

Characterization of PAN-Based Nonburning (Nonflammable) Fibers

TSE-HAO KO

Department of Materials Science, College of Science, Feng Chia University, Taichung, Taiwan, Republic of China

SYNOPSIS

In this article, a continuous stabilization process is used to make nonburning (nonflammable) fibers from polyacrylonitrile (PAN) fibers. The effect of the shrinkage behavior and the stretching process of PAN fibers during the stabilization process on the physical properties, morphology, and flammability of the resultant nonburning fibers is studied for the first time. The higher shrinkage of PAN fibers during the continuous stabilization process is found to increase the diameter, the core proportion, and flammability and decrease the AI value, density, mechanical properties, and formation of oriented molecular chains in the resultant nonburning fibers. The effect of the shrinkage behavior of PAN fibers on the fracture surface of the nonburning fibers is also discussed. The nonburning fibers show a fracture structure radiating from the fiber center to the boundary. The structures are composed of small and fine radial strip-layer-like fibrils. Nonburning fibers developed using an optimum stretch process, not only had increased preferred orientation and density, but also had improved mechanical properties. Those fibers also have sufficient nonflammability. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyacrylonitrile (PAN) fibers have been used as the precursor in making high-performance carbon fibers. An important step in preparing carbon fibers from PAN fibers is to stabilize the precursor from 200–300°C in the air, and then, to carbonize the stabilized fibers at above 1000°C to produce the carbon fibers. However, it is found that stabilized PAN fibers may be used directly in applications where nonburning fibers are required, such as in garments and other appliances for firefighters, building materials, and other applications.

In a laboratory situation, there are two methods for preparing stabilized fibers in a batch process. The fixed-length method requires the PAN fibers to be secured to a rigid frame.¹ The constant load method attaches a weight to the end of the fiber during the stabilization process.^{2,3} It has been established that heat treatment of PAN fibers under a tension load improves the quality of the final car-

bon fibers.^{2,3} Mathur et al.⁴ and Bahl et al.⁵ have pretreated PAN fibers with CuCl to make high-performance carbon fibers. These authors did not discuss the influence of the processing on the properties of stabilized fibers and nonburning fibers during stabilization. In this study, the effect of the stabilization process on the flammability of nonburning fibers will be discussed.

Previous studies⁶ presented the results of our process for modifying PAN fibers with potassium permanganate to produce high-performance carbon fibers. We have discussed the reasons why PAN fibers modified with potassium permanganate can reduce stabilization time and improve the mechanical properties of the resultant carbon fibers.⁷ In another study,⁸ we investigated the morphology and microstructure of a stabilized fiber, nonburning fiber, using optical and electron microscopes. We presented a model for the structure of stabilized fibers. We have done an additional study on the effect of the modification of the PAN fibers on the dynamic mechanical properties of stabilized fibers.⁹ Earlier we also reported on the variation of crystal size in PAN fibers during stabilization. We also provided a model

of the ladder polymer in stabilized fibers transformed from acrylonitrile (AN) units of PAN fibers.¹⁰

In this study, a continuous stabilization process was used to manufacture stabilized fibers, nonburning fibers, from a PAN precursor. The study investigated the effect on the properties of nonburning fibers of different amounts of shrinkage and tension induced in the PAN precursor during the continuous thermal stabilization. This work also provided more information for developing a better process for making nonburning fibers.

EXPERIMENTAL

A special grade of acrylic fiber, Courtelle fiber (Courtaulds Ltd., UK), containing 6% methyl acrylate and 1% (itaconic) acid copolymer was used in this work. A single tow of Courtelle fiber contains 6000 strands of 1.1 denier monofilament.

The precursor was stabilized by means of a continuous process, as shown in Figure 1. The stabilization furnace was divided into four zones (each zone one meter long) and set at different temperature regions, 190°, 225°, 275°, and 300°C, respectively. Two sets of differential speed rollers—feed rollers and pinch rollers—were located at the front and rear of the furnace, respectively. The feed rollers had a variable speed to control the speeds of fibers entering zone 1, and the pinch rollers had a variable speed to control the rate of removal of fibers from zone 4. In this procedure, the feed rollers and take-up rollers were controlled at different speeds. PAN fibers passed through the furnace in 2.25 hours.

Three behaviors were exhibited once stabilization was achieved by heating the fibers fed continuously into the end of the furnace and removed from the other end (Fig. 1). When the speeds of the feed rollers and the pinch rollers are equal, the process is similar to the fixed-length method, which is used in the batch method to prepare stabilized fiber in lab-

oratory situations. In what we will refer to as the overfeed process, the speed of the feed rollers (V_1) was faster than that of the pinch rollers (V_2), with the difference in the speeds being used to control the desired shrinkage of the material. Therefore, the speed ratio of the rollers (V_2/V_1) was lower than 1. In the other process, referred to herein as the stretch process, the speed of the pinch rollers (V_2) was faster than that of the feed rollers (V_1), with the result that the PAN fibers were stretched in the oven during stabilization. In this case, the speed ratio of the rollers was higher than 1. In this study, the speed ratio of the rollers (V_2/V_1) in the overfeed process ranged from 0.7 to 1 and in the stretch process were from 1 to 1.8.

