Viscoelastic Properties and Structure of Poly(acrylonitrile-*co*-methacrylic acid) Polymer Solutions for Gel Spinning at Long Aging Times

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ABSTRACT: The objective of the research is to obtain a more complete understanding of how aging affects the viscoelastic properties of polymer solutions to be used as starting materials for gel spinning of polymer fibers. Specifically, poly(acrylonitrile-*co*-methacrylic acid) solutions were prepared and characterized using rheological measurements and nuclear magnetic resonance spectroscopy. The results indicate that elastic character increased with increasing polymer concentration and that gelation of these solutions continued up to aging times of several weeks. Additionally, comparing the results from the two characterization methods show that while gelation continues to occur, the viscoelastic properties decrease after a critical time point suggesting that a chemical change occurs in the solutions at long times. However, these changes impact the solution dynamics minimally as the effective network properties were similar at the aging times studied here, but considerations for long-term storage of polymer solutions for gel spinning are warranted.
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INTRODUCTION

The use of carbon fibers as a reinforcement in composite materials has enabled the production of structures composed of polymer composite materials for use in transportation applications (land, sea, and air) as well luxury consumer goods such as sports equipment. More recent applications in the area of energy have included structures for harnessing wind energy as well as oil and gas exploration and completion equipment.[1] Combining high strength or high modulus with relatively low density, carbon fibers are an attractive alternative to inorganic fibers for such applications. Accordingly, decreasing the cost and/or improving the mechanical properties of continuous carbon fiber are active research areas for academia, industry, and government agencies. One way to potentially address both research areas is through exploration and subsequent optimization of the production steps.

The majority of commercially available carbon fibers are produced using polyacrylonitrile (PAN)-based polymers as the precursor material. The typical production steps needed to obtain carbon fiber from PAN-based polymers are: synthesis of PAN-based polymers, spinning of the precursor fiber, thermal stabilization in air, carbonization in an inert environment, and graphitization in an inert environment.[2] The PAN polymers used are often copolymers with acrylic acid (AA), methacrylic acid (MAA), or itaconic acid as the addition of comonomers such as these facilitate polymer chain alignment during spinning, ultimately leading to higher carbon yields. Precursor fibers may be produced by a variety of fiber spinning methods including gel,[3] melt,[4,5] wet,[6–8] and dry-jet wet spinning[9,10] as well as electrospinning.[11–13] The resulting fibers generally have diameters in the range of 10–15 μm, except those produced by electrospinning that can be orders of magnitude smaller. The thermal treatment steps of stabilization, carbonization, and graphitization following precursor fiber production convert the PAN-based polymer into a graphitic carbon structure in a stepwise fashion. The resulting fibers generally have diameters in the range of 5–7 μm.[2]

As many of the methods used to produce precursor fibers are solution-based, rheological studies are used to more fully understand the link between polymer solution attributes such as solvent, polymer concentration, polymer molecular weight, homogeneity, and the precursor fiber structure. In particular, rheological characterization has been used to characterize gelation and gel structure in precursor materials for gel spinning.[14–17]

Gelation of PAN-based polymers occurs via thermoreversible and irreversible pathways depending on the system temperature with irreversible gelation occurring at temperatures high enough to liberate HCN from the polymer and induce chemical crosslinking between polymer chains.[18] Thermoreversible gelation is studied more frequently as it is more relevant to the production of precursor carbon fiber. Both crystallite formation and dipole–dipole interactions have been invoked as explanations for the thermoreversible gelation of PAN.[19] Based on the diversity of results and systems reported in the literature, the exact gelation mechanism is likely system-specific where the solution components play an important role in determining the gelation mechanism.[19] This article presents experimental results aimed at obtaining an increased understanding of the rheological and aging behaviors of concentrated PAN copolymer solutions for gel spinning where gelation occurs through a thermoreversible mechanism. Characterization by rheological experiments and nuclear magnetic resonance (NMR) spectroscopy was used to obtain this understanding. While the gelation mechanism is not treated explicitly in these studies, the experiments specifically address the effects of polymer concentration and aging time on the viscoelastic properties of PAN copolymer solutions and how these behaviors may impact the production of carbon fiber through solution stability.

