UV-ASSISTED STABILIZATION OF MELT-PROCESSIBLE PAN CARBON PRECURSOR FIBERS

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Abstract

A novel route for producing carbon fibers from UV-oxidatively stabilized melt-processed PAN precursor fibers is reported. A molecularly designed acrylonitrile (AN)-methyl acrylate (MA)-acryloyl bezophenone (ABP) terpolymer (85/14/1 mole ratio) was melt processed to produce precursor fibers. Incorporation of ABP co-monomer was shown to enhance the UV sensitivity of the precursor. Upon UV irradiation, the precursor formed a crosslinked structure, which helped in oxidative stabilization at 320ºC without breakage of filaments. Stabilized fibers could be carbonized at 1500°C in He atmosphere. Carbonized fibers displayed tensile strengths ranging up to ~ 730 MPa, tensile modulus ranging up to ~ 140 GPa, and strains-to-failure of ~ 1 %. ATR-IR and UV-visible spectroscopic analyses revealed that the UV radiation induces the formation of free radicals that induce cyclization in PAN. A powerful UV irradiance of ~ 1 W/cm^2 accelerated the UV-stabilization process by reducing the processing time to less than one minute.

Introduction

Carbon fibers find wide range applications in high performance composites because of their high stiffness and low density. However, at ~ $10/lb, carbon fibers are significantly more expensive than glass fibers and have not found widespread application in automotive composites. Almost 90% of the carbon fibers are produced from solution-spun polyacrylonitrile (PAN) precursor fibers [1]. PAN based precursor fibers must be thermally stabilized to obtain an intractable structure, which can sustain the severe high temperature processing during carbonization. A schematic of carbon fiber production from PAN based fibers is shown in **Fig 1**.

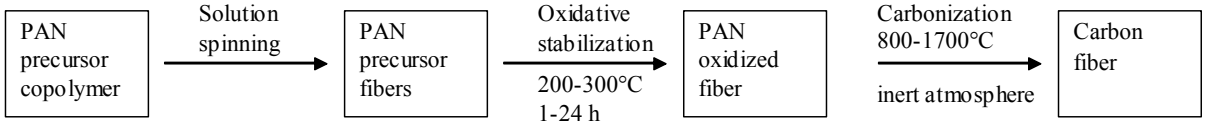

Fig 1: Schematic of carbon fiber manufacturing from typical PAN based precursors

Obtaining carbon fibers from melt-processable polymeric precursors is an attractive way to avoid hazardous solvents that are necessary for solution-spinning of PAN. It is noted that the melting point of PAN is high enough that the polymer actually degrades before it reaches the melting temperature. Therefore, such precursors are not melt-processible. The commercial PAN precursors form a ladder structure and infusible mass after heat treatment. 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 and enable melting of the polymer before its degradation [3-6]. However, unlike solution-spun fibers, melt-processed fibers cannot undergo direct thermo-oxidative stabilization since the fibers melt before the oxidative reaction.

Photo-crosslinking of PAN is a potential technique that has been reported in the literature for stabilization of fibers [7-8]. In a recent study, we have demonstrated that UV assisted stabilization could be a viable route for producing intractable fibers from melt-spun PAN copolymers [8]. However, 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, 9]. Influence of the characteristics of precursor fibers and their stabilization conditions on the microstructure and properties of final carbonized fibers are also discussed.

Experimental

PAN precursor polymer having AN:MA:ABP mole ratio of 85:14:1 (terpolymer) and its control composition AN:MA 85:15 (copolymer) were used in the study (Monomer Polymer, Inc., Feasterville, PA). The chemical structure of the terpolymer is displayed in **Fig 2**.

