

Shear Rheological Properties of Acrylic Copolymers and Terpolymers Suitable for Potentially Melt Processable Carbon Fiber Precursors

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ABSTRACT: In an effort to generate melt processable polyacrylonitrile (PAN) precursor fibers suitable for conversion to carbon fibers, an acrylonitrile/methyl acrylate (AN/MA) copolymer and two acrylonitrile/methyl acrylate/acryloyl benzophenone (AN/MA/ABP) terpolymers were synthesized at molar ratios of 85/15 and 85/14/1, respectively. The termonomer (ABP) was incorporated to accelerate crosslinking via UV irradiation, which serves to prevent relaxation of orientation and flow as the temperature of the fiber is raised during thermooxidative stabilization. Two molecular weights of the terpolymer and one molecular weight of the copolymer were studied to determine the effect of the termonomer, and the effect of molecular weight (MW), on the steady shear viscosity (η) and magnitude of the complex viscosity (η^*). A higher rate of increase of η as a function of time was observed for the high MW terpolymer

relative to that of the copolymer over the temperature range used. Using a temperature sweep and monitoring levels of η^* , a minimum was observed at lower temperatures for both terpolymers. These results suggest that copolymerization with ABP significantly increased the thermally induced kinetics of crosslinking. Comparison of the η and η^* data for the low and high MW terpolymers suggested that molecular weight also significantly reduced the melt stability (increased the kinetics of crosslinking). A chemorheological correlation was then used to quantify the effects of the termonomer and of molecular weight on the kinetics of crosslinking of the AN terpolymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2856–2865, 2004

Key words: polyacrylonitrile; melt processability; copolymerization; crosslinking; stabilization

INTRODUCTION

Currently, carbon fiber precursors are industrially produced via two main techniques: melt spinning of mesophase pitch and solution spinning of high (~ 97 mol %) polyacrylonitrile (PAN) containing copolymers. Carbon fiber precursors produced from mesophase pitch usually lead to high modulus fibers, whereas those produced from PAN precursors (usually a copolymer of acrylonitrile and a suitable comonomer) lead to carbon fibers with a high tensile strength and a high elongation to break ($> 1\%$). Edie¹ reported that PAN-based carbon fibers have approximately three times the value of tensile strength over pitch-based fibers, but the value of the modulus is generally 50% of the pitch fibers. Because carbon fibers generated from mesophase pitch are more expensive,

low cost production may be more easily attainable using PAN-based systems.

Production of PAN-based carbon fibers involves three major steps: precursor fiber formation, thermooxidative stabilization, and carbonization. PAN acrylic textile fibers that serve as carbon fiber precursors are usually generated by wet-spinning.² The precursor fibers are then subjected to a thermooxidative “stabilization” procedure at 220–300°C, during which a crosslinking and cyclization reaction takes place to form a “ladder” structure that can withstand higher temperature heat treatments.² The “stabilized” fibers are then subjected to a high temperature (400–1,200°C) carbonization step in an inert atmosphere for conversion into carbon fibers.²

The precursor for PAN-based carbon fibers is generally copolymerized with a low percentage (2–7 mol %) of a suitable comonomer, such as methyl acrylate (MA), itaconic acid, or methacrylic acid.³ The comonomers enhance solubility and decrease the kinetics of crosslinking during the exothermic stabilization procedure and subsequently reduce heat buildup and thermally induced chain scission reactions.² As a result, improved mechanical properties of the carbon

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fibers are obtained by minimizing the chain scission reactions during the stabilization step.²

PAN-based carbon fibers have found numerous applications in engineering and structural polymer composites for aerospace and defense applications, as well as in sporting goods and automotive applications, because of their high specific strength and modulus and low coefficient of thermal expansion.⁴ However, the prohibitive cost of carbon fiber production has somewhat limited their usage.⁵ The rapid crosslinking reaction that can occur concurrently with the stabilization step requires that acrylonitrile (AN) copolymer precursor fibers be solution processed in the presence of toxic, environmentally unfriendly organic solvents, commonly including dimethyl formamide (DMF) and dimethylacetamide (DMAC).³ These polar organic solvents are usually used in the range of 70–93 wt % solvent (7–30 wt % solids) to permit processing at temperatures well below the onset of the crosslinking reaction.² As a result, high production costs are incurred during carbon fiber production from both solvent use and recovery in the precursor generation step. The thermooxidative procedure requires a significantly longer amount of time than the precursor fiber generation step and prevents continuous carbon fiber generation directly from solution spinning of the precursor. As a result, the stabilization step also significantly contributes to the high production costs associated with PAN-based carbon fibers. For these reasons, there is interest in developing alternative methods to produce PAN-based carbon fibers, in particular suitable for use as reinforcements in automotive structural applications, in a more economical and environmentally friendly manner.

Melt processing of AN copolymers could potentially provide a less expensive and environmentally benign method of carbon fiber production by eliminating the need for solvent use and recovery in the precursor generation step, resulting in reduced capital and operating costs.⁵ Melt spinning would also reduce costs by providing 100% solids throughput on a per pound basis compared to the 7–30 wt. % obtained from solution processing. To melt spin AN precursor fibers, the kinetics of crosslinking described above must be kept to a level that facilitates a relatively stable steady shear viscosity (η) as a function of time. In particular, an arbitrarily selected increase of approximately 10–20% in the levels of η was found to be acceptable over a period of 1,800 s, which was believed to be sufficient to extrude approximately 99% of the material.⁶ However, the precursor fibers must subsequently have the ability to be crosslinked and converted into carbon fiber form following melt spinning.

