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Dynamic oscillatory shear properties of potentially melt processable high acrylonitrile terpolymers

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Abstract

Polyacrylonitrile (PAN) terpolymers consisting of acrylonitrile/methyl acrylate (AN/MA) systems with added amounts of a termonomer (acid based) were synthesized in an effort to generate melt spinnable carbon fiber precursors. The complex viscosity was measured as a function of time in the temperature range of 200–220 °C, and was found to be dependent on both, the amount, as well as the nature of the termonomer. For the different acid termonomers studied, the cyclization/crosslinking reactions occurring during stabilization as evidenced by the increase in viscosity over time of the PAN system ranged in the order, itaconic acid > acrylamide > methyl acrylic acid > acrylic acid (IA > AM > MAA > AA). Dynamic shear experiments indicated that an AN/MA system containing 3 mol% IA seemed well suited for melt spinning and stabilization. A chemorheological correlation was used to describe the viscosity variation in the PAN system as a function of IA content, temperature and time. © 2002 Published by Elsevier Science Ltd.

Keywords: Polyacrylonitrile; Melt processability; Viscosity

1. Introduction

Carbon fibers have several unique and excellent properties such as low density, very high specific strength and stiffness, low coefficient of thermal expansion and good fatigue characteristics [1]. Thus, they are finding numerous applications in the industrial sector as engineering and structural materials. These applications range over several diverse fields such as automotive, sports equipment, aerospace, and defense.

Carbon fibers can be made from various precursors, but carbon pitch and polyacrylonitriles (PAN) are the two main types used industrially. Depending on the requirements of the structural component being produced, the precursor can be chosen to optimize the final mechanical properties of the carbon fibers. Typically, carbon fibers made from pitch-based precursors have higher tensile modulus, whereas those made from PAN-based precursors have higher strengths [2].

In this paper, we will be focusing on PAN-based precursors, which are typically used in applications demanding high tensile strength fibers and a high extension (>1%) to break, such as automotive structural parts. The conventional approach for producing PAN precursors for making carbon fibers is solution spinning. There are a number of disadvantages associated with this approach, which include solvent toxicity, solvent recovery and higher processing costs. For these reasons, there is interest in investigating alternative routes to making PAN fibers in a more economically and environmentally friendly manner.

Because PAN tends to degrade (i.e. crosslink and cyclize) before its melting point is reached (~320 °C), it is solution spun using solvents such as dimethyl formamide and dimethyl acetamide [1]. Our recent research has focused on the development of economical ways to produce carbon fibers using melt spinnable acrylonitrile based precursors [3,4]. This has involved the synthesis of random copolymers composed of AN and MA units. The MA comonomer (typically around 10–15 mol%) helps in disrupting the dipole–dipole interactions present in the AN sequence thereby enabling the melt processability of the AN/MA copolymer. It was seen that a critical comonomer composition was essential in achieving the melt viscosities typically used during melt extrusion/fiber spinning. This trend was exhibited in other comonomer systems such as methyl methacrylate and dimethyl acylamide [4]. The comonomers studied in this work [3,4] are those which have been typically used in industrially solution spun PAN fibers but in smaller amounts (than the critical comonomer composition)

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to impart better mechanical and processing properties to the precursors or to the final carbon fibers. This approach of melt spinning PAN copolymers would obviate the need for toxic solvents typically used in conventional solution spun systems.

The comonomers used were primarily ester-based, which are known to have a diluent effect on the exothermic reactions occurring during stabilization of the precursor fibers [5,6]. Here, the term, 'stabilization', refers to the low-temperature oxidative heating (200–300 °C) of the precursor fibers to transform them into a partially crosslinked ladder-like structure that can be subjected to a high-temperature inert carbonization (800–1200 °C) without melting or fusing of the fibers [1,2]. Although stabilization can also be done in an inert atmosphere, a polymer backbone containing oxygen-bearing groups provides greater stability to the 'stabilized' polymer to sustain high-temperature carbonization treatment. Also, the oxygen containing ladder-like polymer chains fuse during the carbonization process to form carbon fibers possessing superior mechanical properties as compared to those produced by the inert stage stabilization [5].

Although several different melt processable PAN copolymers have been studied [3,4], we have focused on the results obtained for AN/MA system. We found that although melt processability of the AN/MA system was attained for MA content greater than or equal to 10 mol%, the samples required very long times for stabilization at 220 °C (over 24 h). Because stabilization is the most crucial step in the carbon fiber production and governs the properties of the final carbon fibers, long times would imply greatly increased processing costs and might result in poor quality carbon fibers.

The process of stabilization is a complicated process as it involves several intertwined steps of reactions and heat and mass transfer [7]. The ladder-like polymer formation occurs through three distinct steps: initiation, propagation, and termination. The two main types of initiation are free radical and ionic. In PAN homopolymers, free radicals are generated by the cleavage of the C≡N bond which initiates the cyclization reactions. In PAN copolymers, comonomers having an ionic species can undergo fission and start the cyclization process. The initiation process is followed by propagation by a free radical or an ionic mechanism for homopolymers or copolymers, respectively [6]. Free radical propagation is the fastest stage and is exothermic, producing a large amount of heat (6.05 kcal/mol of –CN) [6]. In PAN homopolymers, which are poor heat conductors, this might lead to local hot spots, melting of fibers and loss of orientation, producing very poor quality fibers. Hence, an ionic mechanism for the initiation process which generates heat more slowly (and accomplished at a lower temperature), is preferred and accomplished by incorporation of certain types of monomers in the PAN system [7]. This will be explained in more detail in the following paragraph. The termination of the reaction occurs when the nitrile group stops propagating due to lack of free nitrile groups, chain combination, steric hindrance, species removal as a gas, termination with more active species, etc. [7].

The use of a termonomer in small concentrations (typically <5 mol%) could assist in the cyclization and crosslinking reactions under stabilization conditions while still maintaining the melt processability of the PAN system at lower temperatures. The role of co- or termonomers in stabilization reactions has been documented in Refs. [5–9]. Certain comonomers can enhance the segmental mobility of the polymer chains and reduce the initiation temperature of cyclization. As an illustration, acid comonomers initiate the cyclization reactions at a lower temperature by an ionic mechanism as compared to a free radical mechanism of initiation in a PAN homopolymer and thus aid in the stabilization process as discussed in the preceding paragraph [6]. The exothermic reaction that the PAN system undergoes during stabilization is typically composed of an exothermic cyclization and oxidative reactions. Acid comonomers also help in increasing the separation of the two reactions, observed as the separation of peaks in the DSC, which helps in perfecting the cyclized ladder-like structure of the precursor fibers, leading to carbon fibers with improved mechanical properties [5,6]. The actual reactions may be more complicated than the simplified version presented here [10,11].

Also, it is observed that while all acid comonomers influence the exothermic cyclization reaction, the effect depends on the type and content of the acid comonomer. For example, itaconic acid (IA) contains 2 acid groups, and hence the probability of interaction between the carboxylic acid and nitrile groups is higher than for acrylic acid, which contains only one acid group, leading to better stabilization. Similarly, it was seen that as the amount of acid comonomer increased, the extent of crosslinking reactions also increased [7,9].