EXPERIMENTAL

Materials

Two PAN-co-MAA copolymers were used in this work with different molecular weights. The first polymer had a viscosity average molecular weight (M_v) of 450,000 g/mol and a MAA comonomer content of 4 wt %. Solutions of this copolymer were prepared using distilled dimethylacetamide (DMAc) as the solvent. The second polymer had a M_v of 750,000 g/mol and a MAA comonomer content of 4 wt %. Solutions of this copolymer were prepared using distilled dimethylformamide (DMF) as the solvent. The copolymers were purchased from Japan Exlan, and the molecular weight values were provided by the manufacturer. The solvents were purchased from Sigma-Aldrich and, as indicated above, were distilled before use.

Preparation of PAN-co-MAA Solutions

Prior to solution preparation, the copolymers were dried in a vacuum oven at 40°C for 24 h and then for an additional 24 h at 100°C. The copolymer solutions were prepared by dissolving the desired amount of copolymer in 50 mL of distilled solvent using an overhead stirrer. The mouth of the beaker was covered to minimize solvent loss, and the components were stirred at 100 rpm at 90°C for 60 to 90 min until the solution appeared homogeneous on visual examination. After stirring was completed, the solutions were removed from the heat source and allowed to equilibrate to laboratory conditions.

The concentrations of the solutions were determined using a TA Instruments TGA Q5000 under flowing nitrogen using a flow rate 10 mL/min. To prevent premature solvent loss and improve signal quality, approximately 15–20 mg of the solution was placed in a sealed aluminum pan such as those used for differential scanning calorimetry experiments. At the beginning of the TGA experiment, the lid was punctured, and the pan was placed in a platinum TGA sample holder. The sample was then heated from room temperature to 175°C at a rate of 10°C/min and held isothermally at 175°C for 1 h. The mass of PAN copolymer was taken at the point where the mass signal remained constant, indicating that all of the solvent had evaporated. These tests indicated that the concentrations of the prepared solutions were 7.0, 8.4, 9.3, and 11.6 g/100 mL for the 450,000 g/mol PAN-co-MAA and 5.5 g/100 mL for the 750,000 g/mol PAN-co-MAA.

Rheological Testing

Dynamic frequency sweeps were conducted at room temperature with a Rheometric Scientific ARES rheometer, using a 25-mm diameter parallel plate fixture, a gap setting of 1 mm, and a strain amplitude of 5%. The strain amplitude selected for testing was in the linear viscoelastic range of the samples based on strain sweep data collected at a testing frequency of 100 rad/s. Nominally, data collected at frequencies between 0.1 and 100 rad/s were used for analysis, though data were excluded at the limits of this frequency range on a sample-by-sample basis using torque transducer data. After loading the solution, a thin layer of low-viscosity silicone oil was applied to cover the exposed edge of the sample. The oil was applied to slow solvent evaporation at the exposed edge. Experiments were conducted on all solutions on the day of preparation or after an aging time of 1 day. Tests were performed on selected solutions at different time points after aging at room temperature. The 8.4 g/100 mL solution of the 450,000 g/mol copolymer and the 5.5 g/100 mL solution of the 750,000 g/mol copolymer were tested at time points up to 50 days after solution preparation. For all samples, storage modulus (G') and loss modulus (G'') were calculated by the rheometer software.

NMR Spectroscopy

For the NMR study, a solution containing 750,000 g/mol copolymer was prepared in deuterated DMF at a concentration of 5.3 g/100 mL. The deuterated DMF was obtained from Sigma-Aldrich and used as received. ^{1}H NMR spectra were collected using a Bruker AMX400 spectrometer operating at 400.13 MHz. Tetramethyl-silane was used as an internal standard for the chemical shift reference. A total of 16 scans were accumulated with a relaxation delay of 5 s. A spectrum was also measured with a relaxation delay of 10 s and no changes in relative peak intensities were observed, thus confirming that 5 s was sufficiently long for quantitative work. Spectra were collected on two separate samples obtained from the same solution. One sample was measured at ambient conditions and time points up to eight weeks, and the second sample was measured at a single time point at temperatures between 25°C and 45°C with the accuracy of ± 0.5°C.

