Rheological behavior of polyacrylonitrile and polyacrylonitrile/lignin blends

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ABSTRACT

Dynamic shear rheology study is conducted on the polyacrylonitirile (PAN) solution and composite solutions of PAN with up to 37.5 wt% annual plant lignin (APL) to address current barriers of PAN/lignin blend development as carbon fiber precursor. PAN/APL blends exhibit lower yield stresses, lower relaxation times, and lower viscosities than to PAN solution according to the dynamic frequency sweep measurements from $-7\ ^\circ C$ to $56\ ^\circ C$. Yet an increase of solution activation energy of flow is observed with the increasing lignin content in solution. This is attributed to the potential interactions of PAN and lignin. Solution loss tangents obtained from dynamic frequency sweeps between $-7\ ^\circ C$ and $56\ ^\circ C$ at an oscillatory frequency of 100 rad/s is used to envision the effect of lignin on solution structure during fiber processing.

1. Introduction

Throughout the research and development of advanced textiles, high-performance fibers such as Kevlar®, Dyneema®, Spectra®, and carbon fibers have attracted great attention due to their high specific strength, modulus, and versatile applications. While the exceptional mechanical properties of high-performance fibers are attributed to the highly aligned molecular structure, and minimized defects, voids, and polymer chain entanglements in fiber structure, processing optimization plays a decisive role in the resultant fiber properties [1]. Currently, Kevlar®, Dyneema®, Spectra®, and polyacrlonitrile fibers as carbon fiber precursors are all manufactured from solutions that typically comprised of 5–20 wt% polymers dissolved in designated solvents [1,2]. In order to understand the polymer molecular behavior in solution, rheological characterization of the solution is important. In the past decade, investigation of polyacrylonitrile (PAN) rheology, spinnabiliy, gelation behavior, and coagulation conditions have been an unceasing research focus [3–7]. Recently, interest in low-cost

carbon fiber has called for more cost-effective alternatives for carbon fiber precursor materials and conversion processes. Lignin, as an abundant biorefinery byproduct and a melt-spinnable material, has received increasing attention for its utilization in carbon fiber. However, to date, no demonstration of melt-spun lignin based carbon fiber has been reported that meets the performance target of low cost carbon fiber set by the U.S. Department of Energy [8,9]. More recently, lignin has been proposed to be processed in solution with other polymers, and specifically with PAN, to form blend fiber with further conversion into carbon fibers [10–15]. The addition of lignin is shown to reduce polyacrylonitrile solution viscosity and also has detrimental effect on the fiber spinnability [10,16]. Furthermore, lignin/polymer blends have been reported to result in porous structure [12,13], phase separation [17], reduced drawability [11], and hence limited mechanical properties of the resulting carbon fibers. In order to make the best use of PAN/lignin blend for carbon fiber manufacturing, understanding of the interactions between these two componnets in solutions or in melt is imoortant. In this work, a rheological study of PAN, and PAN/annual plant lignin (APL) solutions is conducted, to understand these interactions.

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2. Experimental

2.1. Materials and solution preparation

Polyacrylonitrile-*co*-methacrylic acid (PAN-*co*-MAA; 4 wt% MAA, Mv = 247,000 g/mol) was acquired from Exlan, Co. (Osaka, Japan) and the annual plant lignin (APL) powder Protobind 2400 from the soda pulping process was provided by GreenValue (Media, PA). Organic solvent dimethylformamide (DMF) was obtained from Sigma-Aldrich and distilled before use. For PAN solution, PAN slurry is initially prepared by adding polymer powder into DMF in a glass reactor with a solid concentration of 15 g/dL, followed by 8 h of stirring at 200 rpm at room temperature to prevent polymer agglomeration. After the stirring process, the slurry is slowly heated to 80 °C in silicone oil bath under continuous stirring at 200 rpm. The solution was then maintained under the same conditions for 5 h before collection. Throughout the solution preparation, a nitrogen stream of 10 standard cubic feet per hour (SCFH) was introduced to avoid solution oxidation in glass reactor. Collected PAN solution then undergoes a 20 min degas process under vacuum at 60 °C before further characterization. For PAN/APL composite solutions, APL solid was dissolved in DMF using orbital shaker (MaxQ 4450, Thermo Scientific.) at 180 rpm and maintained at 40 °C for 8 h before the subsequent addition of PAN powder to form PAN/APL slurry in a glass reactor. PAN/APL solutions were then prepared under identical stirring, heating, and degas conditions, as was done for the PAN solution. In this study, 3.5 g and 9 g of lignin solids are dissolved in 1 dL of DMF with control PAN solids (15 g/dL) to form PAN/APL1 and PAN/APL2 solutions with total solid content of 18.5 g/dL (that is 18.9 wt% lignin with respect to the total solids weight of lignin + PAN), and 24 g/dL (that is 37.5 wt% lignin in total solids) concentrations, respectively.

