

Small-Molecule Additive for Improving Polyethylene-Derived Carbon Fiber Fabrication

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Abstract: A small-molecule additive, diphenylamine (DPA), was successfully employed in the production of strong, light, and high-performing polyethylene (PE)-derived carbon fibers (CFs). The incorporated DPA effectively enhanced the char yield, graphitic structure, and melt-spinnability of the PE matrix, as evidenced by various spectroscopic, thermogravimetric, and rheological analyses. Furthermore, the PE/DPA-derived CFs exhibited sound mechanical properties, with a tensile strength of 0.63 ± 0.13 GPa and modulus of 37.89 ± 5.53 GPa.

Keywords: Carbon fiber, Diphenylamine, Polyethylene, Stabilization, Carbonization

Introduction

High-quality carbon materials have been actively employed in various fields owing to their good mechanical properties [1], electrical and thermal conductivities [2,3], and thermochemical stability. Depending on the target application, carbon materials can be prepared as powder, films, or fibers, among others. For example, carbon powder can be used as a reinforcing filler for tires, and it has been applied as a conducting agent and anode material in lithium-ion batteries [4]. Thin carbon films, owing to their conductivity and optical transparency, have found applications in the field of energy [5-7]. Finally, carbon fiber (CF) is an ideal filler material for the fabrication of CF-reinforced plastic (CFRP) exhibiting excellent mechanical properties and low weight [8,9].

According to a previous report [10], the CFRP market was valued at USD 17.5 billion in 2020 and is expected to reach USD 31.5 billion in 2025, driven by a high demand for composite materials in the aerospace and automobile industries. However, a bottleneck for market growth is the prohibitively high production cost of CFs [11]. In general, the CFs are fabricated via carbonization of polymeric precursors such as polyacrylonitrile (PAN), rayon, lyocell, lignin, and polyethylene (PE). Although CFs prepared using PAN usually exhibit better mechanical properties than those obtained from other precursors, the former are more expensive. The reason for such a high manufacturing cost is that PAN-derived CFs are necessarily prepared by solution spinning. The utilization of toxic organic solvents for CF production is discouraged because it requires additional processing steps (solvent dissolution, recovery, and disposal procedures); moreover, wet-spinning has a slower fabrication speed than the dry-spinning method. The application of melt-spinning for CF production using PAN is challenging

because of the elevated temperatures required: heating PAN to its melting point causes indiscriminate crosslinking and cyclization reactions.

Several efforts have been made to develop new CF precursors, such as a melt-processable PAN synthesized via the introduction of a soft co-monomer [12]. From an industrial perspective, the ability to easily tailor the physical state and properties of a low-cost CF precursor is more desirable than that to precisely define its molecular structure. When the cost of CF fabrication is analyzed in detail, the contribution of the precursor represents approximately 50 % of the total [13,14]. Therefore, it is crucial to find inexpensive CF precursors that are also melt-processable. Some studies have reported the successful fabrication of CFs using PE, one of the most widely used commodity thermoplastics (or melt-processable polymers). PE is characterized by a low cost ensuring a stable supply and price. However, the stabilization of non-carbonizable PE fibers requires a sulfonation step involving the treatment of PE fibers with heated sulfuric acid [15,16]. A very recent study adopted electron beam (E-beam) irradiation prior to the sulfonation step, allowing CF fabrication from PE through significantly milder sulfonation steps [17].

Several other methods can be devised to further improve the properties of CFs obtained with PE as a precursor. In this study, diphenylamine (DPA) was used as a small-molecule additive in PE fibers for more effective CF fabrication. This compound was selected because sulfonation on DPA can provide an excellent carbon precursor with a high char yield and degree of graphitization via direct carbonization without additional stabilization treatments [18]. Because a sulfonation step is also required to fabricate CF from PE, the incorporation of DPA into PE fibers results in a higher char yield and better graphitic structure compared to the neat PE fiber after identical stabilization and carbonization steps. These findings were obtained through characterization of the materials via thermogravimetric analysis (TGA), Raman spectroscopy,

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X-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectroscopy (FTIR). Furthermore, experimental results demonstrated the ability of DPA to act as a plasticizer for PE, thereby lowering the melt viscosity. Because melt viscosity is inversely proportional to melt-spinning throughput, we believe that DPA incorporation could also enhance the speed of CF production with PE as a precursor.

