

Rheological and Thermal Properties of Acrylonitrile-Acrylamide Copolymers: Influence of Polymerization Temperature

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Abstract: An attempt was made to correlate the polymerization temperature and rheological and thermal properties of acrylonitrile (AN)-acrylamide (AM) copolymers. The copolymers were synthesized at different polymerization temperature. The copolymer structure was characterized by gel permeation chromatography (GPC) and Infrared spectrum (IR). The rheological and thermal properties were investigated by a viscometer and differential scanning calorimeter-thermogravimetric (DSC-TG) analysis, respectively. When the polymerization temperature increased from 41 °C to 65 °C, the molecular weight (\bar{M}_w) of copolymers decreased from 1,090,000 to 250,000, while its conversion increased from 18% to 63%, and the polymer composition changed slightly. To meet the requirements of carbon fibers, the rheological and thermal properties of products were also investigated. It was found that the relationship between viscosity and \bar{M}_w was nonlinear and the viscosity index (η) decreased from 3.13 to 2.69, when the solution temperature increased from 30 °C to 65 °C. This suggests the dependence of viscosity upon \bar{M}_w is higher at lower solution temperature. According to the result of activation energy, the sensitivity of viscosity to solution temperature is higher for AN-AM copolymers synthesized at higher polymerization temperature. The result of thermal analysis shows that the copolymers obtained at higher polymerization temperature are easier to cyclization evidenced from lower initiation temperature. The weight loss behavior changed irregularly with polymerization temperature due to irregular change of liberation heat.

Keywords: Acrylonitrile-acrylamide copolymers, Polymerization temperature, Carbon fiber, Rheological and thermal properties

Introduction

It is well known that the mechanical properties of ultimate polyacrylonitrile (PAN)-based carbon fiber depend, to a large extent, on the properties of PAN precursor [1]. Suitable precursor should have small diameter, maximum possible orientation of polymer chain along the fiber axis, high crystalline content, low initial cyclization temperature and broad exothermic peaks, etc, which are determined by the properties of copolymers and spinning process [2-8]. The effect of polymeric structure on the quality of final carbon fiber has been discussed elsewhere [2-6]. In majority of the cases, much attention was focused on the nature and content of comonomer, but few reports were attached on the polymerization parameters. In fact, the polymerization conditions play an important role in the control of polymer structure, such as molecular weight, the degree of branching and stereoregularity of PAN chain, which are directly related to the rheological behaviors of dope and thermal properties of precursor and so further affect the quality of carbon fiber [4-8]. Among them, polymerization temperature is one of the key parameters [9-12].

In this paper, solution copolymerization method was used to synthesize acrylonitrile (AN)-acrylamide (AM) copolymers.

Recently, this method has been a popular method to produce precursor for high performance carbon fiber since it yields polymer with lower stabilization temperature and fewer molecular defects [1]. In the present study, AM, an unpopular and disputed comonomer [13,14], was selected to copolymerize with AN since it has the potential probability to improve the quality of precursor by increasing dope hydrophile [13,15,16]. The objective of the work is to make an attempt to correlate the polymerization temperature to the rheological and thermal properties of copolymers. To date, no studies on such correlation has been reported for the solution copolymerization of AN with AM.

Experimental

AN with purity of 99.99% (analyzed by gas chromatogram) was obtained by distillation. AM (Aldrich Co., 99%), dimethylsulfoxide (DMSO) and azobisisobutyronitrile (AIBN) were used without any further purification.

AN, AM, AIBN and DMSO were poured into a four-necked round bottom flask and flushed with nitrogen for 1 h to remove oxygen. Then the polymerization was carried out for 6 h at different temperature with a mechanical stirring, nitrogen inlet and condenser. To insure effective decomposition of initiator (AIBN), the reaction temperature was usually set beyond 30 °C. On the other hand, the reaction temperature should not be too high which may cause side reactions such

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as oxidation of DMSO [17]. In the present work, the reaction temperature was set 41-65 °C. The concentration of monomers, stirring speed and ratio of AIBN to monomers was 20 wt%, 250 rpm/min and 0.5 wt%, respectively. The AM mole fraction in the feed was 1.5 %. Upon completion of polymerization, the product was precipitated in water and washed several times to eliminate residual monomers and solvent, then vacuum-dried at 50 °C for 12 h.

