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

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To my beloved parent,
(Abang Mahmod Bin Abang Kipli and Salha Binti Majid)
Siblings
(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
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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, ∅ = 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 solvents 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.

ABSTRAK

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, ∅ = 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 diubahkan 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 sekali 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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LIST OF ABBREVIATIONS

PAN	-	Polyacrylonitrile
UHM	-	Ultra-high-modulus
HM	-	High-modulus
IM	-	Intermediate-modulus
HT	-	High-tensile
SHT	-	Super high-tensile
HTT	-	Heat treatment temperature
DMF	-	Dimethylformamide
DMSO	-	Dimethylsulphoxide
FRP	-	Fiber reinforced plastics
AM	-	Acrylamide
DMAc	-	Dimethylacetamide
NaSCN	-	Natrium thiocyanate
$ZnCl_2$	-	Zinc Chloride
$CuCl_2$	-	Cuprum Chloride
CH_4	-	Methane
H_2	-	Hydrogen
HCN	-	Hydrogen cyanide
H_2O	-	Water
O_2	-	Oxygen
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
NH_3	-	Ammonia
FTIR	-	Fourier transform infra-red spectroscopy
XRD	-	X-ray diffraction
TGA	-	Thermogravimetric analysis
DSC	-	Differential scanning calorimetric

LIST OF SYMBOLS

%	-	Percent
˚C	-	Degree Celcius
GPa	-	Giga Pascal
kPa	-	Kilo Pascal
ca	-	Circa
E_c	-	Elastic modulus of carbon fibers
E_p	-	Elastic modulus of precursor fibers
wt. %	-	Weight percent
Φ	-	Jet stretch
>	-	More than
<	-	Less than
GHz	-	Giga Hertz
g/cm^3	-	Gram per centimeter cubic
C_p	-	Centipoise
N	-	Newton
μm	-	Micrometer
nm	-	Nanometer
mm	-	Milimeter
mg	-	Miligrams
mm/min	-	Milimeter per minute
˚C/min	-	Degree per minute
A_c	-	Area under the crystalline diffraction peaks
A_a	-	Area under the amorphous zone
T_g	-	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.

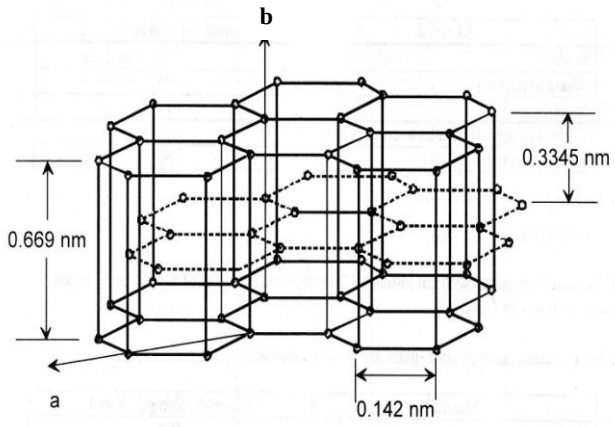

Figure 1.1 The crystal structure of graphite: “a” direction is parallel to the basal planes and “b” direction is perpendicular to the basal planes (Morgan, 2005)

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 polyacrylonitrile, 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.

REFERENCES

Bahrami, S.H., Bajaj, P., and Sen, K. (2003). Effect of Coagulation Conditions on Properties of Poly(acrylonitrile-carboxylic acid) Fibers. *Journal of Applied Polymer Science,* Vol.89, 1825-1837.

Bai, Y-J., Wang, C-G., Lun, N., Wang, Y-X., Yu, M-J., and Zhu, B. (2006). HRTEM Microstructures of PAN Precursor Fibers. *Carbon,* Vol. 44, 1773-1778.

Bajaj, P., Sreekumar, T.V., and Sen, K. (2002). Structure Development during Dry-Jet-Wet Spinning of Acrylonitrile/Vinyl Acids and Acrylonitrile/Methyl Acrylate Copolymers. *Journal of Applied Polymer Science,* Vol.86, 773-787.

