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CARBON FIBERS FROM ORIENTED POLYETHYLENE PRECURSORS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Dong Zhang

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DEDICATION

The author would like to dedicate the paper to his parents in Tianjin, China: Mr. and Mrs Binyue Zhang and to his brother Dr. Biao Zhang at Purdue University for their continuous support.

ABSTRACT

Oriented polyethylene precursors possess extraordinary physical and mechanical properties and a very high carbon content. However, being thermoplastic fibers, they soften and melt at a fairly low temperature, losing their fiber form. The key to success for producing carbon fibers from polyethylene is to introduce crosslinks and make them stable to higher temperatures of carbonization.

In this research, an effort was made to produce carbon fibers from a highly ordered and oriented polyethylene fiber. Sulfonation of the fiber was studied as a method of stabilizing this thermoplastic fiber for higher temperatures required for carbonization. The effect of time, temperature and tension during sulfonation was studied systematically. The progress of reactions and the extent of stabilization were studied by thermal analyses (Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)), burning behavior and color change. Other techniques, such as wide angle x-ray diffraction, fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and optical microscopy were used to investigate the changes in structure and morphology of the fibers with stabilization treatment. Also the physical properties of the carbon fibers produced from these precursors were investigated.

It also shown that highly ordered and oriented polyethylene precursor fibers could be stabilized in sulfuric acid bath between 140 to 160 ^{0}C after treating for about 75 minutes. DSC studies showed that the melting peak of the stabilized fibers had completely disappeared. TGA indicated that the stabilized fibers retain 50% of their weight at 800 ^{0}C, when scanned in a nitrogen environment. The oriented fibers had a strong tendency to shrink before the onset and progress of reactions, and the tension applied during stabilization had a major role in determining the morphology of the stabilized fibers. In the absence of tension, some of the extended chain polyethylene apparently changed to a folded chain structure giving two melting peaks. SEM photographs clearly showed the formation of kink bands due to shrinkage.

The stabilized fibers were carbonized at 1150 ^{0}C for a four minutes in a nitrogen atmosphere. The carbon yield of the fibers was about 70-80% and the carbon content of the fibers was more than 92%, as seen by elemental analysis. The resultant carbon fibers had good mechanical properties, i.e. a tensile strength of 2.1 GPa and Young's modulus of 210 GPa. The elongation of the fiber at break was less than 1%.

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CHAPTER I

INTRODUCTION

Carbon fibers are manufactured by the controlled pyrolysis of organic precursors in fibrous form. Commercial products are based on rayon (or regenerated cellulose), pitch (petroleum and coal tar-based), and PAN (polyacrylonitrile). It is well established in carbon fiber literature that the mechanical properties of the carbon fibers are improved by increasing the crystallinity and orientation, and by reducing the defects in the fiber. The best way to achieve these enhancements is to start with a highly oriented precursor and then try to maintain the initial high orientation of the molecular chains during the process of stabilization and carbonization by applying the necessary tension. Highly ordered and oriented polyethylene fibers like Spectra are available today, with mechanical properties much higher when compared to polyethylene itself or any other organic fiber. If these properties can be translated into the final carbon fiber by careful control of the process, it is conceivable that carbon fibers with excellent mechanical properties can be obtained. The purpose of using different precursors than those normally used today, which produce carbon fibers with poor compressive strength, may help in producing carbon fibers with better compressive properties.

Polyethylene has excellent characteristics which make it useful as a starting material for producing carbon fibers. It has an easily spinnable property and a very high carbon content. However, being a thermoplastic fiber, it softens or melts at around 140 ^{0}C, thereby, losing its fiber form. The key to success in producing carbon fibers from polyethylene is to introduce cross-links and make the polyethylene fiber stable to the higher temperatures required for carbonization.

As it was suggested in the patent [1] by Horikiri et al, polyethylene can be stabilized by heating in a bath containing concentrated sulfuric acid, chlorosulfonic acid or fuming sulfuric acid. The stabilized fiber can be carbonized in an inert environment at a temperature above 1000 ^{0}C. It is claimed that carbon fibers with good mechanical properties can be produced by stabilizing polyethylene in this manner and then carbonizing at 1200 ^{0}C. Postema et al. [2], produced amorphous carbon fibers from linear low density polyethylene by stabilization with chlorosulfonic acid. Being an amorphous carbon fiber, its tensile strength was around 1.15 GPa with a 3% elongation-at-break. Further research was not carried out in this area and, at present, polyethylene is not a precursor for commercial carbon fiber production.

This research is a study to determine the feasibility of producing carbon fibers starting from highly ordered and oriented polyethylene fibers (spectra). Stabilization was carried out using a hot sulfuric acid bath. The progress of

stabilization with different time and temperature of treatment, along with or without tension was studied. The stabilized fibers were subsequently carbonized and characterized by their mechanical and structural properties.

CHAPTER II

LITERATURE REVIEW

2.1 Historical Review

Carbon can occur in three forms [3], i.e., diamond, graphite, and amorphous (or glassy) carbon. However only the crystalline forms have high modulus. Diamond has a three dimensional covalent bonded structure (Figure 1) [3] and graphite has a two dimensional covalent bonded structure. In the graphite structure, the carbon atoms are arranged in the form of hexagonal layers (Figure 2) [3].

The high strength covalent bond between carbon atoms in the layer planes of graphite results in an extremely high modulus, while the weak van der Waal-type bond between the neighboring layers results in a lower modulus in that direction. To obtain high modulus and strength, the layer planes of graphite have to be aligned parallel to the axis of the fiber. In practice, the crystalline units are very small and imperfectly aligned; they contain many faults and defects. Figure 3 [4] shows a schematic representation of the structure of carbon fiber. Note the layers showing the hexagonal units. The term "graphite fiber" is used to describe fibers that have a carbon content in excess of 99%, whereas the term "carbon fiber" describes fibers that have a lower carbon content of 80--95%. The carbon content is a function of the heat

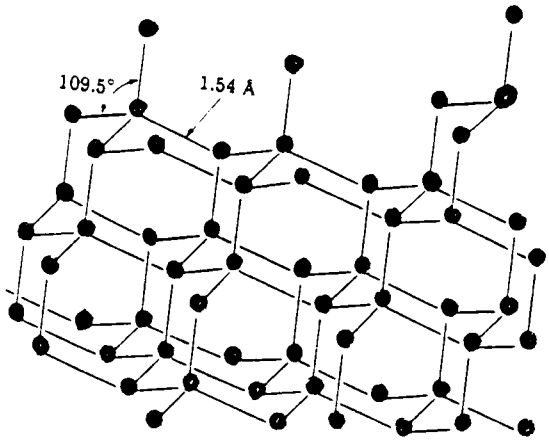


Figure 1. Three Dimensional Covalent Bonded Structure for Diamond [3].

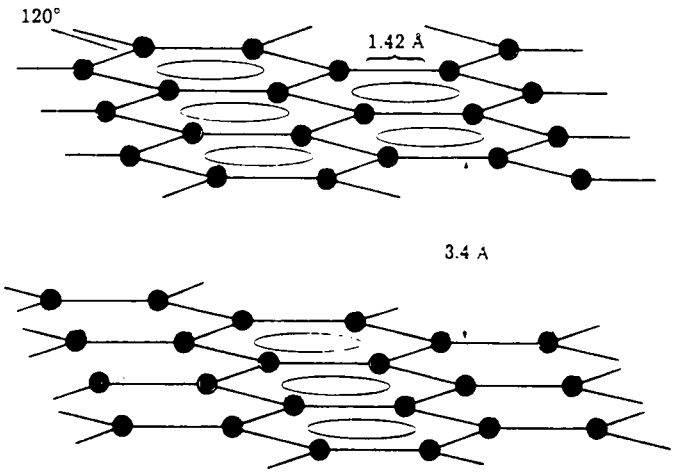


Figure 2. Two Dimensional Covalent Bonded Structure for Graphite [3].

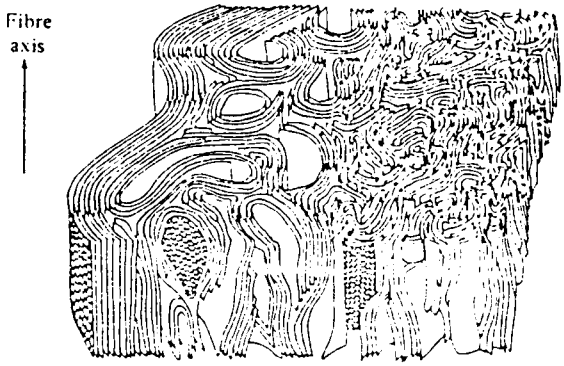


Figure 3. Schematic Representation of Carbon Fiber Structure [4].

treatment process. The currently available carbon fibers are produced from rayon, polyacrylonitrile (PAN) and petroleum or coal tar pitch.

Commercially two types of carbon fibers are produced [5]: Type 1 and Type 2. Type 1 fibers have been graphitized so as to yield highly oriented graphitic layers. Thus Type 1 is a high modulus type. Type 2 fibers have been carbonized to produce enhanced tensile strength. Generally, the fiber modulus increases with the heat treatment temperature, but the strength peaks at some intermediate temperature (Figure 4) [5]. Carbon fibers are also produced from petroleum or coal tar pitch. The molten pitch is spun to produce continuous filaments. During the spinning process, the hydrodynamic effects in the orifice result in substantial orientation of

planar molecules. Because of this, meltblown nonwovens of carbon fibers become possible. Because of low weight and high strength and modulus, carbon fibers find many applications in the aerospace industry. Other applications of carbon fibers are listed in Table I [6].

The current technology for producing carbon fibers generally involves the thermal decomposition of various organic precursors. Carbon fibers based on rayon (or cellulose) were first investigated as long ago as in 1880. It was during this year that Thomas Edison first patented his incandescent lamp [7]. The filaments that he used in the lamp were made of carbon that had been produced by pyrolyzing

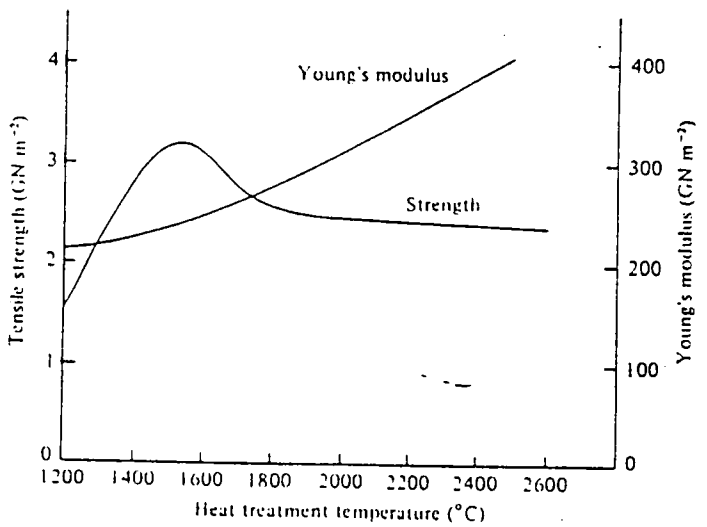


Figure 4. Strength and Modulus of Carbon Fibers with Treatment Temperature [5].

TABLE I. APPLICATIONS OF CARBON FIBERS [6].

1. Brakes, aircrafts, industrial, automotives, racing, carbon fiber composites
2. Friction materials, clutch plates
3. Packings, gaskets, high-temperature insulation
4. Plastics-carbon fiber composites with thermoplastics and thermosets; injection, reaction injection, and compression molding; reinforcement, shielding, conductance, fatigue enhancement
5. Electrostatic dissipants; garments, fabrics, yarns, carpets; composites, circuit board, electric equipment, operating room furniture
6. Electromagnetic shielding, communication equipment, computers, typewriters, telephones, military nuclear blast protection
7. Ablations and ablation coatings and paints
8. Battery electrodes
9. Filler materials
10. Cement reinforcement
11. Conductive paints
12. Synthetic graphite
13. Heating tapes, strips, walls
14. Fire retardation, fire protection equipment, clothing

natural or regenerated cellulose fibers. These carbon fibers were very fragile; they contained numerous pores and were susceptible both to forming "hot spots" and to high-temperature oxidation. In an attempt to overcome these difficulties and extend the life expectancy of the fibers, methods for applying paralytic coatings to the fibers were developed. Over the next 30 years, numerous process patents [8,9] were granted for paralytic coatings, the last going to Whiteney [10] in 1909. At about this time, however, lamps with flexible tungsten fibers became available and interests in carbon fibers dropped significantly. It was not until the mid-1950's that interest in fibrous carbon was again revived. At this time, Soltes [11] and Abbott [12] developed processes for converting both natural cellulose and rayon into fibrous carbon materials. Essentially, the carbon fibers were produced by heat treating the precursor to temperatures of the order of 1000 ^{0}C (1832 ^{0}F) in inert atmospheres. It was discovered that the tensile strengths of these fibers were as high as 40 Ksi (275 MPa) [13]. The driving force behind this renewed interest in carbon fibers was the search for superrefractory reinforcing agents to be used in ablative composites for rocket and missile components. It was also recognized that carbon fibers could be used for a variety of other applications such as resistance heaters; filters for hot, corrosive gases and liquids; reinforced plastics; thermal insulation; and nuclear moderators. In 1959, Union Carbide

Corporation began production of carbon cloths, felts, yarns, and battings using rayon fibers as the precursor materials [14,15]. The carbon fibers were "batch processed" by heat treating the rayon precursors in inert atmospheres at about 900 ^{0}C (1652 ^{0}F), followed by graphitizing the fibers at temperatures greater than 2500 ^{0}C (4532 ^{0}F). The fibers produced by this method possessed tensile strengths between 48 and 130 Ksi (330 and 900 MPa).

In 1960, the potential elastic properties obtainable from highly ordered graphite crystals were demonstrated when Bacon [16] reported on the growth, structure, and properties of graphite whiskers grown in a DC arc at about 3600 ^{0}C (6512 ^{0}F) under the pressure of 92 atm. He showed that when the graphite basal plane (0002) is oriented parallel to the whisker axis, tensile strengths in excess of 3 Msi (20 GPa) and tensile modulus of elasticity values over 100 Msi (690 GPa) were possible. The theoretical maximum tensile modulus of elasticity for graphite parallel to the basal plane is 146 Msi (1000 Gpa) [17]. Methods for obtaining the high degree of preferred orientation in the fibers necessary for the high tensile strength and modulus values were subsequently investigated by a number of researchers. In 1967, a continuous process for making rayon-based carbon fibers was patented by Bacon et al [18]. This development resulted in commercial scale production of continuous lengths of carbon fibers having tensile strengths between 100 and 150 Ksi (690 and 1030 MPa)

and tensile modulus of elasticity values in the order of 6 Msi (40 GPa). The properties of these fibers, however, were still considerably inferior to those of the graphite whiskers. In 1964 Tang and Bacon [19,20] postulated a mechanism, based on infrared, x-ray, and transmission electron microscopy, that described the thermal degradation of cellulose molecules to carbon and graphite. It was shown that the fiber structure in the graphitized filament was directly related to the molecular structure in the starting materials. The tensile modulus of elasticity increased by a factor of two or three when the precursor filaments were subjected to a 150% stretch prior to carbonization [21]. In addition, it was found [22,23] in 1965 that when stress is applied to the continuous fibers at temperatures in excess of 2500 ^{0}C (4532 ^{0}F), plastic deformation occurs within the fiber, tending to orient the graphite basal planes parallel to the fiber axis (i.e. in the direction of applied stress) and hence significantly increases the tensile modulus of elasticity of the fibers. This development led to the commercial production of high-strength, high-modulus Thornel 25 by Union Carbide Corporation. The average tensile modulus of elasticity of this fiber was 25 Msi (170 GPa), whereas the tensile strength averaged 184 Ksi (1270 MPa). By 1970, it was possible, to obtain commercially available rayon-based carbon fibers (Thornel 75) with a tensile modulus of elasticity of 75 Msi (520 GPa) and a tensile strength of 385 Ksi (2650 MPa).

The use of polyacrylonitrile (PAN) as a precursor material for carbon fibers was first reported in a patent application by Tsunoda [24] in 1960. In that patent, Tsunoda revealed that carbon fibers could be processed from PAN precursors by first crosslinking or "stabilizing" the polymer in an oxidizing atmosphere at 220 ^{0}C (428 ^{0}F) and then heat treating the stabilized fibers at 1000 ^{0}C (1832 ^{0}F) in an inert atmosphere. In 1961, Shindo [25] showed the variation in the tensile strength and modulus of the fibers with heat-treatment temperature and also discussed their electrical properties. Shindo reported values of tensile strength on the order of 80--100 Ksi (500--690 MPa) and tensile moduli of elasticity of 25 Msi (170 GPa). In 1964, Watt and Johnson [26] of the Royal Aircraft Establishment filed a patent for high-strength, high-modulus graphitized fibers based on a PAN precursor. Watt and Johnson had independently developed their process without the knowledge that the work had been done previously by Shindo et al [27]. In 1966, carbon fibers of very high tensile modulus of elasticity--70 Msi (480 GPa) and tensile strength--300 Ksi (2070 MPa)--were reportedly made using a PAN precursor by Prescott and Stendege [28] as well as Watt et al [29-31] and Clark and Bailey [32]. The high tensile modulus of elasticity was attributed to the tension that was applied to the fibers during the early stages of their preparation. Since 1966, numerous other patents [33-35] have been granted for carbon fibers based on PAN precursors. Basically, all of these

processes involve first stretching the PAN precursor to obtain a high degree of molecular orientation of the polymer molecules and then subjecting it to a stabilizing treatment in an oxidizing atmosphere while the fibers are held under tension. Subsequently, the fibers are carbonized at temperatures ranging from 1000 to 3000 ^{0}C (1832 to 6332 ^{0}F). The mechanism of stabilization [36-38] as well as the development of the structure and properties [39-44] of carbon fibers have been studied in detail by a number of investigators.

