Melt spinning of AN/VIM copolymers for carbon fiber precursor preparation

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Abstract

Fibers of Polyacrylonitrile (PAN), or commonly referred to as acrylic fibers, have found to have many uses in the world. Acrylic fibers are used as a textile medium for high quality and high performance yarns and fabrics, and also as the main supply of precursors for carbon fibers. The reasoning for this is because of the high carbon yield of 55% in comparison to other materials which have much lower carbon yield. The current issue with the acrylic stock is due to its harsh and costly processing conditions. At present, the acrylic fibers are processed by solution spinning in hazardous solvents requiring stringent solvent reclamation. We will show to solve this problem by the use of copolymers made with acrylonitrile (AN) with 1-vinylimidazole (VIM) creating a Tg of 115 which then can be further plasticized. Melt processing of our AN-VIM copolymer by an extrusion method is then possible by lowering the processing temperatures to obtain fibers, precursor for carbon fiber. Carbon fiber prepared by using the precursor will also be presented.

1. INTRODUCTION

Carbon fibers have reached a very high interest and importance in multiple industries and applications. These include aerospace, automotive, sporting goods, and other industrial avenues [1-2]. Due to this high interest, a need for higher throughput and production of these medium and high performance carbon fibers are necessary. Much research has pertained to the optimization of strength, structure, synthesis, and post-extrusion processing [3].

The commercial PAN precursors degrade before they melt therefore, the precursor fibers are commonly solution-spun (20–30 wt% solution) from polar solvent. However, the solution spinning process requires solvent recovery and higher processing cost. Previous work (e.g. McGrath et al.) [4-5] focused on copolymer and terpolymer systems with melt processability, although these polymers typically required UV stabilization [6-7].

This work is focused on traditional thermal oxidative stabilization after melt processing. Poly (acrylonitile-co-1-vinylimidazole) is delivered as a novel melt-processable carbon fiber precursor. The replacement of solution-spinning by melt-spinning process lowed cost and is a more green process because solution spinning involves the disadvantages of solvent recovery and higher processing cost. The replacement of solvent-based polymerization by water-based polymerization lowed cost and is a more green process since water as a medium is considered an environmentally friendly and economically viable polymerization. This invention will help new business development with low cost manufacturing and equal or better products compared with current carbon fiber products available in the marketplace.
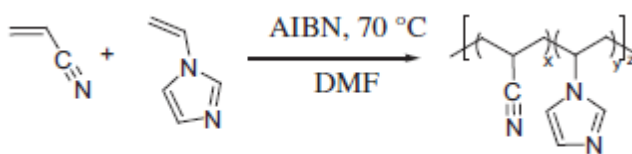
We have found the optimum synthetic condition for the scale-up synthesis of melt processable carbon fiber copolymer precursor. We included not only conventional organic solvent system but also water-borne system. Further study will include the optimum melt spinning condition as well as the conditions of stabilization/carbonization. The main approach that has been devised is using solvent borne system, that has successfully demonstrated melt processable copolymer synthesis and extrusion of the polymer and stabilization.

The mechanical properties of carbon fiber, especially tensile strength and modulus are closely related to the orientation of crystals. The tensile strength and modulus of carbon fibers can be controlled by carbonization temperature; while the modulus increases almost linearly carbon fibers can be controlled by carbonization temperature. While the modulus rises almost linearly with carbonization temperature, the tensile strength peaks at about 1400°C. Thus, by selection of the proper carbonization or graphitization temperatures, carbon fiber with various tensile strength modulus combinations can be produced. In fact, the quality of the ultimate carbon fibers also depends strongly on the composition and quality of the precursor fibers, and the oxidation conditions, as well as the carbonization conditions, generally, the better the orientation of the crystallites, the higher the value of the Young's modulus. The stretching at the carbonization stage is more difficult than that at the spinning and stabilization Therefore, stretching during carbonization must be

carefully controlled. There are three successive stages in the conversion of any precursor into high-performance carbon fibers.

2. MELT PROCESSIBLE CARBON FIBERS

The solution polymerization of AN and VIM by varying feed ratio was carried out in a 250 mL flask fitted with a thermocouple probe, condenser, addition funnel and nitrogen inlet. The flask was charged with 60 mL DMF and purged with nitrogen for 30 min.

Scheme 1. Free radical polymerization of AN with VIM.