Experimental

Experimental Details

Fiber-grade LLDPE pellets (ASPUN 6850A, Dow Chemical, USA) were used for PE fiber spinning. ASPUN 6850A has a density of 0.96 g/cm^3 and a melt flow index of $30 \text{ g}/10 \text{ min}$ at $190 \text{ }^\circ\text{C}$. DPA was purchased from Sigma-Aldrich, USA. The PE/DPA mixture was compounded using the following procedure. First, a DPA solution was prepared using ethanol as the solvent. DPA (5 g) was dissolved in ethanol (500 mL), and the solution was poured into a beaker filled with 100 g LLDPE pellets to reach the designated weight ratio. The mixture was stirred using an overhead mixer (IKA RW20, Germany), and ethanol was evaporated overnight to obtain well-mixed PE/DPA pellets in a dry form. The PE/DPA pellets were processed into films and fibers according to the following procedure. Pellets were hot-pressed at $150 \text{ }^\circ\text{C}$ to obtain films with a thickness of approximately $15 \text{ }\mu\text{m}$. For the fabrication of fibers, pellets were melt-spun into a continuous filament approximately $15 \text{ }\mu\text{m}$ in diameter using a capillary rheometer (Rheograph 20, Goettfert, Germany) with a die hole diameter of $30 \text{ }\mu\text{m}$. PE/DPA films and fibers were converted into carbon materials via the following protocol. They were first treated with E-beam irradiation in a 2.5 MeV irradiation facility (EB Tech, Korea): both films and fibers were exposed to a 2000 kGy dose of E-beam irradiation. The E-beam-treated samples were then stabilized via a sulfonation step. For this scope, PE/DPA samples were immersed in sulfuric acid (98%), and sulfonation was carried out at $95 \text{ }^\circ\text{C}$ for 1 h. Subsequently, the sulfonated samples were thoroughly washed with deionized water for 5 min and then dried in a convection oven at $60 \text{ }^\circ\text{C}$ for 30 min. Finally, the stabilized PE/DPA fibers were carbonized using an alumina furnace (ThermVac Engineering, Korea) at an N_2 flow rate of $20 \text{ L}/\text{min}$. The temperature was increased to $1200 \text{ }^\circ\text{C}$ at a rate of $5 \text{ }^\circ\text{C}/\text{min}$. Heating was stopped as soon as the temperature reached $1200 \text{ }^\circ\text{C}$.

Characterization

Viscosity was measured using a Discovery Hybrid Rheometer HR30 (TA Instruments, USA) with an N_2 flow to minimize the oxidation of the samples during measurements. At the designated temperature, the rotating plate was operated at a shear rate of 10 s^{-1} . FTIR spectroscopy

measurements were conducted with a Jasco FT/IR-6000 (Jasco, Japan) using the attenuated total reflectance mode. TGA was performed using a Q50 instrument (TA Instruments, USA) under an N_2 environment with a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$. Raman spectra of the samples were acquired using a Renishaw inVia Raman spectrometer (Renishaw, U.K.) equipped with a 0.15 mW-rated 514 nm laser; the beam was focused through a $20\times$ optical lens, and the exposure time was set to 30 s with a power output of 1 %. XPS experiments were performed using a K-Alpha XPS instrument (Thermo Scientific, US); a survey scan spanning 0-1350 eV was followed by high-resolution C 1s and O 1s scans. The mechanical properties of the CFs were measured using a FAVIMAT tester (Textechno, Germany); the gauge length was set to 15 mm for all measurements. CF density was determined using a density gradient column (RayRan, UK).

Results and Discussion

The efficient fabrication of PE-based CFs requires an E-beam pre-treatment followed by sulfonation at elevated temperatures. In this study, we prepared PE/DPA composite fibers to improve the current CF fabrication technology relying on PE precursor. Previous studies have shown that DPA produces salt when reacted with sulfuric acid [18]. While pristine DPA completely decomposed even at the relatively low temperature of $200 \text{ }^\circ\text{C}$, DPA treated with sulfuric acid exhibited a significantly higher char yield, reaching 50 wt%. In addition, the obtained carbon material presented a highly graphitic structure. Therefore, we speculated that the introduction of DPA might improve the overall char yield and crystallinity of the PE fibers. Moreover, as a small-molecule plasticizer, DPA might also enhance the flow characteristics of PE/DPA composites compared to pristine PE, thereby improving the spinnability of the fibers.

