PRELIMINARY STUDIES ON THE HEAT TREATMENT PROCESSES FOR PAN CARBON FIBRE

M.A. Baharom, S. Shamsuddin, I. Mustafar, K. Noorsal*, I. Ahmad, H.F.A. Marzuki

Advanced Materials Centre (AMREC), SIRIM Berhad
Lot 34, Jalan Hi-Tech 2/3, Kulim Hi-Tech Park, 09000 Kulim, Kedah.
*(kartini@sirim.my)

RINGKASAN : *Kertas kerja ini melaporkan peringkat awal kajian terhadap proses prapenstabilan dan penstabilan di dalam penghasilan gentian karbon berasaskan PAN (poliakrilonitril). Peringkat pra-penstabilan melibatkan proses rendaman prekursor PAN ke dalam larutan bahan kimia; kalium permanganat ($KMnO_4$), dimetilformamida, dan aluminium klorida (Al_2Cl_6) pada suhu $85°C$. Kajian awal mendapati bahawa hasil rendaman ini memberikan tindakan katalisis yang positif dan ini dapat dilihat dari proses pencirian yang dilakukan. Spektra Fourier Transformasi Infra Merah menunjukkan kehadiran kumpulan C=N pada nombor gelombang 2350 cm^{-1} dan pengurangan kumpulan C≡N pada nombor gelombang 2244 cm^{-1} semasa proses pra-penstabilan. Ini adalah hasil dari pembentukan polimer berbentuk tangga yang berlaku dari tindak balas secara intermolekul ataupun intramolekul semasa proses pensiklikan. Pemerhatian ini disokong oleh analisis terma di mana gentian karbon PAN menunjukkan pengurangan dalam tenaga pengaktifan, suhu permulaan pensiklikan yang awal dan darjah tindak balas pensiklikan yang lebih tinggi berdasarkan kepada aliran haba yang terjana. Pemerhatian yang serupa juga berlaku kepada proses penstabilan pada suhu $200°C$ di mana perubahan struktur gentian PAN berlaku melalui proses pensiklikan. Namun begitu ini juga disusuli dengan pelbagai tindak balas yang saling bertanding semasa proses penstabilan tersebut. Proses pensiklikan ini menghasilkan pengeluaran beberapa spesies gas seperti hidrogen sianida (HCN) dan karbon dioksida. Proses pengoksidaan pula mungkin berlaku semasa penjerapan gas oksigen ke dalam tulang belakang prekursor PAN.*

ABSTRACT : This paper reports the preliminary studies of pre-stabilisation and stabilisation processes in the production of PAN carbon fibre. The pre-stabilisation process involves immersion of PAN precursor in potassium permanganate ($KMnO4$), dimethylformamide (DMF) and aluminium chloride (Al_2Cl_6) at $85°C$ in which a promising catalytical behaviour is demonstrated through the characterisation techniques used. The Fourier Transform Infra Red (FTIR) spectra indicate a distinctive nitrile group of C=N at 2350 cm^{-1} and a decrease of C≡N group at 2244 cm^{-1} during pre-stabilisation process. This is due to the formation of a ladder polymer which occurs intermolecularly or intramolecularly during cyclisation process. Thermal analysis supports this view as the pre-treated PAN fibre showed a reduced activation energy, earlier onset cyclisation temperature and higher degree of cyclisation reaction through its heat flow. Similarly, stabilisation at $200°C$ also indicates chemical structural changes through cyclisation process. Various competing reactions took place during stabilisation. Cyclisation results in the release of a few gaseous species such as HCN and CO_2 while oxidation possibly results in the absorption of O_2 into the PAN precursor backbone.

Keywords : PAN carbon fibre, pre-stabilisation, thermal stabilisation, heat treatment

M.A. Baharom, S, Shamsuddin, I. Mustafar
K. Noorsal, I. Ahmad and H.F.A. Marzuki

INTRODUCTION

Nearly all commercial carbon fibres are produced through conversion of a carbonaceous precursor to a fibre form. The precursor fibre is cross-linked in a stabilisation process, typically in the range of 200 - 300°C before finally being heated at a temperature up to 3000°C in an inert atmosphere to eliminate all non-carbon elements. This eventually turns the precursor to a carbon fibre (Edie, 1998).

This paper details the preliminary studies of the heat treatment process of PAN (polyacrylonitrile) precursor obtained commercially. The future development of the continuous process of PAN fibre heat treatment depends largely on the data collection based on the batch processes carried out at our laboratory, namely pre-stabilisation, stabilisation and carbonisation processes. The batch processes provide data from optimised parameters which is important and highly referred when embarking on the continuous heat treatment process of PAN fibre.

