Study On Polyethylene-Based Carbon Fibers Obtained by Sulfonation Under Hydrostatic Pressure

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Research Article

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Abstract

Carbon bers were prepared using polyethylene bers. The draw ratio of the polyethylene bers and the sulfonation mechanism were investigated under hydrostatic pressures of 1 and 5 bar. The influence of the melt flow index of polyethylene on the sulfonation reaction was studied. Carbon bers were prepared through the sulfonation of linear low-density polyethylene (LLDPE) bers possessing side chains with a high melt flow index. The polyethylene bers, which exhibited thermoplastic properties and plastic behavior, were cross-linked through the sulfonation process. Their thermal properties and mechanical properties changed to thermoset properties and elastic behavior. Although sulfonation was performed under a hydrostatic pressure of 5 bar, it was difficult to convert the highly oriented polyethylene bers because of their high crystallinity, but partially oriented polyethylene bers could be converted to carbon bers. Therefore, sulfonation was performed using partially oriented LLDPE bers with a melt flow index of 20 at 130°C for 2.5 hours under a hydrostatic pressure of 5 bar. The resulting bers were carbonized under the following conditions: 1000°C, 5°C/min, and five minutes. Carbon bers with a tensile strength of 2.03 GPa, a tensile modulus of 143.63 GPa, and an elongation at break of 1.42% were prepared.

1. Introduction

Carbon bers are excellent materials for structural reinforcement in light-weight composites because of their high tensile strength, modulus, high thermal resistance, good chemical stabilities, electrical conductivities, and excellent creep resistance. On the other hand, the high production cost of carbon bers limits their widespread use in the aerospace industry, military industry, high-performance automobile industry, or other special applications not related to price. Therefore, lowering the production cost of the carbon bers is an important issue for expanding their use from the special applications field to the general application field. Among carbon ber production processes, the cost of precursor ber production contributes more than approximately 50% of the total carbon ber production cost. Therefore, reducing the cost of these precursor bers is essential [1–6]. Various materials have been studied to lower the cost of precursor fiber of carbon bers, such as polyethylene, lignin, textile polyacrylonitrile, and melt spinnable polyacrylonitrile. Among these materials, polyethylene has attracted considerable attention owing to its good mechanical performance, high carbon content (86%), and ability to be melt-spun at high production rates, easily available, relatively low cost (<$1/lb), easily deformable property, and high carbon yield when converted to carbon fiber [7–13]. Polyethylene is largely classified into the following: ultra-high molecular weight (UHMWPE), which has extremely long chains of polyethylene that align in the same direction; high-density polyethylene (HDPE), which has short branches with a polymer backbone; linear low-density polyethylene (LLDPE), which is a substantially linear polymer with many short branches; and low-density polyethylene (LDPE), which has a large number of branches (approximately 2% of carbon atoms) with a polymer backbone depending on the manufacturing process. These polyethylene materials exhibit several different characteristics, such as a molecular structure, melt flow index, molecular weight, melting temperature, rheological properties, and mechanical properties [14–18].
Several studies have examined polyethylene-based carbon fibers and various attempts to improve the tensile strength of polyethylene-based carbon fibers have been made [19–28]. J. Kim and J. Lee examined polyethylene-derived carbon fibers using LLDPE. Sulfonation was performed using sulfuric acid over a temperature range of 130 ~ 160°C for 1 ~ 4 hours, followed by carbonization at 950°C for five minutes [29]. B. Barton et al. examined the high modulus low-cost carbon fibers from LLDPE [30]. S. Lee et al. suggested an effective method for polyethylene-derived carbon fibers using an electron beam irradiation process. A melt-spun linear low-density polyethylene fiber was pre-treated with an electron beam under various conditions at an intensity of 500 kGy ~ 1500 kGy. Ninety minutes of sulfonation at 95°C were sufficient for the 1500 kGy irradiated polyethylene fiber to produce carbon fibers with sound mechanical properties [31].

Although carbon fibers were manufactured successfully using various polyethylene materials, such as UHMWPE, HDPE, LLDPE, and LDPE, there is no literature discussing the various types of polyethylene precursor fibers such as high density polyethylene fiber and linear low density polyethylene fiber with different melting index. Also, there were no literature discussing the relationship between orientation and crosslink of the precursor fiber under hydrostatic pressure condition.

