INFRARED STUDIES ON THERMALLY STABILIZED POLYACRYLONITRILE (PAN) FIBER

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ABSTRACT

This study reports the investigation of the fiber when subjected to heating process in the temperature range of 200-300 °C. This was conducted under atmospheric condition with heating rate as low as 1°C/min. The structure of PAN fiber especially the nitrile group ($C\equiv N$) changed significantly with time and heating temperature. A new peak around 1600 cm^{-1} wavenumber, which represented the double bond structure ($C=N$) was observed. That triple bond of nitrile group had been eliminated when the final heating temperature reached 300 °C. In addition, high soaking time could help to accelerate the changes in the PAN fiber structure. This study also found that, regardless of the duration of soaking time, the stabilization of PAN fiber can still be stabilized at 300 °C.

Keywords: Polyacrylonitrile, Stabilization, Infra red.

1.0 INTRODUCTION

There are various types of precursors in producing carbon fiber. Recent studies presented a large variety of carbon fibers derived from PAN (including copolymers), pitch, rayon, pitch and etc [1-6].

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Among the precursors that have been widely used, polyacrylonitrile (PAN) based fibers are the most important fiber that produce high performance carbon fiber [7-9]. Seventy to eighty percent of PAN precursor had been commercially used in producing carbon fiber [10,11]. Howe and Jones [12] also stated that PAN was more favorable compared to pitch due to its better susceptibility than pitch fiber.

Recent studies established that PAN fiber was on a large scale in textile industry and became one of the most suitable and widely applied material for making high performance carbon fiber [13,14]. According to Traceski [15], the total worldwide production of PAN based carbon fiber in 1989 was approximately 19 million lbs per year and increased up to 26 million lbs by next year. In addition, the worldwide outlook demand of PAN carbon fibers are currently amounting to nearly $6 billion pound per year worldwide effort [16,17]. So, the widely available PAN precursor had triggered the production of carbon fiber.

The successful conversion PAN to high strength, high modulus fibers depend in part upon understanding of the thermal and oxidative reaction. Liu *et al.* [18] listed three main steps in converting of PAN based fiber precursor to carbon fiber. They are:

i. Oxidative stabilization, which form ladder structure to enable them to undergo processing at higher temperatures

ii. High temperature carbonization, ($\leq 1\,600\,°C$) to evolve non-carbon atoms and yield a turbostatic structure.

iii. Further heating, up to 2000 °C to improve the orientation of the basal planes and the stiffness of fibers, which also known as graphitization.
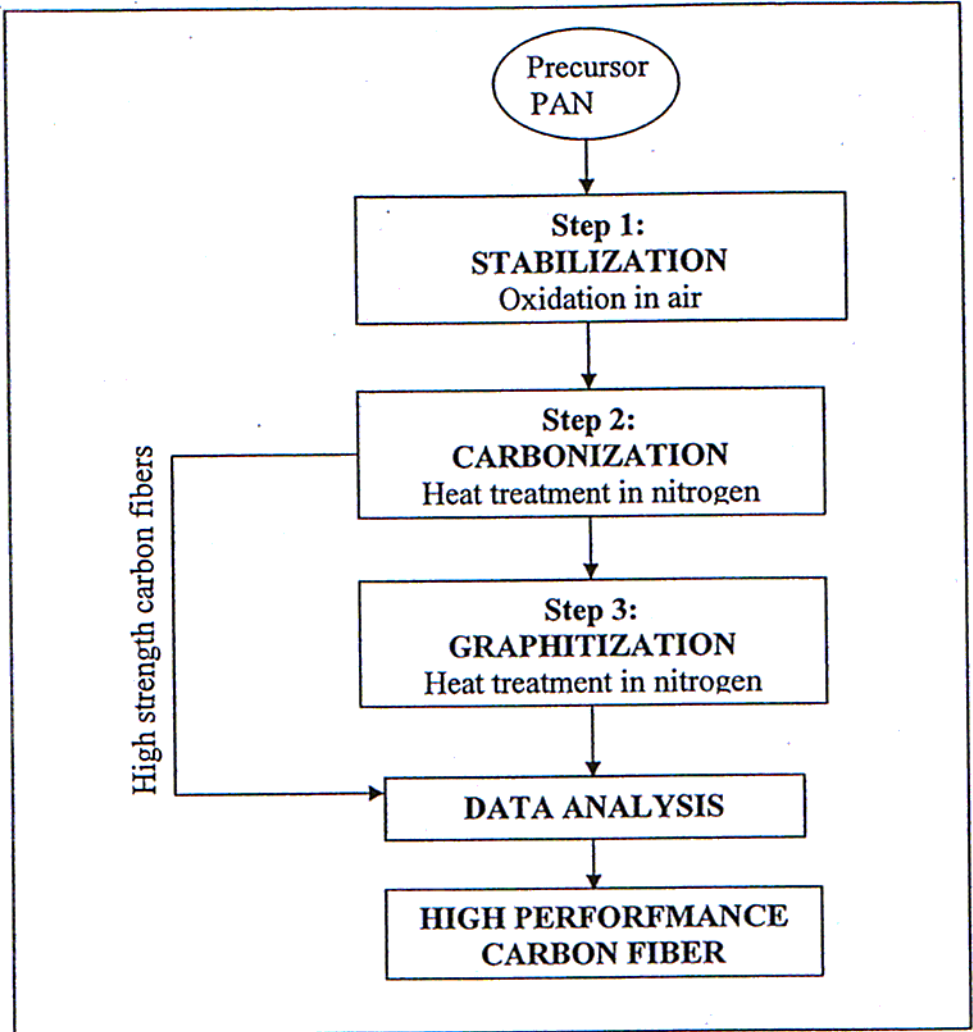
Figure 1 : The conversion process of PAN based carbon fiber.

