

# Thermal characterization of sulfonated polyethylene fibers<sup>1</sup>

Dong Zhang\* and Gajanan S. Bhat

*Textile Materials Research Laboratory, The University of Tennessee, Knoxville, TN 37996 (USA)*

(Received 16 November 1992; accepted 20 April 1993)

## Abstract

Earlier work has shown that sulfonation results in an increase in the melting range of polyethylene fibers. Sulfonation of polyethylene fibers is also reported as a means of stabilization for high temperature treatments. In this study, sulfonation of some highly ordered and oriented polyethylene fibers was carried out to make the fibers infusible. The fibers were treated in concentrated sulfuric acid at different temperatures for varying lengths of time. The changes taking place in the precursor fibers treated under different conditions were investigated by differential scanning calorimetry and thermogravimetric analysis. Fibers treated for sufficient lengths of time showed no melting or recrystallization and retained up to 50% of their weight at 800°C. It was also observed that tension plays a major role in determining the structure and properties of the sulfonated fibers.

## INTRODUCTION

Polyethylene fibers with extremely high strength and modulus are produced from ultra high molecular weight (UHMW) polyethylene, with molecular weights over a million. The fibers are produced from a special gel-spinning technique [1]. Being relatively expensive with superior mechanical properties, these fibers are used mainly for composite applications. The main drawback of these fibers is their lower melting temperature.

Polyethylene fibers were investigated as carbon fiber precursors because of their high carbon content [2]. A highly ordered and oriented polyethylene fiber produced from UHMW polymer has additional advantages as a carbon fiber precursor due to the superior mechanical properties of the starting fiber, which is likely to result in a superior quality carbon fiber. Treatments with sulfuric acid or chlorosulfonation have been investigated

---

\* Corresponding author.

<sup>1</sup> Presented at the 21st Annual NATAS Conference, Atlanta, GA, 13–16 September 1992.

as a means of making the easily meltable polyethylene fibers infusible, so that they can be subsequently carbonized [2, 3]. Interest in chlorosulfonation of superstrong polyethylene fibers has also been in improving the adhesion of these fibers to various matrices by surface modification [4].

The effect of treating in chlorosulfuric acid has been seen in changes in mechanical properties as well as in melting behavior. An increase in the melting temperature has been observed at the initial stages of chlorosulfonation [4]. In the present study, polyethylene fibers with high order and orientation were treated in concentrated sulfuric acid for varying intervals of time at different temperatures. The treated fibers were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in order to understand the changes taking place in the structure of the fibers.

## EXPERIMENTAL

Commercially available ultra high molecular weight polyethylene fibers produced by Allied Fiber Company, Petersburg, VA, were used. Three grades of the fiber, with different fiber diameters (33, 45 and 63 microns) were investigated. The fibers were treated in a concentrated (95%) sulfuric acid bath at different temperatures, ranging from 130 to about 200°C. To prevent melting, the fiber samples were inserted into bath at 130°C and then the temperature was increased in steps of 10°C every 15 min. After treating for the required length of time, the samples were taken out, washed for 30 min in running tap water and dried in an oven at 60°C for 90 min.

To study the effect of tension, the filaments were wrapped as a loop around a stiff steel wire bent in the shape of a C. Although this constraint did not completely prevent shrinkage, the change in dimension was limited with development of tension during the treatment. In the unconstrained case, the sample loops were inserted into the sulfuric acid bath with full freedom to shrink.

The as-supplied fiber and the sulfonated fibers (treated at different temperatures and to varying lengths of time) were characterized by DSC and TGA. A Mettler TA4000 thermal analysis system with DSC25 and TG50 was used for the analysis. DSC scans were made with heating and cooling rates of 10°C min<sup>-1</sup>. TGA scans were made at heating rates of 5, 10, 20 and 100°C min<sup>-1</sup>. Samples were purged with nitrogen or air during scanning and the effect of purge environment was also compared.