Therefore, in this study, carbon fibers were manufactured by selecting HDPE and LLDPE, in which the fiber shape was easy to deform, and they are relatively inexpensive materials. HDPE and LLDPE precursor fibers with various melt flow indices were cross-linked through the sulfonation process. The relationship between fiber orientation and the sulfonation effect under high-pressure conditions was studied, and polyethylene-based carbon fibers were successfully prepared.

2. Experimental

2.1. Materials

Polyethylene fibers were prepared using HDPE pellets (LG Chem., LOTTE Chem., Korea) and LLDPE pellets (LOTTE Chem., Korea). Table S1 lists the specifications of the HDPE pellets and LLDPE pellets. Sulfuric acid 98% (Sigma Aldrich, USA) was used as a cross-linking agent.

2.2. Preparation of the polyethylene precursor fiber

HDPE precursor fibers and LLDPE polyethylene precursor fibers were melt-spun using a single nozzle extruder. Table S2 lists the detailed spinning conditions of the polyethylene precursor fibers and drawing conditions of the polyethylene precursor fibers. The partially drawn HDPE fiber and partially drawn LLDPE fiber stretched well as the melt flow index value increased; hence, a drawing process was performed at different draw ratios for each material.

2.3. Sulfonation and carbonization of the polyethylene fiber

Precursor fibers, HDPE and LLDPE, were cross-linked by sulfonation using the following procedure. Sulfonation was performed using self-designed sulfonation equipment, which could control the
temperature and pressure up to $1 \sim 5$ bar. The single filament fibers, such as HDPE and LLDPE fibers, were wound 50 times on a sulfonation equipment hanger to obtain a multi-filament fiber. The number of filaments in the multi-filaments was 100, and the length was 500mm. A Teflon weight was hung at the end of the multi-filament to give a tension of 4MPa. The prepared samples were immersed in the sulfonation equipment with 98% sulfuric acid. After immersing the specimens in the sulfuric acid, pretreatment was performed at 80°C for four hours. Sulfonation was carried out by varying the sulfonation temperature and pressure conditions of the pre-treated specimens. The sulfonation pressure conditions were performed under pressures of 1 bar and 5 bar, and the sulfonation temperature conditions were a temperature of 130°C and a heating rate of 2°C/min. In the case of HDPE fibers, such as partially drawn and fully drawn fibers, sulfonation was performed for 2, 3.5, and 5 hours. For the LLDPE fibers, such as partially drawn and fully drawn fibers, sulfonation was performed for 2, 2.5, and 5 hours. In the case of LLDPE fibers, because the cross-link reaction was faster than for the HDPE fibers, the specimens treated with 2.5h sulfonation were investigated. In the case of HDPE fibers, the fibers treated with 3.5h sulfonation were analyzed. After sulfonation, the specimens were washed with distilled water for 30 minutes. The washed specimens were then dried in a drying oven at 60°C for two hours.

After sulfonation process, sulfonated polyethylene fibers were hung on a steel hanger for carbonization. The steel weight was hung at the end of the sulfonated polyethylene fiber to give a tension of 4MPa. The prepared specimens were sealed with a quartz beaker and carbonized in a furnace (JSMF-30H, JSR, Korea) in an N$_2$ atmosphere. The temperature was 1000°C for five minutes with a heating rate of 5°C/min. Heating was stopped after reaching the target temperature. Figure S1 presents a sulfonation equipment (Yes solutions Co., Korea) and manufacturing process of the polyethylene based carbon fiber. Figure S2 shows photographs of the before and after carbonization process.

### 2.5. Specimen code

Table S3 list the specimen code of the polyethylene precursor fibers, sulfonated polyethylene fibers and carbonized polyethylene fibers. Carbon fibers were impossible to manufacture from fully drawn polyethylene precursor fibers, whereas they were prepared successfully using partially drawn polyethylene precursor fibers.

### 3. Results And Discussion

#### 3.1. Polyethylene precursor fiber

##### 3.1.1. Mechanical properties of the polyethylene precursor fiber

The tensile strength and initial modulus values of the polyethylene precursor fiber increased with increasing melting flow index of the polyethylene polymer, but the elongation at break of the polyethylene...
precursor fiber decreased (Figure S3). This is because of the difference in molecular weight of the polyethylene polymer (Figure S4).