Balasubramanian, M., Jain, M.K., Bhattacharya, S.K., and Abhiraman, A.S. (1987). Conversion of Acrylonitrile-based Precursors to Carbon Fibers Part 3: Thermooxidative Stabilization and Continuous, Low Temperature Carbonization. *Journal of Materials Science,* Vol. 22, 3864-3872.

Baojun, Q., Ding, P., and Zhenqiou, W. (1986). The Mechanism and Characteristics of Dry-Jet Wet-Spinning of Acrylic Fibers. *Journal of Advances in Polymer Technology*, Vol.6, No.4, 509-529.

Buckley, J.D., and Edie, D.D. (1993). *Carbon-Carbon Materials and Composites*. New Jersey: Noyes Publications.

Chawla, K.K. (1998). *Fibrous Materials*. England: The Press Syndicate of University of Cambridge.

Chen, J.C., and Harrison, I.R. (2002). Modification of Polyacrylonitrile (PAN) Carbon Fiber Precursor via Post-spinning Plasticization and Stretching in Dimethylformamide (DMF). *Carbon,* Vol. 40, 25-45.

Chung, D.D.L. (1994). *Carbon Fiber Composites*. Boston: Butterworth-Heinemann Publisher.

Dong, R., Keuser, M., Zeng, X., Zhao, J., Zhang, Y., Wu, C., and Pan, D. (2008). Viscometric Measurement of the Thermodynamics of PAN

Terpolymer/DMSO/Water System and Effect of Fiber-Forming Conditions on the Morphology of PAN Precursor. *Journal of Polymer Science*, Vol. 46, 1997-2011.

Dong, X-G., Wang, C-G., Bai, Y-J., and Cao, W-W. (2007). Effect of DMSO/H_2O Coagulation Bath on the Structure and Property of Polyacrylonitrile Fibers during Wet-Spinning. *Journal of Applied Polymer Science,* Vol.105, 1221-1227.

Dong, X-G., Wang, C-G., Chen, J., and Cao, W-W. (2008). Crystallinity Development in Polyacrylonitrile Nascent Fibers during Coagulation. *Journal. Polymer Research,* Vol. 15, 125-130.

Donnet, J.B., and Bansal, R.C. (1984). *Carbon Fibers*. New York: Marcel Dekker Inc.

Donnet, J.B., Rebouillat, S., Wang, T.K., and C.M.Peng, J. (Eds.) (1998). *Carbon Fibers*. (3rd ed.). New York: Marcel Dekker Inc.

Doppert, H.L., and Harmsen, G.J. (1973). The Influence of the Stretch Ratio on the Rate of Diffusion in a Wet-Spinning Process. *Journal of Applied Polymer Science,* Vol.17, 893-903.

E-Composite, *Growth Opportunities in Carbon Fiber Composites Market 2006 – 2011*, E-Composites, Inc. 2006.

Edie, D.D. (1998). The Effect of Processing on the Structure and Properties of Carbon Fibers. *Carbon,* Vol.36, No.4, 345-362.

Farsani, R.E., Shokuhfar, A., and Sedghi, A. (2007). Conversion of Modified Commercial Polyacrylonitrile Fibers to Carbon Fibers. *International Journal of Mechanical Systems Science and Engineering* 1, 4 182-185.

Fitzer, E. (Ed.) (1985). *Carbon Fibres and Their Composites*. Berlin: Springer-Verlag.

Gabbott, P. (2008). *Principles and Applications of Thermal Analysis.* Blackwell Publishing Ltd.

Galasso, F.S. (1989). *Advanced Fibers and Composites.* Gordon and Breach Science Publishers.

Gupta, A., and Harrison, I.R. (1996). New Aspects in the Oxidative Stabilization of PAN-based Carbon Fibers. *Carbon,* Vol.34, No. 11, 1427-1445.

Gupta, A.K., and Maiti, A.K. (1982). Effect of Heat Treatment on the Structure and Mechanical Properties of Polyacrylonitrile Fibers. *Journal of Applied Polymer Science*, Vol.27, 2409-2416.

Gupta, B., Revagade, N., Anjum, N., Atthoff, B., and Hilborn, J. (2006). Preparation of Poly(lactic acid) Fiber by Dry-Jet-Wet-Spinning. I. Influence of Draw Ratio on Fiber Properties. *Journal of Applied Polymer Science*, Vol.100, 1239-1249.