Pre-stabilisation is a chemical modification of the PAN fibre precursor prior to the stabilisation process. This modification is believed to affect the stabilisation mechanism through several ways such as decreasing the activation energy of cyclisation, reducing the stabilisation exotherm, increasing the speed of cyclisation reaction and improving the orientation of the molecular chains in the fibre. These modifications are thought to improve the mechanical properties of the resulting carbon fibre (Mittal *et al.,* 1997). Various chemicals are used in the pre-stabilisation process, for example dimethyl formamide (DMF) which has been reported to help in improving the elastic modulus and tensile strength of carbon fibres through removal of surface defects (Chen & Harrison., 2002). The use of succinic acid in post spinning treatment which acts as a plasticiser, has resulted in an increase in stretching by three times and a reduction in the diameter to 1 μm, as opposed to 6 μm obtained from the normal processes (Mittal *et al.,* 1997). On the contrary, in the typical PAN process, the precursor might begin with as-spun diameter of 35 μm and then stretched to a diameter of 10.5 μm before finally shrinking to 7 μm (Edie, 1998). Another precursor potassium permanganate ($KMnO_4$) is believed to reduce the exothermic peak during stabilisation and eventually reduce the stabilisation time.

Stabilisation is an exothermic process which involves heat treatment at lower temperature between 180°C - 300°C, carried out under tension in an oxidative environment. It is considered a crucial step that will determine the final structure of the fibre and its mechanical properties (Bahl *et al.,* 1998). Various possible reactions were suggested, among them being cyclisation, dehydrogenation and oxidation with several interpretations of the chemical structures as reviewed by Bashir (1991).

The stabilised fibre will then undergo a carbonisation process in which the heat treatment can reach up to 1500°C. Tension is applied to the fibre and heating is done in an inert atmosphere.

The heat treatment temperature (HTT) determines the final product of the fibre. A HTT of 1000°C produces Type A carbon fibres with low modulus and low tensile strength. When the HTT is increased to 1400°C, a Type II carbon fibre with high tensile strength and medium modulus will be produced. Type I carbon fibre is produced in a process called graphitisation, in which the HTT reaches 2500°C. The Type I carbon fibre exhibits high modulus with low tensile strength (Ko, 1991). [This paper describes the preliminary studies of pre-stabilisation and stabilisation work carried out on PAN precursor fibre. The carbonisation process is however not discussed in this paper.]

MATERIALS AND METHODS

A special grade of polyacrylonitrile (PAN) fibre tows (Fortafil Fibre Inc.), of average molecular weight 86,200 and approximately 2 wt.% of methyl methacrylate was used in this study. Each tow of the fibre contains about 320,000 filaments (Figure 1). The tow is split into smaller batches for experimental purposes.
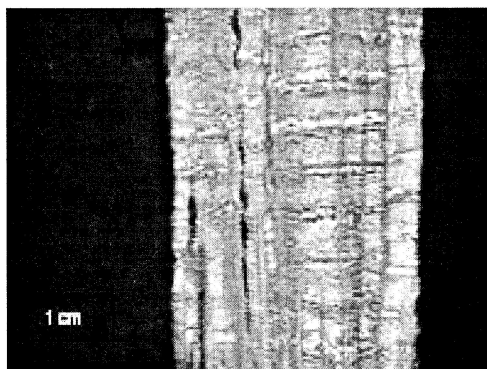

Figure 1. *PAN fibres with 320,000 filaments per tow*

Pre-stabilisation

The PAN fibres were treated with three types of chemical solutions, which include potassium permanganate ($KMnO_4$) (5 wt.%), dimethyl formamide (DMF) (30 wt.%) and aluminium chloride (Al_2Cl_6) (10 wt.%). Immersion in these solutions was carried out for 3 minutes at 85°C in the reagent baths. This was followed by washing with distilled water and dried to a constant weight in an oven prior to further characterisation.