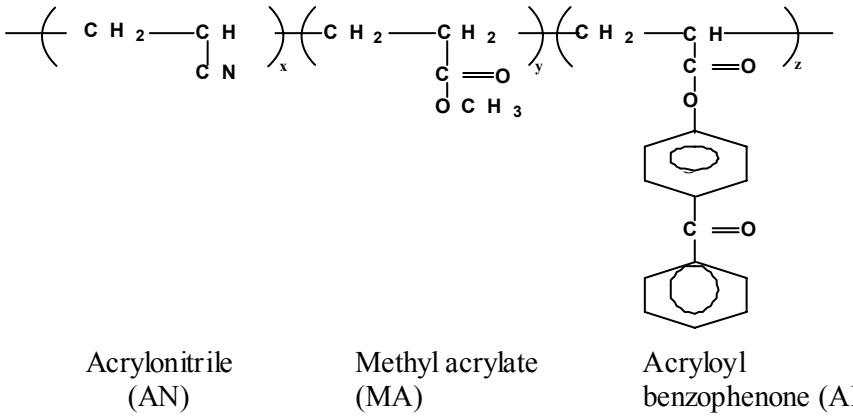

Fig 2: Chemical structure of the terpolymer

Fibers were melt-spun from the precursors using a die of 250 μm diameter and an aspect ratio of ~2 for melt spinning at a temperatures ranging from 200-210^{o}C. The melt-spinning conditions of the two types of fibers are summarized in **Table 1**. To obtain oriented spun-drawn fibers, a maximum winding speed of ~300 m/min was used at different throughput rates (0.14 cc/min and 0.04 cc/min). 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 3 h and ~50 s 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 stabilized fibers were then carbonized at 800°C and 1500°C in He atmosphere in an Astro Furnace.

Table 1: As-spun terpolymer fiber types and their spinning conditions

Fiber Types	Spinning temperature (°C)	Capillary throughput rate (cc/min)	Winding speed (m/min)	Draw down ratio	Fiber diameter (μm)
I	210	0.14	300	120	20
II	200	0.04	275	310	14

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). An average of 10-15 single filament test results was reported. Since fibers could not be directly used for spectroscopic studies, the terpolymer was pressed at 220°C (Carver press 2926) at ~ 20 MPa pressure to obtain thin films. The UV-visible absorption spectra of the precursor at different UV stabilization conditions were recorded on a Shimadzu UV-3100 spectrophotometer at 25°C. Attenuated total reflectance (ATR) IR spectra of the precursors were collected in a Nicolet Magna 550 FTIR spectrometer using a high endurance diamond ATR attachment.

Results and Discussion

Diamond ATR FTIR spectra of high power UV irradiated and the control non-irradiated terpolymer and copolymer samples are displayed in **Fig 3**. For the terpolymer, it was observed that the -C≡N (2242 cm^{-1}) stretching intensity is lowered after high power UV irradiation for ~ 50 s while a broad overlapped peak appears in the frequency range 1560 - 1690 cm^{-1} due to C=C and C=N unsaturations. Such a decrease in -C≡N stretching intensity and the appearance of a new peak was not observed for the control copolymer sample after equivalent UV exposure. Thus, for the terpolymer, UV assisted reactions cause decrease in CN group and development of unsaturation.

The generation of unsaturated chromophores in the terpolymer after UV exposure was investigated by UV-visible spectroscopy. **Fig 4** displays the UV-visible spectra for terpolymer relative to that of the copolymer. Before irradiation, the terpolymer displayed absorbance maximum at 330 nm, whereas, the copolymer did not absorb. The enhanced absorption of UV radiation is due to the presence of benzophenone moiety in the terpolymer. The UV absorbance of the copolymer after 3 h of UV exposure at low power and 110°C appears at wavelengths that are less than 300 nm, having a tail extended in 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 generation of color due to UV exposure is vigorous for the terpolymer. The original UV absorbance at 330 nm is further broadened after 3 h of UV exposure at low power with a long tail extending to 550 nm. The terpolymer turned dark brown after 3 h of irradiation, which indicates a strong UV and violet light absorbance. It is noted that the control terpolymer sample, which was not UV irradiated but underwent same heating cycle (110°C for 3h), was almost colorless and did not show any significant change in the UV-visible spectra (3 symbol in **Fig 4**). The intense brown color for the terpolymer likely results from the accelerated UV assisted cyclization reactions that produce chromophores having a strong UV absorbance. The UV assisted reactions were accelerated during high intensity UV irradiation (for short duration ~50 s) and the extent of reaction is more than that during low power UV irradiation for 3 h as evident from stronger UV and violet light absorbance (**Fig 4**).