Among the conversion steps shown in Figure 1, stabilization process is the most important part in order to produce high performance carbon fiber. Stabilization process, which is conducted at atmospheric condition can change the chemical structure of the fiber and avoiding the PAN polymer from softening and thus resulting in thermally stable fiber [11]. This process is necessary to hold the molecules of the fiber together and

to increase the stiffness through cyclization process [19-22]. Oxygen on the other hand, plays a significant role in the initiation [23]. PAN fiber with optimum stabilization can produce higher modulus fiber than unstablized fiber or even the fiber that was prepared at high temperature stabilization [24].

Recently, the stabilization process plays an important role in converting PAN fiber into an infusible stable ladder polymer by converting the triple bond (C≡N group) to double bond (C=N group) structure [14,25]. The process can develop cross-link between the molecules of PAN fiber [26], which operates at high temperature. Setnescu *et al.*, [27] observed CH_2 and CN groups disappeared completely due to elimination, cyclization and aromatization reactions and formed C=C, C=N and =C–H groups. Although stabilization could be done in an inert atmosphere, a polymer back-bone containing oxygen-bearing groups that evolve in PAN ladder structure (Figure 1.2) could provide greater stability to sustain high temperature processing [28].
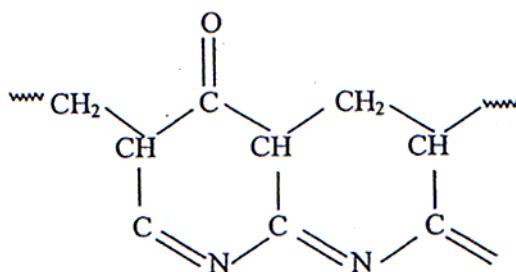

Figure 2 : Ladder PAN Structure [26]

Through IR analysis, PAN fiber showed prominent peaks at 2940 cm^{-1} (– CH stretch), 2240 cm^{-1} (C≡N stretch) and 1452 cm^{-1} (–CH_2 band) wavenumber and for SAF with 1 % IA and 6 % MA, the carbonyl stretch of comonomer units appeared at 1730 cm^{-1} wavenumber [29]. According to Conley and Beron [30], two dominant peaks, at 2940 and 2240 cm^{-1} wavenumber started to decrease at 180 °C due to the formation of cyclization reaction. In addition, after stabilization followed by the pyrolysis process, that two peaks, almost disappeared completely, and subsequently new peaks appeared around 800 cm^{-1} and 1600 cm^{-1}

wavenumber [27]. The changing in peaks were due to the formation of C=C, C=N and =C–H, meanwhile the comonomer of carbonyl peak at 1730 cm^{-1} has also decreased.

2.0 EXPERIMENTAL

2.1 Dope preparation

Introducing comonomer in polyacrylonitrile precursor is an important part in producing high performance carbon fiber. Homopolymer of polyacrylonitrile has a glass transition temperature of T_g= 120 °C. Thus, the polymer is in a glassy phase at ambient temperature. This glassy phase causes spinning to be more difficult due to spinnability and drawbility process. In addition, small fiber diameter in the glassy phase will make the fiber more brittle. By using comonomers it will improve the solubility, spinnability, drawbility process and also will reduce the glass transition temperature. Other advantages of using comonomers include lowering stabilization time, extending the thermal degradation, controlling the heat flux better during oxidative cyclization [31].

In this study, N,N-dimethylformamide or DMF was chose to dissolve PAN and its comonomers. DMF with formula molecule of C_3H_7ON with a molecular structure shown in Figure 2.1 has high-boiling point, low-volatility and polar solvent. The existing hydrogen bonds in DMF structure interacts with water making it, water soluble [32]. This physical characteristic enables DMF the suitable candidate to be PAN polymer solvent.
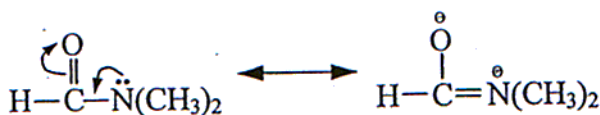
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{N}(CH_3)_2 \quad \longleftrightarrow \quad H-\overset{\overset{\displaystyle \overset{\ominus}{O}}{|}}{C}=\overset{\oplus}{N}(CH_3)_2$$

Figure 3: Molecular structure of dimethylformamide.