3.2. Sulfonated polyethylene fiber

3.2.1. Morphological analysis of the sulfonated polyethylene fiber

Figure 1 shows the cross-section SEM images of the sulfonated LLDPE fibers. Figure 1(a) presents cross-sectional surface SEM images of the LLDPE fibers with a melt flow index of 1.1, 10, and 20 according to the sulfonation time under a pressure of 1 bar and temperature of 130°C.

After the sulfonation treatment, the diameter of all linear density polyethylene fibers increased gradually with increasing sulfonation time. This increase in fiber diameter was attributed to the shrinkage of the longitudinal direction of the linear density polyethylene fiber due to exposure to sulfuric acid during the 130°C sulfonation process. The linear density polyethylene fibers also formed cracks through the fiber axial direction under all sulfonation time conditions. As the LLDPE fibers cross-link through the sulfonation process, the failure mechanism changes gradually from plastic deformation to elastic deformation. This is because the –SO$_3$ crosslinks the CH$_2$ chains of the LLDPE fiber; hence, atomic bonding dominates the molecule instead of intermolecular forces. In this process, residual stress remains in the fiber when shrinkage occurs in the fiber axial direction. Therefore, the fibers with elastic properties do not maintain their original shape and expand, resulting in the formation of cracks. The LLDPE fiber specimens showed a different tendency when sulfonation was performed under a high pressure of 5 bar. Figure 1(b) shows the cross-section SEM images of the LLDPE fibers sulfonated under a pressure of 5 bar and temperature of 130°C. After the sulfonation treatment, the diameters of the LLDPE fiber specimens increased slightly with increasing sulfonation time, but there was almost no change in diameter compared to the HDPE fibers, and the sulfonated fibers showed a clean cross-sectional surface. This is because a high hydrostatic pressure prevents fiber shrinkage. In addition, although the partially drawn polyethylene fiber was treated for a long time, such as 5 h, a neat cross-sectional surface without a core structure was formed, and no cracks were observed through the fiber axial direction. Hence, the diffusion rate of the sulfuric acid into the HDPE fiber is faster under a 5 bar hydrostatic pressure than at 1 bar, so that the residual stress is reduced. In the case of fully drawn LLDPE fiber, phenomena, such as cracks in the fiber axial direction, were more prominent than that of the partially drawn LLDPE fiber. In the case of the fully-drawn LLDPE fibers, due to highly oriented the crystalline region, it is difficult for sulfuric acid to diffuse into the inside of the fiber. As a result, among all specimens including HDPE fibers and LLDPE fibers, the PSL20 specimen sulfonated for 2.5h under 5 bar pressure was sulfonated without cracks or a core structure. HDPE fibers showed poor crosslinking efficiency than LLDPE fibers (Figure S5).

Table S4, S5 lists the changes in diameter and length of the HDPE fibers and LLDPE fibers.

3.2.2. Mechanical properties of the sulfonated LLDPE fiber
Figures 2 present the tensile properties of the sulfonated LLDPE fiber with various sulfonation time under a pressure of 5 bar and temperature of 130°C. In the case of partially drawn LLDPE fiber with a melt flow index of 1.1, 10, and 20 (Fig. 2(a),(b),(c)), the tensile strength and initial tensile modulus values tended to increase with increasing sulfonation time, regardless of the melt flow index, but the elongation at break decreased rapidly.

Hence, the mechanical behavior of the LLDPE changed from plastic behavior to elastic behavior. This is because the properties of the fibers change elastically in that LLDPE, an aliphatic organic compound, is converted to an aromatic organic compound by SO$_3$ from sulfuric acid, and a benzene ring is formed. The cross-linking efficiency was increased dramatically by these branches compared to the HDPE fibers(Figure S6). Therefore, most of the aliphatic components, such as CH$_2$ and CH$_3$, which constitute the main polymer backbone and side chains (branches) of the LLDPE fiber, participated in the reaction with sulfuric acid to form a benzene ring. Thus, the initial tensile modulus of the LLDPE sulfonated fiber was relatively high. In addition, when sulfonation was performed for five hours, the tensile strength of the partially drawn LLDPE fibers decreased. Interestingly, in the case of the fully drawn LLDPE fiber specimen, the tensile strength decreased rapidly. There is a relationship between the increase in crystallinity due to the high orientation of the LLDPE fiber and sulfuric acid penetration. Fibers with high crystallinity are difficult to penetrate by sulfuric acid. Moreover, the axial cracks caused by the residual stress inside the fiber generated during the sulfonation process reduce the mechanical properties of the sulfonated LLDPE fiber.