The mechanical properties of the nonburning fibers were measured by an Instron tensile-testing machine at a crosshead speed of 1 mm/min and a load cell of 10 g with a testing length of 2 cm. In each sample, at least 25 filaments were tested, and the average value was reported. The diameters of all fibers were measured under an Olympus BHT microscope with a closed circuit television camera which magnified the image in order to allow measurement of the diameter of the fibers. Thirty fiber diameters were measured in each experiment and the average measurement of these 30 fibers was calculated.

The preferred orientation of the nonburning fibers was determined by an Rigaku X-ray diffractometer with Cu $K\alpha$ radiation as the source, with a fiber specimen attachment. The precursors were located at around 25 degrees (2θ). The 360° azimuthal circle was used in order to permit the fiber axis to be rotated 360 degrees around the vertical.

$$O(hkl) (\%) = [(360 - H)/360] 100$$

in which H is the half value width in degrees of the curve of (1) versus azimuthal angle.^{6,9} The preferred orientation has a value of 0, if the specimen is com-

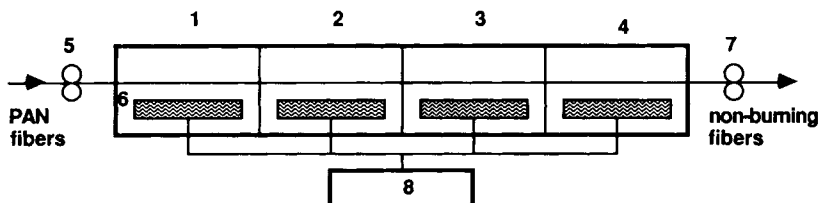


Figure 1 A schematic drawing showing the processing of nonburning fibers from PAN fibers by the continuous stabilization process: 1, 2, 3, 4: stabilization oven; 5: feed rollers; 6: heating mantle; 7: pinch rollers; 8: temperature controller.

pletely unoriented. If the crystallites are all arranged perfectly parallel to one another, the preferred orientation is equal to 100.

A scanning electron microscope (SEM), Topcon model ABT-55, was used to examine the fracture surface. The specimens were coated with Au to provide a better image.

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/cm³ extended from top to bottom.

A Perkin-Elmer model 240C Elemental Analyser was used to carry out the elemental analysis. The samples from the stabilization process were analyzed for carbon, hydrogen, and nitrogen. The oxygen content was determined by difference.

A Mettler TA 3000 thermal analyzer with a differential scanning calorimeter DSC 20 module was used to study the reaction kinetics of the samples. The sample weight was 3.5 mg and the heating rate was 10°C/min, heated to 500°C in air.

Flame retardancy tests were carried out using a model CS-178B ONI Flammability Tester. The Oxygen Index Tester was used for determining the relative flammability of the fibers. The limiting oxygen index (LOI) may be calculated by the following formula:

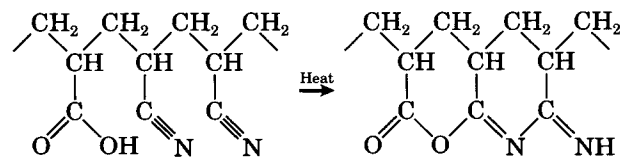
$$\text{LOI, (\%)} = \frac{\text{O}_2}{\text{O}_2 + \text{N}_2} 100$$

where O₂ and N₂ are the volumetric flow (cc/s). In this formula, resulting LOI values with higher numbers are more nonflammable.

RESULTS AND DISCUSSION

X-Ray Studies of Nonburning Fibers

As has been discussed by Watt,¹¹ when PAN fibers are heat-treated in the presence of oxygen above ca. 180°C, the following transformation is thought to take place:



As the stabilization temperature rises above 180°C, C≡N bonds in PAN fibers will convert into

C=N bonds, and then will form ladder polymers in the stabilized fibers. Because of the conversion of C≡N to C=N and the formation of the ladder polymers, the shrinkage behavior (or change in length) of PAN fibers is observed during the stabilization process. Fitzer and Muller¹² have reported that shrinkage of PAN fibers during the stabilization process at temperatures above 180°C is due to chemical effects. We have found that when more shrinkage occurred in the continuous stabilization process, more misoriented molecular chains were formed in the fibers.¹³ This misorientation, however, may lead to poor orientation of the molecular chains in the resulting carbon fibers. Therefore, in order to maintain the orientation of molecular chains throughout stabilization, it is essential to avoid this shrinkage by the application of load to the fiber tow during stabilization. Accordingly Johnson et al.¹⁴ succeeded in developing good carbon fibers only by not allowing the PAN fibers to shrink during the course of stabilization. However, in this study, we are concerned with how to develop better properties in nonburning fibers while developing the fibers using either the shrinkage process or the drawing process.