In order to remove moisture content in PAN polymers, they were heated in the vacuum oven and air oven (Thelco Oven) for 1 day each before the preparation of solution. In dope preparation, 20 wt.% solutions were

chosen to be dissolved in the solvent as proposed by Qin [33]. For mixing temperature, it should be lower than solvent boiling point to inhibit evaporation of solvent during blending process. But the temperature also must not be too low to accelerate the blending and dissolution process.

Finally, this process ensured that a completely homogenous solution was produced. To form the homogenous solution, at least 7-9 hours were needed to blend and to mix the PAN polymers. During this process, it was expected some micro-bubble would produce that could cause bad fiber formation. This bubbles were removed by using ultrasonic treatment (Branson 3510 Ultrasonics) for 48 hours.

2.2 Spinning technique

There are various types of spinning techniques. In 1994, Tsurumi [34] proposed two methods for spinning acrylic fiber; immersion method (wet spinning) and air gap method (dry wet spinning). During this research, the dry/wet spinning method was used to fabricate PAN fiber. Figure 4 has shown a schematic diagram of spinning system that was used during this research.

Spinning solution was extruded through a spinneret to form a nascent fiber at an ambient temperature which introduced dry phase separation through an air gap. The fiber was then immersed into nonsolvent (water) coagulation bath for wet separation and then to the washing treatment bath. The coagulation bath temperature was controlled at 10 °C by refrigeration/heating unit to ensure rapid solidification, while washing bath was kept at ambient temperature. The resulting fiber that had a diameter of 50 μm, was subjected to solvent exchange in water for 1 day before drying at ambient condition.
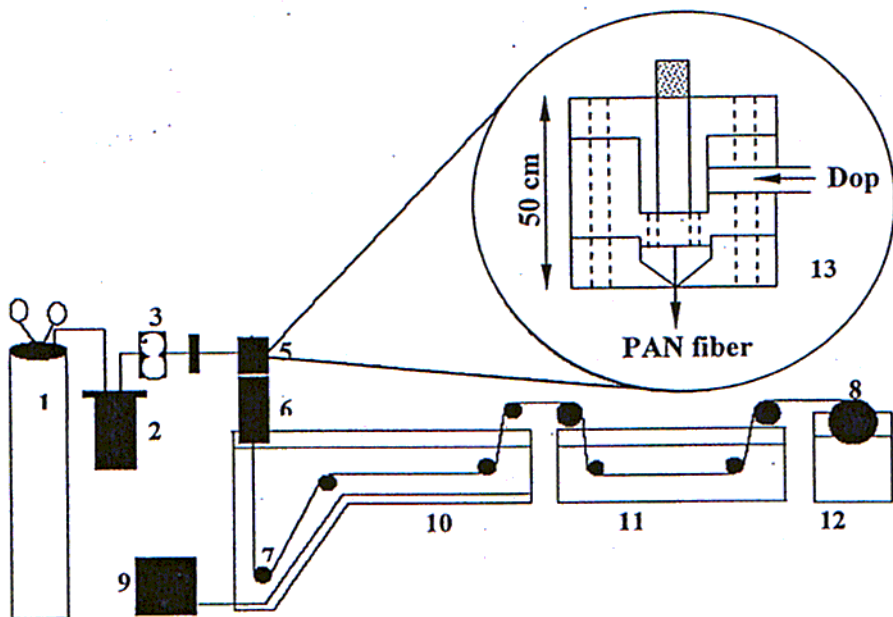
Figure 4: A schematic diagram of PAN fiber spinning system: (1) dope reservoir; (2) gear pump; (3) on line filter, 7mm; (4) spinneret; (5) force convective tube; (6) roller; (7) wind-up drum; (8) refrigeration/heating unit; (9) coagulation bath; (10) washing/treatment bath; (11) wind-up bath; (12) schematic spinneret, modified from [35]