Han, C.D. and Park, J.Y. (1973). A Study of Shaped Fiber Formation. *Journal of Applied Polymer Science*, Vol. 17, 187-200.

He, D-X., Wang, C-G., Bai, Y-J., Lun, N., Zhu, B., and Wang, Y-X. (2007). Microstructural Evolution during Thermal Stabilization of PAN Fibers. *Journal Material Science*, Vol. 42, 7402-7407.

Hou, C., Liang, Y., and Wang, C-G. (2005). Determination of the Diffusion Coefficient of H_2O in Polyacrylonitrile Fiber Formation. *Journal of Polymer Research*, Vol. 12, 49-52.

Hou, C., Qu, R., Wang, C., and Ying, L. (2006). Diffusion Coefficient of DMF in Acrylic Fiber Formation. *Journal of Applied Polymer Science*, Vol. 101, 3616-3619.

Howard, W.H. (1961). Glass Temperatures of Polyacrylonitrile and Acrylonitrile Vinyl Acetate Copolymers. *Journal of Applied Polymer Science*, Vol. V, 303-307.

Http://www.carbonfibrechina.com. Large tow for carbon fiber manufacturer. Retrieved on 21st February 2008.

Http://www.merck.de/. Material safety data sheet (MSDS) for dimethylformamide and dimethylsulfoxide. Retrieved on 13th July 2008.

Http://www.reinforcedplastics.com/view/1110/rapid-growth-forecast-for-carbon fibre-market/. Retrieved on 15th July 2009.

Http://www.sigmaaldrich.com. Material safety data sheet (MSDS) for polyacrylonitrile and acrylamide. Retrieved on 8th August 2008.

Huang, X., (2009). Fabrication and Properties of Carbon Fibers. *Materials*, Vol. 2, 2369-2403.

Ismail A.F., Rahman M.A., Mustafa A., and Matsuura T. (2008). The Effect of Processing Conditions on a Polyacrylonitrile Fiber Produced using a Solvent-

free Coagulation Process. *Journal of Materials Science and Engineering A,* Vol. 485, 251-257.

Jain, M.K., and Abhiraman, A.S. (1987). Conversion of Acrylonitrile-based Precursor Fibres to Carbon Fibres Part 1: A Review of the Physical and Morphological Aspects. *Journal of Materials Science,* Vol. 22, 278-300.

Ji, B-H., Wang, C-G., and Wang, Y-X. (2007). Effect of Jet Stretch on Polyacrylonitrile As-Spun Fiber Formation. *Journal of Applied Polymer Science,* Vol. 103, 3348-3352.

Ji, B-H., Wang, J-H., Wang, C-G., and Wang, Y-X. (2008). Study on the Formation Process of Polyacrylonitrile As-Spun Fiber. *Journal of Applied Polymer Science,* Vol.108, 328-333.

Ji, M., Wang, C., Bai, Y., Yu, M., and Wang, Y. (2007). Structural Evolution of Polyacrylonitrile Precursor Fibers during Preoxidation and Carbonization. *Polymer Bulletin,* Vol. 59, 527-536.

Kannadaguli, M., and Rong, H. (2004). Carbon Fibers (Updated: April 2004) http://web.utk.edu/~mse/pages/Textiles/CARBON%20FIBERS.htm .

Kim, C., Cho, Y.J., Yun, W.Y., Ngoc, B.T.N., Yang, K.S., Chang, D.R., Lee, J.W., Kojima, M., Kim, Y.A., and Endo, M. (2007). Fabrications and Structural Characterization of Ultra-fine Carbon Fibres by Electrospinning of Polymer Blends. *Solid State Communications*, Vol. 142, 20-23.

Knudsen, J.P. (1963). The Influence of Coagulation Variables on the Structure and Physical Properties of an Acrylic Fiber. *Textile Research Journal*, Vol. 33, 13-20.

Ko T-H, (1994). The Influence of Pyrolisis on Physical Properties and Microstructure of Modified PAN fibers during Carbonization. *Journal of Applied Polymer Science,* Vol.43, 589-600.

Kobashi, T. and Takao, S. (1987). Method for the Production of High Strength Polyacrylonitrile Fiber. (U.S. Patent 4,659,529).