RESULTS

Viscoelastic Properties of the PAN-co-MAA 450,000 g/mol Solutions After One Day

Figure 1 shows the trends in G' and G'' as a function of frequency and solution concentration for the solutions containing the 450,000 g/mol copolymer. All data were collected one day after solution preparation. As expected, all of the values increased as
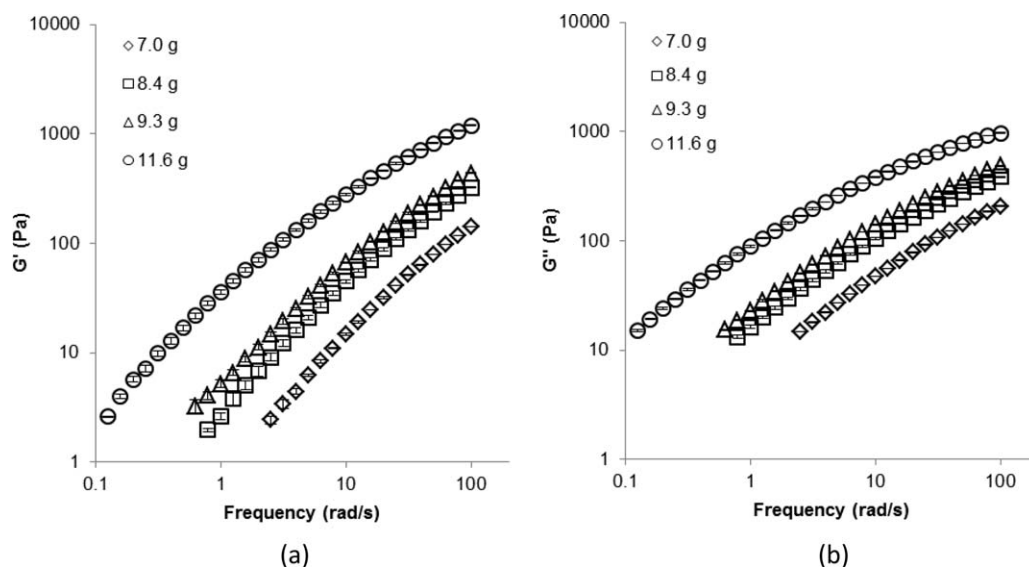
Figure 1. (a) G' and (b) G'' data as a function of oscillation frequency for different polymer concentrations (g/100 mL solvent) for the 450,000 g/mol copolymer solutions. All data were obtained one day after solution preparation. Error bars represent the spread in the experimental data.

the solution concentration increased. The solutions with copolymer concentrations of 7.0, 8.4, and 9.3 g/100 mL DMAc behaved as viscous liquids in the frequency range tested as G'' was greater than G'. However, the solution with a copolymer concentration of 11.6 g/100 mL DMAc showed both elastic and viscous behavior as at a frequency of approximately 40 rad/s, the value of G' was greater than G''. Additionally, the frequency dependence of G' decreased as the copolymer concentration increased, suggesting enhanced elastic character of the solutions at higher copolymer concentrations. The frequency dependence of G'' also decreased as copolymer concentration increased but to a lesser extent. The frequency dependence of G' and G'' were quantified as n' and n'', respectively, using the following equations:

$$G' \sim \omega^{n'} \tag{1}$$

$$G'' \sim \omega^{n''} \tag{2}$$

where n' and n'' are obtained from power law fits of the experimental data at frequencies less than or equal to 10 rad/s. These values are given in Table I. In all cases, the R^2 values associated with these fits were greater than 0.990.

Table I. Power Law Exponents for 450,000 g/mol PAN-*co*-MAA Solutions at an Aging Time of One Day

PAN-*co*-MAA content (g/100 mL solvent)	Power law exponents	
	n'	n''
7.0	1.31	0.84
8.4	1.24	0.82
9.3	1.12	0.81
11.6	1.02	0.73

Long-Term Time-Dependent Studies of PAN-*co*-MAA 450 and 750 K solutions

To understand how the viscoelastic properties change as a function of time, long-term aging studies were undertaken with solutions of both molecular weight copolymers. The concentrations chosen for the study were 8.4 g/100 mL DMAc for the 450,000 g/mol copolymer and 5.5 g/100 mL DMF for the 750,000 g/mol copolymer. Figure 2 shows the G' and G'' data for aging time points of 1, 7, 14, 22, and 50 days for the 450,000 g/mol solution. For this solution, G' increased with time up to aging time of 7 days, and low-frequency responses were impacted more than high-frequency responses. However, measurements at time points of 22 and 50 days showed a decrease in G' at low frequencies. Measurements of G' at 14 days were the same as those taken at 7 days when considering the experimental error. G'' showed similar trends with aging time though an appreciable decrease was not seen until an aging time of 50 days as opposed to 22 days. Similarly, the values of the n' and n'' initially decreased with aging time, remained approximately constant, and then showed a measureable increase at an aging time of 50 days. These data are given in Table II. Visual inspection of the solutions also indicated that a chemical change was occurring in the solution at these extended times because the color of the solutions became dark yellow.