The use of pitch as a precursor material for carbon fibers was reported by a number of investigators [45-47], starting with Otani [48] in 1965. The fibers were generally made by first melt spinning a low-cost, isotropic molten pitch or similar petroleum product and then oxidizing the as-spun filaments. This treatment was followed by carbonization at about 1000 ^{0}C (1832 ^{0}F) in an inert atmosphere. The properties of the isotropic, carbonized fibers were generally poor, tensile modulus of elasticity values being approximately 5-10 Msi (35-70 GPa) [49]. Improvements in this process were reported by Otani et al. [50] in 1969 and by Hawthorne et al. [51,52] in 1970 and 1971. By stretching the fibers either during the initial stages of carbonization or at temperatures above 2500 ^{0}C (4532 ^{0}F), a high degree of basal-plane preferred orientation could be induced, and thus tensile strengths as

high as 375 Ksi (2585 MPa) and tensile moduli of elasticity in excess of 70 Msi (480 GPa) could be attained.

In another method published in 1973, pitch was transformed into a liquid-crystalline (mesophase) state prior to spinning into filamentary form [53,54]. The liquid crystals were formed by extended heat treatment at about 400--450 ^{0}C (752--842 ^{0}F) in an inert gas atmosphere [55]. Once the pitch was at least partially converted to the liquid-crystalline state, the material was spun, oxidized, and subsequently carbonized at 1000--3000 ^{0}C (1832--5432 ^{0}F). The fiber obtained in this manner possessed a high degree of preferred orientation due to the formation of the liquid-crystalline state prior to spinning. Depending on the final heat-treatment temperature, the tensile modulus of elasticity values for these fibers could be as high as 100 Msi (690 GPa) [56]. A similar process was described in 1975 by Fujimaki et al. [57]. The mechanism of mesophase formation was discussed in detail by Riggs [58].

Over the past 15 years, carbon fibers have emerged as the main reinforcement fibers for high performance composite materials [59-61]. The development of strong and stiff carbon fibers for a wide range of applications and their use in lightweight structural parts are among the principal technological achievements of this period.

2.2 Production of Carbon Fibers

Carbon fibers are prepared by the controlled pyrolysis of various organic precursors. Rayon, polyacrylonitrile (PAN), pitch, polyesters [62], polyamides [63], polyvinyl alcohol [64], polyvinylidene chloride [65], poly-p-phenylene [66], and phenolic resins [67,68] have all been investigated as potential precursor materials for producing carbon fibers. Commercial products are based on rayon, pitch and PAN. Rayon-based products were developed first. Mesophase pitch-based carbon fibers seem to have important long-term potential. Most of the commercial high strength carbon fibers are produced from PAN.

2.2.1 Carbon Fibers From PAN

Production of carbon fibers from PAN based precursors consists of a low-temperature oxidative stabilization in air followed by high temperature carbonization in an inert atmosphere. Oxidative stabilization is carried out in the range of 200--350 ^{0}C [69] for sufficient time to render the fibers infusible and flameproof. In this stage, polyacrylonitrile becomes cyclized and forms structures as shown in Figures 5 and 6 [69]. Stabilization allows subsequent chemical degradative reactions during carbonization to proceed without collapse of the fiber or its C-C chain orientation. Temperatures below 200 ^{0}C are impractical since very long time periods are required, while temperatures above 300 ^{0}C usually

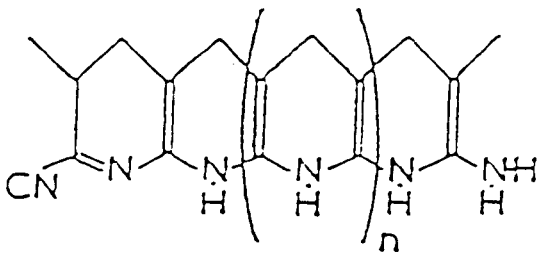


Figure 5. Chemical Structure of cyclized PAN [69].

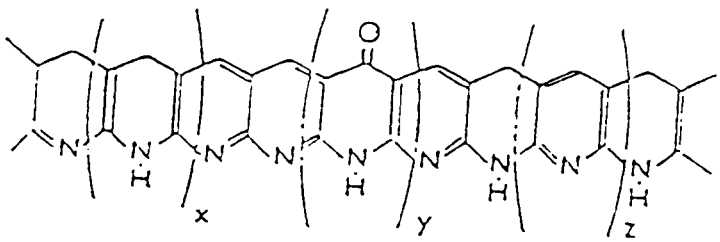


Figure 6. Chemical Structure of Stabilized PAN [69].

cause violent exothermic reactions, resulting in significant weight loss and formation of tarry substances.

Oxidative stabilization is critical to the processing of carbon fibers. Insufficient stabilization can result in "core blow out" during carbonization, yielding hollow carbon fibers of low strength. Proper conditions of rate, time and temperature of heating should be established for optimum stabilization of each precursor. Early workers heated the precursor in air at 220--250 ^{0}C in a batch process. Modern practice is to pass the precursor continuously through an oven divided into several zones with different temperature profiles.

A residence time of 30 minutes to several hours is usually required for complete stabilization. The process is generally carried out in air, although other gaseous media have been explored. Recently it was shown that ammonia in the stabilization environment can reduce the time required for stabilization [69]. But the structures produced from ammonia stabilization were different than that produced by air-only stabilization.

Carbonization of stabilized fibers is carried out in an atmosphere containing inert gases such as nitrogen or argon. The temperature of carbonization is usually decided by the type of application of the resulting carbon fibers. For high strength applications, heating to 1500--1600 ^{0}C is preferred,

while for high modulus applications an additional heat treatment at 2500-3000 ^{0}C is required (Figure 4).

In the 350--1300 ^{0}C range [70], a thermally stable pyridinoid structure is formed which subsequently collapses into a stacked-ring carbon structure to form carbon fiber; the yield is circa 50% based on the precursor. Almost all other noncarbon elements are eliminated as volatiles; only low concentrations of nitrogen remain. These off-gases include substantial amounts of HCN, NH_3, N_2, and H_2O with lesser amounts of CO_2, CO, H_2, and CH_4. Research has shown that there are two principal temperature ranges. In the 350--600 ^{0}C region, the reaction most likely involves those functional groups (chain ends) that do not fit into the condensed ring structure. This leads to some intermolecular cross-linking, which promotes reorganization and coalescence of the cyclized sections and results in evolution of the indicated compounds. In the range of 700--1000 ^{0}C, the main reaction is the intermolecular collapse of the pyridinoid structure. The principal off-gas emission is HCN, with smaller amounts of other nitriles and NH_3.

With increasing process temperature, thermal and electrical conductivity, density, strength, and modulus increase progressively, reflecting increased preferred layer orientation and crystal growth. In the range of 1200--1600 ^{0}C, tensile strength tends to go through a maximum. At 2500 ^{0}C or above for a short time in argon or nitrogen, while still under

tension, some recrystallization occurs. This results in the sliding of the graphite layers over each other and further orientation of the layers parallel to the fiber axis (Figure 7). Although early patents report a relatively long time for carbonization, the modern practice is to pass the stabilized fibers through an increasing temperature profile for a total residence time of only a few minutes.

2.2.2 Carbon Fibers From Cellulose

Carbon fibers from cellulose are obtained by the carbonization of rayon fibers into high-modulus carbon filaments. Rayon is thermosetting, and the carbon yield upon pyrolysis is increased by low temperature oxidation (stabilization) or by heat treatment in the presence of charring agents such as HCl, $ZnCl_2$, or $AlCl_3$. The chemistry of the pyrolysis of cellulose has been investigated by Tang and Bacon [71]. Although the thermal decomposition of cellulose is rather complex, the authors basically distinguish four main stages:

a. desorption of physically adsorbed water (25-150 ^{0}C);

b. dehydration of cellulosic units (150-400 ^{0}C);

c. breakdown of the glucosidic rings (240-400 ^{0}C);

d. formation of the graphite structure (over 400 ^{0}C).

Stage 2 corresponds to an intramolecular process and is concerned with the elimination of OH groups and the formation of C=O and C=C bonds. Thermal cleavages occur during stage 3

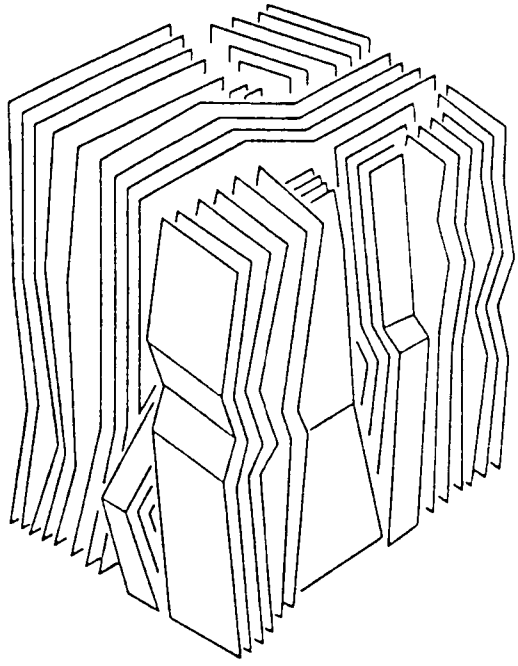


Figure 7. Schematic of Carbon Fiber Structure [70].

and lead to complete breakdown of the cellulosic rings at temperatures higher than 240 ^{0}C. The carbonaceous residue is converted into graphite-like layers by aromatization during stage 4.

The preparation of high-modulus carbon fibers from rayon has been reviewed in detail by Bacon [72] and only a brief description of the important steps is given in this section. During the carbonization of rayon fibers, the original preferred orientation of the cellulosic structure is destroyed and cannot be transferred to an oriented graphitic structure. Even after graphitization of the fibers, there is no preferential orientation of the carbon structure, which consists of entangled ribbons of layer planes about 3nm wide. Longitudinal orientation of the planes may be achieved by graphitization under strain. In fact, carbon yields at temperatures over 2800 ^{0}C, and a straightening of the basal planes is observed in the direction parallel to the applied strain. Elastic moduli as high as 500 GPa can be obtained by stretch graphitization of rayon-based carbon fibers. However, the main disadvantage of this process is the technical difficulty inherent in strain graphitization, which leads to high manufacturing costs.

2.2.3 Carbon Fibers From Pitch

Carbon fibers made from spinning of molten pitches are of interest because of the high carbon yield from the precursors

and the relatively low cost of the starting materials. Processes have been developed with isotropic pitches and with anisotropic mesophase pitches, respectively.

2.2.3.1 Isotropic Pitch

The isotropic pitch or pitch-like material is melt-spun at high strain rates to align the aromatic molecules parallel to the fiber axis [73]. The thermoplastic fiber is then rapidly cooled and carefully oxidized at a low temperature (<100 ^{0}C). The oxidation process is rather slow, to ensure stabilization of the fiber by crosslinking and rendering it infusible. However, upon carbonization, relaxation of the aromatic molecules takes place, which gives carbon fibers with no significant preferred orientation. Hence, as with rayon-based carbon fibers, stress is found to be advantageous during the heat treatment (1500-2200 ^{0}C) to obtain a significant increase of the elastic modulus. The process is:

a. Molten pitch spinning;

b. Low temperature oxidation (stabilization);

c. Carbonization;

d. Graphitization under stress.

The process is not industrially attractive due to the lengthy oxidation step, and only low-quality carbon fibers with no graphitization are produced for uses as fillers with various plastics for thermal insulation materials.

2.2.3.2 Anisotropic Mesophase Pitch

Under thermal treatment, high molecular weight aromatic pitches often form anisotropic liquids, so-called mesophases [74]. Due to the shear stress occurring during spinning, the mesophase molecules are oriented parallel to the fiber axis. The basic concept of this process is that the mesophase is a thermodynamically stable structure that will not relax to an isotropic liquid unless heated above the mesophase-liquid transition temperature. For most pitches, this transition temperature is above its decomposition temperature, so that the preferred orientation of the molecule is partially retained during the carbonization. The process is:

a. Polymerization of commercial pitch to mesophase;

b. Melt spinning;

c. Stabilization in air;

d. Carbonization and graphitization.

The molten pitch precursor is thermally treated above 350 ^{0}C to convert it to a mesophase pitch, which contains both isotropic and anisotropic phases. After spinning, the isotropic part of the pitch is made infusible by thermosetting in air at a temperature below its softening point. The fiber is then carbonized at the temperatures around 1000 ^{0}C.

Basic investigations on the flow properties and the spinning of mesophase pitches have been performed [75]. Since the "green" fiber contains both mesophase and isotropic domains, it was observed that optimal spinning conditions

require that the anisotropic phase become continuous and surround the domains of the remaining isotropic liquid.

The main advantage of this process is that no tension is required during the stabilization or the graphitization step, in contrast to rayon and PAN precursors. To achieve high-performance carbon fibers, however, the spinning process has to be perfectly controlled.

2.2.4 Carbon Fibers from Other Precursors

Saran (vinylidene chloride/vinyl chloride copolymers) is a convenient starting polymer for a fundamental study of carbon fiber preparation because the chemistry of its decomposition is relatively simple [76]. Saran affords the possibility of understanding the roles played by structure, morphology and mode of decomposition in determining the structure and properties of the resultant carbon.

Decomposition of PVDC occurs in two stages. In the range of 140-220 ^{0}C the reaction is limited essentially to the elimination of one molecule of hydrogen chloride which is removed progressively on raising the temperature to about 850 ^{0}C by reactions which are thought to involve condensation of the polyenes by a Diels-Alder mechanism. In most of this work Stage I of the preparation was commenced at 140 ^{0}C in air. The fibers were held under tension at constant length until about 50 per cent of the HCl had been eliminated. This took about five days. The temperature was then raised to 180 ^{0}C and

maintained at that temperature for 12 hours until about 70 per cent decomposition had occurred. Essentially this stage involves polyene formation, which can be represented as

$$-(-CH_2CXCl-)n \xrightarrow{\text{about } 140\ ^0C} -(CH=CX-)-n + nHCl$$

where X is either Cl or H randomly distributed and in the ratio of 83/17.

During stage II, fibers were carbonized under relaxed conditions in a stream of nitrogen in a silica tube heated by a horizontal wire-wound furnace. The temperature was steadily raised to 850 ^{0}C over a period of 12 hours and maintained at 850 ^{0}C for a further 12 hours. This stage involves essentially the elimination of one HCl molecule per vinylidene chloride unit and two hydrogen atoms per vinyl chloride unit. The mechanism of decomposition is thought to involve condensation of neighboring chains (Diels-Alder) to give a three-dimensional crosslinked network followed by elimination of HCl, as shown schematically (Figure 8).

Carbon fibers were then heat treated for 30 min (Stage III) at various temperatures up to 2500 ^{0}C using R.F. heating. It is well known that carbons from PVDC and Saran, unlike those from PVC, do not produce large graphite crystallites when heated to about 2500 ^{0}C. Even after being heated to about 3000 ^{0}C for 30 minutes, the carbon fibers were still glassy

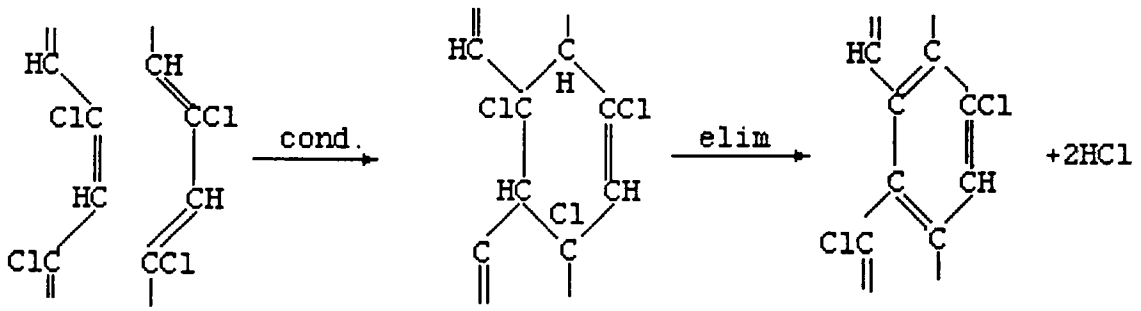


Figure 8. Schematic of Mechanism of Decomposition of Saran Fibers [76].

and exhibited conchoidal fracture similar to that of partially decomposed materials and to the carbon prepared at 850 ^{0}C.

