

# Structure and Properties Development During the Conversion of Polyethylene Precursors to Carbon Fibers

DONG ZHANG\* and QIN SUN

Textiles and Nonwovens Development Center; The University of Tennessee; Knoxville, Tennessee 37996-1950

## SYNOPSIS

In this study, the differences of structure and properties development during stabilization and carbonization between highly oriented and partially oriented polyethylene precursors were investigated. The effect of stabilization temperatures, time, and tension on the conversion process was studied using thermal analysis such as differential scanning calorimetry and thermogravimetric analysis, scanning electron microscopy, and single filament mechanical properties. Comparison of the resultant carbon fibers from these two kinds of precursor fibers showed that using partially oriented polyethylene precursor may reduce the stabilization time and temperature, with a diffusion-controlled process of sulfonation for stabilization. The mechanical properties of the resultant carbon fibers were evaluated.

© 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Carbon fibers are manufactured commercially from rayon (regenerated cellulose), pitch (petroleum- and coal tar-based), and polyacrylonitrile (PAN). Most of the high-strength carbon fibers are PAN-based, and the high modulus carbon fibers are produced from pitch-based precursors. Gel-spun polyethylene fibers have expected advantages as precursors for carbon fiber production. Being a thermal plastic fiber, it softens or melts at about 140°C so it is not studied widely because of the difficulty in stabilizing the precursor fibers. The key to success for conversion of polyethylene precursors to carbon fibers is to set up crosslinks and make the polyethylene fiber stable for the high temperature of carbonization. Earlier research showed that polyethylene fibers can be stabilized by heating in a bath containing concentrated sulfuric acid, chlorosulfonic acid, or fuming sulfuric acid and then carbonized in an inert environment at elevated temperatures.<sup>1,2</sup> Our earlier work<sup>3,4</sup> indicated that highly ordered and oriented polyethylene fibers can be converted to carbon fibers by stabilization in sulfuric acid bath and carboni-

zation in a nitrogen environment for a few minutes. Being a diffusion controlled process of sulfonation, stabilization time can be reduced by using partially oriented polyethylene fibers in this studies, the differences of structure and properties development during stabilization and carbonization between highly oriented and partially oriented polyethylene precursors were investigated. The effects of stabilization temperatures, time, and tension on conversion process were studied using thermal analysis such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and single-filament mechanical properties. Comparison of the resultant carbon fibers from these two kinds of precursor fibers showed that using partially oriented polyethylene precursor may reduce the stabilization time and temperature, with a diffusion-controlled process of sulfonation for stabilization. The mechanical properties of the resultant carbon fibers were evaluated.

## EXPERIMENTAL

### Stabilization of Precursor Fibers

The precursors used were commercially available polyethylene fibers (manufactured by Allied Fiber Co.), one being highly ordered and oriented and the

\* To whom correspondence should be addressed.

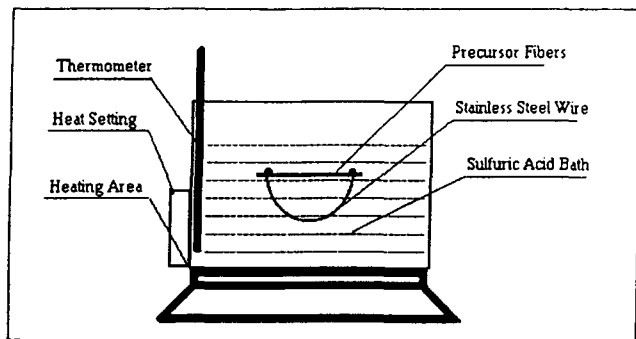


Figure 1 Setup for stabilization.

other partially drawn. Stabilization was carried out in hot sulfuric acid contained in a stainless steel heater bath with a resistance controller to vary the temperature. The actual temperature was monitored using a thermometer. The concentrated (95%) sulfuric acid used was heated to a temperature of 130°C, and the elastic-constrained fiber bundles were inserted into the bath as shown in Figure 1. The temperature was slowly raised up to 180°C in 1 h, as the fibers became stable to higher temperatures of carbonization without melting. After treatment for a predetermined length of time and temperature, the fibers were taken out, washed thoroughly in running tap water, and then dried in a DK-63 constant temperature oven at 60°C for 1 h.

