Effect of Blending Temperature on the

Characteristics of Modified Polyacrylonitrie Homopolymer

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Abstract

This paper examines the modification of polyacrylonitrile (PAN) homopolymer by a blending technique. The discussion on this modified PAN fiber involves the comparison a new concept of comonomer attachment compared to the conventional method. The PAN homopolymer and comonomers (i.e. itaconic acid (IA) and methylacrylate (MA)) were dissolved in dimethylformamide (DMF) at two different temperatures; 70°C (Type 1) and ambient temperature (Type 2). These fibers were fabricated using a simple the dry/wet spinning process before subjected to a stabilization process. FTIR result shows that the peaks (around $1600 cm^{-1}$) indicated that the comonomers in Type 1 fiber were attached to the PAN homopolymer backbone during the dope preparation step. However for Type 2 fibers, the comonomers were only attached to the PAN homopolymer backbone during the stabilization process. Type 1 fibers also have higher weight loss and faster stabilization compared to Type 2 fibers. Therefore, the blending process at heat temperature of 70ºC is claimed as the technique that can modify the PAN homopolymer and make the stabilization process of PAN fibers faster.

Keywords: Polyacrylonitrile, Comonomers, Stabilization, Cross-section, TGA, Infrared

1. Introduction

Polyacrylonitrile (PAN) is a polymer with carbon chain connected to one another. Polyacrylonitrile is hard, horny, relatively insoluble, and a high-melting material (Schwartz, 2002). The main characteristic of the PAN molecule is its bulky nitrile (CN) side groups which characterized by high dipole moment, the lone pair orbital of nitrogen atoms, and the electrons in the p orbital of the nitrile triple bond. Based on previous works (Bahl and Manocha, 1974; Wangxi et al., 2003; Wiles, 2003), PAN is the main precursor material for manufacturing carbon fibers as it can produce carbon fiber with a high carbon yield of up to 50% are thermally stable and extremely oriented molecular structure when subjected to low temperature treatment. Hence, manufacturing of PAB fibers with high tensile and high modulus is of significant interest

In terms of processing path, Liu *et al.* (1994) has listed three main steps in converting PAN based fibers to carbon fibers. They are:

(1) Oxidative stabilization, which form ladder structures to enable them to undergo processing at higher temperatures;

(2) High temperature carbonization, (i.e. up to 1600 ° C) to evolve non-carbon atoms and yield a turbostatic structure;

(3) Further heating, up to 2000 °C to improve the orientation of the basal planes and the stiffness of fibers, which is also known as graphitization.

Among these three steps, the stabilization process is the most important one. It plays a significant role in converting PAN fibers into an infusible stable ladder polymer. Through process triple bonds (C≡N groups) transformed into double bonds (C=N groups) and consequently develop cross-links between the molecules of PAN fiber (David and Ismail, 2002).

Comonomers are also normally used to accelerate the stabilization process and improving the thermal behavior of PAN. There are various types of comonomers such as itaconic acid, acrylic acid, methacrylic acid, methyl acrylate (MA), etc. (Edie and Diefendorf, 1993). Grassie and McGuchan (1972) observed that acrylate and methacrylate comonomers have diluent effect on the exothermic reactions occurring during heat treatment of PAN, while acidic comonomers by having of electrophilic groups could initiate stabilization reactions at a lower temperature. At least 15% of regular PAN textiles are comonomers (Chand, 2000) and most of PAN fiber contains at least 1-1.1% of itaconic acid (IA). Other researchers (Tsai and Wu, 1993) stated that PAN precursors with a few percent of acrylate comonomers also have more preferred orientations, and as a result, the resulting carbon fibers possessed the best mechanical properties. Hence, the objective of this study is to characterize the modified polyacrylonitrile (PAN) homopolymer through blending with comonomers such as itaconic acid and methylacrylate with regards to fiber properties.

2. Experimental

2.1 Dope Preparation

Polyacrylonitrile homopolymer have a glass transition temperature of $120^{o}C$. Thus, at ambient temperature the polymer is in a glassy phase. This state can interrupt the spinning process by reducing the draw ability of the polymer solution. The presence of comonomers in this experiment can reduce this problem which improves the solubility and draw ability in the spinning process. As mentioned before, most researchers have been focusing their study by investigating the minimum amount of methyl acrylate (MA) and itaconic acid (IA) in order to improve the properties of carbon fiber.

In this study, the modification of PAN homopolymers was carried out by blending PAN and its comonomers (i.e MA and IA) using two different techniques. The first technique (Type 1) involved reaction of comonomers and PAN polymer at 70°C, while in the other technique (Type 2), the comonomers were mixed with PAN at ambient temperature. The blending and mixing of the PAN polymers lasts at least 7-9 hours to ensure that a completely homogenous solution can be produced.

2.2 Spinning technique

In this research, the dry/wet spinning method was used to fabricate PAN fiber. The spinning solution was extruded through a spinneret through a 2 cm air gap before entering the coagulation bath. The fiber then immersed into the nonsolvent (water) coagulation bath for wet separation and then to the washing treatment bath. The coagulation bath temperature was controlled at 10°C by a refrigeration/heating unit to ensure rapid solidification, while the washing bath was kept at ambient temperature. The resulting fiber with a diameter of 50μm, was subjected to solvent exchange for 1 day before drying at ambient condition. The specification of spinning conditions is listed in Table 1.

