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Rheological behavior of chitosan derivative/cellulose polyblends from *N*-methylmorpholine *N*-oxide/H_2O solution

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Abstract *O*-carboxymethylated chitosan (*O*-CMCh) aqueous solution (I) and Ethyletheramine Chitosan (EACS) aqueous solution (II) were blended with cellulose *N*-methylmorpholine *N*-oxide solution, and corresponding polyblends (Polyblend I and II) were obtained. The rheology of this three liquids, (cellulose solution, Polyblend I and II), was investigated in this study. Then the influence on rheology, because of the addition of chitosan derivative, was discussed.

Introduction

Cellulose fiber is a favorite undergarment material and it is the most appropriately to be made into antibacterial next-to-skin fabrics due to the safety to human body and the comfort resulted from its high moisture-retentivity. Though the viscose process is a widely used solution-spinning process of cellulose fiber, where the carbon disulfide applied is very harmful while hydrogen sulfide as a byproduct during the process is a notorious air pollutant. Therefore, several promising solvent systems e.g. LiCl/*N*,*N*-dimethylacetamide (DMAc), dimethylformamide (DMF), and *N*-methylmorpholine *N*-oxide (NMMO)/H_2O were utilized and corresponding fibers were developed [1–4].

Chitosan, a de-*N*-acetylated form of chitin, the second most abundant natural polymer obtained from the shells of crab, shrimp and krill, consists mainly of b(1–4)-2-amino-2-deoxy-D-glucose units. Chitosan is also a biopolymer, reported to exhibit a great variety of useful biological properties [5–7] . Recently, the antibacterial and antifungal activities of chitosan have been hold with great interest. Chitosan inhibits the growth of a wide variety of bacteria and fungi [8], showing broad spectra of antibacterial activities, high killing rate and low toxicity toward mammalian cells [9, 10]. Some chitosan derivatives exhibit even stronger antibacterial activity than chitosan does.

Blending chitosan and its derivatives with cellulose can develop antibacterial fiber with little skin reaction. Basing on the similar molecular structures of chitosan and cellulose, Seo et al prepared an antibacterial fiber CHITOPOLY composed of polynosic and chitosan microparticles with a mean size < 5 μm which were blended in ripening viscose via a mechanical blend method [11–14]. We reported a chitosan/*N*,*O*-CMCh/viscose rayon hybrid fiber, which had satisfying physical properties and exhibited excellent antibacterial activity against *Escherchia coli, Staphylococcus aureus* and *Candida albicans*. Moreover, the good moisture-retentivity of viscose rayon also remained after the addition of chitosan [15].

In our previous study, for introducing the environment friendly cellulose spinning process for antibacterial cellulose-based fiber, *O*-CMCh aqueous solution (A) and EACS aqueous solution (B) were blended with cellulose NMMO/H_2O solution and two types of chitosan derivative/cellulose antibacterial blend films (A and B) were prepared. Both Film A and B exhibited satisfying antibacterial activity against *E. coli* even the concentration was only 1 wt%. Rheological property is crucial for spinning. In this paper, *O*-CMCh aqueous solution (I) and EACS emulsion (II) were blended with cellulose NMMO/H_2O solution, and corresponding polyblends (Polyblend I and II) were prepared. The rheology of the three fluids, cellulose solution, Polyblend I and II, was investigated.

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Experimental

Materials

Cellulose was obtained from Tianjin Rayon Factory (Tianjin, China). Its viscosity-average degree of polymerization (DP) was 612, which was determined in cupriethylene diamine solution at 25 °C [16]. Chitosan (molecular weight 1.08×10^6; the degree of deacetylation 0.85), provided by Qingdao Medicine Institute, China, was depolymerized via γ irradiation degradation to a lower molecular weight of 2.0×10^5 [17]. *O*-CMCh and EACS were prepared in our previous study. *N*-methylmorpholine-*N*-oxide (NMMO) aqueous solution (50 wt%) was purchased from BASF, Germany.

Preparation of cellulose solution and Polyblends

10 g Cellulose was pulverized and dipped in 200 mL NMMO/H_2O (50 wt%), heated to 100 °C and stirred for 30 min in vacuum state. Then the cellulose was filtered and dissolved in NMMO/H_2O solution under stirring.

