Redox Synthesis and Thermal Behavior of Acrylonitrile-Methyl Acrylate-Fumaronitrile Terpolymer as Precursor for Carbon Fiber

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Abstract—Redox polymerization of acrylonitrile (AN) with methyl acrylate and fumaronitrile as comonomer and termonomer respectively, were carried out by using sodium bisulfite (SBS) and potassium persulphate (KPS) as initiator at 40 ℃. The effect of methyl acrylate (MA) and fumaronitrile (FN) on the glass transition temperature (T_g) and stabilization temperature has been studied by Differential Scanning Calorimetry (DSC). The degradation behavior and char yield were obtained by Thermogravimetric Analysis. The T_g of poly(AN/MA) copolymers were found to be lower (~70 ℃) as compared to polyacrylonitrile (PAN) (210 ℃). However, by incorporating MA into PAN system, the char yield reduced significantly.It was found that FN reduced the initial cyclization temperature of poly(AN/MA/FN) terpolymer to ~230 ℃ as compared to poly(AN/MA) copolymer (~260 ℃). In addition, FN reduced the heat liberation per unit time during the stabilization process that consequently reduced the emission of volatile group during this process. Thereby, the char yield of poly(AN/MA/FN) 90/4/6 terpolymer is higher at 51% as compared to poly(AN/MA) 90/10 copolymer (45%).

Index Terms—Redox method, synthesis, thermal stability, polyacrylonitrile, terpolymer

I. INTRODUCTION

Thermal behavior of polyacrylonitrile (PAN) has always been the subject of interest because of its commercial values for the production of high performance carbon fiber. The most important in the manufacturing of carbon fibers from PAN is the oligomerization of nitrile groups (during stabilization process) which is influenced by the method of polymerization, nature of comonomers, additives and heat treatment [1,2]. The term stabilization is often used to describe the process involved when heating the PAN precursor at 200-300 ℃ under controlled conditions in order to stabilize it for the succeeding carbonization process and graphitization. This process leads to the formation of a ladder polymer in stabilized fibre. The cyclization of PAN during stabilization is always associated with a large exotherm in DSC curve [1].Acrylate comonomer acts as defects and help to reduce the dipole-dipole interactions and long-range order present in PAN system [3]. Thus, in this study, MA comonomer incorporated into PAN system to disrupt the order of polymer chains in the PAN system, thereby reducing itsglass transition temperature and lowering its processing temperature and consequently facilitating the melt spinning

of PAN system [4]. However, although MA succeed in reducing the T_g [5], it has been reported that MA comonomer results a negative impact on the theoretical carbon yield of PAN system [3].

On the other hand, acidic comonomers change the mechanism of stabilization from a free-radical reaction to an ionic reaction and help in initiating the cyclization reaction to occur at a lower temperature and slower rate [6]. These comonomers help to provide a uniform heat transfer within the PAN system, leading to better precursor fiber properties [7]. In this paper, the role of acid groups that are commonly used by other researchers to facilitate the stabilization process replaced by fumaronitrile (FN) as the termonomer. It has been reported that incorporation of FN slightly reduced the cyclization temperature during stabilization process and greatly increased the char yield of PAN after heat treatment at 900 ℃ [8]. Overall, this study focuses on producing PAN with low T_g so that PAN can undergo melt spinning and yet results in better stabilization process and char yield by using methyl acrylate as comonomer and fumaronitrile as termonomer respectively. Terpolymerization of acrylonitrile with methyl acrylate comonomer and fumaronitrile termonomer is shown in Fig. 1.
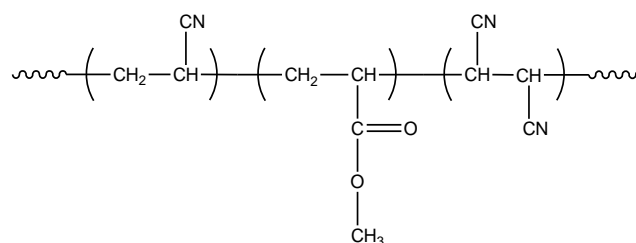

Fig. 1. Terpolymerization of acrylonitrile with methyl acrylate comonomer and fumaronitrile termonomer.