2.3 Structure and Properties of Oriented PE Precursor

Highly-oriented polyethylenes such as spectra have better mechanical properties and higher carbon content than any other organic precursor for carbon fiber. This makes oriented high molecular weight polyethylene fibers attractive precursors for carbon fibers. It is conceived that carbon fibers from spectra will have good mechanical properties.

Polyethylene is obtained usually by free-radical polymerization [77]. The problem in this process is that there is a tendency for short branches (typically ethyl or butyl

groups) to form along the chain. Therefore, the degree of crystallinity in polyethylene is not really high.

In order to increase the degree of crystallinity, one of the most important methods is to produce polyethylene without branches. In 1953, Zieglar first invented a process to produce polyethylene without branches using AlH_3 as the catalyst [78].

Today, linear polyethylene is produced with molecular weights of one to five million [79]. The new fibers are characterized by a 1 - 5 million MW, an especially extended chain polyethylene and a very high degree of crystalline orientation (95 --99%), and crystalline content (60--85%). The generalized extended-chain process begins with a polymer of approximately one to five million MW, which is dissolved in a suitable solvent. The solution serves to disentangle the polymer chains, a key step in achieving an extended-chain polymer structure.

The fibers derived from this type of spinning not only have the excellent inherent attributes of PE, but also possess extraordinary physical properties: low specific gravity, high energy to break, high abrasion resistance, excellent electrical properties, excellent chemical resistance, good UV resistance, low moisture absorption, high specific modulus and strength. Although this is an impressive list, PE has its limitations. Even in extended-chain form, it has relatively low melting point (150 °C). Therefore, what one has to do is to stabilize the precursor fiber to make it

withstand the higher temperatures of carbonization, and at the same time try to maintain its superior performance properties.

2.4 Stabilization of Polyethylene

Stabilization of a precursor is the most important step in carbon fiber production. The stabilized precursor, then, can be carbonized in an inert environment. There are two general approaches to stabilizing a polymeric precursor [80]: (a) by modification of molecular structure, and (b) by using additives. Dependent on the mode of degradation, either or both of these techniques may be employed. When the initiation rate is low, additives can be used. At high initiation rates, additives are less effective, and stabilization by structure modification may be the only practical approach. Additives would be overwhelmed by the large number of radicals formed during initiation.

Thermal degradation in the absence of oxygen (pyrolysis) usually takes place at an elevated temperature. The initiation rate is high and, therefore, additives are not nearly so effective as in the inhibition of low-temperature oxidation or photooxidation. Structure modification in which relatively weak bonds are replaced by bonds of higher dissociation energy is the preferred approach. As an example, polytetrafluoroethylene, with only C-C and C-F bonds in the structure, is much more stable to pyrolysis than is polyethylene. Replacement of C-H bonds with C-F or other

bonds, however, results in a polymer quite different from polyethylene in many other important aspects. The extent to which a specific polymer can be heat stabilized by structural modification or by copolymerization is limited because other properties of the original polymer must usually be held within closely specified limits. Here, we are only interested in stabilization by structure modification and crosslinking of polymer molecules.

2.4.1 Stabilization by Structure Modification

There is wide variation in the stability of polymers to nonoxidative thermal degradation. This can be attributed to differences in dissociation energies of those bonds which make up the structures. At the elevated temperature, bonds may cleave along the backbone chain in a random-scission process or by depolymerization. In other polymers, substituents are split off from the backbone chain. Whatever the mechanism of pyrolysis, it is evident that replacement of weak bonds with others having higher dissociation energy will increase thermal stability. This approach has been applied successfully in a limited number of cases in which weak links or labile substituents are responsible for initiating degradation. Replacement of a few such bonds can usually be accomplished without altering the original polymer properties beyond acceptable limits.

2.4.2 Stabilization by Crosslinking

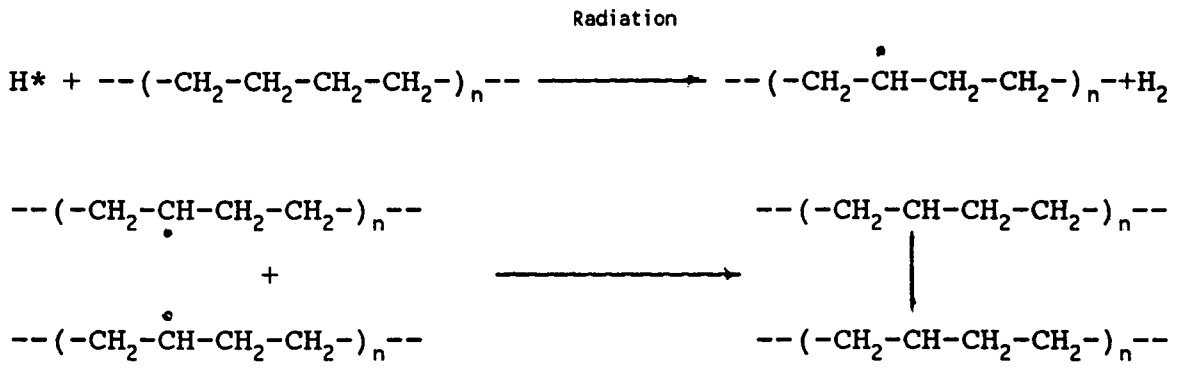
The bonds forming crosslinks in network polymers contribute significantly to thermal stability. Thus thermosets as a general class have greater resistance to heat than do the thermoplastics. Though this approach to stabilization is one more of polymer design than modification, crosslinking can be considered as a special type of structural modification. Some polymers designed for high-temperature resistance take advantage of the inherent stability of network structures. When a single covalent bond in a thermoplastic is broken, chain scission occurs; but, in the densely crosslinked structures, many bonds must be broken before extensive degradation takes place. Thermal stability increases with crosslink density. Crosslinking of polyethylene can take place through radiation and/or chemical agents.

Formation of ethylenic unsaturation during radiolysis has been attributed to elimination of molecular hydrogen in a single step as represented in the radiolysis of polyethylene [81].

$$--(-CH_2-CH_2-CH_2-CH_2-)_n-- \xrightarrow{\text{Radiation}} --(CH_2-CH=CH-CH_2-)_n-- + H_2$$

Formation of molecular hydrogen may also result in the formation of crosslinking of polymers.

$$--(-CH_2-CH_2-CH_2-CH_2-)_n-- \xrightarrow{\text{Radiation}} --(-CH_2-\dot{C}H-CH_2-CH_2-)_n-- + H^*$$



Crosslinking will create bonds in this structure where portions of individual molecules are now rigidly fixed in position relative to each other.

This occurs because the secondary bonds at those positions have been replaced by much stronger covalent bonds. The net result is a more rigid net-work, which in turn is reflected in changes in the bulk properties of the material. In tension behavior, for example, the addition of crosslinks generally results in an increase in modulus and decrease in strain-to-break.

Crosslinking necessarily affects all properties that are influenced by the type and degree of intermolecular bonding. The ability of the polymer to melt or soften and become a liquid is eliminated. Properties such as thermal expansion, conductivity, heat-distortion temperature, hardness, impact strength, and creep are also affected.

Methods of crosslinking are [82]: (1) use of monomer units having a functionality greater than 2; (2) nuclear radiation; and (3) using various chemical agents.

Different methods have been used in stabilizing different precursors. However, almost identical processing temperatures are employed in carbonization and graphitization. Demand for carbon fibers, in variety and quantity has been increasing steadily. Past and projected annual demands for carbon fibers (tones) are shown in figure 9 [83]. As the demand for carbon fibers increases, it is necessary to study other potential precursor fibers such as polyethylene. In this research the new precursor fiber consisting of a highly ordered and oriented polyethylene fiber was investigated as a potential precursor for carbon fibers.

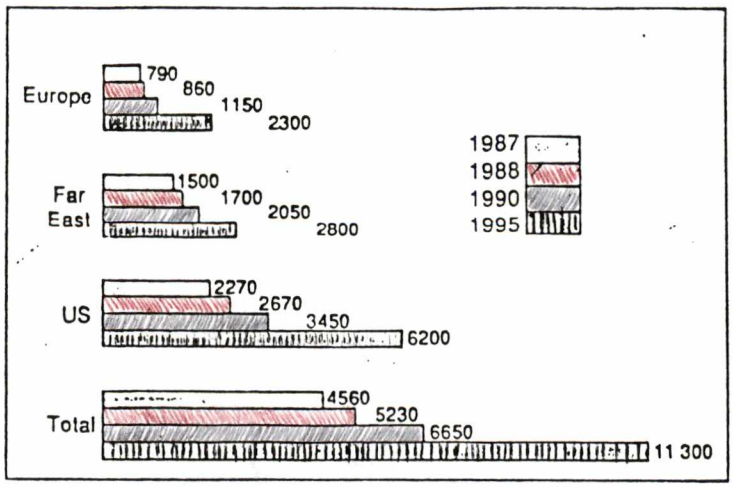


Figure 9. Projected Annual Demands for Carbon Fibers (tones) [83].

CHAPTER III

EXPERIMENTAL DETAILS

3.1 Precursor Fibers

The precursor fibers used were commercial ultra-high molecular weight PE fibers (spectra) produced by Allied Fiber Company. Three different grades of the fiber with varying filament deniers were investigated. The color of the fiber was white and the physical properties are superior to any other organic fiber. Their physical and mechanical properties are listed in Table II. All the samples were multifilament bundles with number of filaments varying from 63 to 200.

3.2 Stabilization of Precursor Fibers

The PE fibers were treated in a concentrated sulfuric acid (95%, H_2SO_4) bath in an elastically constrained way by wrapping the filament loop around a bent steel wire as shown in Figure 10. The stabilization treatments were carried out at temperatures 130 to 200 ^{0}C for different periods of time (5 to 120 minutes). An IKA heater, which is an electrically heated stainless-steel bath, was used. The temperature was controlled by changing the setting and a thermometer was used to monitor the actual bath temperature. After sulfonation, the fibers were thoroughly washed with water and dried in a DK-63

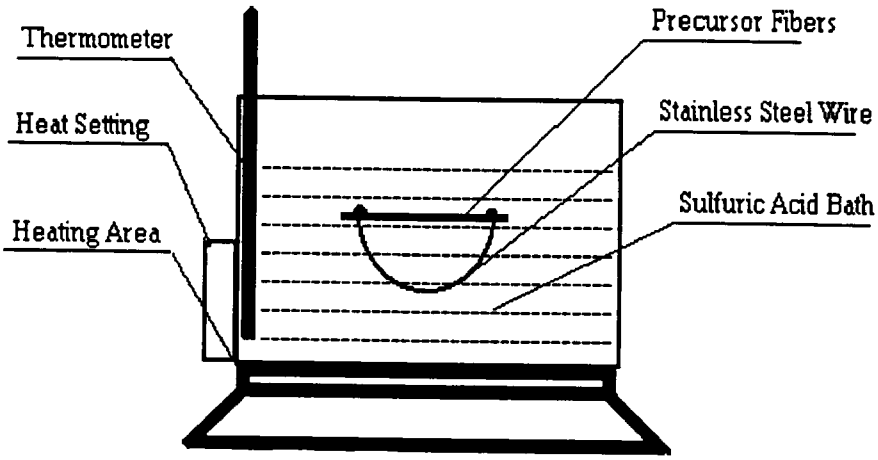


Figure 10. Schematic of Stabilization Bath.

constant temperature oven at 60 ^{0}C for 90 minutes. After completely drying, the fibers were removed from the bent steel wire.

3.3 Carbonization of the Stabilized Fibers

The stabilized fibers were carbonized in a tubular furnace with a ceramic tube as shown in Figure 11. Glass end caps covered the two sides of the ceramic tube. Nitrogen gas was fed from both sides of the glass end caps. The temperature of the heater was controlled by an Omega CN2000 programmable temperature controller. Carbonization was carried out in nitrogen atmosphere at 1150 ^{0}C for four minutes, with a slight tension. 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 four minutes), the fiber was slowly pulled out of the furnace.

3.4 Characterization of the Fibers

3.4.1 Thermal Analyses

Thermal analyses, i.e., differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using the Mettler DSC25 and TGA50, respectively. DSC curves were recorded using 10 ^{0}C/min heating and cooling rates for

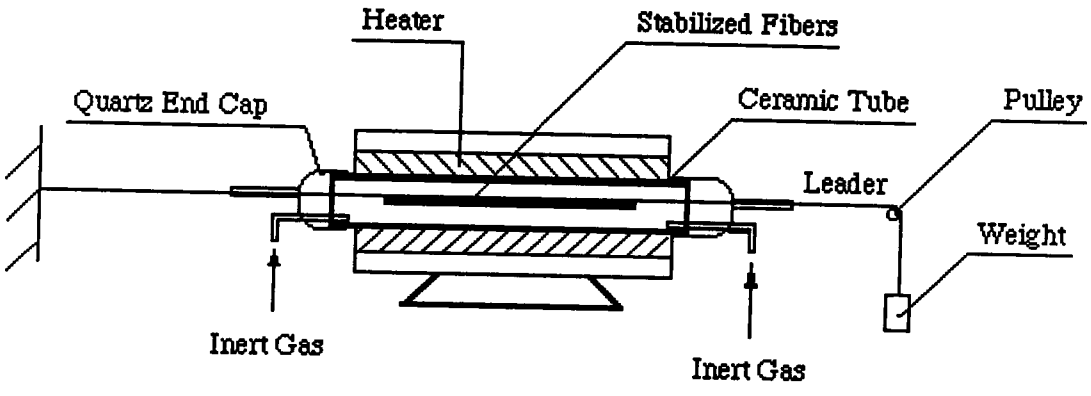


Figure 11. Schematic of Carbonization Furnace.

all the samples in both nitrogen and air environments. TGA scans were recorded by using different heating rates of 5, 10, 20, and 100 ^{0}C/min in air or nitrogen atmosphere. Weight losses of the different samples were determined up to a temperature of 800 ^{0}C. In all the cases, fiber samples were cut up with scissors and the sample weight was kept close to 10 mg.

3.4.2 Color Change

Changes in the color of the samples as stabilization proceeded were monitored visually. The colors were recorded subjectively as white, light yellow, grey and black.

3.4.3 Burning Test

The samples were thrust into a match flame to determine flammability. Samples which do not burn in a match flame can usually be carbonized without disintegration. The results were recorded as samples that passed or failed the burning test.

3.4.4 Elemental Analysis

The selected precursor, stabilized and carbonized samples were analyzed for elemental composition. Elements which were of interest were C, H, O, and S. The measurements were carried out by Leco Corporation, St. Joseph, Michigan. The data reported is an average of three readings with an accuracy of $\pm$ 0.5%.

3.4.5 Tensile Testing

Tensile properties of the stabilized and carbonized fibers were measured using a Table Model (4310) Instron tensile tester, equipped with a 50g load cell, and operated at a cross-head speed of 25 mm/min. All test were carried out with single filaments and the gauge length of the specimen was 10 mm. The tenacity, modulus and elongation-at-break were calculated as an average of 20 samples.

Tensile properties of the precursor fibers were measured with the Instron Table Model tensile tester, which a single filament was held between pneumatic grips under an air pressure of 40 psi. A gauge length of 10 mm was used for testing, at a cross-head speed of one inch/min. The fiber slipped from the clamp. That mean the friction of the maximum pressure was not sufficient to hold the fiber.

3.4.6 Fourier Transform Infrared Spectroscopy

Infrared spectra of the samples were obtained using the IR Microscope and Digilab FTIR Model FTS-40 spectrometer. IR Microscopy scans were obtained on the precursor, as well as on partially stabilized, stabilized, and carbonized fibers. Since the beam energy was concentrated, samples with low throughput could be examined by conventional transmittance measurements.

The fiber sample was mounted as a very thin layer of fibers on a gold coated glass piece (see Figure 12). The

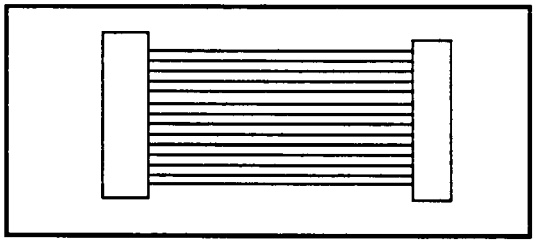


Figure 12. Sample Fibers Mounted for IR Spectrometry

scanning was carried out in air with wavenumbers from 4000 to 700 cm^{-1}. The data were collected, Fourier processed, ratioed with the background and plotted as absorbance spectra.

3.4.7 X-ray Diffraction

Wide angle X-ray diffraction was carried out using a Rigaku Geigerflex diffractometer. The precursor fiber, the stabilized fiber, and the carbonized fibers were scanned at 2^0/min from 30 to 100^0 of 20. X-ray diffraction studies elucidated the changes taking place in orientation of the precursor fibers during stabilization and carbonization. X-ray diffraction photos were taken using a small angle x-ray diffractometer Phillips Model at 30 KV and 20 MA for four hours. The wavelength of x-ray was 1.54183 Å. The samples were prepared by carefully placing the fibers as a parallel array

on the sample holder (a frame with a central circular opening). The distance between the film and the sample was 36.5mm.