3.2.4. Thermal properties of the sulfonated LLDPE fiber

Figure 3 shows the DSC curve of the fully drawn LLDPE fiber and the partially drawn LLDPE fiber with various sulfonation time. The melting temperature and endothermic enthalpy decreased gradually with increasing sulfonation time. In the case of the specimens sulfonated for 5 h, only a weak melting point peak was observed, regardless of the melt flow index of the LLDPE. Moreover, the endothermic enthalpy was also very low, which means that the thermal properties of the LLDPE fibers were cross-linked by SO$_3$ in sulfuric acid to change from thermoplastic to thermoset properties. In addition, the melting point peak disappeared relatively easily because sulfuric acid easily penetrated the amorphous region of the partially drawn LLDPE fibers(Fig. 3(b)). The FSL10 and FSL20 specimens showed complete crosslinking under the sulfonation condition of 5 h. The crosslinking efficiency of the partially drawn LLDPE fiber was superior to the fully drawn HDPE fibers(Figure S7(a)), partially drawn HDPE fibers(Figure S7(b)), and fully drawn LLDPE fibers(Fig. 3(a)). This is due to the thin fiber diameter of LLDPE, large amount of polymer side chains inside the polymer backbone structure, and the proper distribution of amorphous regions. On the other hand, although sulfonation was performed for a long time, such as 5 h, a low endothermic enthalpy still appeared, indicating that the polymers do not participate in the crosslinking reaction and remain aliphatic organic compounds.

3.2.5. Molecular structure change of the sulfonated polyethylene fiber
Figures S8 (a), (b), and (c) show the typical $^1$H NMR spectra of the PL1.1, PL10, and PL20 specimens, respectively. The peak at 0.7–1.3 ppm was assigned to a proton of the CH$_3$ group; the peak at 1.2-1.4ppm corresponded to a proton of the CH$_2$ group, and the peak at 1.4-1.7ppm was attributed to a proton of the CH group. Because the LLDPE is a structure with many side chains (branches), peaks were generated for a large range of primary alkyl, secondary alkyl, and tertiary alkyl groups. On the other hand, there was no peak at 6.5-8.0ppm corresponding to the protons of an aromatic ring. This indicates that pure LLDPE without sulfonation is also an aliphatic organic compound. In the case of HDPE precursor fibers, only two distinct peaks were observed because the HDPE fiber is the dominant structure of the main chain, and peaks of primary alkyl and secondary alkyl were generated in all HDPE samples (Figure S9).

In the case of HDPE and LLDPE fibers treated with sulfonation under a pressure of 1 bar, they were crosslinked with sulfuric acid, and a benzene peak could be observed in the range of 6.5-8.0ppm (Figure S10 and Figure S11), and this benzene peak was remarkably observed under the sulfonation pressure of 5 bar.

Figure 4 (a), (b), and (c) show the typical $^1$H NMR spectrum of the PSL1.1, PSL10, and PSL20 specimens. In the case of partially drawn sulfonated LLDPE fiber that was sulfonated at 5 bar, most of the primary alkyl groups, secondary alkyl groups, and tertiary alkyl groups disappeared, and protons for an aromatic ring were observed at 6.5-8.0ppm. The aromatic peak dominated the molecular structure of the polymer. This result provides conclusive evidence that polyethylene fibers, which were aliphatic organic compounds, were cross-linked by sulfonation and converted to aromatic organic compounds. Aliphatic organic compounds have a relatively weak bond strength of 364kJ/mol and are easily phase-changed and thermally decomposed by the movement of molecular chains at carbonization temperature. On the other hand, aromatic organic compounds are quite strong with a bonding strength of 518kJ/mol, so that they are not decomposed easily even at carbonization temperature. These benzene rings are formed more easily in LLDPE materials with a high melt flow index than LLDPE with a relatively low melt flow index of 1.1. However, in the case of HDPE fiber, even though sulfonated under 5bar pressure, it could not completely changed aromatic polymer due to the molecular structure without branches (Figure S12).

