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The rheological properties of bamboo cellulose pulp/ionic liquid system

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Abstract. In this study, two kinds of spinning solutions were prepared by dissolving bamboo cellulose pulp into 1-ethyl-3-methyl imidazole chloride salt ([EMIM] Cl) and 1-butyl-3-methyl imidazole diethyl phosphate salt ([BMIM]DEP) ionic liquids, respectively. Furthermore, the rotational rheometer was used to test the steady-state rheological properties of above as-prepared spinning solutions. The research results show that both of these two ionic liquids exhibit better solubility to the bamboo cellulose pulp. The apparent viscosities(η_a) decrease with the increased temperature(T) and shear rate(γ) and increase with the increased concentration. The non-Newtonian index(n) declined with the increase of both shear rate and concentration, as well as increased with the build-up temperature. The structural viscosity index($\Delta\eta$) increased with the increased concentration and tended to decrease with temperature rise. Meanwhile, viscous flow activation energy(Eη) decreases with the increased share rate as well as the concentration. According to the results, it can be seen that the bamboo cellulose pulp/[EMIM]Cl with the concentration of 6% at 70℃ exhibits better spinnability.

1. Introduction

Cellulose is a kind of renewable and widely applied resources with environmental protection and biocompatibility. It can be used for energy, materials, chemicals, textiles, paper and other fields[1]. In cellulose's family, plenty of produces are made from the so-called "cellulose generation". The recycled fiber is one of the most important products. There are many kinds of methods to obtain the regenerated cellulose fibers, such as direct melt spinning, enzyme cellulose spinning, Copper-ammonia cellulose solution spinning technology, etc. Among various kinds of such fabrication methods, the application research of new type ionic liquid in this area is more active. For example, Ingildeev[2] reported that the cellulose -ionic liquid was spun by the wet and the dry-wet spinning methods, and found that the regenerated cellulose fibers by the dry-wet spinning were preparing exhibited better strength, crystal orientation degree as well as easier prone to fibrillation. Electrospinning was also used to fabricate cellulose- ionic liquids by Quan S L and co-workers [3]. Furthermore, in order to decrease the viscosity of electrospun solutions, dimethyl formamide(DMF) and dimethyl sulfoxide(DMSO) were used as the cosolvent during the electrospinning process by Härdelin, etc [4]. It is well known that the performance of spinning solutions provide influences not only on the machining performances but also affect the choices of spinning process as well as the fibrous produces' qualities. Accordingly, deep research of the rheological properties of the spinning solutions is particularly important in the process of development of new type of cellulose fibers. China is rich in bamboo resources, relatively high levels in development and utilization of the world [5]. In this paper, by the solubility of bamboo cellulose pulps in different ionic liquids, the influential factors of the spinning solutions rheological properties were studied.

2. Experiment

2.1. Preparation of bamboo cellulose pulp/ionic liquid

The bamboo cellulose pulp/ionic spinning solutions with different concentrations were obtained by mixing and stirring different amounts of bamboo cellulose pulps (Tangshan sanyou group Dongguang pulp Co., Ltd. DP=500， α-cellular content~90%) with 10 g ionic liquid in the three-flake container at 80℃and the certain degree of vacuum until dissolved. Over here, bamboo cellulose pulps were activated by 18% NaOH solution.