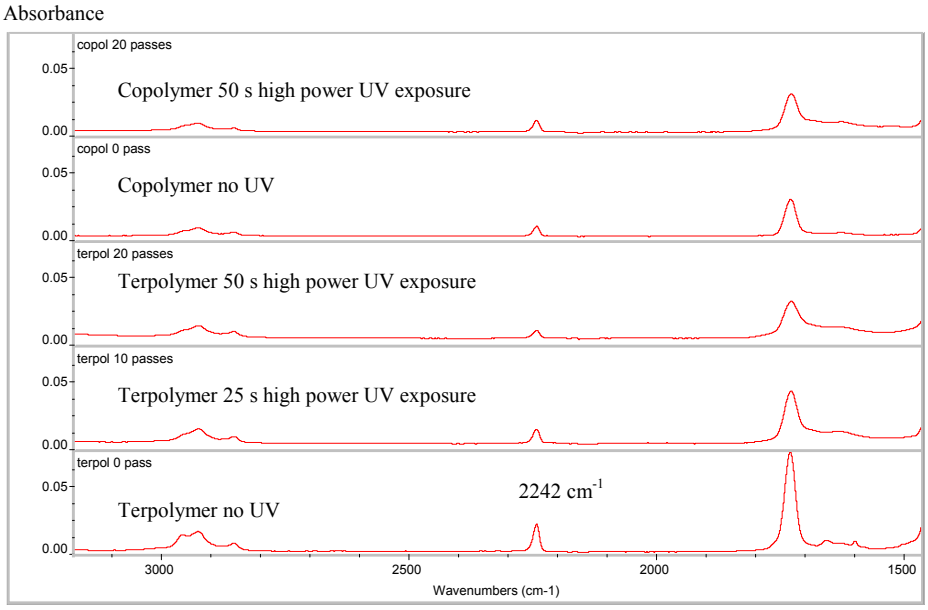

Fig. 3: ATR IR spectra of PAN-based terpolymer and copolymer at different high power UV irradiation times

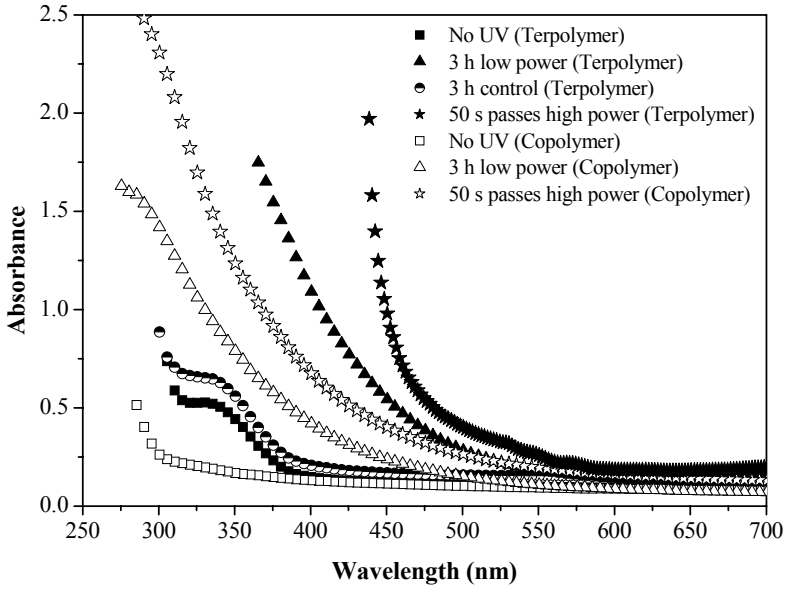

Fig. 4: UV-visible spectroscopy of PAN-based terpolymer and copolymer samples at different condition of UV irradiation

The fibers were successfully stabilized by UV irradiation at 110°C. In the low power UV source, an irradiation time of 3 hours was needed for adequate crosslinking. In contrast, the high power source enabled a drastic acceleration of the process such that the irradiation time could be reduced to ~ 1minute. The non-irradiated precursor fibers dissolved in dimethyl sulphoxide (DMSO) solvent completely. The copolymer sample also remained completely soluble even after UV irradiation in both low and high power unit for 3 h and 50 s, respectively. However, UV irradiated terpolymer fibers produced ~70% swollen colored gel after complete stabilization, establishing the role of ABP moiety in crosslinking the

precursor. It was observed that the stabilization of highly oriented fibers at temperatures higher than 110°C was difficult due to high shrinkage force, which caused fiber breakage during radiation processing and subsequent oxidative stabilization steps.