2.3 Stabilization Process

Stabilization process influences the processing sequence that is used to convert PAN precursors to carbon fibers and will determine whether the final carbon fibers will have desirable properties. In this study, PAN fiber bundles were inserted into a quartz tube and wrapped with stainless steel wires of   type 304 (outer diameter 3 mm) at both end. The quartz tube was inserted into a Carbolite wire wound tube furnace (Model CTF 12/65/550) that can be set to a maximum temperature of 1200°C.

The PAN chain was cross-linked by conducting a slow heating treatment on the PAN fibers. As a result, a new structure of PAN fiber was formed which could withstand high temperature during the carbonization process. The heating rate used was as low as 1ºC/min, in order to avoid shrinkages (Chen and Harrison, 2002). For the final heating process, the temperature was varied from 200-300°C with an increment of 10°C for 1hour soaking time. This stabilization process was conducted with air flow and without air flow. Figure 1 illustrates the stabilization system used in the present work.

2.4 Thermogravimetry Analysis (TGA)

The weight loss of the sample caused by the heating process was studied by TGA using a Mettler Toledo TGA model (TGA/SDTA851^{e}). The sample size was about 40 mg and the analysis was performed under an inert atmosphere (nitrogen gas) at a heating rate of 20°C/min until the temperature reached 1000ºC. The residue after the heating process was analyzed using Mettler STARe software.

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

Analysis of the existence and information on the organic structure of PAN fibers before and after heating treatment was due by infra-red spectroscopy using the potassium bromide (KBr) disk method. In order to mix the polymer with KBr thoroughly we used an agate grinder. The stabilized fibers were grinded into small particle and mixed thoroughly with KBr. The mixture was pressed to form a thin layer, and then the sample was subjected to FTIR analysis.

3. Results and Discussion

3.1 Effect of Different Dope Preparation temperature on Polyacrylonitrile Properties

Polyacrylonitrile was modified with copolymers through a blending technique. As stated before, dimethylformamide (DMF) is suitable to dissolve any polar polymers and usually recommended for the copolymerization of acrylonitrile. By dissolving polyacrylonitrile and its comonomers in DMF, carbanion condition can exist. Carbanion is a condition which the carbon atom bears a negative charge which help to initiate the reaction of comonomers and polyacrylonitrile (Wade, 1999). In this case, two types of polymer solutions have been prepared which produced Type 1 and Type 2 fibers.

The existence of the functional groups of these PAN fiber was determined by using infrared (IR) spectra. Generally the PAN fiber shows 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 2 shows the spectrum of the Type 1 fibers before the fiber was stabilized. The first method caused the comonomers to be fully ionized and could attach the polyacrylonitrile during the preparation of the dope. Thus, peaks similar to those found by Dalton et al. can be observed (Dalton et al., 1999). In Figure 2, there are four important peaks that can be seen. A very sharp and strong peak representing nitrile band is observed at 2245 cm^{-1} and this is due to the dominant functional groups in the polyacrylonitrile structure. The second peak is at 1701.5 cm^{-1} which represents to carbonyl stretching. In conjunction with the peaks at 1072.9 (most likely due to C-O-C bend), the carbonyl peak seems to confirm the presence of methecrylate (H$_2$C=C(CH$_3$)CO$_2$R) as a comonomer. In addition, through the combination of the broad adsorption around 3600-3300 cm^{-1} (due to OH stretch) and the peak in the 1300-1000 cm^{-1} range (due to the C-O stretch and the C-C stretch), the carbonyl peak also confirms the likely presence of an acid comonomer (itaconic acid) (HO$_2$CCH$_2$C(=CH$_2$)CO$_2$H). There are also bands in the regions with 2941.4, 1454.7, 1353.0 and 1270–1220 cm^{-1} wavenumbers which represent the aliphatic CH group vibrations of different modes of CH, CH$_2$ and CH$_3$. However, the essential requirement of the comonomer was proven when the cyclization reaction became faster in stabilization process.   This topic is discussed in section 3.2.

In the second technique, the comonomers could not fully react with the PAN polymer because the PAN powder might have already been dispersed in the solvent. Therefore, the comonomers might only have been dispersed in acrylonitrile as additives. The comonomers which were dispersed in the PAN matrix were attached to the PAN structure when heat was supplied especially in the stabilization process. Based on Figure 3, the important peak (~1700cm^{-1}) which represents attached comonomers is nearly non-existent. The peak at 1700 cm^{-1} is shifted to around 1660 cm^{-1} and this could be evidence that comonomers were dispersed in the PAN matrix. It is because the resonances that form at this peak reduced the stretching frequency of the carbonyl group in both comonomers (Wade, 1999). The resonance reaction is illustrated in Figure 4. The resonance phenomenon could have inhibited the initiation of the cyclization reaction during the heat treatment. As a result, initial observation showed that, there was no significant change in the PAN fiber colour although the temperatures reached 200°C in contrast to the PAN fiber of Type 1.

  It was reported that copolymerization with itaconic acid could initiate the cyclization reaction. Beltz and Gustafson (Beltz and Gustafson, 1996) stated that PAN homopolymer cyclizes slower than any of the co-polymers, resulting in a lower extent of cyclization for the homopolymer than the acidic co-polymers at all reaction times. In addition, with short reaction time, the initial cyclization rate is faster for co-polymers with larger itaconic acid concentrations. However, as stated by Tsai and Lin (1990), in the presence of itaconic acid as additive, the cyclization of PAN precursors can also initiated at a lower temperature thus reducing stabilization time.