2.2 Stabilization Process

Stabilization process influences the processing sequence that are used to convert PAN precursors to carbon fiber which determine either final carbon fiber have proper properties or not. During this process, PAN fiber bundles were inserted into a quartz tube and wrapped with stainless steel wire type 304 (outer diameter 3 mm) at both end. Then, the quartz tube was inserted into Carbolite wire wound tube furnace (Model CTF 12/65/550) that could be set to a maximum temperature of 1200°C. The PAN chain was cross-linked by conducting a slow heating treatment on the PAN fiber. As a result, the new structure could withstand the high temperature condition during pyrolysis. The heating rate used was as low as 1 °C/min, because if heating temperature was more than 5 °C/min, the

fiber would shrink [36]. During the final heating process, the temperature was varied from 200-300 °C with an increment of 10 °C for every 1 and 2 hour of soaking time. Since the shrinkage could occur during the heat treatment and eventually could deteriorate the fiber properties, the stabilization process must be carried out by applying a tension to the fiber, with a permanent weight load. The stabilization system as shown in Figure 5 was used in this research.
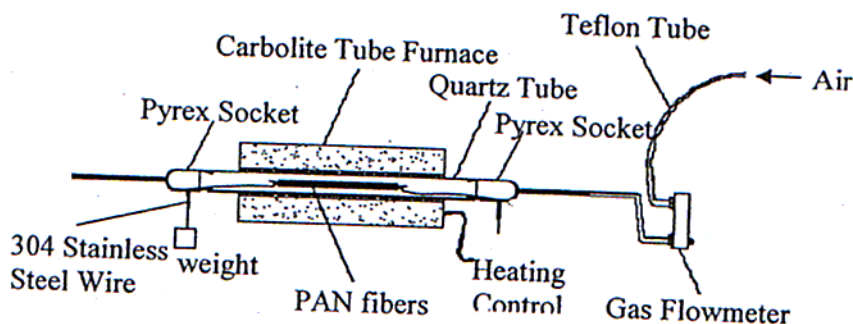

Figure 5: Stabilization heating system

2.3 Fourier Transform Infrared Spectroscopy (FTIR) of PAN fiber.

Fourier Transform Infrared Spectroscopy (FTIR) is one of the methods to determine the existances and information on organic structure. In this study, infrared was used to identify the functional group of PAN fiber before and after heating treatment. The stabilized fibers were grinded into small particle and mixed well with Potassium Bromide (KBr). The mixed were pressed to form a thin layer, then the sample were subjected to FTIR analysis.

3.0 RESULTS AND DISCUSSION

The stabilization process prior to the carbonization of PAN fiber is usually conducted in atmospheric condition which will provide a better stability for PAN fiber. It is known that by changing the stabilization temperature, the molecular structure of the PAN fiber will be affected. In

addition, the conversion of the PAN fiber (having a linear C-H chain with pendant C≡N and C=O/C-O groups) with the presence of oxygen, in the stabilization stage, is expected to cause the following structural changes [37,38]:

1. Cyclization of pendant cyanide groups, leading to a ladder type structure.
2. Dehydrogenation, leading to formation of conjugated double bonds; and
3. Oxidation, leading to a removal of carboxylic acid group (from third comonomer) and loosely bonded hydrogen.

The existence of functional groups PAN fiber were determined using infrared (IR) spectra. PAN fiber showed peaks in the range of 3000-2850 cm^{-1} (–CH stretch), 2260-2240 cm^{-1} (C≡N stretch) and 1465 cm^{-1} (–CH$_2$ band). Figure 3.1 shows the spectrum of the PAN fiber before the fiber was stabilized. As Dalton et al. [29] found in their study, there were four important peaks could be seen in the graft. Very sharp and strong peak assigned to nitrile band (2245.4 cm^{-1}) and this is due to dominant functional groups in polyacrylonitrile structure. There was also peak around 1700 cm^{-1} that represents the carbonyl of comonomer unit which corresponding to itaconic acid (IA) and methyl acrylate (MA). In addition, the bands in the regions 2941.4, 1454.7, 1353.0 and 1270–1220 cm^{-1} wavenumber were the aliphatic CH group vibrations of different modes in CH, CH$_2$ and CH$_3$ [39].
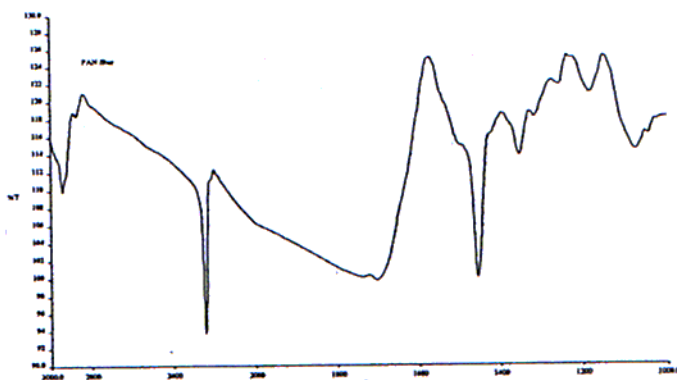

Figure 6: Infrared transmission for PAN fiber.