Stabilisation

Stabilisation process was carried out in an oven (Memmert) at 200°C with applied load of 175g for various soaking times (Figure 2). Each sample weighed about 4g. The heat treated PAN fibre was subjected to further characterisation techniques.
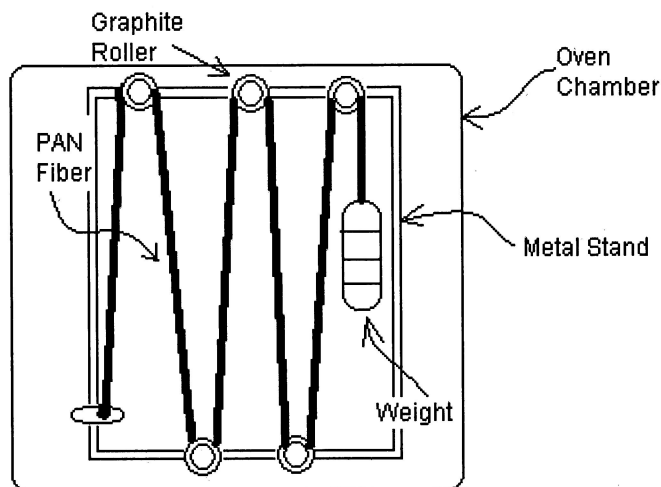
M.A. Baharom, S, Shamsuddin, I. Mustafar
K. Noorsal, I. Ahmad and H.F.A. Marzuki

Figure 2. *Schematic diagram of the batch process of stabilisation*

Thermal Analysis

The exothermic reaction of PAN and stabilised PAN were determined by Differential Scanning Calorimetry (DSC) (Mettler Toledo DSC 821e). The sample weight was 3 mg and the heating rate was $10°C$/min up to $400°C$ with the onset temperature of $25°C$ under an oxygen environment.

Fourier Transform Infra-Red (FTIR)

The changes in the chemical structure of PAN fibre was detected using the FTIR (Nicolet MAGNA - IR 560) spectrometer. The transmittance spectra were collected using the ATR-FTIR at a resolution of 4 cm^{-1} and 360 scans. Samples were tested in its fibre form.

Elemental Analysis

The changes in the carbon, hydrogen and nitrogen were detected through the CHN analyser (Perkin Elmer Series II 2400) and oxygen content was determined by means of the difference between the three elements.

Colour changes

The colour changes of the PAN fibre were recorded visually after the pre-stabilisation and during stabilisation processes.

RESULTS AND DISCUSSION

Effect of pre-stabilisation treatment

PAN fibre changed to brown from clear white when treated with $KMnO_4$ whilst no colour changes were detected in both DMF and Al_2Cl_6 solutions. The reasons for the colour changes were quite unclear though several authors reported that the colour formation could be due to base induced cyclisation, which is similar to the one occurring in thermal stabilisation (Mc. Cartney, 1953; Grassie & Hay 1962). The cyclisation process was believed to be initiated by the permanganate ions as shown in Figure 3. Chemical impregnation of the permanganate ions was also thought to cause a large reduction in the cyclisation exotherm. As the activation energy is reduced, the time required for stabilisation of PAN fibres is also reduced (Mittal & Bahl, 1997). The FTIR and the thermal analysis results showed an agreement with this hypothesis.

Two characteristic peaks at 2941 cm^{-1} and 2244 cm^{-1}, due to the methylene (CH_2) stretch and nitrile ($C\equiv N$) groups, can be detected in the FTIR spectrum of the untreated PAN fibre as shown in Figure 4.
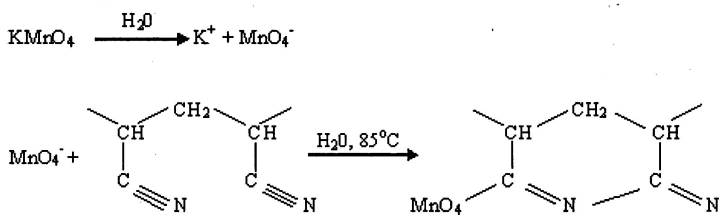

Figure 3. *Proposed reaction mechanism of PAN fibre treated with $KMnO_4$ (Mathur et al., 1993)*
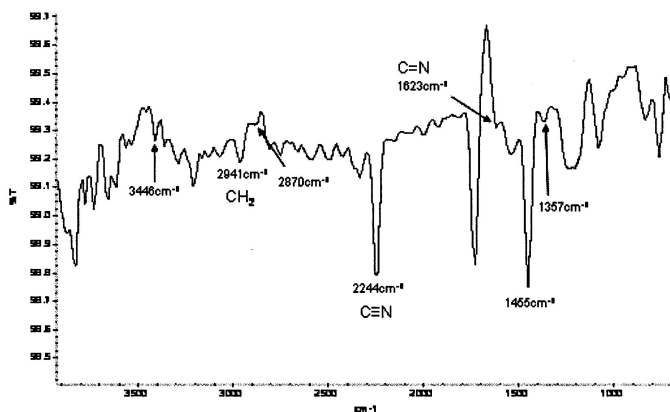

