UV-Assisted Stabilization of Polyacrylonitrile-Based Carbon Fiber Precursors

Marlon Salvador Morales Sandoval
Clemson University

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UV-ASSISTED STABILIZATION OF POLYACRYLONITRILE-BASED CARBON FIBER PRECURSORS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemical Engineering

by
Marlon Salvador Morales Sandoval
December 2013

Accepted by:
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ABSTRACT

Due to their high strength and stiffness coupled with low density, carbon fibers are the preferred reinforcing fibers used in high-performance polymer matrix composites. Consequently, the demand for carbon fibers is expected to grow from 40,000 metric tons to about 150,000 metric tons over the next decade. A large fraction of the increase is anticipated in the industrial sector that is cost-sensitive. Therefore, there is a need for the development of novel processes and precursors to reduce the carbon fiber production cost and expand the use of carbon fibers. This research focuses on the development of an alternative, rapid stabilization route for polyacrylonitrile (PAN) precursor-based carbon fibers. The main goal was to investigate the stabilization reactions induced by the addition of photo-initiators and UV-treatment of polyacrylonitrile (PAN) based precursors. Also, the role of this external photoinitiator on the fiber spinnability, properties of the spun precursor fibers, and the properties of the resulting thermal stabilized and carbonized PAN-based fibers were systematically studied.

Two mechanisms of photo-initiation were investigated: homolytic cleavage and hydrogen abstraction. Solution-cast PAN copolymer samples containing both types of photo-initiators were irradiated for different durations (100 - 600 s) and temperatures (65 - 100°C, i.e., below and above glass transition temperature). FTIR spectra show the formation of carbon-oxygen, carbon-nitrogen, and carbon-carbon double bonds attributed to the development of cyclized structure. Samples containing hydrogen abstraction photoinitiator show higher extents of cyclization among the different set of samples. This observation was also confirmed by higher gel contents. FTIR conversion indices of
samples UV treated above glass transition temperature were higher compared with that for the same specimens UV treated below glass transition temperature, as expected. DSC results show that samples containing hydrogen abstraction photoinitiator enable a higher extent of post-UV thermal stabilization. FTIR spectra of the UV treated samples, when compared with only thermally stabilized specimens, confirm that the addition of 1 wt% photoinitiator to PAN followed by 5 minutes of UV treatment increases the rate of the cyclization reaction and reduces the thermal oxidation time by over an hour, which could significantly reduce the conventional stabilization time by half.

Rheology measurements show no adverse effect on the viscosity of solutions by the addition of the photoinitiator. Fibers containing photoinitiator were successfully wet-spun from PAN-DMSO solution. SEM micrographs show no deterioration of the post-stretched fiber microstructure due to the presence of photoinitiator. After UV treatment, fibers that contained 4,4'-bis(diethylamino)benzophenone display a higher tensile modulus as compared with that of other sets. Wide-angle X-ray diffraction results show no significant decrease in interplanar spacing and size of the crystals within the fibers containing photoinitiator, but such fibers retain a higher extent of molecular orientation after being UV treated. Conversion indices were measured from the WAXD spectra and compared with those for fibers that were only thermally stabilized. These results agree with previous FTIR ones, which established that only 5 minutes of UV treatment leads to a conversion index that is observed in control fibers after more than an hour of only thermo-oxidative stabilization.
After a short UV treatment that induced cyclization and crosslinking, precursor fibers could be rapidly thermo-oxidatively stabilized and successfully carbonized. SEM micrographs show no deterioration of the microstructure or significant skin-core formation of the fibers due to UV treatment and presence of photoinitiator. Fast-thermal stabilized pure polyacrylonitrile carbon fibers contained core-hollow fiber defects due to inadequate thermal stabilization, but such defects were not observed for fast-thermal stabilized fibers that were UV treated and contained photoinitiator. Tensile testing results show fibers containing 1 wt% photoinitiator and UV treated for 5 minutes display higher tensile modulus than all the other set of thermal stabilized and carbonized fibers. WAXD results show a higher development of the aromatic structure and molecular orientation in thermal stabilized fibers. Although no significant increase in interplanar spacing and size of the crystals was observed within the UV-assisted-stabilized carbon fibers containing photoinitiator, but such fibers retain a higher extent of molecular orientation when compared with control pure fibers.

In summary, these results establish for the first time the positive effect of the addition of photoinitiator and UV treatment on the properties of the polyacrylonitrile-based fibers. This novel, dual UV-thermal mechanism can be used to develop processes that can reduce the thermal oxidation time (faster fiber production) while retaining the mechanical properties of the carbon fibers thus produced.
DEDICATION

This work is dedicated to everyone who supported and assisted me, making this work possible, and anyone who makes good use of it.
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to everyone who helped me make this work possible. Thanks to all of the faculty, staff, and students in the ChBE department for helping me throughout my research. I would especially like to thank my advisor, Prof. Amod Ogale, for his guidance, patience and insights during my time at Clemson. I would also like to thank my committee members, Dr. Hirt, Dr. Kitchens, and Dr. Anderson, for their support and valuable suggestions, as well as all former and current members of my research group for their important help and advice.

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I gratefully acknowledge all of the teachers and professors that taught me along my academic life and all the entities that financially supported me during my undergraduate and graduate studies. Just in case, I would like to apologize to and thank anyone who supported me that I accidentally left out from these acknowledgements.
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CHAPTER 1
INTRODUCTION

1.1 Introduction to carbon fibers

Carbon fibers possess excellent physical and chemical properties, such as low density, high strength and stiffness, good resistance to chemical and environmental effects, and ability to withstand high temperatures while maintaining their mechanical properties. Consequently, carbon fibers are the preferred reinforcing fibers used in high-performance polymer matrix composites (1-3). In addition, carbon fibers are used to reinforce ceramic and carbon matrices resulting in a unique class of ultra high-temperature composites (4).

Carbon fibers were first used in 1870 by Thomas Edison as filaments for incandescent bulbs. He used rayon (or cellulose) as a precursor. However, only in the early 1960’s the process of producing carbon fibers from polyacrylonitrile developed at Rolls Royce and the Royal Aircraft Establishment, Farnbororough, UK became popular making carbon fibers available for structural applications (5, 6). Since then, numerous scientific studies and technology development efforts have been devoted to the improvement of the properties and development of new precursors.

Table 1.1 summarizes the properties of different reinforcing materials. Due to the different nature of the carbon fiber precursors and production methods employed, the properties of the resulting carbon fibers can be tailored to a specific use. Figure 1.1 shows the comparison of specific strength and stiffness of different fibrous reinforcement
materials with high tenacity (HT) and high modulus (HM) carbon fibers. When compared with other fibrous reinforcement materials, carbon fibers are the stiffest and strongest reinforcements known, with tensile strengths higher than 7 GPa, approximately five times higher than steel, and tensile modulus as high as 900 GPa. By the use of the adequate precursor and thermal treatment conditions, thermal conductivity values of 1000 W m$^{-1}$ K$^{-1}$ have been achieved, which is approximately three times higher than the one for cooper. On the other hand, carbon fibers with low thermal conductivity values of 4 W m$^{-1}$ K$^{-1}$ can also be produced that are useful for thermal insulation applications. Also, carbon fibers have small thermal expansion coefficients ($-0.5 \times 10^{-6}$ and $10 \times 10^{-6}$ K$^{-1}$ in the axial and radial directions, respectively) when compared with other materials e.g. metals (4, 6-9). This is very important in applications where significant temperature variations are expected. Consequently, carbon fibers find application in different industries such as defense, space, sports, civilian aeronautical, automotive, energy, oil & gas, infrastructure, electronic, and others (8, 10). However, the higher cost of carbon fibers compared with other reinforcing materials has become the primary barrier that limits their use only for the high-performance applications where strength-to-density ratio is critical (3, 11).

Since 2005, the rate of growth of demand for carbon fibers has increased from approximately 360 to 4100 metric tons a year (12). Also, this demand is expected to grow to about 150,000 metric tons over the next decade from current demand of 40,000 metric tons. However, a large fraction of the increase is anticipated in the industrial sector that is cost-sensitive (13). For cost effective products, such as automotive application, there is a
need for the development of novel processes and precursors to reduce the carbon fiber production cost and expand the use of carbon fibers.

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<th>Relative density</th>
<th>Tensile modulus (GPa)</th>
<th>Tensile strength (GPa)</th>
<th>Break strain (%)</th>
<th>Thermal expansivity* (10^-6 K^-1)</th>
<th>Thermal conductivity* (W m^-1 K^-1)</th>
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<td>T-300</td>
<td>1.76</td>
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<td>3.66</td>
<td>1.6</td>
<td>-0.6 (a)</td>
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<td>T-650/35</td>
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<td>241</td>
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<td>1.8</td>
<td>-0.6 (a)</td>
<td>14 (a)</td>
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<td>T1000G</td>
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<td>6.37</td>
<td>2.2</td>
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<td>0.9</td>
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<td>P-100S</td>
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<td>759</td>
<td>2.41</td>
<td>0.3</td>
<td>-1.48 (a)</td>
<td>520 (a)</td>
</tr>
<tr>
<td>K-1100</td>
<td>2.20</td>
<td>931</td>
<td>3.1</td>
<td>0.3</td>
<td>-1.5 (a)</td>
<td>1000 (a)</td>
</tr>
<tr>
<td><strong>Rayon-based carbon fibers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shuttle-grade, rayon-based carbon fibers</td>
<td>1.50</td>
<td>55-62</td>
<td>0.3-0.7</td>
<td>0.5-1.3</td>
<td>--</td>
<td>4</td>
</tr>
<tr>
<td><strong>Other fibers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon carbide (SiC) monofilament</td>
<td>3.00</td>
<td>400</td>
<td>2.4</td>
<td>0.6</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>Boron monofilament</td>
<td>2.60</td>
<td>400</td>
<td>4</td>
<td>1</td>
<td>5</td>
<td>38</td>
</tr>
<tr>
<td>Kevlar</td>
<td>1.45</td>
<td>130</td>
<td>3</td>
<td>2.3</td>
<td>-6 (a)</td>
<td>54 (r)</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.60</td>
<td>76</td>
<td>3.5</td>
<td>4.5</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>C-glass</td>
<td>2.49</td>
<td>69</td>
<td>3.3</td>
<td>4.8</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>S-glass</td>
<td>2.48</td>
<td>85.5</td>
<td>4.6</td>
<td>5.4</td>
<td>5.6</td>
<td></td>
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<td><strong>Other materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mild steel</td>
<td>7.8</td>
<td>208</td>
<td>0.4</td>
<td>10-30</td>
<td>17</td>
<td>60</td>
</tr>
<tr>
<td>Alumina</td>
<td>3.9</td>
<td>380</td>
<td>0.5</td>
<td>10-20</td>
<td>8</td>
<td>25</td>
</tr>
<tr>
<td>Epoxy</td>
<td>1.25</td>
<td>3.5</td>
<td>0.05</td>
<td>3</td>
<td>60</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*a: axial; r: radial
It is well known that carbon does not melt, and so cannot be directly spun into fibers in a single step. Therefore, carbon fibers are produced from precursors. The most popular precursor materials for carbon fiber production are polyacrylonitrile (PAN), pitch, and cellulose (rayon). Today, more than 90% of the global carbon fiber production is PAN-based, approximately 6% is from pitch, and less than 1% is rayon-based (2, 10). All these precursors are first spun into fibers and later through different thermal treatment steps, as explained in more detail in the next sections, converted into carbon fibers. Note that high strength carbon fibers used in structural composites for aerospace applications are mostly derived from PAN precursor fibers (4, 14, 15).
1.2  Carbon fiber precursors

1.2.1  Polyacrylonitrile

More than 90% of the carbon fibers produced globally are derived from polyacrylonitrile (PAN) precursor (10). PAN-based carbon fibers are the strongest fibers with tensile strength values of 7 GPa (8). The wide acceptance of PAN as the main carbon fiber precursor is due to its relatively high carbon yield and flexibility for tailoring of the final structure of the carbon fiber. The carbon yield of PAN ranges between 40 and 50%, approximately twice the carbon yield of rayon which ranges between 10 and 30%. Also, good orientation and crystallinity within the fibers can be achieved during fiber spinning of the PAN-based precursor (4, 14). Figure 1.2 shows the main repeating unit of a PAN polymer chain with the nitrile groups aligning perpendicular to the chain-axis to promote crystallinity.

![Chemical structure of a repeat unit of PAN polymer chain](image)

Figure 1.2: Chemical structure of a repeat unit of PAN polymer chain

The theoretical melting temperature of PAN is above 400°C. This temperature is higher than the degradation temperature of PAN, which starts above about 250°C. This means that PAN degrades before melting. This restricts the use of melt-spinning techniques, but enables solution-spun PAN fibers to be converted to carbon fibers by
reacting it in 200-300°C range. These thermo-oxidative reactions in PAN are highly exothermic \((1)\). To reduce the glass transition temperature, the oxidation rate, and the temperature of initiation of the exothermic reactions, PAN is copolymerized with a small amount of another monomer. This carbon fiber grade PAN-based precursor usually has 93 to 95 percent of acrylonitrile units and the remaining being one or more other co-monomers such as methyl acrylate (MA), acrylic acid (AA), or itaconic acid (IA). These comonomers disrupt the order in PAN leading to a reduction of the temperature of initiation of the cyclization reaction producing carbon fibers with higher mechanical properties than carbon fibers produced from PAN homopolymer \((14, 16, 17)\).

By the addition of plasticizers or increasing the concentration of copolymer (above 10 mol\%) the melting temperature can be lowered and melt spinning can be possible. Unfortunately, excessive order disruption of the polymer chains leads to defect formation and reduction of the final properties of the carbon fibers produced from melt spun PAN-based precursors \((3, 14, 17-19)\).

1.2.2 Mesophase pitch

Mesophase pitch derived from petroleum or coal-tar pitch serves as a carbon fiber precursor due to the high availability of low cost raw pitch, their high carbon content and carbon yield \((4, 20)\). Mesophase pitch-based carbon fibers possess a structure closer to graphite when compared with those obtained from PAN and rayon precursors \((9)\). Figure 1.3 shows a typical polynuclear aromatic hydrocarbon found in mesophase pitch. The carbon fiber yield from pitch-based precursor fibers is approximately 75\%. With a
suitable heat treatment, pitch-based carbon fibers can develop a high degree of graphitization. This highly developed graphitic structure helps to achieve high tensile modulus and thermal conductivity (21). Tensile modulus values as high as 900 GPa, almost 85% the theoretical tensile modulus of graphite, and thermal conductivity values of 1000 W m⁻¹ K⁻¹ have been reported; this conductivity value is approximately three times higher than the one for cooper (4, 8, 9).

![Chemical structure](image)

Molecular weight = 1178 g mol⁻¹  
C/H = 1.50  
Hₐrom/Hₐliph = 1.30  
Cₐrom/Cₐliph = 6.15

Figure 1.3: A typical chemical structure of a polynuclear aromatic hydrocarbon found in mesophase pitch (4)

Some of the drawbacks of pitch-based carbon fibers are that the handling of the fibers is very hard due to their graphitic nature, which makes the fibers very brittle. Thus, pre-pregging of the fibers to produce composite materials is an expensive process. In
addition, highly oriented crystalline structure makes these fibers more flaw-sensitive, which results in lower tensile strengths (as compared with PAN-based carbon fibers) and makes such fibers unsuitable for structural applications (9, 21).

1.2.3 Rayon (cellulose)

Even though rayon-based carbon fibers were the first high performance carbon fibers produced and used in 1870 by Thomas Edison as filaments for incandescent bulbs, today less than 1% of the global carbon fiber production is rayon-based (5). Figure 1.4 displays the repeating unit of the rayon polymer chain. The main drawbacks to rayon-based carbon fibers are lower mechanical properties, low carbon yield, and higher expenses during the stretched-carbonization needed to obtain even moderate mechanical properties in rayon-based carbon fibers. These are some of the reasons that PAN has taken the lead as the main global precursor for carbon fibers over rayon. However, the low thermal conductivity of rayon-based carbon fibers makes them well-suited for high performance thermal insulating carbon felt is used as such applications (4, 7, 20).

Figure 1.4: Chemical structure of a repeat unit of rayon (cellulose) polymer chain
1.3 Properties

1.3.1 Microstructure

Figure 1.5 shows representative SEM images of carbon fibers derived from the three main precursors, namely, PAN, rayon, and pitch. The first feature to notice is the different cross-sectional shapes of each fiber. PAN-based fibers, shown in Figure 1.5a, are wet spun, and so they are not circular. During wet-spinning, when the fibers are solidifying in the coagulation bath, there is a high concentration gradient of solvent across the nascent fiber radius. The skin of the initially circular fiber is the first section to solidify. The solidification of the skin makes more difficult the diffusion of solvent out of the fiber. As the solvent leaves the fiber, bigger voids start to form in the core of the fibers. Later, as the fibers are stretched, these voids are collapsed leading to the formation of kidney or dog bone cross-section shape. The same phenomenon occurs during the wet-spinning of rayon-based fibers, but this type of fibers develops a characteristic crenulated shape as shown in Figure 1.5b. Figure 1.5c, in contrast, shows a very clear circular cross-section shape developed during the melt-spinning stage of the pitch-based carbon fibers. All the shapes displayed by the fibers are determined by the fiber spinning and conditions; these initial shapes are essentially retained through the carbon fiber manufacturing process (4, 22, 23).
Figure 1.5: Representative SEM micrographs of carbon fibers: (a) PAN, (b) rayon, and (c) pitch (4, 22, 23)
Figure 1.6 and 1.7 show schematics of microstructure of PAN-based carbon fiber (22, 24). The microstructure of PAN-based fibers is fibrillar (25). Also, skin-core structure can be observed. In the skin, the undulated layer planes are parallel to surface of the fiber. In the core, the layer planes are less organized and the amplitude of these undulations is higher. The presence of voids between adjacent crystals is higher at the core than near the surface or skin region of the fiber.