Polyblend I and II were prepared as follows: 5 g chitosan derivative powder was dissolved in 90 g de-ionized water. A certain amount of solution was drip fed to cellulose solution under violent stirring to get polyblend in which chitosan derivative/cellulose = 3/100 (w/w).

Rheological measurement

The rheological properties of cellulose NMMO/H_2O solution, Polyblend I and II were performed on the REOLOGICA Stresstech revolving rheometer (cone-plate diameters 30 mm and cone angles 1°). Rheological measurements were carried out at different temperatures.

Results and discussion

Rheological property is essential for spinning. Many factors e.g. additives and temperature may affect the rheological property of the spinning solution. Figure 1 shows the shear stress (τ) $\sim$ shear rate($\dot{\gamma}$) and $\lg \tau \sim \lg \dot{\gamma}$ curves of the three systems: cellulose NMMO/H_2O solution, Polyblend I and II. From Fig. 1 it can be clearly seen that all of the three fluids are non-Newtonian fluid. Their viscosity decreases along with the increase of shear rate.

It is reported that cellulose NMMO/H_2O solution is characterized as a power-law fluid [18]. Thus, it's shear stress and shear rate obey the following equation:

$$\tau = \eta \dot{\gamma}^{\mathrm{n}} \qquad (1)$$

where η is the viscosity and n is the power-law index. When *O*-CMCh or EACS aqueous solution is added to the cellulose NMMO/H_2O solution, the power-law curve is preserved. The relations between $\lg \tau$ and $\lg \dot{\gamma}$ of the three systems are shown in Fig. 1 too. All of the $\lg \tau \sim \lg \dot{\gamma}$ curves give high degree of linear correlation. The slope of the straight line represents the power-law index of the fluid at that temperature. Power-law index is an important parameter in the spinning process. Raising power-law index can make the spinning solution exhibit closer property to Newtonian fluid, and then improve the spinnability. Table 1 gives power-law indexes of the three fluids at different temperatures. The power-law indexes of Polyblend I stemmed from *O*-CMCh aqueous solution are higher than those of cellulose solution at most experimental temperatures, and Polyblend II which was made by blending EACS aqueous solution with cellulose solution gives even higher power-law indexes. Moreover, for all the three systems, the higher the temperature is, the higher the

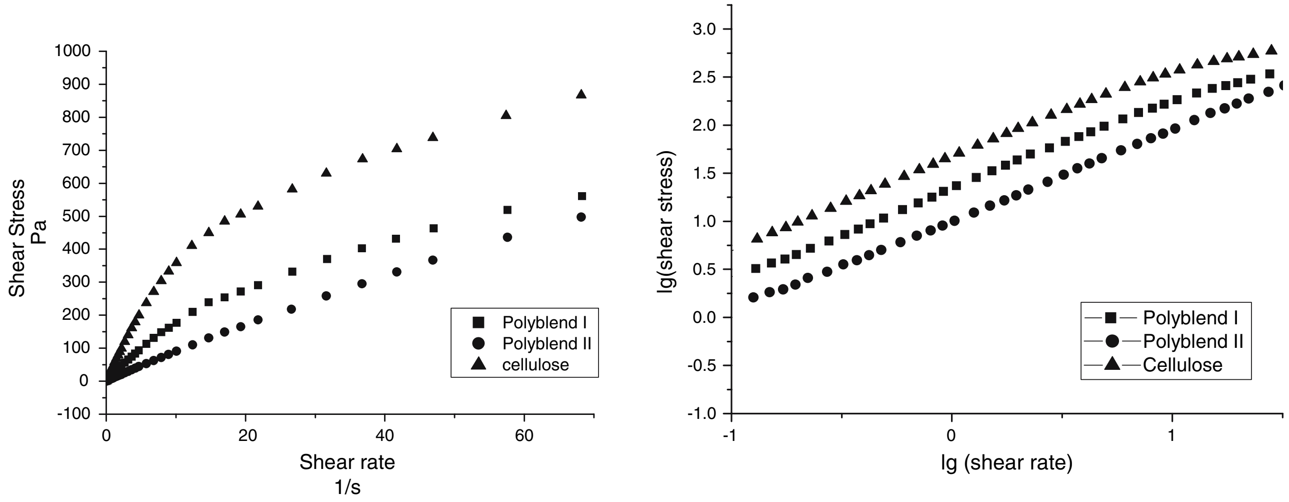

Fig. 1 Shear stress versus shear rate curves of the three dopes(363 K)