In order to observe the change in the molecular structure of the polyethylene fiber in more detail, FT-IR analysis was performed.

Figures S13 show the FT-IR spectra of sulfonated LLDPE fibers. The PL1.1, PL10, and PL20 specimens (Figure S13 (a),(b), and (c)) showed absorptions at 2928 cm$^{-1}$ and 2859 cm$^{-1}$ for the C-H asymmetric and symmetric stretching vibrations, respectively. Absorptions at 1469 cm$^{-1}$ (C-H bending vibration) and 738 cm$^{-1}$ (C-H bending) were detected. All of these peaks were attributed to aliphatic organic compounds in LLDPE. Specimens FSL 1.1, 10, and 20 treated by sulfonation revealed aromatic C-C stretching vibrations and aromatic C-H out of plane bending peaks concomitantly CH$_2$ and CH$_3$ peaks at 1500-1400 cm$^{-1}$ and 674 cm$^{-1}$, respectively. Hence, the aliphatic organic compounds changed to aromatic
organic compounds. On the other hand, in the PSL1.1, 10, and 20 specimens, the CH$_2$ and CH$_3$ peaks disappeared, and only aromatic C-C stretching vibrations (1500-1400 cm$^{-1}$) and aromatic C-H out of plane bending vibrations (674 cm$^{-1}$) were detected. Therefore, the LLDPE fibers changed from aliphatic organic compounds to aromatic organic compounds.

### 3.2.6. Orientation of LLDPE fibers and the molecular structure of sulfonated linear low-density fibers

LLDPE fibers with melt flow index of 20, which had superior sulfonation efficiency than HDPE fibers, were selected, and the orientation characteristics according to fiber drawing and molecular structure of the sulfonated LLDPE were analyzed qualitatively by WAXD.

Figure 5 presents the 2D-WAXD pattern of LLDPE precursor fibers and sulfonated LLDPE fibers with melt flow index of 20. The fully drawn LLDPE fiber (Fig. 5(a)) showed remarkable peaks at $2\theta = 23^\circ$. The X-ray pattern of the fully drawn LLDPE fiber shows that the ring is partially bright in the equatorial direction, and a clear crystal orientation result of the LLDPE fiber appeared. This pattern indicates that the crystalline phase of the LLDPE fiber was well oriented, indicating that the polymer chain axis (c-axis) is oriented parallel to the fiber drawing direction. This means that the level of orientation is improved dramatically by the drawing process. Moreover, the crystalline phase became more oriented along the fiber axis. Figure 5(b) shows the 2D-WAXD pattern of FSL20 specimen. This 2D-WAXD pattern means that the crystal regions lost their orientation and were arranged randomly, indicating that crystals with melting points exist. The presence of crystals with melting points suggests that the fibers may eventually fail to maintain their shape during the carbonization step and may be pyrolyzed. Figure 5(c) shows the 2D-WAXD pattern of PL20 specimen. The partially drawn LLDPE fiber showed remarkable peaks at $2\theta = 23^\circ$. The rings of the X-ray pattern of partially drawn LLDPE fiber appear brightly over a wider area than the fully drawn LLDPE fiber. This indicates that the LLDPE fibers were partially drawn and have relatively isotropic properties compared to the fully drawn LLDPE fibers. Figure 5(d) shows the 2D-WAXD pattern of PSL20 specimen. Very fuzzy rings were observed in the X-ray pattern of the sulfonated LLDPE fiber. These patterns are typically observed in fibers exhibiting isotropic properties. Moreover, it is believed that directional LLDPE fibers are cross-linked by sulfuric acid to form benzene rings. LLDPE changed to an aromatic structure and lost its orientation.

