **10** (1974) 337.
20. O. P. BAHL, R. B. MATHUR and K. D. KUNDA, *Fibre Sci. Tech.* **15** (1981) 147.

21. C. R. BOHN, J. R. SCHAEFGEN and K. D. KUNDRA, *J. Polym. Sci.* **55** (1961) 531.
22. S. B. WARNER, D. R. UHLMANN and L. H. PEEBLES, Jr. *J. Mater. Sci.* **14** (1979) 1893.
23. O. P. BAHL, R. B. MATHUR and T. L. DHAMI, *Mater. Sci. Eng.* **73** (1985) 105.
24. M. K. JAIN and A. S. ABHIRAMAN, *J. Mater. Sci.* **18** (1983) 179.
25. N. GRASSIE and J. HAY, *J. Polym. Sci.* **56** (1962) 189.
26. E. FITZER and D. J. MULLER, *Carbon* **13** (1975) 63.
27. N. POPORSKE and I. MLADENOV, *ibid.* **21** (1983) 33.
28. T. UCHIDA, I. SHINOYAMA, Y. ITO and K. NUKUDA, in Proceedings of 10th Biennial Conference on Carbon, Bethlehem, Pennsylvania, 1971, p. 31.
29. W. WATT, in Proceedings of 3rd Conference on Industrial Carbons and Graphites, London, 1971, p. 431.
30. W. WATT and W. JOHNSON, *Nature* **257** (1975) 210.
31. D. J. JOHNSON, *Phil. Trans. R. Soc.* **A294** (1980) 443.
32. *Idem*, private communication (1983).
33. W. WATT and J. GREEN, in Proceedings of International Conference on Carbon Fibres, their Composites and Applications, Plastic Institute, London, 1971, p. 23.
34. A. K. FIEDLER, E. FITZER and F. ROZPLOCH, *Carbon* **11** (1973) 426.
35. W. WATT, D. J. JOHNSON and E. PARKER, in Proceedings of 2nd International Plastics Conference on Carbon Fibres, Plastics Institute, London, 1974, p. 3.
36. A. OBERLIN and M. OBERLIN, *J. Microscopy* **132** (1983) 353.
37. G. A. COOPER and R. M. MAYER, *J. Mater. Sci.* **6** (1971) 60.
38. T. H. KO, *J. Appl. Polym. Sci.* **43** (1991) 589.
39. T. H. KO, H. Y. TING and C. H. LIN, Preprint, 32nd International SAMPE Symposium and Exhibition, Anaheim, California, Vol. 32, 1987, p. 208.
40. W. WEISWEILER, N. SUBRAMANIAN and B. TERWIESCH, *Carbon* **9** (1971) 755.
41. A. OYA and S. OTANI, *ibid.* **17** (1979) 131.

Received 15 January
and accepted 7 June 1991