The change in color of the samples on sulfonation was observed and recorded as white, light yellow, yellow, gray or black. The burning behavior of the fibers treated to different extents was tested by exposing them to a match flame. The results were recorded as either fail or pass depending on whether they burned or not when exposed to the flame.

## RESULTS AND DISCUSSION

DSC scans of polyethylene fibers treated for different lengths of time are shown in Figs. 1–4. Figures 1 and 2 show the heating curves in nitrogen and air, respectively. Curve (1) is for the precursor in all four figures. With

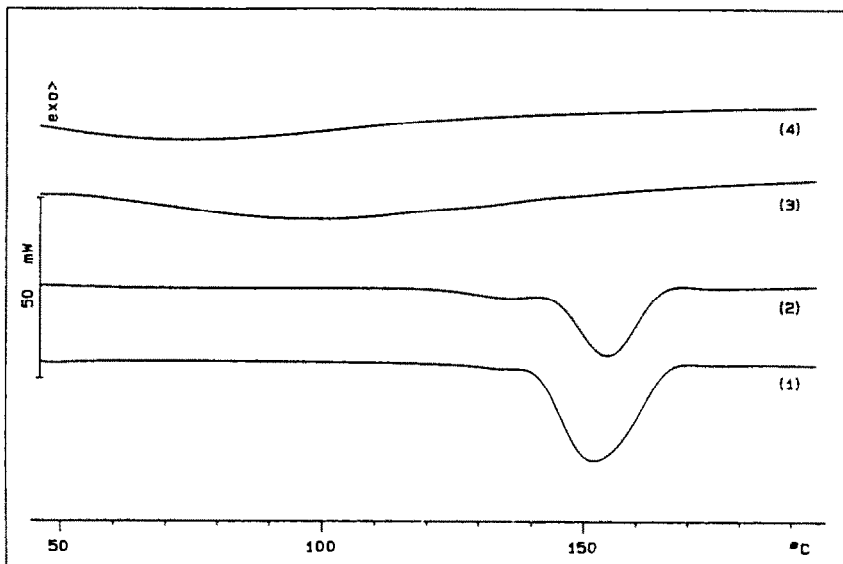


Fig. 1. DSC scans for heating in nitrogen for different fibers: (1) polyethylene; (2) treated till 150°C and 60 min; (3) treated till 160°C and 75 min; and (4) treated till 180°C and 105 min.

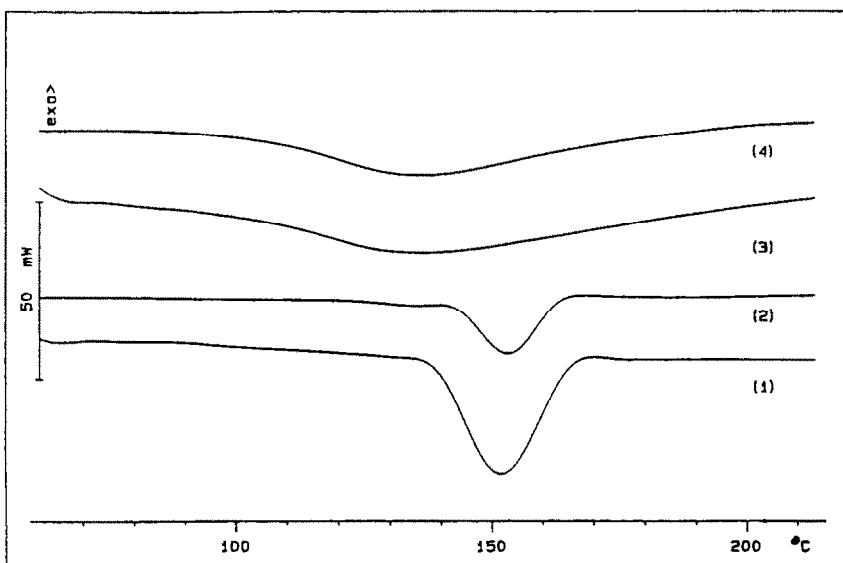


Fig. 2. DSC scans during heating in air for different fibers: (1) polyethylene; (2) treated till 150°C and 60 min; (3) treated till 160°C and 75 min; and (4) treated till 180°C and 105 min.

