



Rheological Behaviour of Polyacrylonitrile in an Ionic Liquid Solution

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ABSTRACT

The ionic liquid of 1-butyl-3-methyl-imidazolium bromide ([BMIM]Br) was used as a good solvent to dissolve polyacrylonitrile (PAN). In order to systematically study the rheological properties of PAN/[BMIM][Br] solutions, the shear rheology of PAN/[BMIM][Br] solutions with a concentration range of 3.0-6.0 wt% was investigated by measuring the complex and dynamic moduli at different temperatures. The effects of solution concentration and temperature on the complex viscosity of PAN/[BMIM][Br] solutions were studied. The solutions exhibited shear-thinning behaviours. The complex viscosity of solutions increased with increase in solution concentration. The heightening of solution temperature lowers the complex viscosity of the solution. Then the storage modulus, G' , and loss modulus, G'' , influenced by the PAN concentration are discussed. Both G' and G'' are increased with the increasing in PAN concentration. The crossover frequency of G' to G'' is shown to decrease as the concentration is increased. Master curves are generated for complex viscosity by employing Carreau and Cross models to fit the experimental data. Both Carreau and Cross models yield good shifted curves for the complex viscosity. The activation energy for each solution concentration was calculated from the Arrhenius plots of the shift factors with respect to temperature. The activation energy for PAN/[BMIM][Br] solutions varies between 4.79 and 8.88 kJ/mol, being slightly higher for the Cross model. The activation energy is increased with the increase in PAN concentration. It can be summarized that 3-5 wt% range of PAN/[BMIM][Br] solution concentrations are considered as dilute solutions, in which PAN molecules are independent of each other without any intermolecular entanglement.

Key Words:

polyacrylonitrile;
ionic liquid;
shear rheology;
1-butyl-3-methyl-imidazolium bromide;
activation energy.

INTRODUCTION

Electrospinning is a fibre spinning technique that produces polymer fibres of nanometer to micrometer in diameters. A large number of synthetic and native polymers including polyethylene oxide, polyacrylic acid, polyvinyl alcohol, polyurethane, polycaprolactone, polyacrylonitrile, poly(*L*-lactic acid), polyamide, silk fibroin and

collagen, etc. have been successfully electrospun [1-7]. In the present, traditional volatile solvents, sodium thiocyanate, dimethyl formamide and dimethyl sulphoxide are widely employed to prepare electrospinning solution. However, there are many disadvantages such as limited dissolving capacity, poor oxidation resistance and especially

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environment pollution due to their volatility. Therefore, the interests of pursuing new solvents to replace traditional solvents in electrospinning processing are growing.

Recently, ionic liquid (IL), a newly generated solvent with particular advantages such as excellent dissolution ability, high thermal stability and ease of recycling has been identified as a green solvent with great potential applications in textile industry [8,9]. Furthermore, the properties of an IL can be easily modified by adjusting the structures of its anion or cation or both, and hence, IL is also termed as designable solvent [10]. Compared with traditional volatile solvents, the advantages of IL as solvent in electrospinning process are obvious. One advantage is that the IL can avoid releasing hazardous vapour owing to its non-volatility and excellent chemical stability [9,11]. Another advantage is that a wide spectrum of organic, organometallic, inorganic compounds and polymers [12,13] are dissolvable in IL, especially for the native cellulose [14], which is difficult to dissolve in common solvents or melt due to its hydrogen-bonded supramolecular structures. Therefore, the application of IL in electrospinning technology could increase the types of materials from which the fibres can be made. On the basis of above advantages, IL may substitute the traditional solvents, and play more and more important roles in textile industrial applications.

In our previous work, the electrospinning of PAN in pure IL 1-butyl-3-methyl-imidazolium bromide ([BMIM][Br]) as well as the key factors which influenced the electrospinning process have been investigated [15]. An alternative method is to produce ultrathin polymer fibres. It has been found that the rheological properties are the most important factors in the electrospinning process of PAN in pure ionic liquid. It is also shown that PAN/[BMIM][Br] with concentrations of 3 wt%, 4 wt% and 5 wt% can be electrospun to fibres by increasing their temperatures to 70°C, 75°C and 85°C, respectively. In that respect it is necessary to study the rheological properties of PAN/[BMIM][Br] solutions at different temperatures. In fact, the polymer rheology is the significant fundamental subject in polymer processing. Through rheological characteristics analysis, Xu et al. examined the spinnability of poly(butylene