Figure 4. *FTIR spectrum of the untreated PAN fibre*

M.A. Baharom, S, Shamsuddin, I. Mustafar
K. Noorsal, I. Ahmad and H.F.A. Marzuki

The peaks at 2941 cm^{-1} and 2870 cm^{-1} correspond to the asymmetrical CH$_2$ stretching and symmetrical CH$_2$ stretching respectively, whilst CH$_2$ vibration at 1455 cm^{-1} corresponds to the scissoring band. A weak absorbance of C=N at 1623 cm^{-1} indicates that a small amount of C=N group exists in the untreated PAN fibre.

All treated PAN fibre shows to a strong new peak at 2350 cm^{-1} which is due to the C=N stretching (Figures 5 - 7), whilst the peak at 2244 cm^{-1} (C≡N stretching) shows a remarkable decrease. The CH$_2$ stretching band at 2941 cm^{-1} occurs in all treated PAN fibre FTIR spectrum. The presence of the CH$_2$ and the C=N groups suggests that a polyimine structure (Figure 3) normally termed as the ladder polymer that resulted from the cyclisation process could be formed during the pre-stabilisation process. The remarkable decrease of CH$_2$ scissoring band at 1455 cm^{-1} is also related to the cyclisation process in which dehydrogenation of the PAN molecule could occur, to form an unsaturated alkene bond. The FTIR results suggest that the cyclisation process appears to be initiated by the permanganate ions, in which the manganese atom is thought to attract the nitrile (C≡N) groups of acrylonitrile unit to initiate the cyclisation reaction. The concentration of the manganese atom in the PAN fibre was however not determined in this work. Similar observation can be seen in the FTIR spectra of DMF and Al$_2$Cl$_6$ solutions, which indicates that the catalytic reaction may be exerted by both chemical solutions. While DMF has been widely used in the catalytical modifications, Al$_2$Cl$_6$ is rarely featured in the literature. This work has attempted to use Al$_2$Cl$_6$ as an alternative catalyst for the pre-stabilisation process.
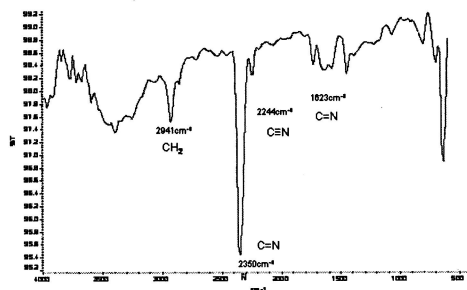

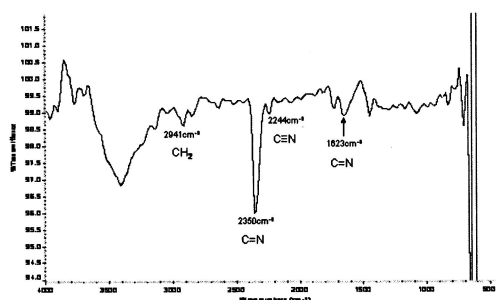**Figure 5.** *FTIR spectrum of PAN fibre treated with KMnO$_4$*

Figure 6. *FTIR spectrum of the PAN fibre treated with dimethyl formamide (DMF)*
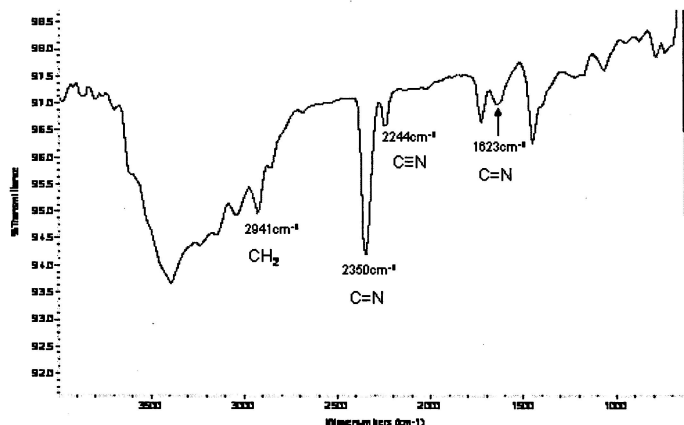
Figure 7. *FTIR spectrum of the PAN fibre treated with Al_2Cl_6*