Note that the structure of rayon-based carbon fibers is also fibrillar (22, 26). PAN-based carbon fibers consist of relatively small misaligned graphite crystallites, in the range of 10 to 50 Å, that are formed during carbonization. These misaligned crystals are the pieces that build the turbostratic structure observed in PAN-based carbon fibers, as shown in Figure 1.8 (14). Rayon-based carbon fibers also have a turbostratic structure, but rayon-based fibers possess an even less developed crystalline structure when compared to PAN-based fibers. Their crystallite sizes fall in the low range of the crystallites sizes of PAN. The low graphitic structure leads to low thermal conductivity values of approximately 15 and 4 W m⁻¹ K⁻¹ for PAN and rayon-based carbon fibers, respectively (7). However, as discussed in the next section, this turbostratic structure can positively influence the mechanical performance of PAN-based carbon fibers.

Figure 1.9 shows schematics of different microstructures of pitch-based carbon fibers (9). In contrast to PAN-based carbon fibers, pitch-based carbon fibers can display a variety of microstructures depending on the initial composition and processing conditions of the precursor pitch. The most preferred microstructures developed by pitch are radial,
flat layer, or random, the most common ones observed in commercial pitch-based carbon fibers. For example, the fiber shown in Figure 1.5c is radial folded.

Figure 1.6: Schematic of microstructure of PAN-based carbon fiber (24)

Figure 1.7: Three dimensional structural model of PAN-based carbon fiber (22)
Pitch-based carbon fibers are able to develop very graphitic structures and a high degree of 3-D order. In contrast with PAN and rayon, relatively large graphite crystallites, larger than 300 Å, can be formed during graphitization. The high graphitic structure developed by pitch-based fibers leads to high thermal conductivity values. Some grades of pitch-based carbon fibers can achieve values of approximately 1000 W m$^{-1}$ K$^{-1}$, which is approximately three times that of copper (5, 6, 9, 24, 27).
1.3.2 Mechanical properties of carbon fibers

Carbon fiber mechanical properties depend on the degree of graphitic structure, which in turn depends on the manufacturing process and nature of the precursor used \( (1, 20) \). Among carbon fibers, PAN based fibers have the highest tensile strength with values higher than 7 GPa, as displayed earlier in Table 1.1 \( (8) \). This behavior can be explained based on how the fibers handle the stress and crack propagation. PAN-based carbon fibers have more disorganized structure with small crystallite size. Then, during tension, cracks need to propagate from one small crystal to next. Thus, the higher interlayer spacing and lack of inherent orientation hinder crack propagation. Also, the folded nature and small size of the crystallites, which can independently fail without causing fiber failure, can explain higher break strain values of the PAN-based carbon fibers. Figure 1.10 shows a model summarizing the mechanism of tensile failure in misoriented crystal: crack initiation (a), propagation (b), and fracture (c) \( (9, 14, 24, 26) \).
Figure 1.10: Model of the mechanism of tensile failure in misoriented crystal: crack initiation (a), propagation (b), and fracture (c) \(^{(9)}\)

In contrast, pitch-based carbon fibers possess the highest tensile modulus among all carbon fibers with values approaching 900 GPa, which is more than 85\% the theoretical modulus for perfect graphite crystal (1060 GPa). The nearly perfect orientation along the fiber axis of the graphite basal planes and good development of the graphitic structure are the causes of such high modulus. However, pitch-based fibers display lower tensile strength and break strain values when compared with those of PAN-based carbon fibers. The same reasons that promote the development of high modulus (i.e. high orientation and larger size of the crystals) also facilitate the propagation of cracks along the crystals within the fiber and make the fiber more brittle and hard to handle \((9, 24, 26)\). The mechanical properties of rayon-based fibers are lower than the ones displayed by the PAN and pitch carbon fibers. However, the very low thermal
conductivity of these fibers makes them useful for the fabrication of high performance insulation composites (4, 7).

1.4 Carbon fiber manufacture

1.4.1 Polyacrylonitrile-based carbon fiber manufacture

Figure 1.11 displays a schematic of the PAN-based carbon fibers manufacturing process (5, 15, 28). The first step consists of the preparation of the PAN precursor solution in a suitable organic solvent, such as dimethyl sulfoxide or dimethylacetamide. Inorganic solvents, e.g. aqueous sodium thiocyanate, can also be used for solution preparation. The concentration of polymer in solution typically ranges between 15 to 30 wt%. After dissolving the precursor, the solution undergoes ripening, which consist of storing the solution at room temperature (25°C) for approximately 1 day before the spinning step. Ripening helps to remove air bubbles, and results in improved rheological properties of the fibers (4, 14). After ripening, the solution is loaded in a tank, filtered to remove impurities, and pumped through a spinnerette.

As mentioned before, the most common carbon fiber grade PAN-based precursors decompose before melting (18, 19). Therefore solution-spinning techniques are the most commonly used during fiber spinning. These solution spinning methods are wet-, dry-jet (a modification of wet-spinning) and dry-spinning (25).
Wet-spinning is the most common technique used for PAN-based fiber production. This technique consists of a die submerged in a coagulation bath, which consists of an anti-solvent(s) or coagulant. The polymer solution is pumped through the die where the nascent polymer solution fibers solidify as the solvent diffuses out of the fibers. Ethylene glycol and water can be used as anti-solvents in the coagulation bath. Different temperatures in the line can be used to control the viscosity of the solution to values between 10 and 100 Pa.s (14).

After coagulation, the fibers are wet-stretched, washed, dry-stretched, and wound up on spools. Stretching is very important because it collapses the voids left by the solvent in the fibers and increases molecular orientation within the fibers, which leads to an enhancement of the mechanical properties (25, 29). Washing helps to remove the remaining traces of solvent from the fibers. It is well documented in the literature that precursor type, concentrations, solvents, temperatures, and drawn-down ratios (i.e., the different processing conditions) used during this wet-spinning process determine the final properties of the fibers (4).
Dry-jet wet-spinning is very similar to conventional wet-spinning with the only difference that the die is not submerged in the coagulant. Rather, the spinnerette, through which the solution is extruded, is a short distance (~10 mm) above the surface of the coagulation bath. This technique allows the polymer chains in the solution to be better orientated before coagulation starts. Some of the advantages of this technique are higher spinning speeds and mechanical properties of the spun fibers when compared with traditional wet-spinning. Also, higher temperatures can be used during the spinning of the solution; thus the concentration of solids in solution can be increased.

Dry-spinning consist of extruding the polymer solution into temperature controlled chamber were hot gases are circulated to evaporate the solvent from the nascent fibers. This method requires a very careful control of the temperature and composition of the gases inside the chamber because these two parameters govern the evaporation rate of solvent from the fibers and their final structure. One of the advantages of this technique is that higher spinning speeds can be achieved. However, dry-spinning is not suitable for the production of tows of large number of filaments, e.g. 50,000, which can be produced using wet-spinning. In addition, the mechanical properties of the spun fibers are inferior when compared with wet-spun fibers (4, 14, 25).

In addition to solution-spun techniques, melt-spinning can also be used. This technique offers the clear advantage of the elimination of solvents during the spinning of the fibers. The addition of plasticizers or the increase of copolymer content can be used to lower the melting temperature of the PAN-based precursor below its decomposition temperature (4, 18). These two methods make the melt-spinning of the PAN-based
precursor possible. PAN-based precursor can be mixed with water and water soluble polyethylene glycol and, by plasticizing effect, lowering the melting temperature of the precursor (14). Also, as the copolymer content increases, the amorphous phase of the PAN-based polymer increases and the glass transition temperature and melting temperature of the PAN-based precursor decreases (16). When the concentration of copolymer is higher than 10 mol%, the PAN-based precursor can be melted and spun to produce fibers (17).

Some of the advantages of the melt-spinning versus wet-spinning are the elimination of the necessity of solvents, solvent recovery, waste water treatment, and higher concentration of polymer in the mixture (when plasticizer is used) (4). Unfortunately, melt-spun fibers present more surface defects and voids than wet-spun fibers. In addition, when the copolymer content is increased, greater disruption of the polymer chains occurs, leading to higher defect formation and reduction of the fiber properties. Thus, the mechanical properties of melt-spun carbon fibers are inferior when compared with wet-spun carbon fibers (14, 17).

As noted in Figure 1.11, thermal treatment steps, i.e. thermal oxidative stabilization and carbonization, have to be conducted for the conversion of PAN into carbon fibers (1). The thermal stabilization process involves the heating of the PAN-based polymer precursor fibers in the range between 200-300°C under tension in air or in another oxidizing atmosphere (24, 30). This heat treatment involves the conversion of the PAN polymer chains into a condensed ring structure with a carbon-nitrogen double bond often know as a “ladder” structure (31). Figure 1.12 shows the cyclization and
dehydrogenation reactions occurring during the thermal stabilization of PAN-based precursors showing the most common functional groups observed. The cyclized PAN structure becomes thermally stable and able to withstand the carbonization step. The thermal stabilization step is considered the most critical step during the production of carbon fibers because the conditions employed during stabilization dictate the final structure and mechanical properties of the resulting carbon fibers. Also, thermal stabilization is the rate-limiting step in the production of PAN-based carbon fibers.

![Diagram of cyclization reaction](image)

**Figure 1.12**: Cyclization reaction involved during thermal stabilization of PAN-based precursors showing the most common functional groups observed (31)

During thermo-oxidative stabilization, heat is produced by exothermic reactions and a temperature gradient is generated within the fiber due to the low thermal conductivity of PAN precursors (≈0.26 Wm⁻¹K⁻¹) (1, 10, 18, 33). The dissipation of this energy is very important and the energy generation can be controlled by using slow heating rates, e.g., 2°C min⁻¹, during the thermal stabilization of the fibers (32, 34, 35).
Simultaneously, post-drawing of fibers must be performed to collapse the voids and to increase molecular orientation \((4, 25, 29)\). However, this orientation is partly lost due to molecular relaxation processes that occur when the PAN precursor fibers are heated up to \(300^\circ\text{C}\) during the stabilization step. Additional tension must be applied during stabilization and carbonization steps in an attempt to regain the molecular orientation. This strategy results in carbon fibers with high strength, but the limited molecular orientation prevents the fibers from developing an ultra high modulus \((18, 36-38)\).

The final step for the conversion of PAN into carbon fibers is carbonization. This step involves the heating of the stabilized PAN-based fibers to approximately 1000-1500°C in an inert atmosphere \((1, 28)\). Tension is again applied on the fibers because during this step the crosslinking of the cyclized polymer chains occurs and a graphite-like structure is formed. A significant fraction of non-carbon atoms are eliminated from the fiber structure. The carbon content of the final carbonized fibers is higher than 80%; this value depends on the final carbonization temperature. Below 600°C, slower heating rates of 5°C min\(^{-1}\) are recommended to slow the formation and facilitate out-diffusion of gases such as methane, water, ammonia, carbon monoxide, carbon dioxide, and hydrogen cyanide. Above 600°C, higher heating rates can be used. In general, during carbonization higher heating rates can be used than during thermal stabilization \((4)\).

Heat treatment above 2000°C is not recommended for PAN-based fibers because it negatively affects the mechanical properties \((14, 34)\). Some of the nitrogen atoms from the original PAN structure still remain in the carbonized structure of the fibers. As the carbon fibers are heated above 1500°C, to say 1800°C, the mechanical properties of these
fibers start to decay due to the removal of the nitrogen, which leaves voids in the carbonized structure and creates defects within the fiber.

1.4.2 Mesophase pitch-based carbon fiber manufacture

Figure 1.13 displays the mesophase pitch-based carbon fiber manufacturing process. First, mesophase pitch is produced from highly aromatic raw petroleum or coal-tar pitch by thermal or catalytic polymerization. The raw pitch is heated at temperature between 400 and 450°C for about 45 hours where part of the initial isotropic material transforms into an optically anisotropic fluid phase, i.e. mesophase or liquid crystalline phase. The conversion during this step ranges between 45 to 60% depending on the type of pitch. Also solvents, such as benzene, heptanes, and toluene, can be used to produce mesophase pitch. In this method, the solvent is mixed with the raw pitch to extract part of the isotropic pitch. The insoluble fraction is then heated between 230 and 400°C, transforming this solvent insoluble fraction into mesophase pitch (4, 5, 8, 20).

Figure 1.13: A schematic of pitch-based carbon fiber manufacture process
After the preparation of the mesophase pitch, this thermoplastic precursor is spun into fibers by melt-spinning. The mesophase precursor is fed into an extruder where it is heated, mixed, and pumped to the top of a die head which has a multi-hole spinnerette. Before passing through the spinnerette, the mesophase pitch is filtered to remove any impurities. The mesophase precursor is heated until the viscosity is around 100 Pa-s. However, this optimum viscosity value may vary depending on the composition of the precursor. Due to high temperature dependence of the viscosity of the mesophase pitch, during the melt-spinning of mesophase pitch, temperature control is very important to keep uniformity in the properties of the spun fibers. Also, during the melt-spinning of the fibers a high degree of orientation of the disk-like molecules is achieved. Because the discotic phase leads to textural orientation (rather than conformational one in PAN), application of tension during the further thermal treatment steps is unnecessary (4).

To avoid softening of the fibers during the carbonization step, as-spun pitch-based fibers need to be stabilized by thermosetting in air. The temperature and duration of this thermal stabilization step depends on chemical composition and the diameter of the fibers. Temperatures of 200-300°C and process duration between 1 hr to 20 hrs are usually used (5, 20). The temperature should be carefully selected: it should not be too high to avoid the sticking of the fibers with each other but not too low to minimize the time required for this step. The principal criteria for the selection of the processing temperature and time are based on the maximization of the final properties of the fibers.

Finally, the thermoset pitch-based fibers are carbonized and graphitized. This process consists of heating the stabilized pitch-based fiber in an inert atmosphere. If the
final temperature of this process is below 1700°C, the fibers have only been carbonized. Graphitization involves the heating of the fibers at temperatures above 2000°C to develop graphitic crystallinity. Carbonization and graphitization can be achieved during the same heating process (4, 5, 9). The higher the temperature employed in this thermal treatment process, the more developed the graphitic structure within the pitch-based carbon fibers will be. This is very important because the properties of the final carbon fibers depend on the level of development of this graphitic structure within the fibers.

1.4.3 Rayon-based carbon fiber manufacture

Similar to PAN, rayon degrades before melting, so wet-spinning processes are required to convert rayon into fibers. To prepare the spinning solution, raw cellulose is dissolved in a basic solution, viz. sodium hydroxide, and carbon disulfide (CS₂). This leads to the formation of cellulose xanthate (20). An acid solution, 10 to 15 wt% sulfuric acid, is used as a coagulation bath. As the solution exits the spinnerette into the coagulation solution a hydrolyzation reaction takes place between the spinning solution and the coagulant, which leads to the formation of cellulose filaments (4).

Rayon-based fibers do not need to be thermally oxidized prior to carbonization. However, when thermal oxidation is conducted, the carbon yield of the fibers is enhanced. Therefore, the fibers are thermally oxidized in air at temperature as high as 400°C. As the temperature during oxidation increases, aromatization and decomposition of the original cellulose structure occurs. Due to this decomposition, the fibers lose most
of their molecular orientation; thus pre-stretching or stabilization under tension is useless (5).

After wet-spinning and thermal oxidation (if conducted), the fibers are carbonized in an inert atmosphere. During this step, tension is very important because increasing the molecular orientation of the developing structure during carbonization enhances the mechanical properties of the rayon-based carbon fibers. Also, due to the fact that the fibers lose most of the molecular orientation during the thermal stabilization step, the plastic deformation undergone by the fibers during this stage can be quite high. These fibers can be stretched as much as 150%. The final temperature employed in this thermal treatment process will control the level of graphitic structure within the rayon-based carbon fibers (4, 20).

1.5 Alternative stabilization routes

As discussed above, the stabilization step is of utmost importance during the production of carbon fibers because creation of a crosslinked polymer network within the precursor fiber is critical to its survival during the subsequent harsh carbonization temperatures. All the precursors discussed above utilize thermo-oxidative reactions as the route for crosslinking. However, in the polymer industry, reactions involving the use of photo-sensitive species to induce polymerization and crosslinking (curing) reactions have become an accepted industrial practice (39-42). For this purpose, various types of radiation, such as ultraviolet (UV), X-ray, gamma, and e-beam, can be used. Of these, UV-based methods have become more popular than other types because it is least
hazardous (43). UV radiation is all radiation between 100 and 400 nm. UV-induced polymerization and curing can proceed through two major ways: free radical or cationic (44). Of the two, cationic initiation has more limited applications, whereas free radical photo-initiation is more popular and widely used for photo-induced polymerization and curing.

Figure 1.14 shows the three major ways of generating free radical intermediates from a photo-excited species (44, 45). Homolytic cleavage involves the bond scission of a single exited species to generate two radicals. This mechanism has been investigated in numerous literature studies (39, 44-46). Hydrogen abstraction consists of the interaction of one excited species with another hydrogen donor molecule to generate two radicals. Electron transfer involves the interaction of a positively charged excited species with a negatively charged molecule to generate two radicals or the interaction of an excited species with a hydrogen donor molecule to generate two radicals. Even though the latter two mechanisms require the interaction of two species, which is not convenient for solid state processes, some molecules can be synthesized with both functional groups, e.g., Michler’s ketone for hydrogen abstraction (44, 45). Note that the location of the UV-absorption bands, solubility, atomic composition, compatibility of the photoinitiator with the system, etc. are some of the criterions needed for the selection of a suitable photoinitiator.

Photo-induced crosslinking of melt-spun PAN-based precursors and successful conversion into carbon fibers has been reported in previous Clemson and related studies (3, 17). These PAN-based terpolymers contained a photo sensitive comonomer, such as
acryloyl benzophenone, incorporated into the polymer chain. However, a modification of
the previous method, where external photoinitiator is added to the conventional PAN-based precursor solution prior to wet-spinning (i.e., without synthesizing the photoinitiator into the polymer chain itself) has not been studied.

It is known that polymerization and stabilization reactions in PAN proceed faster
and at lower temperatures when initiated by UV radiation \((17, 43, 47)\). Reduced
cyclization temperature can also help to maintain molecular orientation during thermal
oxidation, which in turn is important to impart superior modulus and strength properties
to the resulting carbon fibers \((18, 36, 37)\). Alternatively, the incorporation of this UV-based pre-stabilization step may lead to a reduction of the time required for the thermal stabilization step while maintaining the properties of resulting fibers. However, the role
of external photoinitiator added to the polymer solution on the UV-induced cyclization
and crosslinking reactions has not been systematically addressed in previous literature
studies. Also, the rheology of the PAN-dope, wet-spinnability, and the properties of the
carbon fibers thus produced remain unaddressed.