Table 1 Power-law indexes values of the spinning dopes at different temperatures

Temperature		353 K	363 K	373 K	383 K
Power-law indexes (n)	Cellulose	0.811	0.796	0.857	0.807
	Polyblend I	0.777	0.802	0.929	0.844
	Polyblend II	0.796	0.852	0.890	0.928

power-law index is, below 373 K. Along with the rise of temperature, water is vaporized, which results in the errors of test.

Rectified shear rate ($\dot{\gamma}'$) and apparent viscosity (η_a) can be calculated as follows:

$$\dot{\gamma}' = \dot{\gamma}\frac{(3n+1)}{4n} \tag{2}$$

$$\eta_a = \frac{\tau}{\dot{\gamma}'} \tag{3}$$

The apparent viscosity of the three systems at different shear rate and temperature are shown in Fig. 2. The three fluids display close apparent viscosities in the full shear rate scale under this experimental condition. In our previous study, we reported that *O*-CMCh existed as microparticles in Polyblend I . The diameters of *O*-CMCh microparticles in Polyblend I are less than 1 μm [19]. While Polyblend II has lower apparent viscosity than Polyblend I, in other words, the dispersion degree of EACS in Polyblend II is much better than *O*-CMCh in Polyblend II. Cellulose solution can be characterized by an instant quasi-network-structure [20]. Intermolecular force and macromolecule entanglement result in a great number of instant physicocrosslinking sites. When a certain shear stress is exerted on the solution, the physical networks are dissociated and macromolecular chains oriented. Thus the viscosity decreases with an increase in shear rate.

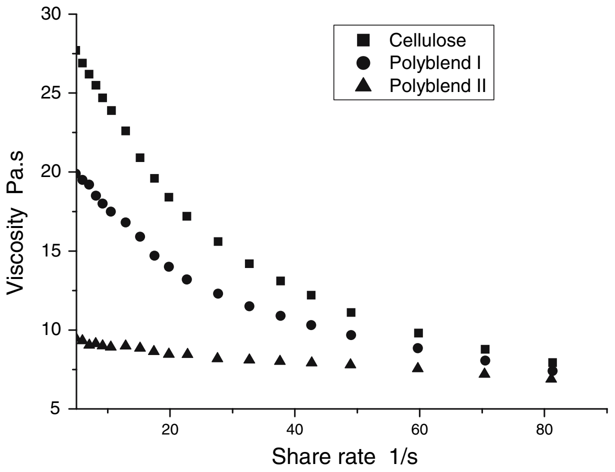

Fig. 2 Viscosity versus shear rate curves of the three dopes(363 K)

The relations between apparent viscosity and shear rate are similar for all the three systems. (c.f. Fig. 2) It is benefit to choose a suitable shear rate for spinning. If the shear rate is too low, the apparent viscosity shows an excessive sensitivity on the undulation of the shear rate, which may result in fluctuation of the fiber quality. On the other hand, if the shear rate is too high, energy will be expense. So from the angle of shear rate, one can select the initiate stage of the apparent viscosity platform to spin.

Structural viscosity index ($\Delta\ \eta$), defined as follows, is another important parameter of spinning solution:

$$\Delta\eta = -\left(\frac{\mathrm{d}\lg\eta_a}{\mathrm{d}\sqrt{\dot{\gamma}'}}\right) \times 100 \tag{4}$$

Structural viscosity index demonstrates the degree of structuralizing of the spinning solution. As mentioned above, intermolecular force and molecule entanglement lead to a great number of instant physicocrosslinking sites in cellulose solution. These crosslinking sites may counterwork the orientation of macromolecules during spinning process and thus affect the fiber quality. Reducing Structural viscosity index can weaken the structuralizing tendency of the spinning solution, and therefore improve the spinnability.