The progression of the preferred orientation change of nonburning fibers is plotted as a function of the speed ratio of rollers in Figure 2. The preferred orientation of nonburning fibers increases with an increasing roller speed ratio up to 1.3, indicating that more ladder polymers were formed parallel to the fiber axis during the stabilization process. The application of insufficient tension (the overfeed process) to PAN fibers led to shrinkage and promoted the formation of partial ladder polymers, which were not parallel to the fiber axis. This misorientation of the ladder polymers led to poor ori-

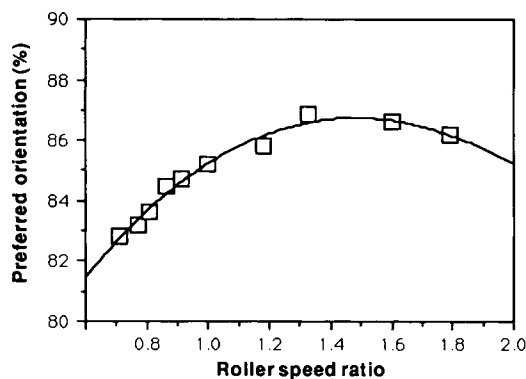


Figure 2 Preferred orientation of nonburning fibers as a function of roller speed ratio during stabilization.

entation of the molecular chain in the nonburning fibers during the overfeed process. However, above a roller speed ratio of 1.3, the preferred orientation of the nonburning fibers showed a slight decrease during the stretch process, indicating that the overstretch would lead to thermal shock and would break down the molecular chain of the ladder polymers. Due to this, a large degree of misorientation and hence defects were introduced in the nonburning fibers.

In our previous study,⁶ we modified the testing method and recommended that the aromatization index (AI) value be a criterion for checking whether the stabilization process has been completed. We also have recommended that this method be used to estimate the amount of ladder polymers. A Rigaku X-ray diffractometer with Cu K_α radiation as the source was used to determine the d spacing and the aromatization index (AI) of nonburning fibers. The AI was measured by following formula:

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

in which I_a is the diffraction pattern give by the ladder polymers at $2\theta \approx 25^\circ$, and I_p is the diffraction pattern given by the PAN crystal at $2\theta \approx 17^\circ$. A higher AI value indicates that there are more ladder polymers in the fibers.

As shown in Figure 3, the AI values, or aromatization index, of nonburning fibers increase with an increasing speed ratio of the rollers. The nonburning fibers developed by the overfeed process had

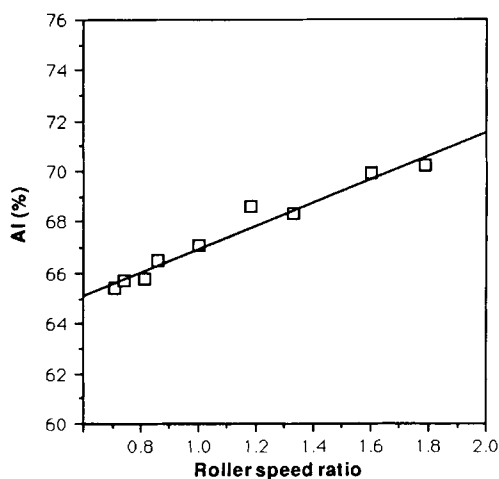


Figure 3 Aromatization index of nonburning fibers as a function of roller speed ratio during stabilization.

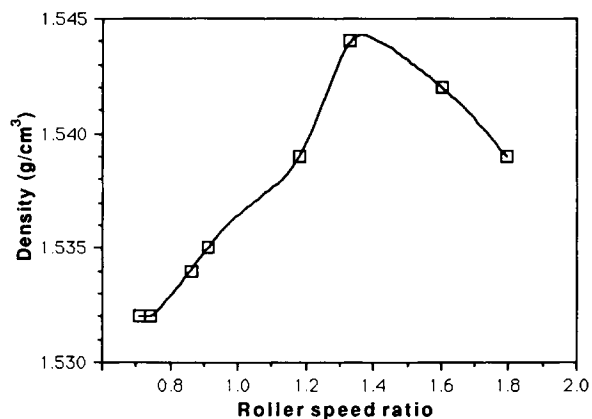


Figure 4 Density of nonburning fibers as a function of roller speed ratio during stabilization.

lower AI values than those fibers developed by the stretch process, indicating that the stretch process could promote the formation of ladder polymers converted from $C\equiv N$ bonds in PAN fibers.

The Density and Diameter of Fibers

The variation of density with the variation in roller speed ratio is shown in Figure 4. The density of nonburning fibers increased with the roller speed ratio up to the speed ratio of 1.3. But, above this speed ratio, there was a remarkable drop in density, which was due to the breakdown of the molecular chain and the introduction of defects in the fibers. As shown in Figure 2, the variation of preferred orientation with the roller speed ratio exhibited the same phenomena, indicating that the overstretch not only decreased the preferred orientation, but also promoted a decrease in density though the ladder polymers were still formed during stabilization. Therefore, greater amounts of ladder polymers and higher AI values do not always indicate that nonburning fibers have better preferred orientation and density.

