UV-Assisted Stabilization Routes for Carbon Precursor Fibers Produced from Melt-Processable PAN Terpolymers

Amit K. Naskar, Robert A. Walker, Sarah Proulx, Dan D. Edie and Amod A. Ogale*
Department of Chemical Engineering, and Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634-0910

** Corresponding author: ogale@clemson.edu*

Introduction

The majority of commercial carbon fibers are produced from solution-spun polyacrylonitrile (PAN) precursors [1]. Since the solution spinning process involves handling and recovery of hazardous solvents, an environmentally benign processing route for PAN is of interest. Melt spinning of PAN by external plasticization was reported earlier with limited success [2]. PAN copolymers of higher comonomer content (10-15 mole %) are alternative melt processible precursors. Comonomers such as methyl acrylate (MA) and vinyl acetate (VA) disrupt long-range order in acrylonitrile (AN) segments allowing the polymer to melt before it degrades [3-6]. However, direct thermo-oxidation can not be used to stabilize melt-spun PAN fibers (since the fibers melt before the oxidative reaction). In a recent study we reported that it might be possible to utilize photo oxidative crosslinking to stabilize melt-spun PAN copolymers [7]. However, in this initial study the process required a prolonged stabilization time. In the present study, we report on the accelerated UV crosslinking of a terpolymer containing a UV sensitive comonomer, acryloyl benzophenone (ABP), which was synthesized in a companion study by McGrath et al. [6].

Experimental

Two compositions of PAN precursor polymers having AN:MA:ABP mole ratio of 85:14:1 (terpolymer) and AN:MA mole ratio of 85:15 (copolymer) were used throughout the study (Monomer Polymer, Inc., Feasterville, PA). Fibers were melt-spun at 220°C using a die diameter of 250 μm and an aspect ratio of ~2. For spectroscopic studies, precursors were pressed at 220°C (Carver press 2926) to obtain 50-60 μm films. The UV-visible absorption spectra of the precursor films were recorded on a Shimadzu UV-3100 spectrophotometer at 25°C. Gel fractions of the precursors were measured after equilibrium swelling (48 h) in dimethyl sulphoxide (DMSO) solvent. The as-spun fiber tows were UV irradiated at ~110°C in low power (100 W) and high power (4.5 kW) mercury arc lamps for 180 min and ~ 1 min durations, respectively. After UV irradiation, the terpolymer fibers were oxidatively stabilized in a forced-circulation oven (ATS 3610) at 320°C for 30 min using a heating rate of 2.5 °C/min. The copolymer fibers could only be heat treated at a maximum rate of 0.2 °C/min. The stabilized fibers were then carbonized at 1500°C in He atmosphere in an Astro Furnace. SEM micrographs of the

fibers were obtained using a field emission scanning electron microscope (Hitachi FE-SEM S-4700). Tensile properties of the fibers at various stages of treatment were measured in a computerized MTI Phoenix tensile testing machine equipped with 500 g load cell (ASTM D 3379-75).

Results and Discussion

After UV irradiation, the copolymer developed only a pale brownish tint, whereas the terpolymer turned dark brown. Irradiated precursors were immersed in DMSO solvent and the gel contents were measured after equilibrium swelling (48 h). Figure 1a and b show the results for low power and high power exposure, respectively. The non-irradiated samples dissolved completely. The copolymer samples also remained almost completely soluble (~0% gel) after 180 min and ~ 1 min of UV irradiation in low and high power units, respectively. However, UV irradiated terpolymer fibers produced ~30% and ~70% gel contents after stabilization for similar periods (as compared with the copolymer), establishing the role of ABP moiety in crosslinking the precursor.