The molecular weight (\bar{M}_w) was characterized by LC-10AD gel permeation chromatography (GPC). Conversion was calculated by the change of weight and the average value for three determinations was used. Infrared spectrum (IR) made by Germany Bruker corporation TENSOR 27 with an affix of attenuated total reflection (ATR) was used to study the molecular structure of copolymers, and the copolymer composition was calculated from the IR spectra using a calibration curve [13]. The rheological properties of AN-AM copolymers were studied by the determination of Newtonian viscosity (η_0). η_0 , namely viscosity at zero shear rate was determined by a viscometer. To eliminate the influence of survival monomers on η_0 , copolymers were washed by abundant water and then dissolved into DMSO to prepare solutions. The solution concentration was prepared as high as possible to meet the industry requirements. In view of the best solubility, the solution concentration was choosed as 6 wt%. Among these samples, PA1 was not studied for rheological properties due to bad solubility. The thermal properties of copolymers, namely differential scanning calorimeter (DSC) and thermogravimetric (TG) curves were characterized by NETZSCH STA 409PC. The samples (by powder) with 5-7 mg weight were heated under nitrogen at 5 °C/min heating rate. The scanning range was 50-450 °C.

Results and Discussion

Copolymerization of AN and AM at Different Reaction Temperature

Table 1 shows the effect of polymerization temperature on \bar{M}_w and conversion. When increasing polymerization temperature from 41 °C to 65 °C, the \bar{M}_w decreased from 1,090,000 to 250,000 and the conversion increased from

Table 1. Effect of polymerization temperature on the copolymerization of AN and AM

Sample code	Reaction temperature (°C)	AM in feed (mol %)	Molecular weight ($\bar{M}_w \times 10^4$)	AM in copolymer (mol %)	Conversion (%)
PA1	41	1.5	109	5.6	18
PA2	52	1.5	71	5.7	38
PA3	55	1.5	53	5.7	44
PA4	60	1.5	36	5.6	58
PA5	65	1.5	25	5.6	63

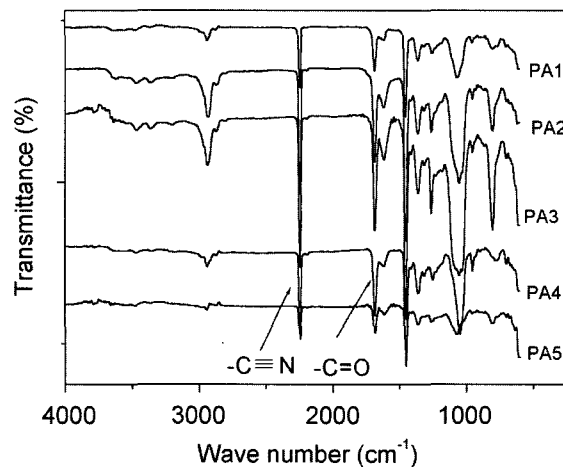


Figure 1. IR spectra of AN-AM copolymers synthesized at different temperature.

18 % to 63 %. This is accordant with the general mechanism of free radical polymerization. At low temperature, less chain transfer reaction occurs. Furthermore, free radicals more tend to terminate by coupling (reaction), which also benefits to the enhancement of \bar{M}_w .

Figure 1 shows the IR spectra of AN-AM copolymers. The bands appearing at 1220-1270, 1345-1375, and 1440-1465 cm^{-1} are assigned to C-H vibrations of different modes. The strong absorption band at 2240 cm^{-1} is assigned to C \equiv N. The band at 1685 cm^{-1} is due to the stretching vibration of the C=O in AM unit. The copolymer composition can be calculated by the ratio of absorption intensity at 2240 cm^{-1} (C \equiv N) to that at 1685 cm^{-1} (C=O) using a calibration curve [13]. The calculated results are listed in Table 1.

In general, the polymer composition is not coincident with the feeding composition due to the difference in reactivity of monomers. The copolymer composition usually varies with the polymerization conversion except in the case of ideal copolymerization [17]. For the estimation of reactivity ratio of AN and AM, some workers [13,18] thought that the reactivity ratio of AN was higher than that of AM, while Lin *et al.* [19] argued that the activity of AM is higher. Whichever, it can be concluded that there is a marked difference in reactivity of AN radical and AM one. As listed in Table 1, the copolymers composition is not accordant with the feeding ratio and the content of AM in the polymer (5.6-5.7 mol %) is always higher than that in the feeding (1.5 mol %). This indicates higher reactivity ratio value of AM than that of AN, which is agreement with the result of Lin *et al.* [19]. It is interesting to be noted that the mole fraction of AM in polymer changes slightly with increasing polymerization temperature. This is absurd in theory unless ideal copolymerization appears. One reason may be that trace AM rapidly uses up due to high reactivity as the progress of reaction. This needs a more critical and in-depth study of the system.