Figure 1.14: Types of free radical Photoinitiation

\[
\begin{align*}
\text{Homolytic cleavage} & \quad \text{Hydrogen abstraction} & \quad \text{Electron transfer} \\
A-B^* & \xrightarrow{hv} A^+ + B^- & A^* + RH & \xrightarrow{hv} AH^+ + R^- & (A^+)^* & + X^- & \xrightarrow{hv} A^+ + X^- \\
& & & & \text{or} & A^* + DH & \xrightarrow{hv} (AH^- \cdot DH^+) & \xrightarrow{hv} AH^- + D^-
\end{align*}
\]
1.6 Objectives

The overall goal of this research was to investigate the stabilization reactions induced by the addition of photo-initiators and further UV-treatment of polyacrylonitrile (PAN) based precursors, and their effect on the final properties of the produced fibers. The specific objectives were to:

1. induce crosslinking and cyclization reactions in polyacrylonitrile by the addition of photoinitiator and further UV treatment;

2. investigate the role of external photoinitiator added to the polymer solution on the rheology of the PAN-solution before fiber spinning, wet-spinnability, and properties of the spun precursor fibers; and

3. study of the effect of the addition of photoinitiator and further UV exposure on the properties of the resulting stabilized and carbonized PAN-based fibers.

Solvent-cast PAN-based films were used throughout the first part of this work to study the photo-induced stabilization reactions. Thus, Chapter 2 addresses the UV-assisted stabilization reactions for PAN-based films. In this chapter, studies were conducted to investigate the crosslinking and cyclization reactions in solution-cast PAN samples induced by the addition of different photoinitiators that generate free radicals. Two different mechanisms, namely, homolytic cleavage and hydrogen abstraction were investigated and results have been published (48). In addition, different UV treatment conditions, such as temperature and duration, were studied. Stabilization indices were
measured and compared with conventional thermally stabilized samples to assess the effectiveness of the UV-treated samples.

In the second half of this study, the role of photoinitiator and UV-treatment on the processing and properties of PAN-based fibers was investigated. In Chapter 3, the role of external photoinitiator added to the polymer solution prior to wet-spinning (i.e., without synthesizing the photoinitiator into the polymer chain itself) on the rheology of the PAN-dope, wet-spinnability, microstructure, and mechanical characterization of the precursor fibers is reported. Wet-spun PAN fibers were used for experimental results investigated in this chapter. In addition, stabilization indices were also calculated and compared with conventional thermal stabilized fibers to measure the conversion achieved by the UV-treated fibers [published as reference (49)].

Chapter 4 addresses the effect of the addition of photoinitiator and further UV exposure on the properties of the resulting thermally stabilized and carbonized PAN-based fibers. In this chapter, the capability of these fibers to withstand further thermal stabilization and carbonization, including accelerated heating rates, and the properties of such fibers after each thermal treatment is reported. This chapter addresses the last thermal treatment stages of the PAN-based carbon production process and the properties of the final PAN-based carbon fibers produced by this novel UV-assisted stabilization method.

Finally, Chapter 5 summarizes the important conclusions drawn from this research and provides recommendations for future work.
References


CHAPTER 2

UV-INDUCED CROSSLINKING AND CYCLIZATION OF SOLUTION-CAST POLYACRYLONITRILE COPOLYMER

2.1 Introduction

As discussed in detail in Chapter 1, polyacrylonitrile (PAN)-based carbon fibers possess outstanding mechanical strength, and have found numerous applications in ultrahigh performance applications (1). These fibers have a low density, of about 1.8 g cm$^{-3}$, and can provide energy efficiency in the civilian aeronautical, energy generation and sports applications, if their cost can be reduced (2).

The rate-limiting step in the conversion of PAN-based precursors into carbon fibers is the stabilization step. Thermo-oxidative stabilization typically involves the heating of the polymer precursor fibers in the range between 200-300°C in air or in another oxidizing atmosphere (3-5). This heat treatment involves the conversion of the PAN polymer chains into a condensed ring structure with a carbon-nitrogen double bond often know as a “ladder” structure (6). This is considered the most critical step during the production of carbon fibers because it determines the final structure and mechanical properties of the resulting carbon fibers (7, 8).

The thermo-oxidative reactions in PAN are highly exothermic (1, 7). Further, thermal conductivity of PAN precursor (like other polymers) is relatively small (~0.26 W m$^{-1}$ K$^{-1}$) (9). Thus, the rate of heat dissipation during the stabilization is a rate-limiting step. If the heat of reaction is not adequately removed in a real process, the core of the
fibers can degrade and result in poor final mechanical properties of the carbon fibers (10-12).

Reducing the rate of reaction and the temperature of initiation of the exothermic reactions can be used to control the heat flux of the fiber during the thermal oxidation step. This is one of the reasons for the use of copolymers of PAN with a low percentage of comonomer such as methyl acrylate (MA), acrylic acid (AA), or itaconic acid (IA). These comonomers disrupt the order in PAN leading to a reduction of the temperature of initiation of the cyclization reactions producing carbon fibers with higher mechanical properties than carbon fibers produced from PAN homopolymer (13). Literature studies have discussed interesting piezo-optic response in photopolymers (14). The acoustic-optic interaction may provide yet another mechanism for manipulating chemical changes and rates within photopolymers.

PAN based terpolymer containing a photo sensitive comonomer, such as acryloyl benzophenone, have been investigated and successfully converted into carbon fibers in previous studies (15). In addition, polymerization and stabilization reactions are known to proceed at lower temperatures when initiated by UV radiation (16, 17). Reduced cyclization temperature can also help to maintain molecular orientation during thermal oxidation, which in turn is important to impart superior modulus and strength properties to the resulting carbon fibers (8, 18-20). Alternatively, the incorporation of this UV-based pre-oxidation step may lead to a reduction of the time required for thermal stabilization process while maintaining the properties of resulting fibers.
Therefore, the overall goal of this research was to investigate UV-assisted stabilization reactions for PAN precursors. The fundamental study reported in this chapter investigates the crosslinking and cyclization reactions in solution-cast PAN samples induced by the addition of photoinitiators that generate free radicals. Specifically, two different mechanisms, namely, homolytic cleavage and hydrogen abstraction, were investigated.

The criteria followed for the selection of the photoinitiators used throughout this research were:

- location of the UV-absorption bands of the photoinitiator;
- solubility of the photoinitiator;
- compatibility of the photoinitiator with the PAN-based precursor;
- atomic composition of photoinitiator (Carbon, Hydrogen, Oxygen, and Nitrogen only);
- type of chemistry involve in the generation of radicals;
- shape and size of photoinitiator and more important shape of radicals generated; and
- stability-reactivity of the generated radicals.

2.2 Experimental
2.2.1 Materials

Poly(acrylonitrle-co-methylacrylate) with a nominal AN/MA ratio of 94:6 and glass transition temperature ($T_g$) of $\sim$82.5°C was used throughout this study. The solvent used for solution-casting of polymer film samples was dimethyl sulfoxide (DMSO). Two different photoinitiators, 1-hydroxycyclohexyl phenyl ketone (denoted as “HPK”) and 4,4’-bis(diethylamino)benzophenone (denoted as “DBP”), were used during this study, as shown in Figure 2.1.

![Figure 2.1: 1-hydroxycyclohexyl phenyl ketone (denoted as “HPK”) and 4,4’-bis(diethylamino)benzophenone (denoted as “DBP”) photoinitiators used throughout the study](image)

Figure 2.2 shows the mechanism by which these photoinitiator generate free radicals when exposed to UV radiation. HPK generates free radicals by homolytic cleavage and has UV absorbance peak at 244 nm in the UVC region (250-260 nm). In contrast, DBP does so by hydrogen abstraction and has UV absorbance peak at 378 nm in the UVA region (320-390 nm) (21-25). All materials were obtained from Sigma-Aldrich (Aldrich Chemical Company, Inc. Milwaukee, WI) and were used as received.
2.2.2 UV-treatment of samples

The PAN-based precursor and photoinitiator were dissolved in DMSO at 70°C. The amount of solids in solution was kept at ~15 wt%. Films were cast from solution and dried at 70°C in a conventional oven for ~24 hours in air. The final thickness of the films was approximately 20 µm. To generate control samples, no photoinitiator was added; the remaining procedure was identical to the one used with the photoinitiator. The films were irradiated with a Nordson 4.5 kW UV curing lamp (Model: 111465A) having a mercury bulb radiation source (bulb model: PM1163). Mercury bulbs are the most widely used UV source, and were used throughout this study. The intensity of the mercury bulb was measured using a high energy UV radiometer (Electronic Instrumentation and Technology, Inc.). Intensity values of approximately 0.228, 0.196, 0.032, and 0.095 W cm\(^{-2}\) were measured for the UVA, UVB, UVC, and UVV ranges, respectively. Films were irradiated for 100, 300, and 600 seconds. The distance between the samples and the UV source was kept constant at approximately 20 cm. A custom-built air cooling system was placed inside the UV chamber to remove the excess of heat generated by the source.
during the UV-treatment. Thus, temperature was controlled during each experiment to study the reactions in two different regimes, 65 and 100°C, that are respectively below and above the $T_g$ of the precursor. All UV treated samples were compared against two types of control films. The first control consisted of pure as-produced PAN film. The second control consisted of samples that were covered by a metal sheet (to avoid UV exposure) but ones that were treated in the same UV chamber to provide similar thermal exposure.

Finally, PAN samples were only thermo-oxidative stabilized (as in conventional processes) to produce control samples whose extent of cyclization could be compared with those of the UV treated samples. The samples were placed on metal frames and heated at 2.5°C min$^{-1}$ to 320°C and held there for 30 minutes. During this thermal oxidation, samples were removed from the oven at 150, 175, 200, 212.5, 225, 240, 255, 270, 280, 300, 320, and 320°C (after 30 minutes) to analyze and quantify the partial extent of the cyclization reaction.

2.2.3 Characterization

Fourier transform infrared spectroscopy (Nexus 870 FT-IR ESP, Nicolet) was used to determine the chemical changes induced during the UV treatment and estimate the extent of the cyclization reaction. Peaks located in the double bond region between 1450 and 1700 wavenumbers (cm$^{-1}$) are associated with the ladder structure (7, 26-28). The scans were conducted from 400 to 4000 cm$^{-1}$ and the transmittance intensities were normalized against the intensity of the 2940 cm$^{-1}$ peak (CH$_2$ asymmetric stretching) for
comparison. The extent of the cyclization reaction was estimated from the following conversion index \((10, 29, 30)\):

\[
\text{Conversion index (\%)} = \frac{I_{1600}}{I_{2240} + I_{1600}} \times 100\%
\]

where \(I_{1600}\) is the measured intensity of the peak located at approximately 1600 cm\(^{-1}\), which corresponds to carbon-nitrogen double bonds associated with the heterocyclic ring structure or ladder structure developed during the thermal oxidation of the PAN-based precursors. \(I_{2240}\) corresponds to the measured peak intensity of the peak located at approximately 2240 cm\(^{-1}\) associated to the carbon-nitrogen triple bond present in the original polyacrylonitrile structure. The peak intensities values used to calculate these conversion indices were raw intensity values given by the FTIR spectrometer without any normalization.

The gel content (insoluble material) is proportional to the extent of cyclization and crosslinking reactions undergone by the samples during the UV treatment. Approximately 100 mg of treated sample was immersed in about 10 mL DMSO and allowed to dissolve at 70°C for over 48 hours under constant agitation. The gel was then separated from the solution using a pre-weighed filter paper, dried in a vacuum oven at 70°C, and the remaining gel mass was measured using a microbalance. The gel fraction of each sample was calculated as the ratio of the remaining insoluble mass and the initial mass of film used in the analysis \((16, 31)\).
Differential scanning calorimetry (Pyris 1 DSC, Perkin Elmer Instruments) was conducted to observe the thermal behavior of the samples after being UV-treated and to quantify the residual heat that a UV treated sample would liberate upon further conventional thermal oxidation. Approximately 4 mg of film sample was heated up to 350°C at a rate of 5°C min\(^{-1}\) in air environment. For each of the characterization techniques used during this study, at least three different measurements were conducted on the different samples. Appendix A gives a complete list of the equipment used during this study.

2.3 Results and Discussion

2.3.1 Influence of PI

Figure 2.3a displays the FTIR spectra of three control specimens: as-produced PAN and two non-UV irradiated but thermally treated samples at 100°C for 300 and 600 seconds. These correspond to the longest treatment times for each set of samples discussed in the following sections. In Figure 2.3b, the section between ~1450 and ~1700 cm\(^{-1}\) displays the double bond region associated with the carbon-oxygen, carbon-nitrogen, and carbon-carbon double bonds present in the ladder structure. This region includes the most significant differences among all the FTIR spectra. The peaks located at 2940, 2865, 2242, 1730, 1454, and 1055 cm\(^{-1}\) have been assigned to \(\text{CH}_2\) asymmetric stretching, \(\text{CH}_2\) symmetric stretching, \(\text{C}≡\text{N}\) stretching, \(\text{C}=\text{O}\) stretching (due to the presence of methyl acrylate), \(\text{CH}_2\) scissor vibration, and \(-\text{C}-\text{C}-\) backbone bending,
respectively (7, 16, 26, 27, 31). These results confirm that simply raising the temperature in the UV-chamber has no discernible effect on the chemical modification of the non-irradiated samples.

Figure 2.3: FTIR spectra of as-produced PAN and two non UV exposed but thermally treated control samples at 100°C for 300 and 600 seconds: (a) over extended wavenumbers, and (b) zoomed-in spectra over the double bond region
Figure 2.4 displays FTIR spectra obtained from samples UV treated at 100°C for 300 seconds, with and without photoinitiators. It is evident that the intensities of this double bond region were higher for UV treated samples containing 1 wt% DBP (hydrogen abstraction photoinitiator) as compared with samples containing 1 wt% HPK (homolytic cleavage) or the controls (pure, UV treated). The conversion index was calculated for each set of samples at 9.0 ± 1.5, 4.6 ± 1.5, 2.2 ± 1.1, 0.1 ± 0.2, and 0 ± 0.2% for samples containing 1 wt% DBP, 1 wt% HPK, UV treated pure, and the two control samples, respectively. At 95% confidence, the conversion index was higher for UV treated samples containing 1 wt% DBP (hydrogen abstraction) compared with other samples containing 1 wt% HPK (homolytic cleavage PI) and UV treated pure samples. Thermally treated samples without UV exposure show no ladder formation. Hence, the presence and type of photoinitiator influences the extent of cyclization of the samples.

Gel contents of these samples were measured at 59 ± 10, 42 ± 10, and 25 ± 10% for specimens containing 1 wt% DBP, 1 wt% HPK, and pure UV treated films at 100°C for 300 seconds, respectively. As expected, the control samples did not produce any gel. These gel fraction measurements are in good agreement with the behavior described by the FTIR results in that samples containing 1 wt% DBP (hydrogen abstraction photoinitiator) are more reacted as compared with the one containing 1 wt% HPK (homolytic cleavage photoinitiator) and pure UV treated sample. These results also confirm that UV-sensitive components can be physically added into the precursor, and not have to be present in the polymer backbone.
The greater double bond formation during UV treatment afforded by the hydrogen abstraction mechanism (over that by homolytic cleavage) can be attributed to the competition between the PAN-based precursor and the photoinitiator. It is known that mercury lamps provide a broad-band output distribution in the UVA, UVB, UVC and UVV regions (32). PAN has an UV absorption peak in the UVC region (~274 nm), which falls in the same UV absorption region as do most of photoinitiators dissociating by homolytic cleavage (21, 23). Specifically, HPK has a UV absorption peak at ~244 nm. Thus, the PAN-based precursor and photoinitiator compete for the same region of the UV spectrum, and energy absorption is inefficient. On the other hand, hydrogen abstraction-type photoinitiators have UV absorption bands at higher wavelengths in the UVA region, specifically ~378nm for DBP (21). This reduces the competition between the PAN-based precursor and photoinitiator for the same region of the UV spectrum. This establishes that
hydrogen abstraction photoinitiators offer a more efficient mechanism, as compared to homolytic cleavage type for UV-induced reactions in PAN-based precursors.

Figure 2.5 displays the DSC results of the residual heat of reaction for PAN-based precursor, with and without photoinitiator, UV-treated at 100°C for 300 seconds. The exothermic heat of reaction observed is a measure of further thermal oxidation that the sample can undergo. It is evident from the results that UV-treated samples display a reduction in the residual heat of cyclization, which may possibly be attributed to three phenomena occurring during the UV-treatment of the precursor: cyclization, crosslinking, and scission of the polymer chains (15, 16, 19, 33, 34). This reduction of the residual heat of reaction of UV treated specimens as compared with samples without UV treatment means that some reaction has already taken place during UV irradiation, albeit at a lower temperature. Interestingly, specimens containing 1 wt% DBP (hydrogen-abstraction PI) show higher heat of reaction compared with that displayed by samples containing 1 wt% HPK (homolytic cleavage PI) and pure UV treated samples. Thus, samples containing 1 wt% DBP will undergo additional thermal cyclization during the further thermal oxidation step, which is desired, even though the same specimens also had displayed higher FTIR double bond conversion percentage and gel content. Thus, DBP is able to absorb more UV energy delivered by the source to react with the PAN-based precursor increasing double bond formation. At the same time, reduction of chain scission and crosslinking which hinder ladder formation during the further thermal oxidation step is observed. By the selection of a suitable photoinitiator, the undesired side reactions (viz. chain scission and crosslinking) can be reduced to favor ladder formation. Since DBP
offered a better performance, it was further investigated with regards to different exposure temperatures and durations.

Figure 2.5: DSC scans of PAN copolymer with and without photoinitiator UV-treated at 100°C for 300 seconds. $\Delta H$ represents the residual heat of cyclization.