### Carbonization of the Stabilized Fibers

The stabilized fibers were carbonized in a ceramic tubular furnace at 1100°C in a nitrogen environment for 2 min with a slight tension as shown in Figure 2. The fiber to be carbonized was tied to a carbon fiber leader at both ends. The tied fiber was slowly pulled into the preheated furnace to place the stabilized fiber in the central zone. After carbonization (about 2 min), the fiber was slowly pulled out of the furnace, which temperature was controlled by an

Omega CN2000 programmable temperature controller.

### Characterization of the Fibers

DSC of the fibers was carried out using a Mettler TA4000 thermal analysis system with DSC 25. The heating rate of 10°C per min was used. The sample chamber was purged with nitrogen gas to maintain an inert environment during the scans. TGA of the fibers was done using the same thermal analysis system with TGA 50. The heating rate of 20°C was used with a temperature range from 50 to 800°C. Different purge gases of nitrogen, helium, and air were used during TGA scans.

Single-filament tensile testing of the carbon fibers was measured using a table model Instron (1130). The single filament, mounted in window with a gauge length of 10 mm, was used with a cross head speed of 1 inch/min. The reported data are an average of 20 measurements. Color change was investigated during the processing. Burning testing was carried out by exposing the samples to a flame.

Wide-angle X-ray diffraction (WAXD) photographs were taken using a Phillips X-ray diffractometer with CuK $\alpha$  radiation (wave length 1.54183 Å). The fibers, mounted in a parallel array on the sample holder, were exposed for 4 h at 30 kV and 20 mA, with a distance of 36.5 mm between the film and the sample. Scanning electron micrographs were obtained using an ETEC Auto-scan scanning electron microscope (Hayward, CA), operating at 20 kV. Samples were coated with gold using a Hummer I Sputter Coater. The fibers were investigated for their cross section as well as surface features. Fiber diameter was determined by SEM photographs.

### RESULTS AND DISCUSSIONS

The precursor fibers were stabilized in a sulfuric acid bath at increasing temperatures for various lengths

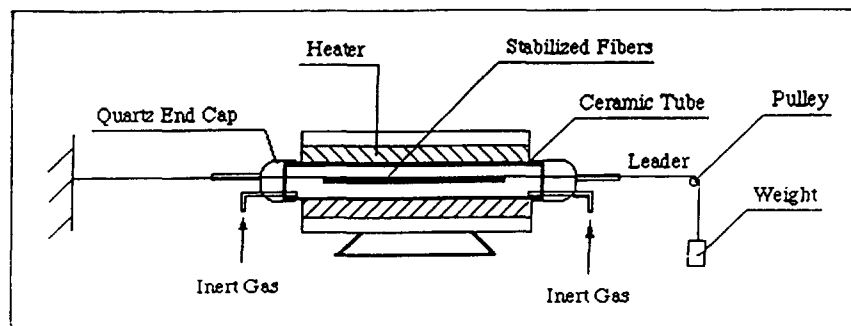


Figure 2 Setup for carbonization.

**Table I Color Changes of the Fibers During Stabilization**

Stabilization Time (min)	Stabilization Temperature (°C) for HOPE/PDPE <sup>a</sup>					
	130	140	150	160	170	180
5	L.Y./L.Y. <sup>b</sup>	L.Y./L.Y.	—	—	—	—
15	L.Y./grey	L.Y./D.grey <sup>c</sup>	—	—	—	—
30	Grey/black	Grey/black	—	—	—	—
45	Grey/black	Grey/black	Black/black	—	—	—
60	Black/black	Black/black	Black/black	Black/black	—	—
75	Black/black	Black/black	Black/black	Black/black	Black/black	—
90	Black/black	Black/black	Black/black	Black/black	Black/black	Black/black

<sup>a</sup> HOPE, highly oriented PE; PDPE, partially drawn PE.