3.4.8 Microscopy

3.4.8.1 Scanning Electron Microscopy

Scanning electron micrographs (SEM) were taken with an ETEC Autoscan 1975 microscope operating at 20 KV. Samples were gold coated using a Hummer I Sputter Coater. Fiber diameters were determined by SEM. Fiber cross sections were scanned to identify any skin-core heterogeneity or the presence of holes. Surface scans were conducted to observe the changes in the surface texture.

3.4.8.2 Optical Microscopy

An Olympus Model CH optical microscope was used to investigate the morphology of the fiber. The cross-sections of the samples were obtained from fiber composites. Spurr low-viscosity embedding media was used to make the composites [84]. Very thin (20-30 um) cross-sections were made using the SPENCER 820 Microtome. Pictures were taken using a camera connected with the microscope. The birefringence of the precursor fibers was measured by the retardation technique [85].

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Precursor

Highly ordered and oriented PE fibers are characterized by a 1 - 5 million MW and a very high degree of crystalline orientation (95-99%) and crystalline content (60-85%) [85]. The fibers are manufactured by a special gel spinning process which leads to extended-chain crystals and extraordinary physical properties. Four different grades of spectra fibers were used and their physical properties are listed in Table II. The very high birefringence values observed are an indication of the high degree of overall orientation. Among the different grades, spectra 1000 (A) has the maximum orientation and tenacity with the fiber diameter being the least. These fibers are drawn to a greater extent than the other grades. However, even in extended-chain form, the fiber has a relatively low melting point (150 ^{0}C) as seen by DSC measurement (4.2). Therefore, to improve the thermal stability of these fibers, stabilization was carried out by treating in a concentrated sulfuric acid bath.

4.2 Effect of Stabilization Time and Temperature

The PE fibers were treated with sulfuric acid at different temperatures, for different periods of time in an

TABLE II. PHYSICAL AND MECHANICAL PROPERTIES OF POLYETHYLENE PRECURSOR FILAMENTS

Sample Specification	Spectra 1000 (A)	Spectra 900 (B)	Spectra 1000 (C)	Spectra Medical Grade (D)
Linear Density (Denier)	4.26	11.76	6.97	6.25
Diameter of Filament (um)	32.7	62.8	45.5	51.8
Strength at Break (MPa)*	335	260	-	-
Elongation at Break (%)*	2.47	3.50	-	-
Young's Modulus (GPa)*	170	120	-	-
Melting Point (^{0}C)	150	150	150	150
Birefringence	0.036	0.020	0.029	0.024

*Reported from [79]

elastically constrained way. The color of the fiber changed with the progress of sulfonation from white via light yellow and grey to black (Table III). The color change on observed darkening is an indication of the development of conjugated structures during stabilization. As the color of the fibers changed, the samples also gained weight and, towards the end of sulfonation, the mass of the fiber increased by 60-80% (Table IV).

DSC curves show a slight increase in the peak melting point of the fiber with an increase in treating time and temperature, with a simultaneous decrease in the heat of fusion (Table V and Figure 13). On continued treatment the melting peaks completely disappeared. The results are consistent with the observations of Postema et al. on chlorosulfonized PE filaments [85]. The melting peak increase was associated with the modification of the crystals having foreign groups in the amorphous domains. As the treating time and temperature increased, degradation began and penetration and diffusion of the molecules of sulfuric acid took place from surface of the crystals in toward their center. On continued heating, crosslinking progressed into the whole of the fiber, which was seen by the disappearance of melting peaks. The endotherm disappeared after a treating time of 75 minutes and a temperature of 160 ^{0}C and the fiber became infusible (Figure 13). Similar results were observed when scanning was done in the air environment (Figure 14).

TABLE III. COLOR CHANGE DURING SULFONATION

Stabilization time (min)	Stabilization Temperature (^{0}C) 130	140	150	160	170	180	190	200
5	L.Yellow	L.Yellow	-	-	-	-	-	-
15	L.Yellow	L.Yellow	-	-	-	-	-	-
30	Grey	Grey	-	-	-	-	-	-
45	Grey	Grey	Black	-	-	-	-	-
60	Black	Black	Black	Black	-	-	-	-
75	Black	Black	Black	Black	Black	-	-	-
90	Black	Black	Black	Black	Black	Black	-	-
105	Black	Black	Black	Black	Black	Black	Black	-
120	Black	Black	Black	Black	Black	Black	Black	Black

Note: (1) Color of the precursor was white.
(2) The sample was spectra 1000 (A).

TABLE IV. MASS INCREASE WITH STABILIZATION TIME AND TEMPERATURE

Sample	Stabilization Time (min)	Maximum Stabilization Temperature (^{0}C)	Mass Increase (%)
A_{15}	60	150	8.23
A_{16}	75	160	47.39
A_{17}	90	170	55.55
A_{18}	105	180	67.39
A_{19}	120	190	77.39
B_{15}	60	150	7.85
B_{16}	75	160	50.43
B_{17}	90	170	60.97
B_{18}	105	180	74.62
B_{19}	120	190	84.12

Note:

(1). Sample A is Spectra 1000.
(2). Sample B is Spectra 900.
(3). All samples were stabilized in sulfuric acid bath with tension.

TABLE V. HEAT OF FUSION FOR DSC OF SAMPLES

Sample	In Nitrogen				In Air			
	Heating		Cooling		Heating		Cooling	
	Tm	ΔH	C_T	ΔH	Tm	ΔH	C_T	ΔH
A_0	150.3	283.4	112.4	165.0	149.6	263.4	113.5	174
A_{15}	153.7	175.5	115.7	147.3	153.0	149.0	97.3	60.7
A_{16}	-	-	-	-	-	-	-	-
A_{17}	-	-	-	-	-	-	-	-
A_{18}	-	-	-	-	-	-	-	-
A_{19}	-	-	-	-	-	-	-	-

Note:

(1). Tm (^{0}C) is melting point.
(2). C_T (^{0}C) is the peak temperature of crystallization.
(3). ΔH (J/g) is heat of fusion of peak.

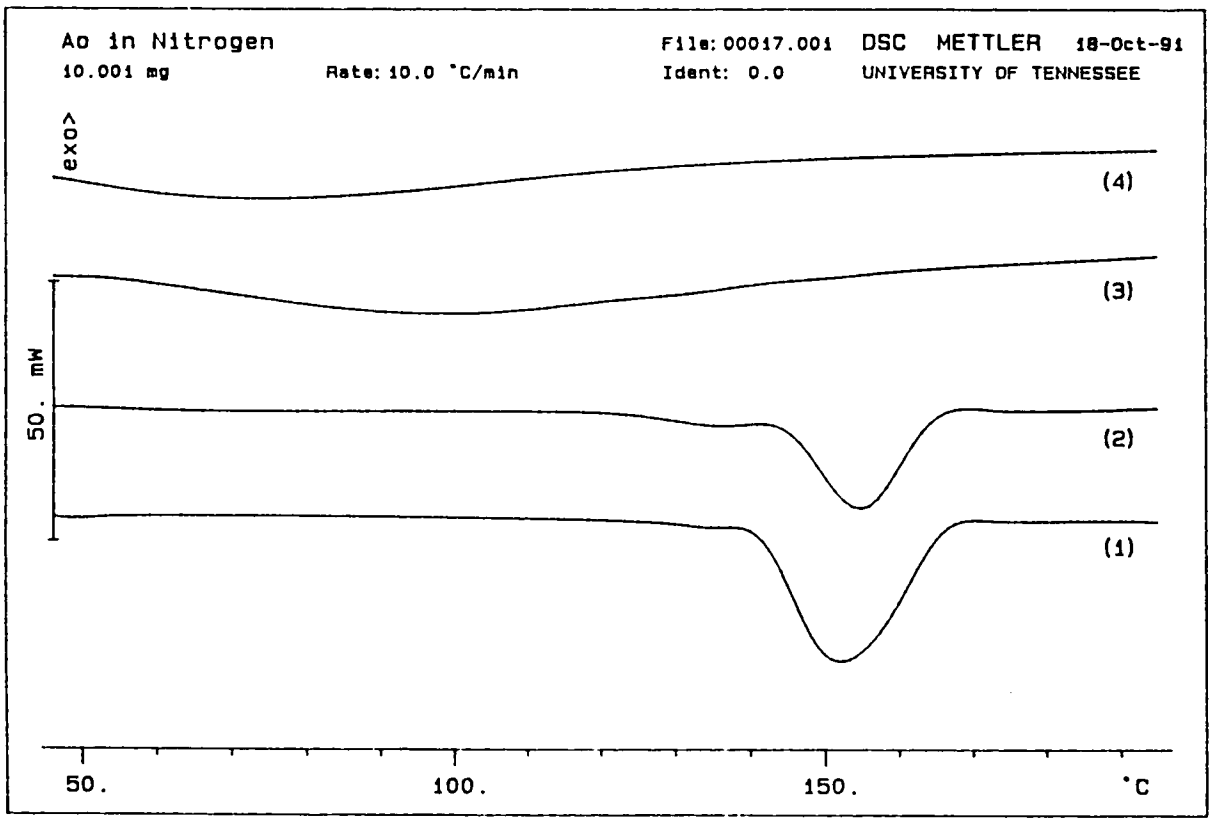


Figure 13. DSC Scans (Heating in Nitrogen) of PE Fibers for Different Stabilization Time and Temperature. Precursor (1); 150 ^{0}C & 60 min. (2); 160 ^{0}C & 75 min. (3); 180 ^{0}C & 105 min. (4).

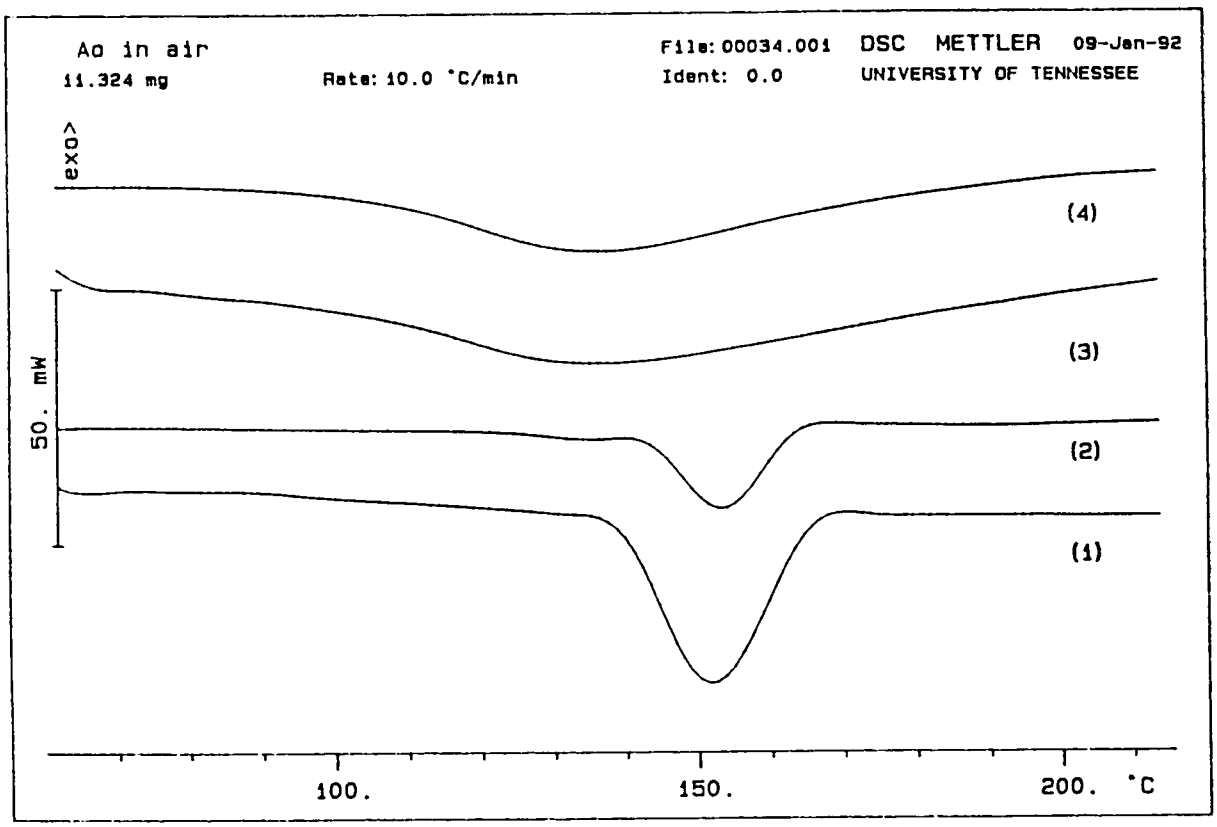


Figure 14. DSC Scans (Heating in Air) of PE Fibers of Different Stabilization Time and Temperature. Precursor (1); 150 ^{0}C & 60 min. (2); 160 ^{0}C & 75 min. (3); 180 ^{0}C & 105 min. (4).

Cooling curves in nitrogen and air are shown in Figures 15 and 16, respectively. The enthalpy of crystallization was larger when scanned in N_2 than in air. That is because no additional chemical reactions took place in the inert environment. In the presence of air during DSC scanning, additional reactions could take place, thereby decreasing the heat of crystallization, as seen by the cooling curve.

TGA showed bigger differences for the samples when scanned in air and nitrogen environments. While scanning in the presence of air Figure 17, the stabilized samples lost about 80-90% of their original weight when the temperature reached 800 ^{0}C, whereas in the case of the nitrogen environment the weight loss was only about 50% (Figure 18). Oxidative degradation took place in air at elevated temperatures and only pyrolysis took place in nitrogen. In both of the atmospheres the weight loss of the precursor PE fiber was 100% when the temperature reached about 500 ^{0}C. Weight retention did not improve beyond a stabilization temperature of 160 ^{0}C and total treating time of 75 minutes.

The results from the burning test, shown in Table VI, are consistent with the DSC and TGA observation. All these observations show the importance of increasing the bath temperature with sulfonation. To start with, the temperature should be lower than 140 ^{0}C, to prevent melting of low melting crystals. As the fibers become stable, the treatment

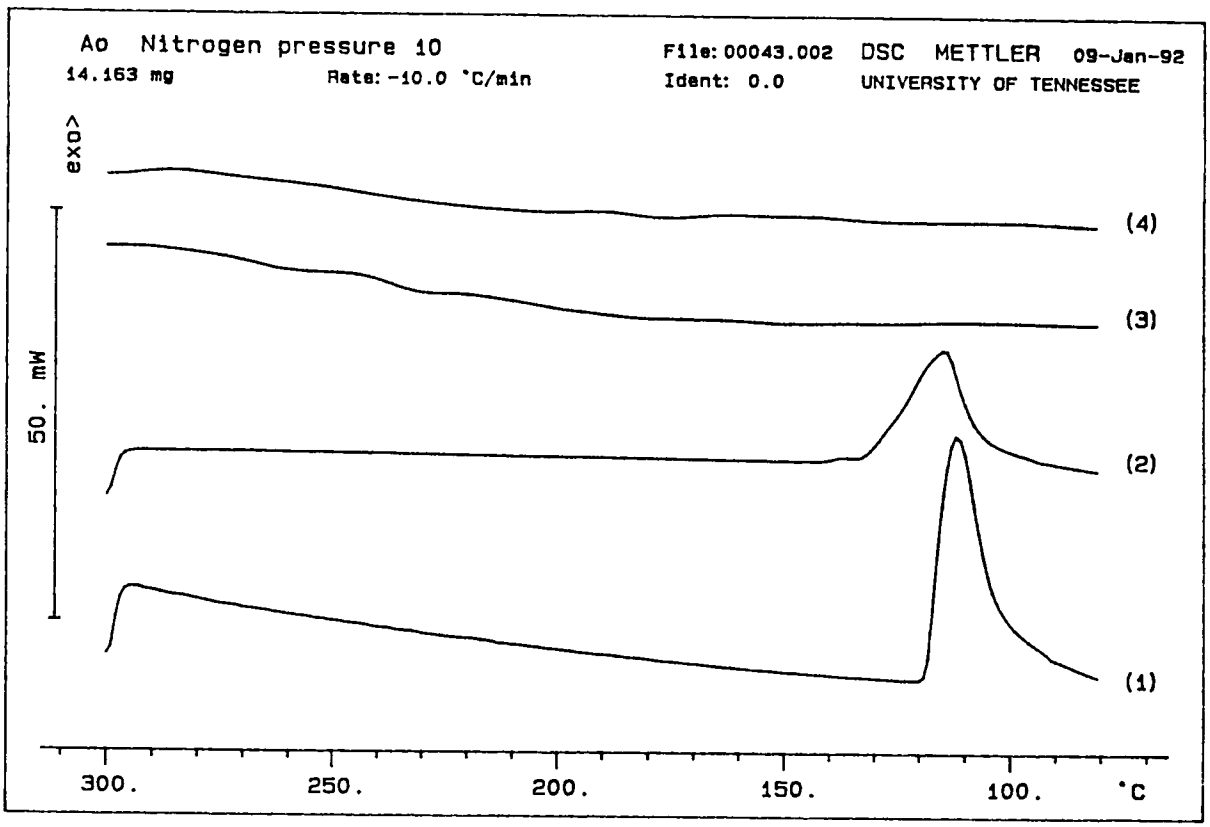


Figure 15. DSC Scans (Cooling in Nitrogen) of PE Fibers of Different Stabilization Time and Temperature. Precursor (1); 150 ^{0}C & 60 min. (2); 160 ^{0}C & 75 min. (3); 180 ^{0}C & 105 min. (4).