II. EXPERIMENTAL

A. Synthesis and Characterization

Polymerization of acrylonitrile (AN) with methyl acrylate (MA) as comonomer and fumaronitrile (FN) as termonomer was prepared by redox method. Polymerization was carried out in a three-necked flask at 40 ℃ under nitrogen atmosphere. The flask was fitted with a condenser and the third neck was used for nitrogen purging. The reaction medium used was water. Sodium bisulfite and potassium persulfate were used to initiate the polymerization. The polymerization was allowed to proceed for 3 hours and the polymer formed was precipitated, filtered, washed successively with methanol and deionized water and dried under vacuum at 45 ℃ till a constant weight was obtained [4]. Polyacrylonitrile

homopolymer and copolymer were also prepared in the same way.

The FTIR spectra of homoPAN, copolymers and terpolymers were recorded on Perkin Elmer GX infrared spectrophotometer using KBr pellets.

B. Composition Analysis of Polymers

The composition of methyl acrylate and fumaronitrile that polymerized was calculated from residual monomer concentration data. The residual monomer concentrations of withdrawn samples were obtained using a Gas Chromatography system. The polymers obtained were firstly mixed with 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 GC analysis [9].

The calibration curve of methyl acrylate (Fig. 3) and fumaronitrile (Fig. 4) were obtained by using GC system. Undecane was used as internal standard (IS) for calibration curve and samples analysis. The peak area served as calibration parameter. On the other hand, the composition of acrylonitrile that polymerized was calculated by the equation:

Polymerized acrylonitrile (g) = polymer conversion (g) – (methyl acrylate + fumaronitrile polymerized) (g)

C. Differential Scanning Calorimetry (DSC)

Samples in powder form (~5) mg were used for DSC. The glass transition temperature (T_g) of the samples were evaluated using a Mettler-Toledo Differential Scanning Calorimeter. The heating rate employed was 10 ℃/min and the samples are heated from room temperature to 200 ℃, cooled back to room temperature at the same heating rate, and reheated again to 200 ℃. The stabilization temperature was obtained by heating the samples from room temperature to 400 ℃ at 10 ℃/min.

D. Thermogravimetric Analysis

Thermogravimetric analysis was carried out using a Mettler-Toledo TGA instrument in nitrogen from room temperature to 950 ℃ at the heating rate of 10 ℃/min. A sample size of ~15 mg in the form of fine powder was used. To establish the relationship between the weight loss and temperature, TG thermograms and DTG curves were obtained.

III. Results and Discussion

A. FTIR Spectroscopy

The comparison of IR spectra of PAN with its copolymer and terpolymer are shown in Fig. 2. In all cases, the bands in the region 2943 cm^{-1} were assigned to C-H stretching in CH, CH$_2$ and CH$_3$. The bands at 1450 cm^{-1}, 1353 cm^{-1} and 1204-1199 cm^{-1} appear due to the C-H vibrations of different modes. The band at 2244 cm^{-1} indicating the absorption of nitrile groups in homoPAN, copolymers and terpolymers. The band in the region 1632 cm^{-1} may be attributed to the hydrolysis of acrylonitrile units during the polymerization process that also found by other researchers [10]. The strong band in the range of 1735 cm^{-1} in copolymer and terpolymer spectra were due to the C=O stretching [11]. The disappearance of bands at 2238-2239 cm^{-1} that due to the

stretching of unsaturated nitriles of FN [12,13] confirming that FN was incorporated into AN and MA to form terpolymers.
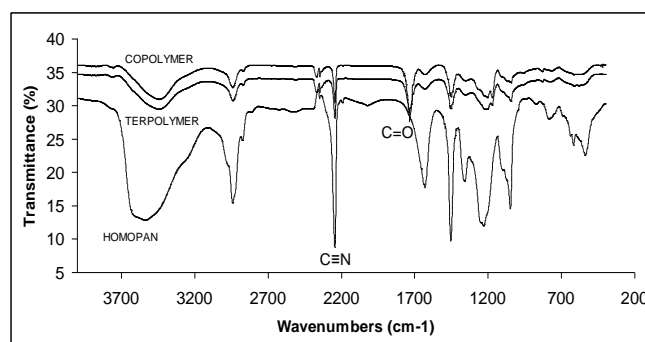

Fig. 2. IR spectra of homoPAN, copolymer and terpolymer.

B. Conversions and Composition Analysis

Table I shows the conversion of polymerization for homoPAN, copolymers and terpolymers. As expected, the conversions of copolymers are about 77-80 % which are lower as compared to the homoPAN (85%). This is probably due to no abnormalities or defects presents in homoPAN chains since polymerization was not incorporated with other monomers. In addition, the method used was the most suitable and typical conditions (3 hours reaction temperature and initiator type) to obtained homoPAN by redoxmethod as reported before [4,14]. Besides, redox polymerization that carried out under mild condition (lower energy of activation) lowers the possibility of side chain reactions hence, giving high yield [15].