3.2 Cross Section of the PAN Fiber

Figure 5 shows the morphology of a PAN fiber produce through a dry-wet spinning process. It is clearly seen that the fiber was free from void. However, flaws can be seen at the surface of the PAN fiber. This flaw might be due to the free solvent system that was applied in the spinning process. The systems caused the mass transfer within the fiber surface and coagulation bath inconsistent and thus produce a bad fiber shape.

Meanwhile, the evenness of the cross-section or fineness of PAN precursors was largely influenced by the flow conditions in the spinneret, and the design of the roller for drawing. Referring to Figure 5, the cross sectional shape of the fiber seems to be slightly kidney bean or round shaped. The formation of the shape is dependent on the center of the fiber, whether it has solidified or not during fiber collection. Rigid fiber skin can also form in the spinning process before the center of the fiber has solidified, and as a result yields the kidney bean shape.

As a comparison, fibers diameter were also measured by scanning electron microscopy (SEM). The diameter of the fibers were in the range of 50-55μm which depended on the size of the spinneret. The fibers of Type 1 were 7% bigger in diameter compared to Type 2 because the Type 1 solution had the highest viscosity due to heating process during dope preparation. Typically a jet stretch of 2.0 is applied during the fabrication process. However, the high value of the jet stretch will cause the PAN fiber from the Type 1 solution tend to break during the spinning process. Therefore, it is

recommended that the jet stretch value is maintained at 1.0 for the fabrication of PAN fibers of Type 1. However, the diameter of fibers is examined to be bigger with a jet stretch of 1.0 under SEM.

3.3 Effect of thermal degradation temperature

The thermal behavior of the samples was investigated by thermogravimetric analysis (TGA) under a nitrogen (N_2) atmosphere until the temperature reached up to 1000ºC. When polyacrylonitrile was heated in the TGA instrument under an inert atmosphere, degradation occurred and the mass decreased as the temperature increased. Typical thermograms of various polyacrylonitrile samples are presented in Figure 6. These thermograms of the PAN powder and PAN fiber (Type 1 and Type 2 PAN fibers) were obtained without stabilization.

From Figure 6, it can be seen that at the beginning of the heating process (below 300°C) there was no weight loss observed in the PAN powder and only a little weight change occurred in the PAN fiber (Type 2). This occurred because the PAN powder did not contain comonomers that initiated the cyclization reaction. A cyclization reaction of the nitrile groups was believed to be the cause of loss of polyacrylonitrile weight during heating. In addition, Devasia *et al.* (2003) also stated that the cyclization of nitrile groups would initiate an exothermic reaction which is then followed by a loss of the polyacrylonitrile weight. However, PAN fibers with side chain comonomers had a larger weight loss because chain scission occurred in the fiber during the cyclization reaction.

Based on Figure 6, significant weight loss occurred around 300-350°C for the PAN powder and PAN fiber of Type 2 (i.e., PAN powder at 313.19°C; Type 2 PAN fibers at 320.2ºC). Meanwhile, for PAN fibers with the comonomers attached to the PAN structure (Type 1), the onset of the thermal decomposition took place at two temperature regions (i.e. 265.63ºC and 376.47ºC). The reason was possibly due to the glassy temperature of polyacrylonitrile at 317°C. This decomposition trend was also discovered by David and Ismail (2002). However in the region at 350-750°C TGA temperatures of the loss of Type 1 PAN fibers were slower. This indicated that the comonomers which attached to the PAN structure (Type 1 PAN fibers) could cyclize the structure faster than others and then stabilized the PAN structure. However, because of the chain scission of the comonomers, the overall weight loss of this fiber is on average the greatest. As shown in Figure 6, the PAN powder has degraded to 66.99% of the total mass, Type 2 PAN fibers lost 61.18% of their weight and Type 1 PAN fibers were left with only about 14.35% of their original weight.

From the percentage loss, the total weight loss of PAN fibers prepared by method 2 is less. It is also shown in Figure 6 that after about 50% weight loss the rate of loss was slow. It is postulated that the molecular crosslinking that occurred in the PAN structure inhibited the weight loss of PAN fibers. It is believed that a cross-linked polymer is more thermally stable than the corresponding thermoplastic polymer. The molecular crosslink in the PAN polymer could crystallize the PAN structure. Zhu *et al.* (2002) discovered that PAN in a crystal structure would decelerate the weight loss in order to produce high carbon yield.

3.4 Effect of stabilization process

For comparison, the fibers that were produced from both methods (method 1 and method 2) were stabilized at the same condition. Figures 7 and 8 show the shifting of the spectrum of PAN samples after heating in air (without air flow) at different temperatures around 200-300°C for 1 hour, in order to develop hydronaphthiridine rings. During stabilization process, thermal heating played an important role to initiate the cyclization reaction. Heat was produced by the cyclization of pendant CN groups of PAN fibers, although they were heated under a nitrogen atmosphere (exothermic reaction). Thus, more heat evolution occurred which caused a lot of CN groups undergo cyclization and form hydronaphthiridine rings. The presence of hydronaphthiridine rings was proved by Memetea *et al.*(1995) and the new bands within 1600-1620 cm^{-1} which were attributed to C=N vibrations appeared. In addition, it is apparent that the carbonyl peak intensities at (~1700cm^{-1}) of PAN fibers (Figures 7 and 8), was shifted to the intensity of the band at 1600 cm^{-1}.

