PREPARATION AND CHARACTERIZATION OF POLYACRYLONITRILE FIBER PRECURSOR USING MULTI-HOLE SPINNERET

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A thesis submitted in fulfilment of the requirements for the award of the degree of Master of Engineering (Gas)

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To my beloved parent,
(\textit{Abang Mahmod Bin Abang Kipli and Salha Binti Majid})

Siblings
(\textit{Abang Mahzrie, Abang Mohd Fardaus and Dayang Zafirah})

and relatives for their inspirational words, best encouragement, undoubted feelings, mind and endless support, inspired and motivated me throughout the success of this research study.
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ABSTRACT

The aims of this study were to prepare and characterize polyacrylonitrile (PAN) fiber as a precursor for carbon fiber production. A dry-jet wet spinning technique with a multi-hole spinneret (10 holes, $\varnothing = 0.350$ mm) and a solvent-free coagulation bath system were adopted in the preparation of PAN fibers precursor. The spinning dope consisted of polymer polyacrylonitrile (PAN) with acrylamide (AM) as an additive. Dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were employed as solvent in the dope formulation. The dopes were prepared at 18 wt.% polymer concentration and coagulation bath temperature was varied between 13 °C to 20 °C. The PAN fibers were characterized using field emission scanning electron microscopy (FESEM), fourier transform infrared (FTIR), differential scanning calorimetry (DSC), thermogravimetry (TGA), x-ray diffraction (XRD) and tensile test. FESEM micrographs showed that at 18 wt.% of polymer concentration, PAN fibers prepared from DMF and DMSO exhibited similar circular cross-sectional structure with different fiber surfaces as coagulation bath temperature increased. Dope prepared from DMF resulted on PAN fibers with rough fiber surface meanwhile PAN fibers produced with DMSO showed smooth fiber surface. Both PAN fibers prepared from DMF and DMSO showed the presence of typical functional groups of precursor fibers particularly nitrile groups which is significant for higher processing temperature. The lowest weight lost was observed approximately 56 wt.% for PAN fibers prepared from DMSO. It showed a significant improvement of the polymer stability which enhanced the carbon yield. The highest glass transition temperature ($T_g$) recorded for PAN fibers fabricated from DMF was 92 °C and both PAN fibers from DMF and DMSO exhibited the highest percentage of crystallinity which was 35 %. The mechanical properties of the prepared fibers are strongly dependent on the type of solvent used during the preparation. PAN fibers prepared from DMSO achieved the maximum of 279.20 kPa on tensile strength while maximum 3.25 GPa Young’s modulus obtained by PAN fibers prepared from DMF. This study concludes that different types of dope solvent and variation of coagulation bath temperature played significant role to determine the fiber structures and properties as well as fabricating PAN fibers via solvent-free coagulation system. The results also elucidate that dry-jet wet spinning technique with a multi-hole spinneret using solvent-free coagulation bath system with 18 wt.% polymer concentration produced PAN fibers continuously without any breakage thus enhanced the production of carbon fiber precursor.
Kajian ini adalah bertujuan untuk menghasilkan dan mencirikan gentian poliakrilonitril (PAN) sebagai prapenanda bagi pengeluaran gentian karbon. Teknik pemutaran pancutan-kering basah yang terdiri daripada pemejam lubang berbilang (10 lubang, $\varnothing = 0.350$ mm) dan sistem takungan pengentalan bebas pelarut telah digunakan untuk penghasilan gentian PAN prapenanda. Larutan pemutaran terdiri daripada PAN sebagai polimer, akrilamid (AM) sebagai bahan tambah. Dimetilformamid (DMF) dan dimetilsulfoksida (DMSO) sebagai pelarut dalam formulasi larutan. Kepekatan polimer disediakan pada 18 wt. % dan suhu takungan pengentalan diubah di antara 13 °C hingga 20 °C. Gentian PAN dicirikan dengan menggunakan mikroskopi imbasan electron pemancaran medan (FESEM), spektroskopi inframerah transformasi fourier (FTIR), pemeteran kalori pengimbasan kebezaan (DSC), analisis gravimetrik terma (TGA), pembelauan X-ray (XRD) dan ujian tegangan. Mikrograf FESEM mendedahkan bahawa pada kepekatan larutan polimer 18 wt.