As shown in Table I, with increasing the % mol in the feed, there is an increase in the comonomer and termonomer content in the copolymer and terpolymer. Besides, the incorporation of MA comonomer into copolymer and terpolymer system is higher (77-100%) as compared to that of AN (73-79%). This is due to the ester monomers that are more reactive in radical copolymerization as reported by other researchers [16]. However in terpolymer system, the incorporation of FN is higher (87-99%) as compared to that of MA and AN. The rate of copolymerization is greatly influenced by the concentration and polarity of the monomers [6]. In water reaction medium, polymerization proceeds according to the suspension polymerization technique, hence, propagation would mostly occur in oligomeric radicals phase as the number of polymer particles increase [17]. In this case, because MA is more hydrophilic, it remains in the aqueous phase, while FN, which is more hydrophobic as compared to that of MA, becomes buried in the growing particle core and has a better chance to polymerize into polymer particles.
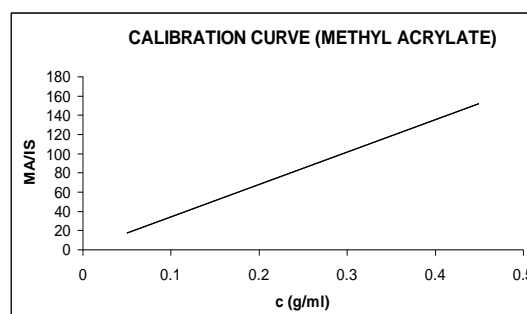

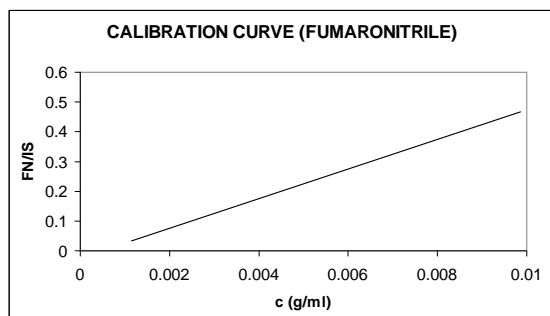Fig. 3. Calibration curve of methyl acrylate (MA) comonomer.

Fig. 4. Calibration curve of fumaronitrile (FN) termonomer.

TABLE I: CONVERSIONS AND COMPOSITION OF MONOMERS IN HOMOPAN, COPOLYMER AND TERPOLYMER.

Monomer in feed (%mol)	Conversions (%)	Observed composition (%mol) AN:MA:FN	Reacted monomer (%) AN:MA:FN
PAN	85	100:0:0	85:0:0
AN:MA:FN			
95:5:0	80	93.82:6.18:0	79:99:0
90:10:0	78	87.32 : 12.68 : 0	76 : 99 : 0
85:15:0	77	83.32:16:68:0	75:86:0
90:2:8	74	88.34 : 2.24 : 9.42	73 : 83 : 87
90:4:6	75	87.63 : 4.48 : 7.89	73 : 84 : 99
90:6:4	76	87.22 : 7.58 : 5.20	74 : 96 : 99
90:8:2	74	88.99 : 8.32 : 2.69	73 : 77 : 99

C. DSC Studies

As shown in Table II, the introduction of MA comonomers greatly lowered the glass transition (T_g) of poly (AN/MA) copolymers to 70 ℃ (20% MA) as compared to PAN (210 ℃). MA acts to defect the regularity sequence along the PANS chains hence reduce the dipolar interaction of PAN chains. Less dipolar interactions increase the free volume of the PAN system, thus enhances the mobility of polymer chains [5,18] and thereby depresses the T_g. Low T_g is favorable in this study because it reflects low T_m that lowering its processability temperature thereby facilitating the melt extrusion/ spinning of PAN [3].

In the poly (AN/MA/FN) terpolymers obtained, it was seen that as the amount of FN increased from 2 to 8 mol %, the T_g of the PAN system increased to ~80 ℃ (Table II). This could be attributed to some potential interaction between the nitrile groups of FN and AN respectively which could reduce the chain mobility and leading to a higher T_g.