During stabilization process, the following Possible reaction are: (1) cyclization of nitrile group and (2) dehydrogenation process that formed ladder polymer structure [40] consisting 40 % acridone, 30 % pyridine, 20 % hydronaphthiridine rings, and 10 % of other structures [41]. The possible molecular structure of the ladder polymer is shown in Figure 7.
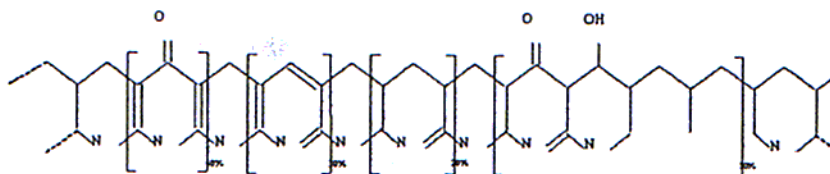

Figure 7 : Proposed ladder structure of stabilized PAN fiber [40].

Figure 7shows the shifting of the spectrum of PAN sample after heating in air at different temperature within 200-300 °C for 1 hour, in order to develop hydronaphthiridine rings. This observation was also proved by Memetea et al. [42]. The presence of hydronaphthiridine rings was proven by the appearance of the new bands within 1600-1620 cm^{-1} which attributed to C=N vibrations. When the nitrile bond (C≡N) was converted to the double bond (C=N), the peak around 2240 cm^{-1} wavenumber was eliminated as the temperature exceeding 300 °C. This phenomenon was caused by cyclization reaction, which started at 200 °C heating temperature (Figure 8). The cyclization changed the aliphatic to cyclic structure (Figure 9) prior to the formation of ladder polymer. This ladder structure was thermally stable and might be able to withstand high temperature during pyrolysis process.
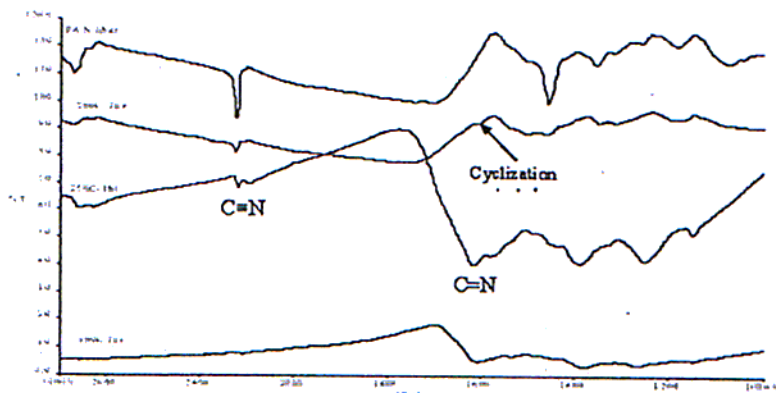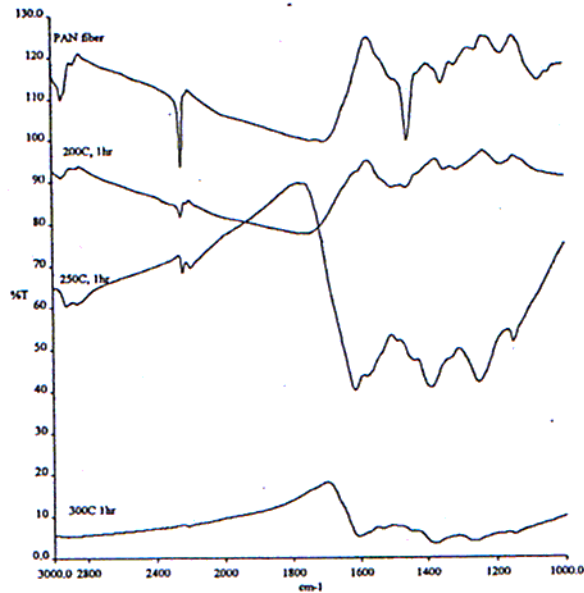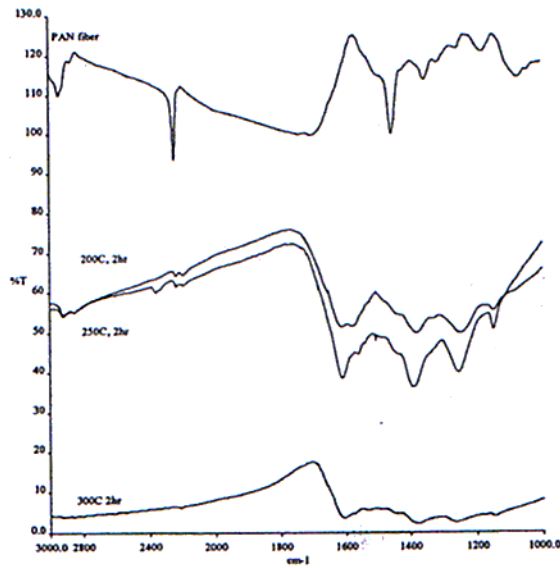

Figure 8: Variation of IR transmission at different final temperature.

