

Preparation and Thermal Behaviour of Acrylonitrile (AN)/Ethyl Acrylate (EA) Copolymer and Acrylonitrile (AN)/Ethyl Acrylate (EA)/Fumaronitrile (FN) Terpolymer as Precursors for Carbon Fibre

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ABSTRACT

Redox polymerization of acrylonitrile (AN) with ethyl acrylate (EA) and fumaronitrile (FN), as comonomer and termonomer respectively, were carried out using sodium bisulfite (SBS) and potassium persulphate (KPS) as initiators at 40°C. The actual composition of monomers in copolymers and terpolymers has been characterized by gas chromatography (GC). The effects of EA and FN on the glass transition temperature (T_g) and stabilization temperature have been studied by Differential Scanning Calorimetry (DSC). The degradation behaviour and char yield were obtained by thermogravimetric analysis. Meanwhile, incorporation of 10 mol% of EA in homoPAN system was found to greatly reduce T_g to 66°C as compared to that of the homoPAN ($T_g=105^\circ\text{C}$). The initial cyclization temperature (T_i) was found to be higher (264°C) in comparison to that of homoPAN (246°C). In addition, the incorporation of EA was also shown to reduce the char yield of copolymer to 40%. When FN was incorporated as termonomer, the char yield of poly(AN/EA/FN) 90/4/6 increased up to 44% after the heat treatment with the lowest T_i (241°C).

Keywords: Acrylonitrile, carbon fibre, copolymer, ethyl acrylate, fumaronitrile, redox polymerization, terpolymer

INTRODUCTION

Carbon fibre has excellent properties such as low density, high stiffness, good resistance toward chemical and environment effects, and the ability to withstand high temperature. Hence, carbon fibre has a lot of applications such as in aerospace industry, sporting goods, automobile, defence applications, and ship structure (Gupta *et al.*, 1991). Carbon fibres can be made from various materials such as rayon, pitch, and polyacrylonitrile (PAN). At present, PAN in fibre form is the most successful precursor for making high performance carbon fibres (Tsai *et al.*, 1991). In this paper, the focus of the study is on PAN-based precursors, which are commonly used in various applications that require high tensile strength fibres and a high extension to break. The most important process involved in the conversion of PAN fibres into carbon fibres is the stabilization process. This process leads to the formation of a ladder polymer. This stabilization process involves some complex reactions of intra and intermolecular cyclizations of PAN that should yield the highest degree of ladder-like structure formation with minimum adverse effects, such as chain scission and defect on chain structure (Gupta *et al.*, 1995). However, it is well known that the cyclization process of

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PAN involves a rapid exothermic process with high heat liberation. The evolution of volatile by products such as H₂O, CO₂, HCN, NH₃ and even nitrogen causes mass loss. The elimination of HCN and NH₃ creates uncyclized gaps in the structure of polymer which retards the process of cyclization (Martin *et al.*, 2001). Hence, it may produce carbon fibre with poor properties after heat treatment. In order to overcome this problem, ethyl acrylate (EA) comonomer was incorporated into the PAN system. EA was used as T_g modifier in AN/EA copolymer system (Jordan *et al.*, 1972). Ester-based comonomers are known to have diluent effect on the exothermic reactions which occur during stabilization of the precursor fibres. Since acrylate comonomer can be randomly polymerized into the PAN system, it acts as defects and helps to reduce the dipole-dipole interactions and long-range order in the PAN system (Rangarajan *et al.*, 2002) that also can be indirectly observed by T_g depression. In addition, this also indicates a low processing temperature of PAN (Rangarajan *et al.*, 2002). However, the incorporation of ester-based comonomer reduces the level of formation of ladder-like structure which further reduces the char yield of PAN that provides a realistic indication of the final carbon content after heat treatment (Tsai *et al.*, 1991). In this study, FN was used as termonomer because it had been shown to increase the char yield of PAN copolymer. In more specific, FN was found to increase the possibility to form ladder-like structure during stabilization and thus lead to a high char yield during carbonization (Jamil *et al.*, 2007). High char yield indicates high carbon content in fibres (Rangarajan *et al.*, 2002), and thus results in carbon fibres with good mechanical properties.

Water is used in the redox method for polymerization, and this gives it some advantages, i.e. polymerization which is carried out in a mild reaction conditions, short reaction time, affords a high conversion and avoids the use of organic solvent (Sarac, 1999).