However, FN initiates the cyclization of the nitrile group at lower temperature as shown in Table III. The T_i for poly(AN/MA/FN) terpolymers are about 230 ℃ which is lower as compared to that of poly (AN/MA) copolymers(~260 ℃). This behavior could be attributed to the interruption of polymer chain sequence provided by the FN group. Since FN has two nitriles groups on its molecule, some intra or intermolecular interactions occurred between FN, acrylonitrile and methyl acrylate thereby ease the initial cyclization process [8]. The DSC thermogram that demonstrated the cyclization behavior of poly (AN/MA/FN) 90/4/6 terpolymer is shown in Fig. 3. It reveals that poly(AN/MA/FN) terpolymer has a broader exothermic peak, indicated by the greater value of ΔT (T_f-T_i) as shown in Table III, suggesting a slower propagation reaction for producing ladder-like polymer [19] as compared to the more intense peak observed for the poly(AN/MA) copolymer (Fig. 3). On the other hand, the total heat of exothermic reaction, ΔH in the case of terpolymers is lower as compared to that of copolymers. The lower ΔH value for terpolymers as compared to that for copolymers suggests a different reaction mechanism that took place during stabilization and relatively much slower propagation [2] as a result of incorporation of FN.

TABLE II: GLASS TRANSITION TEMPERATURE OF PAN, COPOLYMERS AND TERPOLYMERS

AN:MA:FN (mol%)	Glass transition, T_g (℃)
100:0:0	210
Copolymer	
95:5:0	79
90:10:0	75
85:15:0	72
80:20:0	70
Terpolymer	
90:2:8	82
90:4:6	81
90:6:4	75
90:8:2	77

For instance, the $\Delta H/\Delta t$ of AN/MA 90/10 copolymer is 60 $Jg^{-1}min^{-1}$ which is higher as compared to AN/MA/FN 90/4/6 terpolymer (49 $Jg^{-1}min^{-1}$). This shows that the exothermic reaction in the case of AN/MA/FN terpolymer takes much longer time to be completed with lower heat liberation per time. This leads to better heat distribution during stabilization process thereby increases the formation of ladder-like structure that leading to better quality of carbon fiber [2].

TABLE III: DSC DATA OF PAN, COPOLYMERS AND TERPOLYMERS

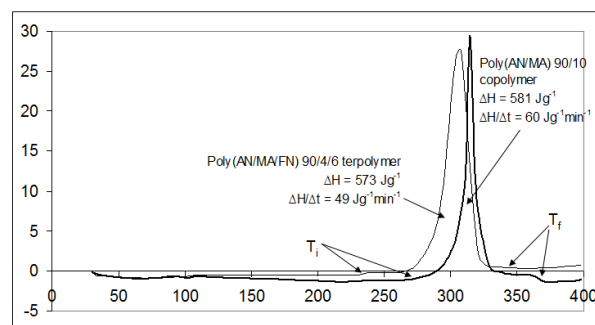| AN:MA:FN (mol%)	T_i (℃)	T_f (℃)	ΔT (℃)	ΔH (Jg^{-1})	$\Delta H/\Delta t$ ($Jg^{-1}min^{-1}$)
100:0:0	246	345	99	758	77
Copolymer					
95:5:0	262	332	70	610	87
90:10:0	270	367	97	581	60
85:15:0	255	342	87	965	111
80:20:0	265	381	116	729	63
Terpolymer					
90:2:8	231	322	91	575	63
90:4:6	231	349	118	573	49
90:6:4	253	352	99	615	62
90:8:2	228	342	114	657	58

Fig. 5. DSC thermogram of poly(AN/MA) 90/10 copolymer and poly(AN/MA/FN) 90/4/6 terpolymer.

D. TGA Studies

The TGA of the samples was carried out to obtain the thermal stability and get an estimate of the carbon yield. As

the samples subjected to heating, it starts to actively cyclize at temperature greater than 220 ℃ leading to char formation at the end of heat treatment. The results give preliminary estimate of the carbon yield of the polymers [20]. As shown in Table III, the char yield of PAN is low at 48% because the heat dissipation is more difficult in a PAN due to its poor conductor of heat [3]. Hence, excessive localized heating can lead to chain scission and lower char yield. On the other hand, values of the char yield of poly(AN/MA) copolymerswere significantly reduced to 33% as the amount of MA increased. This is due to the MA units that act as defects in the PAN chains reduce the formation of ladder-like structure along the polymer chains and resulting in lower char yield [3].However, by incorporating 2-6 mol% of FN in the case of poly(AN/MA/FN) terpolymers, the char yield of terpolymers increases to about 50%. Some interactions between FN units that have two nitrile groups each, and AN system ease the stabilization process hence the chain scission reactions and the loss of volatile products are minimized, leading to lesser weight loss.

