Effect Of High Pressure Homogenization (HPH) On The Rheological Properties Of Pineapple Leaf Cellulose/[BMIM]Cl Solution

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Abstract. Due to the intermolecular and intramolecular strong hydrogen bonds, cellulose possesses high crystallinity, hardly dissolves in ordinary solvents. In the meanwhile, the cellulose, hemicelluloses and lignin were woven into compact structure, that is one of the reasons that natural cellulose poorly soluble in water and other organic solvent [1] Swatloski et al in 2002 first explicitly pointed out that ionic liquid, 1 - butyl 3 - methyl imidazole chloride salt ([Bmim]Cl) had good solubility of cellulose. The ionic liquids, with their excellent physical and chemical property, cause more and more concerns of people increasingly [2]. You can take advantage of the ionic liquid ([Bmim]Cl) good solubility of cellulose by microwave heating way to dissolve cellulose in ionic liquids [3] [4]. As a new type of high-efficient green solvent, ionic liquid has unique properties, which is different from the traditional solvent. The highly effective and safe homogeneous treatment of pineapple leaf cellulose under microwave irradiation was reported in this paper. The rheological properties of pineapple leaf cellulose / [BMIM]Cl had a great change after the high pressure homogenization (HPH). Effect of high pressure homogenization on the rheological properties of pineapple leaf cellulose / [BMIM]Cl solution was investigated by rotational rheometer MARS III Haake (Germany).

Introduction

Nanocellulose was prepared through ball-milling process [5] and hydrolysis method in previous studies [6]. However, mechanical method has the shortcoming of high energy consumption and low production efficiency [7]. Preparation of nanocellulose by hydrolysis method is low efficiency and caused serious pollution to the environment Therefore, how to produce nanocellulose effectively has been a urgent problem.

“Cellulose nanocrystallization technology in liquid phase conditions” was adopted in this study, this technology can reduce the resistance between the cellulose chain and destroy intermolecular and intramolecular hydrogen bonds, then cellulose in a homogeneous condition completed network structure collapse and the molecular chain of self-assembly through high pressure homogenization [8]. The technology with great advantages, such as high conversion
rate, fast, continuous, green, clean process mild reaction conditions, are suitable for the
production of nanocellulose.

The pineapple leaf cellulose / [BMIM]Cl solution in a homogeneous condition takes on high
viscosity, and shear thinning behavior. Effect of high pressure homogenization on the
rheological properties of pineapple leaf cellulose / [BMIM]Cl solution was investigated by
Hakke rheometer (MARSIII). In order to later provides the theory basis for pineapple leaf fiber
products nanotechnology applications.

Experimental

Materials

Pineapple leaves were collected from local plantations by China tropical agriculture science
academy of agricultural machinery research institute. All chemical reagents were of analytical
grade, purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). The ionic
liquid of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) used in this study was synthesized
in previous study.

Natural Cellulose Extraction. Pretreatment of pineapple leaf and dissolution of cellulose:
the original pineapple leaf was pretreated with NaOH solution to remove the impurities.

Homogeneous Solution Preparation. Then cellulose (3wt%) was dissolved in the
synthesized ionic liquid at 40 °C~80 °C by microwave heating with 400W Preparation of 3%
homogeneous pineapple leaf cellulose / cellulose / [BMIM]Cl solution by high pressure
homogenizer: 3% not homogeneous pineapple leaf cellulose / [BMIM]Cl solution was then
passed through a high pressure homogenizer with 45 cycles at 100 MPa pressure [9].

Rheological Properties Of Pineapple Leaf Cellulose / [BMIM]Cl Solution. Rotational
Rheometer MARS III Haake (Germany). Rheometer technical parameters: Temperature range
-150 ~ 600°C; Torque range 0.003 uN.m ~ 200 mN.m; Frequency range 10E-6 ~ 100 Hz;
Normal force scope 0.01~50 N. The pineapple leaf cellulose / [BMIM]Cl solution was
investigated by rotational rheometer MARS III.