Kobayashi, Y., Okajima, S., and Kosuda, H. (1967). Change of Orientation by Thermal Contraction of Polyacrylonitrile Fiber, *Journal of Applied Polymer Science,* Vol. 11, 2525-2531.

Krigbaum, W.R., and Tokita, N. (1960). Melting Point Depression Study of Polyacrylonitrile. *Journal of Polymer Science,* Vol. XLIII, 467-488.

Kruchinin, N.P., Spirova, T.A., Medvedev, A.T., Serkov, A.T., Radishevskii, M.B., Volodin, V.I., Prokhorov, V.A., Krutova, I.N., Egorova, and Grekhova E.V. (1991). Morphological and Structural Features of Polyacrylonitrile Fibers Spun by the Dry-wet Method. Khimicheskie Volokna, No. 3, pp.19-22.

Langley, M. (1973). *Carbon Fibers In Engineering*. United Kingdom, McGraw Hill Book Company.

Lee, K.J., and Chen, Z.Y. (2003). Microstructure Study of PAN-pitch-based Carbon-carbon Composite. *Materials Chemistry and Physics*, Vol. 82, 428-434.

Liu, F., Wang, H., Xue, L., Fan, L., and Zhu, Z. (2008). Effect of Microstructure on the Mechanical Properties of PAN-based Carbon Fibers during High-temperature Graphitization. *Journal of Materials Science,* Vol. 43, 4316-4322.

Liu, J-J., Ge, H., and Wang, C-G. (2006). Modification of Polyacrylonitrile Precursors for Carbon Fiber via Copolymerization of Acrylonitrile with Ammonium Itaconate. *Journal of Applied Polymer Science,* Vol.102, 2175-2179.

Loidl, D., Paris, O., Rennhofre, H., Muller, M. and Peterlik, H. (2007). Skin-core structure and Bimodal Weibull Distribution of the Strength of Carbon Fibers. *Carbon* 45, 2801-2805.

Mikolajczyk, T., Bogun, M., and Kowalczyk, A. (2005). Effect of Fibre-spinning Conditions on the Properties of Nanosilica-containing Precursor PAN Fibres. *July/September 2005*, Vol.13, No.3. 30-34.

Min, B. G., Sreekumar, T.V., Uchida, T., Kumar, S. (2005). Oxidative Stabilization of PAN/SWNT Composite Fiber. *Carbon*, Vol. 43, 599-604.

Minus, M.L., and Kumar, S. February (2005). The Processing, Properties, and Structure of Carbon Fibers. *Overview High-Performance Fibers*, 52-58.

Mittal, J., Mathur, R.B., and Bahl, O.P. (1997). Post Spinning Modification of PAN Fibres-A Review. *Carbon,* Vol.35, No.12, 1713-1722.

Mittal, J., Mathur, R.B., Bahl, O.P., and Inagaki, M. (1998). Post Spinning Treatment of PAN Fibers using Succinic Acid to Produce High Performance Carbon Fibers. *Carbon*, Vol. 36, 893-897.

Moreton, R., and Watt, W. (1974). The Spinning of Polyacrylonitrile Fibres in Clean Room Conditions for the Production of Carbon Fibres. *Carbon,* Vol. 12, 543-554.

Morgan, P. (2005). *Carbon Fibers and Their Composites*. Boca Raton: Taylor and Francis Group.

Muhammad Syukri Bin Abd. Rahaman (2006). Development and Characterization of Carbon Fiber from Polyacrylonitrile Precursor. M.Sc. Thesis. Universiti Teknologi Malaysia, Skudai.

Mukhlis Bin A. Rahman (2006). *Effects of Fabrication Conditions in the Solvent-Free Coagulation Process on the Structural and Mechanical Properties of Polyacrylonitrile/Acrylamide Fibers*. M.Sc. Thesis. Universiti Teknologi Malaysia, Skudai.

Ouyang, Q., Cheng, L., Wang, H., and Li, K. (2008). Mechanism and Kinetics of the Stabilization Reactions of Itaconic Acid-modified Polyacrylonitrile. *Polymer Degradation and Stability,* Vol. 93, 1415-1421.