2.3.2 Influence of UV radiation time and temperature (above and below $T_g$)

Figures 2.6a and b display FTIR spectra of PAN-based copolymer without any photoinitiator (Figure 2.6a) and with 1 wt% DBP (Figure 2.6b). Both set of samples were UV treated at 100°C for 100, 300 and 600 seconds and are compared with as-produced and thermally treated control samples. The conversion indices were measured to be $6.2 \pm 1.5$, $9.0 \pm 1.5$, and $15.2 \pm 1.5\%$ for samples containing 1 wt% DBP UV treated for 100, 300, and 600 s, respectively. In contrast, the conversion indices of pure samples were $0.6 \pm 1.1$, $2.2 \pm 1.1$, and $7.3 \pm 1.5\%$ for the three durations. Figure 2.7 summarizes these
Figure 2.6: FTIR analysis of PAN-based copolymer with and without photoinitiator UV treated at 100°C for 0, 100, and 600s: (a) without photoinitiator, and (b) with 1%wt DBP; compared against as-produced and thermally treated control samples.

conversion indices as a function of UV treatment time for both sets of samples. Increased UV exposure time led to higher double bond formation and higher conversion index in the double bond region. These results are consistent with prior studies that show that PAN precursors can be cyclized by high-intensity UV radiation (15, 19). The cyclized
polymer can subsequently be thermally stabilized for successful conversion into carbon fibers (16). Although there is some evidence of cyclization reaction occurring in UV-treated samples without PI, the double bond region intensity is significantly higher for samples containing photoinitiator.

![Figure 2.7: Conversion index results (with trend line for visual guidance) versus UV treatment time of PAN-based copolymer with and without photoinitiator UV treated at 100°C for 0, 100, and 600s](image)

In addition to the different intensities observed for the different samples, two other differences were observed. Samples without PI show three noticeable peaks located at 1680, 1630, and the clearest at 1520 cm\(^{-1}\). In contrast, samples containing 1 wt% BDP have an extra peak located at 1600 cm\(^{-1}\). This peak is very clear for samples containing PI after UV treatment for only 100 seconds, and it is not significant for samples without PI even after 600 seconds of UV treatment. It is known that radicals are more likely to add to unsaturated groups, such as the nitrile group present in the PAN structure (16, 33, 34).
Thus; it is believed that the generated photoinitiator radicals react with the carbon-nitrogen triple bonds to start the radical cyclization reaction. The peak located at 1600 cm\(^{-1}\), clearly observed for samples containing PI, has been assigned to the carbon-nitrogen double bond. The presence of the 1520, 1600, 1630, and 1680 cm\(^{-1}\) peaks is a clear indicator of the formation of the ladder structure after the UV treatment (7, 26-28).

In contrast, due to the absence of photoinitiator in pure samples, dehydrogenation reaction is believed to be the primary pathway during UV treatment. Hydrogen radicals produced during the UV-treatment combine to form hydrogen, with carbon-carbon double bond formation in the backbone of the precursor or even crosslinking and scission of the polymer chains, presumably in the amorphous region (19, 33, 34). Based on these arguments, the two peaks located at 1630 cm\(^{-1}\) and 1520 cm\(^{-1}\) (the clearest and most intense for UV-treated samples without PI) are believed to be associated with the conjugated carbon-carbon double bond system. The peak located at 1680 cm\(^{-1}\) has been assigned to the carbon-oxygen double bond formation. Although these are the most noticeable peaks, these overlap with other weaker peaks associated with the ladder structure. Conjugated carbon-oxygen and carbon-nitrogen double bonds, carbon-carbon and carbon-nitrogen single bond stretching, and NH in-plane bending have been assigned in the region between 1500 and 1700 cm\(^{-1}\) (7, 26). The presence of photoinitiator affects the extents and how favorable a specific reaction can become over other parallel reactions taking place during the UV treatment of the PAN-based precursors.

To study the effect of polymer mobility on the photo-induced cyclization of PAN-based specimens with and without photoinitiator, samples were UV treated below and
above the $T_g$ of the PAN-based precursor. Figure 2.8a and b summarizes these results. Figure 2.8a shows PAN-based specimens without photoinitiator UV-treated at 65 or 100°C for 600 seconds. These two temperatures are below and above the glass transition temperature of the PAN-based copolymer ($T_g \sim 82.5^\circ C$), respectively. Figure 2.8b, displays another set of samples containing 1 wt% DBP UV treated at the same temperatures of the pure precursor. The conversion indices of the samples without photoinitiator UV treated at 65 and 100°C were 4.7 ± 1.5 and 7.3 ± 1.5%. For samples containing 1 wt% DBP the indices were 6.8 ± 1.5 and 15.2 ± 1.5%, respectively. In both set of samples, specimens UV treated above $T_g$ of the precursor show higher intensities in the double bond region compared with that for the samples UV treated below $T_g$. The presence of photoinitiator plays a bigger role on the extent of the ladder structure formation on samples UV treated above $T_g$ (7.3 vs. 15.2%) compared with the values obtained for samples UV treated below the $T_g$ of the precursor (4.7 vs. 6.8%).

These results can be explained by the fact that the mobility of the polymer chains is limited below the $T_g$ of the precursor, which reduces the reactivity of the precursor. Based on the similarities shown by their respective FTIR spectra, the presence of photoinitiator has little effect on the type of reactions undergone by the samples UV treated at temperatures below the $T_g$ of the precursor. In both set of samples, with and without photoinitiator UV treated below $T_g$, a very prominent peak at 1520 cm$^{-1}$ mainly associated with carbon-carbon conjugated double bonds is observed. The only subtle difference observed between these two spectra is the wider shoulder shown by the sample
Figure 2.8: FTIR analysis of PAN-based copolymer UV treated at 65 or 100°C for 600 s: (a) without photoinitiator, and (b) with 1 wt% DBP; compared against as-produced and thermally treated control samples containing photoinitiator reaching the 1600 cm\(^{-1}\) region, which is associated with carbon-nitrogen double bond present in the ladder structure. Although some carbon-nitrogen double bond formation is observed for samples containing photoinitiator UV treated
below $T_g$, the amount of triple bonds attacked by the photoinitiator radicals during the UV treatment has been reduced by the restricted polymer chain mobility. As discussed earlier, samples containing photoinitiator and UV treated above $T_g$ show higher double bond intensity specially the 1600 cm$^{-1}$ peak related with carbon-nitrogen double bonds. Pure samples are more inclined to form carbon-carbon double bonds when UV treated irrespective of the temperature. The limited mobility of the polymer chains below $T_g$ limits the effect of photoinitiator. Thus, processing temperature (relative to precursor $T_g$) and the composition (type of PI) during this photo-induced oxidation process play an important role in achieving the stabilization reaction.

Finally, Figure 2.9 displays the FTIR spectra of pure PAN-based copolymer at different stages during the traditional thermal oxidation treatment in air. The overall changes involve the reduction of the C≡N stretching peak (2242 cm$^{-1}$), CH$_2$ stretching peak (2937 cm$^{-1}$), CH$_2$ bending peak (2937 cm$^{-1}$), and carbon back bone bending peak (1051 cm$^{-1}$). On the other hand, primary amines (3390 and 3356 cm$^{-1}$), carbon-oxygen double bond (1680 cm$^{-1}$), carbon-nitrogen double bond (1600 cm$^{-1}$), carbon-carbon double bond (1630 cm$^{-1}$), conjugated carbon-carbon double bond corresponding to the heterocyclic ring structure (1520 cm$^{-1}$), carbon-hydrogen in and out of plane deformations (1370 and 805 cm$^{-1}$, respectively), and carbon-oxygen single bond (1150 cm$^{-1}$) appear. All these peaks are related to the cyclized structure produced during the thermal oxidation treatment (7, 16, 26, 27, 31).
Figure 2.9: FTIR spectra of pure PAN-based copolymer at different stages during the traditional thermal oxidation treatment in air.

Figure 2.10 shows the section between ~1450 and ~1700 cm$^{-1}$ of the first four FTIR spectra shown in Figure 2.9 corresponding to as-produced PAN samples, and those thermally treated up to 150, 175 and 200°C. The four spectra indicate the start of the
standard thermally activated cyclization reaction in an oxidizing environment. For the PAN copolymer investigated in this work, chemical changes in the double bond region associated with the ladder structure are observed at temperatures between 150 and 175°C. They appear as shoulders of the two strong peaks (1730 cm\(^{-1}\), methyl acrylate C=O stretching; and 1454 cm\(^{-1}\), CH\(_2\) scissor) belonging to the original PAN copolymer structure. The subtle peaks observed at 175°C belong to the carbon-oxygen double bond (1680 cm\(^{-1}\)) and carbon-carbon conjugated system (1630 and 1520 cm\(^{-1}\)). Between 175 and 200°C, the intensity around 1600 cm\(^{-1}\) starts to become noticeable indicating carbon-nitrogen double bond formation associated with cyclization. These observations indicate that the first reaction to take place during the thermal oxidation is the dehydrogenation reaction by oxygen attack on the polymer chains. The cyclization reaction starts immediately after the dehydrogenation reaction initiates. These observations are

![Figure 2.10: FTIR spectra of as-produced PAN-based copolymer and the same sample thermally treated up to 150, 175, and 200°C](image)

Figure 2.10: FTIR spectra of as-produced PAN-based copolymer and the same sample thermally treated up to 150, 175, and 200°C
consistent with those reported in the literature (11, 28). Notice that the reaction path followed by the thermally treated samples is similar to the one followed by the UV treated samples without photoinitiator described at the beginning of this section.

Based on FTIR spectra displayed in Figure 2.9, the FTIR conversion indices for pure, non-UV treated, thermally stabilized samples are presented in Figure 2.11 as a function of the thermal stabilization time. Also included is the temperature profile followed during these thermal stabilization experiments. These results show that most of the conversion of the precursor occurs during the second half of the thermal treatment process, specifically between 200 and 300°C. In addition, the dashed line indicates the conversion index of 9.0% for a sample containing 1 wt% DBP UV treated at 100°C for 300s. The results show that 300 seconds (5 minutes) of UV treatment of the PAN-copolymer containing 1 wt% DBP are approximately equivalent to the first 4800 seconds (80 minutes) of the thermal oxidation process, i.e., a reduction of approximately half of the time. In addition, during the UV treatment, the sample was kept at 100°C; in contrast, the thermal treated samples have to reach approximately 240°C to achieve the same conversion index. Thus, the same conversion was achieved in a shorter period of time at a lower temperature. The conversion index for UV treated samples in the absence of photoinitiator was approximately 2% and not statistically different from the initial indices for pure PAN samples thermally stabilized (therefore, not included in the figure). These kinetic results indicate the potential for developing a novel and more rapid process for stabilization of PAN-based precursors to produce carbon fibers more efficiently.
2.4 Conclusions

The effect of UV-photoinitiators and UV-radiation on photo-induced stabilization of polyacrylonitrile was investigated. Hydrogen-abstraction was found to be a more efficient mechanism in comparison with homolytic cleavage during the photo-induced cyclization of PAN precursor polymer. FTIR, gel percentages, and DSC results confirm that samples containing 4,4’-Bis(diethylamino)benzophenone (hydrogen abstraction type) achieved higher extents of cyclization than did samples containing 1-hydroxycyclohexyl phenyl ketone (homolytic cleavage type). Also, the presence of 4,4’-Bis(diethylamino)benzophenone enables higher extents of post-UV thermal cyclization.

The presence of photoinitiator is more effective in promoting carbon-nitrogen double bond formation for samples UV treated above the $T_g$ of the precursor in comparison with UV treated samples without photoinitiator and samples UV treated
below $T_g$ where carbon-carbon double bond formation was more favorable. At temperatures below the $T_g$ of the precursor, the presence of photoinitiator does not play a significant role on the extent of the cyclization due to the limited mobility of the polymer chains.

Increasing UV exposure time leads to greater formation and higher FTIR conversion index in the double bond region. The present results confirm that it is possible to produce UV-induced cyclization in PAN-based precursors by the external addition of photoinitiator into the polymer solution (i.e., without necessarily incorporating photoinitiators into the polymer chain itself). Thus, the addition of 1 wt% photoinitiator to PAN and UV treatment for only 5 minutes increases the rate of the cyclization reaction and reduces the thermal oxidation time by over an hour, which could significantly reduce the conventional stabilization time. These results have been published as reference (35).
References


CHAPTER 3

WET-SPUN, PHOTOINITIATOR-MODIFIED POLYACRYLONITRILE PRECURSOR FIBERS: UV-ASSISTED STABILIZATION

3.1 Introduction

As noted earlier in Chapters 1 and 2, high strength carbon fibers used in structural composites for aerospace applications are derived from solution-spun PAN precursor fibers (1-5). However, the higher cost of carbon fibers compared with other reinforcing materials (viz. glass fibers) limits their use for the high-end applications where strength-to-density ratio is critical (4-8). The demand for carbon fibers is expected to grow to about 150,000 metric tons over the next decade from current demand of 40,000 metric tons. However, a large fraction of the increase is anticipated in the industrial sector that is cost-sensitive (9). For cost effective products, such as automotive application, there is a need for the development of novel processes and precursors to reduce the carbon fiber production cost and expand the use of carbon fibers.

For the conversion of PAN into carbon fibers, thermal oxidative stabilization and carbonization steps have to be conducted (4, 10, 11). The thermal stabilization process is believed to be the most important step during the carbon fiber manufacture, because the conditions employed during stabilization will dictate most of the final carbon fiber properties (12-15). Also, thermal stabilization is the rate-limiting step in the production of PAN-based carbon fibers (3, 16). Various details of the thermo-oxidative stabilization and carbonization steps have been discussed in literature studies (17-22), which indicate
that stresses must be applied during stabilization and carbonization steps in an attempt to regain the molecular orientation. This strategy results in carbon fibers with high strength, but the limited molecular orientation prevents the fibers from developing a high modulus (14, 15, 18, 23). To retain molecular orientation, it is desirable to conduct stabilization reactions at lower temperatures, which can be accomplished when such reactions are initiated by UV radiation (24-26). In Chapter 2, it was established that cyclization and crosslinking reactions associated with thermal stabilization start at lower temperatures by the addition of small amounts (1 wt%) of photoinitiator to solution-cast PAN films. Subsequent UV exposure at lower temperatures led to a reduction of the conventional thermal stabilization time (27). This chapter discusses the effect of external photoinitiator added to the polymer solution on the rheology and wet-spinning of the PAN-dope, and characterization of precursor fibers.

3.2 Experimental

3.2.1 Materials

Polyacrylonitrle homopolymer with a molecular weight (Mw) of 233,000 and a glass transition temperature (Tg) of 125°C was used throughout this study. This PAN homopolymer was obtained from Scientific Polymer (Ontario NY). The photoinitiator used throughout this study, 4,4’-bis(diethylamino)benzophenone (denoted as “BDP”), is shown in Figure 2.1. This photoinitiator generates free radicals by hydrogen abstraction and has UV absorbance peak at 378 nm in the UVA region (320-390 nm) (28, 29). The
solvent used in this work was dimethyl sulfoxide (DMSO) with a density of 1.1 g cm$^{-3}$ and viscosity of 0.002 Pa s (both measured at 25 °C). Both, photoinitiator and solvent were obtained from Sigma-Aldrich (Aldrich Chemical Company, Inc. Milwaukee, WI). Also a standard silicon powder reference material was used for line position and line shape during X-ray diffraction studies (NIST reference material® 640d). All materials were used as received.

3.2.2 Fiber spinning

PAN-based precursor and photoinitiator (where applicable) were dissolved in a 99:1 mass ratio in DMSO at 70°C. The amount of solids in solution was kept at ~16 wt%. Fibers were spun from solution using a custom-built wet-spinning unit fitted with a spinnerette that had 100 holes each one with an approximate diameter of 68 µm. A volumetric flow of 0.6 mL min$^{-1}$ was maintained during the spinning of the fibers. The coagulation bath consisted of 70 wt% DMSO / 30 wt% distilled-deionized water. After the coagulation bath, the solidified fibers were passed through a distilled-deionized water washing bath; both baths were kept at ~20°C. The effective length of the coagulation and washing bath were 40 and 80 cm, respectively. The rolls of fibers were placed in an oven and dried at 70°C for about 24 hours. Next, the fibers were post-stretched in a distilled-deionized water bath at approximately 80°C. The effective length of the post-stretching bath was 80 cm. Pure PAN fibers as well as fibers containing 1 wt% of photoinitiator were thus produced.
3.2.3 UV-treatment of samples

The fibers were irradiated with a Nordson 4.5 kW UV curing lamp (Model 111465A). Two different UV sources were used: mercury (model PM1163) and iron halide (model PM1163F) bulb. The intensity of both bulbs was measured using a high energy UV radiometer (model PP2000, Electronic Instrumentation and Technology, Inc.). For the mercury bulb intensity values of approximately 0.228, 0.196, 0.032, and 0.095 W cm\(^{-2}\) were measured for the UVA, UVB, UVC, and UVV ranges, respectively. The intensity values measured from the iron-halide bulb were approximately 0.378, 0.131, 0.014, and 0.236 W cm\(^{-2}\) for the UVA, UVB, UVC, and UVV ranges, respectively. Mercury bulbs are the most widely used UV source and they provide a broad-band output distribution in the four UV regions (26, 30). Iron halide bulbs have the feature of possessing a higher energy emission in the UVA region. As noted earlier, the photoinitiator BDP has a UV absorption peak at 378 nm (UVA). Thus, by choosing an appropriate UV source (mercury vs. iron halide), it may be possible to control the interactions between the UV radiation and the PAN-based precursor or photoinitiator. Besides cyclization, dehydrogenation, and crosslinking, UV radiation acting directly on the PAN precursor leads to chain scission as well, which hinders the stabilization reaction and affects the properties of the resulting fibers (27). Iron halide reduces the amount of energy delivered in the UVC and UVB regions that interact with PAN-based precursors (UV absorption peak at ~274 nm) and delivers more energy in the UVA region where the UV absorption peak of the photoinitiator is located (27). As shown later, the UV profile
of the UV source selected will influence the rate of stabilization reaction, and hence, the properties of the material for a given UV treatment time.

Segments of approximately 10 inches (matching effective length of UV bulbs) were irradiated for 300 seconds at approximately 150°C. The bundle of fibers was held under approximately 0.1 g denier\(^{-1}\) of tension during the UV treatment. The distance between the samples and the UV source was kept constant at approximately 20 cm. A custom-made air cooling system was placed inside the UV chamber to remove the excess of heat generated by the source during the UV-treatment and control the temperature inside the UV chamber. All UV treated samples were compared against two types of control fibers. The first control consisted of pure as-produced PAN fibers. The second control consisted of fibers that were covered by a metal sheet (to avoid UV exposure) but ones that were treated in the same UV chamber to provide similar thermal exposure as that received by UV treated samples (that also experienced the slightly elevated temperatures).

