

Rheological Study on *O*-Carboxymethylated Chitosan/Cellulose Polyblends from LiCl/*N,N*-Dimethylacetamide Solution

Zhi Li, Xupin Zhuang, Xiaofei Liu, Yunlin Guan, Kangde Yao

School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

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ABSTRACT: An *O*-carboxymethylated chitosan (*O*-CMCh) water solution (I) and *N,N*-dimethylacetamide (DMAc) emulsion (II) were blended with a cellulose LiCl/DMAc solution, and corresponding polyblends (Polyblends I and II) were obtained. The rheology of the three fluids, that is, the cellulose solution and Polyblends I and II, was investigated. The cellulose solution was characterized by a power-law fluid. When an *O*-CMCh water solution or DMAc emulsion was added to the cellulose solution, the power-law curve was preserved. The power-law indexes (n) of all three fluids increased along with the temperature. Polyblend I displays an n close to but a little higher than that of the cellulose solution, while Polyblend II shows a much higher power index than those of the

other two fluids. The values of the apparent viscosity (η_a) for all the three fluids are close and decrease along with an increase in the temperature. Adding *O*-CMCh microparticles into Polyblends I and II results in a decrease in the structural viscosity index ($\Delta\eta$) in comparison to that of the cellulose solution, and this effect is very obvious for Polyblend I. A cellulose solution's $\Delta\eta$ declines with the augmentation of temperature, while the $\Delta\eta$'s of both Polyblends I and II show minimum values at about 323 K. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1719–1725, 2003

Key words: rheology; cellulose; *O*-carboxymethylated chitosan; polyblend; spinnability

INTRODUCTION

Cellulose fiber is a favorite undergarment material and it is the most appropriate fiber to be made into antibacterial next-to-skin fabrics due to the safety to the human body and the comfort that results from its high moisture retentivity. Although 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 by-product during the process is a notorious air pollutant. Therefore, several promising solvent systems, for example, LiCl/*N,N*-dimethylacetamide (DMAc), dimethylformamide (DMF), and *N*-methylmorpholine *N*-oxide (NMMO)/H₂O, were utilized and corresponding fibers were developed.^{1–5}

Chitosan is not only one of the most naturally occurring biopolymers, but it is also a biocompatible polymer reported to exhibit a great variety of useful biological properties.^{6–8} Recently, the antibacterial and antifungal activities of chitosan have held great interest. Chitosan inhibits the growth of a wide variety of bacteria and fungi,⁹ showing a broad spectra of

antibacterial activities, a high killing rate, and low toxicity toward mammalian cells.^{10,11} Some chitosan derivatives exhibit even stronger antibacterial activity than that of chitosan. *O*-Carboxymethylated chitosan (*O*-CMCh) provides intensive antibacterial activity.⁹

Blending chitosan and its derivatives with cellulose can develop antibacterial fiber with little skin reaction. Based 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 less than 5 μm , which were blended in a ripening viscose via a mechanical blend method.^{12–15} 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.¹⁶

In our previous study,¹⁷ which introduced an environmental friendly cellulose spinning process for antibacterial cellulose-based fiber, an *O*-CMCh aqueous solution (A) and a DMAc emulsion (B) were blended with a cellulose LiCl/DMAc solution, and two types of *O*-CMCh/cellulose antibacterial blend films (A and B) were prepared. SEM observations indicated that the *O*-CMCh/cellulose polyblend displayed a heterogeneous microstructure. *O*-CMCh microdomains were

Correspondence to: Y. Guan (guanyl@tju.edu.cn).

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dispersed in the cellulose matrix of the blend film. Film A showed a better dispersion of the *O*-CMCh microdomains than did film B. Both films A and B exhibited satisfying antibacterial activity against *E. coli* even when the *O*-CMCh concentration was only 2 wt %. The rheological property is crucial for spinning. In this article, an *O*-CMCh aqueous solution (I) and DMAc emulsion (II) were blended with a cellulose LiCl/DMAc solution, and corresponding polyblends (Polyblends I and II) were prepared. The rheology of the three fluids, the cellulose solution and Polyblends I and II, was investigated.