TABLE IV: CHAR YIELD OF PAN, COPOLYMERS AND TERPOLYMERS

AN:MA:FN (mol%)	Char yield (%)
100:0:0	48
Copolymer	
95:5:0	52
90:10:0	45
85:15:0	37
80:20:0	33
Terpolymer	
90:2:8	48
90:4:6	51
90:6:4	52
90:8:2	54

As an example, Fig. 6 and Fig. 7 show a comparison of degradation behavior between poly(AN/MA) copolymer and poly(AN/MA/FN) terpolymer. The weight loss in the region 30-100 ℃ is the vaporization of moisture. The TGA thermogram corresponding to weight loss of the polymers occurred in 3 steps indicating different types of reactions taking place. The first step is up to 250 ℃, in which the weight loss is not substantial. The degradation occurred at this region to evolve HCN and NH_3 [2]. Then followed by a second step between 250-600 ℃ in which the weight loss is very rapid. The third step starts at 600 ℃ up to 950 ℃ in which the weight loss is quite steady. In the case of poly(AN/MA) copolymer, the DTG curve (Fig. 6) shows that the weight loss in the first step is about 1%, while in the second step starting from 250 ℃ to 600 ℃, the weight loss is very high at 47% and appear as a broad DTG curve. The final step shows a steady and slow weight loss (8%) up to 950 ℃. Overall, the total char yield is 45%

On the other hand, the poly(AN/MA/FN) terpolymer also gives similar results in the first step, the weight loss is not substantial at only about 1%. The weight loss associated with the second step is 43%. The DTG curve (Fig. 7)shows that the degradation occur at a faster rate due to the more intense but smaller peak as compared to that of the poly(AN/MA) copolymer. Whereas in the third step, the weight loss is about 5% and results the total char yield of 51% which is higher as compared to poly(AN/MA) copolymer.
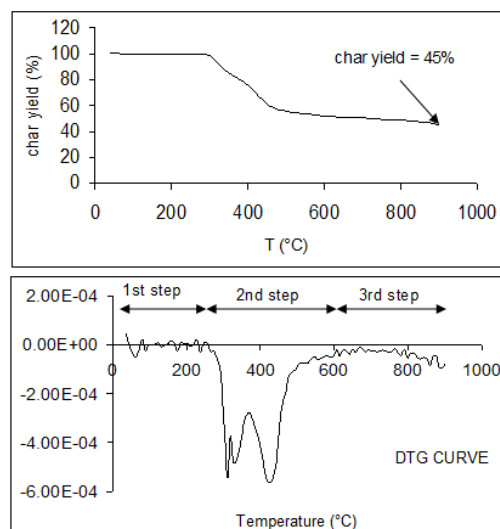

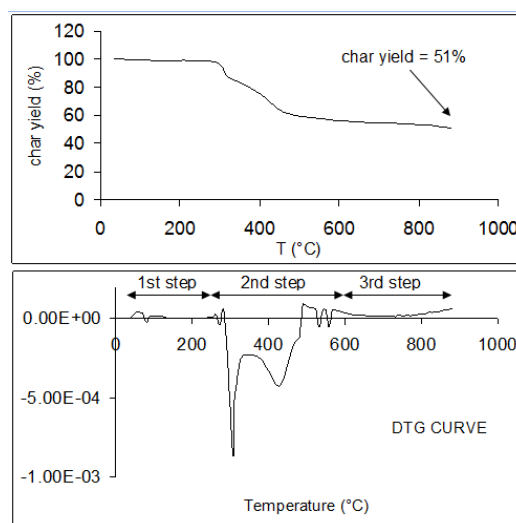Fig. 6. TGA thermogram and DTG curve of poly(AN/MA) 90/10 copolymer.

Fig. 7. TGA thermogram and DTG curve of poly(AN/MA/FN) 90/4/6 terpolymer.

IV. CONCLUSIONS

Poly (AN/MA) copolymer and poly(AN/MA/FN) terpolymer were successfully synthesized by redox method with high monomers conversion; more than 74% conversions. MA comonomer greatly reduced the T_g of copolymers and this indirectly indicates that MA enhanced the mobility of the polymer chains and facilitate their flowability. Thus, poly(AN/MA) copolymers have a potential to undergo melt processability. However, incorporating MA results lower char yield. Fumaronitrile termonomer incorporated into PAN system has been shown to facilitate the stabilization process to occur at lower temperature and lower heat liberation. Thereby, the char yield of poly(AN/MA/FN) terpolymer is higher (54%) as compared to poly(AN/MA) copolymer (45%).

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