2.2. Solution characterizations

Rheological characterization of all solutions is conducted using Discovery Hybrid Rheometer (TA Instruments) in parallel plate geometry, with a 60-mm plate on top and Peltier plate on the bottom with a 1-mm gap size in between. All solutions are stored in an oven maintained at 55 °C. In one set of experiments, isochronal temperature scans of polymer solutions were performed at 1 rad/ sec. The Peltier plate was maintained at 60 °C before loading the solution. During sample loading between the parallel plates, a thin layer of silicone oil was applied to cover the exposed surface of polymer solution to prevent solvent evaporation and moisture absorption during experiment. Ten minutes after loading the samples while maintaining the temperature at 60 °C, sample cooling was initiated from 60 °C to 0 °C, followed by the heating from 0 °C to 60 °C, at a cooling and heating rates of 2 °C/min, and the rheological data was continuously collected at 1 rad/s. In the second set of experiments, fresh solution samples were used and dynamic frequency sweep measurements from 0.1 to 100 rad/s were performed at temperatures in the range of −7 °C to 56 °C (±0.05 °C), with an increment of 7 °C. A fresh sample from the oven maintained at 55 °C was loaded in the rheometer for each temperature run, and this temperature range is chosen to provide an understanding of the polymer solution during fiber spinning and coagulation [18]. In the gel spinning, fiber spinning is typically done at about 75 °C and the gelation/coagulation temperature as low as −50 °C is used. However, we were not able to conduct the rheological experiments in this full temperature range, as solution samples gelled at about −10 °C during sample loading. Therefore, the lowest temperature of study of −7 °C was selected. In the third set of experiments, steady-state shear rheology was determined under a shear rate from 0.015 s^{-1} to 12.6 s^{-1} at room temperature

(21 °C). This was done to demonstrate the equivalence between the steady and the dynamic shear viscosities.

3. Results and discussions

Rheological plots as a function of temperature at a given frequency for PAN and PAN/APL blend solutions are shown in Fig. 1. In each trial, solution sample undergoes a cooling scan from 60 °C to 0 °C, followed by heating from 0 °C to 60 °C. For PAN solution (Fig. 1a.), storage modulus (G′) increases with a decrease in temperature during cooling scan due to the reduced mobility of polymer chains and vice versa during heating. Throughout the cooling and subsequent heating process between 60 °C and 0 °C, PAN solution exhibits thermo-reversibility with the recovery in both G′ and G". During cooling and heating, G" > G′ in the entire temperature range for PAN solution, indicating the liquid-like behavior. As compared to PAN solution, for PAN/APL1 (18.9 wt% lignin) solution (Fig. 1b.), G″ still exhibits fair thermo-reversibility, while G′ does not. In fact, G′ for PAN/APL1 during heating shows upturn at about 37 °C (indicated by the arrow in Fig. 1b). This G′ upturn implies a possible binodal temperature of the blend during heating [19,20]. For PAN/APL2 (37.5 wt% lignin) (Fig. 1c), as compared to PAN/APL1, G′ curve during heating shows even higher degree of deviation from the cooling G′ curve, and appears to show minimum (as shown by the arrow in Fig. 1c). The higher magnitude of the G′ upturn is attributed to the strong dynamic asymmetry of the constituent components (PAN and lignin in the present case), the minimum around 37 °C in G′ curve suggests a transition from binodal point to spinodal point of the blend solutions, where minority-component rich domain and majority-component rich domain develops to alter solution G′ behavior [19]. Moreover, a crossover point of G′ and G″ is observed around 37 °C (indicated by the arrow in Fig. 1c), suggesting the formation of physical gel network through the thermo-rheological interactions between lignin and PAN [21]. Rheological tan δ plot of all solutions is given in Fig. 1d. During cooling, all three samples exhibited comparable tan δ magnitude and slope, indicating similar behavior for the three samples. During heating, tan δ for PAN/APL2 decreases significantly as compared to PAN/APL1 and PAN. Note that the emergence of G′/ G″ crossover point is not observed in the temperature scan of PAN or PAN/APL1 but only in PAN/APL2 solution, and the altered behavior of G′ and tan δ with the increasing lignin content is only shown during the heating scan but not in the cooling scan. These results suggest that the presence of lignin induces polymer gel-network formation, following cooling and subsequent heating. The physical nature of this network has not been understood at this time and should be further studied.

Rheological plots as a function of frequency at various temperatures for PAN, PAN/APL1, and PAN/APL2 are plotted in Figs. S1, S2, and S3, respectively. All solutions exhibit similar shear thinning behavior at increasing frequency as well as a strong viscosity dependence on temperature. Solid content layout of the solution as well as the zero-shear viscosity and the slopes of G′ versus ω and G″ versus ω log-log plot of the solutions at room temperature (21 °C) when ω → 0 are summarized in Table 1. At 21 °C, PAN exhibits slopes of G′ versus ω (1.654), and G″ versus ω (0.992) log-log plots at the terminal region when ω → 0. In comparison, PAN/APL1 exhibits a lower G′ versus ω slope (1.446) and G″ versus ω slope (0.981) compared to PAN. With an increased lignin content, PAN/ APL2 shows further decreased G′ versus ω slope and G″ versus ω slope of 1.426 and 0.974, respectively. At low frequencies, a scaling relationship of G" (ω) ~ ω^2 and G′ (ω) ~ ω^1 indicates liquid-like behavior [4]. In this study, increasing APL content in PAN solution result in decreased slopes of G′ versus ω and G″ versus ω plots, suggesting that APL molecules in the composite solutions promote