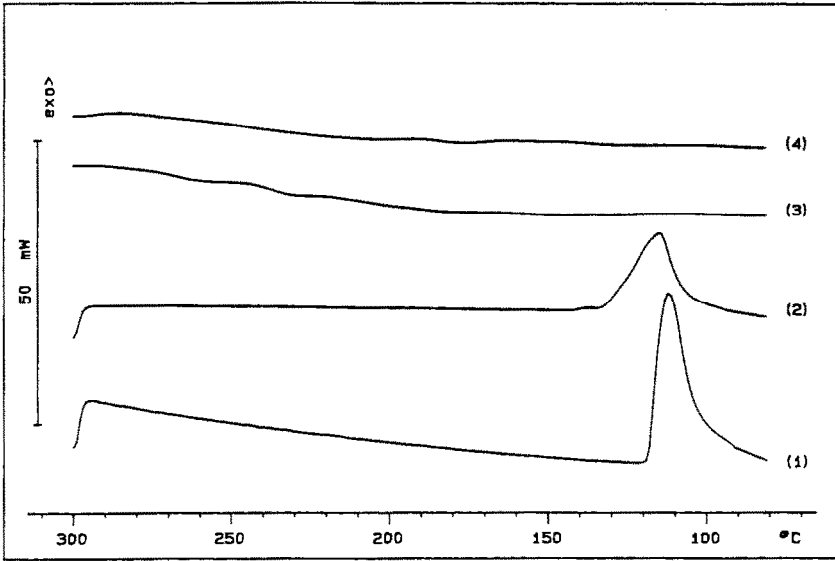


Fig. 3. DSC scans during cooling in nitrogen for different fibers: (1) polyethylene; (2) treated till 150°C and 60 min; (3) treated till 160°C and 75 min; and (4) treated till 180°C and 105 min.

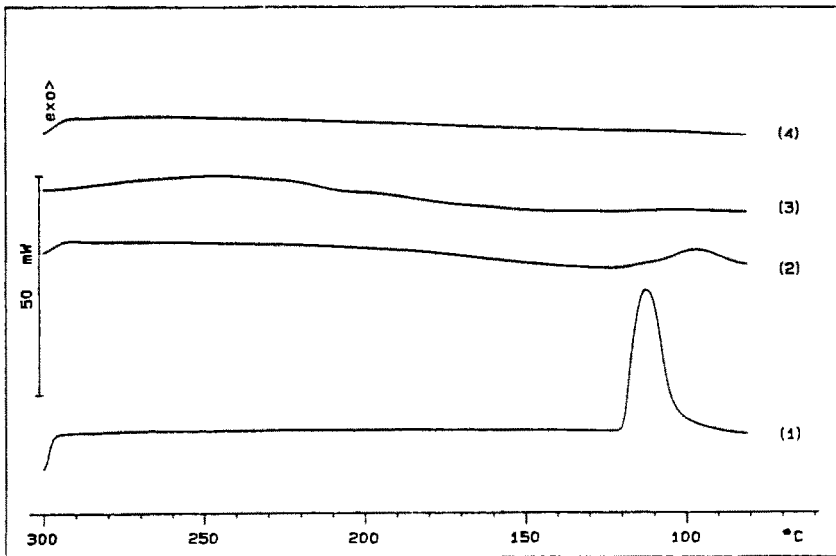


Fig. 4. DSC scans during cooling in air for different fibers: (1) polyethylene; (2) treated till 150°C and 60 min; (3) treated till 160°C and 75 min; and (4) treated till 180°C and 105 min.

continued treatment in the sulfuric acid bath, there is a broadening of the melting peak accompanied by reduction in the enthalpy of melting. DSC data indicate that the fiber becomes stabilized in about 75 min and at 160°C: the melting endotherm is not seen for these samples. The disappearance of the melting peak indicates that most of the polyethylene segments have participated in the crosslinking reaction.