2.2. Instruments and characterization

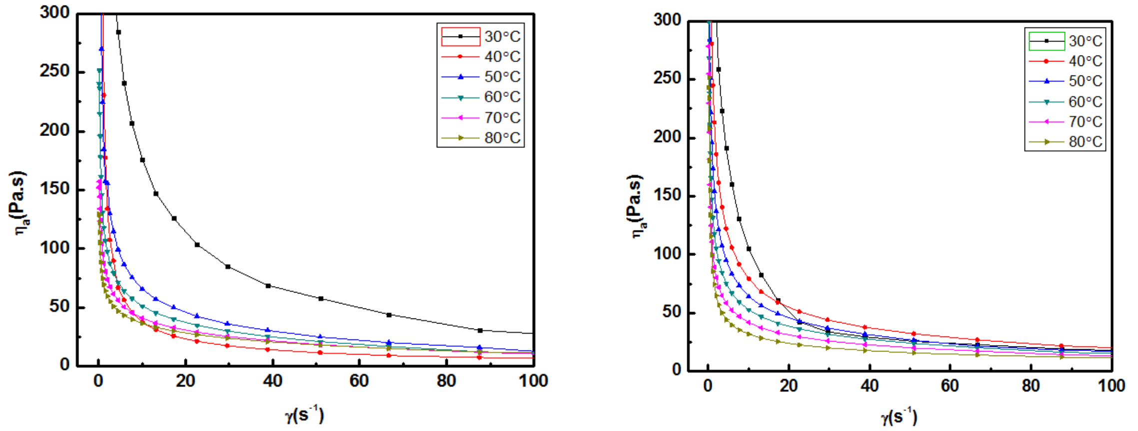
Rotational Rheometer (Bohlin Gemini HR nano-Peltier, clamp: ECT-PP20. The distance: 1000 μm, steady shear rate 0.1-250 S^{-1}) was used to measure the rheology properties of as-prepared spinning solutions (concentration~8%, temperature 80℃). In this work, the rheology properties of bamboo cellulose pulps dissolved in different ionic liquids ([EMIM]Cl and [BMIM]DEP (Ke-neng Material Technology Co., Ltd., Linzhou, China), with different concentration and at different temperatures were studied.

3. Results and discussion

3.1. Apparent viscosity

η_a is an important indicator which reflects the liquidity. It is closely related to temperature, concentration, molecular structures of the liquids.

3.1.1. The influence of temperature. Figure 1 is apparent viscosities of the bamboo cellulose pulp/[EMIM]Cl and bamboo cellulose pulp/[BMIM]DEP with the concentration of 8% between 30℃ to 80℃, respectively. It can be seen obviously that with the increased temperature, the rheological curve moved down for both of above two solution systems, which indicate the behavior of shear-thinning as well as the typical pseudoplastic non-Newtonian fluid. Furthermore, the value η_a decreases at the beginning and then gradually converge by increasing γ. For polymer molecule, when the molecular weight over more than a certain critical value, the flexible long-chain molecules between each other twisted into a knot, forming entanglement between molecular chains. According to the polymer network structure theory, there are two kinds of entanglement between large molecular chains: the tangles of geometry and the bonding of intermolecular. The bound nodes are all with instantaneous degeneration in the polymer fluid that can divide, reconstruct as well as issue in a particular condition to reach the dynamic balance [6]. When the temperature increased, the bound nodes solve quickly by random thermal motion of molecules, and make the gravity center of these molecular chains flowing along the direction of displacement and mutual slippage between the chains, which decrease the entanglement effect between molecules and friction, and enhance the liquidity of the solution and η_a decreased. When the shear rate increases, the disentanglement rate of the bound node is greater than the reconstruction rate, which leads to both of the numbers of bound nodes and apparent viscosity decrease. But when the shear rate increases to threshold, the bound node to reconstruction was restricted, resulting in the viscosity dropping to the minimum value without any further changes.



a-[EMIM]Cl b-[BMIM]DEP

Figure 1. η_a-γ curves of bamboo cellulose pulp/ionic liquid solutions (concentration~8%)

3.1.2. The influence of Concentration. The relationship between η_a and γ of bamboo cellulose pulp/[EMIM]Cl and bamboo cellulose pulp/[BMIM]DEP with different concentrations at 80℃ are shown in Figure 2. It can be seen that the rheological curves move up when concentrations increase. Meanwhile, with the increase of γ, the value η_a down first and then stabilize. However, the value η_a of bamboo cellulose pulp/[BMIM] DEP system is significantly higher than bamboo cellulose pulp/[EMIM] Cl system at the same concentration and shear rate. As we were known, random coil state macromolecules are isolated in dilute solution. When reaching to a certain concentration, polymers contact and through overlapping each other that make the chain sections roughly uniform and form tangles network in such solution. In this kind of uniform distribution of polymer solution, the total number of molecules per unit volume chain should be proportional to the square of the concentration [7]. The greater the concentration, the more molecules bound nodes and friction forces between each node, which increase the apparent viscosity value of the spinning solution. Because the different molecular structure of [BMIM]DEP and [EMIM]Cl, the solvation structural level of cellulose molecule chain in both the liquid is different, which lead to differences in phase geometry bound node and the bonding force of intermolecular, and impact on the flexibility and kinematic of molecular chain in the fluid. Because of the branched chain length of [BMIM]DEP molecules are longer, the