According to the above discussion, the optimum stretch would bring about a higher preferred orientation of the molecular chains and would increase the formation of ladder polymers while resulting in a fiber with a lower diameter, as shown in Figure 5. The overfeed process introduces a degree of shrinkage during stabilization, which promotes the intermolecular addition between two opposite CN groups and leads to the formation of misoriented molecular chains. Therefore, the diameter of nonburning fibers decreased with the increase in the roller speed ratio.

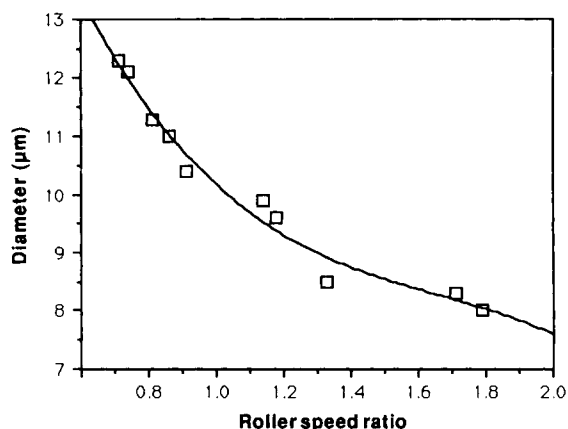


Figure 5 Diameter of nonburning fibers as a function of roller speed ratio during stabilization.

The Morphology of Nonburning Fibers

In this study, the nonburning fibers were embedded in resin and were cut with an LKB ultramicrotome. The cross-section of the fibers, about $0.1 \mu\text{m}$, were examined in an Olympus BHT microscope with a closed-circuit television camera. As shown in Figure 6, transmission optical micrographs of nonburning fibers show the existence of "skin-core" morphology, consisting of an outer ring and a cream-colored core. It has been shown that the formation of the outer ring is due to the attachment of oxygen to the backbone of the ladder polymers in the stabilized fibers.¹⁵⁻¹⁷ The core area would decrease with increasing stabilization time and finally disappear.⁶ In our previous study,¹³ to determine the area of the core, PC, we have devised the following formula:

The proportion of core, PC (%)

$$\begin{aligned}
 &= \frac{\sum R_c^2 \pi}{\sum R_f^2 \pi} \times 100 \\
 &= \frac{\sum \text{core area}}{\sum \text{cross-section of fiber}} \times 100
 \end{aligned}$$

in which R_c is radius of core and R_f is radius of fiber. The radius of core and fiber were measured from a transmission optical micrograph of a cross-section of fibers, as shown in Figure 6. If the fibers are fully stabilized PAN fiber, the PC value is 0.

Figure 7 shows the variation in proportion of core of the cross-section of the nonburning fibers during the stabilization. The proportion of core decreases with the increase in the roller speed ratio. The proportion of core decreases very rapidly during the overfeed process and decreases slightly during the

stretch process, indicating that the shrinkage behavior not only decreases the formation of ladder polymers but also prevents the diffusion of oxygen.

The oxygen content of the nonburning fibers as a function of the roller speed ratio is shown in Figure 8. These results show the strong effect of the roller speed ratio on the diffusion of oxygen in the nonburning fibers. The oxygen content increased during stabilization below the roller speed ratios of 1.2. This finding indicated that the optimum drawing would promote the diffusion of oxygen into the fibers. Between roller speed ratios of 1.2 and 1.6, the oxygen content decreased although the proportion of core still decreased. This indicated that the overstretch would prevent the absorption of oxygen. When the roller speed ratio was above 1.6, the oxygen content increased again. This was due to the degradation of the ladder polymer.¹⁸ This degradation caused the breakdown of molecular chain of ladder polymers in the fibers.