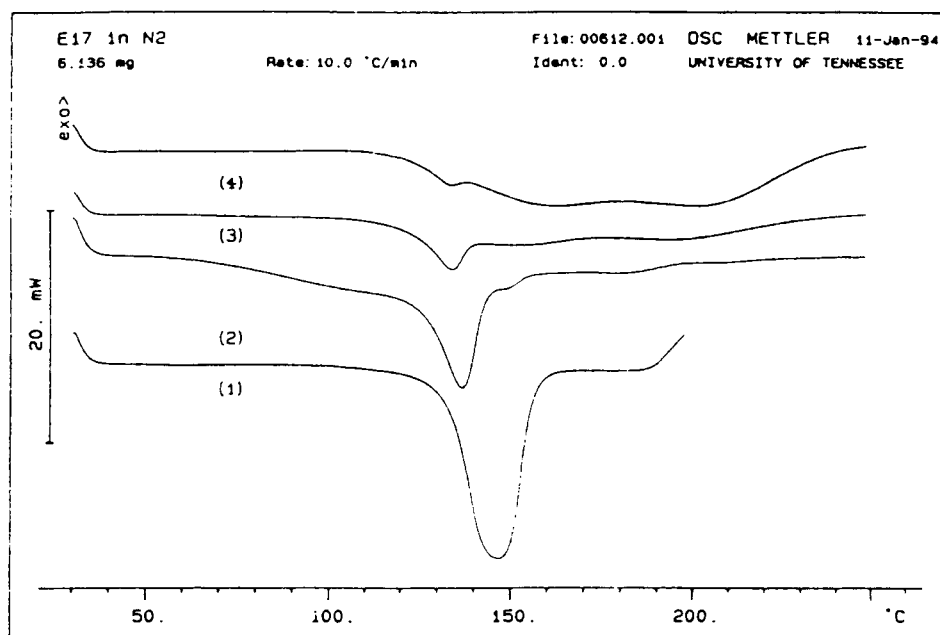
<sup>b</sup> L.Y., light yellow.

<sup>c</sup> D. grey, dark grey.

of time. The color of the fiber changed with the progress of sulfonation from white via light yellow and grey to black (Table I). Being a diffusion controlled process of sulphonation, the color changes for partially drawn polyethylene is faster than that of highly oriented PE, because the crystallinity of partially drawn polyethylene is lower and folded chain crystals existing in partially drawn PE, which leads to enhance the diffusivity of the acids in polyethylene. The change of color is an indication of the development of conjugated structures during the stabilization, and it is the reason of the observed darkening. When the fiber became gray, some fumes

appeared on the surface of the bath. As the fiber became dark, the fumes continued until the end of the stabilization process. After sulfonation, the mass of the fibers increased by 150–160%.

Figure 3 shows the DSC curves of precursor fiber and fibers stabilized at the given temperatures and times. The melting point of the fibers decreased as the stabilization time and temperature increased. That is due to the degradation and change of crystal structures from the extended to the folded. The melting temperature of extended-chain polyethylene is higher than that of folded-chain polyethylene. The endotherm of the melting peak decreased with the