Before examining the features of PE/DPA fibers, composite films were prepared to investigate other general properties such as char yield and changes in chemical structure. The thickness of the PE/DPA films was carefully tuned to match the diameter of the PE/DPA fibers so that the analysis results could be directly applicable to the fiber counterpart. The char yield of the samples was determined via TGA (Figure 1(a)): films with varying PE/DPA weight ratios were prepared as described in the Experimental section and tested by ramping the temperature to $1200 \text{ }^\circ\text{C}$ under an N_2 flow. The as-prepared and E-beam-irradiated samples exhibited very low char yields, and the subsequent sulfonation treatment was necessary to accomplish appreciable char yields. In particular, sulfonation is known as a key process for the transformation of linear PE into a cyclic structure, which is essential to its successful carbonization [15-17]. At the same time, E-beam irradiation is a known support technique for

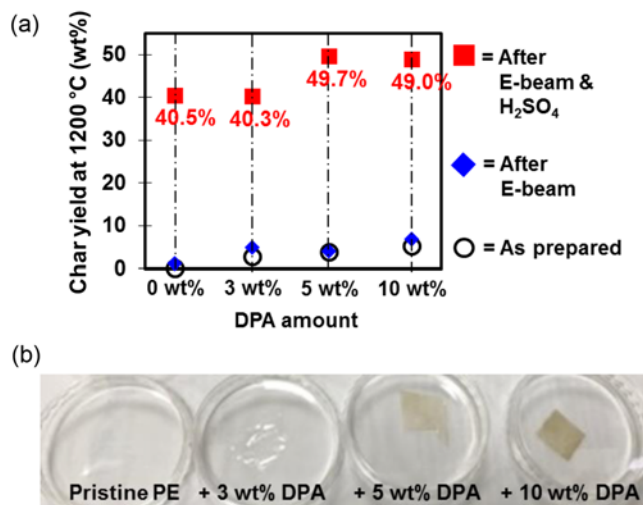


Figure 1. (a) TGA results for PE/DPA films with varying DPA contents. The measurements were performed on the samples as prepared, after E-beam treatment, and after E-beam treatment and sulfonation and (b) Photographs of E-beam-exposed PE/DPA films with varying DPA contents.

maintaining the fibril form [17]. The char yield was positively correlated with the DPA content: while no significant improvement in char yield was observed in the PE/DPA sample with 3 wt% DPA compared to pristine PE, a significant enhancement in char yield (49.0 %) was achieved through the incorporation of 10 wt% DPA. Therefore, we could argue that the inclusion of DPA had a positive effect beyond the nominal contribution of DPA's char yield (which reached 50 % after sulfonation). Theoretically, if the char yields of DPA and PE were considered as simple additive features, the char yields of the PE/DPA films with 5 and 10 wt% DPA would be 40.5 % and 41 %, respectively. This suggests that the inclusion of DPA determined a surplus char yield.

The impact of E-beam irradiation on DPA was evidenced by the trend in color change in E-beam-irradiated PE/DPA films (Figure 1(b)). For an accurate comparison with typical

treatment conditions, the thickness of the PE/DPA films was carefully tuned to be similar to that of usual CF precursor fibers. While the pristine PE film did not exhibit any distinct change in color after 2000 kGy E-beam irradiation, a significant color change was observed in the PE films containing DPA, and a higher DPA content led to a more intense yellow-blackish color. Therefore, we deduced that the color change was due to a chemical modification of the DPA structure. E-beam treatment is known to generate radicals as a consequence of bond breakage [19-21]; for this reason, the observed change in the color of PE/DPA films could be the result of oxidation caused by radicals formed upon N-H bond breakage, which in turn favored the stabilization and carbonization of PE.