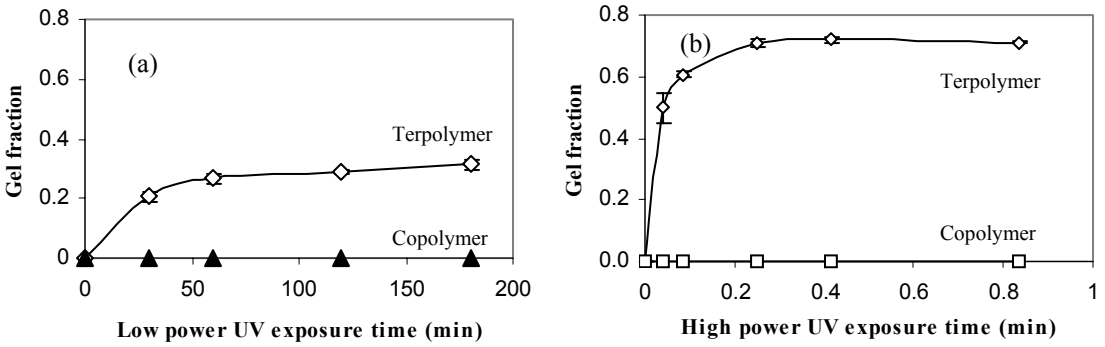

Figure 1: Gel fractions of precursors after UV irradiation: (a) films after exposure in low power unit, (b) terpolymer fibers after multiple passes in high power unit, 1 pass ≈ 2.5 s exposure time

Figure 2 displays the UV-visible spectra for the terpolymer relative to that of the copolymer at different conditions of UV irradiation. Before irradiation (0 min), the terpolymer displayed enhanced absorbance, relative to that of the copolymer, at 330 nm. This difference in the spectra is due to the UV sensistivity of the benzophenone moiety in the terpolymer. The control terpolymer sample, which was not UV irradiated but underwent only the heating cycle (110°C for 180 min), remained almost colorless and did not show any further change in the UV-visible spectra. After low-power UV irradiation for 180 min, the absorbance of the copolymer appears at wavelengths lower than 300 nm, having a low-level tail extended in the violet region (~450 nm). The low level of absorbance in the violet region is consistent with the development of only a brownish tint for the copolymer, without any significant change of color. In contrast, the color generation after UV exposure is vigorous for the terpolymer, which turned dark brown indicating a strong UV and violet light absorbance. The intense brown color for

the terpolymer may be attributed to UV assisted cyclization reactions that produce chromophores having a strong UV absorbance. Finally, it is noted that when the terpolymer was irradiated for only ~ 1 min in the high-power UV source (in contrast to 180 min in low-power), the UV assisted reactions were accelerated even further as evident from intense UV and violet light absorbance.

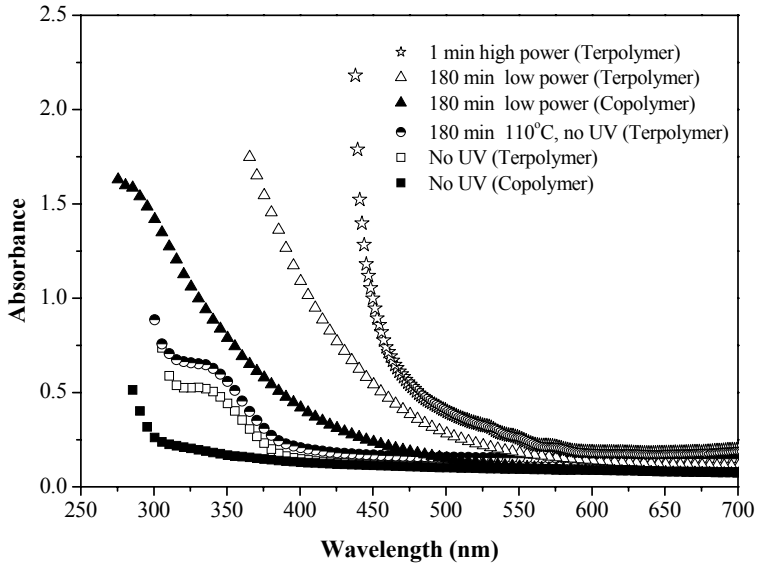

Figure 2: UV-visible spectroscopy of terpolymer and copolymer films at different condition of UV irradiation