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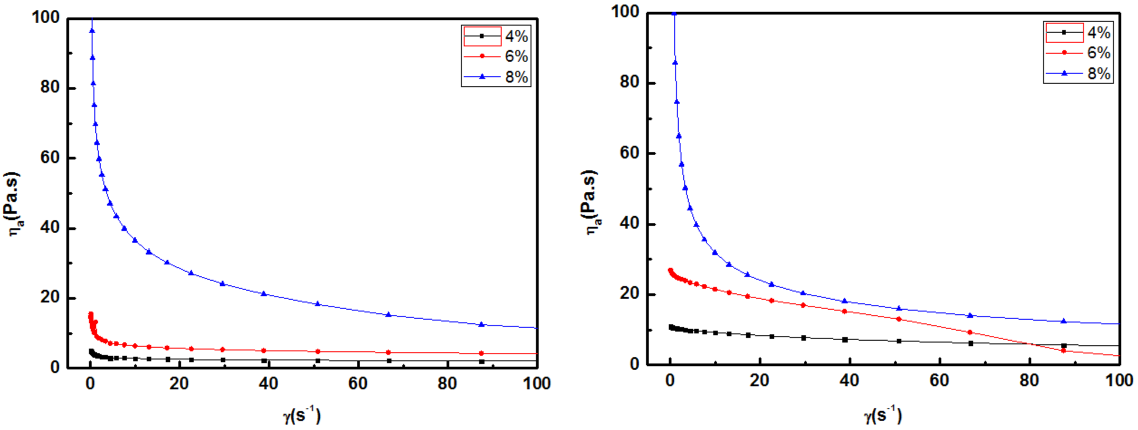
dissolved cellulose chain segment motion resistance is larger, so the apparent viscosity of bamboo cellulose pulp / [BMIM] DEP system is relatively larger as well.



a-[EMIM]Cl b-[BMIM]DEP

Figure 2. η_a-γ curves of bamboo cellulose pulp/ ionic liquid solutions at 80℃

3.2. Non-Newtonian index

The non-Newtonian index is used to represent the degree of polymer fluid deviates from the Newtonian fluid, it can reflect the viscoelastic of spinning solution, and it is usually less than 1. When the non-Newtonian index is much more close to 1, it indicates that spinnability of the spinning solution is better. The non-Newtonian index can be expressed by power law function formula (τ= K γ n), in which the value n can be obtained according to lgτ-lgγcurve graph [8].

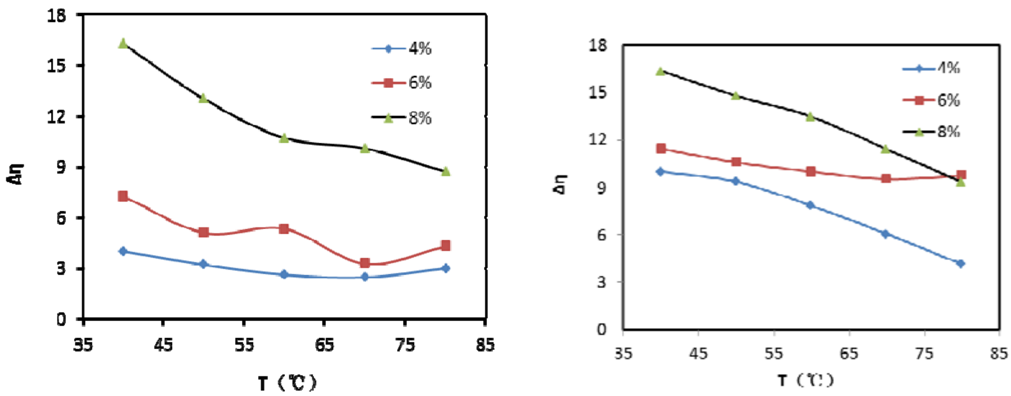
Table 1 shows the non-Newtonian index values of two kinds of bamboo cellulose pulp/ionic liquids with different concentrations and temperatures. With the increase of γ, the non-Newtonian index of solution exhibits a trend of decrease. When the temperatures increase, the non-Newtonian index increased as well. However, under the condition of lower shear rate, the value n changes with some volatility. It is mainly due to that macromolecular chain segment motion are accelerated when the temperature increase, which is advantageous to the molecular chains disentanglement, and makes a decline in sensitivity of the shear rate to the liquidity of the solution. According to Table 1, it can be found that when the concentration is less than 6%, both of above two solutions become much more like the Newtonian fluid. However, with higher concentrations, the non-Newtonian index is still smaller even under low shear rate, indicating a far deviation from the Newtonian fluid. Such above are fit well with the steady-state rheological curve with different spinning fluid concentration. By comparing the solubility and rheological properties, [BMIM]DEP and [EMIM]Cl can be used to preparing cellulose spinning solutions.