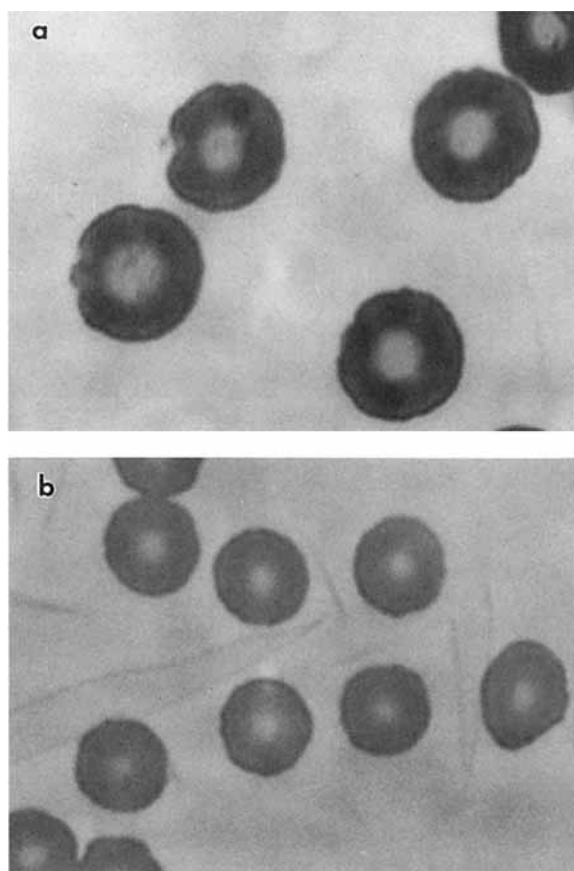


Figure 6 Transmission optical micrograph of cross-section of nonburning fibers developed by (a) the overfeed process, speed ratio of 0.77, (b) the stretch process, speed ratio of 1.54.

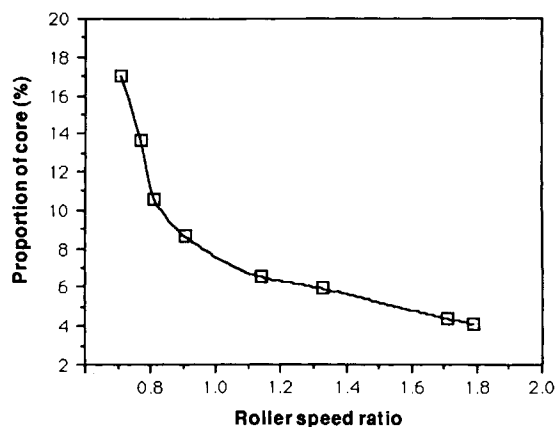


Figure 7 Proportion of core of nonburning fibers as a function of roller speed ratio during stabilization.

In our previous work,⁸ a proposed model of a stabilized fiber was presented, as shown in Figure 9. The stabilized fiber, heat-treated at 230°C for 2 h with a fixed-length method, was composed of lamellar plate-like structures along the fiber axis. The fracture surface of the fibers had some circumferential distribution in the boundary, and the inner zone had a radial distribution, which were examined under a stereoscan.

In this study, a typical fractured end of nonburning fibers (stabilized fibers) is shown in Figure 10(a). The fracture surfaces of the nonburning fibers developed from the stretch process were similar to the findings in our early study.⁸ For those fibers developed from the overfeed process, the fracture surfaces also show a radial structure from the fiber center to the boundary, as shown in Figure 10(b) and 10(c). But, there were small, and fine radial strip-layer-like fibrils in the fibers' centers. This

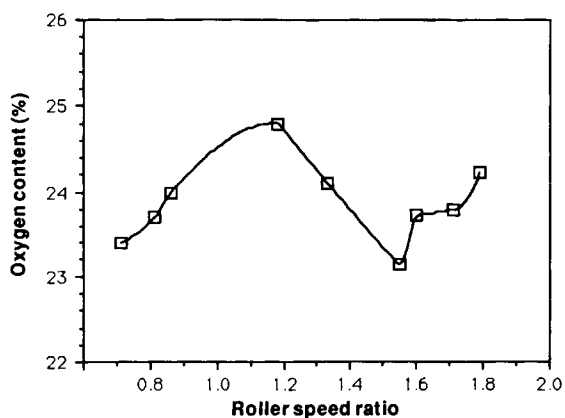


Figure 8 Oxygen content of nonburning fibers as a function of roller speed ratio during stabilization.