Results and Discussion

The Analysis Of The Rheological Properties

Flow Curve of Of Pineapple Leaf Cellulose / [BMIM]Cl Solution. The rheological
properties of cellulose solution play an important role in cellulose forming process [10]. The
study on the rheological properties of cellulose solution and its influencing factors is one of
effective methods to understand its change laws.

As you can see from Fig.1, 3% not homogeneous pineapple leaf cellulose / [BMIM]Cl
solution and 3% homogeneous pineapple leaf cellulose / [BMIM]Cl solution fluid have
undergone a shift from first Newton area to non-newtonian area at a certain range of
experimental shear rate. At lower shear rate, the apparent viscosity of homogeneous system had
no correlation with Shear rate. When the shear rate increased to a certain extent (Critical shear
rate), as shear rate increasing, the apparent viscosity of homogeneous system were decreased
sharply, and behave Shear thinning, show the pseudo-plastic fluid features.
Figure 1. Pineapple Leaf Cellulose / [BMIM]Cl solution apparent viscosity and shear rate (a: 3% not homogeneous pineapple leaf cellulose / [BMIM] Cl solution; b: 3% homogeneous pineapple leaf cellulose / cellulose / [BMIM]Cl solution).

**Non-Newtonian Index Of Pineapple Leaf Cellulose / [BMIM]Cl Solution.** 3% pineapple leaf cellulose / [BMIM]Cl solution was of pseudo-plastic fluid, the relationship between the shear rate and apparent viscosity could also be described by power law model in a certain range of shear rate. The relationship between the apparent viscosity and shear rate as shown in Eq.1:

$$\eta_a = K\gamma^{n-1} \tag{1}$$

Where $\eta_a$ is apparent viscosity, $\gamma$ is shear rate, $K$ is empirical constant, $n$ is non-Newtonian index. The closer that non-Newtonian index is to 1, the closer the Newton fluid movement. The non-Newtonian index is dependent on temperature and shear rate. At the same concentration and shear rate, the viscosity of cellulose / [BMIM]Cl solution is inversely proportional to the temperature.
Rising temperatures can provide enough energy to the molecular segment slipped, reduce the friction between the molecules, so the fluidity of solution increased [11]. The processing fluidity of pineapple leaf cellulose / [BMIM]Cl solution would be improved with the increase of temperature. When the temperature is 70 °C, the effects of temperature increase on the viscosity of 3% not homogeneous pineapple leaf cellulose / [BMIM]Cl solution were negligible, as shown in Table 1.

Table 1. 3% Not Homogeneous Pineapple Leaf Cellulose / [BMIM] Cl Solution in Steady Rheological Properties under Different Temperature.

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>Empirical constant k</th>
<th>Non-Newtonian index n</th>
<th>zero shearing viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>27.22</td>
<td>0.8172</td>
<td>19.75513</td>
</tr>
<tr>
<td>50</td>
<td>10.38</td>
<td>0.8627</td>
<td>7.648328</td>
</tr>
<tr>
<td>60</td>
<td>4.85</td>
<td>0.9185</td>
<td>3.9778</td>
</tr>
<tr>
<td>70</td>
<td>2.199</td>
<td>0.9550</td>
<td>1.973045</td>
</tr>
<tr>
<td>80</td>
<td>1.232</td>
<td>0.9743</td>
<td>1.181046</td>
</tr>
</tbody>
</table>

However, when the temperature is 60 °C, the cellulose chain entanglement was reduced obviously, the results showed that the effects of temperature increase on the viscosity of 3% homogeneous pineapple leaf cellulose / [BMIM]Cl solution were negligible, see Tab. 2.

This phenomenon can be explained that the entanglement between the cellulose molecular chain segments has been destroyed by high pressure homogeneous process [12], thus increased the fluidity of pineapple leaf cellulose / [BMIM]Cl solution.