Extensive efforts have been documented by Bhanu et al.^{7,8} and Rangarajan et al.,^{5,9} which had the goal of establishing a suitable polymerization technique, copolymer composition, comonomer types, and molec-

ular weight to produce melt-spinnable acrylic precursors that can be processed in the range of 200–220°C. These studies focused largely on the use of suitable comonomers (primarily MA) in the range of 10 to 15 mol % to disrupt the long range order and modestly reduce the T_g of AN copolymers, affording melt stability. AN/MA copolymers were preferably generated via a heterogeneous free radical (emulsion) polymerization, and a molar ratio of about 85/15 mol % AN/MA was identified as melt processable. The kinetics of crosslinking was found to be relatively slow, with increases in the levels of η of approximately 3 and 7% over a period of 1,800 s and shear rate ($\dot{\gamma}$) of 0.1 s⁻¹ at 200 and 210°C, respectively. The precursor could be melt spun, but it was noted that an extremely long thermooxidative stabilization procedure was required to prevent the fibers from flowing and losing orientation. As a result, a thermally stable, but photochemically active termonomer (acryloyl benzophenone) was identified that could be terpolymerized to accelerate crosslinking in the drawn precursor fibers via UV irradiation.⁷ However, the effects of addition of the termonomer on the melt stability and rheology of the precursor copolymer were unknown.

Although the overall goal of this study was geared toward production of low cost carbon fibers (< \$5/lb.) with high mechanical properties (e.g., tensile modulus = 170 GPa, tensile strength = 2.7 GPa), the goal of this paper was to determine whether the viscosity levels and melt stability of the AN/MA/ABP terpolymers are suitable for melt spinning. Changes in the steady shear viscosity (η) versus time were measured to quantify the melt stability of the co- and terpolymers in the temperature range 200–260°C. Dynamic oscillatory frequency sweeps, used over the temperature range of 200–220°C, provided information about the frequency dependence of the magnitude of the complex viscosity (η^*). A temperature sweep was also used over the range of 180–280°C, in which the levels of η^* were monitored to determine the temperature dependence of the magnitude of the complex viscosity.

EXPERIMENTAL

Materials

The base copolymer for this study is an 85/15 mol % AN/MA copolymer. The AN/MA/ABP terpolymers are both 85/14/1 mol % copolymers, differentiated as batch 1 and batch 2. The AN/MA and AN/MA/ABP copolymers were produced via a heterogeneous free radical (emulsion) polymerization by Monomer Polymer, Inc. (Feastersville, PA). The emulsion polymerization recipe developed by Bhanu and coworkers⁸ is different from that for solution and suspension polymerizations. One kilogram quantities of each co- and

TABLE I
Intrinsic Viscosity and Molecular Weight Data for the 85/15 AN/MA and 85/14/1 AN/MA/ABP Polymers

AN/MA molar ratio	Intrinsic viscosity (NMP/25°C)	M_n (GPC, g/mol)	M_w (GPC, g/mol)	PDI
85/15	0.50	26,500	65,900	2.5
85/14/1 batch 1	0.36	16,300	27,300	1.7
85/14/1 batch 2	0.52	22,000	41,700	1.9

terpolymer were scaled up, and the co- and terpolymers were available in powder form for rheological measurements.

Molecular weight analyses

Intrinsic viscosities (IV) and number and weight average molecular weights, M_n and M_w , respectively, for each sample are indicated in Table I. Intrinsic viscosities were measured using a Cannon Ubbelohde viscometer. Absolute molecular weight measurements from gel permeation chromatography (GPC) were obtained at 60°C with a Waters 2690 (Waters Associates, Milford, MA) Separation Module equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek T60A) coupled in parallel. NMP containing 0.2M P_2O_5 was used as a solvent. As indicated in Table I, the IV of the 85/15 copolymer and batch 2 are comparable, but batch 1 has a significantly lower IV. The molecular weights of the polymers are decreasing in the order AN/MA copolymer > batch 2 > batch 1. The polydispersity is similar for all three materials, in the range of 1.7–2.5.

Dynamic oscillatory rheology

Dynamic oscillatory rheological measurements were performed using a Rheometrics RMS 800 Mechanical Spectrometer. Frequency sweeps were made over the range of 0.1–100 rad/s using 25.0 mm parallel plates and 1–5% strain. Temperatures in the range of 200–220°C were used. To minimize degradation during measurements of the magnitude of the complex viscosity, η^* , angular frequencies (ω) below 0.1 rad/s were not used because of the length of time required to obtain data. Strain sweeps were performed at 220°C and an angular frequency of 10 rad/s over the range of strain of 0.6 – 100%. The temperature sweep was performed at a rate of 0.033°C/s over the range of 180–280°C, using an angular frequency of 10 rad/s.

Rheological measurement procedure

Specific steps were taken to minimize any significant crosslinking in the copolymers prior to the dynamic oscillatory rheological measurements. Samples were

compression molded into circular samples of 25.0 mm diameter and 1.0 mm thickness using a press at room temperature, which compacted the powder samples using high pressures (~ 60 MPa). As a result, the compacted powder samples had no thermal history prior to loading into the rheometer. During loading, heating, and equilibration of the samples in the rheometer, an inert nitrogen atmosphere was used in the rheometer oven. The presence of oxygen has been shown to accelerate the crosslinking reaction, and use of an inert atmosphere helped to prevent significant degradation prior to rheological measurements.¹⁰

Steady shear viscosity

Steady shear viscosity (η) measurements were carried out using a RMS 800 Mechanical Spectrometer. Measurements were taken using 25.0-mm parallel plates and a sample thickness of 1.0 mm over the temperature range 200–260°C. A shear rate, $\dot{\gamma}$, of 0.1 s⁻¹ was used for the measurements at each temperature. Measurements were conducted for 1,800 s, which was estimated to be significantly longer than the residence time in an extruder.¹¹ Steady shear viscosity data are included in the figures from the beginning of the experiment (time, $t = 0$) to illustrate consistent transient viscosity growth.

RESULTS AND DISCUSSION

In the following sections, the time-dependent steady shear viscosity (η) behavior and both the time and frequency dependence of the magnitude of the complex viscosity, η^* , of a potentially melt processable AN/MA copolymer suitable for use as a carbon fiber precursor are evaluated. The effects of copolymerization of a UV-sensitive terpolymer (ABP) on the viscosity and melt stability are then determined.