Figure 3 shows the trends in G' and G'' at different aging times for the 750,000 g/mol copolymer. For this copolymer, the values of G' were higher than those for the 450,000 g/mol copolymer at frequencies less than approximately 10 rad/s and lower at higher frequencies. The values of G'' were lower across most of the measured frequency range. The magnitude differences at high frequencies could be because of differences in polymer–solvent interactions between the two solutions as different solvents were used. Also, increased solution heterogeneity in the higher molecular weight solution could have contributed to the lower
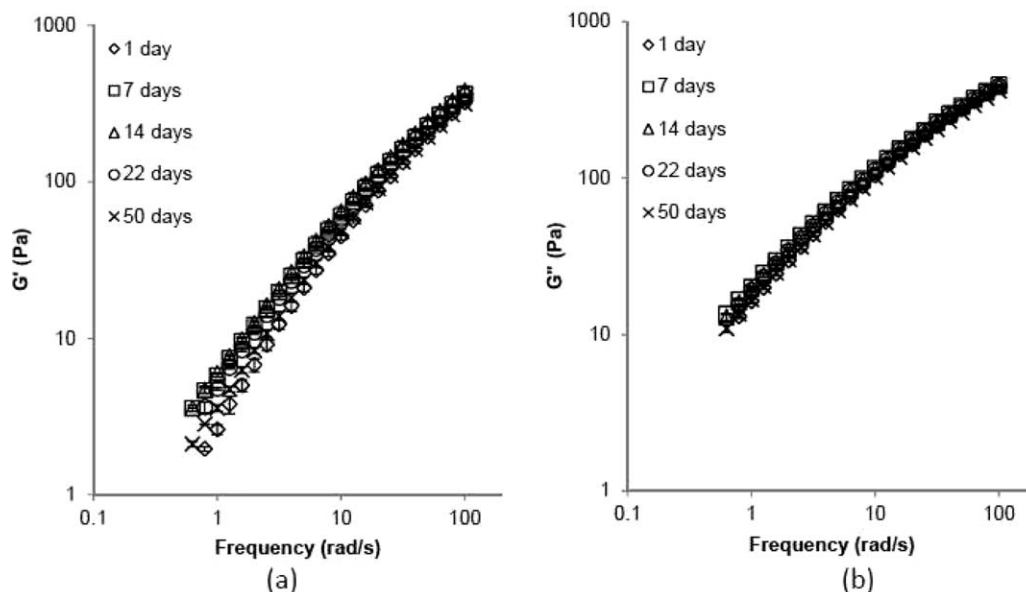
Figure 2. (a) G' and (b) G'' data as a function of oscillation frequency for different aging times at ambient conditions for the 450,000 g/mol copolymer solution with a copolymer loading of 8.4 g/100 mL DMAc. Error bars represent the spread in the experimental data.

value of G' at higher frequencies. Independent of the differences, the higher molecular weight solution showed an enhanced elastic character. The 750,000 g/mol solution showed viscous and elastic behavior in the measured frequency range as the values of G'' were greater than G' at low frequencies, and the opposite situation was observed at higher frequencies. The frequency where G' and G'' were equal served as the boundary between these behaviors and was designated as the crossover frequency. The crossover frequencies are given in Table III. Crossover behavior in the measured frequency range was not seen in the 450,000 g/mol solution at a concentration of 8.4 g/100 mL DMAc.