EXPERIMENTAL

Materials

Cellulose was obtained from the Tianjin Rayon Factory (Tianjin, China). Its viscosity-average degree of polymerization (DP) was 612, which was determined in a cupriethylene diamine solution at 25°C.¹⁸ Chitosan (molecular weight 1.08×10^6 ; degree of deacetylation 0.85), provided by the Qingdao Medicine Institute (Qingdao, China), was depolymerized via γ -irradiation degradation to a lower molecular weight of 2.0×10^5 . To synthesize *O*-CMCh, 15 g chitosan and 9 g monochloroacetic acid were suspended in 150 mL of a sodium hydroxide solution (42%, by weight). The system was reacted at 0°C for 48 h and then the pH was adjusted to 1.0 with hydrochloric acid. After filtration, the solid product was washed with methanol twice. The *O*-CMCh yielded was dried in an oven at 60°C. The degree of substitution determined by pH titration was 0.86.¹⁹

Preparation of cellulose solution and polyblends

Ten grams of cellulose was pulverized and dipped in 200 mL DMAc, heated to 150°C, and stirred for 30 min. Then, the cellulose was filtered and dissolved in an LiCl/DMAc solution (LiCl concentration is 9 wt %) under stirring.

Polyblend I and II were prepared as follows:

Polyblend I: Ten grams of an *O*-CMCh powder was dissolved in 90 g deionized water. A certain amount of the *O*-CMCh water solution was dripped into the cellulose solution under violent stirring to obtain a polyblend in which *O*-CMCh/cellulose = 2/100 (w/w).

Polyblend II: The pH of the *O*-CMCh aqueous solution was adjusted to 14 with 1M NaOH under vigorous agitation to evolve *O*-CMCh and an *O*-CMCh water emulsion was obtained. This emulsion was washed with DMAc several times so that water could be replaced by DMAc and an *O*-CMCh DMAc emulsion was obtained. As with

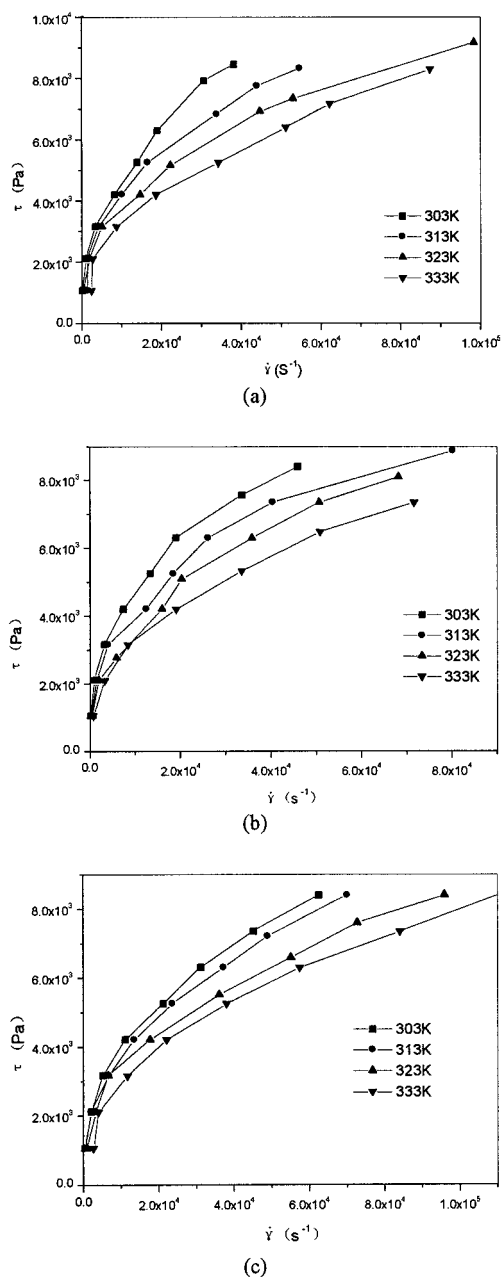


Figure 1 Shear stress versus shear rate curves of the three fluids: (a) cellulose solution; (b) Polyblend I; (c) Polyblend II.

the *O*-CMCh water solution, a certain amount of the DMAc emulsion was also blended with the cellulose solution and then Polyblend II (*O*-CMCh/cellulose = 2/100, w/w) was obtained.

Rheological measurement

The rheological properties of the cellulose LiCl/DMAc solution and Polyblends I and II were performed on a capillary rheometer with a length-to-diameter (l/d) ratio of 47.75/1. Rheological measurements were carried out at different temperatures.