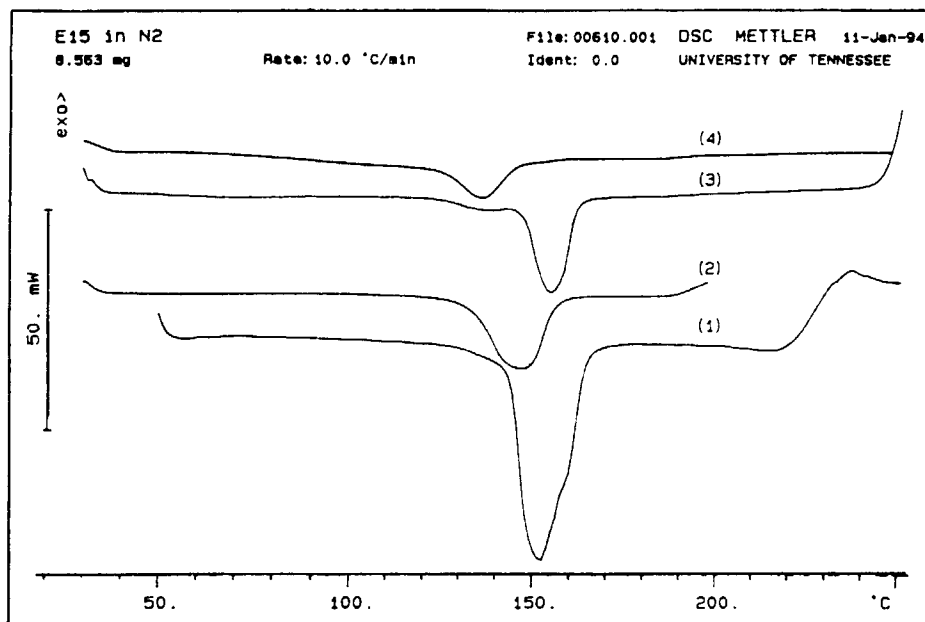
**Figure 3** DSC scans of fiber samples stabilized at different temperatures and time. (1) Precursor; (2) 150°C and 30 min; (3) 160°C and 45 min; (4) 170°C and 60 min.

**Table II** Burning Testing for Stabilized Fibers

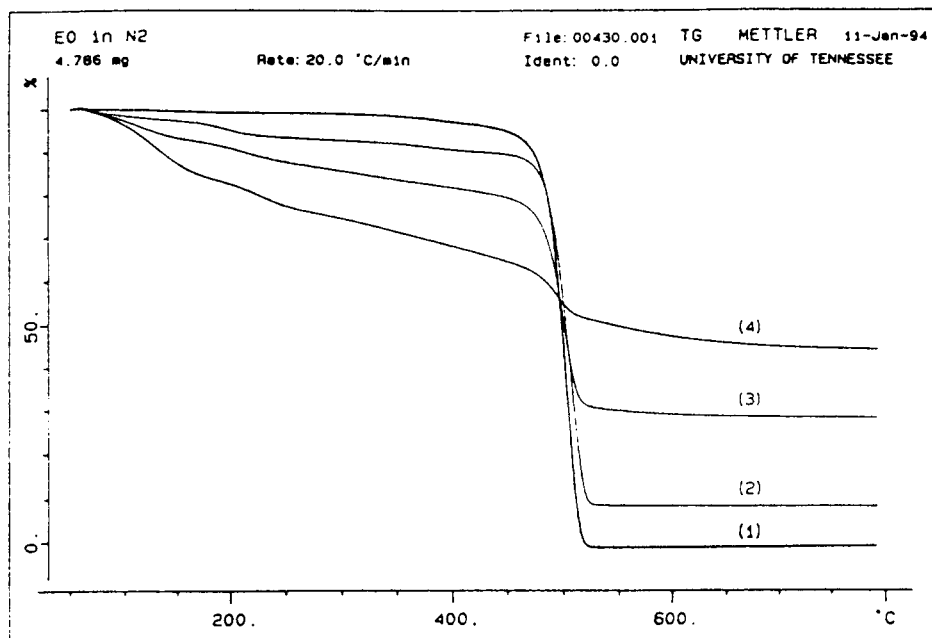
Stabilization Time (min)	Stabilization Temperature (°C) for HOPE/PDPE					
	130	140	150	160	170	180
5	Fail/fail	Fail/fail	—	—	—	—
15	Fail/fail	Fail/fail	Fail/fail	—	—	—
30	Fail/fail	Fail/fail	Fail/fail	Fail/fail	—	—
45	Fail/fail	Fail/fail	Fail/fail	Fail/pass	—/pass	—
60	Fail/fail	Fail/fail	Fail/fail	Pass/pass	—/pass	—/pass
75	Fail/fail	Fail/fail	Fail/pass	Pass/pass	Pass/pass	—/pass
90	Fail/fail	Fail/fail	Fail/pass	Pass/pass	Pass/pass	Pass/pass