However, similar trends with aging time were seen for the 750,000 g/mol solution, indicating that this was a general behavior for these copolymers in DMAc and DMF. The maximum increases in G' and G'' were observed at an aging time of 7 days, and decreases in the values of these properties were seen at an aging time of 50 days. The changes in G' and G'' as a function of time were smaller with respect to those observed for the 450,000 g/mol copolymer solution, leading to differences in the trends seen in the values of n' and n'' for the 750,000 g/mol

Table II. Power Law Exponents for the 450,000 g/mol PAN-*co*-MAA Solution at Different Aging Times

Aging time after solution preparation (days)	Power law exponents	
	n'	n''
1	1.24	0.82
7	1.03	0.78
14	1.05	0.78
22	1.06	0.78
50	1.14	0.80

copolymer solution. Instead of following the trends in crossover frequency, the value of n' continued to decrease as aging time decreased. The value of n'' decreased at an aging time of 7 days and then remained at this value for the duration of the aging study.

Cole–Cole Plots for the Copolymer Solutions

The data obtained from all of the tests were plotted in Cole–Cole plots to understand their relative dynamics as a function of concentration and aging time. These plots are shown in Figure 4. The plot for the 450,000 g/mol copolymer solutions at different copolymer concentrations indicated that the dynamics of these systems were the same because the data from all of the samples fell on the same curve. However, the dynamics of the 450,000 g/mol copolymer solution containing 8.4 g/100 mL DMAc were impacted as a function of aging time. Particularly at larger values of G' and G'' (higher testing frequencies), the data obtained at different aging times are spread apart, supporting the trends seen in separate plots of G' and G''. Conversely, the 750,000 g/mol solution did not show an appreciable change in the system dynamics as a function of aging time as the data fell on a continuous curve. This behavior was not necessarily expected as the values of G' and G'' did decrease with increasing aging time.

NMR Characterization

NMR studies were used to further characterize the structural changes occurring in the solutions with time. A solution containing the 750,000 g/mol copolymer was prepared using deuterated DMF as the solvent. The solvent concentration was 5.4 g copolymer in 100 mL solvent, similar to the concentration used in the rheological experiments on this copolymer. Figure 5 shows the NMR spectra for the solution as a function of aging time up to eight weeks. These spectra show three resonances for the PAN copolymer. Two of the resonances were found at the
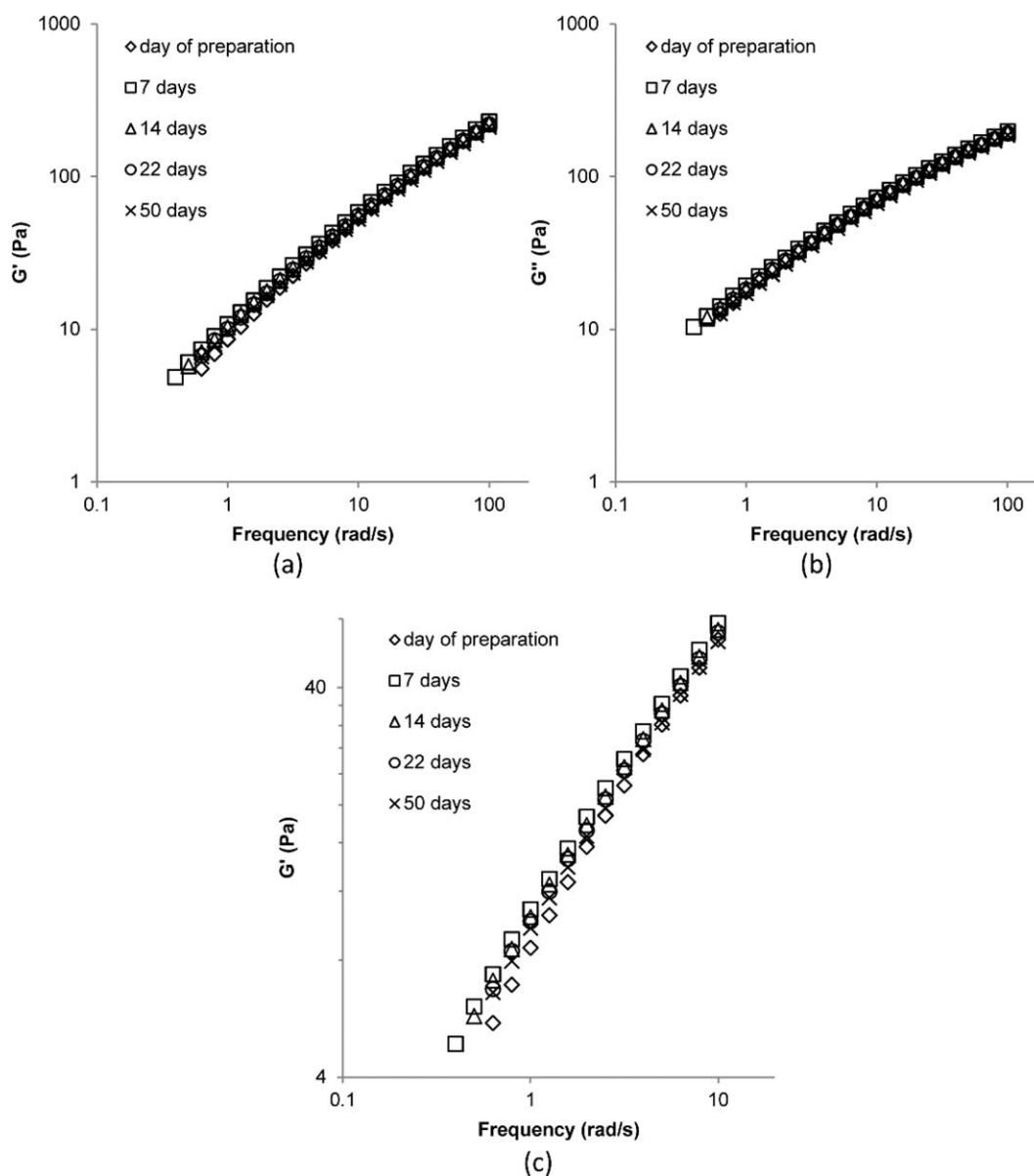
Figure 3. G' (a) and G'' (b) data as a function of oscillation frequency for different aging times at ambient conditions for the 750,000 g/mol copolymer solution with a copolymer loading of 5.5 g/100 mL DMAc. G' data obtained at frequencies of 10 rad/s and lower are shown separately in (c). Error bars were removed for clarity. Spread in the experimental data is approximately equal to the size of the symbols.