MATERIALS AND METHODS

The homoPAN, copolymers and terpolymers in this study were synthesized using the redox method. The three-necked flask was fitted with a condenser, stirrer, and nitrogen inlet tube. Deionized water was used as a reaction medium with potassium persulfate (KPS) and sodium bisulfite (SBS) as initiator. Polymerization was carried out at 40°C for 3 hours under a nitrogen atmosphere. The polymer formed was precipitated, filtered, and washed successfully with deionised water and methanol. The polymers obtained were dried under vacuum at 45°C till a constant weight was obtained. The actual composition of ethyl acrylate and fumaronitrile that polymerized was calculated from the residual monomer concentration data. The residual monomer concentrations of the withdrawn samples were obtained using the gas chromatography (GC) system. The polymers obtained were firstly mixed with a defined amount of methanol to precipitate and isolate the polymer from the reaction medium (water). The residual monomer remains in water. A defined portion of supernatant was injected for the GC analysis (Rintoul *et al.*, 2005). In addition, the calibration curves of ethyl acrylate and fumaronitrile were obtained using the GC system. Undecane was used as the internal standard for calibration curve and sample analysis. The peak area served as the calibration parameter. On the other hand, the composition of acrylonitrile that polymerized was calculated using the following equation:

$$\text{Polymerized acrylonitrile (g)} = \text{polymer conversion (g)} - (\text{ethyl acrylate} + \text{fumaronitrile polymerized}) \text{ (g)} \quad (1)$$

The fourier transform infrared spectroscopy (FTIR) spectra of homoPAN, copolymers, and terpolymers were recorded on the Perkin Elmer GX infrared spectrophotometer using KBr pellets. Meanwhile, the samples in powder form (~5) mg were used for the DSC analysis. The glass

transition temperatures (T_g) of the samples were evaluated using the Mettler-Toledo differential scanning calorimeter (DSC). The heating rate employed was 10°C/min and the samples were heated from room temperature to 200°C, cooled back to room temperature at the same heating rate, and reheated again to 200°C. The temperature during the stabilization process was obtained by heating the samples from room temperature to 400°C at 10°C/min. The thermogravimetric analysis was carried out using a Mettler-Toledo TGA instrument in nitrogen from room temperature to 950°C at a heating rate of 10°C/min. A sample size of ~15 mg in the form of fine powder was used to determine the weight loss of polymers.

RESULTS AND DISCUSSION

Conversion of Polymerization and Actual Composition

As shown in Table 1, homoPAN achieved the highest conversion (85%). This is due to the non-abnormalities or defects present in the polymer chains since polymerization was not incorporated with other monomer (Jamil *et al.*, 2007). In the case of AN/EA copolymer, the incorporation of EA into copolymer was 86-89%, which is higher as compared to that of the AN (68-76%). In the case of terpolymers, the incorporation of EA into terpolymers was also the highest (82-87%) as compared to that of the AN (62-68%) and FN (77-80%). The rate of copolymerization is greatly influenced by the concentration and polarity of the monomers (Bhanu *et al.*, 2002). In water reaction medium, polymerization was proceeded according to the suspension polymerization mechanism; hence, propagation would mostly occur in oligomeric radicals phase as the number of polymer particles increased (Wan *et al.*, 2005). In this case, it remains in the aqueous phase since FN is more hydrophilic, whereas EA (which is more hydrophobic as compared to FN) is buried in the growing particle core and has a better chance to polymerize into polymer particles.

TABLE 1
Actual composition of PAN, poly(AN/EA) and poly(AN/EA/FN)

Feed (%mol), M AN/EA/FN	Conversion (%)	Composition (%mol), m AN/EA/FN	Reacted monomers (%) m/M x 100 AN/EA/FN	Actual composition (%mol)
100/0/0	85	85/0/0	85/0/0	100/0/0
Copolymer				
95/5/0	77	71.88/4.45/0	76/89/0	94/6/0
90/10/0	76	66.15/8.70/0	74/87/0	88/12/0
85/15/0	73	57.81/12.90/0	68/86/0	82/18/0
80/20/0	-	-	-	-
Terpolymer				
90/2/8	65	55.73/1.74/6.40	62/87/80	87/3/10
90/4/6	69	59.90/3.44/4.62	67/86/77	88/5/7
90/6/4	66	56.25/5.16/3.12	63/86/78	87/8/5
90/8/2	70	60.94/6.56/1.56	68/82/78	88/9/2