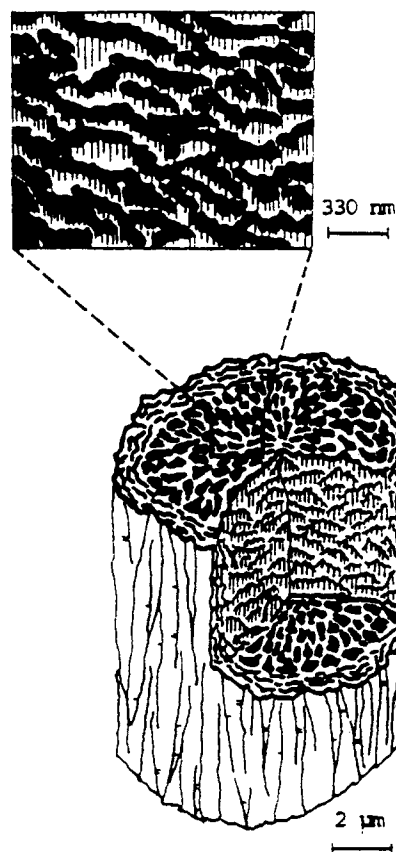


Figure 9 Structure model for a nonburning fiber.⁸

area increased with the increase in the extent of the overfeed of fibers during stabilization. We attributed this structure in the center of the fibers to the overfeeding and the shrinkage during stabilization, which promoted the intermolecular addition between CN groups of opposite neighboring molecular chains. This misoriented ladder polymer would decrease the oxygen diffusion from the surface to the interior. Layden¹⁹ studied the formation of core area in fibers and found that the temperature at the interior was higher than at the exterior during stabilization. Therefore, the cyclization reaction at the interior was higher than at the exterior. This led to a higher misorientation of molecular chains at the interior than at the exterior. There seemed to be no absolute relationship between the skin-core morphology which was examined under optical microscopy and the radial structure which was found with a stereoscan. From the skin-core morphology, we can determine the oxygen diffusion during stabilization. The different radial structures in nonburning fibers examined by stereoscan reveal whether nonburning fibers were developed by the over-feed process or the stretch process.

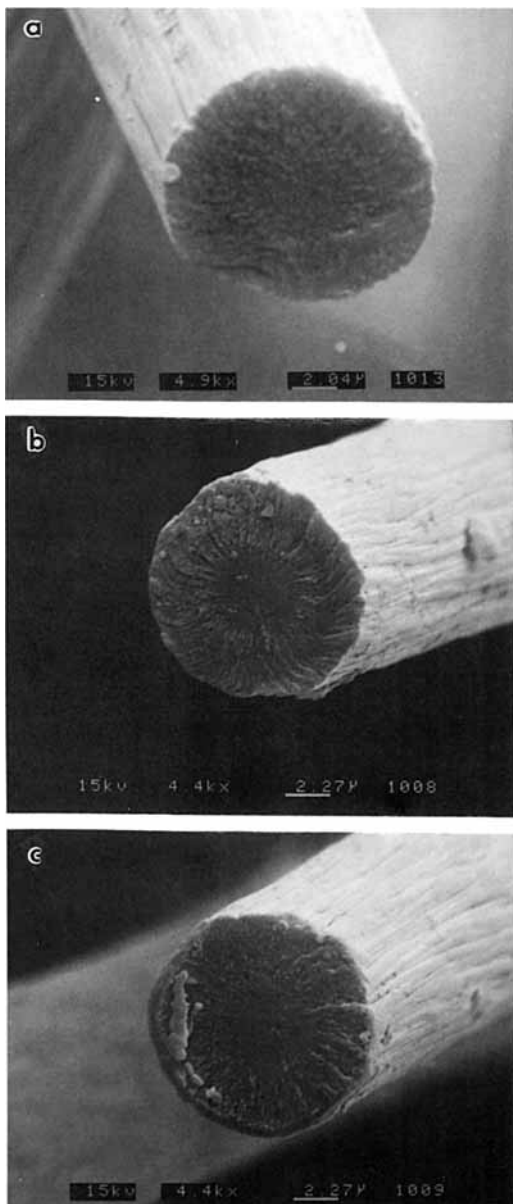


Figure 10 SEM images of nonburning fibers developed from: (a) the stretch process, speed ratio of 1.33; (b) the overfeed process, speed ratio of 0.86; (c) the overfeed process, speed ratio of 0.77.

Mechanical Properties and Flame Retardancy Tests

During stabilization, $C\equiv N$ bonds in PAN fibers are converted into $C=N$ bonds and form ladder polymers, and the cohesive energy between the relative chains drops appreciably.¹¹ The extent of decrease in strength depends on the percentage conversion of $C\equiv N$ to $C=N$.²⁰ We have found that the tensile strength of PAN fibers stabilized at 230°C from 1

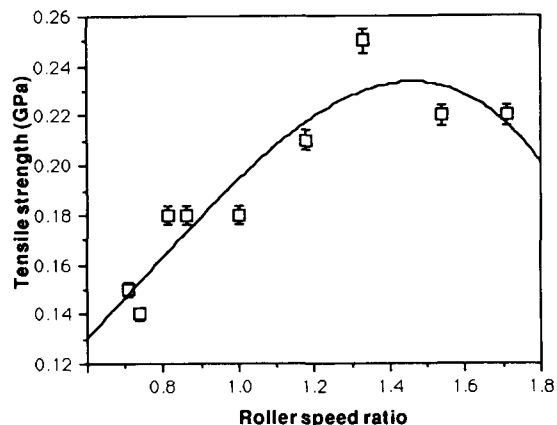


Figure 11 Tensile strength of nonburning fibers as a function of roller speed ratio during stabilization.

to 10 h in air decreased with the increase in stabilization time.⁶ In this study, all samples were developed at the same temperature and in the same amount of time. The only varying condition during the stabilization process was the roller speed ratio.