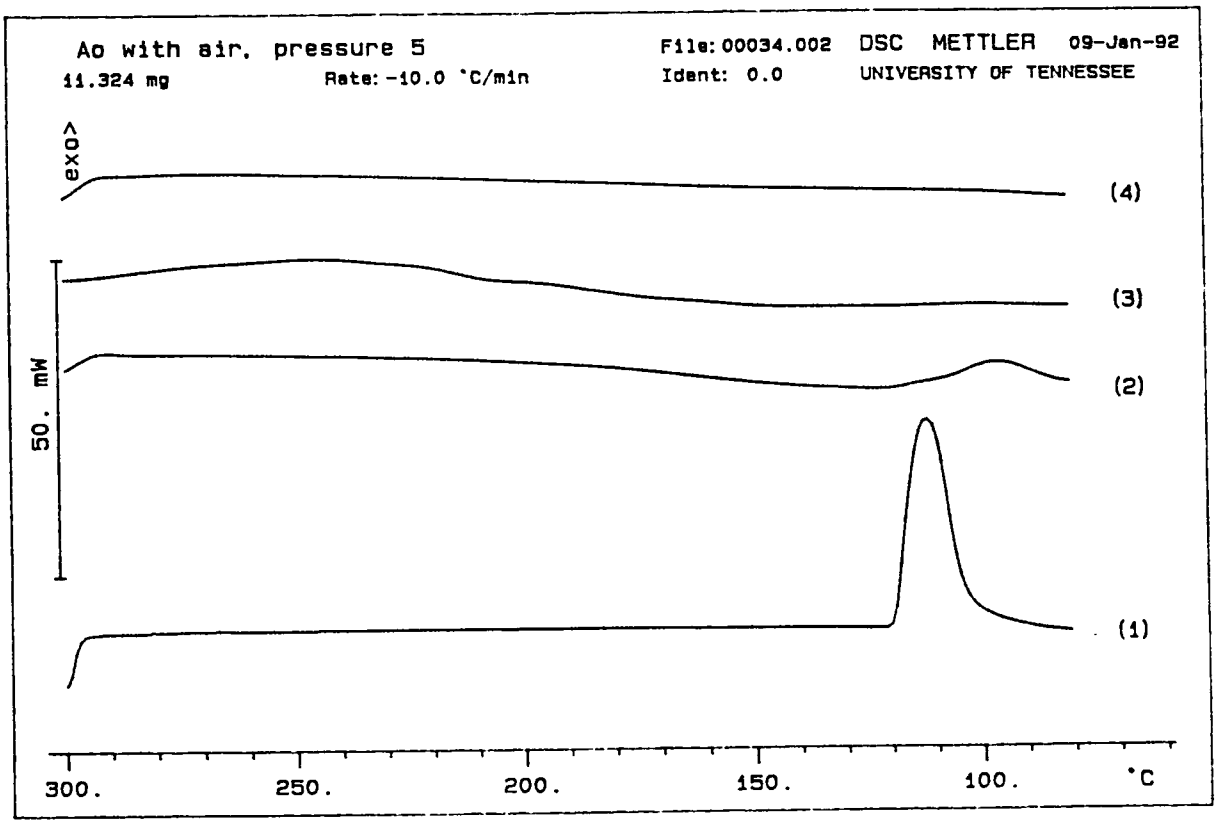


Figure 16 DSC Scans (Cooling in Air) of PE Fibers of Different Stabilization Time and Temperature. Precursor (1); 150 ^{0}C & 60 min. (2); 160 ^{0}C & 75 min. (3); 180 ^{0}C & 105 min. (4).

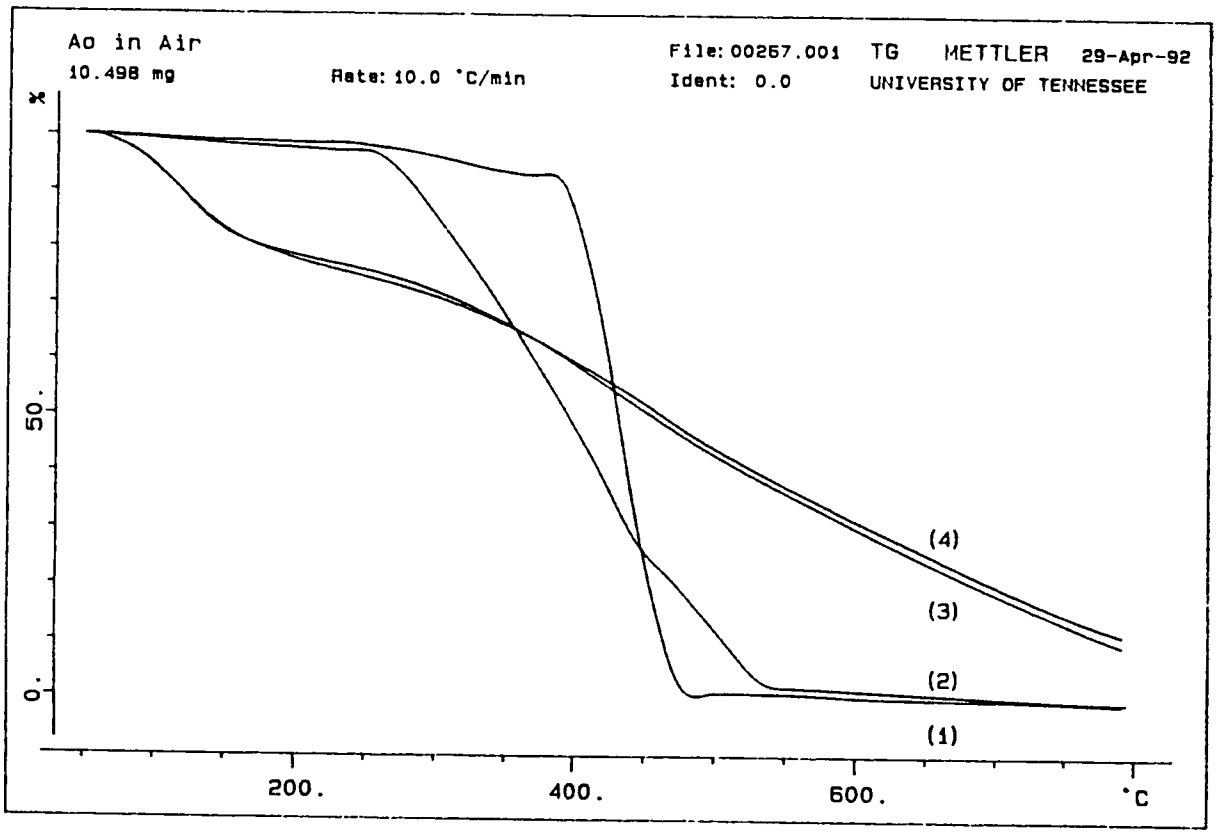


Figure 17. TGA Scans (in Air) for the Samples: Precursor (1); 150 ^{0}C & 60 min. (2); 160 ^{0}C & 75 min. (3); 180 ^{0}C & 105 min. (4).

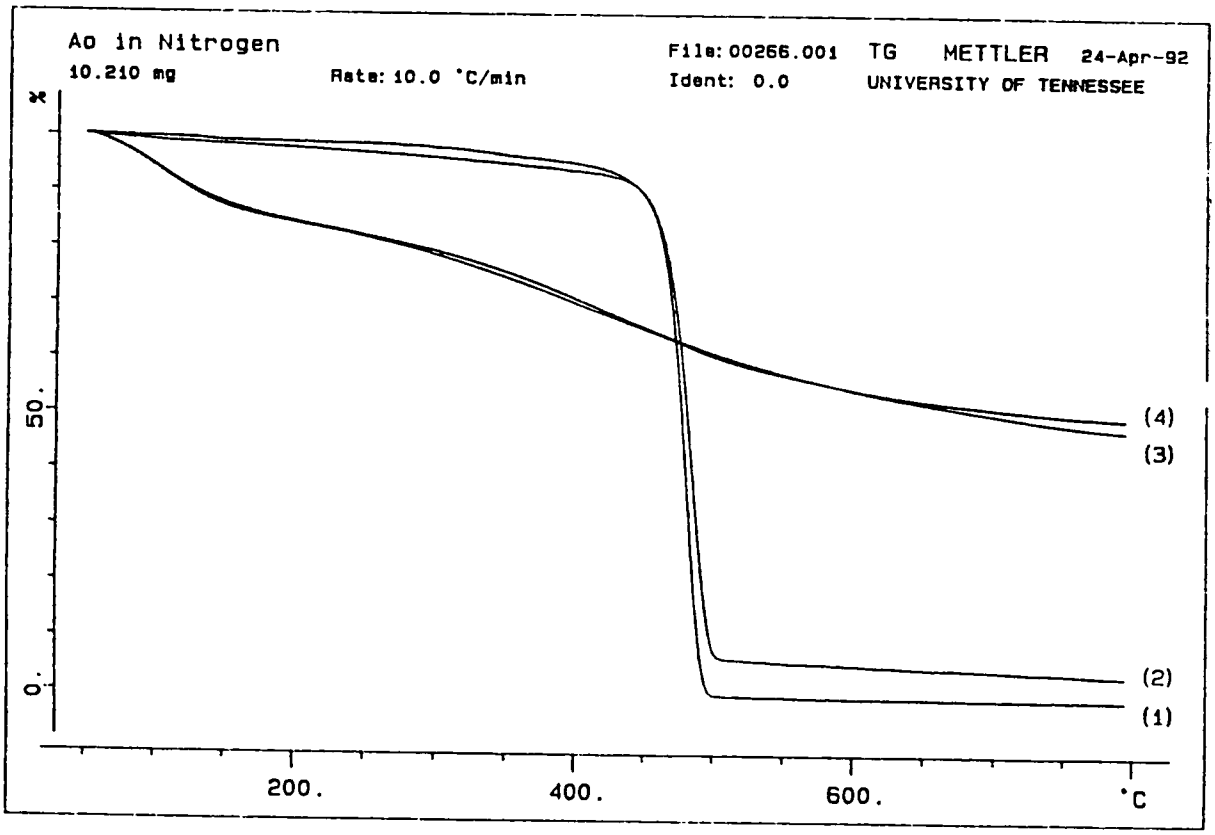


Figure 18. TGA Scans (in Nitrogen) for the Samples: Precursor (1); 150 ^{0}C & 60 min. (2); 160 ^{0}C & 75 min. (3); 180 ^{0}C & 105 min. (4).

TABLE VI. RESULTS FROM BURNING TEST OF SAMPLES STABILIZED AT DIFFERENT TIME AND TEMPERATURE

Stabilization Time (min)	Maximum Stabilization Temperature (^{0}C)							
	130	140	150	160	170	180	190	200
15	F	-	-	-	-	-	-	-
30	F	F	-	-	-	-	-	-
45	F	F	F	-	-	-	-	-
60	F	F	F	P	-	-	-	-
75	F	F	F	P	P	-	-	-
90	F	F	F	P	P	P	-	-
105	F	F	P	P	P	P	P	-
120	F	P	P	P	P	P	P	P

Note:
The sample is spectra 1000 (A).

temperature can be increased, which still maintaining the fibrous form. When the temperature is not increased beyond 130 ^{0}C, the sample fails the burning test even after two hours of treatment, indicating that the stabilization reactions occur at a much slower rate. To reach the stabilized state in a short period, it is important that the treatment temperature be raised slowly as the fiber becomes more and more stable.

4.3 Effect of Tension during the Stabilization

DSC of PE fibers stabilized without any tension at 140 ^{0}C for 30, 60, and 90 minutes are shown in Figure 19. Partially stabilized fibers showed a double melting peaks. The first peak, attributed to a lamellar structure and folded chain crystals, disappeared with the increase in treating time to two hours. The second peak, attributed to fibrils, shifted to a slightly lower temperature as a consequence of relaxation of molecular chains and the conversion of extended chain crystals into folded chain crystals. After prolonged treating time both the peaks disappeared. The same results were obtained by increasing the treating temperature (Figure 20). The double peak disappeared on treatment at 160 ^{0}C for 110 minutes for unconstrained sulfonation. In the case of stabilization under tension, no double peaks were observed (Figure 13). This is due to the fact that the crystal structure was not altered noticeably during stabilization under tension. It took

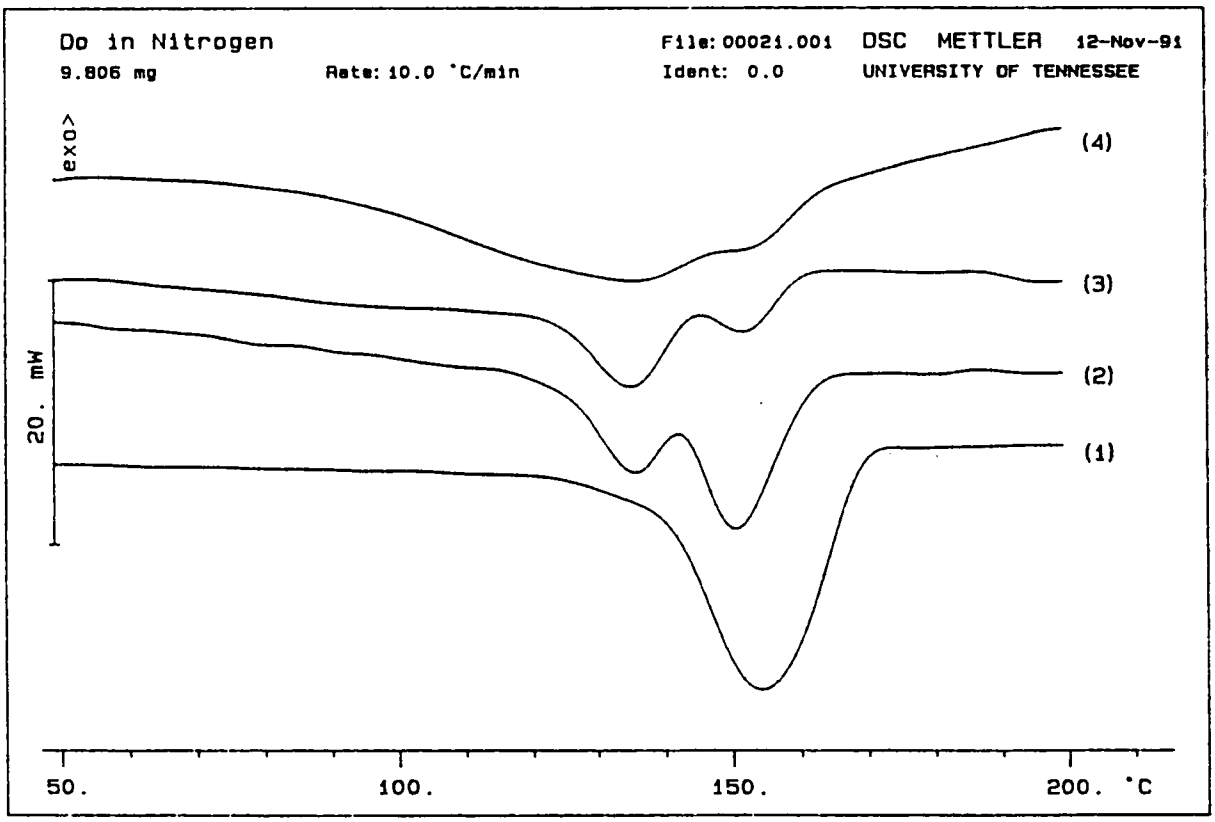


Figure 19. DSC Scans of Samples for Different Treating Time at 140 ^{0}C. Precursor (1); 30 min. (2); 60 min. (3); 120 min. (4).