succinate-*co*-butylene terephthalate)s with different molecular weights [16]. He et al. studied the effect of solution concentration on viscosity, and solution viscosity on diameters of electrospun nanofibres [17]. Luo et al. pointed out the relationship between the viscoelastic behaviour and chemical structure of the poly(butylene succinate-*co*-terephthalate)s (PBST) fibres by investigating the tensile properties and viscoelastic behaviour of PBST fibres [18]. There are some reports on rheological characterization of natural cellulose solutions in ionic liquids [19-23]. Also, the rheological properties of 8-20 wt% PAN/[BMIM][Cl] concentrated solutions under different temperatures and molecular weights of PAN are investigated by Wang et al. [24,25]. Yet there are few reports on the relationship between the rheological behaviour and electrospinnability of polymer spinning solutions. The concentration and temperature are the key factors influencing rheological behaviour of polymer spinning solutions. In this article, we systematically studied the rheological properties of PAN/[BMIM][Br] solutions with a concentration range of 3-6 wt% at different temperatures. To realize the structure of PAN chain in [BMIM][Br] solution, we identified the dilute regime and semi-dilute regime by plotting the concentration versus zero shear viscosity. The significance of electrospinning of PAN/ionic liquid solutions lies in providing an alternative environmental friendly method to produce ultrathin polymers fibres.

EXPERIMENTAL

Polyacrylonitrile with a molecular weight of 75,000 was purchased from Shanghai Chemical Fibers Institute. The ionic liquid [BMIM][Br] was synthesized according to the literature [26]. Briefly, 0.3 mol of 1-bromobutane and an equal amount of 1-methylimidazole were added to a 250 mL round-bottom flask fitted with reflux condenser. The reaction was conducted at 80°C for 48 h under the protection of nitrogen atmosphere till the formation of a colourless viscous liquid. The viscous liquid was washed three times with 50 mL portion of ethyl acetate in a separation funnel and then dried at 70°C in vacuum.

PAN/[BMIM][Br] solutions with concentrations of 3 wt%, 4 wt%, 5 wt% and 6 wt% were prepared by dissolving each appropriate amount of the PAN sample into 20 mL [BMIM][Br] solution in a flask. The mixture was then stirred at 110°C for approximately 2 h until the PAN sample was completely dissolved. When the PAN/[BMIM][Br] solutions with high concentrations were prepared, it was necessary to remove air bubbles from inside the solutions by using ultrasonic transmitter. The solutions were sealed and stored at room temperature for further tests.

The rheological properties of PAN/[BMIM][Br] solutions were measured with a Bohlin Gemini 200 Advanced Rheometer (Malvern Instruments, UK), and controlled rheometer with a 40 mm parallel-plate geometry. The chosen gap was about 150 μm for all the measurements. The viscoelastic domain was tested by performing a dynamic strain sweep test, for each solution at the temperature of 80°C. Then the complex viscosity (η^*), as well as the storage modulus, G' , and loss modulus, G'' , were measured by performing dynamic frequency sweep tests over an angular velocity range of 0.1-30 s^{-1} . All experiments were conducted at temperatures of 50°C, 60°C, 70°C, 75°C and 80°C. The zero shear viscosity was determined by the ORIGIN 8.0 graphing software to fit complex viscosity data to Carreau or Cross models. The water absorption for ionic liquids could not be avoided during the rheological measurements, but it could be neglected within one hour of experimental duration because of the reproducibility of time-temperature superposition [19].

RESULTS AND DISCUSSION

Figure 1 illustrates the dynamic strain sweep test. The results gave some indication that the complex viscosity is constant on most of the tested strain range so that 1% strain was chosen for all dynamic frequency tests to measure complex viscosity and dynamic modulus. The effects of solution concentration on complex viscosity at different temperatures are shown in Figures 2a-2d. The solutions exhibit shear-thinning behaviour and the onset of shear thinning shifts to higher angular velocity with increasing temperature. Due to the entangled PAN