While a few papers concerned with the speculation of the role of acid co- and termonomers in stabilization reactions have been published [5,6,8,9], the influence on the melt processability of PAN system has not been determined. Acid co- and termonomers reduce the temperature for cyclization reactions [5,6], and hence they would promote a more rapid increase in viscosity and could have a detrimental effect on the melt processability of the polymer in the extruder and spinnerette. Because our objective is to obtain a melt processable PAN system which could also undergo effective stabilization, we need to address the issue of the effect of acid termonomers in terms of the feasibility of both melt processing and later stabilization. Based on literature studies [8,9], we decided to investigate the role of termonomers (<5 mol%) such as itaconic acid (IA), methacrylic acid (MAA), acrylic acid (AA), and acrylamide (AM), on the melt viscosity and flow behavior of the PAN system. We wanted to study their efficacy as termonomers in aiding the stabilization reactions of the PAN system, while maintaining its melt processability. Also, we fit a chemorheological

Table 1
Composition and intrinsic viscosity data for various terpolymers

Terpolymer system	Molar feed ratio	Observed molar composition	Intrinsic viscosity (NMP/25 °C)	T_g (DSC) (°C)
AN/MA/IA	85/14/1	86.9/11.5/1.6	0.55	93.0
	85/13/2	86.2/10.9/2.9	0.49	96.0
	85/12/3	86.8/9.5/4.2	0.43	104.0
	85/11/4	84.9/10.2/5.9	0.43	111.0
AN/MA/AM	85/13/2	86.1/11.6/2.3	0.44	90.9
AN/MA/AM	85/11/4	85.4/10.1/4.5	0.44	93.6
AN/MA/MAA	85/11/4	85.4/10.1/4.5	0.44	93.5
AN/MA/AA	85/11/4	87.0/9.3/3.7	0.55	90.6

model to the viscosity vs. time data, which could provide information regarding the cure kinetics of the PAN system. This would allow the correlation of the viscosity buildup as a function of temperature, time and the acid termonomer content and help in tailoring and designing the PAN system to limit or get the desired viscosity rise during melt processing or stabilization stages, respectively.

2. Experimental

2.1. Materials

The monomers, acrylonitrile (AN), methyl acrylate (MA), itaconic acid (IA), methacrylic acid (MAA), and acrylamide (AM), the initiator, 2,2′-azo-bis-isobutyronitrile (AIBN), and the chain transfer agent, dodecyl mercaptan, were obtained from Aldrich. *N*,*N*-dimethyl formamide (DMF) solvent was obtained from EM Sciences and was used as received. The liquid monomers were passed over alumina prior to use to remove the inhibitor.

2.2. Precursor synthesis

The solution polymerization was conducted using a 500 ml necked flask fit with a condenser, glass stirrer, nitrogen inlet tube and thermocouple probe. First, the flask was charged with 50 ml DMF, and purged with dry nitrogen for 15 min. Next, the mixture of monomers, AIBN, and mercaptan were added. The solid monomers were weighed separately and added to DMF, before adding the liquid mixture. The total monomer content was kept constant at 375 mmol in all the experiments (Table 1). The polymerization was carried out at 70 °C for 6 h. The polymer so obtained was purified by precipitation from 50-fold excess of de-ionized water and dried under vacuum for 24 h at 70 °C.

2.3. Characterization

Composition Determination: ^{1}H and ^{13}C NMR spectra were obtained with a Varian Unity 400 spectrometer in DMSO-d as solvent using 5 and 10% w/v solutions. For the IA containing terpolymers, the acid content in the feed was varied from 1 to 4 mol%, keeping the AN content fixed at 85%, and changing the MA content accordingly. Intrinsic viscosity measurements were performed using a Cannon Ubbelhode viscometer. Absolute molecular weight measurements from gel permeation chromatography (GPC) were conducted at 60 °C with Water 2690 Separation Module equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek T60A) coupled in parallel. NMP containing 0.02 M P_2O_5 was used as a solvent. The acid content of the terpolymers prepared using IA and MAA was estimated from non-aqueous titration using 0.1 N methanolic KOH (as per ASTM method D 3644-98).

2.4. Thermal analysis

The glass transition temperatures of the PAN samples were evaluated using a Perkin Elmer differential scanning calorimeter (DSC) DSC-7. The heating rate was constant at 10 °C/min and the sample (6–10 mg) was heated from room temperature to 200 °C, cooled back to room temperature at the same heating rate and reheated again to 200 °C, all under nitrogen.

Gravimetric thermal analysis was carried out using a Perkin Elmer Thermo Gravimetric Analyzer (TGA) TGA-7. The test consisted of simulating a thermo-oxidative stabilization reaction for the PAN copolymer. The sample (10–20 mg) was heated in air at 10 °C/min to 220 °C, maintained in air for 3 h, then heated from 220 to 550 °C at 10 °C/min in N_2 and maintained at 550 °C for 3 h.

The cyclization peaks were obtained from differential thermal analysis (DTA) using a Seiko Systems TG/DTA 220. This was studied by heating a sample in N_2 or air at 10 °C/min from room temperature to 350 °C.

2.5. Rheology

Sample preparation consisted of compression molding circular discs of 25.0 mm diameter and 1 mm thickness at 200 °C. The complex viscosity of the PAN copolymer samples was measured using a RMS 800 Mechanical Spectrometer. Henceforth, this viscosity is taken to represent the melt viscosity, which is in most cases a reasonable assumption [12]. Frequency sweeps (between the range of 0.1–100 rad/s) were carried out using parallel plates at 0.1% strain and 220 °C unless specified otherwise. Strain sweeps

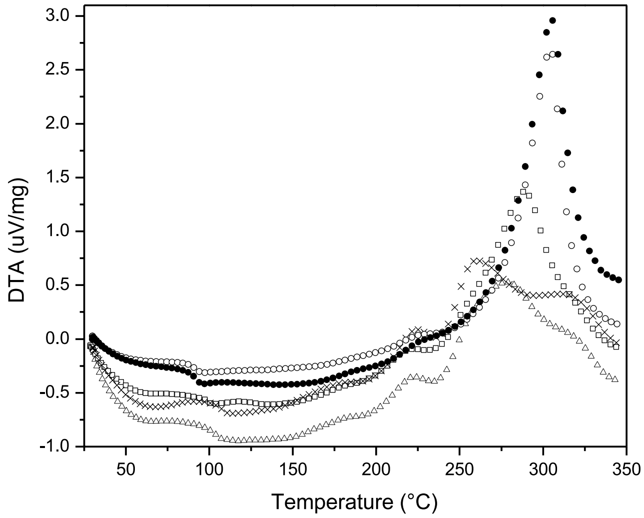

Fig. 1. Effect of content of termonomer (IA, mol%) on cyclization temperature (°C) of PAN system. DTA Plots: (1% (●), 1% (○), 2% (□), 3% (△), 4% (×)), all samples done under nitrogen except (●) which was done in air.

were conducted in order to determine the linear viscoelastic range of response. The time sweeps were carried out at 0.1% strain, and, angular frequency of 10 rad/s at 220 °C for 30 min. The temperature sweep of the AN/MA/IA sample (composition of feed: 85/12/3) was conducted at 2 °C/min from 160 to 240 °C at 10 rad/s and 0.1% strain.