Strain sweeps

To ensure that dynamic oscillatory measurements were made in the linear viscoelastic region for the polymers in this study, strain sweeps were performed at 200°C. The temperature 200°C was chosen because the kinetics of the crosslinking reaction was slow at

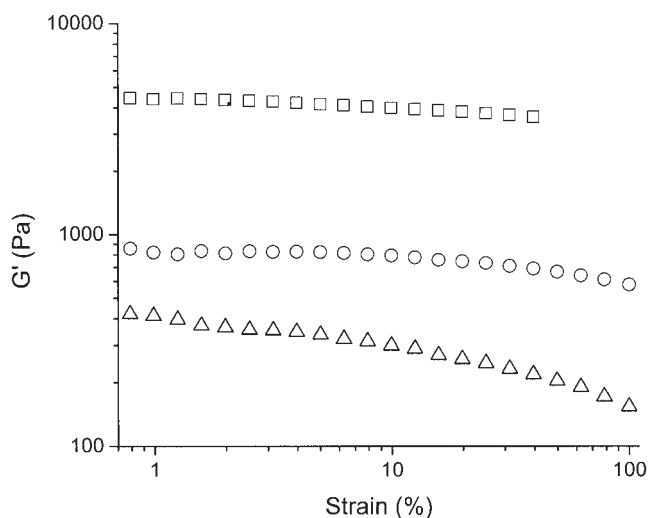


Figure 1 Strain sweeps at $\omega = 10$ rad/s and 200°C for (□) AN/MA copolymer; (○) batch 2 terpolymer; (△) batch 1 terpolymer.

this temperature, and accordingly significant thermal degradation did not occur during the measurements. The data in Figure 1 indicate that the storage modulus, G' , is constant up to a strain of 10% for the AN/MA copolymer and the batch 2 terpolymer and is constant up to approximately 5% strain for the batch 1 terpolymer. As a result, strains above 5% were not used for any of the dynamic oscillatory measurements to ensure that the measurements were made in the linear viscoelastic regime. The values of G' are consistent to those obtained for other AN copolymers with varying molecular weight⁹

Melt viscosity of AN/MA copolymer

Dynamic oscillatory measurements

The dependence of the magnitude of the complex viscosity, η^* , as a function of angular frequency, ω , was evaluated for a melt processable 85/15 AN/MA copolymer suitable for use in the manufacture of carbon fibers. Values of η^* obtained over the temperature range of 200 – 220°C are shown in Figure 2. The low frequency (0.1 rad/s) values of η^* decrease by a factor of 2 between 200 and 220°C . A similar decrease in η^* is observed over the range of frequencies used, 0.1 – 100 rad/s. At each temperature, the general shape of the curves is the same, but the copolymer does not reach a zero shear viscosity, η_0 , at the lowest measured frequency of 0.1 rad/s at any of the temperatures used. Above an angular frequency of approximately 10 rad/s, η^* appears to decrease at a higher rate (as a function of ω) than at the lower frequencies.

We assumed that the levels of η^* are representative of the steady shear viscosity (η) levels. This assumption is confirmed by the steady shear data in Figure 2,

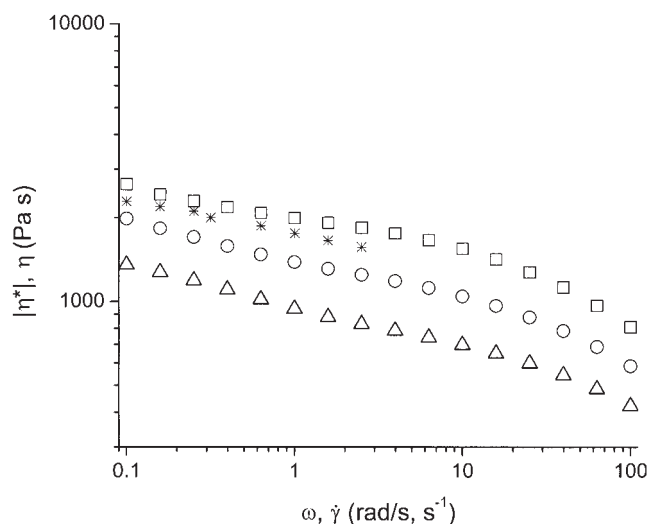


Figure 2 Magnitude of the complex viscosity of AN/MA copolymer at (□) 200°C ; (○) 210°C ; (△) 220°C . *Steady shear viscosity at 200°C .

(obtained for shear rates ($\dot{\gamma}$) from 0.1 – 2.51 s^{-1} at 200°C). The levels of η approach those of η^* at the lowest measured rate and frequency of $\dot{\gamma} = 0.1$ s^{-1} and $\omega = 0.1$ rad/s, respectively, and deviate by less than 15% at the highest measured rate of 2.51 s^{-1} . Values of η for rates above 2.51 s^{-1} could not be measured because edge fracture occurred. These results suggest that the Cox–Merz rule¹² holds reasonably well for this material and that the dynamic oscillatory (complex viscosity) measurements are representative of the steady shear measurements.

The data in Figure 3 evaluate the temperature dependence of η^* . Levels of η^* for the AN/MA copol-

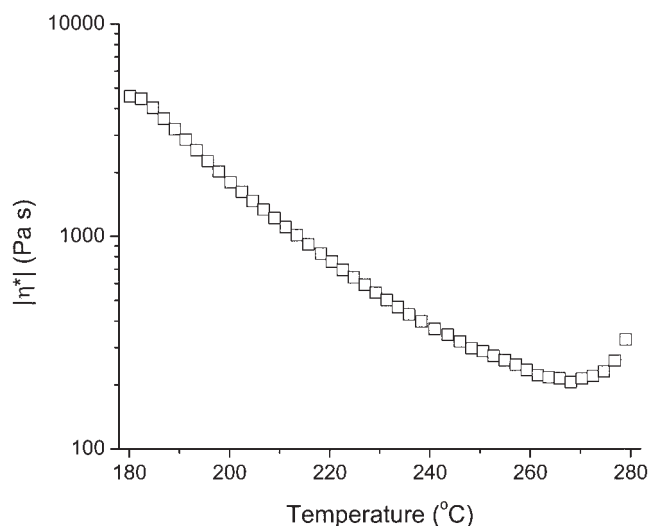


Figure 3 Temperature dependence of the complex viscosity (magnitude) of the AN/MA copolymer. Heating rate $0.033^{\circ}\text{C}/\text{s}$, $\omega = 10$ rad/s, strain = 2%.