% gentian PAN yang disediakan dari DMF dan DMSO mempamerkan struktur keratan rentas bulatan yang sama dengan permukaan gentian yang berbeza semasa suhu takungan pengentalan ditingkatkan. Larutan yang dihasilkan daripada pelarut DMF mempamerkan permukaan gentian yang kasar sementara larutan yang dihasilkan daripada pelarut DMSO mempamerkan permukaan gentian yang licin. Kedua-dua gentian PAN yang dihasilkan menggunakan pelarut DMF dan DMSO menunjukkan kehadiran kumpulan berfungsi gentian PAN yang lazim terutama kumpulan berfungsi nitril amat penting untuk suhu pemprosesan yang tinggi. Kehilangan berat yang terendah dimiliki oleh gentian PAN yang dihasilkan menggunakan pelarut DMSO iaitu dianggarkan sebanyak 56 wt.%. Ia menunjukkan peningkatan yang ketara pada kestabilan polimer yang telah meningkatkan penghasilan karbon. Suhu peralihan kaca (T_g) yang tertinggi adalah 92 °C direkodkan oleh gentian PAN yang dihasilkan menggunakan larutan DMF. Kedua-dua gentian PAN yang dihasilkan menggunakan larutan DMF dan DMSO mempamerkan peratus kehabluran yang tertinggi sebanyak 35 %. Sifat mekanik gentian adalah sangat bergantung kepada jenis pelarut yang digunakan semasa penyediaan larutan polimer. Dalam kajian ini, maksimum kekuatan tegangan 279.20 kPa telah dicapai oleh gentian PAN yang dihasilkan menggunakan pelarut DMSO sementara modulus Young yang maksimum ialah 3.25 GPa telah dicapai oleh gentian PAN yang dihasilkan menggunakan pelarut DMF. Kajian ini menunjukkan bahawa jenis pelarut dan suhu takungan pengentalan yang berbeza memainkan peranan yang penting dalam menentukan struktur dan sifat gentian serta penghasilan gentian PAN yang berkualiti melalui sistem takungan pengentalan bebas pelarut. Keputusan kajian ini juga menunjukkan bahawa teknik pemutaran pancutan-kering basah bersama pemejam lubang berbilang yang menggunakan sistem takungan pengentalan bebas pelarut dengan kepekatan larutan polimer 18 wt.% telah berjaya menghasilkan gentian PAN secara berterusan tanpa pematahan sepanjang pemprosesan pemutaran sambil meningkatkan keluaran gentian prapenanda karbon.
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<td>Polyacrylonitrile</td>
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<tr>
<td>UHM</td>
<td>Ultra-high-modulus</td>
</tr>
<tr>
<td>HM</td>
<td>High-modulus</td>
</tr>
<tr>
<td>IM</td>
<td>Intermediate-modulus</td>
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<tr>
<td>HT</td>
<td>High-tensile</td>
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<tr>
<td>SHT</td>
<td>Super high-tensile</td>
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<td>HTT</td>
<td>Heat treatment temperature</td>
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<td>DMF</td>
<td>Dimethylformamide</td>
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<td>DMSO</td>
<td>Dimethylsulphoxide</td>
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<td>FRP</td>
<td>Fiber reinforced plastics</td>
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<td>AM</td>
<td>Acrylamide</td>
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<tr>
<td>DMAc</td>
<td>Dimethylacetamide</td>
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<td>NaSCN</td>
<td>Natrium thiocyanate</td>
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<td>ZnCl₂</td>
<td>Zinc Chloride</td>
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<td>CuCl₂</td>
<td>Cuprum Chloride</td>
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<td>CH₄</td>
<td>Methane</td>
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<td>H₂</td>
<td>Hydrogen</td>
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<tr>
<td>HCN</td>
<td>Hydrogen cyanide</td>
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<td>H₂O</td>
<td>Water</td>
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<td>O₂</td>
<td>Oxygen</td>
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<tr>
<td>CO</td>
<td>Carbon monoxide</td>
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<td>CO₂</td>
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<td>NH₃</td>
<td>Ammonia</td>
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<tr>
<td>FTIR</td>
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LIST OF SYMBOLS