3. Results and discussion

In the following sections the thermal and rheological properties of the the PAN terpolymers are discussed. The primary system studied was AN/MA/IA terpolymer. Other terpolymers included in this study are AN/MA/MAA, AN/MA/AM, and AN/MA/AA.

3.1. Compositional determination

A BP/Amoco melt processable AN/MA copolymer, Amlon, was used as a standard for the PAN terpolymers synthesized in this study. Amlon was found to have a composition of 90 mol% of AN and 10 mol% of MA [4]. It would be desirable to study the potential melt processability of PAN terpolymers having molecular weights similar to Amlon. In this paper, we have used intrinsic viscosity measurements as a measure of the molecular weight. Hence, the various terpolymers, prepared by homogeneous solution polymerization, had intrinsic viscosity ($[\eta]$) values of 0.4–0.5 dl/g (NMP, 25 °C), similar to the value observed for Amlon (~0.5 dl/g). The composition of the terpolymers was characterized by a combination of proton NMR and non-aqueous titration techniques, as reported previously [13], and shown in Table 1. The IA content (mol%) of terpolymers was found to be more than that supplied in the feed (Table 1). In this paper, we have referred to the terpolymer samples in terms of their feed amounts unless specified otherwise. The AN/MA/AM terpolymers were prepared using 2 and 4 mol% of AM, whereas the AN/MA/MAA and AN/MA/AA terpolymers were synthesized using 4 mol% of the corresponding termonomers, MAA and AA. The MAA and AM content (mol%) of the terpolymers was also observed to be more than that in the feed (Table 1). It is well known in literature that acid monomers have reactivity ratios generally greater than 1 [13,14]. AN and MA, on the other hand, have shown reactivity ratios close to 1 [13]. This could explain the slightly higher values of acid termonomer in the PAN terpolymer system. It should be noted that the composition of AN/MA/AM terpolymer (Table 1) was calculated from ^{13}C NMR because of the overlapping of peaks observed in proton NMR.

3.2. Thermal analyses

3.2.1. Effect of extent of termonomer

We had reported previously that the PAN homopolymer had a T_{g} of 106.4 °C [3]. It was also seen that for random copolymerization with MA, the T_{g} of an AN/MA copolymer (85/15 mol%) with $[\eta]$ of ~0.5 dropped to 85 °C [3]. Thus, copolymerizing MA in the PAN sequence depressed the T_{g} and enhanced the mobility of the polymer chains, facilitating their flowability and potential melt processability beyond the critical amount of about 10 mol% MA [3,4].

The effect of adding IA as a termonomer on the T_{g} and cyclizing behavior of the AN/MA system would be interesting to observe. In the PAN terpolymers synthesized in this paper, the amount of MA decreased as the amount of IA increased (as the total amount of MA and IA comonomers is maintained at 15 mol%). It was seen that as the amount of IA increased from 1 to 4 mol%, the T_{g} of the PAN system gradually increased (Table 1). Although MA and IA are both added to solution spun PAN systems as comonomers, the effect of each monomer is different. MA primarily acts to increase the free volume of the PAN system and reduce the dipole–dipole interaction of the AN groups [5], which is indirectly observed by the T_{g} depression. IA, on the other hand, as discussed earlier, initiates the cyclization of the nitrile group at a lower temperature by an ionic mechanism and facilitates the stabilization process [8,9]. In fact, it can be seen from Table 1 that the 4 mol% IA system shows a higher T_{g} than the PAN homopolymer. This could be attributed to some potential interaction between the carboxylic groups in IA and the nitrile groups in AN, which could reduce the chain mobility, leading to a higher T_{g} of PAN terpolymer as the amount of IA increases.

The cyclization behavior of the PAN terpolymers is shown in the DTA plots in Fig. 1. The peak temperatures for cyclization of PAN homopolymer and AN/MA (85/15) copolymer have been reported to be about 288 and 290 °C, respectively [3]. Also, the initiation temperature for cyclization was above 260 °C in both the systems. With the inclusion of IA as a termonomer, two features were observed in the DTA traces of the AN/MA/IA system. The initiation temperatures for cyclization dropped to about 200 °C and did not change significantly with varying amounts of IA. This could suggest that the stabilization reaction is facilitated in the presence, and by the nature, of the acid group rather than by the amount of acid monomer, as also reported by other workers [8,9]. The DTA scans also reveal a broader exotherm peak in the presence of termonomer IA, suggesting a slower reaction, as compared to the more intense peak observed for the AN/MA system. Multiple exothermic peaks are observed for the AN/MA/IA system (the single peak could be resolved into a doublet of peaks) as opposed to a single strong exothermic peak observed for both PAN homopolymer and AN/MA copolymer. Gupta et al. [8] attributed the doublet peaks to the exothermic cyclization and oxidative reactions, which proceeded fairly simultaneously, but the initiation of the oxidation reaction preceded the onset of cyclization. They assigned the first peak to the oxidative and cyclization reactions and the second peak to the secondary oxidative reactions leading to chain scissions which caused the evolution of HCN, CO_2, and CO. As can be seen in our DTA plots, the low temperature shoulder and the doublet peak resolution are found to become more evident with increasing amounts of IA. In fact, Gupta et al. [8] have reported detecting a triplet, corresponding to each of the dehydrogenation (or oxidation) and cyclization steps at low IA concentrations of about 0.5 mol%. However, they also found that as the amount of IA increased (to about 2 mol%), the triplet peaks merged to form a doublet. Contrary to the findings of their work, the cyclization peaks in our samples could be clearly discerned into doublets and triplets with increasing amounts of IA (to about 4 mol% IA in the feed), which seems to corroborate the speculation that IA helps in spreading the dehydrogenation and oxidation reaction rates over a broader temperature range.

On resolving the peak into doublets, the area under the first peak corresponding to the primary oxidation and cyclization decreased with increasing amounts of IA (lower temperature peaks), whereas the area under the second peak (higher temperature) corresponding to the secondary oxidation increased. This behavior was attributed to termonomers reducing the cyclization reactions due to the interruption of the AN sequence and some steric hindrance provided by the IA group. The promotion of the secondary reactions is attributed to the nature of the termonomer-acid, which increases the amorphous content of the PAN and helps in assisting molecules to come closer with the acid groups. The major reason for the superiority of IA in promoting these reactions over the other acid comonomers is the occurrence of two acid groups, which increases the probability of interaction between the carboxylic group and nitrile group, in spite of dipole–dipole interaction. Owing to the dicarboxylic structure of itaconic acid, if one of the carboxylic groups moves away due to dipolar repulsion, the other carboxylic group moves to the vicinity of the nitrile group and takes part in the cyclization reaction [5,6]. Thus, although the acid monomers tend to reduce the rate of primary oxidation, the overall effect is to increase the exothermicity and hence the favorability of the stabilization reaction. It is to be noted that all our samples were studied under nitrogen whereas Gupta et al. [8] had performed their analyses under both nitrogen and air atmospheres. They noted that the trend followed was similar under both atmospheres, although exothermic reactions were promoted more under air than nitrogen, as was seen from the larger heat of reaction values for the former. We studied the difference in the thermal behavior of the AN/MA/IA samples under air and nitrogen for the 85/14/1 composition. It can be seen from Fig. 1, that the plots are very similar showing that not much variation occurs for our sample. This difference in behavior of our samples relative to that reported in the literature can be attributed to the nature of our terpolymers (AN/MA/IA) as compared to the copolymers (AN/IA) studied in literature. Because the MA in our system (>10 mol%) succeeds in disrupting the long-range order of PAN, the acid termonomer might not be as affective a crosslinking agent as in the AN/IA copolymer. This would imply that the atmospheric conditions of the thermal analysis in our case might not be as crucial as for the results obtained by Gupta and coworkers [8].