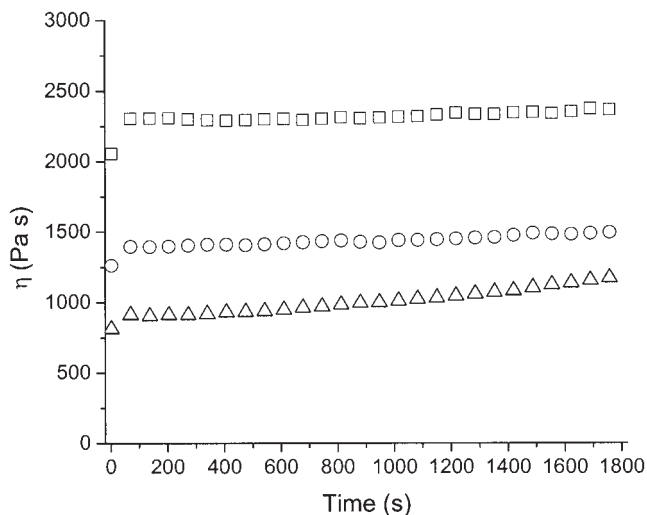


Figure 4 Time dependence of the steady shear viscosity for the AN/MA copolymer at $\dot{\gamma} = 0.1 \text{ s}^{-1}$ and (□) 200°C; (○) 210°C; (△) 220°C.

polymer continue to decrease up to a temperature of approximately 268°C, at which η^* begins to increase. These results suggest that 268°C is the maximum temperature at which melt processing should be performed, above which the kinetics of crosslinking becomes too rapid. The temperature sweep used to obtain the data in Figure 3 is a relative comparison that is rate dependent, i.e., for a slower heating rate, it is possible that a minimum in η^* would be observed at a lower temperature. To address this issue, the changes in viscosity as a function of time (melt stability) are determined, which are of particular interest at temperatures below 268°C, where the kinetics of crosslinking may be slow enough to facilitate melt processing.

Steady shear viscosity

To quantify the melt stability of the AN/MA copolymer system, changes in the steady shear viscosity, η , were measured as a function of time. If levels of η increased with increasing time, then it was implied that crosslinking was occurring. Previously, the time dependence of η^* was used to quantify the melt stability of the material.⁵ However, copolymers for which minimal increases in η^* were observed (over the measurement time) became intractable during monofilament extrusion through a capillary rheometer.¹³ It was believed that measuring η as a function of time would more closely mimic melt extrusion, in which a high degree of mixing introduces the reactive nitrile groups of the polymer chains to each other. During the small strain dynamic oscillatory measurements, the polymer oscillates back and forth over a

small value of strain, and, as a result, the polymer chains did not mix to the same extent.

Values of η for the AN/MA copolymer in Figure 4, which were obtained at a shear rate, $\dot{\gamma}$, of 0.1 s^{-1} , provide an indication of the melt stability of the AN/MA copolymer over the temperature range of 200–220°C. At 200 and 210°C, the kinetics of the crosslinking reaction is slow, and as a result the level of η only increases by 3 and 7%, respectively, over a 30-min measurement. At 220°C, a 31% increase in the level of η is observed. These results suggest that the kinetics of the crosslinking reaction increases significantly between 210 and 220°C. At 200 and 210°C, the levels of η are suitable for extrusion, and the kinetics of crosslinking appears slow enough to produce carbon fiber precursors with minimal degradation. These results have been confirmed experimentally.¹¹

In general, increasing the temperature above 220°C has been shown to significantly increase the kinetics of crosslinking.² The data in Figure 5 illustrate the time dependence of η over the temperature range of 220–260°C and $\dot{\gamma} = 0.1 \text{ s}^{-1}$. The level of η increases by a factor of 6 over a period of 1,800 s at 240°C and by a factor of 126 over a period of 735 s at 260°C. These results indicate that the kinetics of crosslinking significantly increases between 220 and 240°C and, to a greater extent, between 240 and 260°C. In fact, significant degradation had occurred during sample loading and temperature equilibration prior to the η measurements (which took approximately 360 s) at 260°C. This is somewhat apparent in the results in Figure 5, in which an increase is observed in the levels of η from 240 to 260°C at time $t = 0$, contrary to the expected decrease of levels of η with increasing temperature. Studies have shown that the kinetics of crosslinking

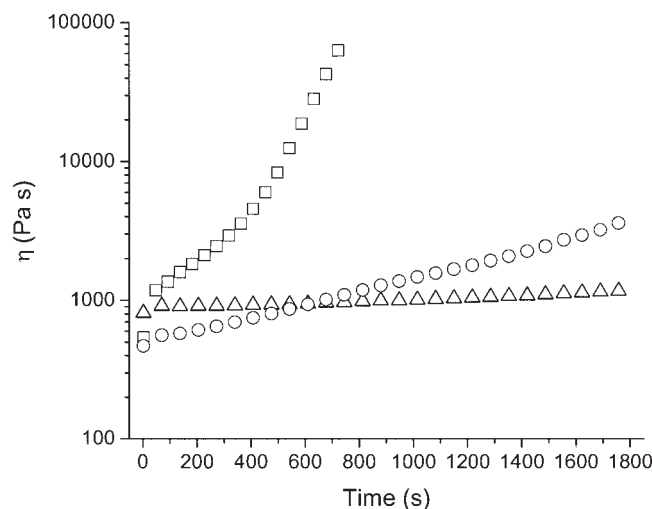


Figure 5 Time dependence of the steady shear viscosity of the AN/MA copolymer at $\dot{\gamma} = 0.1 \text{ s}^{-1}$ and (□) 260°C; (○) 240°C; (△) 220°C.