### 3.3. Polyethylene-based carbon fibers

#### 3.3.1. Morphological analysis of the polyethylene-based carbon fibers

Figure S14 shows SEM images of the polyethylene-based carbon fiber prepared from partially drawn LLDPE fiber with a sulfonation pressure of 1 bar at 130°C for 2.5h. All fibers had a hollow shape with an empty center part, showing that cracks formed through the axial direction of the carbon fiber. This is because sulfuric acid does not penetrate the fibers and cross-linking reactions by sulfonation proceeded only in the part of the fiber that reacted. Thus, it could not develop into carbon fibers with superior
mechanical properties. In addition, in the case of partially drawn sulfonated HDPE fiber subjected to sulfonation under the same sulfonation conditions, the shape of the fiber was not maintained and all decomposed thermally; thus, SEM analysis was impossible.

The polyethylene-based carbon fiber sulfonated under a pressure of 5 bar exhibited different morphological characteristics from polyethylene-based carbon fiber sulfonated at 1 bar.

Figure 6 shows the polyethylene-based carbon fibers prepared by partially drawn HDPE fibers with sulfonation pressure of 5 bar at 130°C for 3.5h and partially drawn LLDPE fiber with sulfonation pressure of 5 bar at 130°C for 2.5h. In the case of CH0.6 (Fig. 6(a)), CH7 (Fig. 6(b)), and CH18 (Fig. 6(c)), the carbonized fibers did not maintain a circular cross-section but had a sharp shape, such as a pentagonal structure and a hexagonal structure, as well as a hollow interior. This is because the fiber has an irregular cross-sectional shape and a hollow cross-section due to the poor cross-linked efficiency of the HDPE fiber. Although sulfuric acid permeated into the HDPE fiber under the sulfonation conditions in a high-pressure hydrostatic atmosphere, the cross-linking reaction by SO₃ did not occur actively because of the molecular structure of the HDPE fiber with only the main chain. In addition, the mechanical properties of the CH0.6, CH7, and CH18 specimens were extremely low and could not be measured.

In the case of the specimen carbonized with partially drawn sulfonated LLDPE fiber, the specimen exhibited a completely different tendency compared to the high-density polyethylene-based carbon fiber. Figure 6 (d), (e), and (f) present cross-section SEM images of the LLDPE-based carbon fiber. The CL1.1, CL10, and CL20 specimens showed a completely filled fiber cross-section. This means that sulfuric acid diffused and penetrated well into the LLDPE fibers and cross-linked due to the high sulfonation hydrostatic pressure of 5 bar and the molecular structure of the LLDPE fiber, which contained a large number of branches with the polymer main chain. The hollow cross-section was not observed in the CL1.1 and CL10 specimens, but a long crack was formed in the fiber axial direction, which was attributed to residual stress caused by thermal hysteresis in the carbonization process. In contrast, in the CL20 specimen, the cross-section image of the carbon fiber revealed a circular shape, no cracks, and a reasonably clean surface. This indicates that the cross-linking reaction of the partially drawn LLDPE fiber with a melt flow index of 20 was extremely stable during the sulfonation process at 5 bar, 130°C, and 2.5h, resulting in an aromatic structure. Furthermore, even in the carbonization process, the fibers could not decompose at high temperatures.

**3.3.2. Thermal properties of the polyethylene-based carbon fibers**

Figure S15 shows the TGA weight loss curve of the partially drawn polyethylene fiber (PL20), partially drawn sulfonated polyethylene fiber (PSL20) sulfonated for 2.5h at 5 bar, 130°C, and carbon fiber-based LLDPE fiber (CL20). In the case of the PL20 specimen, pyrolysis proceeded rapidly at 400 to 500°C, and the residual weight was 0%. This means that the polyethylene fibers have low thermal stability at high temperatures. A comparison of PSL20 and PL20 showed that the thermal decomposition of PSL20 proceeded in stages. There was no significant weight loss in the temperature range of 400 to 500°C, and
the residual weight was 42.7%. This means that PSL20 became quite thermally stable due to cross-linking by sulfuric acid. In the case of carbonized fiber, however, it was extremely stable even at high temperatures. No significant pyrolysis occurred, and the residual weight was 94.9%.