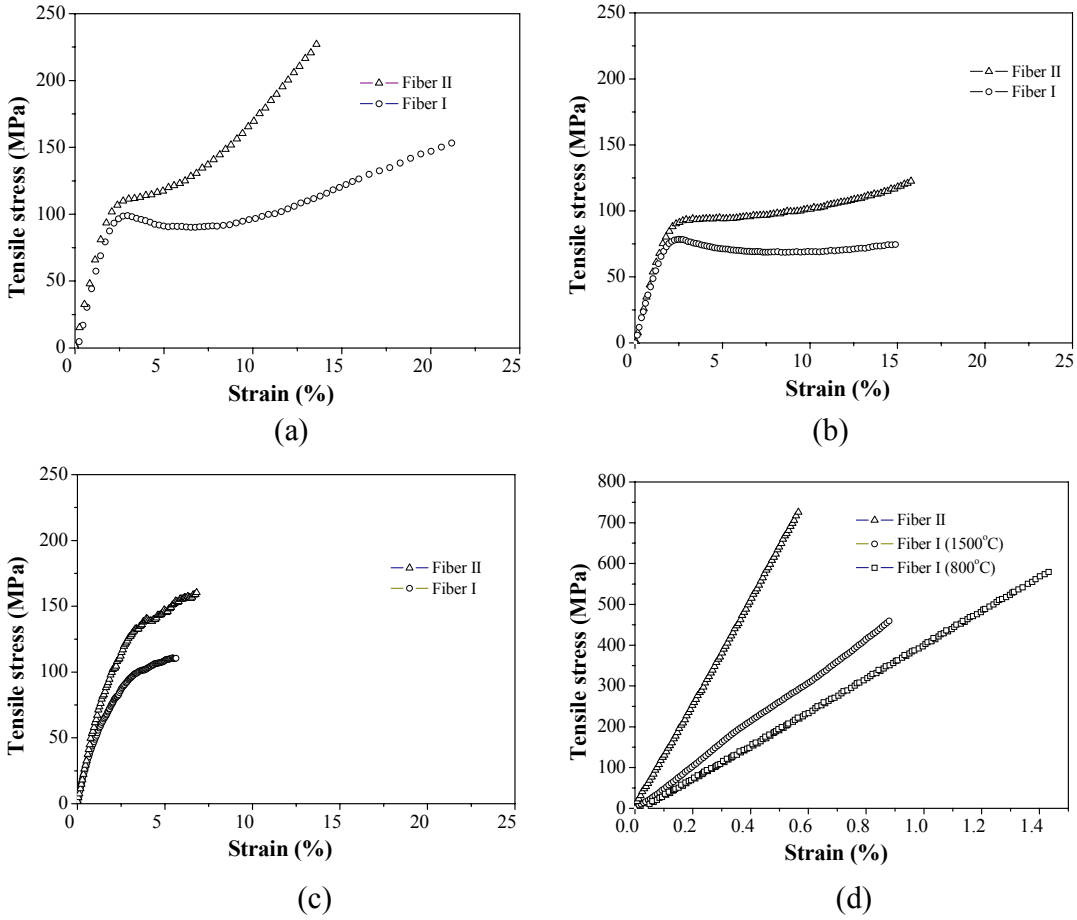

Fig 5: Tensile stress-strain plots for (a) as-spun, (b) low power UV irradiated, (c) oxidized and (d) carbonized fibers

The tensile stress-strain plots for the as-spun fibers are displayed in **Fig 5a**. Properties of the precursor fibers were tailored by choosing suitable melt-processing conditions. The more oriented Type II fibers display better properties than Type I fibers at all stages. Increase in draw ratio caused increased modulus, yield and tensile strengths with lowering in fiber diameter and ultimate elongation. **Figs 5b-c** display the tensile stress-strain plots for the low power UV-irradiated, and oxidatively stabilized fibers, respectively. UV crosslinking not only prevents fiber breakage due to melting during oxidative stabilization but also retards relaxation of fiber through loss in orientation. After UV irradiation, the modulus of the fibers decreased slightly and tensile strength decreased significantly due UV-assisted crosslinking and other associated reactions. Oxidation causes cyclization of the fiber and improves strength and lowers strain-to-failure.