160

(a)

(b)

Figure 9 IR Transmission at different condition; (a) IR for 1 hr soaking time, (b) IR for 2 hour soaking time
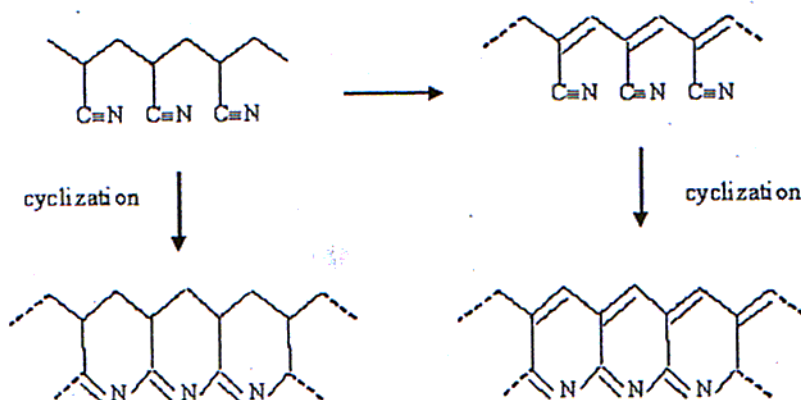
Figure 10 : Cyclization reaction during stabilization

Figure 9 shows the comparison between the IR spectrum of the stabilized PAN fiber with 1 and 2 hour soaking time. Cyclization reaction that occurred during stabilization process could change the molecular structure of the PAN fiber especially in the nitrile stretch (Figure 10). The nitrile stretch was changed significantly when high soaking time was applied at 200 °C of heating temperature. Thus it can be said that, during the 2 hour soaking time, the cyclization reaction may have started at temperature less than 200 °C. At 200 °C heating temperature and 2 hour soaking time, the greatest peak around 1600 cm^{-1} wavenumber representing the double bond structure (C=N, C=C) appeared. However, for 1 hour soaking time, the appearance of this peak was hardly observed. Obviously, with higher soaking time, the change of the PAN fiber structure into the ladder polymer structured is faster. Meanwhile, the IR spectrum of the stabilized PAN fiber at 300 °C heating temperature was similar for both 1 hour and 2 hour soaking time.

The shifting of the stabilized PAN fiber spectrum with soaking time (i.e. 1 hour and 2 hour) at 280 °C heating temperature is shown in Figure 3.6. As being proposed before, the nitrile peak as well as the comonomer peaks shifted when the temperature increased. For 1 hour soaking time, the peak of the nitrile group still exist even up to 280 °C. Similar phenomenon occurred for 2 hour soaking time which meant that the PAN fiber was not fully stabilized. Despite of showing an improvement in the structure changing rate, high soaking time could not reduce the possible temperature of the stabilization process, found to be

162

300 °C. Thus it can be concluded that, the stabilization of PAN fiber was not affected by the duration of the soaking time.
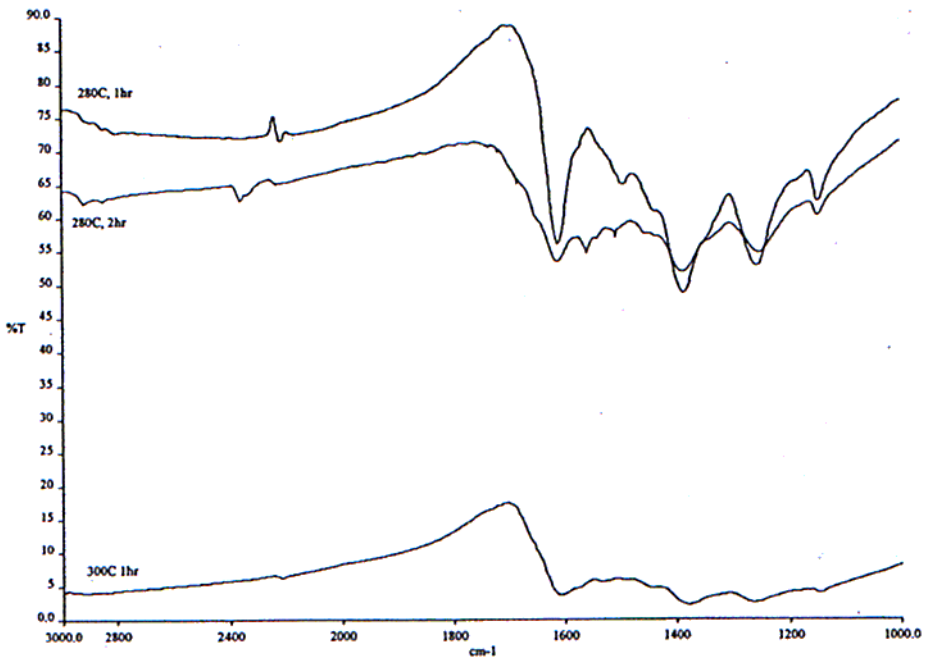

Figure 11: IR transmission at 280 °C and 300 °C

4.0 CONCLUSIONS

It was found that, the changes of the PAN fiber structure occurred as the fiber was subjected to low heating rate of stabilization process. In stabilization process, the important peak like nitrile stretch was found to be reducing with increasing stabilization temperature. The stabilized PAN structure was observered by the reduction in the nitrile stretch. From the experiment it can be concluded that:

1. High soaking time could change the structural peak significantly at 200 °C heating temperature.
2. Low soaking time was enough to stabilize the fiber at 300 °C heating temperature.