3.3.3. Mechanical properties of the polyethylene-based carbon fiber

Figure S16 shows the stress-strain curve of the polyethylene-based carbon fiber (CL20). The tensile strength, tensile modulus, and elongation at break of the carbon fiber, which were confirmed through the stress-strain curve, were 2.03 GPa, 143.63 GPa, and 1.42%, respectively. Carbon fibers exhibited completely elastic properties and high strength, suggesting that the aromatic structure polymer was carbonized at 1000°C.

3.3.4. Cross-link mechanism and carbonization mechanism of the LLDPE fiber and elemental composition.

Figures S17 and S18 show schematic diagrams of the cross-linking mechanism and carbonization mechanism of the polyethylene-based carbon fibers through polyethylene precursor fiber analysis, mechanical and chemical structure analysis of sulfonated polyethylene fibers, and carbon fiber analysis. Table S6 lists the compositions of C, H, O, N, and S in the carbon fiber prepared from partially drawn HDPE fibers and fully drawn LLDPE fibers.

4. Conclusion

This paper reported the preparation of carbon fibers using HDPE fibers and LLDPE fibers. The draw ratio of the polyethylene fibers and the sulfonation mechanism under hydrostatic pressure conditions of 1 bar and 5 bar were investigated.

The influence of the melt flow index of polyethylene on the sulfonation was studied. The LLDPE fibers having a side chain and a low melt flow index were converted successfully to carbon fibers.

Polyethylene fibers, which exhibited thermoplastic properties and plastic behavior, were cross-linked through a sulfonation process. The thermal properties and mechanical properties were changed due to the thermosetting properties and elastic behavior. The sulfonation process changed the thermal and molecular structure properties of polyethylene in depth according to NMR spectroscopy, FT-IR spectroscopy, DCS, wide-angle X-ray scattering analysis, and SEM analysis. The transition from aliphatic polymers to aromatic polymers was an important issue.

Although sulfonation was performed under a hydrostatic pressure of 5 bar, it was difficult to convert the HDPE and LLDPE fibers to aromatic polymers because of their high crystallinity.

Therefore, using a linear low-density polyethylene fiber with a melt flow index of 20 and side chains in the polymer structure that can form a low diameter, sulfonation was performed at 130°C for 2.5 hours under...
a hydrostatic pressure of 5 bar. This was followed by carbonization under carbonization conditions of 1000°C, 5°C/min, and 5min. The resulting carbon fibers had a tensile strength, tensile modulus, and tensile elongation of 2.03 GPa, 143.63 GPa, and 1.42%, respectively.

Declarations

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Figures
Figure 1

SEM images of the cross-sectional surface of the LLDPE fibers with a melt flow index of 1.1, 10, and 20 according to the sulfonation time under a pressure of 1 bar, 5bar and temperature of 130°C (a) Sulfonated fiber under 1bar pressure, (b) Sulfonated fiber under 5bar pressure.
Figure 2

Tensile strength, initial tensile modulus, and elongation at break of the sulfonated LLDPE with various sulfonation time under a pressure of 5 bar and temperature of 130°C (a) Sulfonated LLDPE fiber with melt flow index of 1.1, (b) Sulfonated LLDPE fiber with melt flow index of 10, (c) Sulfonated LLDPE fiber with melt flow index of 20.
Figure 3

DSC curves of the LLDPE fibers with melt flow index of 1.1, 10, and 20 according to the sulfonation time under a pressure of 5 bar and temperature of 130°C (a) Fully drawn sulfonated LLDPE fiber, (b) Partially drawn sulfonated LLDPE fiber.
Figure 4

$^1$H NMR spectrum and hydrogen peak assignments of sulfonated partially drawn LLDPE fibers under sulfonation conditions of 5 bar for 2.5h (a) PSL1.1, (b) PSL10, (c) PSL20.
Figure 5

2D-WAXD pattern of LLDPE precursor fibers and sulfonated LLDPE fibers with melt flow index of 20 at a sulfonation time of 2.5h under a pressure of 5 bar and temperature of 130°C (a) FL20, (b) FSL20, (c)PL20, (d)PSL20.
Figure 6

Polyethylene-based carbon fibers prepared from partially drawn HDPE fibers and partially drawn LLDPE fiber with a sulfonation pressure of 5 bar at 130°C for 3.5h, 2.5h (a) CH0.6, (b) CH7, (c) CH18, (d) CL1.1, (e) CL10, and (f) CL20.

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