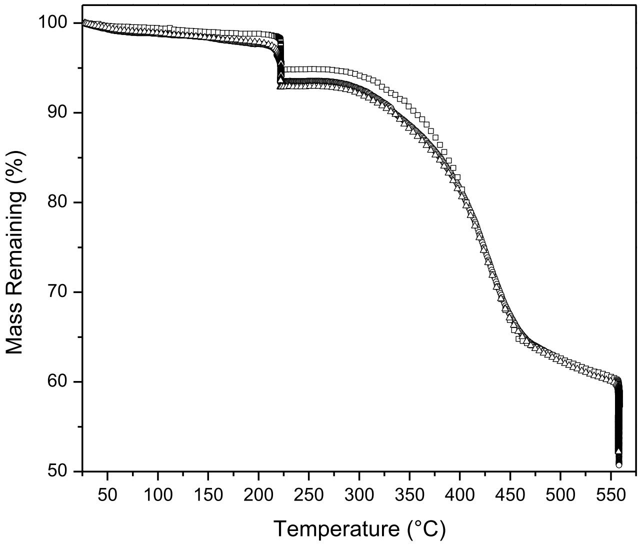

Fig. 2. Effect of content of termonomer (IA, mol%) on char yield (wt%) of PAN system. TGA plots (values represent mol% IA, and char yield (wt%): 1%, 54.7% (□), 3%, 52.2% (△), 4%, 50.7% (○)). Thermo-oxidative stabilization test procedure: heat in air at 10 °C/min to 220 °C, maintain in air for 3 h, heat from 220 to 550 °C in N_2, maintain in N_2 at 550 °C for 3 h.

The TGA plots were used to determine the *carbon content* of the IA based systems (Fig. 2). As reported previously, the AN/MA copolymer system had a char yield of about 56% [3]. In order to determine the char yield of the PAN system, which could provide a more realistic indication of the final carbon content (for conversion to carbon fiber under actual test conditions), the stabilization reaction carried out in air/oxygen during the real carbon

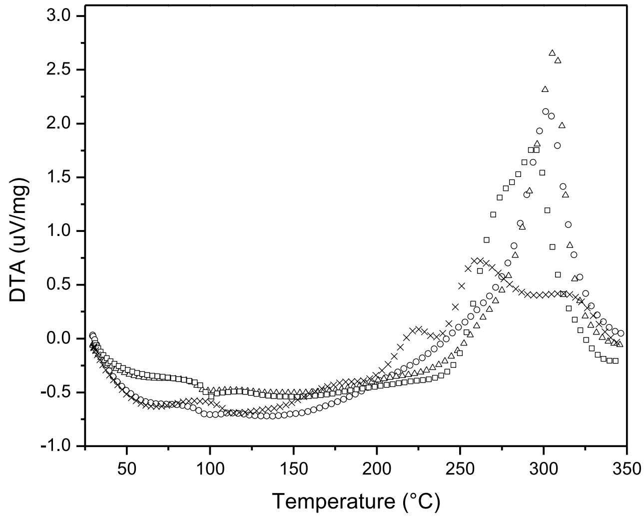

Fig. 3. Effect of nature of termonomer (4 mol%) on cyclization temperature (°C) of PAN system. DTA plots: (IA (×), AM (□), AA (△), MAA (○)), all samples done under nitrogen.

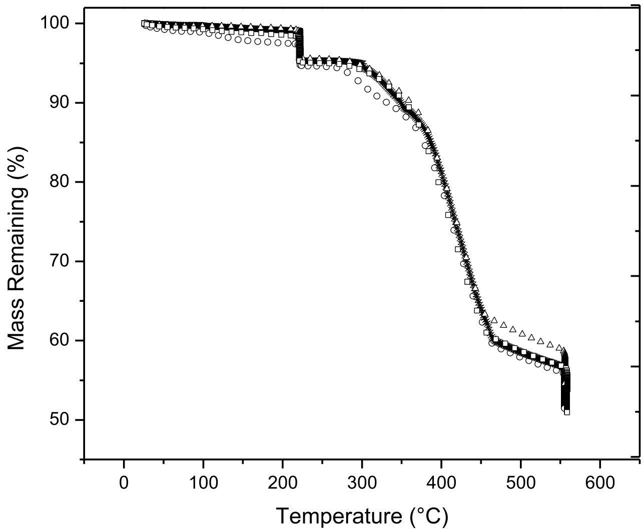

Fig. 4. Effect of nature of termonomer on char yield (wt%) of PAN system. TGA plots: (IA (∗), AM (□), MAA (△), AA (○), control (–)). Thermo-oxidative stabilization test procedure: heat in air at 10 °C/min to 220 °C, maintain in air for 3 h, heat from 220 to 550 °C in N_2, maintain in N_2 at 550 °C for 3 h.

fiber manufacture was simulated using the TGA. It has been seen from the literature that oxygen acts in two opposing ways during stabilization [5]. On the one hand, it initiates the formation of activated centers for cyclization, whereas, on the other hand, it retards the reactions by increasing the activation energy. Despite this, the use of oxygen is preferred because it results in the formation of oxygen containing groups in the backbone of the ladder polymer, which help in fusion of the ladder chains during the carbonization reactions. The PAN terpolymer was stabilized by heating a small sample to 220 °C in air, maintaining it at 220 °C in air for 3 h, then heating it to 550 °C and heating in N_2 at 550 °C for 3 h. This is similar to the stabilization treatment for a PAN precursor fiber, prior to carbonization for conversion to carbon fibers. It can be seen from the TGA plot in Fig. 2 that up to 550 °C, the weight loss curve is fairly similar for all the PAN systems. The AN/MA copolymer had a fairly rapid drop in weight up to about 450 °C, then the drop was more gradual, and the sample was found to lose about 44% of its initial mass after heat stabilization at 550 °C [3]. The char yield of the AN/MA/IA for increasing amounts of IA was similar (~52%). This lead us to conclude that higher levels of the IA termonomer (up to 4 mol%) do not significantly reduce the char yield. The slight variations in the char yield with increasing amounts of IA are within experimental error. Gupta et al. [8,9] had reported similar values of char yields for a series of AN/IA copolymers.

3.2.2. Effect of nature of the termonomer

Keeping the amount of termonomer constant (4 mol%), we studied the effect of changing the nature of the acid group of the termonomer on the T_g, cyclization behavior, and char yield. IA, AM, MAA, and AA were the different termonomers studied. As can be seen in Table 1, the T_g values changed in the order AN/MA/IA > AN/MA/AM > AN/MA/MAA > AN/MA/AA > AN/MA. This roughly corresponds to the order of acidity observed for the various acid termonomers. Fig. 3 shows the cyclization behavior of the AN/MA/acid termonomer systems. MAA and AA are the weaker acids, hence their terpolymers (containing 4 mol% acid termonomer) tend to exhibit a DTA plot similar to those of 1–2 mol% IA-based terpolymers. This is consistent with the fact that IA has two acid groups in each molecule compared to one in the case of the other termonomers studied. On the other hand, AM tends to show a broader exotherm indicating that its nature is more acidic than MAA and AA. The triplet nature of the peaks is very clearly evident for the IA system.