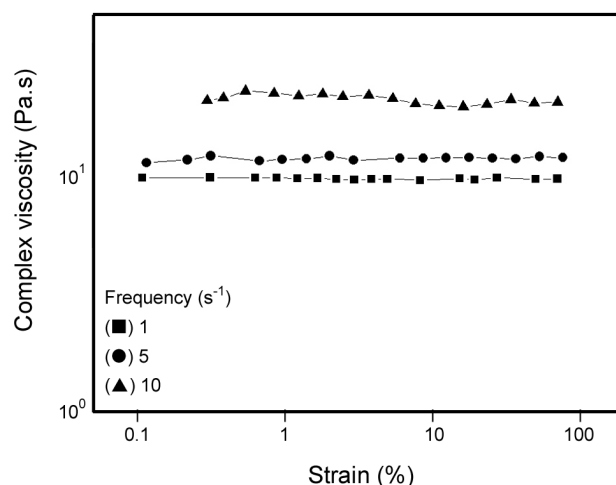


Figure 1. Dynamic strain sweep test of 4 wt% PAN/[BMIM][Br] solution at 70°C.

molecules gradually disrupted by the rising temperature, the PAN solution displays shear thinning at higher angular velocity. The complex viscosity of PAN/[BMIM][Br] solution increased with the increased solution concentration. It has been accepted that with the increase of polymer concentration in solution, the amount of chain entanglement or physical cross-linking increased and the intermolecular force was also enhanced, which are disadvantageous to the orientation and motion of molecular chain [27]. The concentration of a polymer solution is one of the key factors which influences its electrospinnability [28]. In our previous study, when the concentrations of PAN were below 2 wt% or above 6 wt%, the solutions were either very dilute or very viscous for electrospinning. This indicates that the formation of uniform fibres requires appropriate polymer concentrations [29], that is, the chain entanglements mentioned above.

The effects of temperature on complex viscosity of PAN ionic liquid solutions are shown in Figures 3a-3d. By comparing the complex viscosity of PAN/[BMIM][Br] solutions at different temperatures, it was found that with higher solution temperature the complex viscosity of the solution is lowered while the critical shear rate of shear thinning is increased. The influence of temperature of spinning solution on the viscosity could be explained by following theory: the viscous flow of polymer can be pictured as taking place by the movement of molecules or segments of