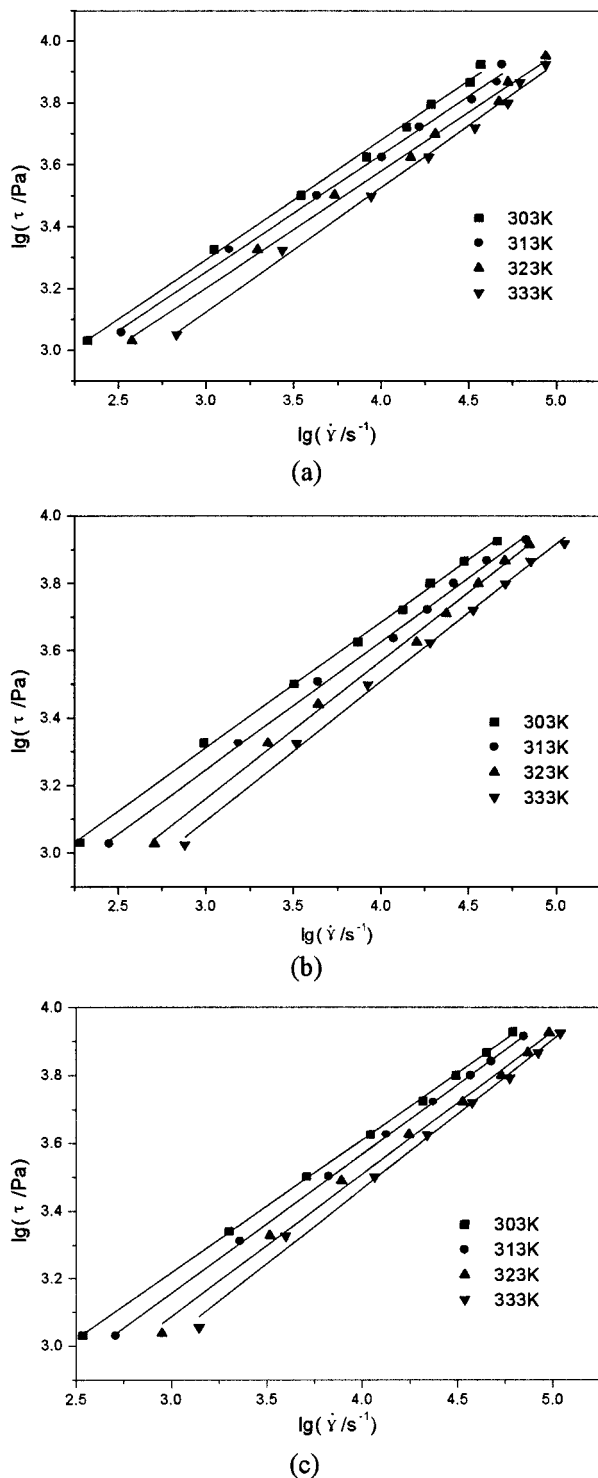


Figure 2 lg τ–lg γ̇ curves of the three systems: (a) cellulose solution; (b) Polyblend I; (c) Polyblend II.

RESULTS AND DISCUSSION

The rheological property is essential for spinning. Many factors, for example, additives and temperature, may affect the rheological property of the spinning solution. Figures 1 and 2 show the shear stress (τ)–shear rate (γ̇) and lg τ–lg γ̇ curves of the three systems:

the cellulose LiCl/DMAc solution and Polyblends I and II. From Figure 1, it can be clearly seen that all the three fluids are non-Newtonian fluids. Their viscosity decreases along with increase of the shear rate.

Wang et al. reported that a cellulose LiCl/DMAc solution is characterized as a power-law fluid.²⁰ Thus, its shear stress and shear rate obey the following equation:

$$\tau = \eta \dot{\gamma}^n \tag{1}$$

where η is the viscosity and n is the power-law index. When the O-CMCh water solution or DMAc emulsion is added to the cellulose solution, the power-law curve is preserved. The relations between lg τ and lg γ̇ of the three systems are shown in Figure 2. All the lg τ–lg γ̇ curves give a high degree of linear correlation. The slope of the straight line represents the power-law index of the fluid at that temperature. The power-law index is an important parameter in the spinning process. An increasing power-law index can make the spinning solution exhibit a closer property to the Newtonian fluid and then improve the spinnability.

Table I gives power-law indexes of the three fluids at different temperatures. The power-law indexes of Polyblend I stemming from the O-CMCh water solution are higher than those of the cellulose solution at all the experimental temperatures, and Polyblend II, which was made by blending the O-CMCh DMAc emulsion with the cellulose solution, gives even higher power-law indexes. Moreover, for all three systems, the higher the temperature, the higher is the power-law index, and this law acts much more markedly in Polyblend II.