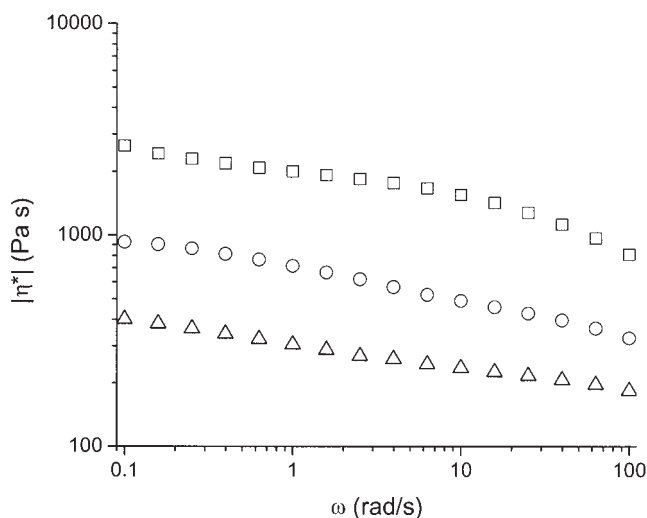


Figure 6 Frequency dependence of complex viscosity (magnitude) at 200°C for the (□) AN/MA copolymer; (○) batch 2 terpolymer; (△) batch 1 terpolymer.

for this AN/MA copolymer becomes sufficiently rapid at 260°C for thermooxidative stabilization of the precursor fibers.¹³ However, relaxation of the fibers during the stabilization step resulted in loss of orientation and carbon fibers with poor mechanical properties.¹³

Characterization of AN/MA/ABP terpolymer

To prevent flow and loss of orientation of the precursor fibers during thermooxidative stabilization, a UV sensitive monomer, acryloyl benzophenone (ABP), was terpolymerized with AN and MA to accelerate the kinetics of the crosslinking reaction via UV irradiation. In the following sections, the effects of ABP on the melt stability and levels of η and η^* are evaluated.

Molecular weight

The polymerization method was almost identical for synthesizing both the AN/MA copolymer and the AN/MA/ABP terpolymer, and similar molar compositions of AN (85 mol %) were used. Therefore, it was expected that the molecular weight and intrinsic viscosities of the polymers would follow similar trends, i.e., for an increase in molecular weight, the intrinsic viscosity would correspondingly increase. The GPC data in Table I indicate that the molecular weights and molecular weight distributions follow the trend AN/MA > batch 2 > batch 1. However, the intrinsic viscosities (IV) follow the trend batch 2 > AN/MA > batch 1, which is interesting considering that IV is expected to scale directly with weight average molecular weight (M_w). The data suggest that copolymerization of only 1 mol % of the ABP termonomer causes

the IV to scale to a different power of molecular weight (corresponding to a significantly different value of “ a ” in the Mark-Houwink equation¹⁴) than with the AN/MA copolymer.

Complex viscosity measurements

Dynamic frequency sweeps and a temperature sweep were used to determine the effect of copolymerization of the ABP termonomer on the levels of η^* . The same temperature ranges were used as for the AN/MA copolymer for direct comparison of the dependence of η^* on angular frequency and temperature. Levels of η^* for the AN/MA/ABP terpolymers and the AN/MA copolymer are shown in Figures 6 and 7 at 200 and 220°C, respectively. As expected, levels of η^* increase with (increasing) molecular weight over the range of frequencies used at both temperatures, with the highest levels obtained for the AN/MA copolymer and the lowest levels for the batch 1 terpolymer. However, the shape of the curves is slightly different upon copolymerization with ABP. The data at 200°C suggest that, above $\omega = 10$ rad/s, levels of η^* for the AN/MA copolymer decrease with increasing ω at a higher rate than both of the terpolymers. At 220°C, it appears that a plateau in η^* at the low frequency range ($\omega < 0.3$ rad/s) is observed for both of the ABP terpolymers, which is not observed at either temperature for the AN/MA copolymer.

A temperature sweep was used over the temperature range 180–280°C to determine the effect of ABP on the temperature dependence of the levels of η^* . As seen from the data in Figure 8, a minimum in η^* for the lower molecular weight (batch 1) AN/MA/ABP terpolymer is observed at approximately 260°C, which

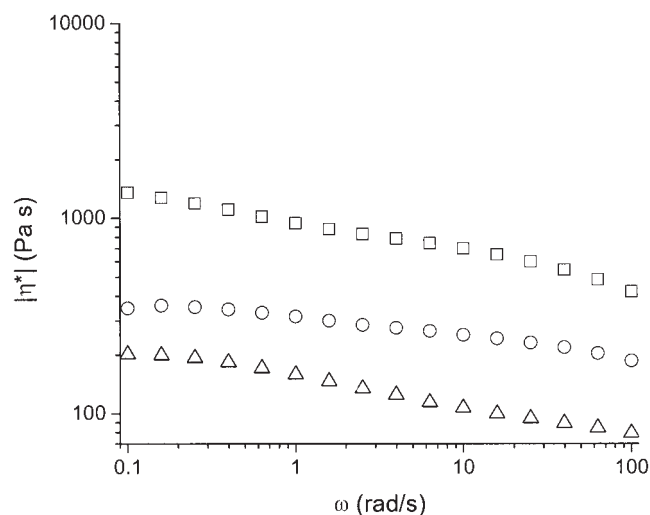


Figure 7 Frequency dependence of complex viscosity (magnitude) at 220°C for the (□) AN/MA copolymer; (○) batch 2 terpolymer; (△) batch 1 terpolymer.