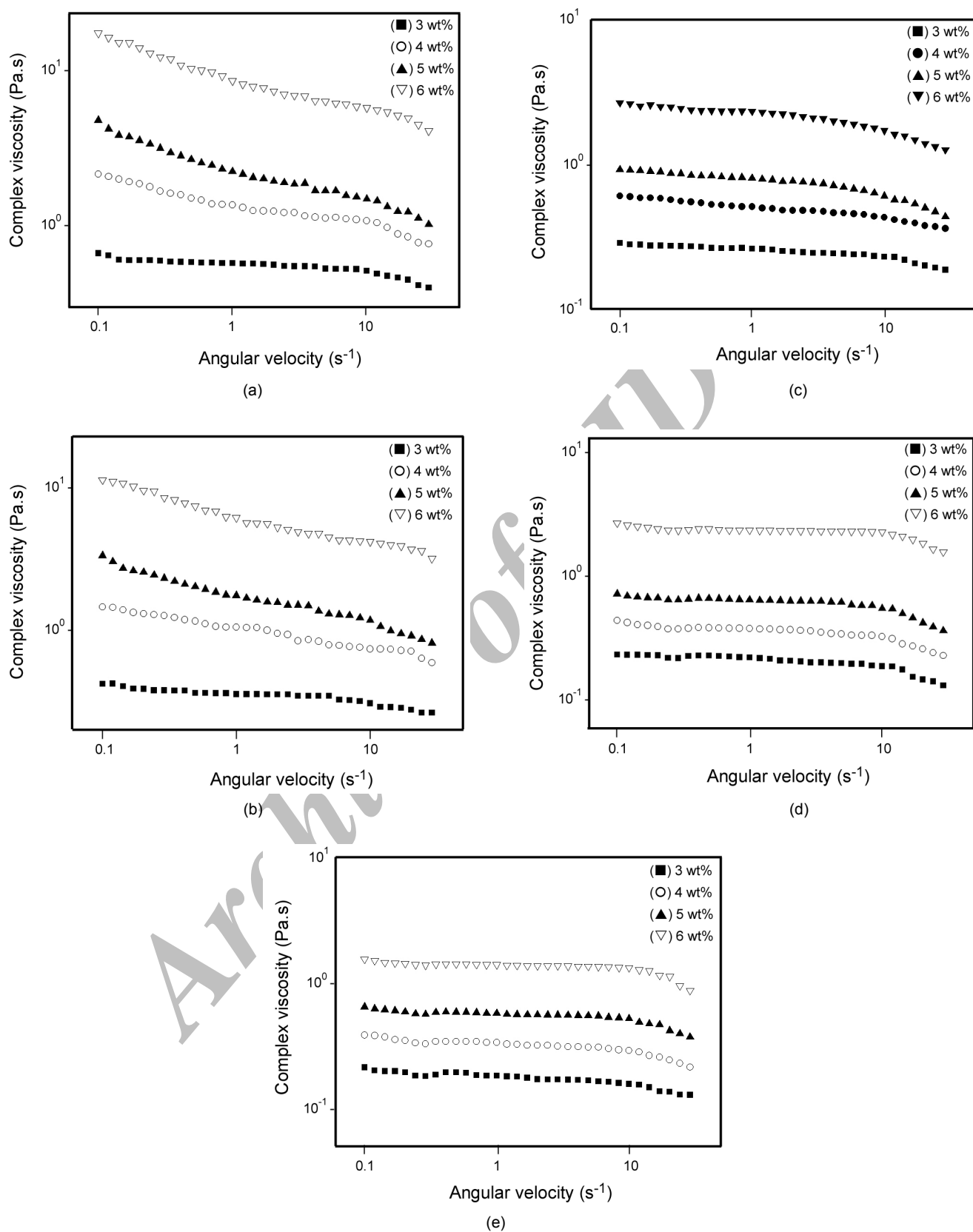


Figure 2. The effects of solution concentration on complex viscosity of PAN/[BMIM][Br] solutions at: (a) 50°C, (b) 60°C, (c) 70°C, (d) 75°C and (e) 80°C.