Then the monomers, AIBN and chain transfer agent, 1-dodecanethiol were added drop wise into the flask over a period of 2e5 h. The polymerization reactions were carried out at 70 C with continuous stirring. The copolymer was precipitated in de-ionized water, filtered and washed with methanol and hexane to remove residual monomers and then dried in vacuum oven for two days till constant weight was obtained (Fig. 1a).
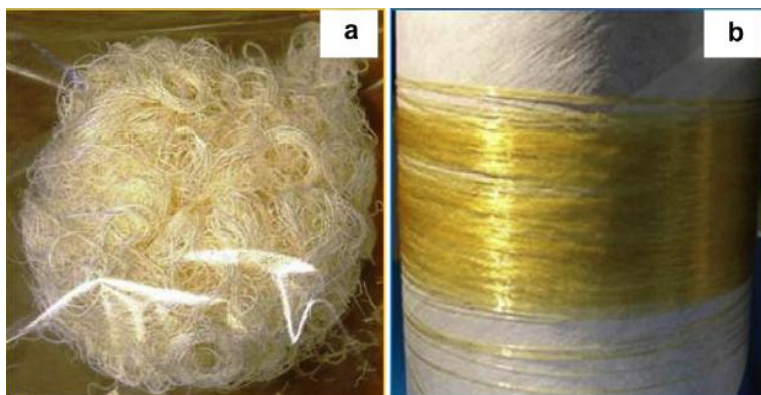

Figure 1. Photograph of (a) 82/18 AN/VIM copolymer as precipitated and (b) melt spun fiber of 82/18 AN/VIM copolymer.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analysis of copolymers was performed on a Shimadzu IR-Affinity 1 with a Pike attenuated total reflectance modular insert (Figure 2). Differential scanning calorimetry (DSC) was

performed on a Mettler DSC instrument in nitrogen at a heating rate of 10 C min

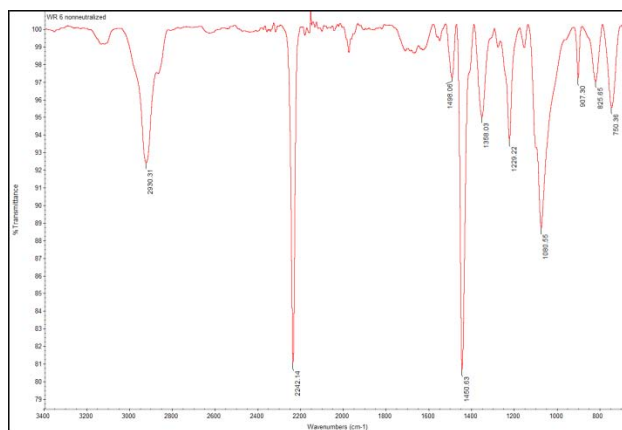1. The glass transition temperature (Tg) was obtained from a second heating cycle (Figure 3).

Figure 2. shows the ATR-FTIR spectrum of typical water based AN-VIM polymer. 2930 cm-1 (backbone CH2 stretch-ing), 2242 cm-1 (CN stretching), 1450 cm-1 (CH2 band of backbone). 1229 cm-1 (C-N ring stretching),1080 cm-1 (C-H ring in-phase bending).
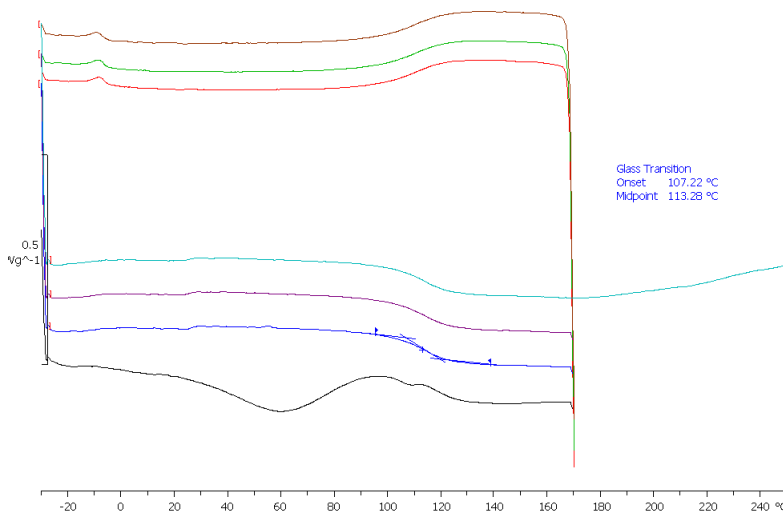

Figure 3. DSC thermogram of 82/18 AN/VIM copolymer showing a glass transition temperature of 107 ºC.