FTIR Spectroscopy

A representative FTIR spectrum of homoPAN, together with its copolymer and terpolymer, is shown in Fig. 1. In all cases, the bands in the region 2943 cm^{-1} were assigned to C-H stretching in CH, CH_2 , and CH_3 . Meanwhile, the bands at 1450 cm^{-1} , 1353 cm^{-1} , and $1204\text{--}1199\text{ cm}^{-1}$ appear due to the C-H vibrations of the different modes. The band at 2244 cm^{-1} indicates the absorption of nitrile groups in homoPAN, copolymers, and terpolymers. The band in the 1654 cm^{-1} region may be attributed to the hydrolysis of acrylonitrile units during the polymerization process which was also found by other researchers (Bajaj *et al.*, 1996). The strong band in the range of 1735 cm^{-1} in the copolymer and terpolymer spectra were due to the C=O stretching (Bajaj *et al.*, 1993). The disappearance of bands at $2238\text{--}2239\text{ cm}^{-1}$, which was due to the stretching of unsaturated nitriles of FN (Jensen, 2003), confirmed that FN was incorporated together with AN and EA to form terpolymers.

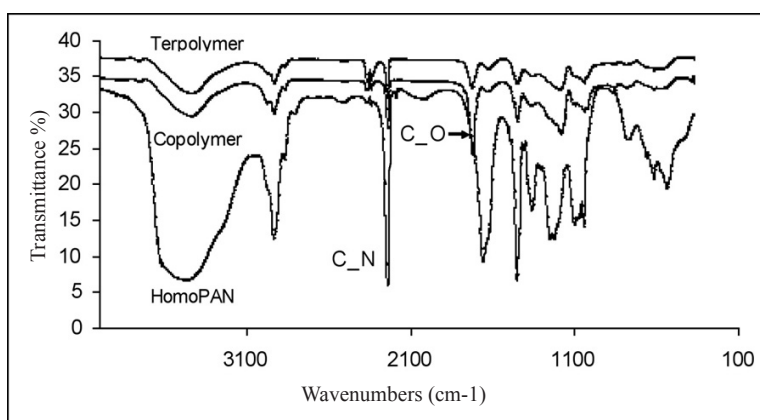


Fig. 1: IR spectrum of homoPAN, copolymer and terpolymer

DSC Analysis

Table 2 shows the glass transition temperature (T_g) of PAN, copolymers, and terpolymers. The T_g of the copolymers is lower as compared to that of the homoPAN (105°C). It is well known that homoPAN has a high T_g , and this is attributed to high chain stiffness resulting from strong dipole-dipole interaction (Min *et al.*, 1994). Meanwhile, AN/EA copolymers exhibited lower value of T_g . This can be ascribed to the introduction of EA that reduces the intermolecular interactions between the polymer chains due to structure loosening (Gupta *et al.*, 1989). From all the samples obtained, the AN/EA copolymer of 10 mol% EA was found to have achieved the lowest T_g (66°C). However, as the amount of EA increased to 15 and 20 mol%, the T_g increased to 68°C and 70°C , respectively. This might be due to the non-optimized amount of EA that hindered the chain mobility sterically, and subsequently increased T_g (Gupta *et al.*, 1989).

In the case of terpolymers, T_g is higher as compared to that of the copolymers. This might be due to the incorporation of FN monomer with polar nitrile group that further increased the intermolecular interactions in the PAN system (Gupta *et al.*, 1989; Bajaj *et al.*, 2001).

TABLE 2
Glass transition temperature of homoPAN, copolymers and terpolymers

AN:EA:FN (mol %)	Glass transition temperature, T_g (°C)
100:0:0	105
Copolymer	
95:5:0	81
90:10:0	66
85:15:0	68
80:20:0	70
Terpolymer	
90:2:8	81
90:4:6	74
90:6:4	70
90:8:2	67