progress of stabilization. The endotherm disappeared after sufficient sulfonation due to the penetration and diffusion of sulfuric acid molecules from the surface of the crystals to their center. When crosslinking progressed to the whole fibers, they became infusible for further carbonization. A burning test was carried out by exposing the samples to a match flame. Table II shows the results of burning tests. The stabilized fibers could pass the burning test, whereas other samples failed. Compared with highly oriented polyethylene, the stabilization temperature and time can be reduced for partially drawn polyethylene.

Figure 4 shows the DSC scans for the differences between the highly oriented polyethylene and partially drawn polyethylene. Both the melting temperature and endotherm of melting peak for partially drawn polyethylene are lower than those of highly oriented polyethylene. At the same stabilization conditions, the stabilized extent for partially drawn polyethylene is more than that of highly oriented polyethylene. This can be seen from the different endotherms for partially drawn polyethylene and highly oriented polyethylene. This is due to the same reason as mentioned above, that there are lower crystallinity and folded chain crystals existing in



**Figure 4** DSC scans for differences between highly oriented polyethylene and partially drawn polyethylene. (1) Highly oriented polyethylene; (2) partially drawn polyethylene; (3) HOPE stabilized at 150°C for 60 min; (4) PDPE stabilized at 150°C for 30 min.

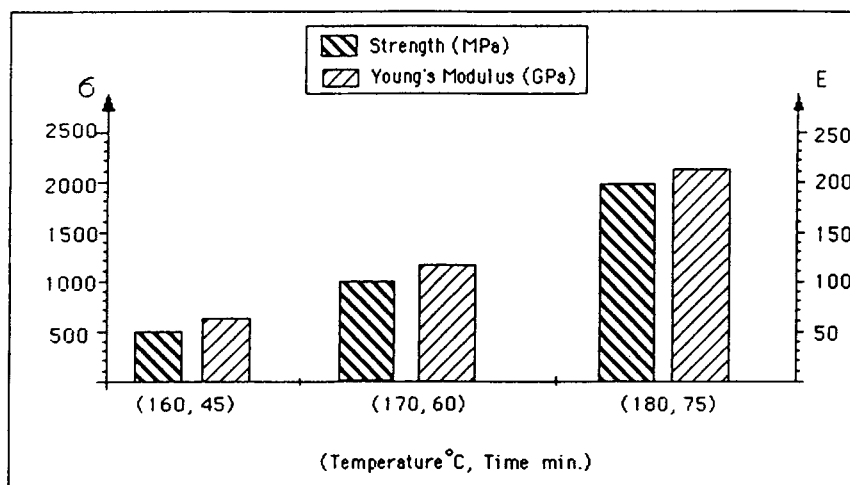


**Figure 5** TGA scans (in nitrogen) of fiber samples stabilized at different temperatures and time. (1) Precursor; (2) 150°C and 30 min; (3) 160°C and 45 min; (4) 170°C and 60 min.