Meanwhile, the intensity of the 2240 cm^{-1} wavenumber in these figures (Figures 7 and 8), which associated to a stretching vibration of C≡N bonds and the strong band around 2930 cm^{-1} representing the CH_2 groups in the polymer chain were hardly changed or reduced. These could result in alterations in molecular structure of polyacrylonitrile. The changes in the PAN intensities also depend on the concentration of comonomers that are used in an experiment. According to Wangxi et al (2003), an increase in the amount of comonomers will cause a reduction in cyclization temperature. Hence, a lower cyclization temperature will avoid the unstable cyclization that occurs in pure PAN and leads to chain-breaking. However, as the content of itaconic acid increased slightly, the conversion of acrylonitrile decreased greatly. This phenomenon had been explained by Tsai and Lin (1991).

From the IR result, it showed that the Type 1 fiber started the cyclization reaction at a lower temperature compared to Type 2 fiber. The intensity of the nitrile peak for the Type 1 fiber (Figure 7) reduced faster than Type 2 fibers (Figure 8). This is because the preparation of dope by method 2, the comonomers were only reacting as additives to the fiber during stabilization process. Whereas the Type 1, the comonomers were attached to the PAN polymer during dope preparation. The additive reactions in the PAN structure were confirmed by Tsai and Lin (1990), whereas the additives could also

reduce the initial cyclization temperature of modified PAN fibers than PAN homopolymer. The mechanism of the reaction as additives is illustrated in Figure 9. In addition, in the stabilization process, the colour of fibers of Type 1 also became yellow at a lower temperature compared to fibers of Type 2 which started to be yellow at a higher temperature.

Typically, in stabilizing the PAN fiber in air, the other main reaction namely oxidation process will also occur. The oxidation process takes place by means of dehydrogenation and crosslinking. The hydrogen moles continue to decrease with progressive oxidation as a result of in dehydrogenation reaction. Wang, (1998) also discovered the same phenomenon in this dehydrogenation reaction which could assist in stabilizing the PAN structure. Subsequently, these reactions helped in increasing the peak around at 1600 cm^{-1} which is represented as a double bond. This unsaturated bond caused by cyclization and the dehydrogenation reaction improved the stability of PAN fibers and reduced chain scission when the fibers were subjected to high temperature processing. The cyclization and dehydrogenation reactions are concluded from Figure 10.

4. Conclusion

Modified polyacrylonitrile (PAN) homopolymer was spun using dry/wet spinning process. Based on the results presented and discussed, this section summarizes the important conclusions from each of the major portions of this work.

(1) PAN homopolymers have been successfully modified by reacting them with comonomers. The heat applied during dope preparation (Type 1) caused an interaction between comonomers and PAN homopolymer. Subsequently, a peak around 1660-1700cm^{-1} was observed.

(2) The modification of PAN homopolymers at the temperature of 70ºC underwent the stabilization process faster than modification at ambient temperature because this can attach to the PAN structure at the heated temperature.

(3) High weight loss of the fibers is likely to be by the large fiber diameter which can cause inconsistent heat treatment. Moreover, with attached comonomers (Type 1 fibers) the weight loss could be increased.

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Table 1. Specification of spinning conditions