Table 1. Non-Newtonian Index of bamboo cellulose pulp/ionic liquid solutions

Ionic liquid	Concentration %	Shear rate s-1	Temperature ℃					
			30	40	50	60	70	80
[EMIM]Cl	4	0.1～1	0.98	0.99	0.98	0.99	0.99	0.98
		1～10	0.74	0.86	0.91	0.93	0.92	0.86
		10～100	0.49	0. 76	0.79	0.83	0.86	0.86
	6	0.1～1	0.95	0.96	0.98	0.98	0.99	0.96
		1～10	0.69	0.76	0. 78	0.79	0.91	0.82
		10～100	0.42	0.57	0.67	0.74	0.82	0.82
	8	0.1～1	0.47	0.48	0.56	0.69	0.76	0.73
		1～10	0.46	0.47	0.52	0.61	0.65	0.70
		10～100	0.20	0.26	0.34	0.34	0.42	0.49
[BMIM]DEP	4	0.1～1	0.94	0.97	0.98	0.99	0.99	0.97
		1～10	0.65	0.80	0.84	0.89	0.93	0.94
		10～100	0.37	0.57	0. 65	0.73	0.79	0.84
	6	0.1～1	0.93	0.95	0.97	0.99	0.99	0.97
		1～10	0.61	0.73	0.75	0.86	0.89	0.93
		10～100	0.35	0.45	0.51	0.63	0.73	0.80
	8	0.1～1	0.38	0.53	0.55	0.58	0.61	0.65
		1～10	0.35	0.48	0.54	0.55	0.60	0. 54
		10～100	0.26	0.41	0.40	0.46	0.51	0.56

3.3. *Structural viscosity index*

Δη can be used to characterize the spinning fluid structured degree which is an important parameter of the spinnability of spinning solution. It is expressed as $\Delta\eta=(-\ d\lg\eta/d\gamma^{1/2})\times 10^2$. According to the linear fitting curve slope (from lgη- $\gamma^{1/2}$ curve), Δη can be calculated under different temperatures and concentrations. In the non-Newtonian area, Δη＞0. The smaller of Δη and the smaller of the spinning fluid structured degree and the better spinnability.



a-[EMIM]Cl b-[BMIM]DEP

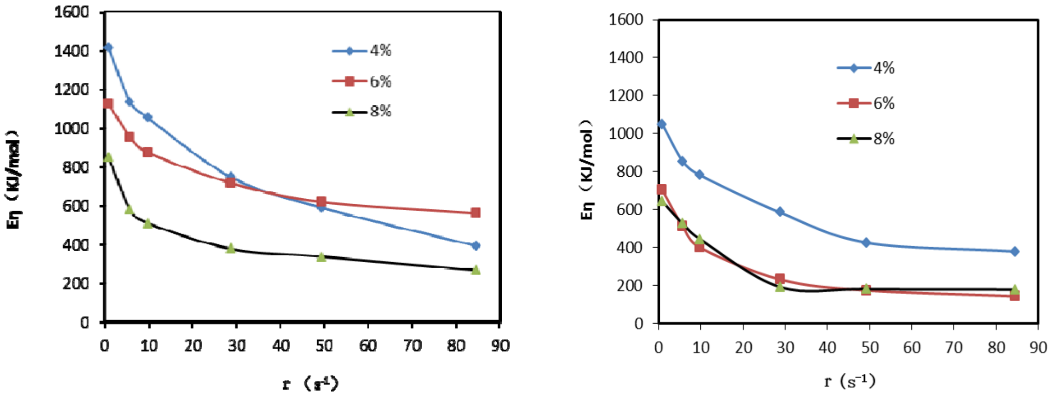
Figure 3. Δη-T curves of bamboo cellulose pulp/ionic liquid solutions