Finally, PAN fibers were only thermo-oxidative stabilized (as in conventional processes) to produce control samples whose extent of cyclization could be compared with those of the UV treated samples. The samples were stabilized under tension (0.1 g denier\(^{-1}\) below 200°C and 0.05 g denier\(^{-1}\) above 200°C), heated at 2.5°C min\(^{-1}\) to 300°C, and held there for 30 minutes. During this thermal oxidation, samples were removed from the oven at 150, 175, 200, 225, 250, 275, 300, and 300°C (after 30 minutes) to analyze and quantify the partial extent of the cyclization reaction.
3.2.4 Characterization

To determine the flow characteristics of the PAN-dopes, the solutions were tested for their rheological response using an ARES LS0012701 advanced rheometer with a cone-and-plate fixture for small shear rates (0.1-30 s\(^{-1}\)) and an ACER 2000 capillary rheometer for high shear rates (30-30,000 s\(^{-1}\)). The cone-and-plate fixture had a diameter of 25 mm and a cone angle of 0.1 radian. The capillary employed during the experiments had a “L/D” value of 30. All testing was conducted at room temperature (~25°C). The viscosities values for each solution were fitted using the generalized Newtonian or Carreau model (Equation 3.1). Where \(\eta(\dot{\gamma})\) is the predicted shear viscosity, \(\dot{\gamma}\) is the shear rate, \(\lambda\) is the time constant, \(\eta_0\) is the zero shear rate viscosity, \(\eta_\infty\) is the infinite shear rate viscosity, and \(n\) corresponds to the power law index. For polymer solutions, the solvent viscosity is usually used for the \(\eta_\infty\) parameter (31, 32).

\[
\frac{\eta(\dot{\gamma})-\eta_\infty}{\eta_0-\eta_\infty} = [1 + (\lambda \dot{\gamma})^2]^{(n-1)/2}
\]

Fourier transform infrared spectroscopy (Nexus 870 FT-IR ESP, Nicolet) was used to confirm the presence of photoinitiator in the fibers after being wet-spun and post stretched in hot water. The scans were conducted from 400 to 4000 cm\(^{-1}\) and the transmittance intensities were normalized against the intensity of the 2940 cm\(^{-1}\) peak (CH\(_2\) asymmetric stretching) for comparison.

Morphological analysis of fibers was conducted by scanning electron microscopy with a Mitsubishi 4800 SEM unit. To retain the cross section shape and other physical
features of the fibers, the fibers were submerged into liquid nitrogen for approximately 1 minute and later broken. To determine the effective diameter of the fibers (with and without photoinitiator) Image-Pro Plus 7.0 (Media Cybernetics, Inc.) analysis software was used to measure the cross section area of each type of sample and the effective diameter calculated from these area measurements. At least 40 cross section areas were measured for each type of fiber.

A PHOENIX single filament tensile testing unit (Measurements Technology Inc.) was used to measure the mechanical properties of the different fibers types produced along this work. The single fibers were mounted on 25 mm paper tabs. At least 20 samples per type of fibers were prepared and tested.

Wide angle X-ray diffraction (WAXD) analysis was conducted on bundles of fibers using a Rigaku-MSC (Houston, TX) X-ray diffraction unit. The X-ray diffraction pattern was captured through image plate and the analysis of WAXD generated images were analyzed using Polar v2.6.7 (Stonybrook Technology and Applied Research, STAR). The curve fitting of the spectra was done using OriginPro 7 (v7.0383, OriginLab Corporation). The unit generates an X-ray beam with a wavelength of 1.5406 Å (Cu target). The diameter of the X-ray beam hitting the sample was ~0.5 mm. The distances between the X-ray source and sample and the sample and the image plate detector were approximately 70 and 12 cm, respectively. Operation conditions of the X-ray source were 45 kV and 0.65 mA. The gas used for most of the beam path was helium. Each bundle of fibers was mounted on a 10 mm paper tab and sprinkled with silicon standard powder.
The exposure time per sample was approximately 2 hours. Plane spacing and crystal size were calculated using the equations below:

\[ \lambda = 2d \sin \theta \quad 3.2 \]

\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 +hk +k^2}{a^2} \right) + \frac{l^2}{c^2} \quad 3.3 \]

\[ l_a = \frac{0.89\lambda}{B \cos \theta} \quad 3.4 \]

\[ B^2 = B_M^2 - B_S^2 \quad 3.5 \]

For these equations, \( \lambda \) corresponds to the wavelength of the X-ray beam, \( d \) is the distance between adjacent planes in the set \((hkl)\), \( \theta \) is the angle of incidence of the X-ray beam, \( a \) and \( c \) are the lattice parameters of the hexagonal structure, \( l_a \) is the crystal size, \( B \) is the corrected full width at half-maximum (FWHM) intensity of the spectrum peak (in terms of \( 2\theta \) scale), \( B_M \) is the measured FWHM, and \( B_S \) is the system broadening determined, in this case, by the silicon standard. Equations 3.2 and 3.3 were employed to calculate the interplanar spacing of the crystals. Equation 3.2 corresponds to the Bragg’s law and Equation 3.3 corresponds to the lattice geometry equation for hexagonal crystal structure observed in PAN. Equations 3.4 and 3.5 were employed to calculate crystal size. Equation 3.4 corresponds to Scherrer formula. Warren’s broadening correction
(Equation 3.5) was used to correct the system broadening on each WAXD scan (33-40). Also, conversion or aromatization index was determined using the following equation (37, 41, 42):

\[
\text{Conversion index} (\%) = \frac{A_A}{A_A + A_P} \times 100\%
\]

where \( A_A \) is the area of the peak associated with the aromatic structure around \( \theta = 25^\circ \) and \( A_P \) correspond to the area of the (100) crystal peak of PAN at \( \theta = 17^\circ \). In addition, the Rigaku-MSC diffractometer is capable of measuring the orientation of the crystal in the fibers. These azimuthal scans were conducted on the most prominent peak of the PAN spectra, which is the (1 0 0) peak. Appendix A gives a complete list of the equipment used during this study.

3.3 Results and Discussion

3.3.1 Spinning of fibers containing photoinitiator

Figure 3.1 displays steady shear viscosity versus shear rate results for PAN solutions with and without BDP. The open symbols represent the viscosity values measured at lower shear rates (0.1-30 s\(^{-1}\)) using the cone-and-plate fixture. The solid symbols correspond to the viscosity values measured at higher shear rates (30-30,000 s\(^{-1}\)) using the capillary rheometer. Both types of solutions displayed a shear-thinning behavior at high shear rates with an approach to Newtonian plateau at shear rates less than about
0.5 s\textsuperscript{-1}. The Carreau model was used to fit the viscosity data. For pure and BDP containing dopes, power law indices of 0.558 ± 0.028 and 0.544 ± 0.011, time constants of 1.85 ± 0.78 and 1.54 ± 0.35 s, and zero shear rate viscosity of 250 ± 34 and 232 ± 8 Pa s, respectively, were obtained. At 95% confidence, the presence of photoinitiator in the solution did not significantly affect the viscosity of the dope. Thus, the presence of photoinitiator has no adverse effect on the viscosity of the dopes. This observation was generally consistent with the fact that the concentration of BDP in the actual solution was small (~0.16 wt%).

Figure 3.1: Viscosity versus shear rate results for PAN solutions with and without photoinitiator (at ~25°C)

All wet-spinning experiments were conducted at room temperature (~25°C). During the spinning of both types of fibers, the total amount of solids in solution was held at about 16 wt%. Higher dope concentrations (17 - 21 wt%) were difficult to spin on
a continuous basis for both types. A linear take up velocity of 190 cm min\(^{-1}\) was employed during the spinning of the fibers. The drawing ratio was kept in between 1.15 and 1.2. The drawing ratio used during the post-stretching step was approximately 3. Higher drawing ratios led to fiber breakage during spinning and post-stretching. Pure PAN fibers as well as fibers containing 1 wt% of photoinitiator were successfully produced.

Figure 3.2 displays representative SEM micrographs of as-produced PAN fibers. Figures 3.2a and 3.2b correspond to pure PAN fibers and those containing 1 wt% BDP, respectively. Both types of fibers show the characteristic kidney shape of wet-spun PAN-based fibers (5, 11, 21, 36, 38). No noticeable deterioration or change in the microstructure of the fibers containing photoinitiator was observed when compared with pure control fibers. Thus, the presence of photoinitiator does not significantly affect the morphology of the fibers. The diameter of pure and 1 wt% BDP PAN fibers were 11.9 ± 0.3 and 11.4 ± 0.3 µm, respectively. At 95% confidence level, there was no significant difference between the effective diameters of the pure fibers and the fibers containing 1 wt% BDP.

To identify the presence of photoinitiator in the fibers after spinning and post-stretching, FTIR analysis was conducted on pure and 1 wt% BDP post-stretched fibers. Figure 3.3 shows the comparison between the FTIR spectra of the pure and 1 wt% BDP fibers. The peaks located at 2940, 2865, 2242, 1454, and 1055 cm\(^{-1}\) have been assigned to CH\(_2\) asymmetric stretching, CH\(_2\) symmetric stretching, C≡N stretching, CH\(_2\) scissor vibration, and -C-C-C- backbone bending, respectively (10, 15, 27, 43, 44). The spectrum
of the fibers containing 1 wt% DBP shows two extra peaks associated with the presence of photoinitiator in the fibers located at 1595 and 1525 cm\(^{-1}\). The 1595 cm\(^{-1}\) peak has been assigned to the C=O stretching and the 1525 cm\(^{-1}\) to the C=C stretching (in ring), respectively. These two peaks are a proof of the presence of photoinitiator in the fibers after the spinning process. Thus, photoinitiator is retained in the fibers after coagulation and post-stretching despite the out-diffusion of the solvent during the coagulation stage.

Figure 3.2: Representative SEM micrographs of as produced PAN fibers: (a) pure PAN fibers, (b) fibers containing 1 wt% BDP
3.3.2 Influence of UV radiation

Figure 3.4 displays representative micrographs of control and active samples UV-treated either with a mercury or iron halide bulb. Figure 3.4a and 3.4b correspond to thermally exposed non-UV treated pure PAN fibers (control #1) and thermally exposed non-UV treated fibers containing 1 wt% BDP (control #2), respectively. Figure 3.4c and 3.4d are representative micrographs of pure and 1 wt% BDP-PAN fibers UV treated with the iron halide source, respectively. Figure 3.4e and 3.4f correspond to pure and 1 wt% BDP-PAN fibers UV treated with the mercury source, respectively. In all cases the fibers retained the characteristic kidney shape of wet-spun PAN-based fibers \((5, 11, 21, 36, 38)\). At 95% confidence level, there was no significant difference between the effective diameters among the different samples. Another important observation is that the UV-
treatment of the fibers did not lead to skin-core structure formation on any of the UV treated fibers. Skin-core structure is undesired during the stabilization of PAN-based fibers because leads to poor quality (mechanical properties of the) stabilized and carbonized fibers \((5, 7, 16, 19, 34, 37)\).

Figure 3.5 shows representative tensile testing curves of each set of samples. Figure 3.5a corresponds to as-produced, thermally exposed, and UV treated with either iron halide or mercury bulb pure PAN fibers. Figure 3.5b shows the same treatment conditions but for fibers containing 1 wt% BDP. The limit of linear proportionality was approximately 1% for all samples. Figure 3.5 also shows that the upper and lower yield points seem very close to the proportionality limit. Also, a small necking section is observed just before breakage. Table 3.1 summarizes the tensile testing results conducted on single filaments. These tensile properties of the PAN fibers are consistent with those reported in the literature: 10-25% for the breaking strain, 0.1-0.7 GPa for strength, and 1-10 GPa for tensile modulus \((1, 7, 8, 12, 14, 18, 42, 45, 46)\).

Tensile testing results shown in Table 3.1 indicate that, at 95% confidence, there is significant difference in the breaking strain between pure and 1 wt% BDP fibers; the presence of photoinitiator reduces the elongation capabilities of the fibers by ~1%. These results show no significant statistical differences, at 95% confidence, between the ultimate tensile strength among different specimens. On the other hand, at 95% confidence, the two set of fibers containing 1 wt% BDP UV treated for 300 s (5 minutes) with either mercury or iron halide displayed higher tensile modulus than the other set of
Figure 3.4: Representative SEM micrographs of PAN fibers with and without photoinitiator after being UV treated: (a) thermally exposed pure PAN fibers, (b) thermally exposed fibers containing 1 wt% BDP, (c) pure PAN fibers UV treated with iron halide bulb, (d) 1 wt% BDP PAN fibers UV treated with iron halide bulb, (e) pure PAN fibers UV treated with mercury bulb, and (f) 1 wt% BDP PAN fibers UV treated with the mercury bulb
Figure 3.5: Representative tensile testing curves of each set of samples: (a) pure PAN, (b) PAN fibers containing 1% BDP

samples. In addition, these tensile testing results show that fibers containing 1 wt% BDP UV treated with a mercury source exhibit the highest tensile modulus of all eight set of samples (significant at 95% confidence). This proves the combined positive effect of the addition of photoinitiator and 300 s of UV treatment on the fibers.
Table 3.1: Single filament tensile results with 95% confidence intervals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Modulus (GPa)</th>
<th>Max Stress (GPa)</th>
<th>Break Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>7.0 ± 0.3</td>
<td>0.24 ± 0.01</td>
<td>16.4 ± 0.5</td>
</tr>
<tr>
<td>Pure, 150°C</td>
<td>7.1 ± 0.3</td>
<td>0.24 ± 0.01</td>
<td>14.9 ± 1.2</td>
</tr>
<tr>
<td>1 wt% BDP</td>
<td>7.0 ± 0.3</td>
<td>0.26 ± 0.01</td>
<td>14.3 ± 0.5</td>
</tr>
<tr>
<td>1 wt% BDP, 150°C</td>
<td>7.1 ± 0.4</td>
<td>0.25 ± 0.01</td>
<td>14.0 ± 0.8</td>
</tr>
<tr>
<td>Pure, 300s Fe, 150°C</td>
<td>6.8 ± 0.3</td>
<td>0.22 ± 0.01</td>
<td>15.2 ± 1.4</td>
</tr>
<tr>
<td>Pure, 300s Hg, 150°C</td>
<td>7.0 ± 0.3</td>
<td>0.24 ± 0.01</td>
<td>16.7 ± 0.5</td>
</tr>
<tr>
<td>1 wt% BDP, 300s Fe, 150°C</td>
<td>7.5 ± 0.3</td>
<td>0.23 ± 0.01</td>
<td>13.5 ± 1.3</td>
</tr>
<tr>
<td>1 wt% BDP, 300s Hg, 150°C</td>
<td>7.7 ± 0.2</td>
<td>0.25 ± 0.01</td>
<td>13.8 ± 0.8</td>
</tr>
</tbody>
</table>

The higher tensile modulus shown by the 1 wt% BDP fibers UV treated with the mercury bulb compared with the same fibers UV treated with the iron halide bulb can be explained based on the differences in the spectral output of each type of bulb. Mercury bulbs deliver more energy in the UVC region and iron halide bulbs produce higher energy output in the UVA region (matching the UV absorption region of BDP). PAN has a UV absorption peak in the UVC region (~274 nm). Thus, the samples UV treated with the mercury bulb display a higher combined effect of the photoinitiator radicals, produced by the interaction of the photoinitiator with the UVA region, and UVC radiation directly interacting with the polymer chains. As mentioned earlier, the emission of UVC radiation is lower for iron halide bulbs compared with mercury bulbs. Therefore, the interaction between the radiation emitted by the iron halide bulb and the polymer chain is lower and the photoinitiator radicals are the ones that mainly interact with the polymer chains (27). These results are very encouraging since the final mechanical
properties of the carbon fibers depend greatly on the mechanical fibers of the precursor fibers (2, 6, 10, 21, 22, 35, 38).

Figure 3.6 shows representative wide angle X-ray diffractograms of as-spun pure, post-stretched pure, and post-stretched with 1 wt% BDP PAN fibers. Integrated 2-theta scans, displayed in Figure 3.6a, show the first peak at ~17° corresponding to the (1 0 0) plane of the PAN precursor. The second peak corresponds to the combination of the amorphous halo at ~26° and the (1 1 0) plane peak of PAN at ~29.5° (35-39, 47-49). Silicon standard was added to each of the different fiber samples as a calibration standard. This silicon standard shows three sharp peaks at 28.44°, 47.3°, and 56.12° corresponding to its (1 1 1), (2 2 0), and (3 1 1) planes, respectively.

As noted before, the orientation of the crystals in the fibers was measured from the azimuthal scans conducted on the (1 0 0) peak of the PAN spectra. Figure 3.6b shows the azimuthal scans of (1 0 0) peak of as-spun pure, post-stretched pure, and post-stretched with 1 wt% BDP PAN fibers. Sharp azimuthal peaks for a given set of planes mean higher orientation, whereas, broad peaks indicate low orientation. As expected, post-stretched PAN fibers have significant higher orientation in comparison with that of as-spun fibers. Similar orientation is achieved for pure and 1 wt% BDP PAN fibers after being post-stretched. To compare the crystal orientation in the different set of fibers, the full-width-at-half-max (FWHM) was measured for each azimuthal scan. The smaller the FWHM value, the more oriented are the crystals within the fibers.
Table 3.2 summarizes the WAXD results obtained from all the different set of samples. After post-stretching, the interplanar spacing between the (1 0 0) plane was reduced and the orientation and crystal size was increased for pure and 1 wt% BDP-PAN fibers. Also, the results show no negative effects (at 95% confidence) for the interplanar
spacing and size of the crystals within the fibers containing photoinitiator as compared with pure control fibers. In a previous study, it was shown that PAN-based precursors containing 1% BDP UV treated for 300 s show higher extents of cyclization reaction as compared with other set of samples (27). Here, WAXD results show that during the UV treatment (cyclization reaction) these samples are able to retain their molecular orientation. This is not the case for pure UV treated samples. The retention of the orientation of the polymer chains within the fibers can lead to more polymer chains undergoing cyclization, leading to higher conversions. These results agree well with the tensile testing results that show superior mechanical properties for samples containing 1% BDP and UV treated for 300 s due to the fact that they are able to retain molecular orientation. For this system, higher molecular orientation leads to higher mechanical properties of the fibers (10, 15, 18, 21-23).