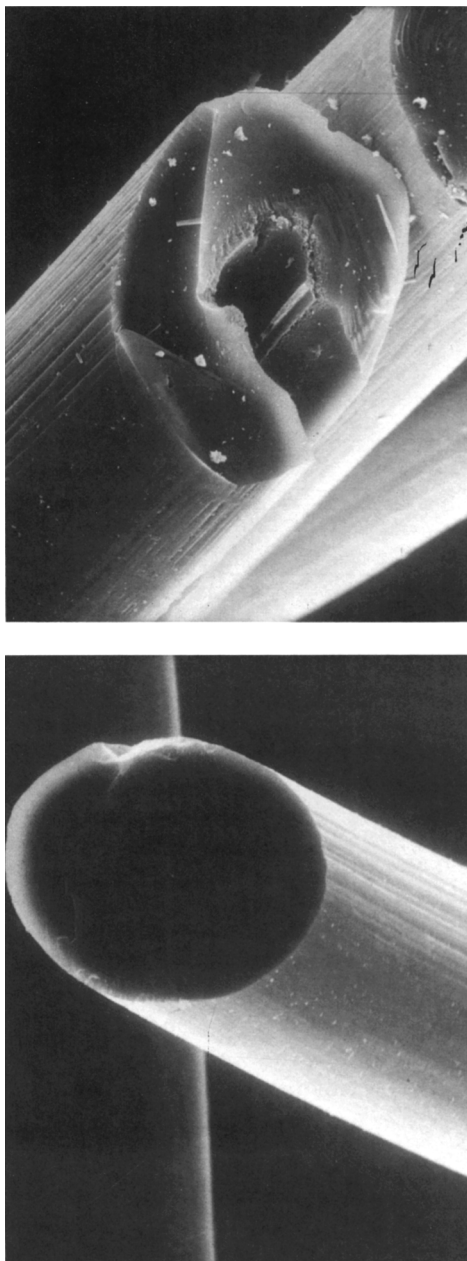
partially drawn polyethylene. The precursor fiber shows a melting peak of 145°C, whereas the partially stabilized fiber decreased in endotherm. Stabilized fibers shows the broadened melting peak and DSC curve became straight for resultant carbon fibers.

TGA scans (Fig. 5) of samples show the weight retention increased with increasing stabilization time and temperature. Decomposition temperature for the polyethylene precursor is about 500°C. Weight retention of the stabilized fibers was about 50% at 800°C in a nitrogen environment. However,

in the case of an air environment, the weight loss was about 100% for all the samples. TGA scans of stabilized fibers in different environments show the differences in weight retention. In a helium environment, the weight retention is 5% higher than that in nitrogen at 800°C. That means carbon yield can be increased for carbonization in a helium environment. However, helium is more expensive than nitrogen. As shown, the weight retention is 0% at 800°C in the case of an air environment due to both oxidation and degradation taking place in the pres-



**Figure 6** Tensile properties of resultant carbon fibers.

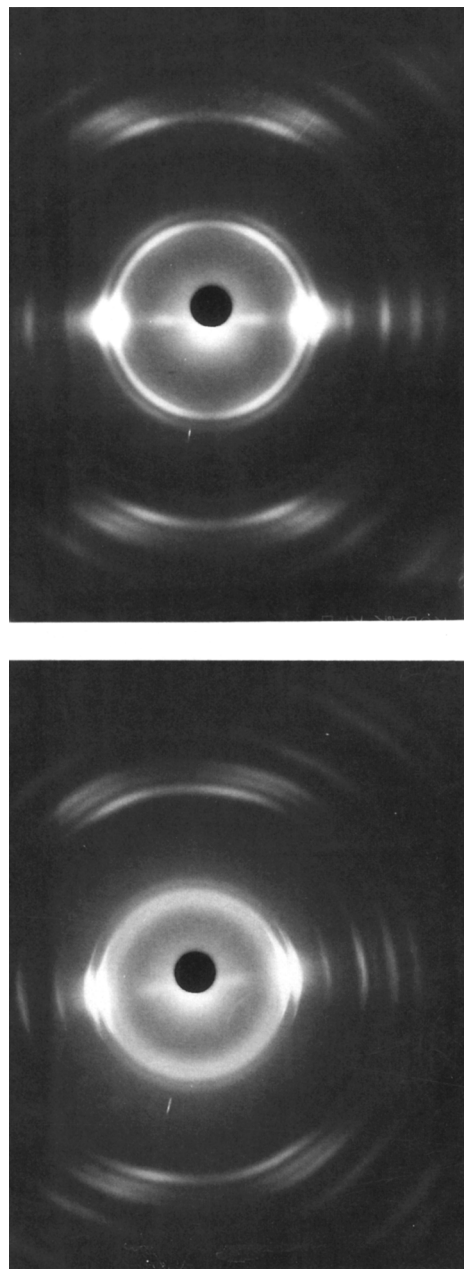


**Figure 7** SEM photographs of resultant carbon fibers from (a) insufficient stabilization and (b) sufficient stabilization.

ence of oxygen at elevated temperature, whereas only pyrolysis took place in nitrogen and helium at elevated temperatures.