Thus far, we have postulated that the aforementioned increment in char yield was due to an escalation in the sulfonation reaction, including oxygen functionalization and cyclization, enabled via radical formation in DPA during E-beam irradiation. In Figure 2(a), a subtle difference can be observed between the FTIR spectra of the pristine PE sample and the one acquired after sulfonation, which involves both the doublet peak spanning 2700-2900 cm^{-1} and a peak at approximately 1500 cm^{-1} , which represent C-H stretching and bending, respectively [22]. In contrast, in the spectra of PE/DPA samples with higher DPA contents, the intensity of both these peaks decreased significantly upon sulfonation, which strongly indicates crosslinking and cyclization (Figure 2(b-c)). The reduction in peak intensity became more significant with increasing DPA content, hinting at the role of DPA in promoting crosslinking and cyclization via sulfonation. Moreover, while the signature band of the -OH bond at approximately 3500 cm^{-1} emerged only slightly in the spectrum of pristine PE after sulfonation, it appeared distinctly in the FTIR spectra of the PE/DPA samples, confirming the role of DPA in promoting sulfonation.

Next, the influence of DPA on carbon structure formation was investigated. Carbonized PE/DPA samples were first analyzed using Raman spectroscopy (Figure 3). Both D and G bands at 1400 and 1600 cm^{-1} , respectively, were observed in all samples, confirming the successful formation of a

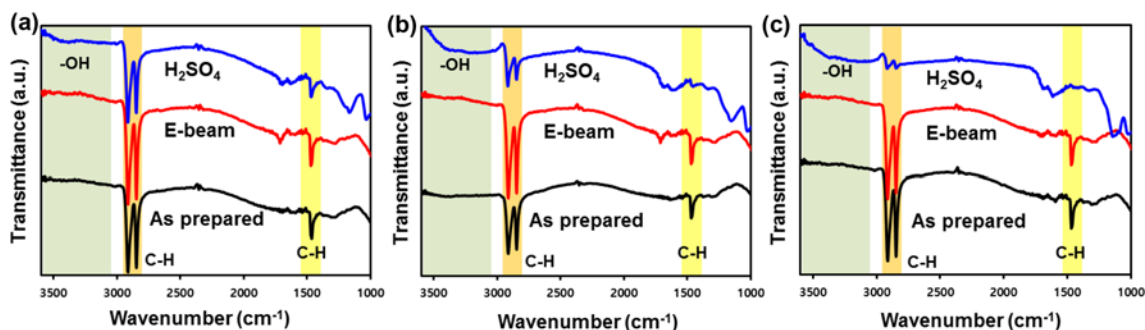


Figure 2. FTIR spectra of PE samples containing (a) 0 wt% DPA, (b) 3 wt% DPA, and (c) 10 wt% DPA. The measurements were performed on samples as prepared, after E-beam treatment, and after E-beam treatment and sulfonation.

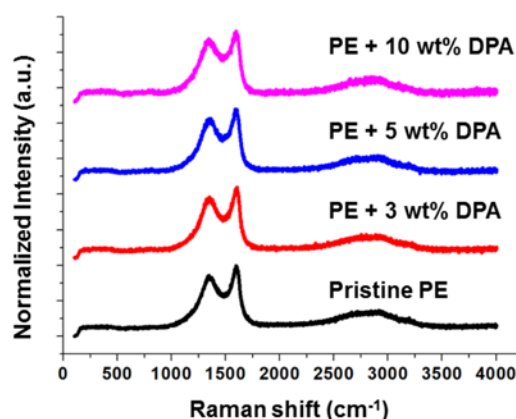


Figure 3. Raman spectra of carbon samples fabricated from PE/DPA composites subjected to both E-beam treatment and sulfonation.

carbon structure. However, Raman analysis was ineffective for the determination of structural differences. The ratio of the D and G band intensities is known to be strongly related to the crystallinity of the carbon structure [23,24]; however, the D and G band ratios of the carbonized PE/DPA samples were all at the same level. Detailed information on the carbon structure could be obtained from XPS analysis (Table 1), which provided the proportion of sp^2 carbon atoms in the absence and presence of DPA. While the sp^2 carbon content was 58.1 % in the carbonized pristine PE, the value notably increased to 61.5 % in the carbonized PE/DPA sample with 10 wt% DPA.

In addition to accelerating sulfonation and assisting carbon structural development, DPA had a positive influence on spinnability by lowering the viscosity. Considering the melting and spinning temperatures of PE, which are approximately 120 and 150 °C, respectively, the viscosity of the samples was measured at temperatures ranging from 135 to 170 °C. Interestingly, over the entire temperature range, rheology experiments showed that the samples with higher DPA contents had lower viscosities (Figure 4), thereby suggesting an improvement in spinnability following the incorporation of DPA.