The catalytic effect of the chemical solutions used is further supported by the DSC thermograms obtained for this work. Figure 8 shows the thermogram of the untreated PAN fibre heated in the presence of oxygen. An exothermic reaction begins at about $232^\circ C$ before rising quite rapidly to its fusion temperature at $271^\circ C$ (Table 1). Many authors attributed this exotherm peak to the formation of the ladder polymer as a result of the cyclisation reaction (Bashir, 1991; Ko *et al.*, 1988). The exothermic reaction for the $KMnO_4$ treated fibre starts at an earlier onset temperature of $215^\circ C$ before reaching its peak at $266^\circ C$. Similar observation can also be seen for the DMF and Al_2Cl_6 treated fibres in which both start at an earlier onset temperature of $217^\circ C$ and $221^\circ C$ respectively before reaching their peak. An earlier onset temperature for the cyclisation process suggests that the cyclisation process can be initiated earlier, thereby reducing the time for a complete stabilisation process. The shorter time frame for the cyclisation process of the treated PAN precursor is evident in Table 1 when compared with the untreated PAN precursor fibre.

The treated PAN precursor fibres show a remarkable reduction in the activation energy when compared with the untreated ones (Table 1). The lower value of the activation energy indicates that lesser energy is required in completing the cyclisation process and this again enhanced the catalytical behaviour of the three solutions used in treating the fibre. The amount of heat used in forming the cyclisation process is reflected in the heat flow values in which the treated fibres show a slightly higher value than the untreated ones (Table 1). This observation may be attributed to a larger degree of cyclisation reaction induced by the catalytic solutions (Mathur *et al.*, 1993).

M.A. Baharom, S, Shamsuddin, I. Mustafar
K. Noorsal, I. Ahmad and H.F.A. Marzuki

Table 1. DSC studies of the untreated and treated PAN fibres

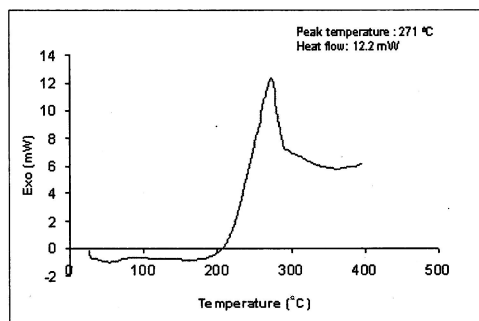| Sample	Onset temperature (°C)	Activation energy, E_a (J/mol)	Heat flow (mW)	Peak temperature (°C)	Time (min)
Untreated PAN fibre	232	470	12.2	271	68.0
PAN fibre treated with $KMnO_4$	215	250	15.7	266	59.3
PAN fibre treated with DMF	217	198	16.3	266	55.9
PAN fibre treated with Al_2Cl_6	221	145	15.5	267	53.4

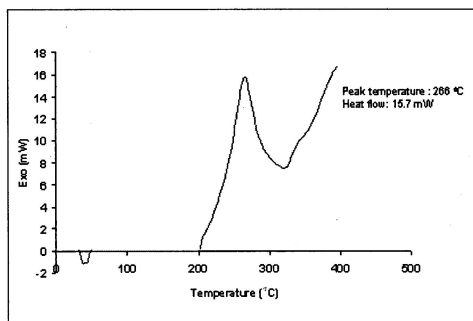**Figure 8.** DSC thermogram of the untreated PAN fibre

Figure 9. DSC thermogram of PAN fibre treated with $KMnO_4$
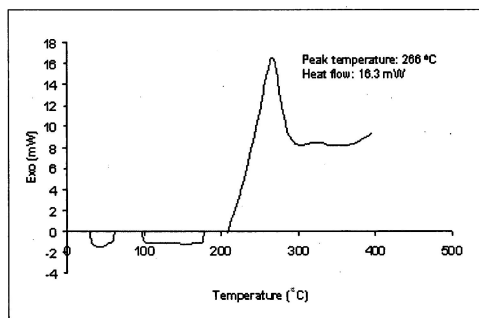

Figure 10. DSC thermogram of PAN fibre treated with DMF
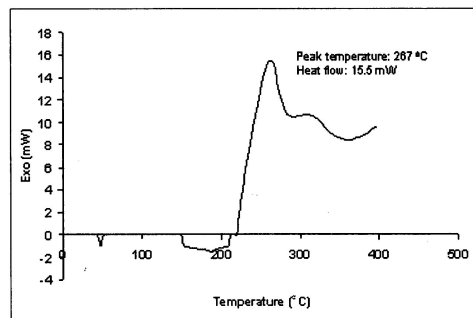