163

3. Nitrile bond was eliminated when the heating temperature reached 300 °C, regardless of soaking time, thus the fiber was already stabilized.

5.0 ACKNOWLEDGEMENT

6.0 REFERENCES

1. J. D Buckley. (1993). *Carbon–carbon overview.* In: J. D. Buckley & D. D. Edie eds. *Carbon–Carbon Materials and Composites.* Park Ridge, NJ: Noyes. 1–17.

2. M. L Greene. R. W. Schwartz. & J. W. Treleaven. (2002) Short Residence Time Graphitization of Mesophase Pitch-Based Carbon Fibers. *Carbon.* **40.** 8. 1217–1226.

3. Manocha & M. Lalit. (2003). High performance carbon–carbon composites. *Sādhanā..* **28.** 1&2. 349–358.

4. S. Ozbek. & D. H. Isaac. (2000). Strain-induced Density Changes in PAN-based Carbon Fibers. *Carbon.* **38.** 14. 2007–2016.

5. C. Sauder, J. Lamon & R. Pailer. (2001). Thermomechanical Properties of Carbon Fibers at High Temperature (Up to 2000 °C). *Comp.Sci.and Tech..* **62.** 4. 499-504.

6. Wiles & B. Kenton. (2002). Determination of Reactivity Ratios For Acrylonitrile/Methyl Acrylate Radical Copolymerization Via Nonlinear Methodologies Using Real Time FTIR. M.Sc Thesis. Faculty of the Virginia Polytechnic Institute and State University.

7. O. P. Bahl & L. M. Manocha. (1974). Characterization of Oxidized PAN Fibers. *Carbon.* **12.** 4. 417.

8. O. P. Bahl & R. B. Mathur. (1979). Effect of Load on the Mechanical Properties of Carbon Fibres From Pan Precursor. *Fiber Sci. Tech.* **12.** 1. 31.

9. Z. Wangxi, L. Jie & W. Gang. (2003). Evolution of Structure and Properties of PAN Precursors During Their Conversion to Carbon Fibers. *Carbon.* **41.** 14. 2805–2812.

10. J. B. Donnet & O. P. Bahl. (1987). Encyclopedia of Physical Science Technology. 2nd ed. 515-529.

11. M. L. Clingerman. (2001). Development and Modelling of Electrically Conductive Composite Materials. Ph.D. Thesis. Michigan Technological University.

12. J. Y. Howe & L. E. Jones. (2004). Influence of Boron on Structure and Oxidation Behavior of Graphite Fiber. *Carbon.* **42.** 3. 461–467.

13. O. P. Bahl, R. B. Mathur & K. D. Kundra. (1981). Structure of PAN Fibers and Its Relationship with Resulting Carbon Fiber Properties. *Fib. Sci. and Tech.* **15.** 2. 147-151.

14. M. C. Yang & D. C. Yu. (1996). Influence of Precursor Structure on the Properties of Polyacrylonitrile-Based Activated Carbon Hollow Fiber. *Appl. Polym. Sci.* **59.** 1725-1731.

15. Traceski & T. Frank. (1999). Assessing Industrial Capabilities for Carbon Fiber. Secretary of Defense (Acquisition & Technology). unpublished.

16. A. H. Tullo. (2000). Chemical and Engineering News. **78.** 11

17. V. A. Bhanu, P. Rangarajan, K. Wiles, M. Bortner, M. Sankarpandian, D. Godshall, T. E. Glass, A. K. Banthia, J. Yang, G. Wilkes, D. Baird & J. E. McGrath. (2002). Synthesis and Characterization of Acrylonitrile Methyl Acrylate Statistical Copolymers As Melt Processable Carbon Fiber Precursors. *Polymer.* **43.** 18. 4841–4850.

18. J. Liu, P. H. Wang & R. Y. Li. (1994). Continuous Carbonization of Polyacrylonitrile-Based Oxidized Fibers: Aspects on Mechanical Properties and Morphological Structure. *Appl. Polym. Sci.* **52**.7. 945–950.

19. N. Grassie, J. N. Hay & I. C. McNeill. (1962). Thermal Coloration and Insolubilization in Polyacrylonitrile. *Polym Sci.* **56**. 189–202.

20. T. Takata, I. Hiroi & M. Taniyama. (1964). Coloration in Acrylonitrile Polymers. *Polym Sci Part A.* **2**. 1567–1585.