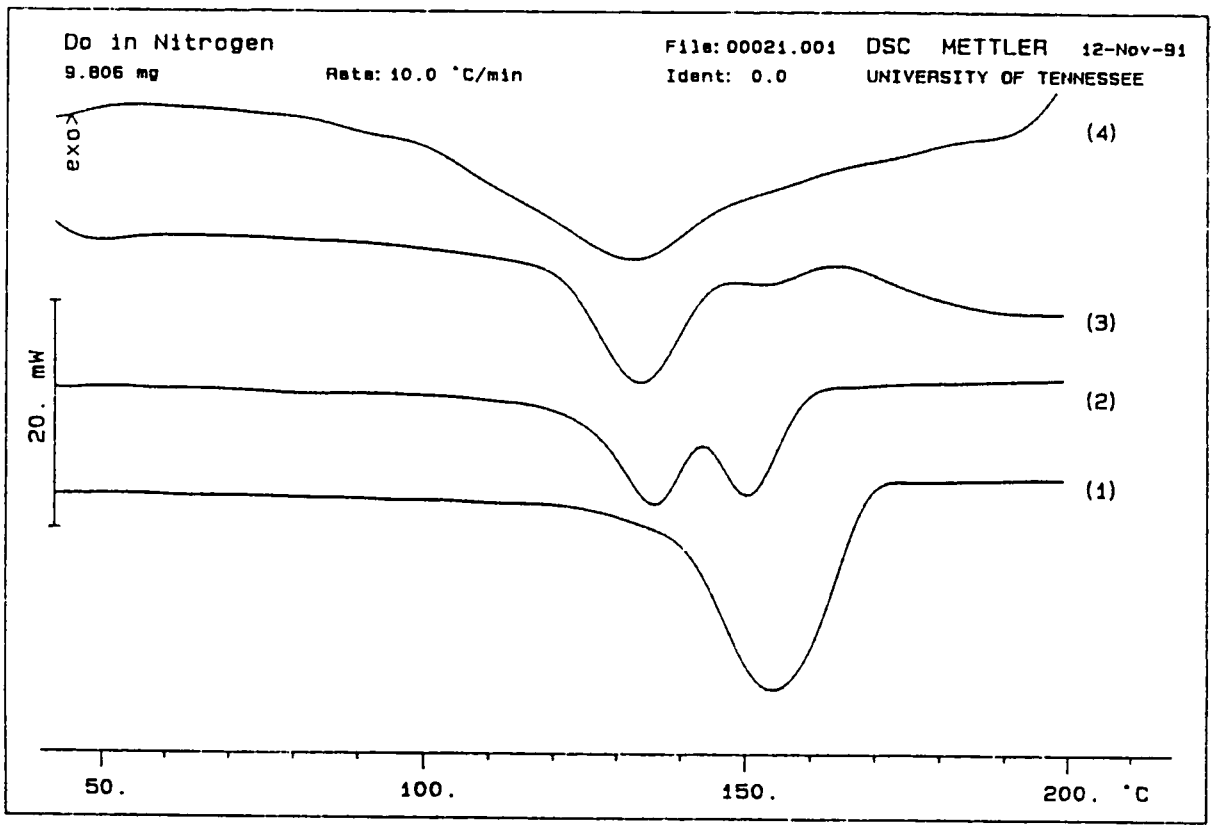


Figure 20. DSC scans of Samples with Increasing Treatment Temperature. Precursor (1); 140 ^{0}C & 45 min. (2); 150 ^{0}C & 50 min. (3); 160 ^{0}C & 110 min. (4).

additional time to stabilize the sample D, because its diameter was larger than than that of sample A. In the case of sample A, 75 minutes was necessary to stabilize the fiber at 160 ^{0}C.

During unconstrained stabilization, the fibers shrank considerably, in some cases even losing their fiber form at elevated temperatures. The resultant fiber was so brittle that it was difficult to handle it for further carbonization. SEM photographs showed the presence of kink-bands on the surface of fibers treated with low or no tension. Therefore, applying tension during the stabilization process is very important. Tension helps in maintaining the orientation of the molecules in the precursor fiber, and is likely to result in a stabilized fiber with good mechanical properties suitable for further carbonization.

4.4 Change in Structure

4.4.1 Elemental Composition

The precursor was comprised of about 84% carbon and 14% hydrogen. Calculated values are C=85.7% and H=13.3%, neglecting contributions from catalysts and chain ends. On stabilization, there is a big increase in oxygen content. Surprisingly, the sulfur content was only about 3%. It appears that the role of sulfur is only in initiating the crosslinking

reactions, with oxygen being the major element in crosslinked structures.

The carbon content of the carbon fiber exceeded 92%. The carbon fiber also had a sulfur content of 2.7% and oxygen content of 1.1% (see Table VII). Carbonization was done at 1150 ^{0}C, which is lower than commercial carbonization temperatures where temperatures as high as 1500-1700 ^{0}C are used. A higher carbonization temperature should reduce the content of other elements in the carbon fiber. FTIR spectra were obtained to determine the functional groups in the stabilized and carbonized fibers.

4.4.2 Fourier Transform Infrared Spectroscopy

FTIR spectra were obtained to qualitatively evaluate the changes in structure on stabilization and carbonization. With the fiber samples, it is not possible to obtain spectra for quantitative measurement. The FTIR spectrum of the precursor (Figure 21) shows a very sharp and strong peak at wavenumbers of 2853-2990 cm^{-1}. This is due to the CH or CH_2 antisymmetric and symmetric stretching, which is the main group in polyethylene. The peak of 1450-1475 cm^{-1} is due to the CH_2 scissoring vibration. Other peaks between 700-1250 cm^{-1} may be due to the CH out-of-phase deformation.

The spectrum of a partially stabilized fiber (Figure 22), shows high absorbency at wavenumbers 1580-1750 cm^{-1}, assigned

TABLE VII. RESULTS OF ELEMENTAL ANALYSIS

Sample Specification	Percent Carbon	Percent Hydrogen	Percent Sulfur	Percent Oxygen
Polyethylene Precursor Fiber	83.7	14.1	-	-
Stabilized Precursor for 105 min at 180 ^{0}C	53.4	10.9*	3.0	32.7
Carbonized Fiber	92.5	3.7*	2.7	1.1

Note:

(1). * Calculated by substraction.

(2). Sample A, i.e., Spectra 1000 was selected as the precursor fiber, followed by stabilization and carbonization.

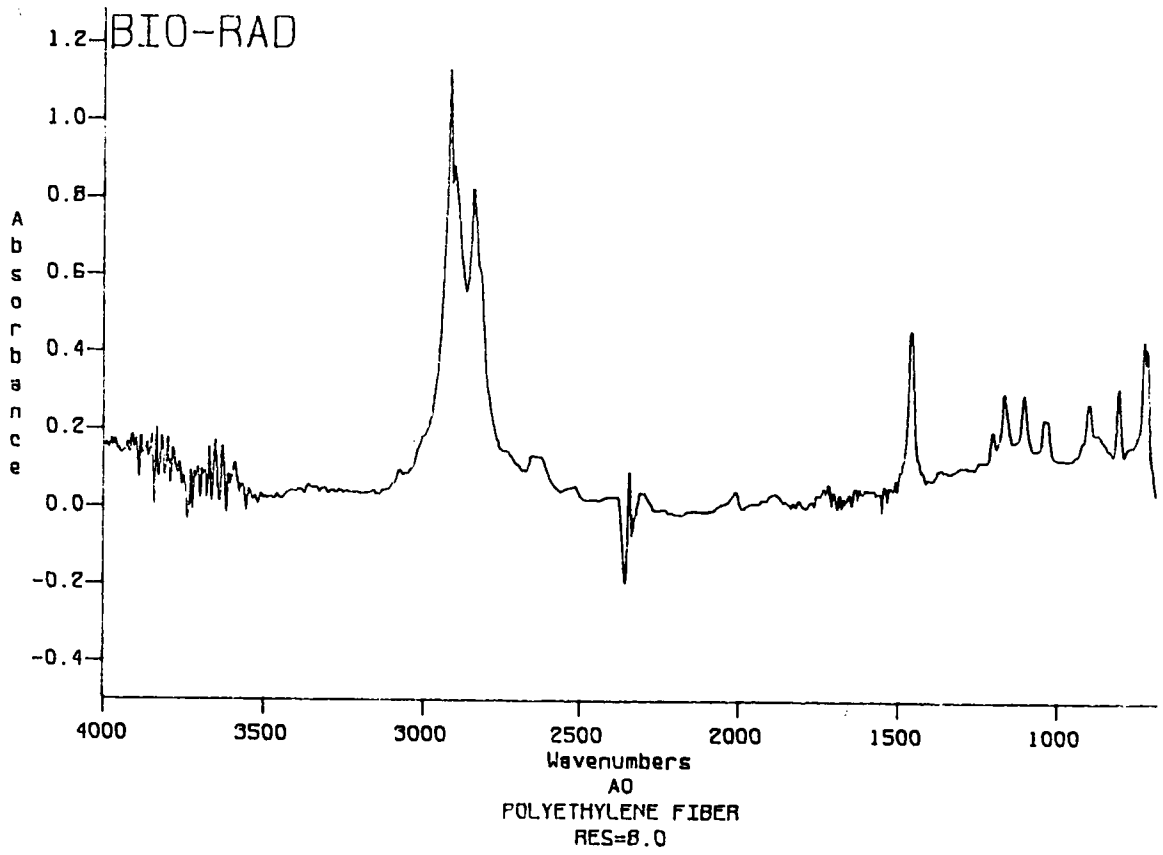


Figure 21. FTIR Spectrum of a Precursor Fiber

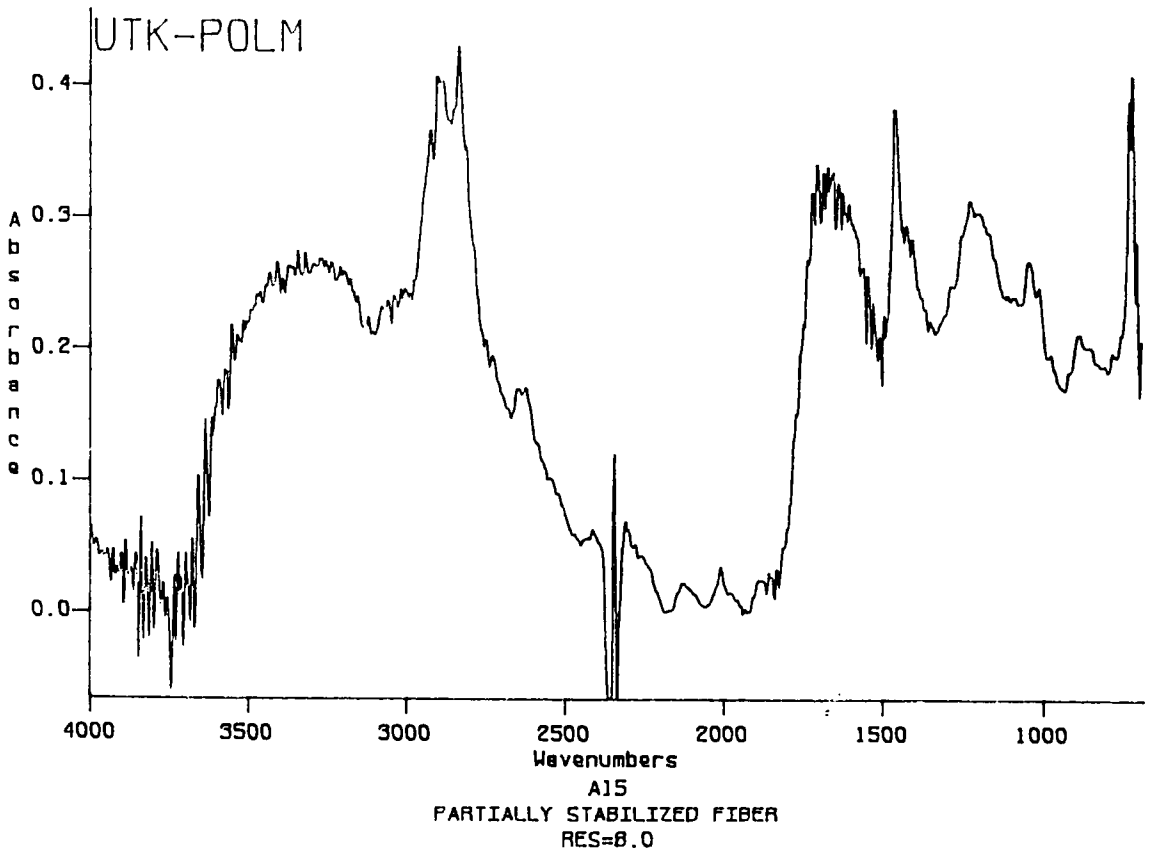


Figure 22. FTIR Spectrum of a Partially Stabilized Fiber

to the =CO vibration. The peaks observed at 2850-2950 cm^{-1} are the same as in polyethylene. That means only a portion of the polyethylene was converted to a stabilized structure. The other peaks below 1500 cm^{-1} may be the C=C vibration and the CH out-of-phase deformation.

For fully stabilized fibers (Figure 23), the peak due to CH_2 vibration disappeared and all of the polyethylene was changed into the stabilized structure. The peak at 1600 cm^{-1} is due to the =CO stretching and the wide peak of 1000-1280 cm^{-1} is assigned to the C=C vibration as is the peak below 950 cm^{-1}. The wide range of absorbance at 900 to 1300 cm^{-1} may be due to the C-O-C stretching. This suggests that the main crosslinking may be with the oxygen group.

From the FTIR spectrum of carbon fibers (Figure 24), one can see that the wide peak of 3000-3500 cm^{-1} is due to the moisture in the fiber. The peak at about 1700 cm^{-1} is the C=O stretching and wide peak below 1500 cm^{-1} may be the ring vibration, C=C stretching and C-C vibration. Elemental analysis showed that sulfur exists in the stabilized fibers. However, its functional groups could not be detected in FTIR spectrum, because the characteristic wavenumbers for S-containing groups are lower than 700 cm^{-1} and the FTIR equipment could scan only between 4000-700 cm^{-1}.

The FTIR spectrum shows mainly the aromatic rings in carbon fibers. Other functional groups such as -NH are due to