Extrusion was made possible by using the Malvern Rosand RH-7 capillary rheometer. Using this type of processing equipment allowed for the incorporation of not only heat to soften the polymer synthesized, but also to allow for increased pressure to reduce the viscosity of the semi-molten material. Fibers were created with small diameter sized, after annealing and drawing had taken place (Figure 4). Fibers had average diameter of 36 μm before they were subjected to stabilization and carbonization.
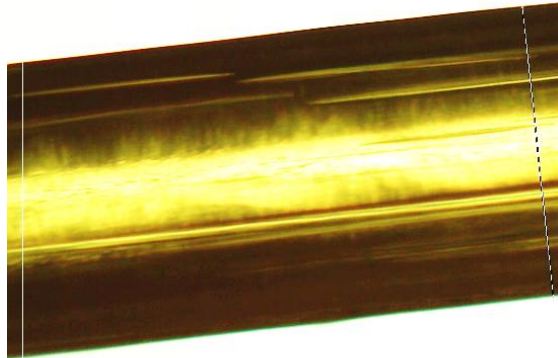

Figure 4. As-spun AN/VIM copolymer fiber with a diameter of 36 μm.

Stabilized fibers are the second stage in the production of forming carbon fiber. This step takes place in an oven under tension and an oxygen rich environment. This allows for oxidation to take place and begin the process of forming a ladder polymer. The typical temperature for this to take place for PAN based polymers is around 280 – 300 °C. It has been found that the copolymer AN/VIM has an onset of oxidation at 250 °C. The fibers will be hung using a weight and the temperature slowly ramped to 100 °C for 8 hours with steam then ramped up to 300 °C for 30 minutes before being brought down to room temperature, as can be shown in the chart in figure 5. All of these are performed under atmospheric conditions with steam or water.
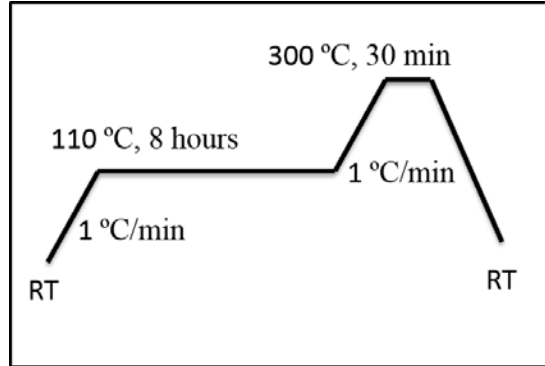
Figure 5. The heating program for stabilization of AN/VIM copolymer.

Carbonization, or otherwise known as denitrogenization, is the last and final step in creating carbon fiber products. It is the step where the nitrogen in the ladder polymers are removed and allowed for the ladders to network together in a large lattice, leaving only carbon chains. This step requires an oxygen deficient atmosphere with a high inert atmosphere, typically nitrogen, to allow for the carry-off of nitrogen-containing compounds. It requires high temperatures and under high tensions to allow for the chains to form the carbon lattice of carbon fibers. The typical temperatures for carbonization are 950 °C to 1100 °C.

The fibers that have been stabilized are combined together into a fiber tow of approximately 5-10 fibers together. The fibers are placed into the Thermo Scientific tube furnace (figure 55) that is connected to a temperature controller. A constant line of N2 gas is supplied to the end of the glass tube of the furnace at a rate of 40 mL/min, or a pressure of 50-100 psi. The tube is flushed with N2 gas for 15 minutes at a minimum. The tube furnace is then set to a temperature of 950 °C – 1000 °C at a rate of 1 °C per minute. The temperature is remained for approximately 15 – 30 minutes then returned to room temperature.
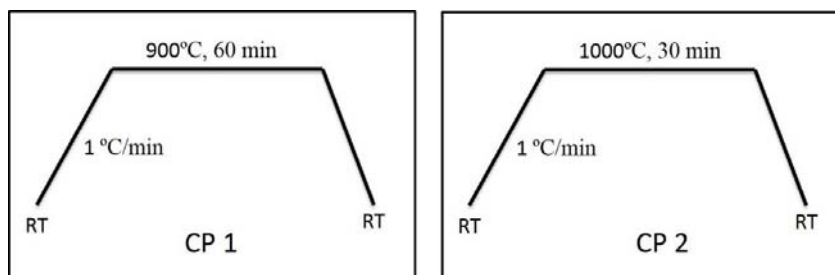

Figure 6. Schemes of the typical carbonization programming for carbon fibers which can vary for ending temperatures of 900 °C (CP1) or 1000 °C (CP2).