Thus it can be seen the fluidity of 3% pineapple leaf cellulose / [BMIM]Cl solution were markedly improved and the processing temperature was reduced through the high pressure homogeneous process, would facilitate a more effective pineapple leaf cellulose utilization.

Table 2. The 3% Homogeneous Pineapple Leaf Cellulose / [BMIM] Cl solution in Steady Rheological Properties under Different Temperature

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>Empirical constant k</th>
<th>Non-Newtonian index n</th>
<th>zero shearing viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>6.146</td>
<td>0.9166</td>
<td>4.864357</td>
</tr>
<tr>
<td>50</td>
<td>2.981</td>
<td>0.9563</td>
<td>2.687698</td>
</tr>
<tr>
<td>60</td>
<td>1.434</td>
<td>0.9797</td>
<td>1.380468</td>
</tr>
<tr>
<td>70</td>
<td>0.8115</td>
<td>0.9872</td>
<td>0.820834</td>
</tr>
<tr>
<td>80</td>
<td>0.5076</td>
<td>0.9919</td>
<td>0.533822</td>
</tr>
</tbody>
</table>

The Tab. 1 and Tab. 2 shows that the non-Newtonian index of 3% pineapple leaf cellulose / [BMIM] Cl solution is to gradually close to 1 as the temperature rises, indicated that the higher
temperature can increase the energy of homogeneous system, intensify the molecular segment motions and decrease the number of entanglement node, reduce the dependency of the apparent viscosity on shear rate, improve the fluidity of 3% pineapple leaf cellulose / [BMIM] Cl solution. The non-Newtonian index of 3% pineapple leaf cellulose / [BMIM] Cl solution is more close to 1, explained that 3% pineapple leaf cellulose / [BMIM] Cl solution is closer to Newtonian fluid after HPH treatment.

**Viscous Flow Activation Energy Of Pineapple Leaf Cellulose / [BMIM]Cl Solution.**

Viscous flow activation energy ($E_\eta$) of polymeric fluid shows that the relationship between viscosity and temperature, reflects the dependency of viscosity and temperature, as shown in Eq.2 (Arrhenius Equation):

\[ \eta = A \exp \left( \frac{E_\eta}{RT} \right) \]  

(2)

Where $A$ is the constant that stands for polymer characteristics and relative molecular mass under specific shear stress, Where $R$ is the gas constant(8.314), $T$ is the absolute temperature, $E_\eta$ is the viscous flow activation energy. Calculation of critical shear rate are shown in Tab. 1 and Tab. 2. In Arrhenius Equation we take its log, as shown in Eq.3:

\[ \lg \eta = \lg A + \frac{E_\eta}{RT} \]  

(3)

The $E_\eta$ values of 3% not homogeneous pineapple leaf cellulose / [BMIM] Cl solution and 3% homogeneous pineapple leaf cellulose / [BMIM] Cl solution at 40 °C was 2.16 and 1.14, respectively.

The greater the $E_\eta$ values is, the greater effect temperature has on system viscosity. The smaller the $E_\eta$ values is, the smaller the influence of the temperature on system viscosity. The $E_\eta$ values of cellulose / [BMIM] Cl solution showed that HPH process can reduce the influence of temperature on the system viscosity of pineapple leaf cellulose / [BMIM] Cl solution The overall processing stability of the pineapple leaf cellulose / [BMIM] Cl solution can be improved by importing HPH process during processing procedure.

**Summary**

The fluidity of pineapple leaf cellulose / [BMIM]Cl solution were improved through the HPH process, and the processing temperature was reduced, would facilitate a more effective pineapple leaf cellulose utilization. At the same time can reduce the effects of temperature on the system viscosity of pineapple leaf cellulose / [BMIM]Cl solution. HPH process can improve the overall processing stability of the pineapple leaf cellulose / [BMIM] Cl solution.

**Acknowledgement**

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**References**