Figure 11. DSC thermogram of PAN fibre treated with Al_2Cl_6

PAN fibre treated with DMF solution, despite starting at slightly lower onset temperature, exhibits a slightly higher amount of heat flow amongst other catalytic solutions and implies the greater conversion of the nitrile (C≡N) group to C=N in the cyclisation process. Treatment with Al_2Cl_6 shows the lowest activation energy is required for the cyclisation process. This may be due to a large amount of cyclisation reaction occurring in the pre-stabilisation step. When the PAN fibre proceeds with the heating treatment in the DSC, the uncyclised unit of PAN fibre is lower and this is demonstrated through the low activation energy. This suggests that Al_2Cl_6 has the ability to generate higher cyclisation rate than its counterpart and shows a potential in this catalytic work.

Effect of stabilisation treatment

Stabilisation process was initially carried out independently from the pre-stabilisation treatment using the commercially available PAN fibre with co-monomer of methyl methacrylate. Incorporation of the co-monomers was believed to reduce the cyclisation reaction rate, hence the fusion and breaking of fibres could be avoided due to overheating and sharp exothermic reaction (Wangxi *et al.,* 2003). It will be the future work of these studies to investigate the effect of stabilisation treatment on the fibres treated with the basic chemical solutions and the effect of adding different co-monomers. This paper details the elemental analysis, FTIR studies and the thermal analysis work carried out on the stabilised PAN fibre at 200°C.

Changes of the PAN fibre colour were detected from dark yellow to brown and finally black throughout the soaking time. Many authors attributed the colour changes of PAN fibre during thermal stabilisation to the degradation of PAN which led to colouration. The degradation relates to the changes of the PAN fibre structure in which a fully heteroaromatic cyclic structure was formed. The cyclisation concept was adopted and modified by other researchers (Grassie *et al.,* 1958; Burlant and Parsons, 1956; La Combe, 1957) and this partially aromatic structure is also called a ladder polymer (Figure 12).
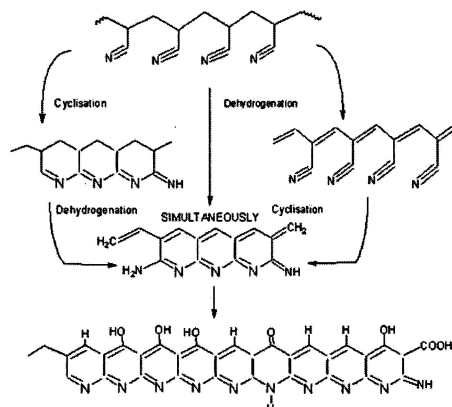

Figure 12. *Possible chemical reactions in the formation of the ladder polymer during thermal stabilisation process (Bahl et al., 1998).*

35

M.A. Baharom, S, Shamsuddin, I. Mustafar
K. Noorsal, I. Ahmad and H.F.A. Marzuki

Figure 12 shows the possible reaction paths in forming the ladder polymer. Dehydrogenation, cyclisation and oxidation are considered as the main reactions taking place in the thermal stabilisation process. Dehydrogenation normally precedes cyclisation but often many authors would prefer a simultaneous reaction of both dehydrogenation and cyclisation. These reactions are also thought to be responsible for the colour changes of the PAN precursor. Studies (Bahl et al., 1998) have indicated that cyclisation involves oligomerisation of nitrile groups. The triple bond of a nitrile group changes to a double bond, and the nitrogen of this nitrile group forms a bond with the carbon of the succeeding nitrile group of the chain. The cyclisation process is initiated at several points of the PAN molecule during the heat treatment and grows until the end group reaches another cyclised unit.

The cyclisation is not continuous throughout the chain, leaving some uncyclised units at random in the molecular chain. Chain scission occurs at the sites of the uncyclised units and often contributes to the loss of weight, hence the evolved gas species. HCN is one of the gaseous products during the chain scission of the uncyclized units and NH_3 could be produced from the terminal imine structure.