TGA studies were done on PAN systems having about 4 mol% acid termonomer. Fig. 4 shows the weight loss of the sample as it undergoes the simulation of the stabilization and carbonization stages at a heating rate of 10 °C/min as discussed in Section 2. The nature of the plots was similar for the most part, showing that the nature of the acid group did not significantly affect the rate of weight loss. Higher weight loss was obtained with the control (AN/MA) as compared to the acid termonomers, AM, MAA, and AA. This could be due to the presence of acid groups on the latter which slows down the rate of the highly exothermic reaction [8,9]. Thereby the chain scission reactions and the loss of volatile products are minimized, leading to lesser weight loss. However, they also serve as initiators for cyclization reactions to occur. As the amount of acid termonomer increases, the reaction sites associated with these reactions also increase, leading to the initiation of cyclization reactions at a number of places in the polymer chain simultaneously. This would lead to increased heat generation and

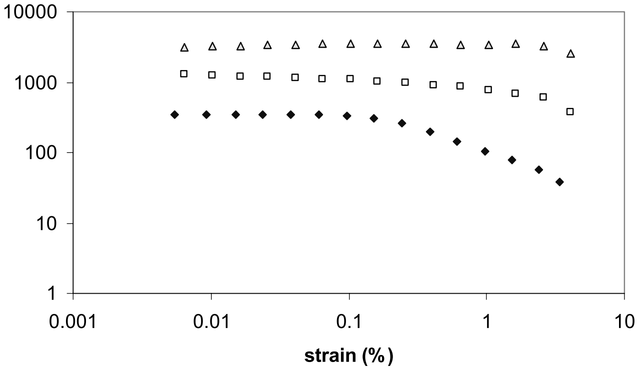

Fig. 5. Strain sweep of AN/MA/IA (81/14/1) at 200 °C and at different frequencies (η^*, Pa s vs. strain (%)), 100 rad/s (◆), 10 rad/s (□), 1 rad/s (△).

loss of volatile chain scission products such as HCN and NH_3. Hence, the increased number of acid groups would actually decrease the carbon yield, which is evidenced for 4 mol% IA, which contains two carboxylic acids for every molecule of IA. It is to be noted that these weight loss variations for different systems are not highly significant because the measurement error is about ±3 wt%.

3.3. Melt viscosity

Although the samples have been characterized for their composition and thermal transitions, the flow characteristics are necessary to provide insights into their feasibility to be melt spun. During stabilization, the cyclization and cross-linking reactions occurring in the PAN system typically lead to a viscosity buildup.

In this section the magnitude of the complex viscosity ($|\eta^*|$) is reported as follows. Strain sweeps on AN/MA/IA containing 1 mol% IA and Amlon were studied at different frequencies in order to determine the linear viscoelastic region. It is seen in Figs. 5 and 6 that up to about 0.2% strain, the systems are linearly viscoelastic for all the frequencies studied. Hence, a strain of 0.1% was chosen for all our dynamic frequency and time sweeps. It was also observed that as higher frequencies were approached, the strains at which the linear viscoelastic behavior was exceeded were smaller. For example, the AN/MA/IA was linearly viscoelastic up to a strain of about 5% at 1 rad/s, whereas it dropped to about 0.15% at 100 rad/s. This behavior was similar in all the IA samples studied and did not vary greatly with extent of IA. This trend was similar to that observed for Amlon.

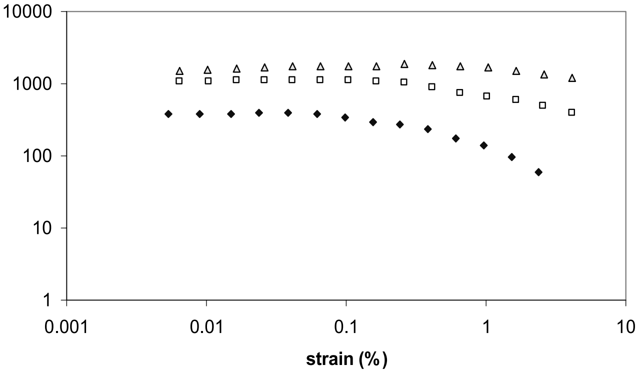

Fig. 6. Strain sweep of Amlon at 220 °C and at different frequencies (η^*, Pa s vs. strain (%)) 100 rad/s (◆), 10 rad/s (□), 1 rad/s (△).

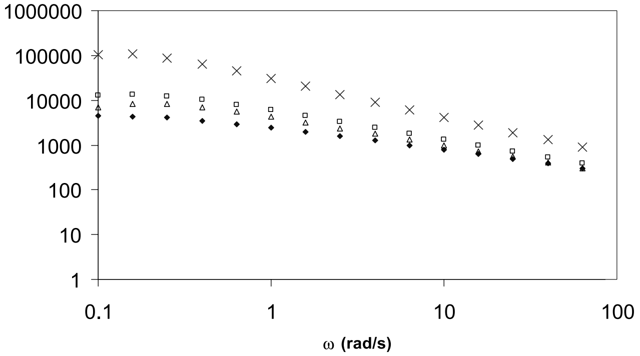

Fig. 7. Effect of content of termonomer (IA, mol%) on complex viscosity (η^*, Pa s) of PAN system. Frequency (ω rad/s) sweeps at 200 °C, 1% (◆), 2% (□), 3% (△), 4% (×), intrinsic viscosity: 0.45 dl/g in NMP at 25 °C.

3.3.1. Effect of amount of termonomer

The terpolymers containing IA had a low frequency (0.1 rad/s) complex viscosity ($|\eta^*|$) value of about 10 000 Pa s at 200 °C (Fig. 7) and did not vary much with amount of IA. Only the terpolymer containing 4 mol% IA had a higher complex viscosity at this frequency. The four terpolymers had a similar $[\eta]$, and hence, the only variable changing was the MA/IA ratio. The PAN copolymer containing AN/MA of 85/15 (mol%) and having $[\eta]$ of 0.45 had a low frequency value of $|\eta^*|$ of about 1000 Pa s. Thus, incorporation of the IA monomer tends to increase the low frequency value of $|\eta^*|$. This can be related to the T_g values measured by means of the DSC, which also increased with higher amounts of IA. Because we want to extrude PAN at about 200 °C, we want to ensure that it is stable under these conditions. Hence, the comparative rise in the viscosity of terpolymers containing different amounts of IA was studied as a function of time (time sweep plot) at 200 °C. A somewhat arbitrary time of 30 min based on residence time in an extruder was chosen as the time limit over which the stability was monitored [3]. As seen from Fig. 8, the PAN systems containing less than 3 mol% IA showed a moderate rise in the complex viscosity in 30 min at 200 °C, ranging from 55 to 200% of their initial value. On the other hand, an IA content of 4 mol% produced a rather rapid viscosity increase in 30 min at 200 °C of about 430% relative to its initial value. As the initial value of the complex viscosity at the start of the stability sweep is also higher for the 4 mol% IA system, it appears from this study that less than 4 mol% IA is required for melt processing the PAN terpolymers $[\eta] \sim 0.5$ dl/g).