Rheological Behavior of AN-AM Copolymers

In the carbon fiber community, spinnability of copolymers has arrested a great deal of interest. Spinnability can be assessed by rheology measurements. Among them, viscosity is one of the main aspects in rheology and represents the fluidity of solution. Table 2 and Figures 2-5 show the rheology behaviour of AN-AM copolymers (PA2, PA3, PA4, and PA5) with different molecular weight (\bar{M}_w). Due to high \bar{M}_w (1,090,000) results the difficulty in dissolving, the sample PA1 is not studied here.

Table 2. Data of Arrhenius activity energy

Sample code	PA1	PA2	PA3	PA4	PA5
$\bar{M}_w \times 10^4$	109	71	53	36	25
ΔE_{η_0} (kJ/mol)	-	24.0	22.1	21.5	24.4

PA1 solution was not prepared due to bad solubility.

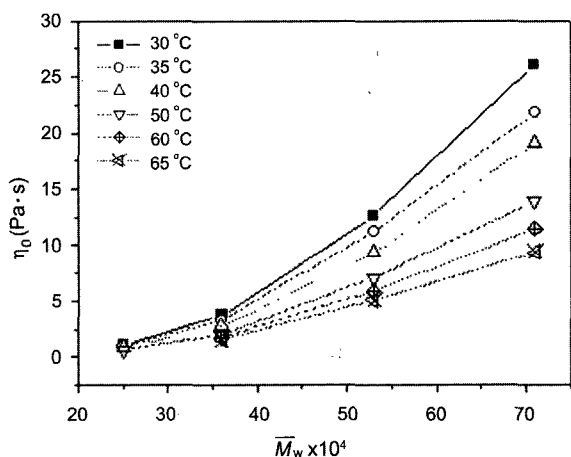


Figure 2. Dependence of viscosity on the molecular weight; copolymer conditions ($\bar{M}_w \times 10^4$): 71 (PA2), 53 (PA3), 36 (PA4) and 25 (PA5).

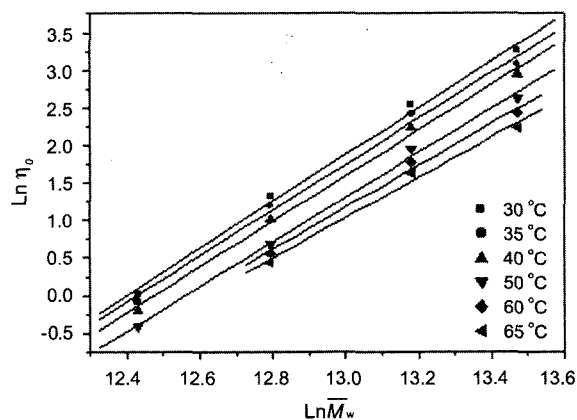


Figure 3. Linear fits for $\ln \eta_0 - \ln \bar{M}_w$ at different solution temperature of AN-AM copolymers; copolymer conditions ($\ln \bar{M}_w$): 13.5 (PA2), 13.2 (PA3), 12.8 (PA4) and 12.4 (PA5).

Figure 2 shows the dependence of Newtonian viscosity (η_0) upon \bar{M}_w . As \bar{M}_w increases, there is a significant increase in η_0 . This is due to the higher the \bar{M}_w is, the more the number of chain entanglements are, and the more difficultly the chains move. As a result, the viscosity of the solution increases. It is apparent that the dependence of solution viscosity on \bar{M}_w is not linear and can be described by the following equation [20]:

$$\eta_0 = K \bar{M}_w^n$$

where K and n are empirical constants. The n value means the degree of dependence of η_0 on \bar{M}_w , which can be calculated by the slope of $\ln \eta_0 - \ln \bar{M}_w$ plots. A good linear fits of $\ln \eta_0 - \ln \bar{M}_w$ is shown in Figure 3, suggesting the viscosity of AN-AM copolymers solution is proportional to the n order of \bar{M}_w . The temperature 30, 35, 40, 50, 60, 65 °C, as identified in Figure 3, represents the temperature of AN-AM copolymers solution. The influence of solution temperature on n value is plotted in Figure 4. It is observed that the value of n is reduced from 3.13 to 2.69 upon increasing the solution temperature from 30 °C to 65 °C. Higher n value at lower solution temperature means that the degree of dependence of η_0 on \bar{M}_w is greater, namely η_0 is more sensitive to \bar{M}_w at lower temperature. This can be explained by the fact that the polymer chains more tend to entangle at lower temperature and thus lower the fluidity of solution. Therefore at lower temperature η_0 increases rapidly with \bar{M}_w increasing, which can be also observed from Figure 2, corresponding higher n value.