Figure 3.7 displays the WAXD spectra of pure PAN fibers at different stages during the traditional thermal stabilization in air. Figure 3.7a and 3.7b correspond to the integrated 2-theta scan and the azimuthal scan of the PAN (1 0 0) peak, respectively. Table 3.3 summarizes the lattice parameters calculated from the spectra shown in Figure 3.7. Between room temperature and 150°C, the (1 0 0) peak becomes sharper and an increase in orientation and crystal size is observed in the fibers. Literature studies have discussed interesting effects of induced anisotropy due to the applied UV radiation (50). However, as observed in the conventional thermal stabilized samples, most of the induced anisotropy in the current samples can be attributed to the fact that the samples are under tension during processing.
Table 3.2: WAXD results with 95% confidence intervals

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Iₐ (Å)</th>
<th>a (Å)</th>
<th>(1 0 0) FWHM (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PURE as spun</td>
<td>31.1 ± 3.2</td>
<td>6.048 ± 0.025</td>
<td>75.2 ± 2.5</td>
</tr>
<tr>
<td>1 wt% BDP as spun</td>
<td>29.4 ± 3.3</td>
<td>6.064 ± 0.029</td>
<td>75.8 ± 2.0</td>
</tr>
<tr>
<td>PURE after stretch</td>
<td>42.3 ± 1.9</td>
<td>6.001 ± 0.020</td>
<td>26.1 ± 0.9</td>
</tr>
<tr>
<td>1 wt% BDP after stretch</td>
<td>45.8 ± 2.2</td>
<td>6.019 ± 0.019</td>
<td>24.6 ± 1.4</td>
</tr>
<tr>
<td>PURE (150°C, NO UV, control)</td>
<td>41.8 ± 1.8</td>
<td>6.028 ± 0.038</td>
<td>28.3 ± 0.9</td>
</tr>
<tr>
<td>1 wt% BDP (150°C, NO UV, control)</td>
<td>42.4 ± 0.4</td>
<td>6.034 ± 0.015</td>
<td>25.3 ± 0.2</td>
</tr>
<tr>
<td>PURE, 300s Fe UV, 150°C</td>
<td>43.8 ± 1.0</td>
<td>6.032 ± 0.010</td>
<td>29.8 ± 1.3</td>
</tr>
<tr>
<td>PURE, 300s Hg UV, 150°C</td>
<td>43.6 ± 1.4</td>
<td>6.047 ± 0.025</td>
<td>29.7 ± 0.6</td>
</tr>
<tr>
<td>1 wt% BDP, 300s Fe UV, 150°C</td>
<td>48.9 ± 4.9</td>
<td>6.029 ± 0.021</td>
<td>25.7 ± 1.8</td>
</tr>
<tr>
<td>1 wt% BDP, 300s Hg UV, 150°C</td>
<td>46.3 ± 1.5</td>
<td>6.036 ± 0.016</td>
<td>25.6 ± 1.1</td>
</tr>
</tbody>
</table>

Between 150 and 225°C, growth of the crystal size is mainly observed. At 225°C, dramatic changes are observed in the spectra. Between 225 and 250°C, the crystal size stops increasing, and around 250°C, the (1 0 0) PAN peak starts broadening and becomes weaker. This indicates an increment on the interplanar spacing and a reduction on the crystal size and orientation of the original PAN structure. In contrast, a strong aromatic peak starts to emerge. This evolution of structure is consistent with that reported in the literature (15, 37, 41, 46).
Figure 3.7: WAXD spectra of pure PAN fibers at different stages during traditional thermo-oxidative stabilization: (a) integrated 2-theta scan; (b) azimuthal scan of the PAN (100) peak

Based on WAXD spectra displayed in Figure 3.7, the conversion indices for pure, non-UV treated, thermally stabilized samples are presented in Figure 3.8 (and Table 3.3) as a function of the thermal stabilization time. Also included is the temperature profile followed during these thermal stabilization experiments. The dashed lines indicate the
Table 3.3: WAXD results with 95% confidence intervals of pure PAN fibers at different stages during traditional thermal stabilization in air

<table>
<thead>
<tr>
<th>Fiber Temperature (°C)</th>
<th>$I_a$ (Å)</th>
<th>$a$ (Å)</th>
<th>(100) FWHM (°)</th>
<th>C. I. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>42 ± 2</td>
<td>6.001 ± 0.020</td>
<td>26.1 ± 0.9</td>
<td>1 ± 2</td>
</tr>
<tr>
<td>150</td>
<td>90 ± 2</td>
<td>6.025 ± 0.013</td>
<td>20.3 ± 1.1</td>
<td>1 ± 2</td>
</tr>
<tr>
<td>175</td>
<td>107 ± 2</td>
<td>6.012 ± 0.020</td>
<td>20.1 ± 0.9</td>
<td>2 ± 2</td>
</tr>
<tr>
<td>200</td>
<td>119 ± 2</td>
<td>6.001 ± 0.020</td>
<td>21.2 ± 1.0</td>
<td>2 ± 2</td>
</tr>
<tr>
<td>225</td>
<td>126 ± 4</td>
<td>6.003 ± 0.018</td>
<td>22.1 ± 0.9</td>
<td>1 ± 2</td>
</tr>
<tr>
<td>250</td>
<td>134 ± 4</td>
<td>6.009 ± 0.017</td>
<td>21.3 ± 0.9</td>
<td>16 ± 8</td>
</tr>
<tr>
<td>275</td>
<td>98 ± 2</td>
<td>6.040 ± 0.020</td>
<td>21.3 ± 1.2</td>
<td>37 ± 5</td>
</tr>
<tr>
<td>300</td>
<td>13 ± 1</td>
<td>6.198 ± 0.124</td>
<td>79.6 ± 5.5</td>
<td>52 ± 14</td>
</tr>
<tr>
<td>300 (after 30 min)</td>
<td>10 ± 1</td>
<td>6.438 ± 0.049</td>
<td>100.4 ± 2.1</td>
<td>70 ± 2</td>
</tr>
<tr>
<td>1 wt% BDP, 300s Fe UV, 150°C</td>
<td>49 ± 5</td>
<td>6.029 ± 0.021</td>
<td>25.7 ± 1.8</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>1 wt% BDP, 300s Hg UV, 150°C</td>
<td>46 ± 2</td>
<td>6.036 ± 0.016</td>
<td>25.6 ± 1.1</td>
<td>14 ± 2</td>
</tr>
</tbody>
</table>

conversion indices of the samples containing 1 wt% DBP UV treated with mercury or iron halide UV source at 150°C for 300 s. The results show that 300 seconds (5 minutes) of UV treatment of the PAN-based precursor containing 1 wt% DBP are approximately equivalent to the first 5000 seconds (about 83 minutes) of the thermal oxidation process, i.e., a reduction of approximately half of the time needed for conventional stabilization process. This correlation between conversion index and processing time is consistent with that obtained from our previous study using FTIR spectra (27). The other conversion indices for UV treated samples in the absence of photoinitiator were not statistically different from the initial indices for pure PAN samples thermally stabilized, and not included in the figure. These kinetic results indicate the potential for developing a novel
and more rapid process for stabilization of PAN-based precursors to produce carbon fibers more efficiently.

![Figure 3.8: Correlation between stabilization temperature and conversion indices (with trend line) of pure PAN fibers during the thermal stabilization step](image)

In Chapters 3 and 4 PAN homopolymer was used during fiber spinning to study the interaction polyacrylonitrile-photoinitiator in a more isolated system. Appendix B contains the FTIR spectra comparison between PAN-based Copolymer (used in Chapter 2) and PAN homopolymer (used in Chapters 3 and 4). Both PAN-based precursors contained 1 wt% of photoinitiator (BDP) and were UV-treated for 300 s at temperatures approximately 20% higher than their respective $T_g$ (~82.5°C for the copolymer and ~125°C for the homopolymer). These FTIR results also confirm that the presence of photoinitiator and further UV treatment have similar effects on both types of PAN-based precursors.
3.4 Conclusions

The successful spinning of PAN fibers containing small concentrations of photoinitiator [4,4’-bis(diethylamino)benzophenone] added externally into the spinning dope (i.e., without incorporating photoinitiators into the polymer chain itself) was demonstrated. It was confirmed that the photoinitiator is retained in the fibers after the coagulation and post-stretching steps. PAN fibers containing 1 wt% photoinitiator showed neither deterioration nor significant morphological differences as compared to pure fibers. Further UV treatment for a short period of time (5 minutes) of the PAN fibers with 1 wt% photoinitiator led to enhancement of the tensile modulus. Tensile testing results indicated that fibers containing photoinitiator show higher tensile modulus for all set of samples, confirming the positive influence of photoinitiator and further UV treatment in the fibers. This increase of the tensile modulus for fibers containing photoinitiator was largely attributed to the retention of molecular orientation after being UV treated as shown by the WAXD results. These results are very encouraging since the final mechanical properties of the carbon fibers depend greatly on the mechanical properties of the precursor fibers, which in turn, depend on the orientation of the crystals within the fibers. Conversion indices calculated from WAXD spectra prove that the addition of 1 wt% photoinitiator to PAN and UV treatment for only 5 minutes increases the rate of the cyclization reaction and reduces the thermal oxidation time by over an hour. These results have been published as reference (51).
References


CHAPTER 4

CHARACTERIZATION OF UV-ASSISTED STABILIZED POLYACRYLONITRILE-BASED CARBON FIBERS

4.1 Introduction

As discussed earlier in Chapter 1, high strength carbon fibers are used in structural composites for aerospace applications (1-3). However, their higher cost as compared with other reinforcing materials (viz. glass fibers) limits their use for the high-end applications where strength-to-density ratio is critical (2-6). Also, as noted earlier in Chapters 2 and 3, thermal stabilization is the rate-limiting step in the production of PAN-based carbon fibers and contributes to the high cost (1-11). During thermo-oxidative stabilization, heat is produced by exothermic reactions and a temperature gradient is generated within the fiber due to the low thermal conductivity of PAN precursors (~0.26 Wm\(^{-1}\)K\(^{-1}\)) (1, 2, 7, 12, 13). The dissipation of this energy is very important and the energy generation can be controlled by using slow heating rates during the thermal stabilization of the fibers making this process the most time consuming step during the thermal treatment of the fibers (14, 15). Simultaneously, post-drawing of fibers must be performed to collapse the voids and to increase molecular orientation (8, 16, 17). However, this orientation is partly lost due to molecular relaxation processes that occur when the PAN precursor fibers are heated up to 300°C during the stabilization step. Additional stresses must be applied during stabilization and carbonization steps in an attempt to regain the molecular orientation. This strategy results in carbon fibers with
high strength, but the limited molecular orientation prevents the fibers from developing an ultra high modulus \((8, 10, 13)\). Therefore, as noted in the beginning of this dissertation, there is a need for the development of novel processes that allow the acceleration of these exothermic reactions in a controlled manner to avoid fiber degradation and retain molecular orientation.

PAN based terpolymer containing a photo sensitive comonomer, such as acryloyl benzophenone, have been investigated and successfully converted into carbon fibers as reported in previous literature studies \((5, 17)\). In addition, polymerization and stabilization reactions are known to proceed faster and at lower temperatures when initiated by UV radiation \((17-19)\). In the current research, Chapters 2 and 3 discussed initiation of cyclization and crosslinking reactions associated with thermal stabilization at lower temperatures by the external addition of a small amount \((1 \text{ wt\%})\) of photoinitiator. Subsequent UV exposure at lower temperatures led to a reduction of the conventional thermal stabilization time, as studied on solution-cast films in Chapter 2, and published as reference \((20)\). Fibers containing photoinitiator added externally into the polymer solution prior to wet-spinning (i.e., without incorporating photoinitiator into the polymer chain itself) were successfully wet-spun. After further UV treatment, fibers containing photoinitiator showed higher tensile modulus and molecular orientation as compared with pure UV treated and pure control fibers, as established earlier in Chapter 3 and published as reference \((21)\). Finally, this chapter reports on the capability of these fibers to withstand further thermal stabilization and carbonization, including accelerated heating rates, and the properties of such fibers after each thermal treatment step.
4.2 Experimental

4.2.1 Materials

Polyacrylonitrile homopolymer with a molecular weight ($M_w$) of 233,000 and a glass transition temperature ($T_g$) of 125°C was used throughout this study. This PAN homopolymer was obtained from Scientific Polymer (Ontario NY). 4,4’-bis(diethylamino)benzophenone (denoted as “BDP”) was the photoinitiator used in this study and is shown in Figure 2.1. This photoinitiator generates free radicals by hydrogen abstraction and has UV absorbance peak at 378 nm in the UVA region (320-390 nm) (22, 23). The solvent used in this work was dimethyl sulfoxide (DMSO). Both, photoinitiator and solvent were obtained from Sigma-Aldrich (Aldrich Chemical Company, Inc. Milwaukee, WI). Also a standard silicon powder reference material was used for line position and line shape during X-ray diffraction studies (NIST reference material® 640d). All materials were used as received.

4.2.2 Fiber spinning

PAN-based precursor and photoinitiator (where applicable) were dissolved in a 99:1 mass ratio in DMSO at 70°C. The amount of solids in solution was kept at ~16 wt%. Fibers were spun from solution using a custom-built wet-spinning unit fitted with a spinnerette that had 100 holes nominally 68 µm in diameter. A volumetric flow of 0.6 mL min$^{-1}$ was maintained during the spinning of the fibers. The coagulation bath consisted of 70 wt% DMSO / 30 wt% distilled-deionized water. After the coagulation bath, the
solidified fibers were passed through a distilled-deionized water washing bath; both baths were maintained at ~20°C. The effective length of the coagulation and washing bath were 40 and 80 cm, respectively. A draw down ratio of ~1.2 was used during the wet-spinning of the PAN-based fibers. The as-spun fibers were placed in an oven and dried at 70°C for about 24 hours. Next, the fibers were post-stretched in a distilled-deionized water bath maintained at ~80°C. The effective length of the post-stretching bath was 80 cm. A draw down ratio of ~3.0 was used during the post-stretching step. Pure PAN fibers as well as fibers containing 1 wt % of photoinitiator, with an average effective diameter of ~11.6 µm, were thus produced and used as the initial fibers throughout this study.

4.2.3 UV-treatment of fibers

The fibers were irradiated with a modified Nordson 4.5 kW UV curing lamp (Model 111465A). A mercury arc bulb (model PM1163) was the UV source used throughout this work. Such UV sources are available commercially and widely used to provide a broad-band output distribution in the four UV regions (19, 20, 24). The chamber was modified to provide temperature control and the experiments reported in this study were all conducted at approximately 150°C. The intensity of this bulb was measured using a high energy UV radiometer (model PP2000, Electronic Instrumentation and Technology, Inc.). Intensity values of approximately 0.228, 0.196, 0.032, and 0.095 W cm⁻² were measured for the UVA, UVB, UVC, and UVV ranges, respectively. Fiber tows approximately 10 inches long were irradiated for 300 seconds. The bundle of fibers was held under approximately 0.1 g denier⁻¹ of tension during the UV treatment. The
distance between the samples and the UV source was kept constant at approximately 20 cm.

4.2.4 Thermal treatment of fibers

Fiber bundles were thermally stabilized in air atmosphere using a heating rate of 2.5°C min⁻¹ from 25°C to 300°C, and held there for 30 minutes. Tension was applied to the samples during thermal oxidation by dead-weight loading. A tension of 0.1 g denier⁻¹ was applied at temperatures below 200°C, and 0.05 g denier⁻¹ above 200°C. As indicated in earlier studies, the external addition of small amounts (~1 wt %) of photoinitiator followed by a short (5 minutes) UV treatment increased the rate of the cyclization reaction (20, 21). Based on these results, UV treated fibers with photoinitiator were placed in a pre-heated oven at 225°C and rapidly heated. Then, using a heating rate of 2.5°C min⁻¹, the fibers were heated to 300°C, and held there for 30 minutes. A tension of 0.05 g denier⁻¹ was applied on these samples. Note that the total duration of this fast-thermal stabilization step was only 60 minutes which was less than half of 140 minutes used for the conventional thermal stabilization step.

Thermally stabilized fibers were then carbonized under a tension of 0.07 g denier⁻¹ in an inert environment (helium). This was accomplished by dead-weight loading using a custom-designed graphite fixture, which could be mounted inside of a graphite furnace ASTRO HP50-7010. Heating rate of 10°C min⁻¹ was used to a maximum temperature of 1200°C, and the fibers held at 1200°C for 1 hour. All UV treated and thermally stabilized and carbonized samples were compared against three types of control
fibers. The first two controls consisted of conventionally thermal stabilized pure PAN fibers and non-UV treated fibers but containing photoinitiator. The third control consisted of fast-thermal stabilized pure PAN fibers without UV treatment. These controls were produced to confirm that the improvement in the mechanical properties and the reduction in the thermal stabilization time are due to the combined positive effect of the presence of photoinitiator and UV treatment of the samples.

4.2.5 Characterization

Morphological analysis of fibers was conducted by scanning electron microscopy with a Mitsubishi 4800 SEM unit. To retain the original cross-section shape and other physical features, the fibers were cryo-fractured in liquid nitrogen. To determine the effective diameter of the fibers, Image-Pro Plus 7.0 (Media Cybernetics, Inc.) analysis software was used to measure the cross section area of each type of sample. The effective diameter calculated from these area measurements is reported only as a reference. At least 40 cross-section areas were measured for each type of fiber.

A PHOENIX single filament tensile testing unit (Measurements Technology Inc.) was used to measure the mechanical properties of the different fibers types produced along this work. The single fibers were mounted on 25 mm paper tabs. At least 20 samples per type of fibers were prepared and tested.