The variations in tensile strength and Young's modulus of nonburning fibers stabilized with different roller speed ratios are shown in Figures 11 and 12, respectively. The tensile strength of fibers increased rapidly up to roller speed ratios of 1.3, and then decreased gradually with additional increases in the roller speed ratios. There was similar phenomena in the variation of Young's modulus. These findings indicate that the nonburning fibers developed with the stretch process had better mechanical properties than those fibers developed with the overfeed process. But, when the roller speed ratio was higher than 1.3, this overstretch process also led to a decrease in mechanical properties, due to the

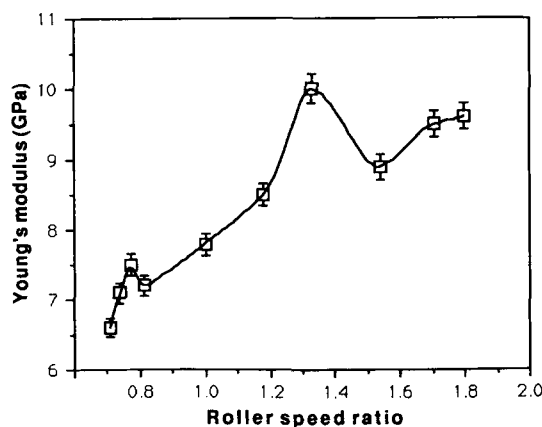


Figure 12 Young's modulus of nonburning fibers as a function of roller speed ratio during stabilization.

breakdown of molecular chains and the formation of misoriented ladder polymers in the fibers.

Houtz²¹ found that the color of PAN fibers changed from white to brown at about 200°C. This coloration change was the result of a chemical reaction in which adjacent nitrile side groups react with each other to produce a sequence of conjugated C=N bonds running parallel to the main chain backbone. We have studied the coloration reaction and a series of color changes of PAN film during the stabilization process, finding similar coloration changes.⁹ However, when the fibers were heat-treated at 230°C in nitrogen for 20 h, the color of PAN fibers changed from white to carmine. These fibers burn down easily and gases evolve in the flame. When these fibers are heat-treated in an atmosphere containing oxygen, oxygen will bind to the backbone of the ladder polymers and form stable structures. In such conditions, the color of these fibers immediately changes from carmine to black. Therefore, as shown in Figure 13, the fibers show no exotherm and no melting point, so they will not burn in flames in air, but rather will glow red, turning black again when they cool.

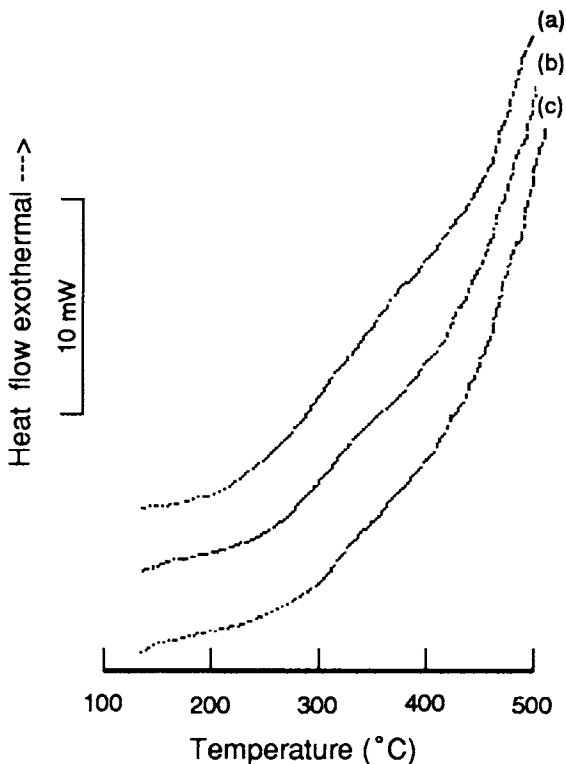


Figure 13 DSC curves of nonburning fibers developed from: (a) the stretch process, speed ratio of 0.77; (b) the overfeed process, speed ratio of 0.86; (c) the over-feed process, speed ratio of 1.33 (heating rate: 10°C in air).

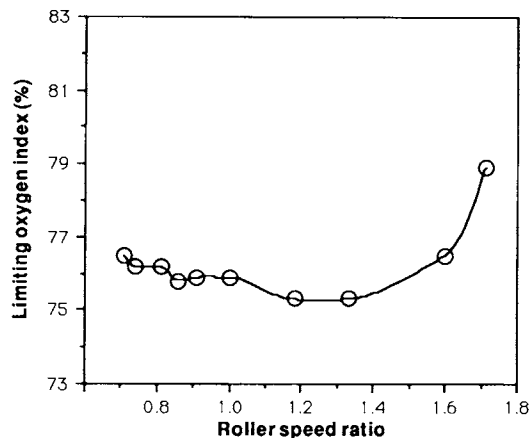


Figure 14 Limiting oxygen index (LOI) of nonburning fibers as a function of roller speed ratio during stabilization.

A flame retardancy test was carried out to test the flammability of each type of fiber. Limiting oxygen index is used for determining the relative flammability of rubbers, plastics, and fibers. The variation of LOI with the roller speed ratio is shown in Figure 14. In this study, the LOI value of all samples was higher than 75%. This is quite high compared to Nomex[™], a commonly used fire-retardant cloth, which has a value of 28%.