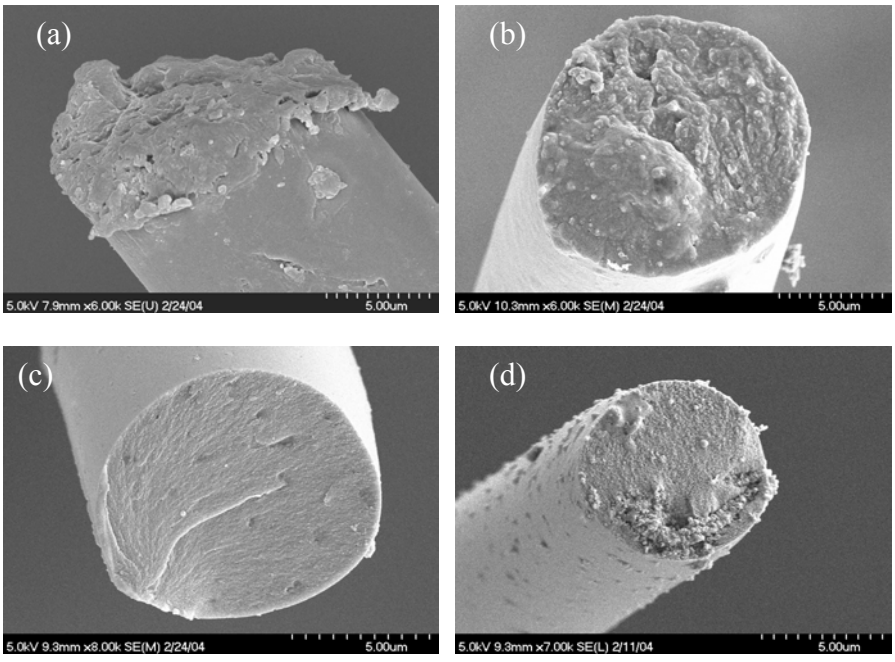

Figure 3: SEM fractographs of (i) as-spun, (ii) UV irradiated, (iii) oxidized and (iv) carbonized fibers

After UV assisted crosslinking, terpolymer precursor fibers were successfully oxidatively stabilized at 320°C and then carbonized at 1500°C. As displayed in Figures 3(a)-(d), the ductile as-spun fibers (rough pattern on fractograph) progressively became brittle on stabilization and carbonization. Occasional voids were detected in the core of the carbon fiber. Tensile stress-strain plots of the fibers at various stages of treatment are displayed in Figure 4. The moduli of the precursor fibers were similar (~ 6 GPa). As expected, UV irradiation reduced the tensile strength of as-spun fibers (from 230 to 115 MPa) and increased strain-to-failure (~16 %) due to crosslinking. After oxidation the strength (160 MPa) of the fibers increased and strain-to-failure (~ 7 %) decreased significantly. The carbonized fibers displayed tensile strengths and moduli as high as 730 MPa and 140 GPa, respectively. Although the modulus of the carbonized fibers was acceptable, the tensile strengths were lower than those of commercial carbon fibers due to defects such as those visible in the micrograph of Figure 3d. Research is underway to improve carbon fiber properties by eliminating void formation during heat treatment. Nevertheless, this study demonstrates that melt-spinning, combined with UV-assisted stabilization, is a viable solvent-free route for producing PAN-based carbon fibers.

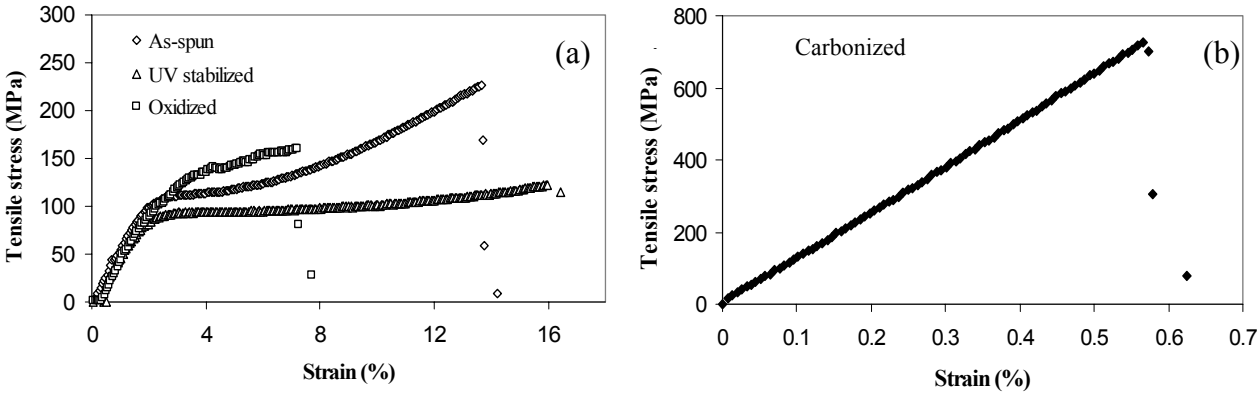

Figure 4: Tensile stress-strain plots of (a) precursor and (b) carbonized fibers

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