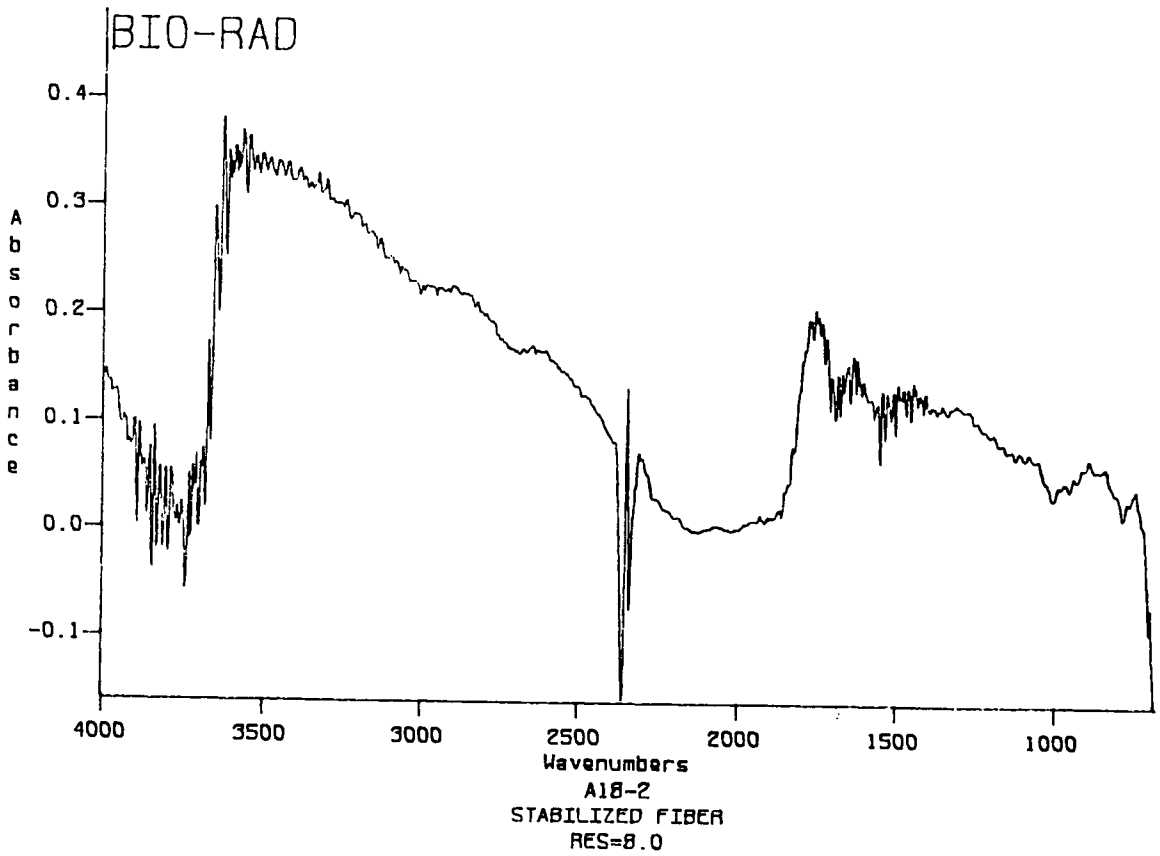


Figure 23. FTIR Spectrum of a Stabilized Fiber

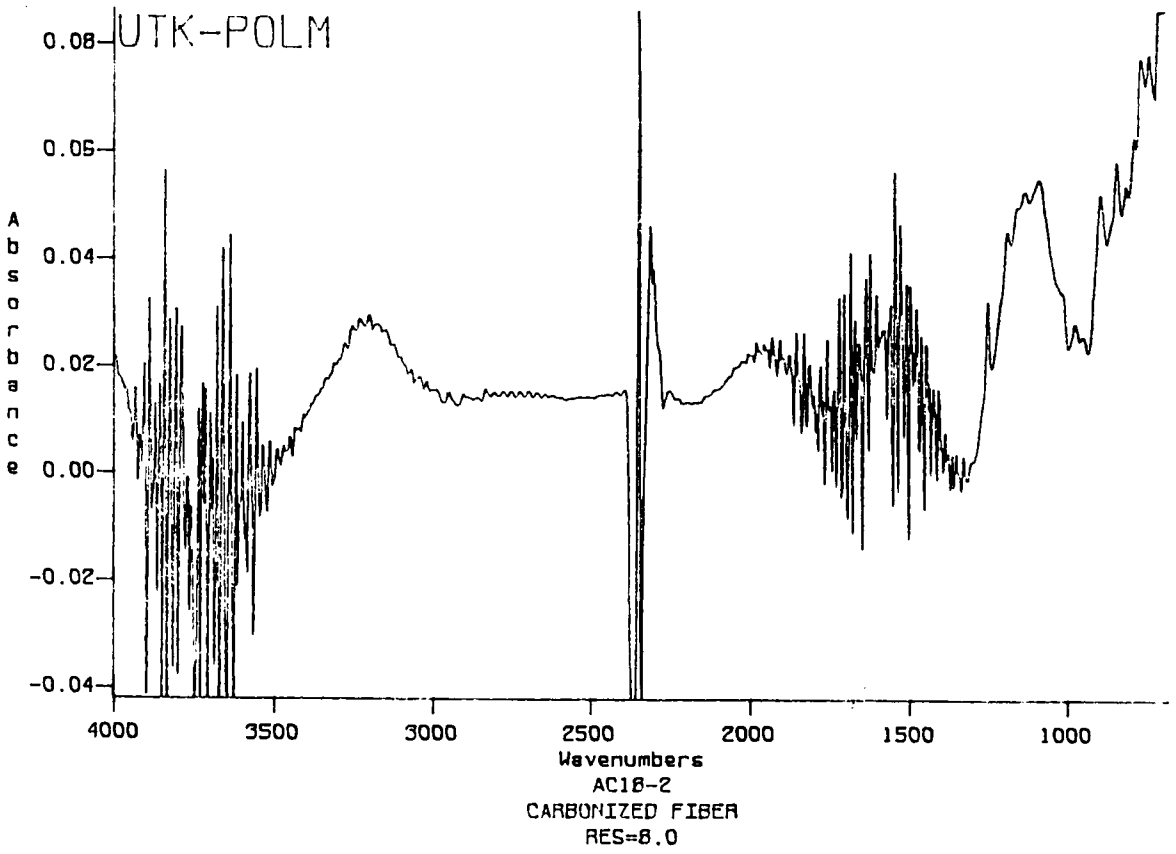


Figure 24. FTIR Spectrum of a Carbonized Fiber

the fact that carbonization was carried out in a nitrogen atmosphere, -OH is due to the presence of moisture in the fiber, and the CO_2 peak occurs because of the scanning done in air.

4.5 Change in Morphology

4.5.1 X-ray Diffraction

In order to determine the changes in orientation and crystalline structure of the fibers, wide angle x-ray diffraction studies were conducted. The precursor fiber shows a high degree of crystallinity (Figure 25). The crystallinity decreased as the time and temperature of stabilization increased. The crystallinity of the precursor fiber decreased with increased stabilization because of the penetration of sulfuric acid molecules into the crystal structure of the fiber. The final carbon fiber also does not show any evidence of crystallinity. The low carbonization temperature is the reason for the lack of detectable crystallinity in the resultant carbon fiber. It is reported that carbonization at higher temperatures can increase the crystallinity of carbon fibers [86].

X-ray diffraction patterns show a high crystal orientation pattern in precursor fibers (Figure 26). A photograph of partially stabilized fiber (Figure 27) shows a

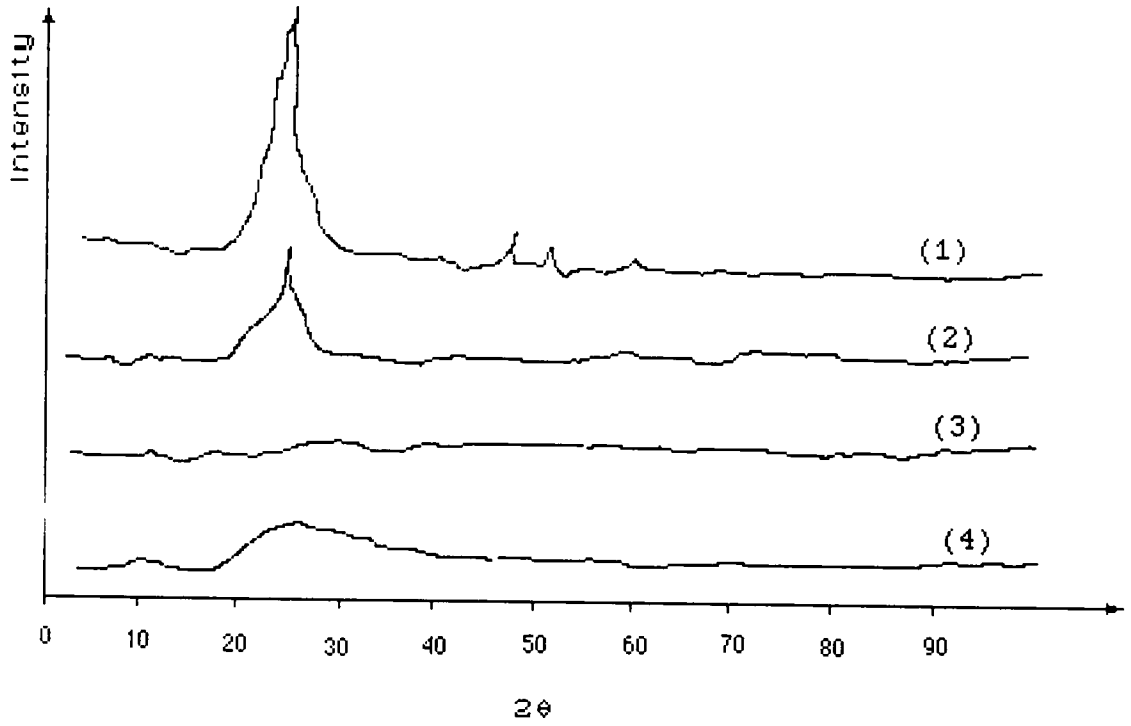


Figure 25. Wide Angle X-ray Diffraction for Precursor (1), Partially stabilized (2), Stabilized (3), and Carbonized (4) Fibers.

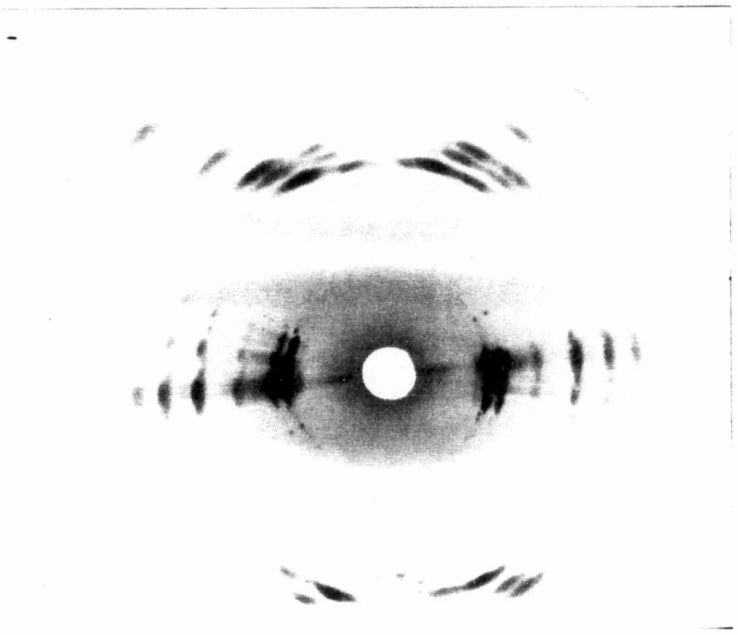


Figure 26. X-ray Photograph for Precursor Fibers

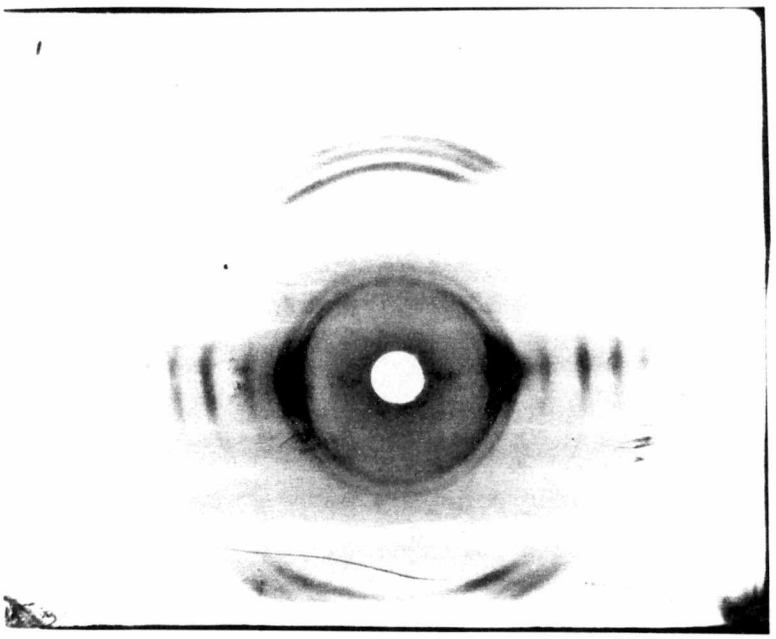


Figure 27. X-ray Photograph for Partially Stabilized Fibers

crystal pattern with reduced orientation. That means some of polyethylene crystal structure still existed in this fiber. The decrease in orientation is due to the fact that sufficient tension was not applied during stabilization in the hot sulfuric acid bath. For stabilized fibers, the x-ray diffraction photograph (Figure 28) shows only diffuse amorphous scattering indicating the complete disappearance of crystalline entities. The carbonized fibers (Figure 29) also did not show any strong peaks, but only a faint ring. This pattern indicates that order is still developing and no detectable orientation exists.

4.5.2 Optical Microscopy

Optical microscopy pictures show that the effect of time and temperature on stabilization is consistent with other observations. The diffusion and penetration of molecules of H_2SO_4 increased toward the center of the fiber as time and temperature increased. From Table III, one can see the color change during stabilization. From photographs using optical microscopy obtained on cross-sections for different time and temperatures of stabilization (Figure 30), one can see the precursor fiber is white, whereas the partially stabilized fiber shows the black circle outside and white color in the center zone. As the stabilization continued, the black zone spread to the center of the fiber and the white color zone

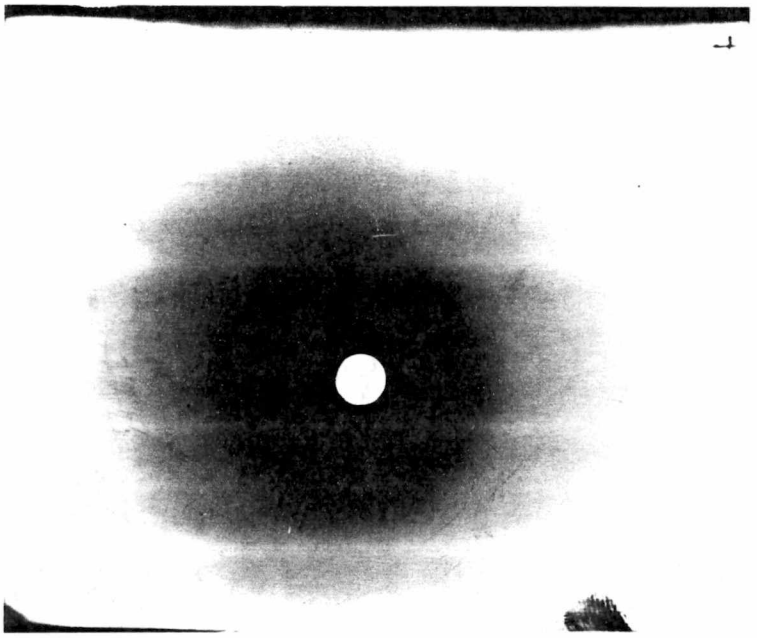


Figure 28. X-ray Diffraction Photograph for Stabilized Fibers.

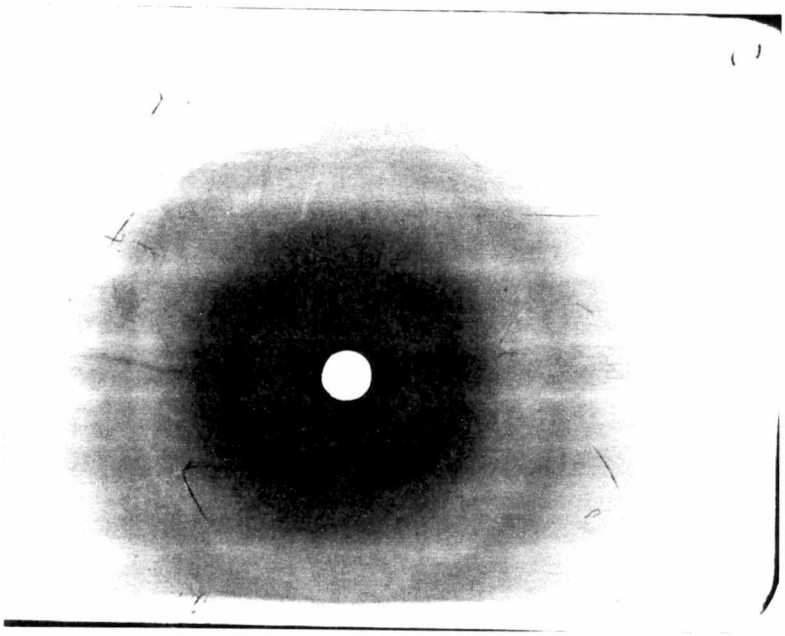
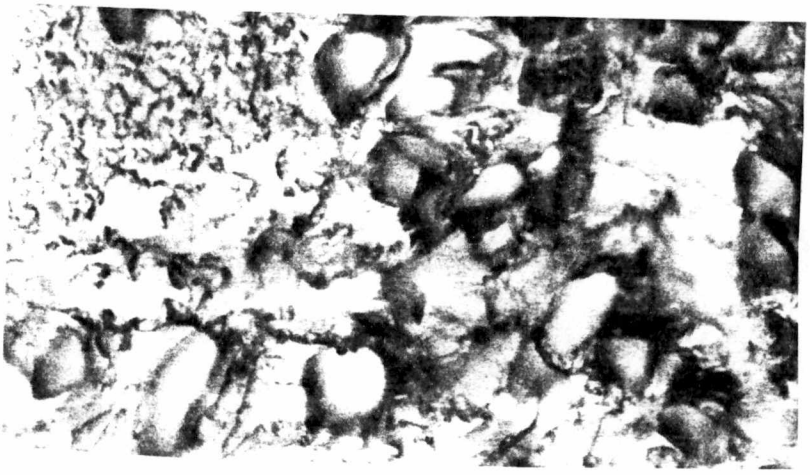
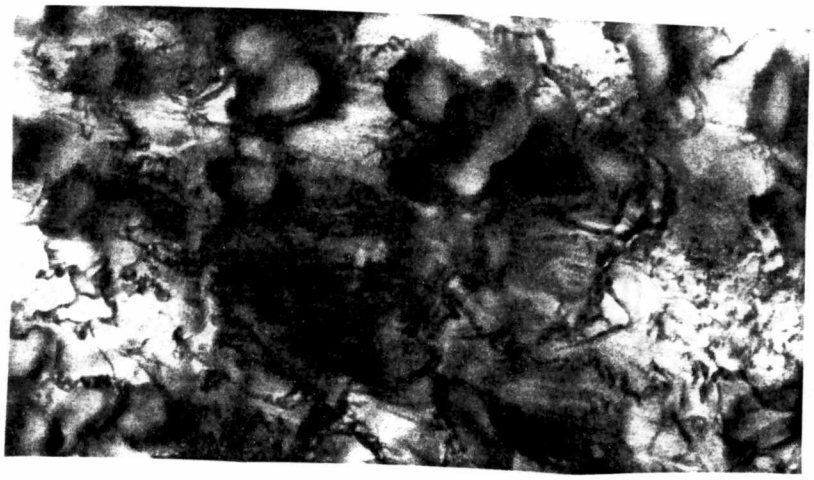


Figure 29. X-ray Diffraction Photograph for Carbonized Fibers.

(a).



(b).



(c).

