THE EFFECT OF COAGULATION BATH TEMPERATURE ON THE MECHANICAL PROPERTIES OF PAN-BASED CARBON FIBER

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ABSTRACT

The objective of this research is to produce and characterize PAN fibers in order to produce high performance carbon fibers. The PAN fiber was produced using a simple dry – wet spinning process where the polymer solution was extruded through an air gap following by coagulation process. The formation of PAN fiber was controlled by coagulation temperature inside the bath and the jet stretch. Low coagulation bath temperature was responsible to retard the coagulation rate and controlling the diffusion of solvent and non-solvent inside and at the surface of the PAN fiber. Stretching was applied to the as-spun fiber in order to align the molecular chain along the axis thus increases the crystallinity of PAN fiber and to help in raising the Young's modulus. The crystallinity of PAN fiber was determined using X-ray diffraction. The mechanical properties of PAN fiber such as Young's modulus and tensile strength were examined in order to investigate the effect of coagulation bath temperature and jet stretch. The PAN fiber produced at a 15 °C coagulation bath and 3 jet stretches exhibited the highest tensile strength and Young's Modulus of 0.96 GPa and 5.21 GPa respectively.

Keywords – PAN fibers, dry – wet spinning, carbon fibers, mechanical properties.

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1.0 INTRODUCTION

Carbon fiber is the most popular advanced material that has been commercialized for the past 35 years. It has a wide range of applications such as in structural materials likes composites and numerous researches have been conducted related to it [1]. Its high strength and stiffness, combined with their lightweight, making the fiber attractive to high-volume applications ranging from sporting goods to aircraft structures [2,3]. There are various types of precursors used by manufactures to produce high performance carbon fibers such as polyacrylonitrile (PAN), cellulose, pitch, coal and rayon [1,2]. Amongst them, PAN is widely used for carbon fibers precursor for the present manufacture of carbon fibers because its advantages compared to other precursors such as higher melting point, high degree of molecular orientation, thermally stable and greater yield of the carbon fiber [4-7]. High quality PAN precursor has less micro voids [8], small diameter [9,11,13-15], low comonomers content [10,13-15] and high modulus and tensile strength [4,9,11,12,16]. The final mechanical properties of carbon fibers are significantly influenced by the coresponding properties of their precursors [11,17]. In fact, a study revealed, what appears to be a direct correlation between the primary Young's modulus of various PAN-based precusors and the resulting carbon fibers. A plot of carbon fiber modulus (E_c) versus precusor modulus (E_p) depicted a straight line passing through the origin [4,11]. The average ratio of E_c and E_p was found to be about 20 [4,11,16,17].

The formation of carbon fibers involves a lot of major steps. At the final stage, the carbon fibers are catogarized into three types depending on the last treatment temperature [2,9]. Normally, the performance of carbon fibers are determined by their Young's modulus and tensile strength. These two parameters are closely related to structural of carbon fibers. Therefore, the formation of PAN fiber is a crucial part in order to get the best arrangement of PAN fiber molecules that are suitable for carbon fiber applications. Some researches reported that some defects should be controlled in the earlier processing stages to produce high modulus carbon fibers [6]. PAN homopolymer is generally not used for fiber spinning because its copolymers are more soluble, thus the preparation and storage of spinning dope are easier [19]. The resulting fibers from

copolymers are also more extensible and less prone to fibrillation. The dope made from homopolymer gels very quickly, but the addition of comonomers tends to decrease the gelation rate, therefore the dope is easier to handle. Comonomers also affect the stabilization process. Besides alleviating the exothermic energy during stabilization process [19], they also reduce the initiation temperature of cyclization reaction [13,19,20] and increase the speed of cyclization reaction [13,20].

During spinning process, the dope is extruded through a spinneret into an air gap, then, emerged into the coagulation bath and the PAN will precipitate into fibril form [1,8]. The shear field tends to orient the solidified PAN structure parallel to the direction of flow. Edie [1] discovered that mass transfer at the surface of fibers was relatively slow because the solvent concentration of coagulation bath was relatively high. This prevented the solvent from leaving the fibers immediately. The solvent diffused radially through the solidifying fiber faster than it can diffuse away from the fiber surface. As a result, the solvent concentration was uniform across the fiber's cross-section during solidification. Therefore, the fiber shrinks uniformly in the radial direction, giving the circular cross-section that is characteristic of wet spun. However, if the polymer concentration in the spinning solution is low, a relatively rigid fiber skin can also form in this process before the center of the fiber has solidified, yielding the dog-bone shape fiber. This so-called 'skin-core' effect phenomenon is determined by the relative rates of diffusion of solvent and precipitation agent into the fiber and of polymer solvent from the fiber.