Carbon fibers that were made showed a low diameter of 15 µm (Figure 7) and had a high tensile strength of 1800 MPa (Figure 8). The fibers also showed a high modulus of 179 GPa (Figure 9).
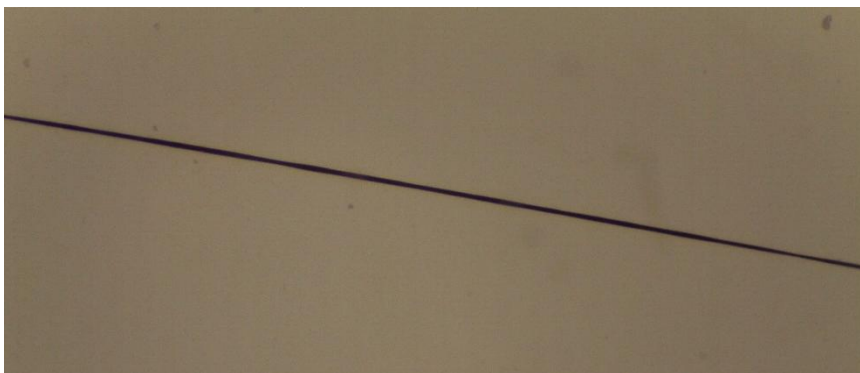

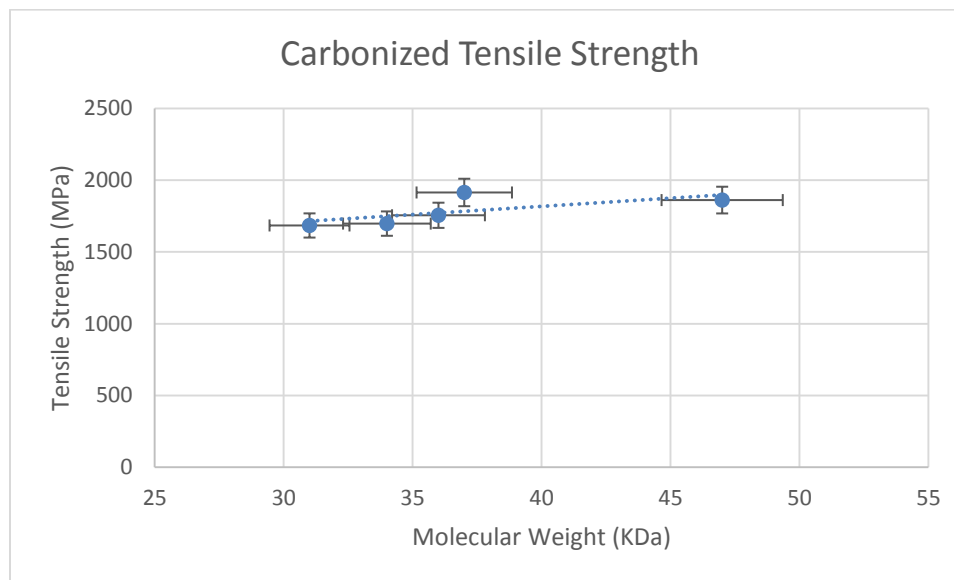Figure 7. Optical microscopy at a 40x of carbon fiber with an average diameter of 16 µm.

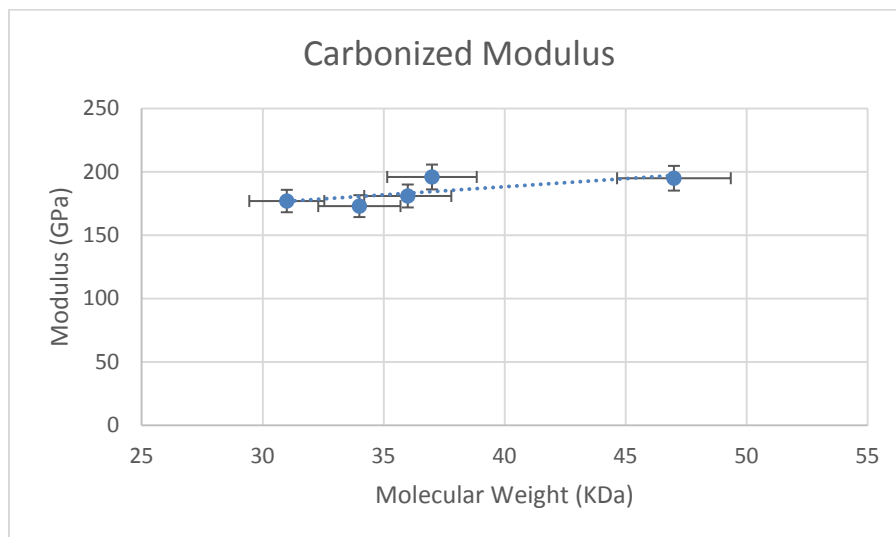Figure 8. Tensile strength of carbon fiber in respects to the molecular weight of the original AN/VIM copolymer batch.

Figure 9. Modulus of carbon fiber in respects to the molecular weight of the original AN/VIM copolymer batch.

3. CONCLUSIONS

It has been shown that a melt processable carbon fiber precursor can be synthesized and extruded like a typical melt processable polymer. This fiber can then be transformed into carbon fiber by optimizing the parameters of stabilization and carbonization. This benefits the ability to create an economically and environmentally friendly carbon fiber total process.

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