\%
\degree C
\text{GPa}
\text{kPa}
\text{ca}
\text{E}_c
\text{E}_p
\text{wt. \%}
\Phi
>
<
\text{GHz}
g/cm^3
\text{C}_p
\text{N}
\text{\mu m}
nm
nm/min
\text{^\circ} C/min
\text{A}_c
\text{A}_a
\text{T}_g
\varnothing
- Percent
- Degree Celcius
- Giga Pascal
- Kilo Pascal
- Circa
- Elastic modulus of carbon fibers
- Elastic modulus of precursor fibers
- Weight percent
- Jet stretch
- More than
- Less than
- Giga Hertz
- Gram per centimeter cubic
- Centipoise
- Newton
- Micrometer
- Nanometer
- Milimeter
- Miligrams
- Milimeter per minute
- Degree per minute
- Area under the crystalline diffraction peaks
- Area under the amorphous zone
- Glass transition temperature
- Diameter
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CHAPTER 1

INTRODUCTION

1.1 Research Background

Carbon fibers are very thin black fibers. It can be much thinner than human hair. Each carbon filament thread is a bundle of many thousand carbon filaments. A single such filament is a thin fiber with a diameter of 5 to 8 micrometers and consists almost exclusively of carbon. Carbon fibers consist of 99.9% of chemically pure carbon (Fitzer, 1985). They can be short or continuous. Their structure can be crystalline, amorphous or partly crystalline (Chung, 1994). The crystalline form has the crystal structure of graphite as shown in Figure 1.1.

![Figure 1.1](image)

**Figure 1.1** The crystal structure of graphite: “a” direction is parallel to the basal planes and “b” direction is perpendicular to the basal planes (Morgan, 2005)
Historically, there are three types of carbon fiber precursors: 1) cellulose (rayon), 2) mesophase pitch and 3) polyacrylonitrile (PAN) (Buckley and Edie, 1993). Carbon fibers from cellulose (rayon) precursor are no longer produced because of the high cost of conversion to carbon. Furthermore, the reaction is more complicated than just simple dehydration and the carbon yield is only of the order of 25-30 %. Pitch precursor, however has a higher yield of 85 % with a high resultant modulus but due to their more graphitic nature, they will have poorer compression. At present, all commercial carbon fibers are produced from PAN precursor.

Carbon fiber properties are significantly dependant on the precursor properties. In order to convert precursor to carbon fiber, three basic requirements of precursor are needed, i.e. (1) it should be easily converted to carbon fiber, (2) it offers a high carbon yield and (3) it allows to be processed economically. PAN has become the attraction as a precursor because of its continuous carbon backbone and the nitrile groups are ideally placed for cyclization reaction to occur which forms ladder structure to enable them throughout higher processing temperatures (Rahaman et al., 2007; Sedghi et al., 2008).

Generally, precursor fibers can be fabricated by various methods such as wet spinning, dry spinning, melt spinning and dry-jet wet spinning. Subsequently, precursor fibers will undergo heat treatment processes. Heat treatment process is significant as it is a conversion stage of precursor fibers into carbon fibers. There are normally three successive stages involving oxidation or stabilization in air, carbonization in an inert environment and graphitization. Precursor fibers are first stretched and simultaneously oxidized in the temperature range of 200-300 °C (Minus and Kumar, 2005; Kannadaguli and Rong, 2004). At this stage, ladder structure will form to allow them to be processed at higher temperature. After oxidation, the fibers are then carbonized in the range of 1000 °C to 1700 °C in an inert atmosphere (Minus and Kumar, 2005). During this heating process the non-carbon elements are removed as volatiles and yield a turbostatic structure. Finally, the fibers are treated at temperature 1500 °C to 3000 °C depending on the fiber type all through graphitization to further improve the basal planes orientation and fiber stiffness.
1.2 Problem Statement

Carbon fibers have been popularly used worldwide as replacement for steel and metal as an alternative material for reinforcement usage. Intensive researches have been continuously carried out to produce an excellent quality of carbon fibers. Dong X-G et al. (2007) and Jain et al. (1987) reported that the properties of carbon fibers mainly depend on the quality of the precursor fibers. There are few precursors that can be used to produce carbon fiber such as polycrylonitrile, pitch and rayon.

Polyacrylonitrile has been found to be the most suitable precursor to obtain carbon fiber with excellent performance (Wang Y-X et al., 2007a). About 90% of the carbon fibers produced are made from PAN fibers (Rahman et al., 2007; Rahaman et al., 2007; Gupta and Harrison, 1996). PAN-based carbon fiber generally has a higher tensile strength than a fiber based on any other precursors due to its high melting point, thermally stable, low weight loss during heat treatments and a high degree of molecular orientation (Mukhlis, 2006).

In spite of all the advantages mentioned on the PAN fiber, there are drawbacks in achieving good mechanical properties of PAN-based carbon fiber. There are the spinning difficulties involving factors such as polymer solution concentration, dope viscosity, coagulation bath temperature and residence time. Finding the optimum polymer solution concentration is a critical factor, in order to successfully spin the fiber. Ji et al. (2007) reported that higher polymer content accompanies the increase of the viscosity whereas Bahrami et al. (2003) reported that with an increase in the concentration of the polymer in the dope the spinnability can be improved, the tenacity increased and the porosity reduced in the cross section of the fiber. Increasing the polymer concentration improves the homogeneity of the fiber structure by reducing the generation of large voids, increasing the density and slightly improving the tenacity (Knudsen, 1963).