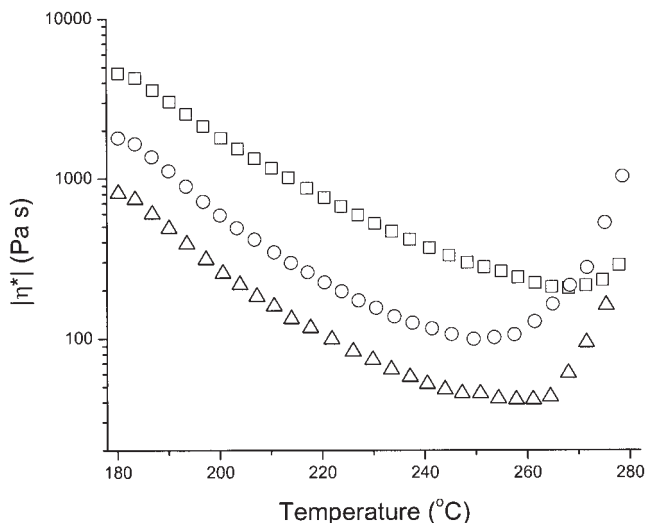


Figure 8 Temperature dependence of the complex viscosity (magnitude) of the (□) AN/MA copolymer; (○) batch 2 terpolymer; (△) batch 1 terpolymer. Heating rate 0.033°C/s, $\omega = 10$ rad/s, strain = 2%.

is slightly lower than that obtained for the AN/MA copolymer. However, η^* is a minimum for the higher MW ABP terpolymer (batch 2) at approximately 252°C. These results suggest that the addition of ABP may increase the thermally induced kinetics of the crosslinking reaction for a given molar composition and molecular weight, indicated by the upturn in η^* for both terpolymers at lower temperatures than that observed for the AN/MA copolymer (268°C). Between the two terpolymers, the data also suggest that an increase in MW increases the kinetics of crosslinking. The following discussion rationalizes this observation. A polymer with a specific MW will increase its size when it first branches, and will continue to increase MW as more branches are formed between the growing polymer chains and one approaches network formation. If the starting MW is increased, then the initially larger polymer chains require less chemistry to obtain enhanced viscosity. As a result, viscosity growth will be faster if the starting MW of a crosslinking polymer is increased. Because zero shear melt viscosity is generally proportional to the 3.4 power of the weight average molecular weight (M_w), it is also expected to build at a significantly faster rate as the initial MW is increased.

Steady shear viscosity

The effect of the ABP termonomer on the melt stability was quantified by tracking η as a function of time over the temperature range of 200–240°C. The data in Figures 9, 10, and 11 illustrate the levels of η as a function of time at $\dot{\gamma} = 0.1$ s⁻¹ and 200, 220, and 240°C, respectively. Values of η at 200°C indicate almost identical

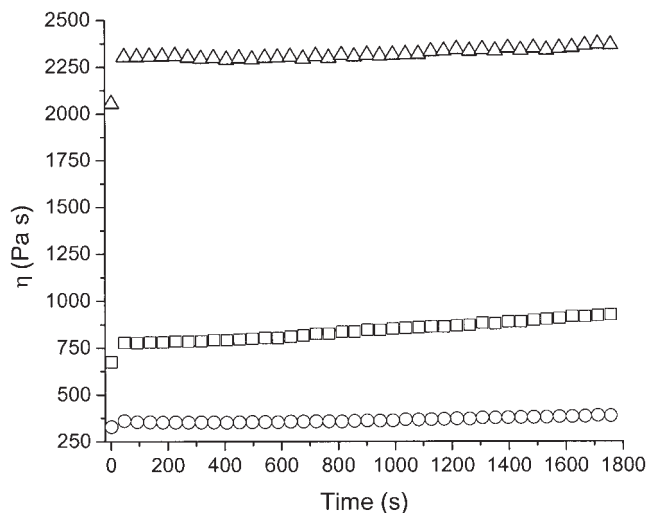


Figure 9 Time dependence of the steady shear viscosity at 200°C, $\dot{\gamma} = 0.1$ s⁻¹ for (△) AN/MA copolymer; (□) batch 2 terpolymer; (○) batch 1 terpolymer.

melt stability (η) trends for the three materials, suggesting that the kinetics of crosslinking was occurring at similar (slow) rates for each polymer. Levels of η only increased by 3 and 8% for the AN/MA copolymer and batch 1 terpolymer, respectively, and by 21% for the batch 2 terpolymer. Levels of η versus time at 220°C indicate a 45% increase for the batch 2 terpolymer, followed by 21 and 11% for the AN/MA copolymer and batch 1 terpolymer, respectively. It is apparent from the data in Figure 11 that the kinetics of crosslinking becomes much more significant for all three polymers at 240°C, indicated by the 16-, 7-, and 6-fold increase in the levels of η for the batch 2, AN/MA, and batch 1 polymers, respectively. As expected,

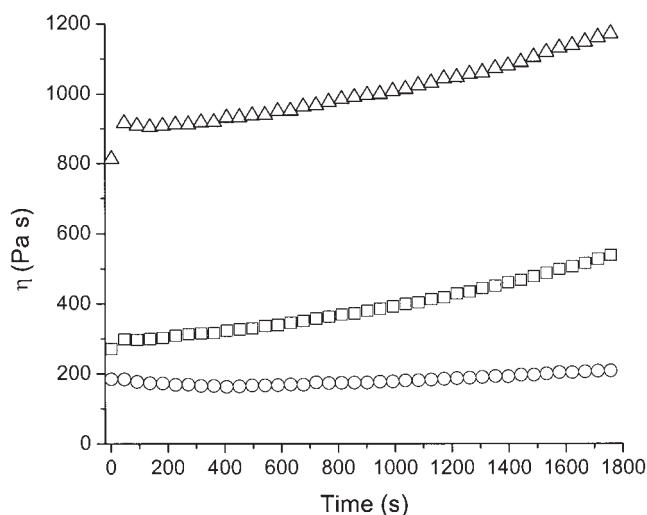


Figure 10 Time dependence of the steady shear viscosity at 220°C, $\dot{\gamma} = 0.1$ s⁻¹ for (△) AN/MA copolymer; (□) batch 2 terpolymer; (○) batch 1 terpolymer.