Finally, CFs were fabricated from a PE/DPA composite following the process shown in Figure 5. Briefly, PE/DPA

Table 1. Results of XPS analysis on carbon samples fabricated from PE/DPA composites subjected to both E-beam treatment and sulfonation

	sp^2 (%)	sp^3 (%)	C-O, C-N (%)	C=O (%)	O-C=O (%)	π - π (%)
Neat PE	58.1	18.1	9.4	4.7	6.9	2.7
3 wt% DPA	60.2	10.8	11.5	7.9	5.2	4.6
5 wt% DPA	61.0	11.7	11.9	6.0	5.7	3.8
10 wt% DPA	61.5	12.1	10.5	6.7	5.7	3.5

pellets containing 10 wt% DPA were melt-spun into a precursor fiber and transformed into CFs via consecutive E-beam irradiation, sulfonation, and carbonization. As a result, CFs were successfully fabricated with no defects such as hollow cores or surface cracks (Figure 6). In addition, PE/DPA-based CFs exhibited sound mechanical properties with a tensile strength of 0.63 ± 0.13 GPa and modulus of $37.89 \pm$

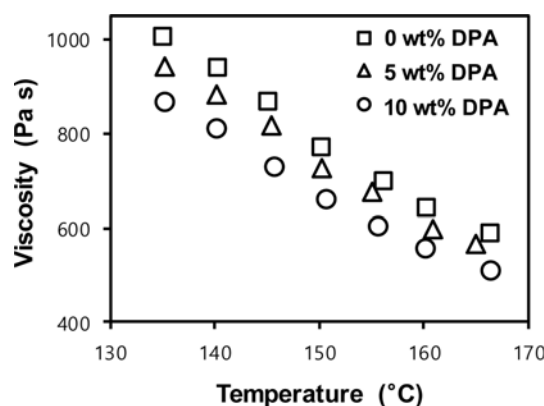


Figure 4. Steady-shear viscosity of PE/DPA samples with varying DPA contents measured with a rheometer operated at different temperatures and a shear rate of 10 s^{-1} .

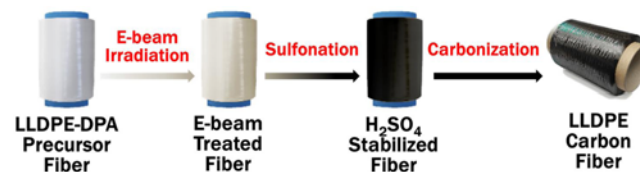


Figure 5. Schematic describing production process for PE/DPA derived CF.

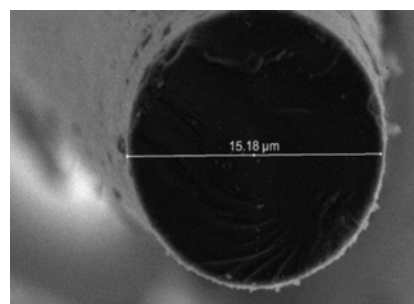


Figure 6. Scanning electron microscopy image of a CF fabricated from PE/DPA with 10 wt% DPA content.

Table 2. Mechanical properties of CFs fabricated from PE/DPA composite containing 10 wt% DPA. Errors indicate standard deviations based on 17 measurements

Avg. tensile strength (GPa)	Avg. modulus (GPa)	Elongation (%)	Char yield (%)
$0.63 (\pm 0.13)$	$37.89 (\pm 5.53)$	$1.69 (\pm 0.26)$	49.0

5.53 GPa (Table 2).

Conclusion

A small-molecule additive, DPA, was used to drive the production of strong, light, and high-performing PE-derived CFs. Based on various spectroscopic, thermogravimetric, and rheological analyses, we found that the incorporated DPA helped to enhance the char yield, graphitic structure, and melt-spinnability of the PE matrix. The fabricated PE/DPA-derived CFs exhibited sound mechanical properties with a tensile strength of 0.63 ± 0.13 GPa and modulus of 37.89 ± 5.53 GPa. We strongly believe that additional optimization can further improve the fiber properties and hope that this study will be useful to researchers working on the development of PE-derived CFs.

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