21. J. Brandrupa & L. H. Peebles Jr. (1968). On the Chromophore of Polyacrylonitrile. IV. Thermal Oxidation of Polyacrylonitrile and Other Nitrile-Containing Compounds. *Macromolecules.* **1**. 1. 64–72.

22. N. Grassie & R. McGuchan. (1971). Pyrolysis of Polyacrylonitrile and Related Polymers. III. Thermal analysis of preheated polymers. *Eur. Polym.* **7**. 1357–1371.

23. P. H Wang. (1998). Aspects on Prestretching of PAN Precursor: Shrinkage and Thermal Behavior. *Appl Polym Sci.* **67**. 7. 1185–1190.

24. T. H Ko. (1991a). The Influence of Pyrolysis on Physical Properties and Microstructure of Modified PAN Fibers During Carbonization. *Appl. Polym. Sci..* **43**. 3. 589-600.

25. T. K Ko. (1991b). Influence of Continuous Stabilization on the Physical Properties and Microstructure of PAN-Based Carbon Fibers. *Appl. Polym. Sci.* . **42**. 7. 1949-1957.

26. L. I. B. David & A. F. Ismail. (2002). Influence of the Thermastabilization Process And Soak Time During Pyrolysis Process on the Polyacrylonitrile Carbon Membranes For O_2/N_2 Separation. *Mem. Sci..* **213**. 1-2. 285–291.

27. R. Setnescu, S. Jipa, T. Setnescu, W. Kappel, S. Kobayashi & Z. Osawa. (1999). IR and X-Ray Characterization of the Ferromagnetic Phase of Pyrolysed Polyacrylonitrile. *Carbon.* **37**. 1–6.

28. P. Rangarajan, V. A. Bhanu, D. Godshall, G. L. Wikels, J. E. McGrath & D. G. Baird. (2002). Dynamic Oscillatory Shear Properties of Potentially Melt Processable High Acrylonitrile Terpolymers. *Polymer.* **43**. 9. 2699-2709.

29. S. Dalton, F. Heatley & P. M. Budd. (1999). Thermal Stabilization of Polyacrylonitrile Fibers. *Polymer.* **40**. 20. 5531–5543.

30. R. T. Conley, & J. E. Beron. (1963). Examination of the Oxidative Degradation of Polyacrylonitrile Using Infrared Spectroscopy. *Appl. Polym. Sci..* **7**. 5. 1757-1773.

31. J. Mittal, R. B. Mathur & O. P. Bahl. (1997). Post Spinning Modification of PAN Fibers. *Carbon.* **35**. 12. 1713-1722.

32. H. M. Sirat, H. Ahmad, B. Zakaria, & M. S. Idris. (2000). *Kimia Organik-kumpulan berfungsi.* Malaysia: Universiti Teknologi Malaysia.

33. J. Qin. (1992). The Enhancement of Microvoids in Acrylic Fibers. *Appl. Polym. Sci. .* **44**. 6. 1095-1105.

34. T. Tsurumi, T. Nakajima, K. Kajiwara & J. E. Mclntyre eds. (1994). Solution In Spinning. *Advanced Fiber Spinning Technology.* Cambridge, England: Woodhead Publishing Ltd. 70.

35. A. F. Ismail, I. R. Dunkin, , S. L. Gallivan & Shilton. (1999). Production Super Selective Polysulfone Hollow Fiber Membranes for Gas Separation. *Polymer.* **40**. 6499-6506.

36. E. Fitzer, W. Frohs & M. Heine. (1986). Optimization of Stabilization and Carbonization of PAN Fibers and Structural Characterization of the Resulting Carbon Fibers. *Carbon..* **24**. 4. 387-395.

37. G. C. Pandey, A. Kumar, A. C. Boccara & D. Fournier. (1998). *Proceeding Control and Quality.* November,. 129.

38. C. Boccara, D. Fournier, A. Kumar & G. C. Pandey. (1997). Nondestructive Evaluation of Carbon Fiber by Mirage-FTIR Spectroscopy. *J. Appl. Polym. Sci.* **63**. 13. 1785

39. P. Bajaj, D. K. Paliwal & A. K. Gupta. (1993). Acrylonitrile Acids Copolymers, Synthesis and Characterization. *J Appl. Polym Sci.*. **49**. 823-833.

40. R. C. Bansal & , J. B. Donnet. (1994). *Carbon Fibers*. 2nd ed. New York: Marcel Dekker Inc.

41. T. Takahagi, I. Shimada, M. Fukuhara, K. Morita, & A. Ishitani. (1986). XPS Studies On The Chemical Structure Of The Stabilized Polyacrylonitrile Fiber In The Carbon Fiber Production Process, *J. Polym. Sci., Polym.Chem.*. **24**.11. 3101-3107.

42. L. T. Memetea N. C. Billingham, & E. T. H. Then. (1995). Hydroperoxides In Polyacrylonitrile And Their Role In Carbon-Fiber Formation. *Polym Deg and Stab.*. **41**. 2. 189-201.