There are various parameters influencing the coagulation processes including polymer composition, coagulation bath composition, coagulation bath temperature and jet stretch [8,14]. The polymer composition in the spinning solution plays an important role in fiber morphology and density [14]. Increase in polymer concentration improves the homogeneity of the fiber structure as the incidence of larger void is reducing [8]. Viscous solution contains more polymer molecules than less viscous solution. This contributes to higher packing of polymer molecules per unit volume inside the PAN fiber. As a result, the gel fiber density also increases. The polymer solution also influences polymer molecules during drawing process.

Coagulation bath temperature has great influence on coagulation process. This parameter is responsible in controlling coagulation rate and the diffusion of solvent and non-solvent. Various researchers reported the effect of the coagulation bath temperature on the structure morphology of PAN-based [8,14,15]. Moreover, low bath temperature improves fiber structure that has always been related to the coagulation rates [8]. At low temperature, coagulation is retarded, and more time is available for an internal adjustment of osmotic stresses. In addition, slower coagulation results in less skin formation, and this leads to smaller and fewer voids. As far as the cross section is concerned, at low coagulation temperatures, the outward diffusion of the solvent predominates, resulting in a reduction of diameter. However, at higher temperature, the coagulation takes place by the counter diffusion of the solvent and non solvent, with an increased influx of water to an outflow of solvent. This may lead to the bulging of fiber diameter, which almost in the coagulated form. The coagulation process is also dependent on the jet stretch, which is the first take-up velocity to the theoretical polymer dope velocity at the exit of capillary. The fiber will stretch during spinning process in order to align the molecular chain along the axis, removing the micro voids those may exist in the fiber and helps in raising the Young's modulus [8]. The jet stretch must not be too high because it may break the molecular chain of the fiber.

Recently, the development of solvent free coagulation bath is considered due to the environmental impact of solvent usage. Although the solvent concentration is one of the factors that control the coagulation process, the optimum soaking time will be determined so that the PAN fibers have identical quality to the PAN fibers that are produced using conventional methods. By controlling the temperature and concentration of coagulation bath simultaneously, a huge coagulation system would be required so as to complete the coagulation process of PAN fibers. Such system requires huge amount of solvent in order to maintain solvent concentration in coagulation bath. If the coagulation process needs low temperature, extensive amount of coolant must be used for cooling purposes. Therefore, the aim of this research is to investigate the conditions of PAN fibers formation that provide good characteristics and properties using

solvent free coagulation bath system in order to produce high performance carbon fibers.

2.0 EXPERIMENTAL SET UP

2.1. Polymer Solution Preparation

The polymer solution was prepared by the dissolution of finely PAN powder (Aldrich 18131-5) in DMF at 80 °C for at least 5 hour in order to get homogeneous solution. Two percent of polymer was acrylamide (AM), which was blended with PAN during this process. Subsequently, polymer solution degassed in order to remove bubbles using ultrasonic bath (Branson 3510 Ultrasonic).

2.2. Dry-wet spinning

The fiber spinning was carried out on a spinning machine design by Membrane Research Unit with single hole spinneret of 200 μm diameter. The air gap between the spinneret and coagulation bath was kept at 10 mm. The wind-up drum speed (V_D) was kept at three or four fold faster than extrusion velocity (V_S). The jet stretch can be calculated using the following equation:

$$Jet\ Stretch = \frac{V_D}{V_S} \qquad (i)$$

The temperature of the coagulation bath was varied from 9 °C to 15 °C. After the spinning process, the PAN fibers were undergone drying process for an hour. The fibers were dried in Memmert oven for 1 hour at 50 °C.

2.3. Tensile testing of individual fibers

Mechanical properties (tensile strength and Young's Modulus) of the fibers were obtained using ASTM 3379-75 guidelines. The fiber diameters were measured from the optical image taken under an inverted microscope. The selected fiber was centered and mounted onto slotted

paper tabs with a 1 in. (25.4 mm) gauge length. Upon loading the mounted sample in the grips of the Instron tester, the center portion of the tab was cut with scissors [9]. The sample was then stressed at a constant crosshead speed of 5.00 mm/min until failure.

2.4. X-ray analysis

Wide angle X-ray scattering was performed on PAN fibers tow in order to observe crystallinity of PAN fibers. X-ray diffraction of the samples was obtained on a Philips PW1710 X-ray diffractometer with nickel-filtered Cu Kα radiation at a 1 ° scan rate. For orientation measurements, the fiber samples were wounded on an aluminum sample holder in such a manner that the individual filaments were parallel. The 2θ angle of 16.9 ° was used to determine the fiber orientation and to capture an azimuthal scan. The crystallinity of the samples was calculated according to this equation:

$$Crystallinity = \frac{A_c}{A_c + A_a} \times 100 \qquad (ii)$$

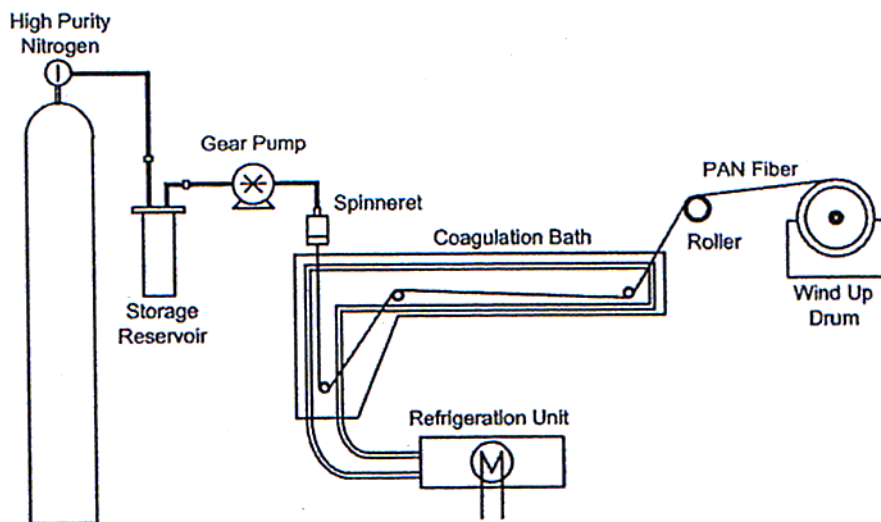where the A_c and A_a are the areas under the crystalline and amorphous curves, respectively.

Figure 1: The laboratory scale for dry-wet spinning process

Table 1: Spinning conditions of PAN fibers

Spinning Dope	PAN/AM/DMF
AM weight % in Polymer	2.0
Polymer Concentration	15,16, 17 and 18 wt %
DopeTemperature	Ambient Temperature
Spinneret Diameter	200 μm
Air Gap Distance	5 mm
Extrusion Velocity, V_s	46 cm/sec
Wind-Up Drum Velocity, V_d	92 to 184 cm/sec
Jet Stretch (V_s/V_d)	2 to 4
Soaking Time	4 to 7 sec
Coagulation Bath Composition	100% H_2O
Coagulation Bath Temperature	9, 12, 15 and 17°C

3.0 RESULTS AND DISCUSSION

3.1. Effect of the coagulation bath temperature on mechanical properties of PAN fibers

The mechanical properties of PAN fibers produced at different coagulation temperatures are represented in Table 2. The tensile strength and Young's modulus were found to be increasing with increasing coagulation bath temperature. The tensile strength of the gel fibers produced at a 9 °C and 15 °C of coagulation bath temperature were 0.82 GPa and 0.96 GPa, respectively. Similarly, the modulus increased from 2.01 GPa to 5.21 GPa when the coagulation bath temperature was increased from 9 to 15 °C. The mechanical properties of PAN fibers produced using solvent free coagulation bath were almost equivalent to the PAN-based carbon fibers that are commercially available. For example, the elastic moduli of the PAN fiber that were produced by Toray (T_2) and Hercules using solvent coagulation bath was 4.34 GPa and 5.38 Gpa, respectively [14].

Based on Table 2, it was found that the improvement in the mechanical properties was due to the enhancement in crystallinity of PAN fiber. The crystallinity refers to the alignment of molecular chains in PAN fiber and

the ratio of crystalline over amorphous region, which is higher in high crystalline fiber. At low temperature of coagulation bath, the coagulation rate was relatively slow. The as-spun fiber was still in gel form and the bonds between polymer chains were weak because of the solvent present. Therefore, the PAN fiber produced at low temperature was easily broken due to high jet stretch. As the temperature increased, the coagulation rate became faster and caused the polymer chains to get close to each other. The high jet stretch applied during spinning process aligned the polymer chains in parallel. At 15 °C coagulation bath temperature, the as-spun fiber consisting semi-gel phase and the fiber was suitable for stretching process. However, by increasing the coagulation bath temperature up to 20 °C, resulted in formation of a fully solid phase fiber due to rapid coagulation process. Although the jet stretch can be applied to the PAN fiber at certain limit, overstretching the fibers will result in breaking the PAN fibers caused by void formation. The void inside the PAN fiber acted as weak linkages or sites for breakage [8].

Table 2: Result for three samples PAN fiber with different coagulation temperature

Coagulation Temperature, °C	Crystallinity, %	Tensile Strength, GPa	Young's Modulus, GPa
9	79	0.82	2.01
12	83	0.93	2.54
15	84	0.96	5.21

4.0 CONCLUSION

From the results obtained, several conclusions can be made;
1. The alignment of PAN fiber molecule chains depends on the temperature of coagulation bath and pre-determined maximum jet stretch.
2. The PAN fiber produced at this temperature displayed 84 % crystallinity as well as 0.96 GPa and 5.21 GPa of tensile strength and Young's modulus, respectively.

3. It is expected that the mechanical properties of PAN fibers can be further improved if the polymer composition and the soaking time are considered during PAN fiber fabrication.

5.0 ACKNOWLEDGEMENTS

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