Table 2 presents the changes in elemental composition of the analysed samples expressed in weight percentage (wt. %). Oxygen content was calculated as the difference between the elements present in the samples. The analysis shows an increment of oxygen content whilst there is a decrease in all other major elements such as carbon, hydrogen and nitrogen with increasing soaking time (heating time) at 200°C. The suggested cyclisation process involves releasing of HCN as its side product and this is reflected in the decrease of the C, H and N content of the samples. Since the thermal stabilisation was conducted in air at 200°C, the higher uptake of oxygen is expected due to possible oxidation process. Laffont et al. (2004) suggested that different competing phenomena can be observed in the stabilisation step. First, absorption of N and O from air during heating and second, the release of different gas species such as HCN, NH_3 and CO_2. The elemental analysis showed that both reactions could take place as there is an increase in the O content and a decrease in C, H and N content.

Table 2. Changes in the elemental content at various soaking times at 200°C.

Soaking time (min)	C (wt. %)	H (wt. %)	N (wt. %)	O (wt. %) (difference)
0	65.93	6.12	24.23	3.72
20	66.07	5.20	24.17	4.56
30	65.75	5.62	24.08	4.55
40	65.55	5.59	23.84	5.02
50	65.32	5.50	23.74	5.44
60	65.33	5.64	23.62	5.41
120	63.99	5.08	23.09	7.84

The structural changes during stabilisation is analysed by the FTIR spectra (Figure 13), obtained for both stabilised and unstabilised PAN precursor. The FTIR spectrum for unstabilised PAN (Figure 4) shows vibration bands associated with the nitrile group (C≡N) at 2241 cm^{-1} and aliphatic C-H bands related to C-H, CH_2 and CH_3 at 2930 - 2870, 1451 and 1363 cm^{-1} respectively. The presence of C=O at 1733 cm^{-1} indicates the presence of the co-monomer, methyl metacrylate.

Upon stabilisation, some chemical structural changes can be seen in the FTIR spectrum. The most prominent one is the decrease of the C≡N peak intensity which suggests that intermolecular or intramolecular cross-linking might have taken place forming the cyclisation reaction. The peak at 1593 cm^{-1} which is assigned to a mixture of C=N, C=C and N-H by many authors (Fochler *et al.,* 1985), appears to be quite dominant. The C=O peak disappears and this could correlate to possible loss of CO_2 gas during the stabilisation process. The methyl methacrylate co-monomer formed a possible chemical linkage with the PAN backbone during the precursor production. This chemical linkage through the carbonyl group breaks and is lost in the form of CO_2 during the thermal stabilisation process.
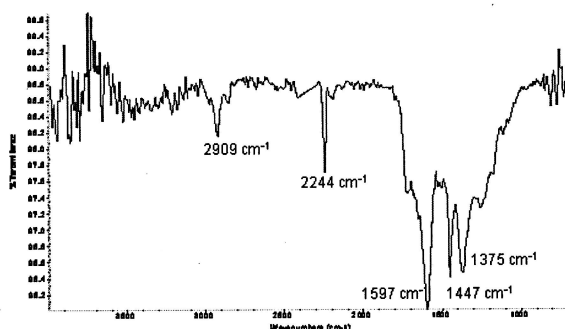

Figure 13. *FTIR spectra of stabilised PAN precursor at 200 °C*

The thermal analysis depicts an unfinished cyclisation process of the stabilised PAN precursor. When both thermograms were compared, the stabilised PAN precursor still shows an exothermic peak in the temperature regime of 200°C to 350°C with a peak at 272°C. The unstabilised PAN precursor exhibits a broad peak at 280°C, with onset temperature at 232°C, (Table 3, Figure 14).

Table 3. DSC studies of the stabilised and unstabilised PAN precursor

Sample	Onset temperature (°C)	Activation energy, E_a (J/mol)	Heat flow (mW)	Peak temperature (°C)	Time (min)
Unstabilised PAN	232	470	12.2	271	68
Stabilised PAN	215	250	15.7	266	48

M.A. Baharom, S, Shamsuddin, I. Mustafar
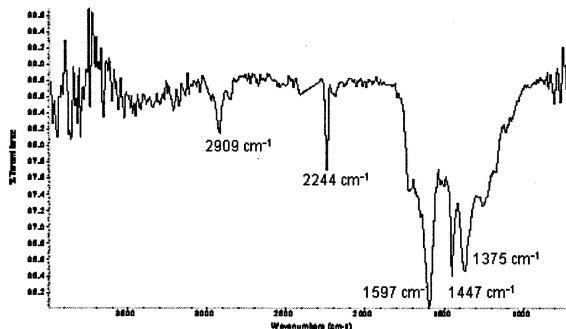K. Noorsal, I. Ahmad and H.F.A. Marzuki

Figure 13. DSC thermogram for (a) unstabilised and (b) stabilised PAN precursor

The stabilised PAN fibre exhibits a much lower activation energy which indicates some catalytic effect in the cyclisation process. This is supported by its shorter cyclisation time (Table 3). The heat flow is slightly higher and this suggests that a higher degree of cyclisation has occurred. The stabilisation at 200°C is not able to induce a complete cyclisation process and this is in agreement with a previous report that the complete cyclisation is expected at higher temperatures, greater than 600°C (Bahl *et al.,* 1998). It is also possible that heating in the DSC would generate further cyclisation for the unreacted chemicals generated from the incomplete cyclisation process.