Dope viscosity also plays an important role in the spinnability of PAN fiber. A very low viscosity may lead to dope fracture whereas a high viscosity may slow down the spinning speed and coagulation rate (Bajaj et al., 2002). Both, coagulation bath temperature and residence time as well have a huge effect on the coagulation process. Coagulation bath temperature is responsible for controlling the mass-
transfer and the counter-diffusion of the solvent and non-solvent thus influences microscopic and morphological structures as well as mechanical properties of PAN fibers (Rahman et al., 2007; Bahrami et al., 2003; Bajaj et al., 2002). Rahman et al. (2007) reported that a short residence time prevented further inward diffusion of non-solvent towards the center of PAN fibers and the higher the residence time, the more non-solvent diffuses towards the PAN fibers.

The drawback of conventional technique is the high amount of solvent content in the coagulation bath to fabricate PAN fibers for carbon fibers production which could probably cause cancer for a long period of exposure as well as damage the system (Ismail et al., 2008). In addition, it would increase the electrical consumption. According to Bajaj et al. (2002), dry-jet wet spinning technique improves the PAN fibers mechanical properties. Work by Mukhlis (2006) showed that dry-jet wet spinning process via solvent-free coagulation bath with a single-hole spinneret has been successfully carried out and produced PAN fibers with competitive mechanical properties. However, the use of a single-hole spinneret is impractical as it has to take long time to produce PAN fibers precursor in bundle. The big volume of precursor fibers is needed especially during tensile and application testing. Tagawa and Miyata (1997) reported that for composites reinforced, carbon fibers were used in continuous form. Moreover, there is still no study reported on the usage of multi-hole spinneret via solvent-free coagulation bath to produce PAN fibers. Most of previous studies demonstrated that the use of a multi-hole spinneret with high concentration of solvent content in the coagulation bath to produce PAN fibers (Bahrami et al., 2003; Bajaj et al. 2002).

The present study further investigated the use of a multi-hole spinneret and improved the understanding of spinning conditions in solvent-free coagulation bath and to enhance the PAN-based carbon fiber performance and production. Therefore, this study attempts to prepare and characterize PAN fiber precursor with certain polymer concentration for carbon fiber production using a multi-hole spinneret along with the suitability of dry-jet wet spinning conditions.
1.3 Research Objectives

Based on the above problem statements, the objectives of this research are:

(i) To study the effects of the different types of solvent used in the dope solution formulation on the structural of PAN fibers with a multi-hole spinneret.
(ii) To study the effects of coagulation bath temperature, residence time and solvent-free coagulation bath on the structure of PAN fibers.
(iii) To investigate the characteristics of PAN fibers based on the morphology and mechanical properties.

1.4 Research Scopes

In order to achieve the above mentioned objectives, the scopes of this research have been identified:

(i) Preparation of several spinning solutions using DMF and DMSO solvent, respectively and study on the 18 wt.% polymer concentration in fabricating PAN fibers using dry-jet wet spinning technique with a multi-hole spinneret (10 holes) in the solvent-free coagulation bath.
(ii) Investigating the effects of solvent type used during dope solution formulation on the PAN fibers structure.
(iii) Investigating the effects of coagulation bath temperature by varying the coagulation bath temperature at 13 °C, 16 °C and 20 °C on the morphological structure of PAN fiber.
(iv) Characterizing the PAN fibers based on the Field Emission Scanning Electron (FESEM), Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD), Differential Scanning Electron (DSC), Thermogravimetric (TGA) and Tensile Test machine for the PAN fibers performance.
1.5 **Significance of Study**

The significance of the present study are:

(i) PAN fibers precursor fabricated using dry-jet wet spinning with multi-hole spinneret in a solvent-free coagulation system is potential in fiber technology due to the reduction of time consumption as well as enhance the fiber production.

(ii) The solvent-free coagulation bath system could be considered for fabricating PAN fibers precursor as it allows the precursor fibers to be processed economically due to the usage of 100 % water in the coagulation bath as well as minimizing the environmental issue.

(iii) Using solvent-free coagulation bath with multi-hole spinneret, the PAN fibers resulted in an acceptable Young’s modulus of 3.25 GPa compared to Rahman *et al.* (2007) study of 2.93 GPa.