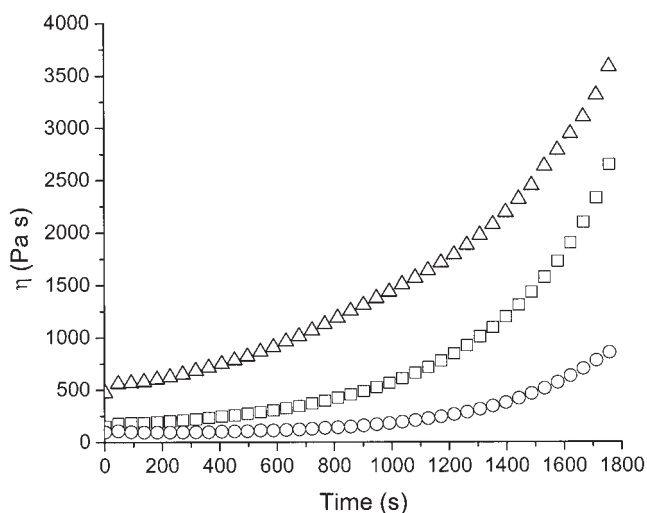


Figure 11 Time dependence of the steady shear viscosity at 240°C, $\dot{\gamma} = 0.1 \text{ s}^{-1}$ for (Δ) AN/MA copolymer; (\square) batch 2 terpolymer; (\circ) batch 1 terpolymer.

the levels (number values) of η in Figures 9–11 correlate directly with molecular weight, with the highest molecular weight (85/15 AN/MA) copolymer having the highest levels of η over the measurement time, followed by the batch 2 and batch 1 terpolymers, respectively. Also, the data suggest that the rate of increase of η as a function of time, which directly correlates to an increase in the kinetics of degradation, becomes higher with increasing temperature for all three polymers. However, the data in Figures 9–11 indicate that the highest IV copolymer (batch 2 terpolymer) was observed to have the highest magnitude of increase in (levels of) η , followed by the AN/MA copolymer and batch 1 terpolymer. Hence, the data suggest that the magnitude of increase of η as a function of time correlates better to IV than MW, especially when comparing polymers of the same AN content (in this case, 85 mol %) but different comonomer (and/or termonomer) contents.

Chemorheology of AN/MA and AN/MA/ABP polymers

During melt extrusion of co- and terpolymers of AN, MA, and ABP, the viscosity will increase as a result of crosslinking and cyclization, which will be dependent on both processing temperature and residence time in the extruder. The ability to quantitatively describe the changes in viscosity as a function of temperature and time, as well as to identify the effects of molecular weight and ABP, was next evaluated by the use of a chemorheological model. The model, which is similar to that used to describe curing in epoxy resins,¹⁵ is represented by the functions in eqs. (1)–(3), which were applied to the steady shear (time dependent)

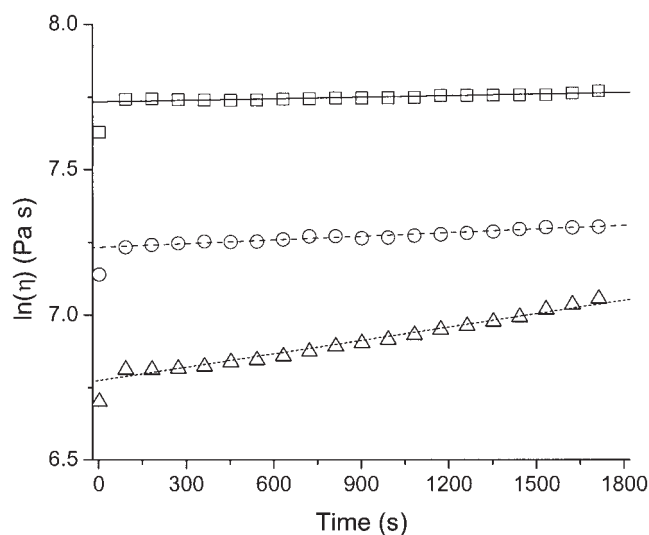


Figure 12 Plots used to obtain k and η_r parameters in eq. (1) for the AN/MA copolymer. Open symbols are steady shear viscosity data at $\dot{\gamma} = 0.1 \text{ s}^{-1}$ and (\square) 200°C; (\circ) 210°C; (Δ) 220°C. Lines are linear fits of the data at (—) 200°C; (---) 210°C; (- - -) 220°C.

viscosity data to describe the crosslinking kinetics of the AN/MA and AN/MA/ABP polymers:

$$\ln \eta(t) = \ln \eta_r + kt \quad (1)$$

where

$$\eta_r = \eta_\infty \exp\left(\frac{\Delta E_\eta}{RT}\right) \quad (2)$$

and

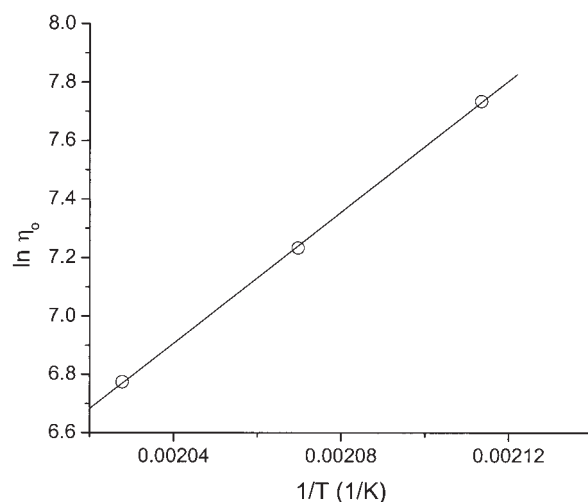


Figure 13 Plot to determine constants in eq. (2) for the AN/MA copolymer. Open symbols are experimental data obtained from the intercepts of the plots in Figure 12. Solid line is a linear fit of the data.