Specifications	Conditions
Spinning dope composition	20 wt.% polymer
	80 wt.% Dimethylformamide
Spinning dope temperature	Ambient temperature (27ºC)
Air distance	10 cm
Spinneret dimensions	Hole diameter 200 µm
Force convection gas	Nitrogen
External bath composition	Tap Water
External bath temperature	10 ºC
Jet stretch	1.0 to 2.0
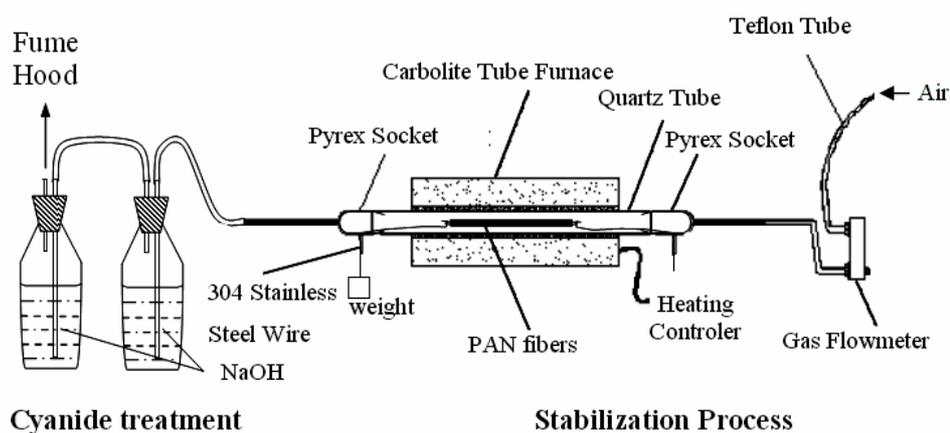
Figure 1. Stabilization heating system.
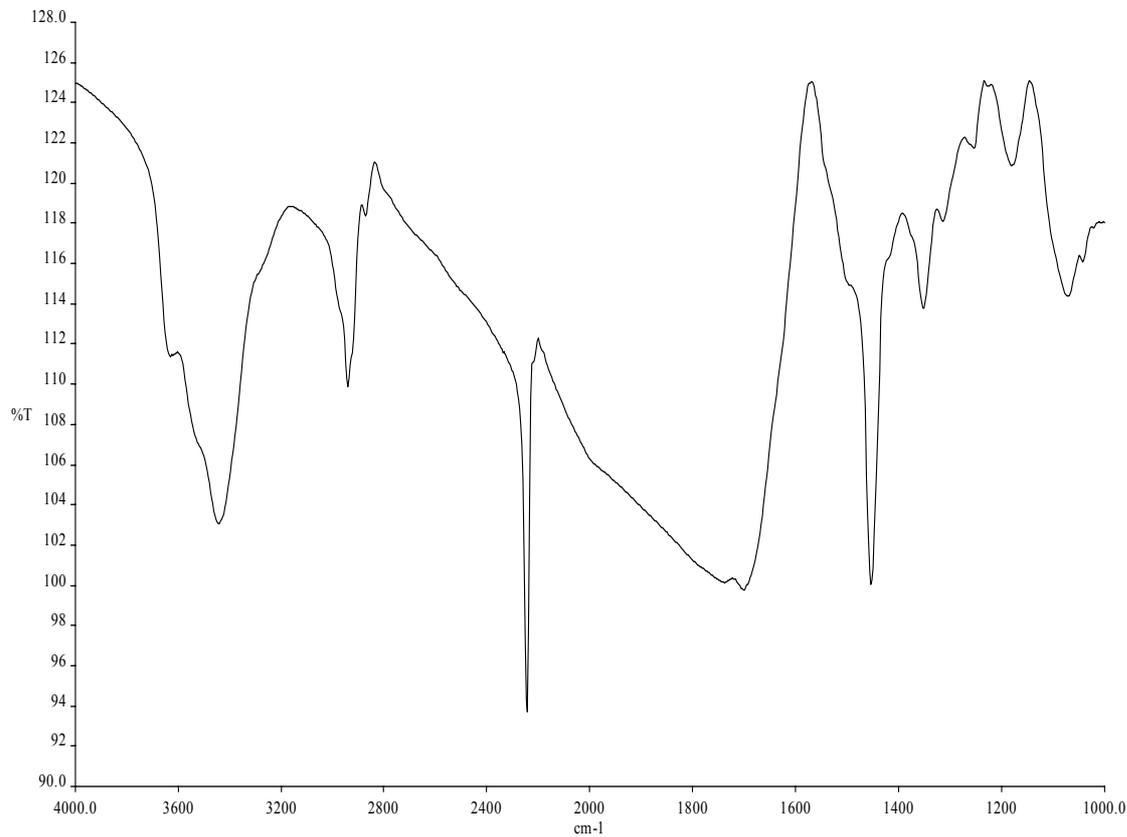
Figure 2. Infrared transmission for PAN fiber (Type 1).
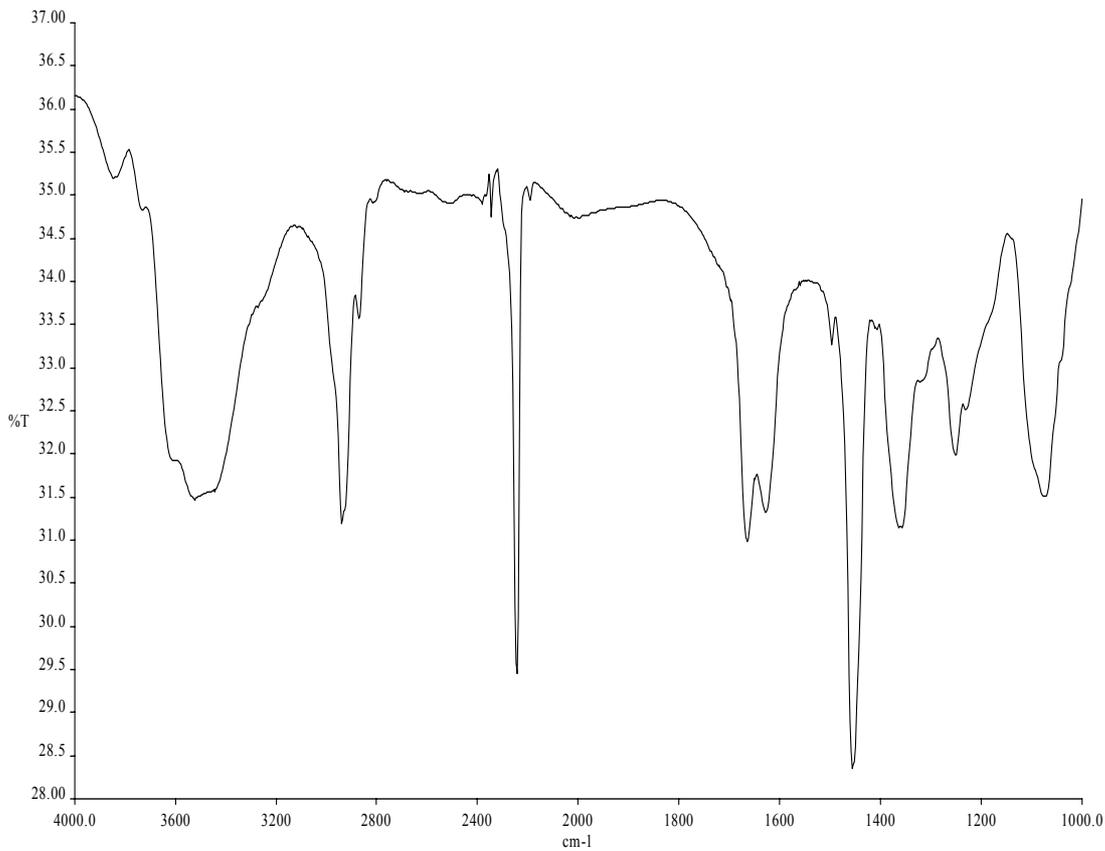
Figure 3. Infrared transmission for PAN fiber (Type 2).
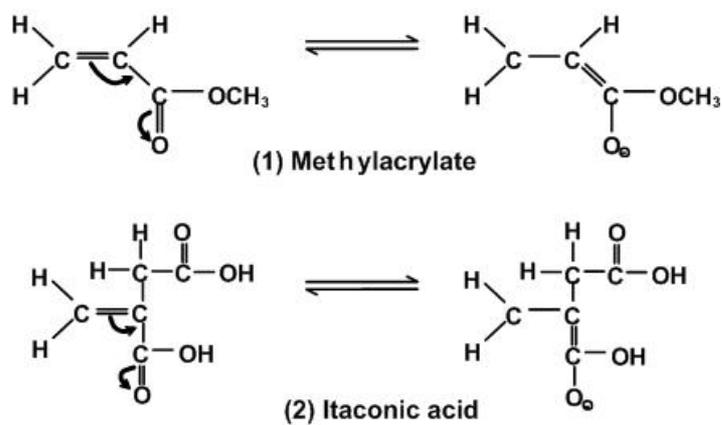