Table III. Crossover Frequency Values and Power Law Exponents for the 750,000 g/mol PAN-*co*-MAA Solution at Different Aging Times

Aging time after solution preparation (days)	Crossover frequency (rad/s)	Power law exponents	
		n'	n''
0	48.2 ± 0.5	0.82	0.62
7	40.8 ± 2.0	0.77	0.60
14	43.7 ± 2.9	0.76	0.60
22	44.1 ± 2.2	0.76	0.60
50	47.3 ± 0.1	0.75	0.60

expected chemical shifts: a multiplet for the methyl group of the MAA between 1.3 and 1.5 ppm and a singlet for the methylene group of acrylonitrile and MAA at 2.1 ppm. The third resonance, associated with the methine group, appeared as a doublet. The resonance peak located at approximately 3.6 ppm was investigated as a possible signature of gelation. The intensity of this peak systematically increased as aging time increased while the other peaks remained at nearly constant intensity over the aging period.

Further evidence to support the association of the resonance peak at approximately 3.6 ppm with physical gelation of the copolymer solutions was its response to increased temperature. As shown in Figure 6, NMR spectra were collected at six
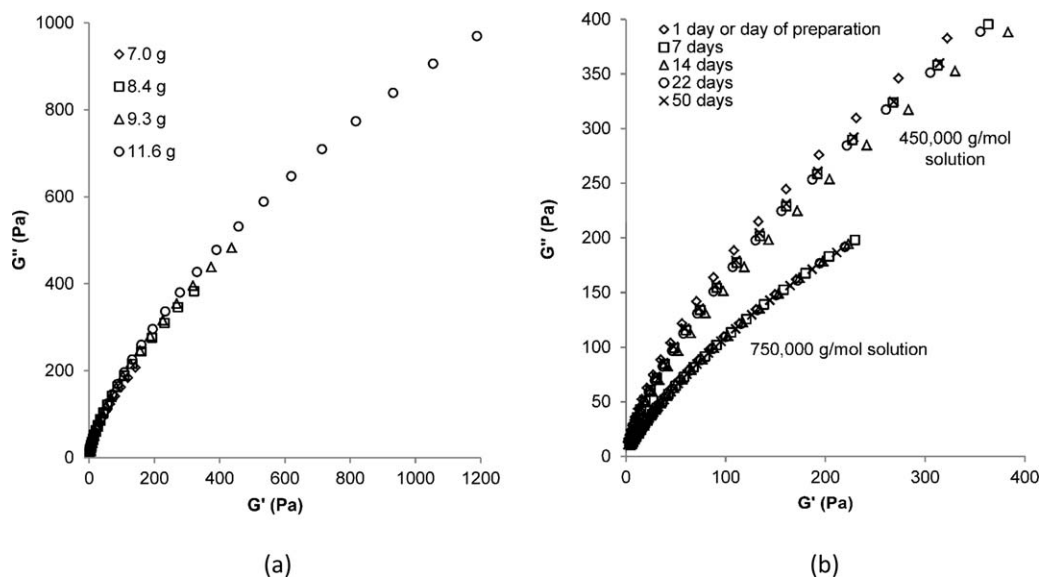
Figure 4. Cole–Cole plots for (a)the 450,000 g/mol solutions at 1 day after preparation and (b) for the solutions subjected to aging studies.