Wide angle X-ray diffraction (WAXD) analysis was conducted on bundles of fibers using a Rigaku-MSC (Houston, TX) X-ray diffraction unit. The X-ray diffraction pattern was captured on an image plate and the images were analyzed using Polar
software v2.6.7 (Stonybrook Technology and Applied Research, STAR). The curve fitting of the spectra was done using OriginPro 7 (v7.0383, OriginLab Corporation). The unit generates a collimated X-ray beam with a wavelength of 1.5406 Å (Cu target) and a diameter of ~0.5 mm. The distances between the X-ray source and sample and the sample and the image plate detector were approximately 70 and 12 cm, respectively. Operation conditions of the X-ray source were 45 kV and 0.65 mA. Each bundle of fibers was mounted on a 10 mm paper tab and sprinkled with NIST-grade silicon standard powder for accurate allocation of 2-theta position. The exposure time per sample was 2 hours.

The crystal plane spacing was calculated using Bragg law (Equation 3.2) and lattice geometry equation for hexagonal crystal structure (Equation 3.3) observed in the initial PAN-based precursor and final carbon fibers. The crystal size was calculated using Scherrer formula (Equation 3.4), whereas the Warren’s method (Equation 3.5) was used to correct the system broadening on each WAXD scan (25-33). Also, conversion or aromatization indices were determined on stabilized fibers using Equation 3.6 (21, 28, 34).

In addition, the Rigaku-MSC diffractometer is capable of measuring the orientation of the crystal in the fibers. These azimuthal intensity scans were measured for the most prominent peak of the initial PAN precursor and final carbonized fibers, which are the (1 0 0) and (0 0 2) peak, located at approximately 17° and 25°, respectively. Appendix A gives a complete list of the equipment used during this study.
4.3 Results and Discussion

4.3.1 Influence of UV radiation and photoinitiator: Thermal stabilized fibers

4.3.1.1 Morphology

Figure 4.1 displays representative SEM micrographs of thermal stabilized PAN fibers with and without photoinitiator. Figure 4.1a and 4.1b correspond to pure PAN fibers and those containing 1 wt% BDP, respectively. Figure 4.1c and 4.1d are representative micrographs of pure and 1 wt% BDP-PAN fibers, both UV treated with the mercury source, respectively. These first four specimens were conventionally thermal stabilized (140 minutes step). Figure 4.1e and 4.1f correspond to pure non-UV treated fibers and 1 wt% BDP-PAN UV treated fibers, respectively. These two last specimens were fast-thermally stabilized (60 minutes step), as described in the experimental section. All fibers retained the characteristic kidney shape of wet-spun PAN-based fibers (3, 8, 27). The effective diameter of pure and 1 wt% BDP PAN fibers were 9.0 ± 0.2 and 8.9 ± 0.1 µm, respectively. At 95% confidence level, there was no significant difference between the effective diameters among the different samples. In addition, no noticeable deterioration or change in the microstructure of the UV treated fibers containing photoinitiator was observed when compared with pure control fibers. Thus, the presence of photoinitiator and further UV treatment do not significantly affect the morphology of
Figure 4.1: Representative SEM micrographs of thermal stabilized PAN fibers with and without photoinitiator: (a) pure PAN fibers, (b) fibers containing 1 wt% BDP, (c) pure UV treated PAN fibers, (d) 1 wt% BDP PAN UV treated fibers, (e) fast-thermal stabilized pure PAN fibers, and (f) fast-thermal stabilized UV treated 1 wt% BDP PAN fibers
the fibers. Another important observation is that the UV-treatment of the fibers did not lead to any obvious skin-core structure formation in any of the UV treated fibers. Skin-core structure is undesired during the stabilization of PAN-based fibers because it leads to poor quality (mechanical properties of the) stabilized and carbonized fibers (3, 4, 11, 14, 28).

4.3.1.2 Mechanical properties

Figure 4.2 shows representative tensile response of various samples. Figure 4.2a corresponds to conventionally thermally stabilized non-UV treated and UV treated pure PAN fibers as well as non-UV treated fast-thermal stabilized pure PAN fibers. Figure 4.2b shows the same treatment conditions but for fibers containing 1 wt% BDP. The limit of linear proportionality was approximately 1% for all samples. Table 4.1 summarizes the tensile testing results conducted on single filaments. These tensile properties of the PAN fibers are consistent with those reported in the literature for experimental grade PAN fibers: 3-10% for the breaking strain, 0.1-0.5 GPa for strength, and 3-15 GPa for tensile modulus (4, 5, 9, 13, 34).

Tensile properties presented in Table 4.1 indicate that, at 95% confidence, there are significant differences in the breaking strain and ultimate tensile strength between pure and 1 wt% BDP fibers. The presence of photoinitiator reduces the elongation capabilities of the non-UV treated fibers containing photoinitiator by approximately half and the ultimate tensile strength by ~15%. These reductions could be possibly attributed
Figure 4.2: Representative tensile testing curves of each set of thermal stabilized fibers:
(a) pure PAN, (b) PAN fibers containing 1% BDP

to the voids (defects) left by the unreacted photoinitiator during conventional thermal stabilization. Another observation was that during the mounting of the fibers for tensile testing excessive fiber fusion was observed on pure UV treated fibers. Fiber fusion facilitates the formation of defects on the fibers. It seems that the main phenomenon taking place during the UV treatment at temperatures slightly above of the glass
transition temperature of the PAN precursor without photoinitiator is fiber fusion and, as shown in previous studies, polymer chain relaxation (21). This leads to a significant reduction in the elongation capabilities of the fibers by approximately half and the ultimate tensile strength by ~25% between pure UV treated and pure control fibers, at 95% confidence. Pure fast-thermal stabilized fibers also show a significant reduction in the elongation capabilities of the fibers by approximately 35% and the ultimate tensile strength by ~25%, at 95% confidence, when compared with pure control fibers. These fast-thermal stabilized pure fibers also showed considerably fiber fusion, similar to the one observed on UV treated pure fibers. Fast heating rates during thermal stabilization led to the formation of skin-core structure in the fibers, which is not desired because it negatively affects the mechanical properties.

Table 4.1: Single filament tensile results of thermal stabilized fibers with 95% confidence intervals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (GPa)</th>
<th>Max stress (GPa)</th>
<th>Break strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>9.6 ± 0.3</td>
<td>0.24 ± 0.01</td>
<td>6.6 ± 0.8</td>
</tr>
<tr>
<td>1% BDP</td>
<td>9.7 ± 0.4</td>
<td>0.20 ± 0.02</td>
<td>3.7 ± 0.6</td>
</tr>
<tr>
<td>Pure, 300s Hg, 150°C</td>
<td>9.6 ± 0.6</td>
<td>0.19 ± 0.02</td>
<td>3.4 ± 0.5</td>
</tr>
<tr>
<td>1% BDP, 300s Hg, 150°C</td>
<td>11.2 ± 0.7</td>
<td>0.26 ± 0.02</td>
<td>5.3 ± 1.1</td>
</tr>
<tr>
<td>Pure, FAST</td>
<td>9.7 ± 0.3</td>
<td>0.19 ± 0.01</td>
<td>4.3 ± 0.3</td>
</tr>
<tr>
<td>1% BDP, 300s Hg, 150°C, FAST</td>
<td>10.8 ± 0.5</td>
<td>0.25 ± 0.01</td>
<td>4.8 ± 0.8</td>
</tr>
</tbody>
</table>

On the other hand, the two set of fibers containing 1 wt% BDP UV treated for 300 s (5 minutes) display higher tensile modulus and ultimate tensile strength than all the other set of samples, at 95% confidence. Specifically, conventionally thermal stabilized
fibers containing 1 wt% BDP UV treated with a mercury source exhibit the highest tensile modulus and ultimate tensile strength of all six set of samples (significant at 95% confidence). This proves the combined positive effect of the addition of photoinitiator and 300 s of UV treatment on the fibers. The addition of photoinitiator and further UV treatment of the fibers could be used to increase the mechanical properties of the fiber during conventional thermal stabilization or reduce the thermal oxidation time (faster fiber production) while retaining the mechanical properties of the carbon fibers thus produced.

4.3.1.3 Wide Angle X-Ray Diffraction

Figure 4.3 shows representative wide angle X-ray diffractograms of the most relevant set of samples: conventionally thermal stabilized UV treated 1 wt% BDP PAN fibers, fast-thermal stabilized pure PAN fibers, conventionally thermal stabilized pure PAN fibers, and initial pure PAN fibers before thermal oxidation for comparison. Integrated 2-theta scans, displayed in Figure 4.3a, show the first peak at ~17° corresponding to the (1 0 0) plane of the PAN precursor. The second peak corresponds to the combination of the amorphous halo at ~26° and the (1 1 0) plane peak of PAN at ~29.5° (26, 27, 29, 35, 36). After the thermal stabilization step, an extra peak associated with the aromatic structure emerges at ~25° (21, 28, 34). Silicon standard was added to each of the different fiber samples as a calibration standard. This silicon standard shows three sharp peaks at 28.44°, 47.3°, and 56.12° corresponding to its (1 1 1), (2 2 0), and (3 1 1) planes, respectively.
Figure 4.3: Representative WAXD spectra of Thermal-Oxidized (TO) fibers: (a) 2-Theta scans, (b) Azimuthal scans of the PAN (100) peak, and (c) Azimuthal scans of the developing aromatic peak.
As indicated before, the orientation of the crystals in the fibers was measured from the azimuthal scans conducted on the (1 0 0) peak of the PAN and aromatic peak of the thermal oxidized fibers spectra. Figure 4.3b and 4.3c show the azimuthal scans of (1 0 0) and aromatic peak, respectively. Sharp azimuthal peaks for a given set of planes mean higher orientation, whereas, broad peaks indicate low orientation. As expected, due to the cyclization reaction undergone for all thermal oxidized fibers, a significant lost of orientation of the (1 0 0) peak of the initial PAN structure was observed in thermal oxidized fibers. On the other hand, the devolvement of orientation due to the formation of the aromatic peak is observed on thermal oxidized samples, as shown in Figure 4.3c. To compare the crystal orientation in the different set of fibers, the full-width-at-half-max (FWHM) was measured for each azimuthal scan. The smaller the FWHM value, the more oriented are the crystals within the fibers.

Table 4.2 summarizes the WAXD results obtained from all the different set of samples. At 95% confidence, the interplanar spacing between the (1 0 0) plane increased and the orientation and crystal size of the original PAN structure decreased in thermal stabilized fibers when compared with initial pure PAN fibers. Based on the WAXD spectra, the conversion indices were calculated for each sample. The conversion indices achieved by the samples containing 1 wt% DBP UV treated at 150°C for 300 s after thermal stabilization are higher than the other sets of samples meaning higher cyclization of PAN. Also these two sets of samples are able to develop a higher level of orientation of the newly form aromatic structure, at 95% confidence. These results agree well with the tensile testing results that show superior mechanical properties for thermal stabilized
samples containing 1% BDP and UV treated for 300 s due to the fact that they are able to develop higher molecular orientation. For this system, higher molecular orientation leads to higher mechanical properties of the fibers (7, 10, 13, 16). Observe that the duration of the thermal stabilization step for some of the UV treated samples containing photoinitiator was less than half the thermal stabilization time used for the control fibers. These results indicate the potential for developing a novel and more rapid process for stabilization of PAN-based precursors to produce carbon fibers more efficiently.

Table 4.2: WAXD results of thermal-oxidized fibers and initial fibers (for comparison) with 95% confidence intervals

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>l_a (Å)</th>
<th>(100) FWHM (°)</th>
<th>Aromatic Peak FWHM (°)</th>
<th>C. I. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Pure (before thermal stabilization)</td>
<td>6.001 ± 0.020</td>
<td>42.3 ± 1.9</td>
<td>26.1 ± 0.9</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Pure</td>
<td>6.438 ± 0.049</td>
<td>10.5 ± 0.9</td>
<td>100.4 ± 2.1</td>
<td>71.2 ± 1.9</td>
<td>70.4 ± 2.4</td>
</tr>
<tr>
<td>1% BDP</td>
<td>6.470 ± 0.026</td>
<td>9.7 ± 0.7</td>
<td>106.1 ± 3.7</td>
<td>71.6 ± 1.9</td>
<td>68.2 ± 1.5</td>
</tr>
<tr>
<td>Pure, 300s Hg, 150°C</td>
<td>6.471 ± 0.048</td>
<td>10.4 ± 0.5</td>
<td>105.6 ± 3.3</td>
<td>70.9 ± 2.9</td>
<td>70.5 ± 1.4</td>
</tr>
<tr>
<td>1% BDP, 300s Hg, 150°C</td>
<td>6.557 ± 0.042</td>
<td>10.6 ± 0.6</td>
<td>129.7 ± 3.7</td>
<td>63.9 ± 2.2</td>
<td>78.9 ± 3.7</td>
</tr>
<tr>
<td>Pure, FAST</td>
<td>6.521 ± 0.046</td>
<td>9.8 ± 0.7</td>
<td>163.4 ± 5.8</td>
<td>77.8 ± 1.6</td>
<td>65.2 ± 1.5</td>
</tr>
<tr>
<td>1% BDP, 300s Hg, 150°C, FAST</td>
<td>6.502 ± 0.058</td>
<td>10.6 ± 1.1</td>
<td>124.5 ± 2.8</td>
<td>64.4 ± 1.7</td>
<td>77.0 ± 1.6</td>
</tr>
</tbody>
</table>

In contrast, at 95% confidence, fast-thermally stabilized pure control fibers show higher level of degradation of the initial PAN structure, which is shown by the FWHM of the (1 0 0) peak, but lower conversion index and orientation of the aromatic structure are achieved. Note that in a previous study, it was demonstrated that during the thermal
stabilization of PAN using the same amount of tension the orientation of the PAN polymer chains decreases, i.e. higher FWHM of the (1 0 0) peak, as the conversion index increases (21). All these results indicate that fast thermal stabilization of PAN precursors leads to excessive degradation of the PAN precursor, formation of skin-core structure within the fibers, and reduction of the mechanical properties of the fibers.

4.3.2 Influence of UV radiation and photoinitiator: Carbon fibers

4.3.2.1 Morphology

Figure 4.4 displays representative SEM micrographs of carbonized PAN fibers with and without photoinitiator. Figure 4.4a and 4.4b correspond to pure PAN fibers and those containing 1 wt% BDP, respectively. Figure 4.4c and 4.4d are representative micrographs of pure and 1 wt% BDP-PAN fibers, both UV treated with the mercury source, respectively. These first four specimens were conventionally thermal stabilized. In contrast, Figure 4.4e and 4.4f correspond to fast-thermally stabilized non-UV treated pure and UV treated 1 wt% BDP-PAN fibers, respectively. In all cases the fibers retained the characteristic kidney shape of wet-spun PAN-based fibers (3, 8, 27). The effective diameter of pure and 1 wt% BDP PAN fibers were 6.6 ± 0.1 and 6.4 ± 0.1 µm, respectively. At 95% confidence level, there was no significant difference between the effective diameters among the different samples.
Figure 4.4: Representative SEM micrographs of carbonized PAN fibers with and without photoinitiator: (a) pure PAN fibers, (b) fibers containing 1 wt% BDP, (c) pure UV treated PAN fibers, (d) 1 wt% BDP PAN UV treated fibers, (e) fast-thermal stabilized pure PAN fibers, and (f) fast-thermal stabilized UV treated 1 wt% BDP PAN fibers
No noticeable deterioration or change in the microstructure was observed on UV treated fibers containing photoinitiator when compared with pure control fibers. Thus, the presence of photoinitiator and UV treatment did not significantly affect the morphology of the fibers. Another important observation is that the UV-treatment of the fibers did not lead to any obvious skin-core structure formation. However, this is not the case for fast-thermally stabilized pure fibers. Figure 4.5 shows SEM micrographs of defects observed on fast-thermal stabilized pure PAN carbon fibers attributed to inadequate thermal stabilization: (a) core-hollow fiber, (b) fused hollow fibers.
stabilization. Figure 4.5a and 4.5b display a core-hollow fiber and fused hollow fibers, respectively. Note that these core-hollow fiber defects were not observed in any of the other set of samples. This demonstrates skin-core structure formation in fast-thermally stabilized pure PAN fibers. As mentioned before, skin-core structure is undesired during the stabilization of PAN-based fibers because leads to poor quality (mechanical properties of the) stabilized and carbonized fibers (4, 11, 14, 28).

4.3.2.2 Mechanical properties

Figure 4.6 displays representative tensile response of various carbonized fibers. Figure 4.6a corresponds to conventionally thermal stabilized non-UV treated pure and UV treated pure as well as fast-thermal stabilized pure PAN fibers. Figure 4.6b shows the same treatment conditions but for fibers containing 1 wt% BDP. Table 4.3 summarizes the tensile testing results conducted on single filaments. These tensile properties of the PAN fibers are consistent with those reported in the literature for commercial and experimental grade PAN-based fibers: 0.3-2.5% for the breaking strain, 0.1-6.5 GPa for strength, and 30-500 GPa for tensile modulus (4, 5, 8, 13, 37, 38).

Tensile testing results shown in Table 4.3 indicate that, at 95% confidence, there are significant differences in the breaking strain and ultimate tensile strength between pure control and pure UV treated fibers. The UV treatment reduces the elongation capabilities of the pure fibers and the ultimate tensile strength by approximately one third. These reductions could be possibly attributed to the excessive fiber fusion observed on pure UV treated fibers leading to defects on these fibers. As mentioned before, it is
suspected that the main phenomena taking place during the UV treatment at temperatures slightly above the glass transition of the PAN precursor without photoinitiator are fiber fusion and polymer chain relaxation leading to a significant reduction in the elongation capabilities and ultimate tensile strength of the fibers.

Figure 4.6: Representative tensile testing curves of each set of carbonized fibers: (a) pure PAN, (b) PAN fibers containing 1% BDP
Table 4.3: Single filament tensile results of the produced carbon fibers (CF) with 95% confidence intervals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (GPa)</th>
<th>Max stress (GPa)</th>
<th>Break strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>153.5 ± 6.6</td>
<td>1.47 ± 0.17</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>1% BDP</td>
<td>150.2 ± 10.1</td>
<td>1.40 ± 0.20</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>Pure, 300s Hg, 150°C</td>
<td>157.6 ± 6.2</td>
<td>1.05 ± 0.13</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>1% BDP, 300s Hg, 150°C</td>
<td>184.8 ± 10.4</td>
<td>1.65 ± 0.12</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>Pure, FAST</td>
<td>137.9 ± 4.8</td>
<td>1.22 ± 0.18</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>1% BDP, 300s Hg, 150°C, FAST</td>
<td>170.6 ± 6.0</td>
<td>1.60 ± 0.11</td>
<td>1.0 ± 0.1</td>
</tr>
</tbody>
</table>

Pure fast-thermal stabilized fibers also show a significant reduction in the tensile modulus of the fibers by ~10% and the ultimate tensile strength by ~20% (at 95% confidence) when compared with pure control fibers. For these specimens considerably fibers fusion is observed as well, similar to the one observed on pure UV treated fibers. Fast heating rates during thermal stabilization lead to the formation of skin-core structure in the fibers confirmed by core-hollow fibers (Figure 4.5) which is not desired because is harmful and negatively affects the mechanical properties of the produced fibers as indicated by the tensile testing results.