During the spinning process, the dope temperature is an important parameter and the solution viscosity changes with solution temperature. The sensitivity of viscosity to temperature can be evaluated from Arrhenius activation energy (ΔE_{η_0}), which is a measurement of the intensity of intermolecular interaction of the macromolecules in the solution. Figure 5

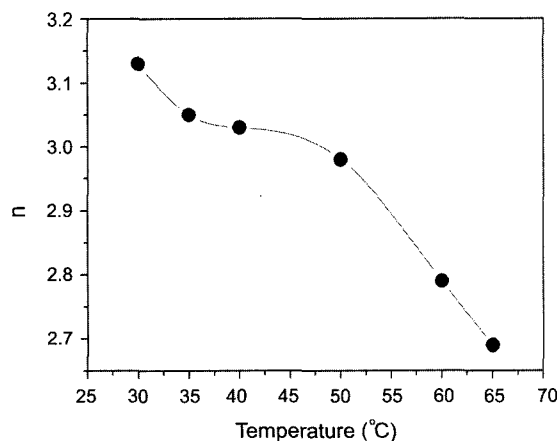


Figure 4. Change of n values with different solution temperature of AN-AM copolymers.

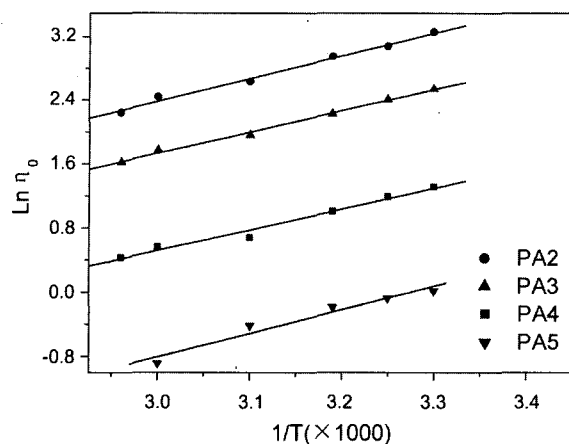


Figure 5. $\ln \eta_0 - 1/T(\times 1000)$ plots for AN-AM copolymers synthesized at different temperature (PA1 solution was not prepared for bad solubility).

illustrates the $\ln \eta_0 - 1/T(\times 1000)$ plots for AN-AM copolymers, and ΔE_{η_0} can be calculated from the slope of plots. The calculated results are shown in Table 2. It is clear that the value of ΔE_{η_0} decreases with the reduction of \bar{M}_w except in the case of sample PA5, suggesting the sensitivity of viscosity to temperature is higher for AN-AM copolymers with higher \bar{M}_w . This may be attributed to the raise of intermolecular interaction force as a result of increase in \bar{M}_w . Another interesting phenomena is also observed in Table 2, that is, ΔE_{η_0} shows high value (24.4 kJ/mol) in PA5 despite of low molecular weight (250,000). This is a surprising result. Usually, the lower the \bar{M}_w is, the chain rigidity is higher which leads that the chains move more difficultly [20]. In the case of PA5, the influence of chain rigidity (or submissiveness) on chain movement may be greater than that of intermolecular interaction. Thus the polymer chain moves more difficultly and shows high ΔE_{η_0} value in PA5.

Thermal Analysis

Cyclization is one of the key reactions in the stabilization process, which involves oligomerization of nitrile groups initiated by miscellaneous atoms [1,14,21]. The cyclization is closely related to the structure of AN-AM copolymers such as \bar{M}_w . Furthermore, the cyclization is considered to be

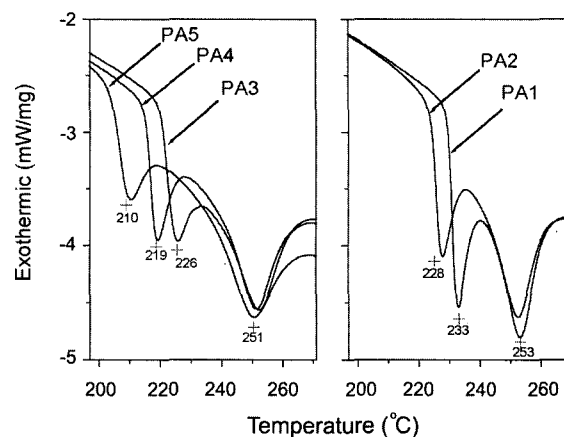


Figure 6. DSC curves of AN-AM copolymers under nitrogen atmosphere.