The tensile stress strain plots of the carbonized fibers are displayed in **Fig 5d**. Fibers I and II carbonized at 1500°C display diameters of ~ 13 and 7 μm, tensile modulus of ~ 55 and ~130 GPa, respectively, and tensile strengths ranging up to ~700 MPa. To determine the effect of carbonization temperature, fibers (Type I) were also carbonized at 800°C and the fibers were found to have a lower modulus (~42 GPa) and a little higher strain-to-failure than

those carbonized at 1500°C. As expected, the extent of ordered structure was lower at a lower carbonization temperature.

The tensile properties of these fibers at various stages, including the final carbonized state, are summarized in **Table 2**. Retention of fiber orientation with minimum relaxation during stabilization is desired. Results of precursor and carbonized fibers (type I) after high dosage irradiation are also summarized in **Table 2**. After high power UV irradiation, the modulus decreased slightly but the strain-to-failure increased significantly. However, high energy UV irradiated fibers after oxidation and carbonization display higher modulus than those from low power irradiation.

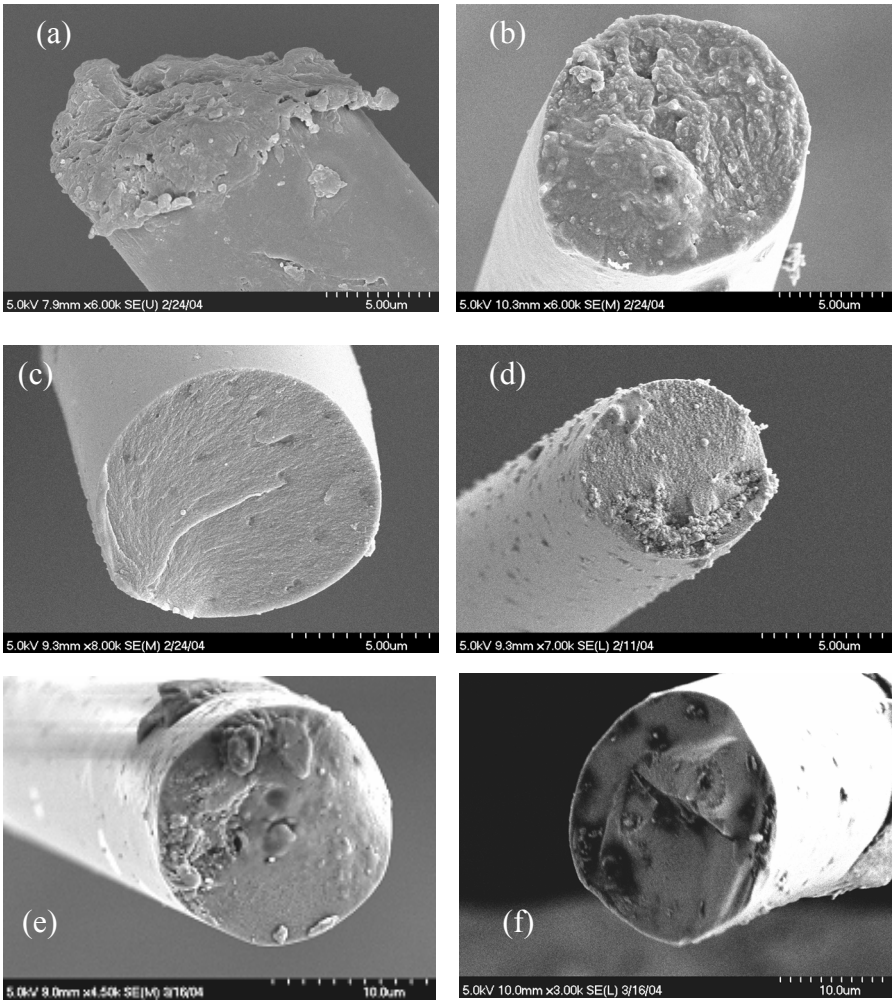

Fig 6. SEM micrographs of PAN based terpolymer fibers: (a) as-spun II, (b) low power UV irradiated II, (c) oxidized II, (d) carbonized II and (e)-(f) carbonized I fibers stabilized by high power UV radiation

Figs 6a-d displays the SEM fractographs of type II fibers at different stages of processing, i.e., as-spun, UV crosslinked, oxidatively stabilized and carbonized fibers. As-spun fibers show ductility (rough failure pattern), which progressively disappears after crosslinking and cyclization steps and failure pattern becomes brittle (catastrophic failure). Cross-section of failed carbon fibers (**Fig 6d**) shows defects inside the fiber. The modulus of the carbonized fibers II was very good (~130 GPa), but defects such as those visible in the micrograph of **Fig 6d** caused failure at a low strain level (~0.6 %) resulting in lower tensile