For UV treated fibers containing photoinitiator, the results are significantly different, the two set of fibers containing 1 wt% BDP UV treated for 300 s (5 minutes) display higher tensile modulus and ultimate tensile strength than all the other set of samples. Specifically, conventionally thermal stabilized UV treated fibers containing 1 wt% BDP exhibit the highest tensile modulus of all six set of samples (at 95% confidence). An improvement in the tensile modulus of approximately 20% was observed in conventional thermal stabilized UV treated fibers containing 1 wt% BDP when
compared with conventional thermal stabilized control pure PAN fibers. The addition of photoinitiator and further UV treatment of the fibers increase the mechanical properties of the fibers during conventional thermal stabilization.

Fast-thermal stabilized UV treated fibers containing 1 wt% BDP exhibit higher tensile modulus and ultimate tensile strength when compared with conventional and fast-thermal stabilized pure fibers. UV treated fast-thermal stabilized fibers containing 1 wt% BDP show around 10%, 15%, and 25% improvement in the tensile modulus when compared with conventional thermal stabilized pure, conventional thermal stabilized 1 wt% BDP fibers, and fast-thermal stabilized pure control fibers, respectively. In addition, fast-thermal stabilized fibers containing 1 wt% BDP display approximately 33% improvement in the ultimate tensile strength when compared with fast-thermal stabilized pure control fibers. It is important to note that, besides the demonstrated improvement in the mechanical properties, the fast-thermal stabilization step takes less than half the duration of the conventional thermal stabilization (60 vs. 140 min, respectively). This proves the combined positive effect of the addition of photoinitiator and 300 s of UV treatment on the fibers. The addition of photoinitiator and further UV treatment of the fibers could be used to increase the mechanical properties of the fiber during conventional thermal stabilization or reduce the thermal oxidation time (faster fiber production) while retaining the mechanical properties of the carbon fibers thus produced.
4.3.2.3 *Wide Angle X-Ray Diffraction*

Figure 4.7 shows representative wide angle X-ray diffractograms of the most relevant set of carbonized samples: conventionally thermal stabilized UV treated 1 wt% BDP PAN fibers, fast-thermal stabilized pure PAN fibers, and conventionally thermal stabilized pure PAN fibers. Integrated 2-theta scans, displayed in Figure 4.7a, show the first peak at ~25° corresponding to the (0 0 2) plane of the turbostratic structure of PAN-based carbon fibers. The second peak at ~42° corresponds to the (1 0 0) plane (31-33, 39). As mentioned earlier, silicon standard was added to each of the different fiber samples as a calibration standard.

The orientation of the crystals in the fibers was measured from the azimuthal scans conducted on the (0 0 2) peak which is the most prominent peak of the carbon fiber WAXD spectra. Figure 4.7b shows the azimuthal scans of (0 0 2) peak. To compare the crystal orientation in the different set of fibers, the full-width-at-half-max (FWHM) was measured for each azimuthal scan. The smaller the FWHM value, the more oriented are the crystals within the fibers.

Table 4.4 summarizes the WAXD results obtained from all the different set of samples. At 95% confidence, fast-thermally stabilized pure carbon fibers show smaller crystal size values and level of orientation as compared with conventionally thermal stabilized pure carbon fibers. These results agree well with the lower mechanical properties and core-hollow defects observed on this set of fibers. All these results indicate that fast thermal stabilization of pure PAN precursors leads to excessive degradation of
the PAN precursor, formation of skin-core structure within the fibers, lost of orientation, smaller crystal size, and reduction of the mechanical properties of the fibers.

This is not the case for carbonized UV treated fibers containing photoinitiator. The results shown in Table 4.4 indicate no negative effects (at 95% confidence) for the (0 0 2) d-spacing and size of the crystals within the UV treated fibers containing
photoinitiator as compared with all the other types of carbon fibers. Also these two sets of samples are able to develop a higher level of orientation when compared with the other groups of carbon fibers. These results agree well with the tensile testing results that show superior mechanical properties for carbonized fibers containing 1% BDP and UV treated for 300 s due to the fact that they are able to develop higher molecular orientation. For this system, higher molecular orientation leads to higher mechanical properties of the fibers (7, 8, 10, 13, 16). All these results prove the combined positive effect of the addition of photoinitiator and 300 s of UV treatment on the fibers prior thermal stabilization. At the same thermal treatment conditions, it was possible to enhance the mechanical properties of the final carbon fibers by the addition of photoinitiator and 300 s of UV treatment. In addition, with this novel process, it was possible to reduce the thermal stabilization time by more than half keeping the final mechanical and physical properties of the produced carbon fibers. All this can be used in the development of a novel and more rapid process for stabilization of PAN-based precursors to produce carbon fibers more efficiently.

Table 4.4: WAXD results of carbon fibers with 95% confidence intervals

<table>
<thead>
<tr>
<th>Sample</th>
<th>( l_c ) (Å)</th>
<th>(0 0 2) d-spacing (Å)</th>
<th>(002) FWHM (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>14.4 ± 0.2</td>
<td>3.586 ± 0.004</td>
<td>45.4 ± 0.7</td>
</tr>
<tr>
<td>1% BDP</td>
<td>14.1 ± 0.3</td>
<td>3.585 ± 0.007</td>
<td>45.4 ± 0.8</td>
</tr>
<tr>
<td>Pure, 300s Hg, 150°C</td>
<td>14.0 ± 0.6</td>
<td>3.586 ± 0.011</td>
<td>46.1 ± 0.8</td>
</tr>
<tr>
<td>1% BDP, 300s Hg, 150°C</td>
<td>14.0 ± 0.2</td>
<td>3.575 ± 0.011</td>
<td>43.4 ± 0.7</td>
</tr>
<tr>
<td>Pure, FAST</td>
<td>13.4 ± 0.3</td>
<td>3.597 ± 0.009</td>
<td>46.1 ± 0.6</td>
</tr>
<tr>
<td>1% BDP, 300s Hg, 150°C, FAST</td>
<td>14.4 ± 0.5</td>
<td>3.580 ± 0.008</td>
<td>44.2 ± 0.3</td>
</tr>
</tbody>
</table>
4.4 Conclusions

A rapid, dual-stabilization route for the production of carbon fibers from polyacrylonitrile-based precursor fibers was successfully demonstrated. Photoinitiator, 4,4’-bis(diethylamino)benzophenone, was effectively added to PAN solution before the fiber wet-spinning step to UV-induce crosslinking and cyclization reactions in the produced polyacrylonitrile-based fibers. After UV treatment, precursor fibers could be rapidly thermo-oxidatively stabilized and successfully carbonized. SEM micrographs show no noticeable deterioration, skin-core structure, or change in the microstructure of the UV treated fibers containing photoinitiator after thermal stabilization and carbonization. On the other hand, fast-thermal stabilized pure PAN carbon fibers show core-hollow fiber defects attributed to inadequate thermal stabilization. Note that these core-hollow fiber defects were not observed in any of the other set of samples.

Tensile testing results show fibers containing 1 wt% photoinitiator UV treated for 300 s (5 minutes) display higher tensile modulus and ultimate tensile strength than all the other set of thermal stabilized and carbonized fibers. Specifically, conventionally thermal stabilized UV treated fibers containing 1 wt% BDP exhibit the highest tensile modulus and ultimate tensile strength of all six set of thermal stabilized and carbonized fibers. This was not the case for pure UV treated and fast-thermal stabilized pure PAN fibers which display a reduction in their mechanical properties when compared with control pure conventionally thermal stabilized fibers. These reductions were attributed to the lost of molecular orientation and excessive fiber fusion leading to defect formation. Wide
Angle X-ray diffraction results confirm that the fast thermal stabilization of pure PAN precursors leads to excessive degradation of the PAN precursor, formation of skin-core structure within the fibers, lost of orientation, smaller crystal size, and reduction of the mechanical properties of the fibers. On the other hand, no negative effects were observed on the (0 0 2) d-spacing and size of the crystals within the UV treated fibers containing photoinitiator as compared with all the other types of carbon fibers. In addition, UV treated fibers containing photoinitiator were able to develop a higher level of orientation when compared with all the other sets of thermal stabilized and carbonized fibers.

The results obtained in this study prove the combined positive effect of the addition of photoinitiator and UV treatment, on the fibers prior thermal stabilization, in the properties of the thermal stabilized and final carbon fibers. At the same thermal treatment conditions, it was possible to improve the mechanical properties of the thermal stabilized and carbonized fibers. In addition, with this novel process, it was possible to reduce the thermal stabilization time by more than half keeping the final mechanical and physical properties of the produced carbon fibers. This can be used in the development of a novel and more rapid process for stabilization of PAN-based precursors to produce carbon fibers more efficiently.
References


(Symposium N) and the 3rd Ion Engineering Conference; Elsevier: Netherlands, 1997; Vol. 121, pp 349-56.


CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This final chapter presents concluding remarks based on the most important findings presented and discussed in Chapters 2 through 4.

In Chapter 2, it was established that it is possible to produce UV-induced cyclization in PAN-based precursors by the external addition of photoinitiator into the polymer solution, i.e., without incorporating photoinitiators into the polymer chain itself. FTIR, gel content, and DSC results confirm that samples containing 4,4’-Bis(diethylamino)benzophenone (BDP) that undergo hydrogen abstraction type mechanism achieved higher extents of cyclization than did samples containing 1-hydroxycyclohexyl phenyl ketone (HPK) that undergo homolytic cleavage. Also, the presence of BDP enables higher extents of post-UV thermal cyclization. Therefore, hydrogen-abstraction was found to be a more efficient mechanism in comparison with homolytic cleavage during the photo-induced cyclization of PAN precursor polymer.

Increasing UV exposure time leads to greater formation and higher FTIR conversion index in the double bond region. As expected, at temperatures below the $T_g$ of the precursor, the presence of photoinitiator does not play a significant role on the extent of the cyclization due to the limited mobility of the polymer chains. FTIR and WAXD based conversion indices demonstrate that the addition of 1 wt% photoinitiator to PAN and UV treatment for only 5 minutes increases the rate of the cyclization reaction and
reduces the thermal oxidation time by over an hour, which could significantly reduce the conventional stabilization time by half.

The successful spinning of PAN fibers containing small concentrations of photoinitiator BDP added externally into the spinning dope was demonstrated in Chapter 3. It was confirmed that the photoinitiator is retained in the fibers after the coagulation and post-stretching steps. PAN fibers containing 1 wt% photoinitiator showed neither deterioration nor significant morphological differences as compared to pure fibers.

The UV treatment for a short period of time (5 minutes) of the PAN fibers with 1 wt% photoinitiator led to enhancement of the tensile modulus. Tensile testing results indicated that fibers containing photoinitiator and UV-treated show higher tensile modulus. This increase is largely attributed to the retention of molecular orientation after being UV treated as shown by the WAXD results.

After UV treatment, precursor fibers could be rapidly thermo-oxidatively stabilized and successfully carbonized. SEM micrographs show no discernible deterioration, skin-core structure, or change in the microstructure of the UV treated fibers containing photoinitiator after thermal stabilization and carbonization. In contrast, fast-thermal stabilized pure PAN carbon fibers show core-hollow fiber defects attributed to inadequate thermal stabilization.

Tensile results establish that fibers containing 1 wt% photoinitiator UV treated for 300 s (5 minutes) display higher tensile modulus and ultimate tensile strength than did all other sets of thermal stabilized and carbonized fibers, as presented in Chapter 4. Without the photoinitiator and UV treatment, pure PAN-fibers that were fast-thermal stabilized
display a reduction in their mechanical properties when compared with control pure-PAN fibers that were conventionally thermal stabilized (slow rate). SEM, tensile testing, and WAXD results confirm that the fast thermal stabilization of pure PAN precursors leads to excessive degradation of the PAN precursor, formation of skin-core structure within the fibers, lost of orientation, fiber fusion, smaller crystal size, and reduction of the mechanical properties of the fibers.

In summary, a rapid, dual-stabilization route for the production of carbon fibers from polyacrylonitrile-based precursor fibers was successfully demonstrated. The results obtained in this study prove the combined positive effect of the addition of photoinitiator and UV treatment on the fibers, prior thermal stabilization, in the properties of the thermal stabilized and final carbon fibers. At the same thermal treatment conditions, it was possible to improve the mechanical properties of the thermal stabilized and carbonized fibers. In addition, with this novel process, it was possible to reduce the thermal stabilization time by more than half while retaining the final mechanical and physical properties of the carbon fibers. This concept can be used in follow-up studies for the development of novel, rapid processes for stabilization of PAN copolymer-based precursors to produce carbon fibers more efficiently.

5.2 Recommendations for future work

In Chapter 2, most of the early work involved the use of gel fraction measurements, a time consuming technique. For future work in similar systems, the use
of FTIR over gel content measurements is strongly suggested to measure the conversions and amount of cyclized material.

In Chapter 3, to maximize orientation and improve the mechanical properties of the experimental grade PAN precursor fibers, modifications of the wet-spinning set-up are suggested. Specifically, an upgraded winding unit with a more precise speed control and traversing movement is needed to reduce fiber defect. Also during the fiber spinning step, heated tubes are recommended to deliver the polymer dope to the die to control the viscosity of the solution and to increase the concentration of polymer precursor in the polymer solution. By increasing the precursor concentration, the amount of solvent that has to diffuse out of the nascent fiber during coagulation is reduced. This can potentially reduce the formation of voids. During fiber spinning, the feeding pump was working at the low end of its pumping capabilities. To maximize the equipment capabilities, the use of a spinnerette with higher number of holes is recommend to produce more fibers per bundle, and to scale-up the fiber production process.

In Chapter 4, during the carbonization step, a heating rate of 10°C min$^{-1}$ was used below 600°C. This value is on the high end of the recommended heating rates. To maximize the mechanical properties of the final carbon fibers, the use a lower heating rate, e.g. 5°C min$^{-1}$, is recommended because below 600°C a considerably amounts of gases still are released during carbonization treatment of the fibers.
Appendix A

List of Equipment Used During this Study

• The casting of the films was conducted with a GARDCO 6”, 2 path applicator (3 & 10 MIL), Cuts 440-C SS
• The wet-spinning of the fibers was conducted with a custom made wet-spinning unit (Alex James & Associates Inc.)
• The thermal stabilization of the samples was conducted with Applied Test Systems Oven (Model: 2404/SRC/20AMP)
• The carbonization of the fibers was conducted with a Laboratory Hot Press (Thermal Technology LLC, Model: HP50-7010)
• Samples were irradiated with a Nordson 4.5 kW UV curing lamp (Model 111465A)
• Two different UV sources were used: mercury (model PM1163) and iron halide (model PM1163F) bulb
• High energy UV radiometer (model PP2000, Electronic Instrumentation and Technology, Inc.) was used to measure the intensity distribution of each bulb
• Small shear rates (0.1-30 s⁻¹) viscosity measurements: ARES LS0012701 advanced rheometer with a cone-and-plate fixture (Thermal Analysis Instruments)
• High shear rates (30-30,000 s⁻¹) viscosity measurements: ACER 2000 Advanced Capillary Extrusion Rheometer (Rheometric Scientific)
• Fourier Transform Infrared (FTIR) Spectroscopy: Nexus 870 FT-IR ESP (Nicolet)
• Differential Scanning Calorimetry (DSC): Pyris 1 DSC (Perkin Elmer Instruments)
• Morphological analysis of fibers: Mitsubishi 4800 SEM unit

• Mechanical properties measurement of fibers: PHOENIX 200 single filament tensile testing unit (Measurements Technology Inc.)

• Wide angle X-ray diffraction (WAXD) analysis of fibers: Rigaku-MSC (Houston, TX) X-ray diffraction unit. The conditions used during the analysis were:
  - Equipment used: Rigaku-MSC (Houston, TX)
  - Analysis of image plates: Polar v2.6.7 (Stonybrook Technology and Applied Research, STAR)
  - Curve fitting: OriginPro 7 v7.0383 (OriginLab Corporation)
  - X-rays wavelength: 1.5406Å (Cu target)
  - Beam diameter: ~0.5mm
  - Distance between x-ray source and sample: ~70 cm
  - Distance between sample and image plate: ~13 cm
  - Working conditions of the x-ray source: 45 kV and 0.65 mA
  - Gas used for most of the beam path: Helium
  - Exposure time per sample: ~2 hours
Appendix B

FTIR Spectra Comparison Between UV-Treated PAN-based Copolymer and UV-Treated PAN Homopolymer

Figure B-1: FTIR Spectra Comparison Between UV-Treated PAN-based Copolymer and PAN Homopolymer. Both UV-treated at temperatures approximately 20% higher than their respective T_g (~82.5°C for the copolymer and ~125°C for the homopolymer): (a) over extended wavenumbers, and (b) zoomed-in spectra over the double bond region.
In Chapters 3 and 4 PAN homopolymer was used during fiber spinning to study the interaction polyacrylonitrile-photoinitiator in a more isolated system. Figure B-1 shows the FTIR spectra comparison conducted between PAN-based Copolymer (used in Chapter 2) and PAN homopolymer (used in Chapters 3 and 4). Both PAN-based precursors contained 1 wt% of photoinitiator (BDP) and were UV-treated for 300 s at temperatures approximately 20% higher than their respective $T_g$ (~82.5°C for the copolymer and ~125°C for the homopolymer). These results confirm that the presence of photoinitiator and further UV treatment have similar effects on both types of PAN-based precursors. The FTIR spectra of pure non-UV treated copolymer and homopolymer controls have been included for comparison purposes.