temperatures between 25°C and 46°C. As the temperature was increased the intensity of the peak decreased. Additionally, the main methine resonance at 3.4 ppm increased in intensity as the temperature increased. At the highest temperature investigated in this experiment, the peak at approximately 3.6 ppm disappeared suggesting that the physical bonding of the gel was disrupted.

The NMR results were consistent with the rheology up to aging times of approximately two weeks. The results from both experiments, rheology and NMR spectroscopy, showed structural changes in the solutions consistent with increased gel formation: increasing elastic character of the solutions through increases in G' and G'' at low frequencies and increasing intensity in the resonance at approximately 3.6 ppm, respectively. However, at aging times greater than two weeks, the results from the experiments differed. The dynamic moduli calculated from rheological measurements began to decrease with respect to those calculated at earlier time points, but the intensity of the resonance peak continued to increase. Based on the color change observed in the solutions used for rheological experiments, some form of chemical degradation likely occurred that could have resulted in chain scission of the copolymer. However, the same level of color change was not observed in the solutions contained in capillary tubes for NMR experiments, and the NMR data do not indicate a change in the chemical
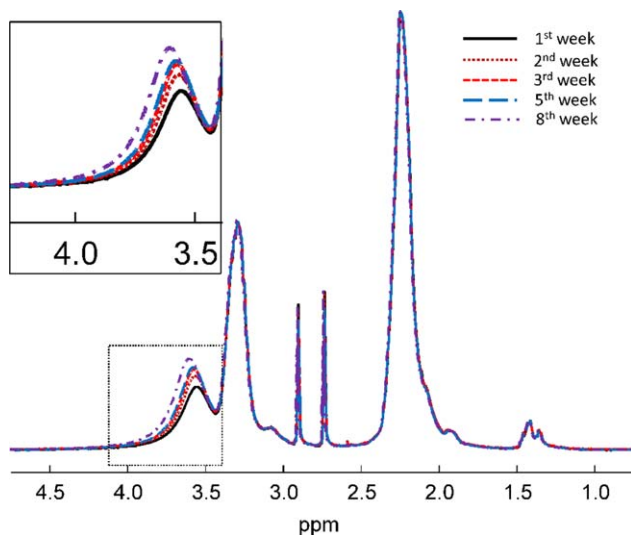

Figure 5. ¹H spectra of the PAN-*co*-MAA solution at various aging times at ambient temperature. The inset shows the peak at ∼ 3.6 ppm, which was observed to increase in intensity as aging time increased. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
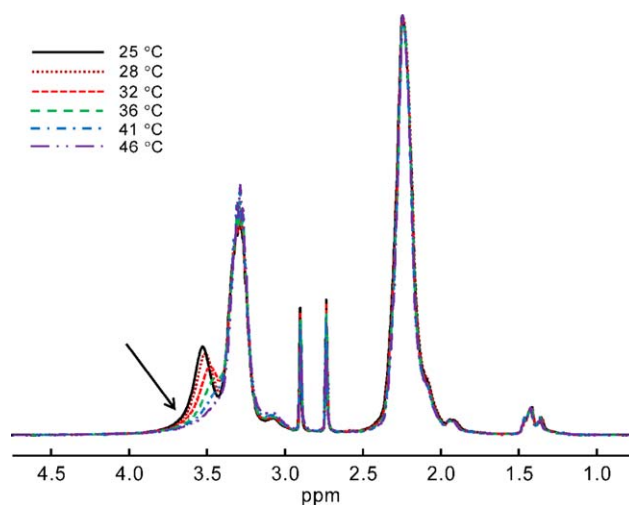