decisive to govern the weight loss behaviors. Figure 6 shows DSC curves of AN-AM copolymers in nitrogen atmosphere, in which two clearly separated exothermic peaks appear due to the introduction of AM [22]. Upon heated in nitrogen atmosphere, the only exothermic reaction is just cyclization and so the presence of two exothermic peaks could be assigned to two different cyclization mechanism, corresponding to ionic mechanism for the first one and free radical mechanism for the second one, respectively [22]. Apparently, the exothermic behavior is different for samples obtained at different polymerization temperature. Samples obtained at higher polymerization temperature tend to easier cyclization. For example, the initiation temperature is 233 °C for PA1, however, which is ahead of 23 °C for PA5. In all cases, the second exothermic peak shows no apparent change and the peak temperature (T_{pk2}) just drifts from 251 °C to 253 °C. The analysis data of DSC is shown in Table 3. As discussed above, the samples properties are affected by polymerization temperature, namely remarkable reduction in \bar{M}_w and slight change in composition upon increasing polymerization temperature. It is reasonable that PA5 with lower initiation temperature because weaker force of intermolecular interaction is expected in copolymers with lower \bar{M}_w . The lower \bar{M}_w is also responsible for the broader exothermic reaction of copolymers [21]. In all cases, the total heat liberation ΔH changes irregularly with sample

Table 3. Parameters for the thermal properties of AN-AM copolymers

Sample code	Condition	T_i (°C)	T_{pk1} (°C)	T_{pk2} (°C)	T_f (°C)	H (J/g)	TG (%)
PA1	Nitrogen	230	233	253	262	425	43
PA2	Nitrogen	224	228	252	262	390	44
PA3	Nitrogen	220	226	252	264	442	47
PA4	Nitrogen	215	219	251	262	418	41
PA5	Nitrogen	204	210	251	263	423	46

T_i : initiation temperature of the exotherm, T_f : final temperature of the exotherm, T_{pk1} : peak temperature at the first peak, T_{pk2} : peak temperature at the second peak, ΔH : total heat liberating, TG: thermogram (from 50 °C to 450 °C).

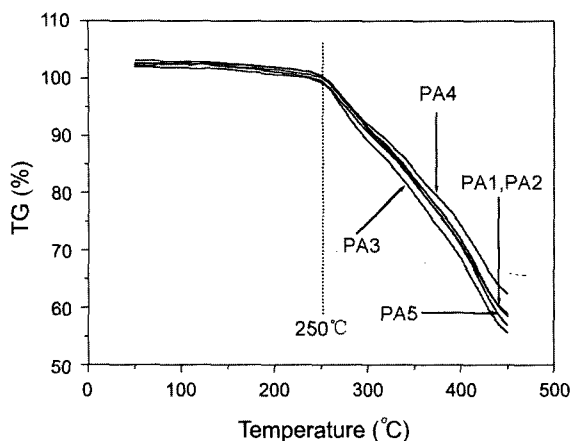


Figure 7. Thermogravimetric curves of AN-AM copolymers under nitrogen atmosphere.

properties, suggesting the amount of nitriles to oligomerize is not directly affected by \bar{M}_w .

TG curves of AN-AM copolymers recorded under nitrogen atmosphere are shown in Figure 7. It is clear that the weight loss occurs in two stages. There is little weight loss with a very slow rate below 250 °C (stage I), such weight loss might be caused by nitrile cyclization [23]; thereafter, the weight loss abruptly decreases at a quite fast rate between 250-450 °C (stage II) which is related to chain scissions [23]. This suggests that chain scissions are the main cause of weight loss under nitrogen atmosphere. Furthermore, according to the discussion of DSC above, the cyclization should complete before 250 °C. This also indicates that the little weight loss in stage I is caused by cyclization. But this does not mean that the weight loss is not related to the cyclization. On the contrary, the greater the extent of cyclization, the smaller the weight loss should be. From the data of DSC, the extent of cyclization shows irregular variation with the change of \bar{M}_w , which can be evidenced from H values in Table 3. As a result, the weight loss changes irregularly (shown in Table 3).

Conclusions

AN-AM copolymers have been synthesized at different polymerization temperature to meet the requirement of spinning and stabilization processes based on rheological and thermal studies. An attempt was made to correlate the polymerization temperature with sample properties. As discussed above, the polymerization temperature affects \bar{M}_w and conversion significantly, however, the polymer composition changes slightly. Rheological studies show that the solution viscosity of copolymers obtained at lower polymerization temperature is more sensitive to the solution temperature, evidenced by higher activation energy value. According to the thermal analysis, the copolymers obtained from higher polymerization temperature are easier to take place cyclization with lower

initiation temperature. Among these copolymers obtained at different polymerization temperature, there is no regular trend in the cyclization extent, resulting the irregular weight loss behaviors.

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