strength of the carbonized fiber in comparison to the commercial fibers. Carbonized fibers produced after high power UV irradiation (**Fig 6e-f**) displayed similar defects in the SEM micrographs, which caused low tensile strength. Ongoing studies are being conducted to improve carbon fiber properties by reducing defect generation during heat treatment process.

Table 2: Tensile properties of PAN based terpolymer fibers

Fiber type	Parameters		As-spun	UV-irradiated	Oxidized	Carbonized @1500°C	Carbonized @800°C
I	Modulus (GPa)	Low power*	5.16 ± 0.32	4.09 ± 0.26	3.94 ± 0.57	52.9 ± 7.7	42.2 ± 2.6
		High power*		3.87 ± 0.49	5.51 ± 0.26	65.5 ± 13.2	
	Tensile strength (MPa)	Low power	155.9 ± 6.1	78.8 ± 12.6	119.6 ± 15.3	451.8 ± 162.0	442.8 ± 168.5
		High power		111.3 ± 8.8	159.3 ± 11.1	300.7 ± 76.2	
	Strain-to-failure (%)	Low power	22.2 ± 2.7	13.5 ± 8.2	6.9 ± 1.8	0.90 ± 0.30	1.05 ± 0.4
		High power		47.9 ± 8.8	5.8 ± 1.0	0.54 ± 0.26	
II	Modulus (GPa)		6.85 ± 0.35	5.10 ± 0.89	6.02 ± 1.2	126.0 ± 15.6	
	Tensile strength (MPa)		234.8 ± 10.7	116 ± 20.5	159.5 ± 30.2	594.1 ± 147.5	
	Strain-to failure (%)		14.6 ± 0.9	16.5 ± 4.4	7.5 ± 2.1	0.42 ± 0.11	

* power of radiation during UV- stabilization process

Conclusions

The molecularly designed, polyacrylonitrile (AN)-methyl acrylate (MA)-acryloyl benzophenone (ABP) (85/14/1) terpolymer precursor could be successfully melt–spun at ~210°C. A novel UV stabilization route was developed for the terpolymer fibers, where ABP acts as a UV sensitive component. High power UV irradiation accelerated the stabilization process, which required less than one minute of irradiation time. Stabilized fibers could be oxidatively cyclized at 320°C for 2.5 h, followed by carbonization at 1500°C for 1h. Carbonized fibers displayed tensile strengths ranging up to ~ 730 MPa, tensile modulus ranging up to ~ 140 GPa, and strains-to-failure of ~ 1%. Scanning electron microscopy revealed the presence of defects in the fiber core, particularly in the cases of high power UV irradiated fibers, which decreased the tensile strengths of the carbon fibers. Ongoing research is devoted to the optimization of the process. Overall, this study demonstrates a viable alternate route to obtain carbon fibers from melt-spun precursors through accelerated UV assisted stabilization.

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