Figure 4. Resonance or conjugation phenomenon occurs in comonomers.
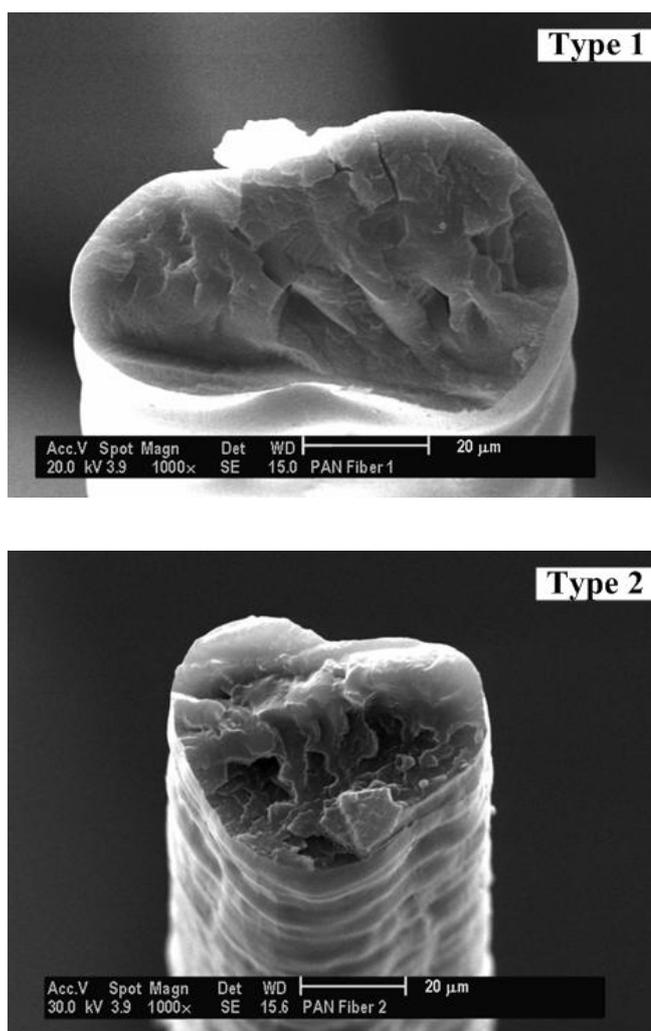
Figure 5. The cross section of PAN Fiber with different types of
dope preparation: (a) for Type 1 and (b)for Type 2 (Magnification: 1000×)
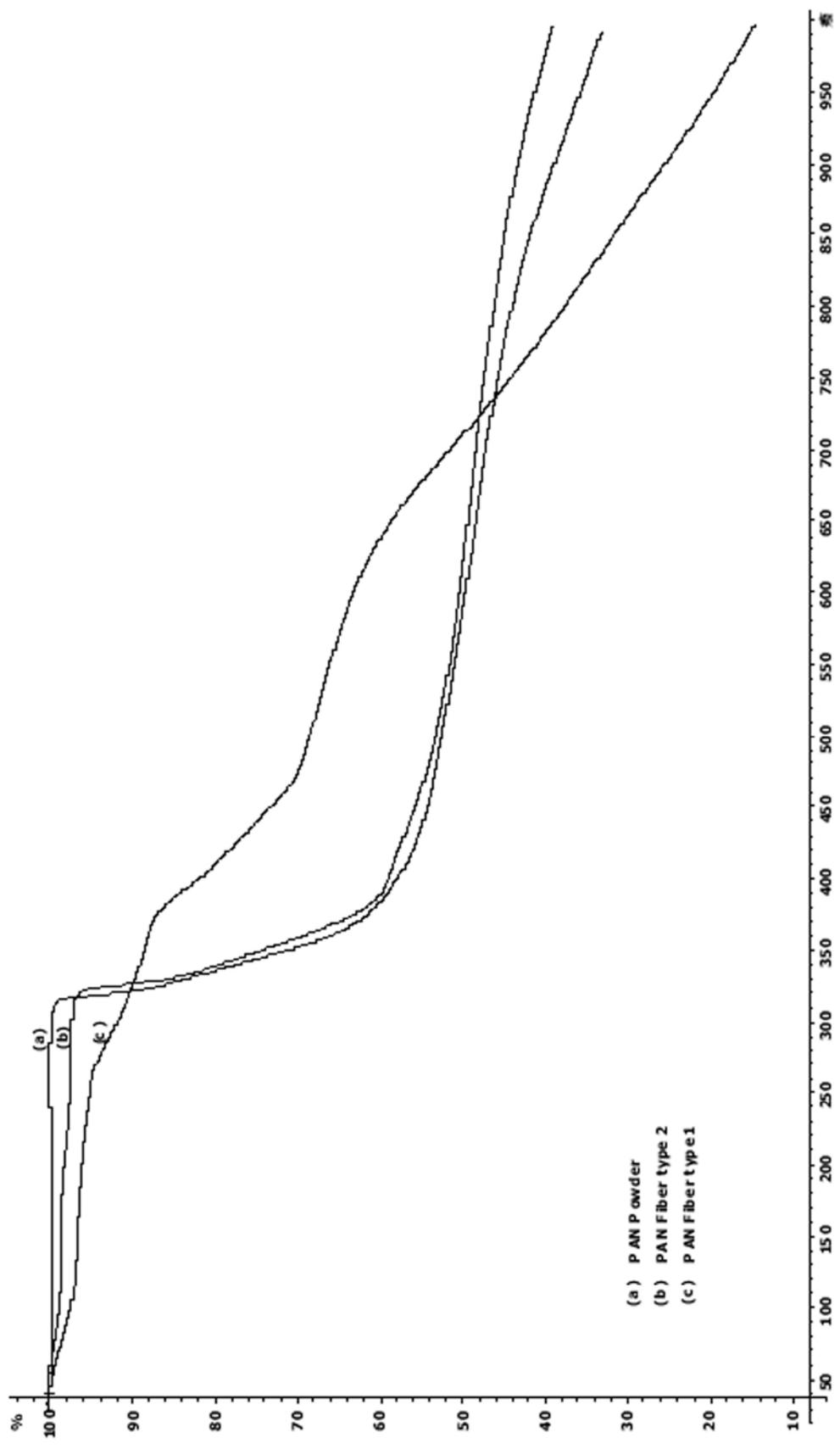
Figure 6. TGA curves of PAN powder and PAN fiber with different dope preparation