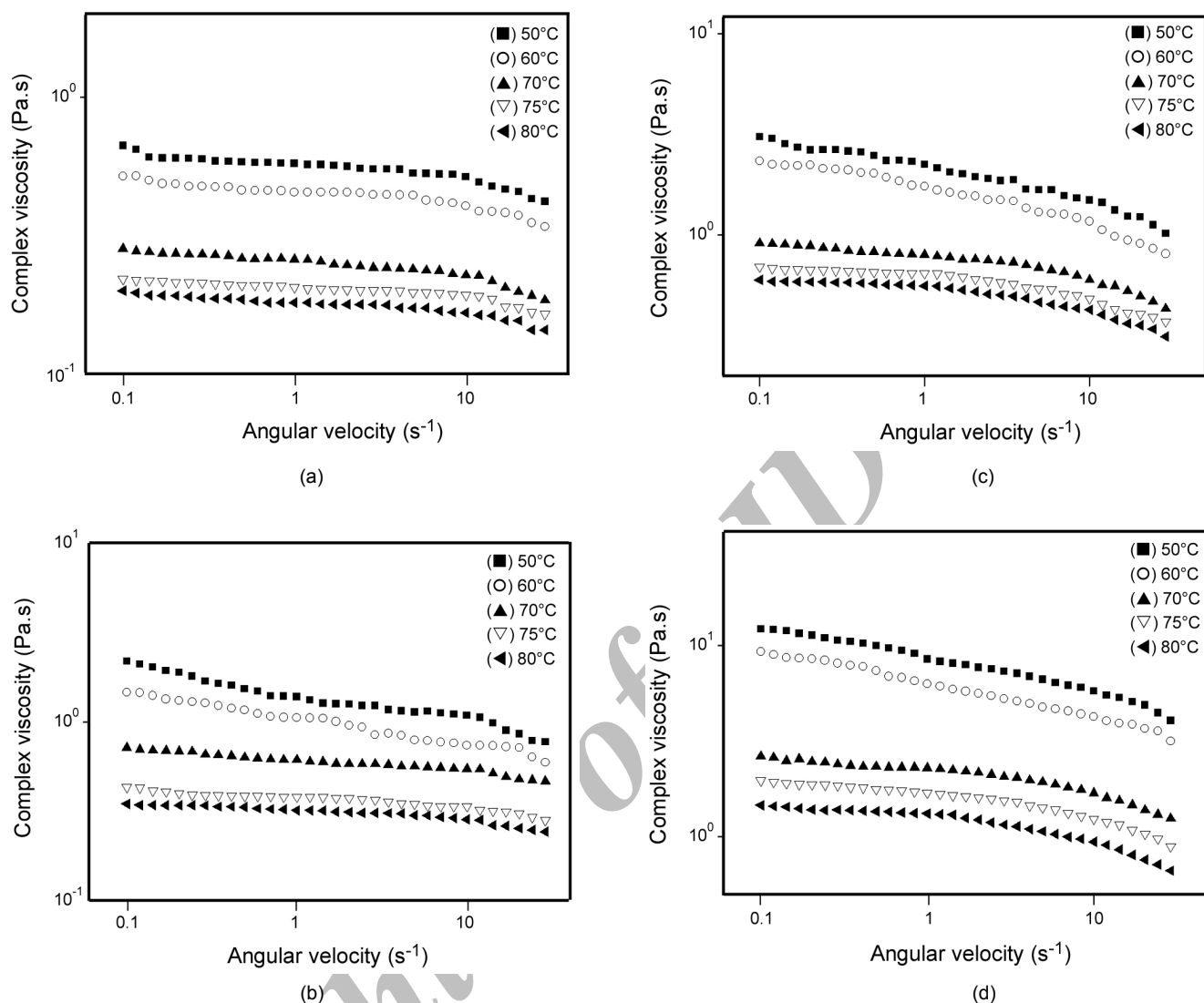


Figure 3. The effects of temperature on complex viscosity of PAN/[BMIM][Br] solution with concentrations of: (a) 3 wt%, (b) 4 wt%, (c) 5 wt% and (d) 6 wt%.

molecules in jumps from one place in a lattice to a vacant hole. The total "hole concentration" can be regarded as a space free of polymer, or "free volume" [27]. By increasing the temperature of polymer solution, more energy for random thermal motion of the molecules was supplied, which benefits the orientation of molecular chain along the shear direction and the diffusion of segments to the vacant hole. This indicates that by appropriate increase of the temperature of high viscosity polymer/ionic liquid the spinning solutions could reduce the viscosity and improve the electrospinnability thereof.

As it is shown in Figure 4, both storage modulus (G') and loss modulus (G'') are increased with the

increasing of PAN concentration. This result indicates that both the viscosity and elasticity of the system are increased. The shift of the crossover point of G' and G'' could reflect the change in degree of physical cross-linking of the system under study. The crossover frequency of G' to G'' is shifted to the left as the concentration increases (it would be out of range at 3% and still can be estimated to be $100 \text{ rad}\cdot\text{s}^{-1}$). This trend could be explained by the enhancement of chain entanglement or cross-linking caused by increase of PAN concentration [20]. The results of the dynamic modulus at 50°C , 60°C , 75°C and 80°C are not illustrated but they display the same trend as that of the 70°C solutions.

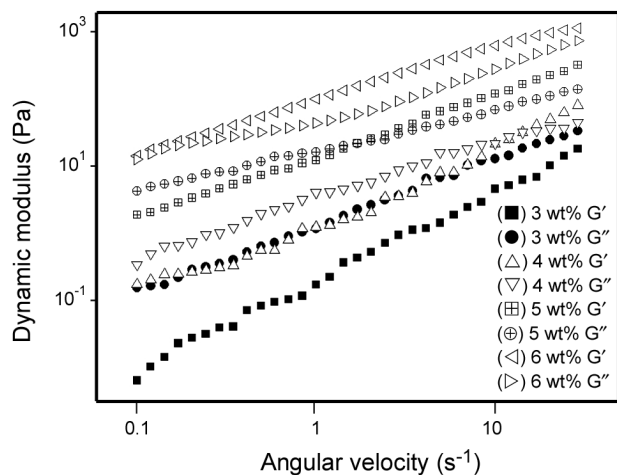


Figure 4. Dynamic modulus G' and G'' as functions of angular velocity. The concentrations of PAN/[BMIM][Br] are 3 wt%, 4 wt%, 5 wt% and 6 wt%; temperature: 70°C.