For the overfeed process, the LOI value of the nonburning fibers decreased with decreases in shrinkage. For the stretch process, the LOI value of the fibers increased with the increase in the roller speed ratio. The nonburning fibers developed by the overfeed process at a roller speed ratio lower than 1, have a higher LOI value than those fibers developed from the stretch process (where the roller speed ratio is higher than 1.4). This phenomena is very interesting. The nonburning fibers developed with the shrinkage process had poor preferred orientation, AI, density, oxygen content, and mechanical properties; however, those fibers had higher LOI values and higher diameters. Therefore, it seemed that stable ladder polymeric structures (higher AI value) and well-oriented molecular chains were not absolute determining factors of the nonflammability of the fibers. The oxygen content and the diameter of fibers also affected the flammability of the nonburning fibers. Our research will look more closely into this phenomena in the near future.

CONCLUSIONS

This study used an overfeed process and a stretch process in the continuous stabilization process for

preparation of nonburning fibers. We found that the optimum stretch not only increased the formation of oriented ladder polymers and density but also improved the mechanical properties. The nonburning fibers developed from the overfeed process had better nonflammability than those fibers developed from the optimum stretch process. Because of the formation of misoriented ladder polymers in the overfeed processed nonburning fibers the diffusion of oxygen was prevented by the resulting misoriented molecular chains. Therefore, these fibers had a large core area and formed small and fine radial strip-layer-like structures in the fibers' center.

In this article, we also found that under our testing conditions there was no absolute relationship between nonflammability and the stable ladder polymers, or the oriented molecular chains. The oxygen content and the diameter of the fibers also affected the nonflammability of the nonburning fibers.

The author gives thanks to Dr. P. Chiranairadul and Mr. W. L. Chou for their help in the lab, Dr. Jin-Shy Tsai (the Catalyst Research Center, China Technical Consultants, Inc.) for his help in testing the flammability of the fibers, and Mr. Carlos McEvelly for proofreading the manuscript. Professor Ko also is especially grateful to the National Science Council of the Republic of China for financial support of this project (No: NSC 81-0405-E035-04).

REFERENCES

1. W. Watt, D. J. Johnson, and E. Parker, *Proc. 2nd Conf. on Carbon Fibers*, Plastic Institute, London, 1974, p. 3.
2. W. Watt, L. N. Phillips, and W. Johnson, *The Engineer (London)*, **221**, 815 (1966).
3. W. Watt and W. Johnson, *Appl. Polym. Symp.*, **9**, 215 (1969).
4. R. B. Mathur, D. Gupta, O. P. Bahl, and T. L. Dhimi, *Fibre Sci. Technol.*, **20**, 227 (1984).
5. O. P. Bahl, R. B. Mathur, and T. L. Dhimi, *Mater. Sci. Eng.*, **73**, 105 (1985).
6. T. H. Ko, H. Y. Ting, and C. H. Lin, *J. Appl. Polym. Sci.*, **35**, 631 (1988).
7. T. H. Ko and C. H. Lin, *J. Mater. Sci. Lett.*, **7**, 628 (1988).
8. T. H. Ko, H. Y. Ting, C. H. Lin, and J. C. Chen, *J. Appl. Polym. Sci.*, **35**, 863 (1988).
9. T. H. Ko, P. Chiranairadul, H. Y. Ting, and C. H. Lin, *J. Appl. Polym. Sci.*, **37**, 541 (1989).
10. T. H. Ko, H. Y. Ting, and C. H. Lin, *J. Appl. Polym. Sci.*, **36**, 553 (1989).
11. W. Watt, *Third Conf. on Ind. Carbons and Graphites, London*, 1971, p. 431.
12. E. Fitzer and D. J. Muller, *Makromol. Chem.*, **144**, 117 (1971).
13. T. H. Ko, P. Chiranairadul, and C. H. Lin, *Polym. Eng. Sci.* (to appear).
14. W. Johnson, L. N. Phillips, and W. Watt, Br. Pat. 1,110,791 (1968).
15. W. Watt and W. Johnson, *Nature*, **257**, 210 (1975).
16. N. Grassie and J. N. Hay, *J. Polym. Sci.*, **56**, 189 (1962).
17. S. B. Warner, L. H. Peebles Jr., and D. R. Uhlmann, *J. Mater. Sci.*, **14**, 565 (1979).
18. M. M. Kanovich and A. P. Rudenko, *Khimicheskie Volokna*, **3**, 19 (May-June 1982) (USSR).
19. G. K. Layden, *Carbon*, **10**, 59 (1972).
20. O. P. Bahl and L. M. Manocha, *Carbon*, **12**, 417 (1974).
21. R. C. Houtz, *Text. Res. J.*, **20**, 786 (1950).

Received January 14, 1992

Accepted March 19, 1992