Figures 3 and 4, which show the crystallization during cooling, better reflect the extent of reaction that has taken place. If the polymer segments are already reacted, they reduce the crystallization potential, thereby reducing the enthalpy of crystallization. Samples that are completely stabilized do not show any crystallization peak. The trend seen in melting behavior is also seen in crystallization, i.e., with continued treatment, the crystallization peak disappears. There was a difference in the scans in the presence of air or nitrogen. When scanned in air, the samples showed the disappearance of the crystallization peak at a shorter treatment time (or lower treatment temperature) compared to the DSC scans in nitrogen for the same samples. This is due to the fact that during scanning in the presence of air, there is a continuation of the stabilization reactions, leaving fewer unreacted segments to crystallize. However, in an inert environment, or in the absence of oxygen, stabilizing reactions do not continue on heating. This observation indicates that the partially stabilized fibers may be heated in air under suitable conditions to continue the reactions further.

Figure 5 shows the TGA scans (in nitrogen) of the samples. The TGA

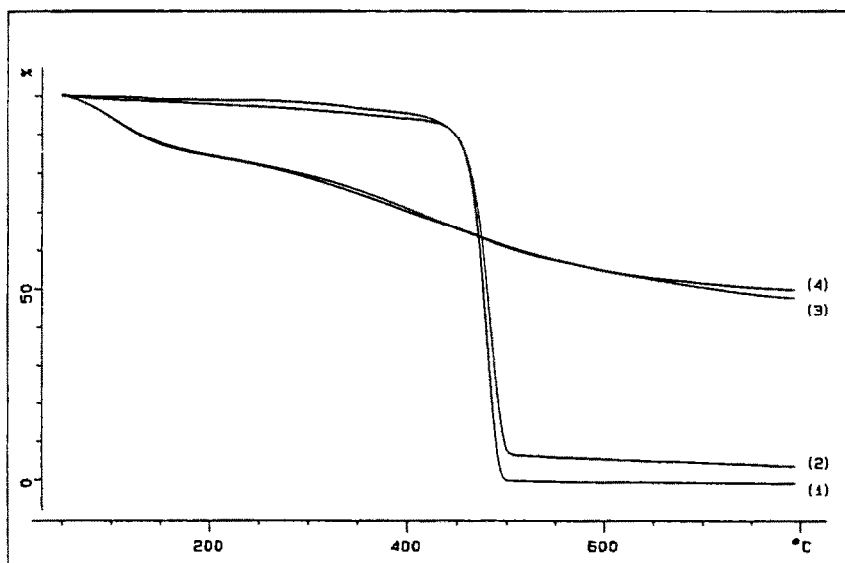


Fig. 5. TGA of fibers scanned in nitrogen: (1) polyethylene; (2) treated till 150°C and 60 min; (3) treated till 160°C and 75 min; and (4) treated till 180°C and 105 min.