Padhye, M.R., and Karandikar, A.V. (1987). Effect of Thermal and Solvent Treatment on the Viscoelastic Behavior of PAN Fiber in the Glass-Rubber Transition Region. *Journal of Applied Polymer Science*, Vol. 33, 1675-1682.

Pakshver, E.A., Semenova, N.A., and Neverov, A.P. (1977). Glass Transition Temperature of As-spun Polyacrylonitrile Fibre. Plenum Publishing Corporation. No. 2, 40-41.

Paul, D.R. (1968a). A Study of Spinnability in the Wet-spinning of Acrylic Fibers. *Journal of Applied Polymer Science*, Vol. 12, 2273-2298.

Paul, D.R. (1968b). Diffusion During the Coagulation Step of Wet-Spinning. *Journal of Applied Polymer Science*, Vol.12, 383-402.

Peng, G-Q., Wen, Y-F., Yang, Y-G., Liu, L., and Wang, W. (2009) Effect of Dope Extrustion Rate on the Formation and Characterization of Polyacrylonitrile Nascent Fibers during Wet- Spinning. *Polymer Bulletin*. 62, 657-666.

Pfeiffer, R.E., and Peacher S.E. (1980). Process for Melt-spinning Acrylonitrile Polymer Fiber. (U.S. Patent 4,220,617).

Preta, I.F.C., Sakata, S.K., Garcia, G., Zimmermann, J.P., Galembeck, F., and Giovedi, C. (2007). Thermal Behavior of Polyacrylonitrile Polymers Synthesized under Different Conditions and Comonomer Compositions. *Journal of Thermal Analysis and Calorimetry*, Vol. 87, 657-659.

Rahaman, M.S.A., Ismail, A.F., and Mustafa, A. (2007). A Review of Heat Treatment on Polyacrylonitrile Fiber. *Journal of Polymer Degradation and Stability*, Vol. 92, 1421-1432.

Rahman, M.A., Ismail, A.F., and Mustafa, A. (2007). The Effect of Residence Time on the Physical Characteristics of PAN-based Fibers Produced using a Solvent-free Coagulation Process. *Journal of Material Science and Engineering A*, Vol. 448, 275-280.

Reichardt, M., Pieper, C.,Nogaj, A., Sandhu, S.S., and Gärtner, E. (1983). Process for the Production of High-strength Filaments from Dry-spun Polyacrylonitrile. (U.S. Patent 4,421,708).

Rosenbaum, S. (1965). Polyacrylonitrile Fiber Behavior. I. Mechanisms of Tensile Response. *Journal of Applied Polymer Science*, Vol. 9, 2071-2084.

Saufi, M.S. and Ismail, A.F. (2002). Development and Characterization of Polyacrylonitrile (PAN) Based Carbon Hollow Fiber Membrane. *Songklanakarin Journal Science Technology,* 843-854.

Sedghi, A., Farsani, R. E., and Shofukor, A. (2008). The Effect of Commercial Polyacrylonitrile Fibers Characterizations on the Produced Carbon Fibers Properties. *Journal of Materials Processing Technology*, Vol. 198, 60-67.

Seymour, R.B., and Porter, R.S. (1993). *Manmade Fibers: Their Origin and Development*, Elsevier Science Publisher Ltd.

Shimada, T.O., and Imai, K. and Miyahara, N. (1990). Process for Preparing a Carbon Fiber of High Strength. (U.S. Patent 4,925,604).

Shimamura, M., Minakuchi, H., Sakai, H., Kuwabara, T., Yuki, K., Abe, T., and all of Iyo-gun. (1971). Process for the Preparation of Acrylic Fibers with Odd-shaped Sections. (U.S. Patent 3,621,087).

Simitzis, J., and Soulis, S. (2008). Correlation of Chemical Shrinkage of Polyacrylonitrile Fibres with Kinetics of Cyclization. *Polymer International,* Vol. 57, 99-105.

Smith, C. (2001). *Environmental Physics*. Published by Routledge Taylor & Francis Group.

Soon Wai Loon (2006). *Effects of Coagulation Temperature and Polymer Concentration on the Morphology and Mechanical Properties of Polyacrylonitrile Precursor Fiber Fabricated through Solvent-Free Coagulation Process*. B.Eng. Thesis. Universiti Teknologi Malaysia, Skudai.