The technique of reduced variables is employed here to generate master curves for shear viscosity. The temperature shift factor can be defined as [30]:

$$a_T = \frac{\eta_0(T) \cdot T_0}{\eta_0(T_0) \cdot T} \quad (1)$$

where $\eta_0(T)$ and $\eta_0(T_0)$ represent zero-shear viscosities of the PAN/[BMIM][Br] solutions at temperature T and reference temperature T_0 , respectively. Based on this shift factor, the reduced complex viscosity, η_r^* , and reduced angular velocity, ω_r , are obtained according to the equations below:

$$\eta_r^* = \eta^*(\omega, T) \frac{\eta_0(T_0)}{\eta_0(T)} = \eta^*(\omega, T) \frac{T_0}{a_T T} \quad (2)$$

$$\omega_r = \omega \cdot a_T \quad (3)$$

Assuming that the Cox-Merz rule is valid for the PAN/[BMIM][Br] solution rheology, the three-parameter Carreau and Cross viscosity models [31] are used to predict the zero-shear viscosity from the complex viscosity data. The three-parameter Carreau viscosity model is given by:

$$\eta = \eta_0 [1 + (\lambda \dot{\gamma})^2]^{(n-1)/2} \quad (4)$$

and the three-parameter Cross model is given by:

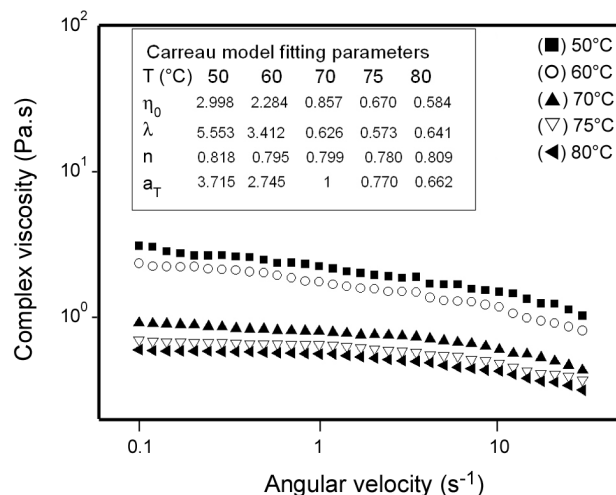


Figure 5. Complex viscosity curves and Carreau model fitting results for 5% PAN/[BMIM][Br] solution.

$$\eta = \frac{\eta_0}{1 + (\lambda \dot{\gamma})^{(1-n)}} \quad (5)$$

where λ is a time constant and n is the power-law exponent. From the "Arrhenius type dependence" of a_T as a function of temperature, the activation energy for shear flow is determined as follows:

$$a_T = \exp \left[\frac{\Delta E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (6)$$

where ΔE_a is the activation energy and R is the universal gas law constant.

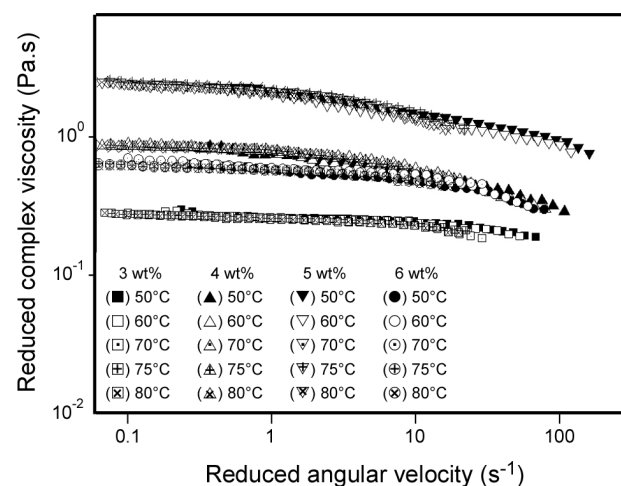


Figure 6. Master curves for complex viscosity (Carreau model parameters).