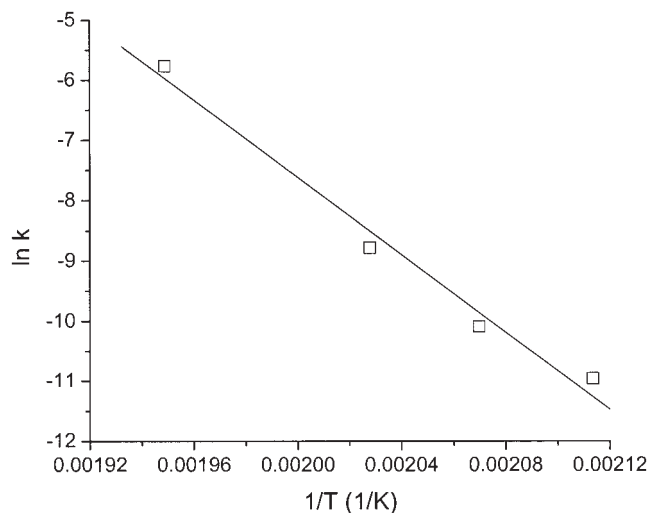


Figure 14 Plot to determine constants in eq. (3) for the AN/MA copolymer. Open symbols are experimental data obtained from the slopes of the plots in Figure 12. Solid line is a linear fit of the data.

$$k = k_{\infty} \exp\left(\frac{\Delta E_k}{RT}\right) \quad (3)$$

In eq. (1), k and η_r are temperature dependent rate and viscosity constants, respectively, and t is time. For eqs. (2) and (3), ΔE_{η} and ΔE_k are the activation energies associated with the temperature dependence of k and η_r , respectively, and T is temperature. Steady shear viscosity versus time data, obtained at 200, 210, 220, and 240°C for each polymer (at $\dot{\gamma} = 0.1 \text{ s}^{-1}$), were used to plot $\ln \eta$ versus time at each temperature. The slopes and intercepts of these plots were used to obtain k and η_r , respectively, at each temperature and composition. The data at 240°C was only used to obtain a slope for the value of k , because (as previously discussed) significant degradation had occurred by time $t = 0$ at 240°C, which would provide a value for the intercept (and subsequently η_r) of a system that had crosslinked to a significant extent. The natural logarithm of both k and η_r were then plotted as a function of $1/T$, from which the slope and intercept of a linear fit of the data for each polymer provided the required constants in eqs. (2) and (3). Linear fits of the natural logarithm of η versus time are shown in Figure 12, which were used to obtain k and η_r for the AN/MA copolymer.

Although not shown here, similar plots were used to obtain k and η_r for the AN/MA/ABP terpolymers. Linear fits of the plots of the natural logarithms of η_r and k versus $1/T$ (obtained from the data shown in Fig. 12) were used to obtain values for η_{∞} and k_{∞} from the intercepts and $\Delta E_{\eta}/R$ and $\Delta E_k/R$ from the slopes, respectively, and are shown in Figures 13 and 14 for the 85/15 copolymer. Although not shown here, similar plots to those in Figures 13 and 14 were used for both terpolymers. Correlation coefficients greater than 0.98 were obtained for all linear fits of the data. The data in Table II illustrate the values of the constants in eqs. (1)–(3) obtained for the three AN copolymers.

For comparison to the η^* data in Figure 8, eq. (1) was differentiated with respect to temperature ($d\eta/dT$) to obtain an estimate of the temperature at which viscosity (of the model) is a minimum. As the temperature increases, the viscosity drops because of the activation energy of flow, but increases as the kinetics of the cyclization and crosslinking reaction increases. The temperature at which $d\eta/dT = 0$ represents a balance between the activation energy of flow and the kinetics of crosslinking and indicates the maximum value at which processing of the AN copolymers should be performed. The temperature, T , listed in Table II is the value at which the minimum in viscosity was calculated for each polymer. A temperature of approximately 258°C was calculated for the minimum viscosity of the 85/15 copolymer, which is significantly lower than that of 268°C observed in the data in Figure 8. For the batch 1 terpolymer, a temperature of approximately 262°C was calculated, which is only 2°C different from the measured value. The calculated value for the batch 2 terpolymer was approximately 268°C, which is significantly higher than the measured value of 252°C. The calculated temperatures in Table II suggest that copolymerization of ABP increases the temperature at which the viscosity (of the model) is a minimum. These results suggest increased melt stability, implying a reduction in the thermally induced kinetics of crosslinking. However, it is interesting that, between the two terpolymers, the kinetic model predicts a higher temperature for the higher MW (batch 2) terpolymer. Based on the time-dependent viscosity data in Figures 9–11, we expected that the model would predict a lower temperature for the batch 2 terpolymer because η for the batch 1 terpolymer is

TABLE II
Parameters Obtained from Chemorheological Analysis in eqs. (1)–(3)

Molar composition (mol %)	k_{∞} (s^{-1})	$\Delta E_{\eta}/R$ (K)	$\Delta E_k/R$ (K)	η_{∞} (Pa s)	T (°C)
85/15	3.97E + 24	11,202	−32,125	1.19E-07	258.4
85/14/1 batch 1	3.69E + 13	9,404	−19,489	7.75E-07	261.7
85/14/1 batch 2	1.68E + 11	11,641	−16,622	1.59E-08	267.9

observed to increase at a slower rate as temperature is increased. It is possible that premature crosslinking (prior to $t = 0$) introduced error in the values of η_r , which would have propagated in the determination of the constants in eq. (2). The error also would have been magnified from use of logarithmic plots of the data to determine these constants and may be the source for the discrepancy between the measured (from Fig. 8) and calculated temperatures (Table II) at which viscosity is a minimum.

CONCLUSION

This study has identified the temperature and time dependence of η , as well as the temperature and angular frequency dependence of η^* , of a melt processable 85/15 mol % AN/MA copolymer and two 85/14/1 mol % AN/MA/ABP terpolymers. Based on previous studies, the melt stability and the levels of η and η^* of both terpolymers appear to be suitable for melt processing at temperatures between 200 and 220°C. Changes in η versus time and in η^* versus temperature suggest that copolymerization of ABP increases the kinetics of thermal degradation, resulting in decreased melt stability. Comparison of the η and η^* data for the two terpolymers suggests that the kinetics of crosslinking also has a significant dependence on molecular weight. For a specific molar composition (in this case, 85 mol %), changes in η versus time suggest that levels of η correlate well to molecular weight, but that the magnitude of the increase in η as a function of time correlates better to intrinsic viscosity. A chemorheological model suggests that copolymerization with ABP slows the kinetics of the crosslinking reaction. However, the model may be somewhat in error

due to the difficulty in isolating and measuring the activation energy of flow without the additional effects of crosslinking (thermal degradation).

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