(a) PAN Powder
(b) PAN Fiber type 2
(c) PAN Fiber type 1
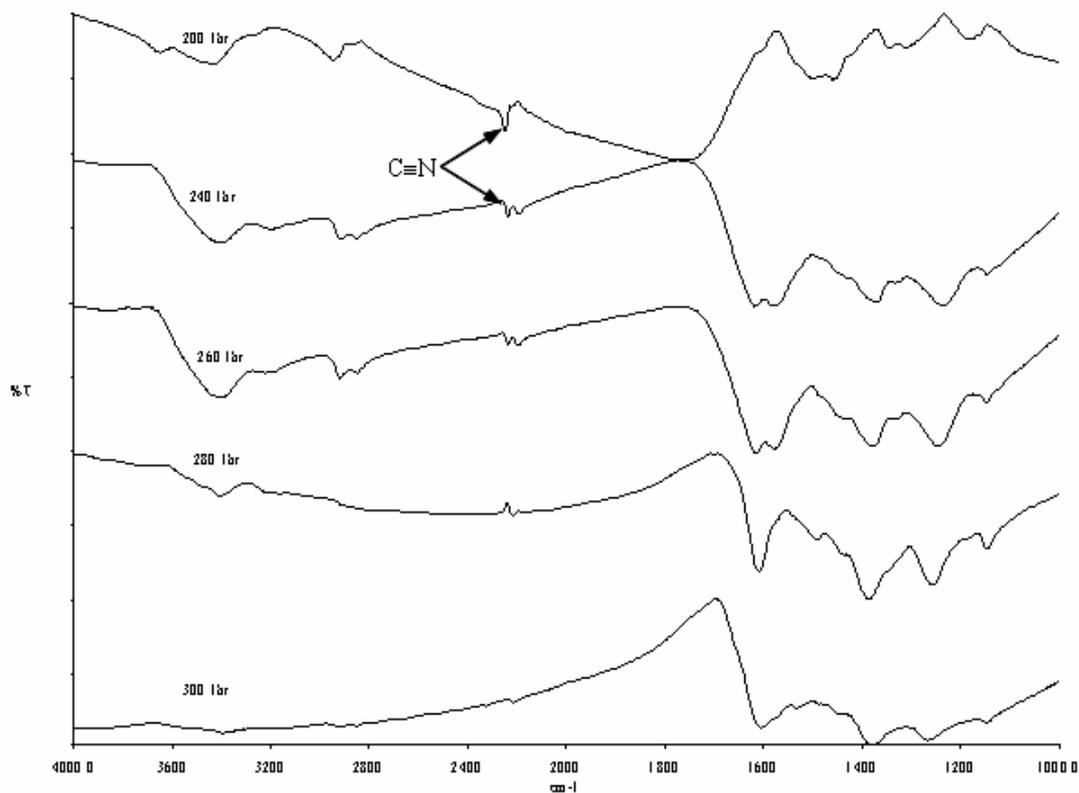
Figure 7. IR spectrum of stabilized PAN fiber (Type 1) in air.
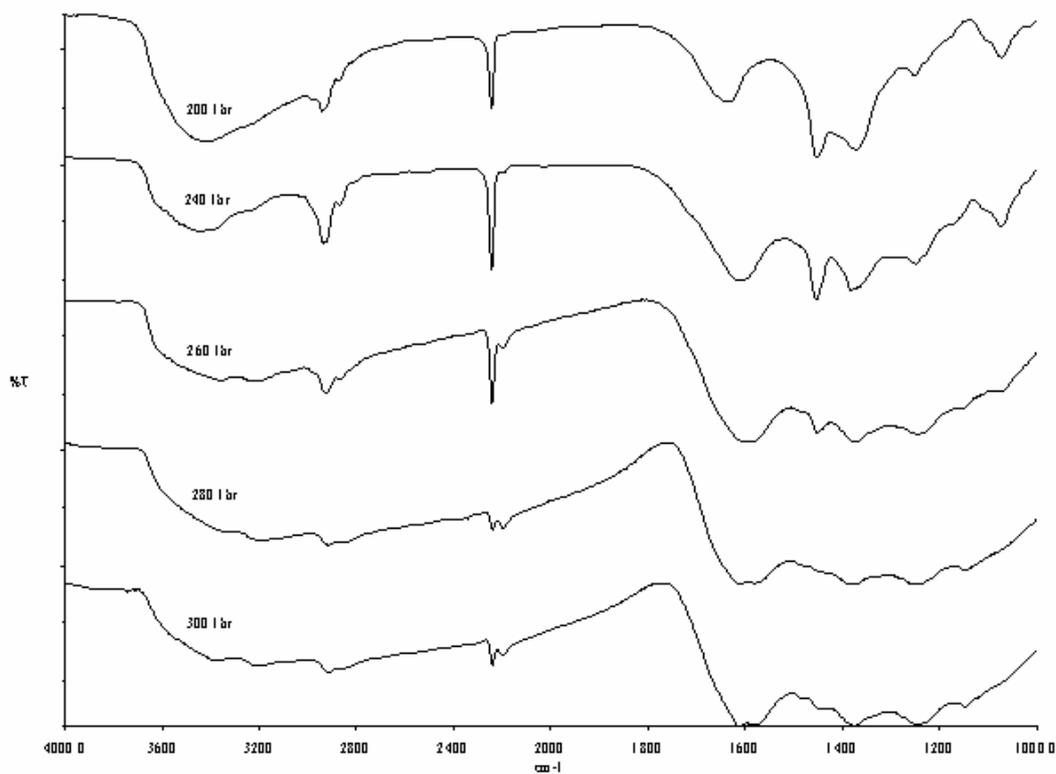
Figure 8. IR spectrum of stabilized PAN fiber (Type 2) in air.
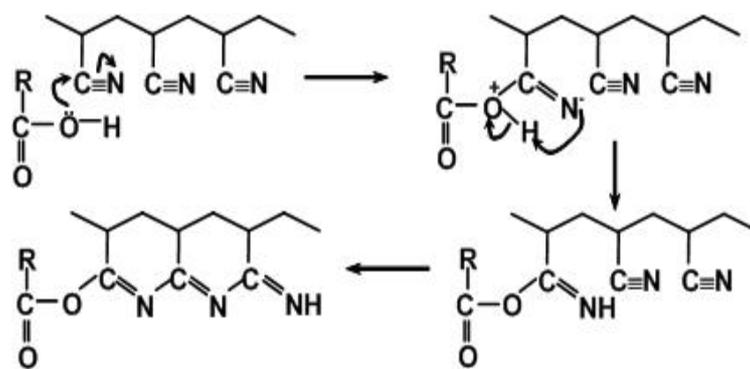
Figure 9. Comonomers react as an additive to initiate cyclization reaction (Tsai and Lin, 1990).
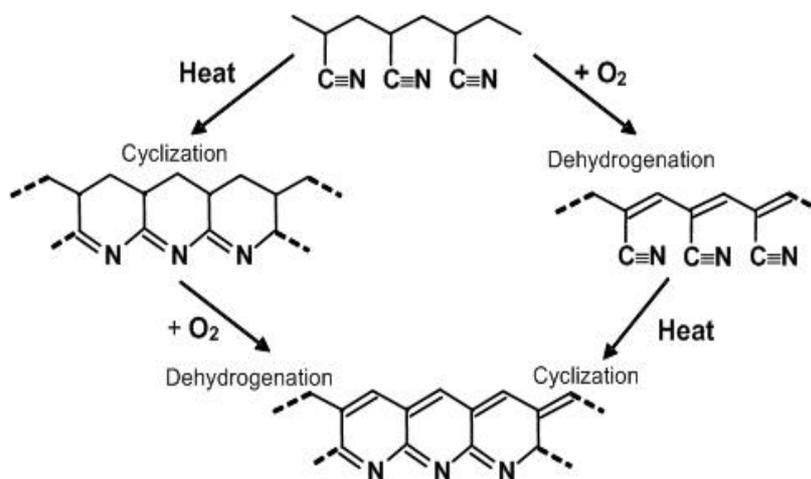
Figure 10. Cyclization and dehydrogenation reaction during stabilization process.