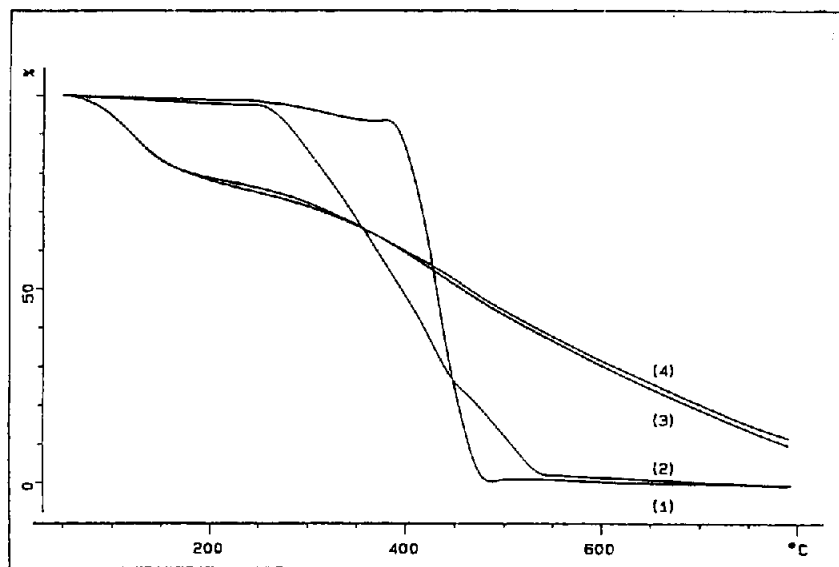


Fig. 6. TGA of fibers scanned in air: (1) polyethylene; (2) treated till 150°C and 60 min; (3) treated till 160°C and 75 min; and (4) treated till 180°C and 105 min.

results are consistent with the DSC observations: the weight loss decreased on treating the fiber in sulfuric acid. The weight loss of the stabilized fiber was about 50% at 800°C. It is also to be noted that there was a weight gain of up to 80% during stabilization, which results in a high carbon yield based on the precursor. The TGA scans of the same fibers in air (Fig. 6) show that the samples lost most of the weight due to oxidation with no material remaining after 800°C. In both air and nitrogen, the precursor and the partially stabilized fiber lose weight over a narrow temperature range, while the well-treated fibers lose weight continuously.

TGA scans of a partially stabilized sample scanned in nitrogen at different heating rates are shown in Fig. 7. The higher the heating rate, the lower the weight loss. At a heating rate of 5°C min<sup>-1</sup>, the stabilized fiber lost about 65% of its mass, while at a scanning rate of 10°C min<sup>-1</sup>, weight loss was less than 55%. The differences between heating rates of 10, 20 and 100°C min<sup>-1</sup> were marginal. The results indicate that the samples are not very sensitive to heating rate, unless the rates are lower than 10°C min<sup>-1</sup>. This also has a consequence in that the rate of heating to higher temperatures of processing, such as carbonization, will have an effect on the yield as well as on the structure and properties of the processed fiber.

Changes in color and the results of the burning test for a fiber with the progress in stabilization are shown in Table 1. These observations are consistent with the results from DSC and TGA. Although samples turned black after about 45 min treatment, they did not pass the flame test. The fibers became infusible after approaching 160°C or in about 60 min

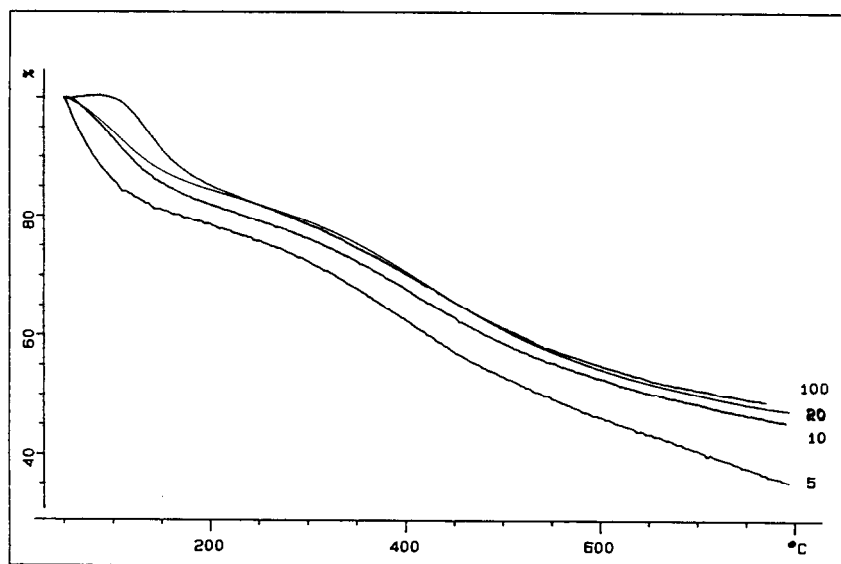


Fig. 7. TGA of a partially treated fiber scanned in nitrogen at different heating rates.