CONCLUSION

Preliminary work shows that $KMnO_4$, DMF and Al_2Cl_6 used in the pre-stabilisation process exhibit a promising catalytic behaviour in initiating the cyclisation process to form the ladder polymer, in which if put into use, will reduce the time taken for the stabilisation process. The stabilisation process which was carried out independently of the pre-stabilisation process showed an incomplete cyclisation reaction that was reflected in the thermal analysis work. This phenomenon indicates the stabilisation process needs a higher temperature to complete the cyclisation throughout the polymer backbone.

ACKNOWLEDGMENT

REFERENCES

Bahl, O. P., Shen, Z., Lavin, J.G., Ross, R.A. (1998). Manufacture of carbon fibers. In: Donnet, J. P., Wang, T.K., Rebouillat, S., Peng, C.M., editors. Carbon Fibres, New York: Marcel Dekker; pp 1-83.

Bashir, Z. (1991). A critical review of the stabilisation of polyacrylonitrile. *Carbon,* **29**: pp 1081 - 1090.

Burlant, W.J. & Parsons, J. L. (1956). Pyrolysis of polyacrylonitrile. *J. Polym. Sci.,* **22(101)**: pp 249 - 256.

Chen, J.C., Harrison, I. R. (2002). Modification of polyacrylonitrile (PAN) carbon fibre precursor via post spinning, plasticisation and stretching in dimethyl formamide (DMF). *Carbon,* **40**: pp 25 - 45.

Edie, D. D. (1998). The effect of processing on the structure and properties of carbon fibres. *Carbon,* **36(4)**: pp 345 - 362.

Fochler, H. S., Mooney, J. R., Ball, L. E., Boyer, R. D., and Grasselli, J. G. (1985), Infrared and NMR spectroscopic studies of the thermal degradation of polyacrylonitrile. *Spectrochimica Acta,* **41A (1/2)**; pp 271 - 278.

Grassie, N. & Hay, J. N. (1962). Thermal coloration and insolubilisation in polyacrylonitrile. *J. Polym. Sci.,* **22(163)**: pp 189-202.

Grassie, N., Hay, J. N., McNeill, I. C. (1958), Colouration in acrylonitrile and methacrylonitrile polymers, *J. Polym. Sci.,* **31(122)**: pp 205 - 206.

Ko, T. -H., Ting, H.-Y., Lin, C.-H. (1988). Thermal stabilisation of polyacrylonitrile fibres. *J. Appl. Polym. Sci.,* **35**; pp 631 - 640.

Ko, T.-H. (1991). The influence of pyrolysis on physical properties and microstructure of modified PAN fibres during carbonisation. *J. Appl. Polym. Sci.,* **43**: pp 589 - 600.

La Combe, E. M. (1957). Colour formation in polyacrylonitrile, *J. Polym. Sci.* **24(105)**: pp 152 - 154.

Laffont, L., Monthioux, M., Serin, V., Mathur, R.B., Guimon, C., Guimon, M.F. (2004). An EELS study of the structural and chemical transformation of PAN polymer to solid carbon. *Carbon* (in press).

Mathur, R. B., Mittal, J. and Bahl, O. P. (1993). Bimodification of polyactylonitrile (PAN) fibres, *J. Appl. Polym. Sci.,* **49**; pp 469 - 476.

Mc. Cartney, J. R. (1953). Alkaline degradation of polyacrylonitrile. *U.S. Bur. Stand. Linc.* No. 525.

M.A. Baharom, S, Shamsuddin, I. Mustafar
K. Noorsal, I. Ahmad and H.F.A. Marzuki

Mittal, J., Mathur, R. B., & Bahl, O. P. (1997). The post spinning modification of PAN fibres - A Review. *Carbon*, **35(12)**: pp 1713 - 1722.

Wangxi, Z., Jie, L. & Gang, W. (2003). Evolution of structure and properties of PAN precursors during their conversion to carbon fibres. *Carbon*, **41**; pp 2805 - 2812.