Tensile properties of the resultant carbon fibers are shown in Figure 6. There are no significant differences for tensile properties of carbon fibers between the two precursors. The tensile strength and Young's modulus of the carbon fibers reached 2.0 and 200 GPa, respectively, at stabilization time 1 h

and temperature 180°C. The elongation of the carbon fibers at break was less than 1%. It is well established in carbon fiber literature that two types of carbon fibers have been obtained depending on the temperatures of carbonization.<sup>5</sup> Type I fibers are graphitized at temperatures above 2500°C so as to yield highly oriented graphite layers. Thus, the type I fiber is a high-modulus fiber. Type II fibers are carbonized at 1000–1500°C to produce maximum strength. Therefore, the tensile properties of the



**Figure 8** X-ray diffraction photographs of fiber samples: (a) precursor; (b) partially stabilized.

polyethylene-based carbon fibers can be improved by increase in carbonization temperatures beyond the limitation of the carbonization equipment. The properties of the carbon fibers depend not only on the carbonization conditions but also on the stabilization conditions. As seen, tensile strength and Young's modulus of the carbon fibers increased as the stabilization time and temperature increased, resulting in increased extent of stabilization. The carbon fibers from sufficient stabilization (as seen in DSC scans) have good structure and properties, whereas insufficient stabilization results in poor structure and properties of the carbon fibers. Using partially drawn polyethylene precursor results in reduction in stabilization temperature and time.

The SEM photographs show carbon fibers with different degrees of stabilization. As shown in Figure 7(a) and (b), the carbon fiber from sufficient stabilization shows a smooth cross-section (a), whereas the one from insufficient stabilization shows a hole in the cross-section (b), which leads to production of hollow carbon fibers. After sulfonation and carbonization, the surface of the fibers was not smooth any more. The changes in morphology of the fibers during stabilization were documented by WAXD. The X-ray diffraction photographs of the precursor and a partially stabilized fiber are shown in Figure 8 whereas the intensity and the arc lengths indicate the presence of oriented crystals in the precursor fiber, with the progress of stabilization the fiber lost orientation as well as crystallinity. The molecules that involved in reaction do not crystallize, thus resulting in reduced crystallization. The decrease in orientation was due to the lack of sufficient tension during stabilization to prevent the relaxation of

chains from partially melted crystals. Therefore, tension is being controlled in stabilization and carbonization so that a polyethylene-based carbon fiber with excellent tensile properties may be produced.

## CONCLUSION

It was shown that carbon fibers can be manufactured from partially drawn polyethylene and highly oriented polyethylene precursors. Both precursor fibers can be stabilized by sulfonation and the stabilization time decreased to 45 min from 130 to 170°C compared with highly oriented polyethylene fibers. The stabilized fibers can be carbonized at 1100°C for 2 min. Tensile properties of the carbon fiber, at this stage, were reasonably good with tensile strength of 2 GPa and Young's modulus of 200 GPa. The elongation at break was less than 1%. These precursors are quite promising and, by controlling tension during stabilization, carbon fibers with superior mechanical properties may be produced.

## REFERENCES

1. S. Horikiri, *U.S. Pat.* 4070446 (1978).
2. A. R. Postema, H. De Groot, and A. J. Pennings, *J. Mater. Sci.*, **25**, 4216 (1990).
3. D. Zhang, *J. Thermopl. Comp. Mater.*, **6**, 38 (1993).
4. D. Zhang, *J. Polym. Polym. Comp.*, **2**, 159 (1994).
5. R. Moreton, W. Watt, and W. Johnson, *Nature*, **213**, 690 (1967).

*Received March 4, 1996*

*Accepted March 12, 1996*