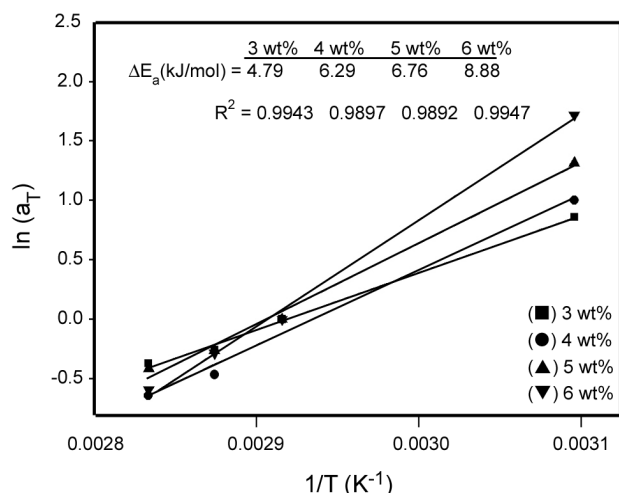


Figure 7. Arrhenius plot for the shift factors of all solution concentrations (Carreau model).

Figure 5 displays the complex viscosity curves of 5% PAN/[BMIM][Br] solution at 50°C, 60°C, 70°C, 75°C and 80°C and the Carreau model fitting parameters. Figure 6 shows the master curves for different concentrations of solution. These curves were obtained by shifting the complex viscosity curves at 50°C, 60°C, 75°C and 80°C on the reference viscosity curve at 70°C. The change of testing temperature brings about only a change in zero-shear viscosity, without modifying the general pattern of shear thinning shown for all viscosity curves. The Arrhenius plot of $\ln(a_T)$ versus $1/T$ is shown in Figure 7. From the slope of the linear fit, the

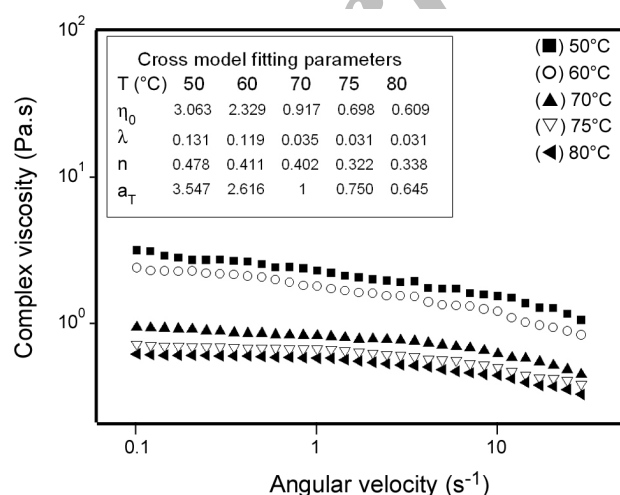


Figure 8. Complex viscosity curves and Cross model fitting results for 5 wt% PAN/[BMIM][Br] solution.

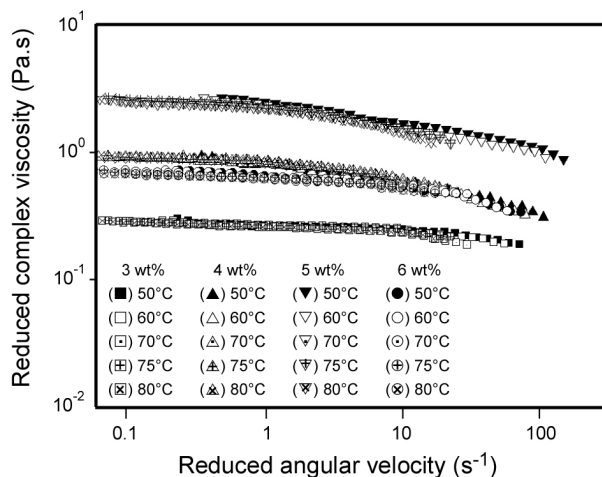


Figure 9. Master curves for complex viscosity (Cross model parameters).

activation energy for each concentration of solution was calculated and shown in the inset of the figure.