Stoyanov, A.I. (1982). Influence of the Content of Polymer with Different Molecular Weights in Spinning Solutions on Properties of Acrylic Fibers. *Journal of Applied Polymer Science*, Vol. 27, 235-238.

Tagawa, T., and Miyata, T. (1997). Size Effect on Tensile Strength of Carbon Fibers. *Material Science and Engineering* A238, 336-342.

Tan, L., Chen, H., Pan, D., and Pan, N. (2008). Investigating the Spinnability in the Dry-Jet Wet Spinning of PAN Precursor Fiber. *Journal of Applied Polymer Science,* Vol. 110, 1997-2000.

Tsai, J-S and Wu, C.J. (1993). Effect of Cross-section Evenness for Polyacrylonitrile Precursor on the Properties of Carbon Fibre. *Journal of Material Science Letters* 12, 411-413.

Tsai, J-S. (1994). Orientation Change for Polyacrylonitrile Precursor during Oxidation. *Journal of Materials Science Letters* 13, 1162-1163.

Tsai, J-S., and Lin, C-H. (1991a). Effect of Comonomer Composition on the Properties of Polyacrylonitrile Precursor and Resulting Carbon Fiber. *Journal of Applied Polymer Science*. Vol. 43, 679-685.

Tsai, J-S., and Lin, C-H. (1991b). The Effect of Molecular Weight on the Cross Section and Properties of Polyacrylonitrile Precursor and Resulting Carbon Fiber. *Journal of Applied Polymer Science*, Vol. 42, 3045-3050.

Walczak, Z.K. (1977). *Formation of Synthetic Fibers*, Gordon and Breach Science Publishers Inc.

Wang, C-G., Dong, X-G and Wang, Q-F. (2009). Effect of Coagulation on the Structure and Property of PAN Nascent Fibers during Dry Jet Wet-spinning. *Journal Polymer Research,* Vol.16, 719-724.

Wang, Y-X., Wang, C-G., and Yu, M-J. (2007b). Effects of Different Coagulation Conditions on Polyacrylonitrile Fibers Wet Spun in a System of Dimethylsulphoxide and Water. *Journal of Applied Polymer Science,* Vol. 104, 3723-3729.

Wang, Y-X., Wang, C-G., Wu, J-W., and Jing, M. (2007a). High Temperature DSC Study of Polyacrylonitrile Precursors during Their Conversion to Carbon Fibers. *Journal of Applied Polymer Science,* Vol.106, 1787-1792.

Wangxi, Z., Jie, L., and Gang, W. (2003). Evolution of Structure and Properties of PAN Precursors during Their Conversion to Carbon Fibers. *Carbon,* Vol. 41, 2805-2812.

Warner, S.B., Uhlmann, D.R. and Peebles, L.H. (1979). Oxidative Stabilization of Acrylic Fibres. *Journal of Materials Science,* Vol. 14, 1893-1900.

Wu, G.P., Lu, C.X., Zhang, R., Wu, X.P., Ren, F.Z., Li, K.X., He, F., and Ling, L.C. (2004). Effect of Moisture on Stabilization of Polyacrylonitrile Fibers. *Journal of Materials Science*, Vol. 39, 2959-2960.

Ying, L., Hou, C., and Qun, W. (2007). Rheological Behavior of Acrylonitrile/Ammonium Acrylate Copolymer Solutions. *Journal of Applied Polymer Science*, Vol.103, 2320-2324.

Yu, M., Wang, C. Bai, Y., Wang, Y., and Xu, Y. (2006a). Influence of Precursor Properties on the Thermal Stabilization of Polyacrylonitrile Fibers. *Polymer Bulletin* 57, 757-763.

Yu, M., Wang, C., Bai, Y., Wang, Y., and Zhu, B. (2006b). Evolution of Tension during the Thermal Stabilization of Polyacrylonitrile Fibers under Different Parameters. *Journal of Applied Polymer Science*, Vol. 102, 5500-5506.

Zeng, X.., Hu, J., Zhao, J., Zhang, Y., and Pan, D. (2007). Investigating the Jet Stretch in the Wet Spinning of PAN Fiber. *Journal of Applied Polymer Science*, Vol.106, 2267-2273.