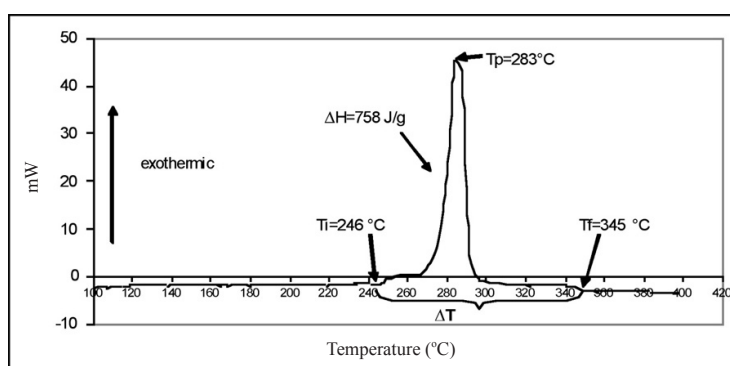


Fig. 2: DSC thermogram of homoPAN

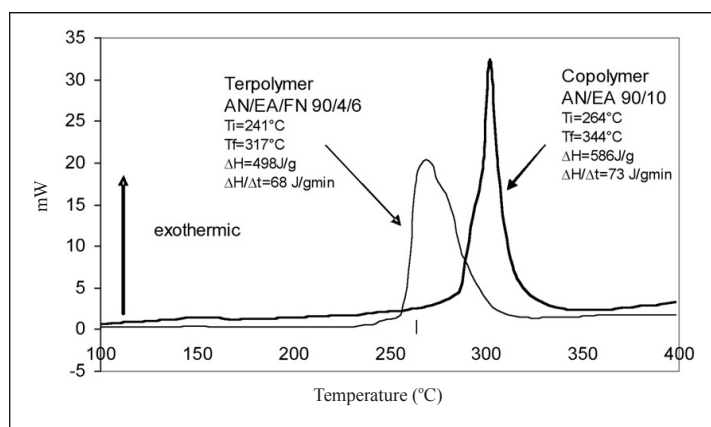


Fig. 3: DSC thermogram of copolymer and terpolymer

Figs. 2 and 3 show a comparison between DSC thermogram of PAN, copolymer, and terpolymer. The exothermic peak of homoPAN has a singlet, sharp, intense, and narrow peak starting from 246°C to the final temperature, i.e. 345°C. The heat liberated during the reaction (ΔH) was 758 Jg⁻¹. The singlet, intense, and narrow peak indicates that the rate of propagation is very high after the initiation of cyclization reaction through a radical mechanism (Gupta *et al.*, 1995). On the other hand, the exothermic process that involves heat evolution accomplished at the lowest rate in the case of AN/EA/FN 90/4/6 copolymer (68 Jg⁻¹min⁻¹), indicating that the exothermic reaction takes much longer time to be completed with lower heat liberation per time (Bajaj *et al.*, 1993). This is favourable in the production of carbon fibre because it reduces defects in polymer chains and increases the formation of ladder-like structure, and hence produces carbon fibre with good mechanical properties (Bajaj *et al.*, 1993).

Amongst homoPAN, copolymer and terpolymer, the AN/EA/FN 90/4/6 terpolymer achieved the lowest rate of heat liberation (68 Jg⁻¹min⁻¹), as compared to homoPAN and AN/EA copolymer. This indicates that FN slightly affects stabilization process by facilitating the cyclization reaction, as reported previously (Jamil *et al.*, 2007).

Thermogravimetric Analysis (TGA)

Table 3 shows the char yield obtained from the TGA thermogram. The char yield of copolymers is lower (40%) as compared to that of homoPAN (48%). The incorporation of EA enhances the level of degradation due to the higher amount of chain scission instead of the formation of the ladder-like structure. According to Rangarajan *et al.* (2002), other researchers have reported that there is an increase in weight loss with the increase in the comonomer content due to the disruption of nitrile sequence which ultimately results in poor char yield of carbon fibre. However, incorporating 6mol% of FN in the case of terpolymers increased the char yield to 46%. There might be a different degradation process of terpolymer as compared to that of copolymer. There are 4 stages in oxidative degradation. In the case of AN/EA 90/10 copolymer (Fig. 4), the weight loss in the region 30-100°C involved the vaporization of moisture. The weight loss in the first zone (100-240°C) is only 1.25% due to the evolution of HCN and NH₂ (Bajaj *et al.*, 1993). The second zone (240-350°C) has a rapid weight loss with a maximum weight loss of 31.94%. This is the most important stage because it is associated with the formation of ladder-like structure which produces volatile products (HCN, NH₂ along with other products such as CO₂ and H₂O) and subsequent chain scission (Bajaj *et al.*, 1996). This is followed by little weight loss of about 18.68% in the region 350-480°C. The final zone (480-900°C) showed a steady and slow weight loss (8.01% weight loss) up to 900°C and gave a char yield of 40%.