Figure 3 exhibit the relationships between Δη and T of two kinds of bamboo cellulose pulp/ionic liquid systems with different concentrations. With the increases concentration, Δη increase. And Δη decreases when the temperature increases. When the temperature reaches at 70℃, Δη is relatively lower. Thus, in this work, it can be seen that 70℃ is the better spinning temperature. Furthermore, the value Δη of bamboo cellulose pulp/[EMIM]Cl is smaller than that of bamboo cellulose pulp/[BMIM]DEP at the same temperature and concentration, indicating a relatively good spinnability.

3.4. Viscous flow activation energy

Eη is a physical quantity to describe the fluid viscosity on the temperature sensitivity, which represents the polymer chain segment that be used to overcome the barrier (the minimum energy of chain segment transition from original location to near "holes"), and can be affected by polymer molecular structures, intermolecular forces, molecular weight, shear rate, polymer concentration, temperature, solvent and so on. If Eη is larger, the viscosity will be more sensitively to temperature changes, which is not conducive to the fiber forming. Within a small scope of temperature interval, the spinning solution viscosity can be expressed by Arrhenius formula, $\eta = Ae^{E\eta/RT}$. Based on logarithm on the equation, figure lnη～1/T, the Eη can get from the straight slope [9].

Figure 4 are Eη of bamboo cellulose pulp/ionic liquid solutions. It can be seen that with the increase of spinning solution concentration as well as the shear rate, Eη decrease. especially in the low shear rate range that the change of Eη is more.. Accordingly, the value Eη of the bamboo cellulose pulp/[EMIM]Cl is larger than that of bamboo cellulose pulp/[BMIM]DEP at the same concentration, indicating that the viscosity of bamboo cellulose pulp/[EMIM]Cl is more sensitive to temperature. To the bamboo cellulose pulp/[BMIM]DEP system, there is only a bit influence of the concentration to Eη when the solution concentration exceeds 6%. Such phenomena might be due to that the temperature plays an important role in macromolecular chain disentanglement at low shear rate. However, when the shear rate is higher, γ plays the main role in disentanglement, so that leads to the Eη lower, and the sensitivity to the temperature is decreased also. When solution concentration was increasing, the number of tangle molecule point also increased accordingly, due to the limited effect of temperature on the disentanglement, the sensitivity of viscosity to temperature is reduced. Since the anion of [EMIM]Cl exhibit strong ability to accept the hydrogen bonds, and the alkyl chain of its cationic groups is shorter, so the bonding force between [EMIM]Cl and cellulose molecules is relatively larger, when the cellulose chain segment transit from the state of in situ to the near "holes", a larger barrier must to be overcome, which needs more energy, thus the Eη value is relatively higher. Therefore, in the process of spinning, both temperature and uniformity of the solutions should be kept stabilization to prevent the excessive volatility of the system viscosity.



a-[EMIM]Cl b-[BMIM]DEP

Figure 4. Eη-γ curves of bamboo cellulose pulp/ionic liquid solutions at 80℃

4. Conclusions

- In the range of 30℃～80℃, η_a of bamboo cellulose pulp/[EMIM]Cl and bamboo cellulose pulp/[BMIM]DEP solutions decrease with the increase of temperature as well as shear rate, and increase along with the increased concentration, which shows as shear thinned, and can be classified as a typical non-Newtonian fluid.
- In the range of concentration 4%～8%, the non-Newtonian index decrease with the increased shear rate and concentration, and also exhibits an increasing trend when the temperature increased. Meanwhile, Eη declines when the shear rate and concentration declined. Δη reduce with the temperature up and increase with the increased concentration.
- At the same temperature and concentration, Δη of the bamboo cellulose pulp/[EMIM]Cl system is lower than bamboo cellulose pulp/[BMIM]DEP, and Eη is larger. According to analysis results mentioned above, bamboo cellulose pulp/[EMIM]Cl solution exhibits good spinnability with the concentration of 6% at 70℃.

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