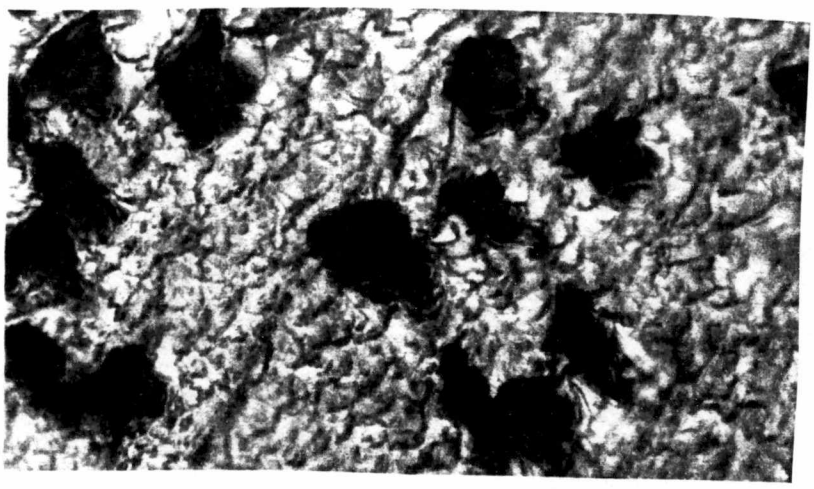


Figure 30. Optical Microscopy Pictures of (a). Precursor Fibers, (b). Partially Stabilized Fibers, and (c). Stabilized Fibers.

decreased, with the whole fiber becoming black upon completion of stabilization.

The slow progress of reactions from the fiber surface in toward the center of the fiber is a clear indication that the process is diffusion controlled. This explains the differences in stabilization kinetics seen in fibers of different diameter as mentioned in section 4.3. For producing carbon fibers without any hole, it is important that the stabilization be complete all the way to the center of the fiber.

4.5.3 Structure Studies By DSC

As can seen in Figure 19, some of the partially stabilized fibers showed two melting peaks. To study the changes in morphology near the melting region, the precursor was annealed at 150 and 160 ^{0}C. Figure 31 shows the DSC patterns of PE fibers for preheating at and above their melting point (150 ^{0}C) in an oven without tension. On preheating at 150 ^{0}C for ten minutes, the DSC shows only one melting peak. That means, around the melting point for 10 min., the extended chain crystal structure does not change and only relaxation of molecular chains took place. After preheating above its melting point for ten minutes, some of the extended chain crystals change into folded chain crystals and double melting peak is observed. The peak at a lower temperature is due to the melting of folded chain crystals and the peak at the higher temperature is due to the melting of

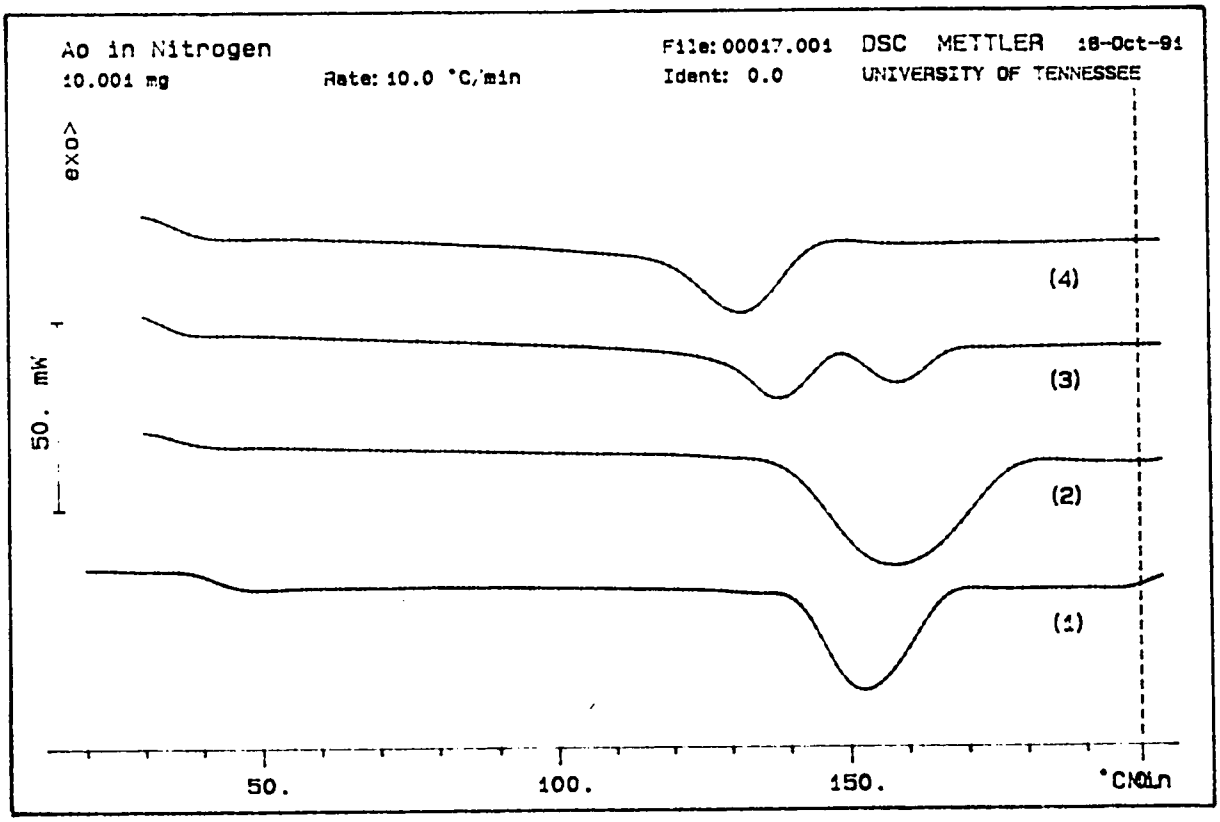


Figure 31. DSC Scans for PE Fiber Preheated Below or Above Its Melting Point. Precursor Fiber (1); Preheated at 140 ^{0}C for 10 min (2); 160 ^{0}C for 10 min (3); 160 ^{0}C for 30 min (4).

unchanged extended chain crystals. Increasing preheating time above the melting point resulted in only one melting peak in DSC pattern. This is because all of the extended chain crystals were converted to folded chain crystals.

The double melting peak observed during actual stabilization without tension is due to the melting and recrystallization of some of the extended chain crystals in the folded chain form. This has a consequence that a lack of tension leads to loss in orientation of molecules, which might significantly affect the properties of the carbon fibers.

4.6 Characterization of Carbon Fibers

The different stabilized PE fibers were carbonized by pyrolysis at 1150 ^{0}C in a nitrogen atmosphere for four minutes under constant tension. The weight loss of the fiber after carbonization was 50-60%. Tensile strength and Young's modulus of the resultant carbon fibers are shown in Figure 32. The tensile strength and Young's modulus reached 2.1 GPa and 210 GPa, respectively, for a stabilization time of 90 minutes and a temperature of 170 ^{0}C. The elongation of the carbon fiber at break was less than 1% for the same case. It is well established in carbon fiber literature that two types of carbon fibers can be obtained depending on the temperatures of carbonization [5]. Type I (high modulus) fibers are produced by treating at temperatures above 2500 ^{0}C so as to yield highly oriented graphitic layers. Type II (high strength)

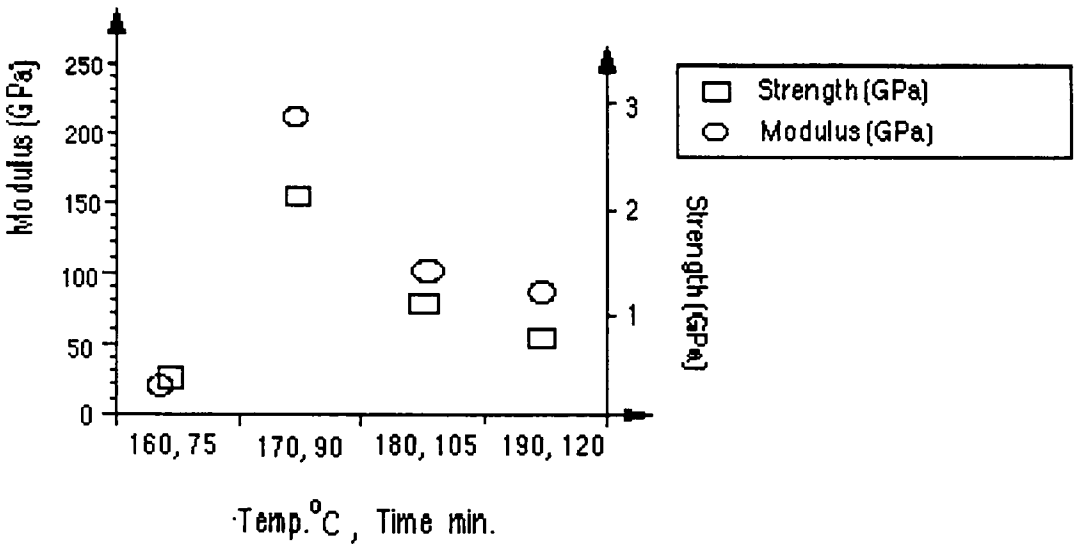
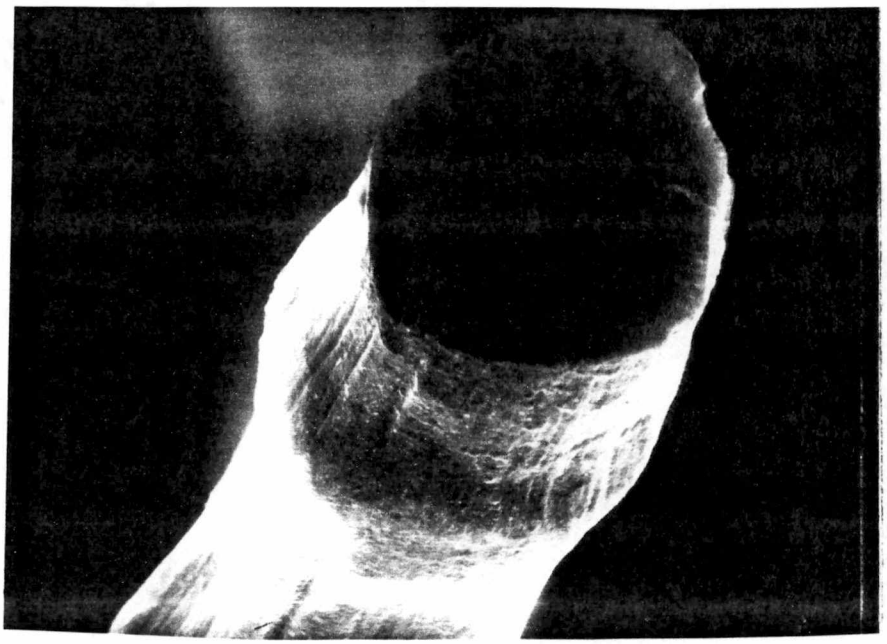


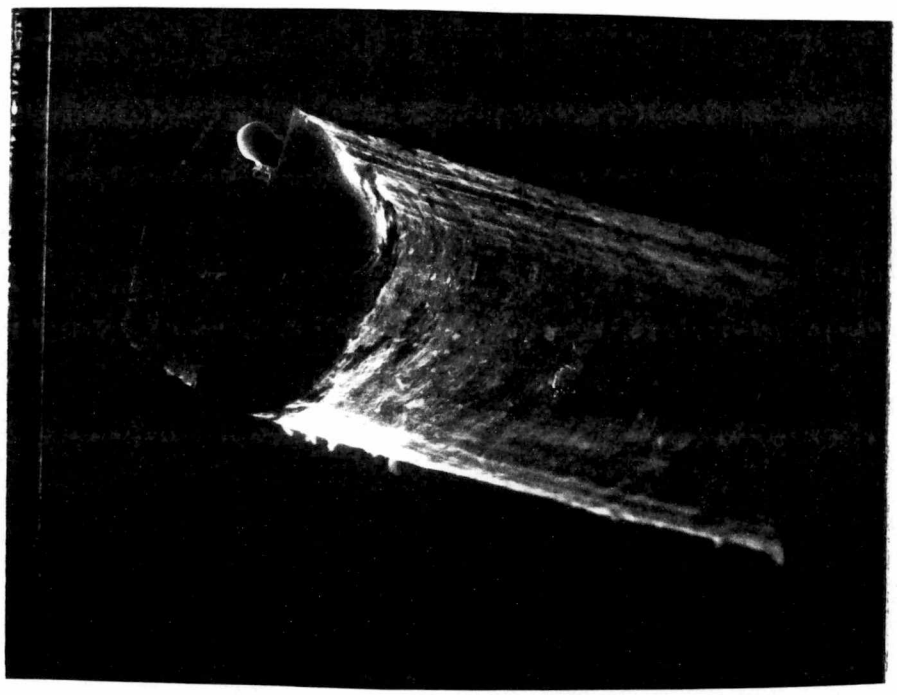
Figure 32. Tensile Properties of Carbon Fibers for Different Stabilization Temperature and Time.

fibers are produced by thermal treatment around 1000-1500 ^{0}C to achieve maximum strength. Generally, the fiber modulus increases with the heating temperature, but the strength goes through a maximum at one temperature and then decreases. So, it is conceivable that higher strengths can be achieved by treating at higher temperatures. The maximum temperature that could be achieved with the furnace temperature less than 1200 ^{0}C, which limited the treatment temperature in the present case.

Figure 33 shows SEM photographs of carbon fibers without and with slight tension during stabilization. The kink-bands (Figure 33 (a)) of the carbon fiber were due to the shrinkage of fibers during stabilization at low tension, which decreased the tensile strength of the carbon fiber. It is possible that the kink-bands in the carbon fiber, leading to modification of the surface, may increase the bonding force between the fiber and the matrix if composites are made from this carbon fiber. Figure 33 also shows the surface and cross-section of the carbon fiber which was stabilized under slight tension. It was very difficult to control the tension during stabilization in the concentrated H_2SO_4 bath, especially at higher temperatures. However, the results indicated the importance of tension during stabilization.



(a)



(b)

Figure 33. SEM Micrograph of the Carbon Fibers Stabilized with low tension

CHAPTER V

CONCLUSIONS

The feasibility of producing carbon fibers from highly ordered and oriented polyethylene fibers was investigated. The main conclusions follow:

The highly ordered and oriented PE fiber can be made infusible by crosslinking in the presence of sulfuric acid from 130-160 ^{0}C for at least 75 minutes. Although stabilization has to be started at a lower temperature (lower than melting temperature), increasing in stabilization temperature can reduce the time required for stabilization. TGA indicates that the stabilized fibers retain 50% of their weight at 800 ^{0}C in N_2 environments.

FTIR spectra indicated the presence of oxygen functional groups in the stabilized fibers. Elemental analysis indicated the presence of a small amount of sulfur (about 3%), with oxygen contents greater than 30 percent. That means that oxygen has a major role in the formation of crosslinks in the fibers. The role of sulfur may only be in initiating the crosslinking reactions.

Tension is very important during stabilization so that the fibers can maintain their fibrous form and initial orientation. Applying proper tension during both stabilization and carbonization can increase the mechanical properties of

the carbon fibers. Tension also influences the morphology of the fibers. The larger the diameter of the precursor fibers, the more time that is required to stabilize the fibers.

The stabilized PE fiber can be carbonized to carbon fibers at 1150 ^{0}C in a few minutes with proper tension. The carbon yield based on the precursor was in the range of 75-80%. Elemental analysis showed that the carbon content of the resultant fibers was about 92%. Higher temperatures of carbonization may reduce the other elements in carbon fibers.

The resultant carbon fiber had reasonably good mechanical properties, considering the fact that the tension was not controlled during stabilization and carbonization temperature was low. The combination of increasing stabilization tension to reduce the relaxation and using higher carbonization temperatures can lead to an improvement in mechanical properties of the polyethylene-based carbon fibers.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE STUDY

In order to improve mechanical properties of carbon fibers, the effect of proper tension during stabilization should be studied. Since it is very difficult to control tension in a hot sulfuric acid bath during stabilization, other stabilization environments should possibly be investigated so that the orientation of precursor fibers can be maintained and that carbon fibers with better mechanical properties can be obtained. Stabilization in an SO_2 gaseous environment might be investigated so that the tension can be controlled fairly easily during stabilization.

Other spectroscopic techniques should be used to investigate all the functional groups and microstructure of the fibers at different stabilization and carbonization conditions, so that the relationships between chemical structure and physical properties can be established. ESCA (Electron Spectroscope for Chemical Analysis) and AES (Auger Electron Spectroscopy) might be used to understand the changes in chemical structure of the samples.

Quantitative measurements might be made with optical microscopy to study the role of diffusion kinetics. Fibers with different diameters can be compared with respect to color

change, especially the movement of the black color inward from the fiber surface.

The use of regular polyethylene fibers instead of highly ordered and oriented polyethylene should be investigated also. The reactions may be faster in regular PE and tension control might be less critical.

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