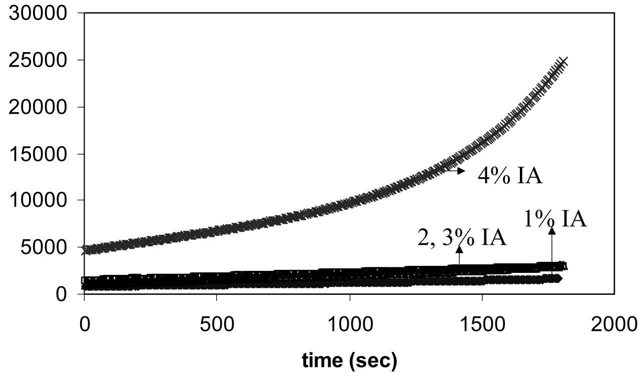

Fig. 8. Effect of content of termonomer (IA, mol%) on time stability of PAN system. Time sweeps (complex viscosity, η^* (Pa s) vs. time in seconds) at 200 °C, 1% (◆), 2% (□), 3% (△), 4% (×).

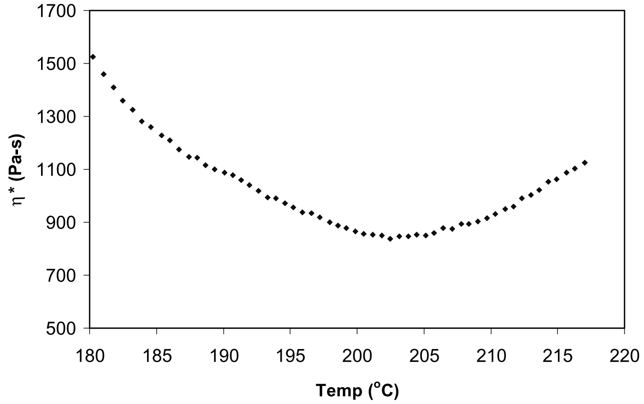

Fig. 10. Temperature sweep of AN/MA/IA (85/12/3) system at 10 rad/s: complex viscosity (η^*, Pa s) vs. temperature (°C).

Stabilization of the terpolymer is typically performed under oxidative conditions at 220–300 °C [5]. An arbitrary temperature of about 220 °C was chosen for this work based on our previous studies [3,13]. The effect of heat treatment on flowability was studied by observing the complex viscosity rise of the sample at 220 °C for about 30 min. During stabilization, a rapid increase in viscosity is desired in order to prevent any polymer flow and also to ensure that the system can be held under tension in order to prevent shrinkage and loss of orientation in the precursor fiber. From Fig. 9, it can be seen that $|\eta^*|$ increased exponentially with time at 220 °C. This will be discussed in more detail in Section 3.3.3. As the IA content increased, $|\eta^*|$ rose rapidly. For the 1 mol% IA-based terpolymer, $|\eta^*|$ reached about 700% of its initial value after 30 min (1800 s). The viscosity of the higher IA-based terpolymers reached about 3500% of the initial values in progressively shorter times, 1680 s (2 mol% IA), 1110 s (3 mol% IA) and 890 s (4 mol% IA). Based on viscosity data at 200 °C, it had seemed that a sample containing less than 4 mol% IA was required for melt processing. However, the stabilization stage (at 220 °C) is promoted by increasing the amount of IA in the PAN terpolymer. Thus, from the time stability studies, it is speculated that terpolymers containing 3 mol% IA seem the most suitable for melt spinning at 200 °C followed by rapid stabilization at 220 °C (Table 2).

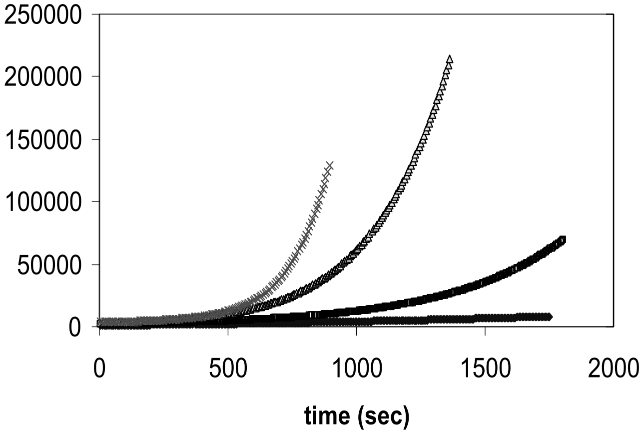

Fig. 9. Effect of content of termonomer (IA, mol%) on time stability of PAN system under stabilization conditions: time sweeps (complex viscosity, η^* (Pa s) vs. time in seconds) at 220 °C, 1% (◆), 2% (□), 3% (△), 4% (×), intrinsic viscosity: 0.45 dl/g in NMP at 25 °C.

We did an additional temperature sweep from 160 to 220 °C at 2 °C/min on the 3 mol% IA system in order to optimize the temperature for extrusion/spinning. Based on Fig. 10, it appears that extrusion and spinning would best be carried out at a temperature of about 203–205 °C which is where the minimum value in viscosity is reached. The viscosity drop with increasing temperature is opposed by the viscosity buildup occurring due to the cyclization/crosslinking reactions in the PAN terpolymer. These cyclization/crosslinking reaction rates increase with higher temperature, and beyond 205 °C lead to a greater viscosity rise than the viscosity drop associated with improved flowability. Thus, the optimum temperature for extrusion/melt spinning of AN/MA/IA (85/12/3, $[\eta] = 0.45$) seems to be about 200–205 °C.

3.3.2. *Effect of nature of termonomer*

Figs. 11–13 show the effect of type of acid termonomer (4 mol%) on the complex viscosity at 200 °C, the time stability at 200 °C, and the time stability at 220 °C, respectively. All the terpolymers, except those containing 4 mol% IA, showed very similar frequency and time sweeps at 200 °C (melt spinning conditions). This could be attributed to the number of acid groups of IA being two for every molecule of acid termonomer added to the system. Hence, the rate of

Table 2
Model parameters for AN/MA/IA viscosity rise (dynamic sweep)

Amount of IA in feed (mol%)	1.0	2.0	3.0	4.0
i (IA observed by NMR)	1.6	2.9	4.2	5.9
k at 200 °C (s^{-1})	0.000382	0.00052	0.000616	0.0007
k at 220 °C (s^{-1})	0.001228	0.002114	0.0031	0.0041
$-\Delta E_k/R$ (°C)	13 673	16 340	18 854	20 616

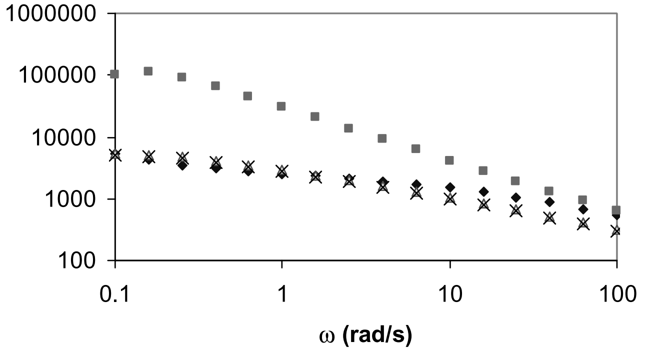

Fig. 11. Effect of nature of termonomer on complex viscosity (η^*, Pa s) of PAN system. Frequency (ω rad/s) sweeps at 200 °C, AM (◆), IA (■), MAA (△), AA (×), intrinsic viscosity: 0.45 dl/g in NMP at 25 °C.

reactions promoted by IA would be higher as compared to the other acid termonomers studied in this work. Similarly, while undergoing stabilization, it was seen that the viscosity buildup changed in the sequence IA > AM > MAA > AA at 220 °C. It is interesting to note that the acidity of the acid groups present in these monomers also changes in the same order. This shows that the nature and acidity of the termonomer significantly affects the rate of viscosity buildup. The results are consistent with the reportedly higher efficiency of IA in inducing the cyclization of AN/IA copolymer [8,9]. Thus, depending on the viscosity of the PAN system needed during processing and the rate of viscosity buildup required during stabilization, we can select the type and amount of termonomer.