TABLE 3
Weight loss and char yield of PAN, copolymer and terpolymer

Monomer feed (mol%)	Weight loss (%)				Char yield (%)
	Zone 1 (30-250°C)	Zone 2 (250-350°C)	Zone 3 (350-480°C)	Zone 4 (480-900°C)	
PAN	1.61	23.21	13.17	14.27	47.74
AN/EA/FN					
90/10	1.25	31.94	18.68	8.01	40.12
90/2/8	0.98	27.79	17.65	6.46	47.12
90/4/6	0.36	29.86	14.54	8.87	46.37
90/6/4	0.65	30.14	13.67	10.31	45.23
90/8/2	1.14	31.78	13.41	10.80	42.87

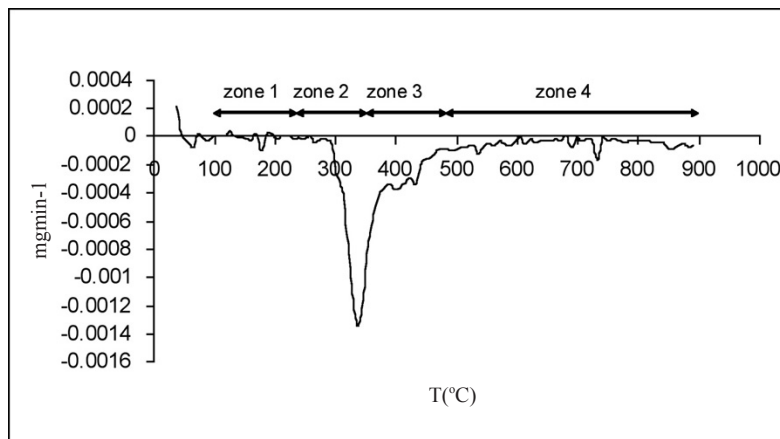


Fig. 4: DTG curve of AN/EA copolymer

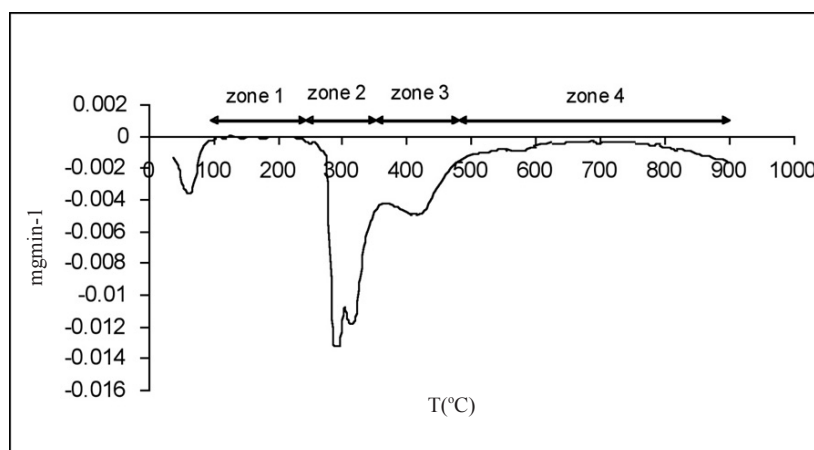


Fig. 5: DTG curve of AN/EA/FN terpolymer

On the other hand, the AN/EA/FN 90/4/6 terpolymer (see Fig. 5) has a different degradation pattern. The weight loss in the first zone is 0.36%, followed by 29.86% weight loss in the second zone. The weight loss in the third zone is 14.54% and the weight loss in fourth zone is 8.87%. This gave a char yield of 46% which is higher as compared to that of the AN/EA copolymer. This is due to the incorporation of FN which has increased the formation of ladder-like structure during the stabilization process, and subsequently increases the char yield of terpolymer (Jamil *et al.*, 2007).

CONCLUSIONS

Using the redox method in this study, the polymerization was achieved with a maximum conversion of 77% and 70% in the case of AN/EA copolymer and AN/EA/FN terpolymer respectively. Meanwhile, the introduction of EA had successfully reduced T_g of copolymer to 66°C as compared to that of the homoPAN (105°C). The initial cyclization temperature of copolymer increased

to 264°C as compared to that of the homoPAN (246°C). The incorporation of EA comonomer also reduced the char yield to ~40% which is unfavourable to the mechanical properties of PAN precursors. In order to overcome this problem, FN has successfully been incorporated into the terpolymer system to increase the thermal stability of terpolymers and consequently increase the char yield to 47%. FN was found to facilitate the exotherm process by reducing T_i to 241°C and the rate of heat liberation to 68 Jg⁻¹min⁻¹.

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