Because all of the three fluids are shear thinning fluids, their Δ^{η} are always greater than 0. Δ^{η} at a certain shear rate can be regarded as the slope of the tangent at that shear rate point.

Suppose $y = -\lg\eta_a$ and $x = \sqrt{\dot{\gamma}'}$, one can fit the above $-\lg\eta_a \sim \sqrt{\dot{\gamma}'}$ curves with cubic polynomial as follows:

$$y = ax^3 + bx^2 + cx + d \tag{5}$$

Table 2 shows the results of the cubic polynomial fitting of the three fluids at different temperatures. The cubic polynomial fitting for the curves obtained under this experimental conditions give high accuracy because all of the correlation coefficients (r^2) almost equal 1.

Deduce Eq. 5 one can get:

$$\frac{\mathrm{dy}}{\mathrm{d}x} = 3ax^2 + 2bx + c \tag{6}$$

then:

$$\Delta\eta = -\left(\frac{\mathrm{d}\lg\eta_a}{d\sqrt{\dot{\gamma}'}}\right) \times 100 = \left(3a\sqrt{\dot{\gamma}'}^2 + 2b\sqrt{\dot{\gamma}'} + c\right) \times 100 \tag{7}$$

Hence the Δ^{η} at a certain $\sqrt{\dot{\gamma}'}$ point can be calculated. Figure 3 illustrates the $\Delta^{\eta} \sim \sqrt{\dot{\gamma}'}$ curves of the three fluids

Table 2 The results of the cubic polynomial fitting of the three fluids at different temperatures

Object	Temp. (K)	*a*	*b*	*c*	*d*	r^2
Cellulose NMMO/H_2O solution	353	−7.0238E−4	0.00985	0.06407	−1.89764	0.99642
	363	−1.5389E−4	0.0075	0.05251	−1.94472	0.99544
	373	−1.8309E−5	0.00584	0.02329	−1.68039	0.98612
	383	−8.2305E−4	0.01366	0.01419	−1.53215	0.99838
Polyblend I	353	−4.072E−4	0.00916	0.05718	−1.965	0.99547
	363	−7.0238E−4	0.00985	0.06407	−1.89764	0.99642
	373	4.853E−4	−0.00376	0.02488	−0.97849	0.93742
	383	−6.3515E−4	0.01021	0.01583	−1.37361	0.99359
Polyblend II	353	−9.5169E−4	0.01616	0.00757	−1.70146	0.99585
	363	−5.6914E−4	0.01131	3.18E−5	−1.4401	0.9857
	373	3.880E−4	−0.00192	0.03003	−1.23234	0.9724
	383	8.583E−4	−0.01337	0.07731	−1.07983	0.92992

at different temperatures. In Polyblend I and II, Chitosan derivative microparticles disperse uniformly within the system, obstruct the entanglement of the cellulose macromolecule chains, and, to a certain extend, decline the intermolecule force. Therefore, the instant quasi-network-structure is partially destroyed. Tensile strength and elongation of the blend films in the dry state are given in Fig. 4. Both of them show a continuous little decrease with the content of EACS increase.

The addition of Chitosan derivative reduces the Δ^{η} of the fluid. Because Polyblend I has a better *O*-CMCh dispersion degree, it shows the lowest Δ^{η} among the three fluids. Δ^{η} is also affected by temperature. (c.f. Fig. 3) For cellulose solution and Polyblend II, Δ^{η} decreases with the increase of the temperature. For Polyblend I, however, Δ^{η} shows a minimum value, Polyblend I gives the lowest Δ^{η} at 373 K. (c.f. Fig. 3) So 373 K could be regarded as the most befitting temperature for the polyblend spinning from the angle of Δ^{η}.