Similarly, the effect of changing amounts of a termonomer, AM, on the complex viscosity in terms of the frequency and time sweeps of PAN system is shown in Figs. 14 and 15. It was observed that frequency and time sweeps for both 2 and 4 mol% systems were very similar at 200 °C, whereas at 220 °C the viscosity rise in 4 mol% was substantially higher than for the 2 mol% terpolymer. Again, the most significant inference derived from the study of these systems is that we can tailor the type and amount of termonomer in order to get the viscosity stability/rise that we desire during the melt spinning/stabilization reactions.

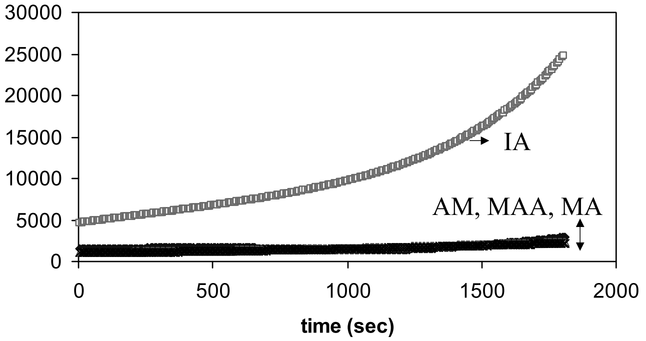

Fig. 12. Effect of nature of termonomer on time stability of PAN system. Time sweeps (complex viscosity, η^* (Pa s) vs. time in seconds) at 200 °C, AM (◆), IA (□), MAA (△), AA (×), intrinsic viscosity: 0.45 dl/g in NMP at 25 °C.

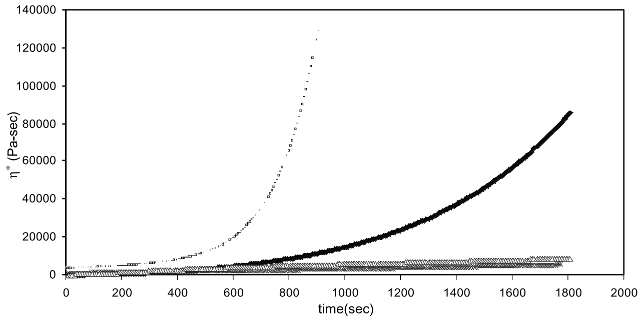

Fig. 13. Effect of nature of termonomer on time stability of PAN system under stabilization conditions: time sweeps (complex viscosity, η^* (Pa s) vs. time in seconds) at 220 °C, AM (◆), IA (□), MAA (△), AA (×), intrinsic viscosity: 0.45 dl/g in NMP at 25 °C.

3.3.3. Chemorheology of IA-based PAN terpolymers

During the extrusion of PAN terpolymers based on AN, MA, and IA, the viscosity will increase with time and melt temperature as a result of cyclization and crosslinking. It is desirable to quantitatively describe the changes in viscosity as a function of temperature, IA content, and time in order to establish melt spinning conditions. For this reason, we evaluated the potential of chemorheological models used to fit the cure kinetics of systems such as epoxy resins, unsaturated polyesters, phenolics and polyurethanes to describe the cyclization and crosslinking kinetics of AN/MA/IA systems [15].

The following functions used to describe the cure kinetics of crosslinking systems were applied to the viscosity data

$$\ln \eta(t) = \ln \eta_0 + kt \tag{1}$$

where

$$\eta_0 = \eta_\infty \exp(\Delta E_\eta/RT) \tag{2}$$

and

$$k = k_\infty \exp(\Delta E_k/RT) \tag{3}$$

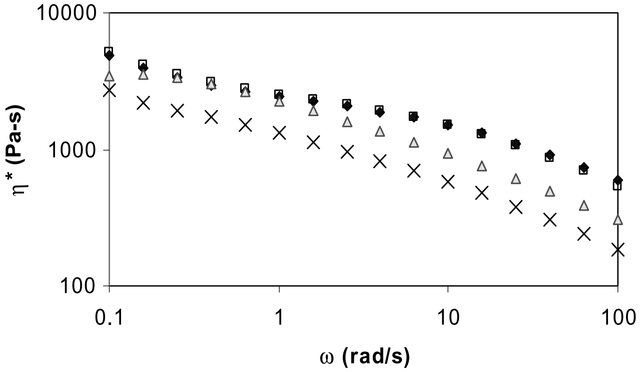

Fig. 14. Effect of extent of AM as termonomer (mol%) and temperature on complex viscosity (η^*, Pa s) of PAN system: frequency (ω rad/s) sweeps, 2%, 200 °C (◆), 4% 200 °C (□), 2%, 220 °C (△), 4%, 220 °C (×), intrinsic viscosity: 0.45 dl/g in NMP at 25 °C.

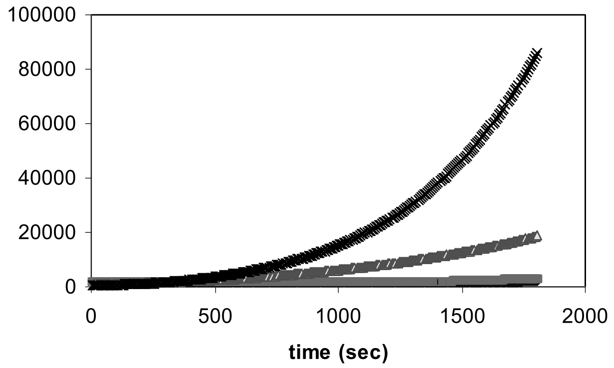

Fig. 15. Effect of extent of AM as termonomer (mol%) and temperature on time stability of PAN system. Time sweeps (η^*, Pa s vs. time, s), 2%, 200 °C (◆), 4% 200 °C (■), 2%, 220 °C (△), 4%, 220 °C (×), intrinsic viscosity: 0.45 dl/g in NMP at 25 °C.