Cross model fitting parameters and the fitted results are presented in Figures 8-10 in the same way as the results from the Carreau model. It can be seen from Figures 5 and 8 that Carreau model underpredict the zero-shear viscosity, as compared with Cross model, a fact that was also observed by other investigators [20]. From Figures 6 and 9, it can be observed that both Carreau and Cross models yield good shifted curves for the complex viscosity. The activation energy for PAN/[BMIM][Br] solutions varies between 4.79 and 8.88 kJ/mol, being slightly

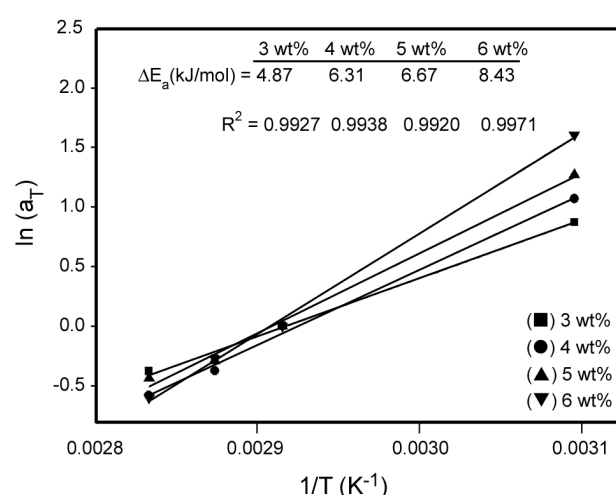


Figure 10. Arrhenius plot for the shift factors of all solution concentrations (Cross model).

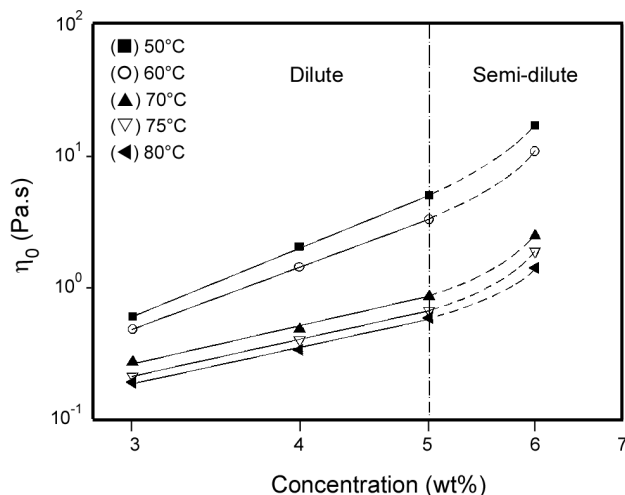


Figure 11. Concentration dependence of zero shear viscosity, η_0 . C^* indicates the overlap concentration.

higher for the Cross model. The activation energy is increased with the increase of PAN concentration. This trend is also reported by other groups on PAN/DMF spinning solution [32,33]. This could be supported by the fact that the fibres may only be formed as the temperatures of PAN solutions are above the critical electrospinning temperature [34].

The concentration dependence of zero shear viscosity (η_0) of PAN/[BMIM][Br] solutions at different temperatures is plotted in Figure 11. It can be stressed that 3-5 wt% PAN/[BMIM][Br] solutions are considered as dilute solutions due to linearly increase of η_0 (solid lines) with increasing concentration. The linear viscous behaviour indicates that PAN molecules are independent unentangled chains in this concentration range. The zero shear viscosity increases non-linearly (dotted curves) when the concentration is above 5 wt%, indicating that 6 wt% solutions should be considered as semi-dilute solutions [19].

CONCLUSION

We performed systematic studies on the rheological properties of PAN/[BMIM][Br] solutions with a concentration range of 3.0-6.0 wt% at different temperatures with a rheometer. The complex viscosity of PAN/[BMIM][Br] solution increased with the increase of the solution concentration. The effects of temperature on complex viscosity of

PAN/[BMIM][Br] solutions show that heightening of solution temperature would lower the complex viscosity of the solution. Both storage modulus (G') and loss modulus (G'') increased with the increasing in PAN concentration. The crossover frequency of G' to G'' is shown to decrease as the concentration increased, which indicates that the chain entanglement or cross-links enhanced with the increased PAN concentration. Carreau and Cross models were employed to yield master curves for the complex viscosity. It can be observed that they yield good shifted curves for the complex viscosity. The activation energies for solutions of each concentration were calculated from the slope of $\ln(a_T)$ versus $1/T$. The activation energy for PAN/[BMIM][Br] solutions varies between 4.79 and 8.88 kJ/mol. The concentrations within 3-5 wt% range of PAN/[BMIM][Br] solutions are considered as dilute solutions and a 6 wt% solution as a semi-dilute solution by plotting of concentration versus zero shear viscosity to evaluate the dilute, semi-dilute and concentrated regimes.

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