treatment time. If the temperature is not increased, it will take several hours due to the slower reaction kinetics, as shown by the isothermal treatment [5]. At 140°C the samples needed a treatment time of at least two hours to pass the burning test, while at 130°C, even after two hours of sulfonation, the samples continued to burn on exposure to a match flame, indicating that the samples were not completely stabilized. Increasing the treatment as the fibers become slightly stable is very important. However, to start with, it is necessary that the treatment temperature be lower than the temperature at which the fiber starts to melt.

TABLE 1

Color changes and burning test results

Sample description		Color	Burning
Max. temp./°C	Total time of treatment/min		
130	15	Light yellow	Failed
140	30	Grey	Failed
145	45	Black	Failed
150	60	Black	Failed
160	90	Black	Passed
180	120	Black	Passed
200	150	Black	Passed

### Effect of tension

Because the fibers used had an extremely high level of order and orientation, they had a tendency to shrink at the higher temperatures of treatment used in this study. The results shown so far were from fibers treated under some dimensional constraint, which did not allow large levels of shrinkage. To really observe the effect of not allowing any tension to develop, some fibers were treated in the sulfuric acid bath without any dimensional constraint. Those samples showed large shrinkage, sometimes even losing the fiber form. Figure 8 compares the DSC scans of a partially treated fiber with and without constraint. The fibers treated without constraint show two melting peaks at the intermediate stage of stabilization, although both peaks disappeared on continued treatment. The additional melting peak which appeared at a lower temperature is due to the formation of folded chain crystals, which were formed due to the partial melting and recrystallization of some of the extended chain crystals during the process of sulfonation.

To confirm that the observed double melting peak is due to changes in the crystalline structure as a result of thermal effects, and that treatment with sulfuric acid has nothing to do with it, some annealing studies were made. Figure 9 shows the DSC scans of the original fiber, two samples which were preheated for 10 min at 150 and 160°C, and the reheating of the earlier scanned precursor sample. The sample preheated at 150°C show only one peak corresponding to extended chain crystals indicating that at that temperature and time there was not enough melting and relaxation

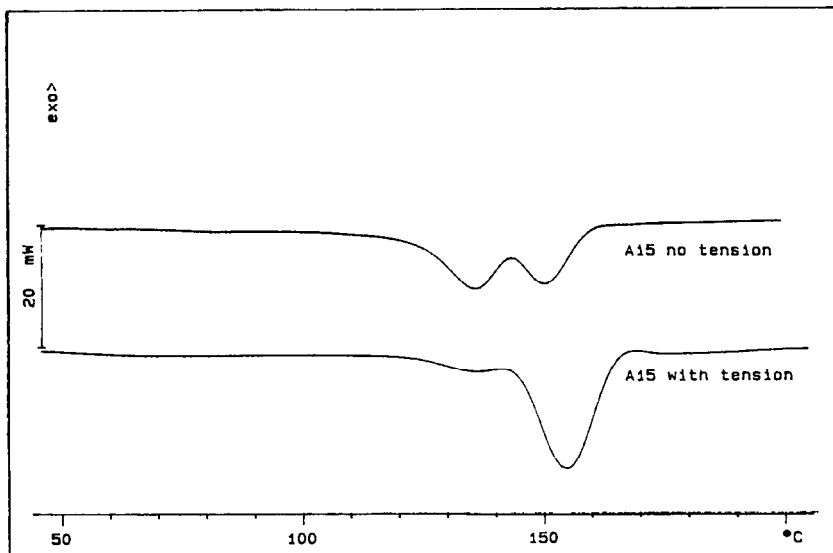


Fig. 8. DSC scans of a fiber partially treated with and without tension.