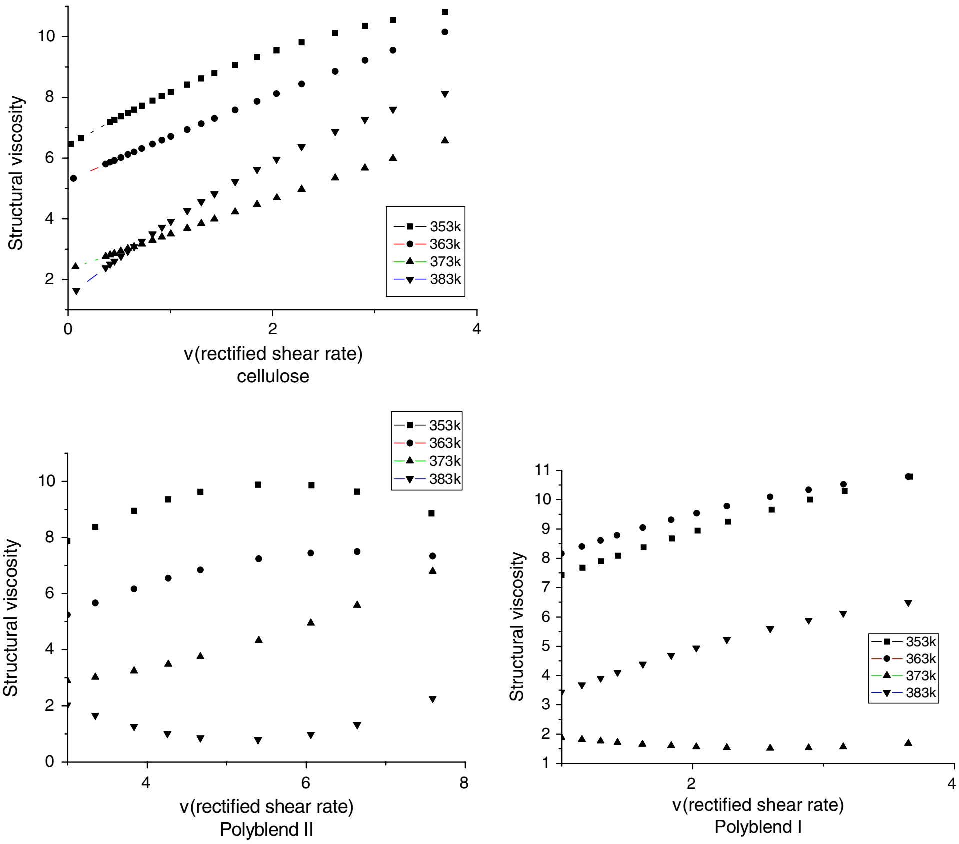

Fig. 3 $\Delta^{\eta} \sim \sqrt{\dot{\gamma}}$ plots of three spinning dopes

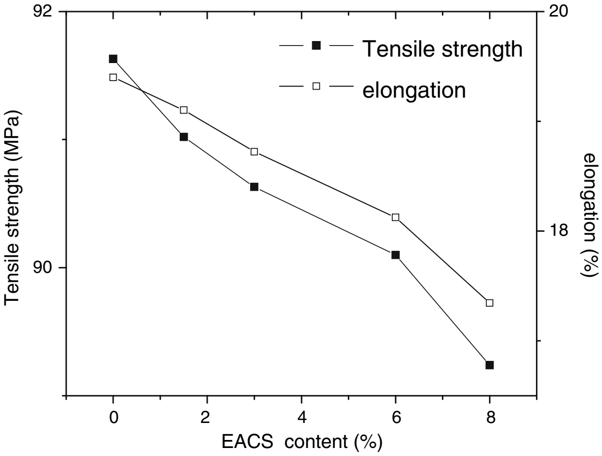

Fig. 4 Mechanical properties of blend films with different EACS content

Conclusions

Cellulose NMMO/ H_2O solution is characterized as a power-law fluid. When *O*-CMCh or EACS aqueous solution is added to the cellulose solution, the power-law curve is preserved. The power-law indexes (n) of all the three fluids, cellulose solution, Polyblend I and II, rise along with the temperature. Polyblend I displays an n close to but a little higher than that of cellulose solution, while Polyblend II shows a higher power-index than the other two fluids. Apparent viscosity η_a of all the three fluids are close to each other and decrease along an increase in temperature. Polyblend I and II display a lower Structural viscosity index (Δ^{η}) than cellulose solution. Moreover, this phenomenon is much obvious in Polyblend II.Cellulose solution's Δ^{η} drops with enhancing temperature, while Δ^{η} of both Polyblend I show similar minimum values at ca. 373 K.

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