Figure 6. ¹H spectra of the PAN solution as a function of temperature. The peak at ∼3.6 ppm is observed to decrease in intensity and eventually disappear as the solution temperature is increased. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure of the solution with time. Possible explanations for the discrepancy in long-time behavior are related to differences in the solvents used for the two experiments and different levels of exposure to air. The solutions used for rheology were prepared using distilled DMF, whereas the solutions used for NMR spectroscopy were prepared with deuterated DMF. Also, the solutions used for rheology had a larger head space in the container and were opened to remove samples for testing. The solutions used for NMR were sealed in a capillary tube and not exposed to air after preparation.

DISCUSSION

The experiments presented in this paper were undertaken to more fully understand the effects of aging at ambient conditions on the gelation behavior and structural stability on polymer solutions used to produce carbon fibers through gel spinning. The particular experimental methods used, rheology and NMR, provide complementary phenomenological and structural data for the solutions, facilitating this increased understanding. Two main materials design variables were investigated: solution concentration and aging time. Two different molecular weights were used; however, unambiguous conclusions cannot be drawn regarding the effect of molecular weight as the different solvents were used with the different molecular weight copolymers and differences in solution homogeneity may have played a role in the results obtained here. Increases in solution concentration and aging time up to a critical point corresponded to decreased values of n' and n'', indicating increased elastic character of the solutions though for different reasons. Increasing solution concentration would increase elastic character through changes in network structure related to polymer chain entanglement and not strictly differences in gelation. Whereas aging time should relate to changes in network structure related to the formation of physical bonds between polymer chains associated with gelation. This distinction is supported by the Cole–Cole plots. With regard to solution concentration, the single curve seen in the Cole–Cole plot indicated that the dynamics of the solutions were similar in the concentration range studied and similar levels of gelation were achieved in these solutions one day after preparation. Longer aging times for the 450,000 g/mol copolymer solution resulted in changes to the solution dynamics, presumably because of gelation up to an aging time of 14 days. The data for longer aging times showed a change in the network structure that was likely because of some chemical degradation pathway.

Conversely, the long-term aging behavior of the 750,000 g/mol copolymer solution showed a different behavior. The values for n' and n'' did not increase after a certain time point, and the Cole–Cole plot indicated that the solution dynamics were not changing as a function of time even though the values of G' and G'' decreased at long aging times and the NMR data obtained from a similar solution with a deuterated solvent suggested that gelation was occurring over the aging time period. Whereas it is not impossible to discount the effect that the deuterated solvent could have on the gelation dynamics, these results taken together suggested that chemical degradation and gelation may be occurring simultaneously at long aging times.

Overall, these changes impacted the solution dynamics minimally, suggesting that the effective network properties were similar at the aging times studied here.

Several rheological studies have been conducted on PAN solutions to understand gelation in this system because of its relevance to carbon fiber manufacture,[15–18,20–26] and the results presented here are largely consistent with those published previously. However, few efforts have included characterization of aging behavior at long times, which was the motivation of this study. Our focus has been on the thermoreversible gelation process relevant to the likely storage conditions of the solutions prior to gel spinning and not on irreversible gelation processes that generally occur at higher temperatures.[18,21,22] Overall, these results suggest that long-term storage (beyond approximately one week) could lead to degradation of the solution. If the degradation is related to a decrease in the polymer molecular weight or a change in polymer structure, then it is anticipated that the properties of the PAN precursor fibers would be impacted by these changes to the solution's structure.

CONCLUSIONS

This study concerned structural characterization of polymer solutions relevant to gel spinning of carbon fiber precursor fibers. The results reported here suggest that different processes, gelation and degradation, are occurring simultaneously in the solutions when aged at ambient conditions for long times. Ultimately, these changes in solution structure would be expected to impact precursor fiber structure and properties, suggesting that solution storage conditions and duration should be taken into consideration during carbon fiber production.

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