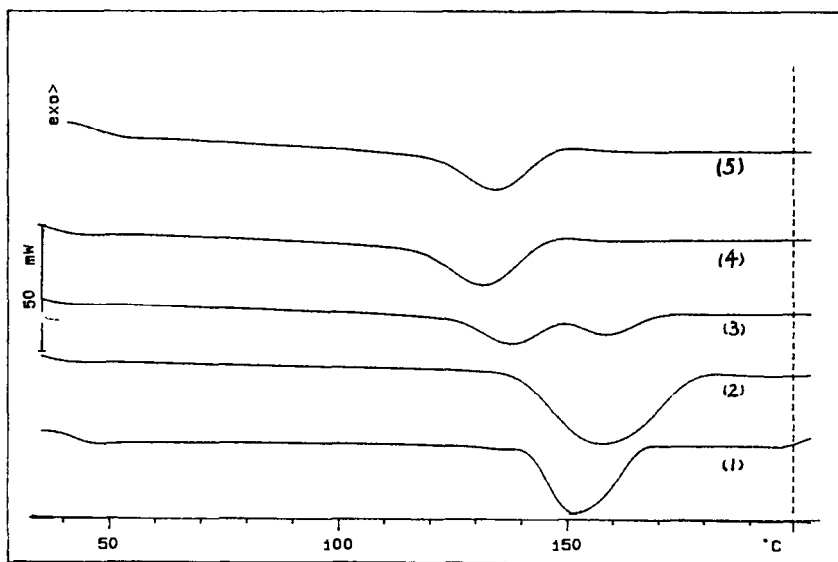


Fig. 9. DSC scans of: (1) polyethylene fiber; (2) annealed at 150°C for 10 min; (3) annealed at 160°C for 10 min; (4) annealed at 160°C for 30 min; and (5) reheating of sample 1.

taking place. The samples annealed at 160°C for 10 min show two melting peaks indicating the partial melting and recrystallization in the folded chain form. However, prolonged heating at 160°C resulted in a single peak with a lower melting temperature. Again, in the case of reheating, because the sample was completely melted and recrystallized in the DSC capsule without any tension, only one melting peak is observed at the lower temperature. This is because, in the absence of tension, the molten polyethylene could only recrystallize in the lower-melting folded chain form.

## CONCLUSIONS

Highly ordered and oriented polyethylene fibers became infusible on heating in sulfuric acid for a sufficient time. The temperature had to be increased slowly from below the melting point of the fiber, as the fiber was sulfonated, to increase the rate of reaction. DSC scans of the sulfonated fibers did not show any melting or crystallization peaks. In the case of partially treated fibers, a lower crystallization enthalpy was seen during scanning in air due to continued reaction during the measurement. TGA showed that the sulfonated fibers lost only 50% of their weight, while the precursor had shown complete loss of material. The effect of tension or dimensional constraint during the sulfonation treatment was seen to be very important. In the absence of any dimensional constraint, the fibers shrank considerably. This shrinkage was accompanied by changes in the crystalline

structure of the fibers. A portion of the extended chain polyethylene crystals melted and recrystallized in the folded chain form resulting in double melting peaks in the partially treated fibers without any dimensional constraint. This high level of relaxation is likely to result in poor mechanical properties as the effect of higher orientation in the precursor cannot be taken advantage of.

#### REFERENCES

- 1 G.C. Weeden and T.Y. Tam, *Modern Plastics*, 63(3) (1986) 63.
- 2 S. Horikiri, US Patent 4 070 446, 1978.
- 3 A.R. Postema, H. De. Groot and A.J. Pennings, *J. Mater. Sci.*, 25 (1990) 4216.
- 4 A.R. Postema and A.J. Pennings, in A.E. Zachariades and R.S. Porter (Eds.), *High Modulus Polymers*, Marcel Dekker, New York, 1988, p. 431.
- 5 D. Zhang, M.S. Thesis, The University of Tennessee, Knoxville, TN, 1992.