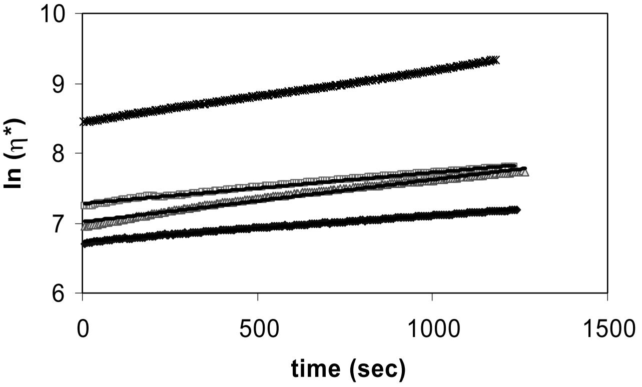

Fig. 16. Cure kinetic model correlation with experimental data for AN/MA/IA system with varying IA concentrations (mol%) at 200 °C ($\ln(\eta^*)$ vs. time, s), 1% (◆), 2% (□), 3% (△), 4% (×), (symbols represent experimental data, solid line represents model).

In these equations, k_∞ and E_k are temperature independent functions of i, the molar mount of IA in the terpolymer as observed by non-aqueous titration (Table 1). It is to be noted that i here refers to the IA content in the terpolymer and not in the feed amount as reported for the DSC and TGA analyses. Here, t is time, T is temperature, k is the rate constant, $\eta(t)$ is the viscosity at time t, and η_0 is the viscosity at time $t = 0$ at a given temperature. The temperature dependence of η_0 and k are given in terms of the activation energies ΔE_η and ΔE_k, respectively. Thus, Eqs. (1)–(3) are correlations that relate the viscosity to temperature, time and IA content. In order to determine the constants given in Eqs. (1)–(3), we first plotted ln η vs. time for each of the AN/MA/IA samples at each temperature and for different amounts of IA. Fig. 16 shows the experimental data (denoted as symbols) at 200 °C. The slope and intercept of these plots yielded k and η_0, respectively.

Using the viscosity variation with time and IA content ($i = 1.6$–5.9, or IA of 1.0–4.0 mol%) at three temperatures, 200, 210 and 220 °C, we obtained all the parameters used in Eqs. (1)–(3). The $|\eta^*|$ data used for analysis was recorded at $\omega = 10$ *rad/s*. The natural logarithms of η_0 and k were then plotted as a function of $1/T$, which gave the values of η_∞, and k_∞, as intercepts, and, $\Delta E_\eta/R$, and $\Delta E_k/R$ as slopes, respectively. We assumed here that η_∞ and ΔE_η were functions of the molecular weight of the terpolymer as well as the amount of IA. The $[\eta]$ of all the AN/MA/IA samples was similar, and hence the molecular weight would also be similar. Therefore, we assumed here that η_∞ and ΔE_η were functions of the amount of IA alone. Graphs of ln k_∞ vs. i, and ln $\Delta E_k/R$ vs. i, both gave linear plots ($R^2 = 0.973$). From these graphs, we obtained the following relationships for the variation of k_∞ and $\Delta E_k/R$ with i:

$$k_\infty = 1.022 \times 10^7 i^{3.66} \tag{4}$$

$$\frac{\Delta E_k}{R} = 1626i + 11\,436 \tag{5}$$

Although η_∞ and ΔE_η can be obtained similarly, the error associated with their measurement would be higher. Due to the time required to bring the sample to the desired temperature (typically about 5–7 min for a 1 mm thick sample), the cyclization/crosslinking reactions were probably already initiated at time $t = 0$, and η_0 would represent a system which is partially crosslinked. The higher the temperature of the study, the greater would be the extent of the reactions and the corresponding rise in viscosity. Therefore, the value of η_0 obtained experimentally was not used to obtain the values of η_∞ and ΔE_η.

Fig. 16 shows the comparison of the model with the experimental data at 200 °C. Excellent correlations were observed for $i = 1.6$ and 2.9 ($R^2 > 0.99$) (corresponding to IA of 1 and 2 mol%, respectively) and good correlation for $i = 4.2$ ($R^2 \sim 0.978$) (corresponding to IA of 3 mol%) at both 200 and 220 °C. Similarly, a good correlation was observed for the samples having an i of 5.9 (corresponding to IA of 4 mol%) at 200 °C ($R^2 \sim 0.98$). However, at 220 °C, the η_0 computed for these samples (having an i of 5.9) by the correlation was about 35% lower than the experimentally observed value. The difference between the two values was due most likely to the sample being partially crosslinked at time zero, and the actual η_0 would be smaller than the experimentally obtained η_0.

Eq. (1) can be differentiated with respect to temperature to get an estimate of the temperature at which the viscosity is minimum. This temperature would represent the value at or below which the melt processing of the PAN terpolymer should be performed in order to achieve good flowability. As the reaction temperature is increased, the viscosity of the polymer drops due to the activation energy and increases due to the crosslinking reactions and cyclization. The temperature at which the viscosity is a minimum can be obtained by setting $\mathrm{d}\eta/\mathrm{d}T = 0$. The parameters needed for getting this value of temperature are k_∞, $\Delta E_k/R$, $\Delta E_\eta/R$, and $\mathrm{d}T/\mathrm{d}t$. The sample was experimentally monitored at a heating rate of 2 °C/min ($\mathrm{d}T/\mathrm{d}t = 0.033$ *°C/s*). This analysis was studied for a sample of AN/MA/IA of 85/11/3 ($i = 4.2$)

using the parameters obtained from the correlations and verified with the experimental result presented in Fig. 10. In order to get an accurate value of $\Delta E_\eta/R$, the slope corresponding to a plot of ln η vs. $1/T$ in the temperature range 170–180 °C was used (from Fig. 10). At these temperatures, the crosslinking/cyclization rates are fairly low and the viscosity change is primarily due to the activation energy, thereby giving good estimates of $\Delta E_\eta/R$. A value of $T = 203.8\,^\circ C$ was obtained using the correlation parameters, which agrees excellently with the value of 203.5 °C obtained experimentally, corresponding to the temperature at which viscosity obtained is minimum (Fig. 10). Also, the stabilization at temperatures higher than 203.8 °C is favorable in order to achieve fast cyclization and good viscosity buildup. It is to be noted that this value of temperature would change with the amount of IA used in the terpolymer. Thus, the above model should be very useful for obtaining the optimum conditions for doing the melt processing and stabilization of the terpolymer.

4. Conclusions

PAN terpolymers based on AN, MA, and IA, have been synthesized and tailored to potentially meet the requirements of both melt spinnability and stabilization based on rheological characterization. Thermal analyses of the PAN terpolymers showed that the char yield would not be changed significantly on incorporation of small amounts (less than 4 mol%) of termonomer. Also, small amounts of acid termonomers were found to significantly affect the rate of oxidation and cyclization reactions. The initiation of the exothermic reactions was considerably hastened and the different types of exothermic reactions (oxidation/dehydrogenation, cyclization and secondary oxidation) were separated in the DSC peaks obtained. The nature and the amount of the termonomer were found to considerably influence these results. It was seen that the buildup of viscosity was also dependent on both the amount as well as the type of termonomer. For the different acid termonomer studied, the extent of crosslinking as evidenced by the viscosity buildup ranged in the order IA > AM > MAA > AA. A chemorheological analysis of the IA-based PAN terpolymers showed that curing models used to describe the crosslinking behavior of polymer samples could fit to the viscosity buildup as a function of temperature, time and amount of IA. A temperature of ~205 °C was suggested to be the optimum temperature to do the melt processing of AN/MA/IA sample of $[\eta] \sim 0.5$ based on this analysis.

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