The rectified shear rate (γ̇') 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 rates and temperatures are shown in Figure 3. The three fluids display close apparent viscosities in

TABLE I
Power-law Indexes of the Three Systems at Different Temperatures

Systems	Power-law indexes			
	303 K	313 K	323 K	333 K
Cellulose solution	0.38	0.38	0.38	0.40
Polyblend I	0.37	0.38	0.41	0.41
Polyblend II	0.39	0.41	0.42	0.44

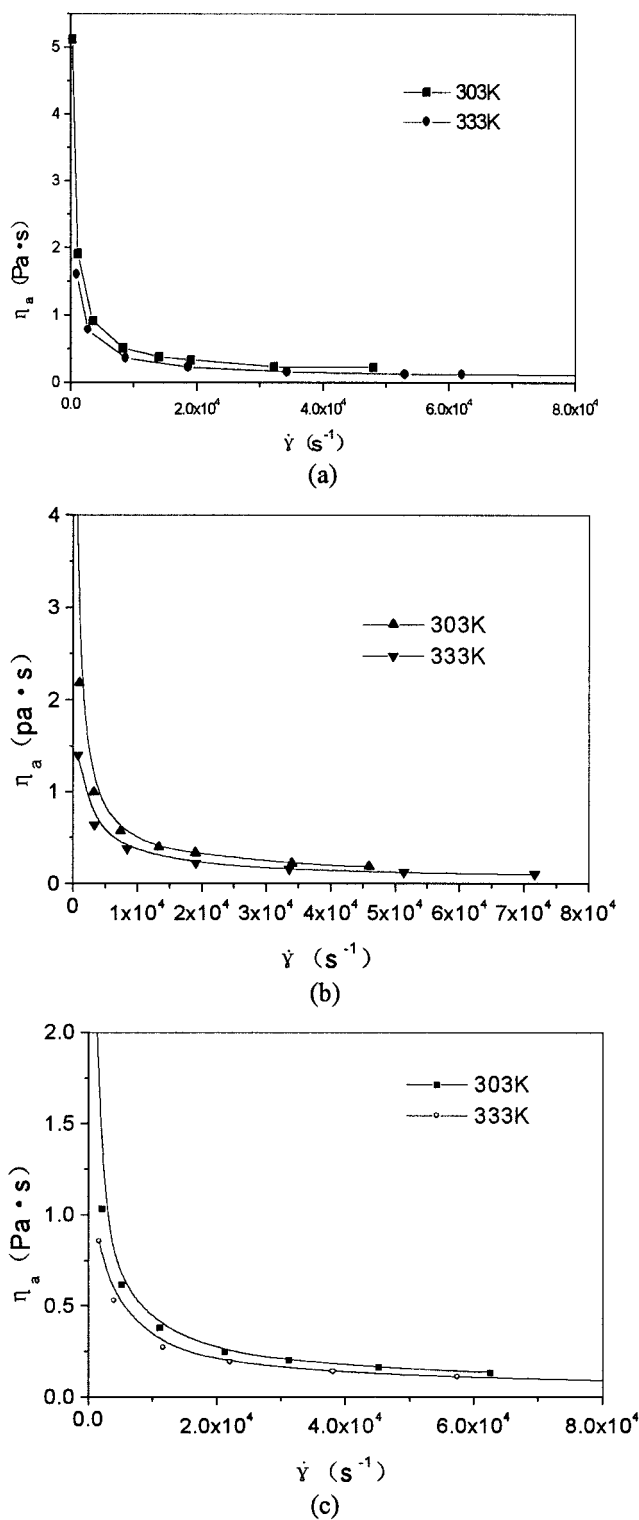


Figure 3 Apparent viscosities versus shear rates: (a) cellulose solution; (b) Polyblend I; (c) Polyblend II.

the full shear rate scale under this experimental condition. In our previous study,¹⁷ we reported that *O*-CMCh existed as microparticles in both Polyblends I and II. The diameters of the *O*-CMCh microparticles in Polyblend I are less than 1 μm , which are smaller than

those in Polyblend II (6–10 μm). In other words, the dispersion degree of *O*-CMCh in Polyblend I is much better than that in Polyblend II. The cellulose solution can be characterized by an instant quasi-network-structure. Intermolecular force and macromolecule entanglement result in a great number of instant physico-crosslinking sites. When a certain shear stress is

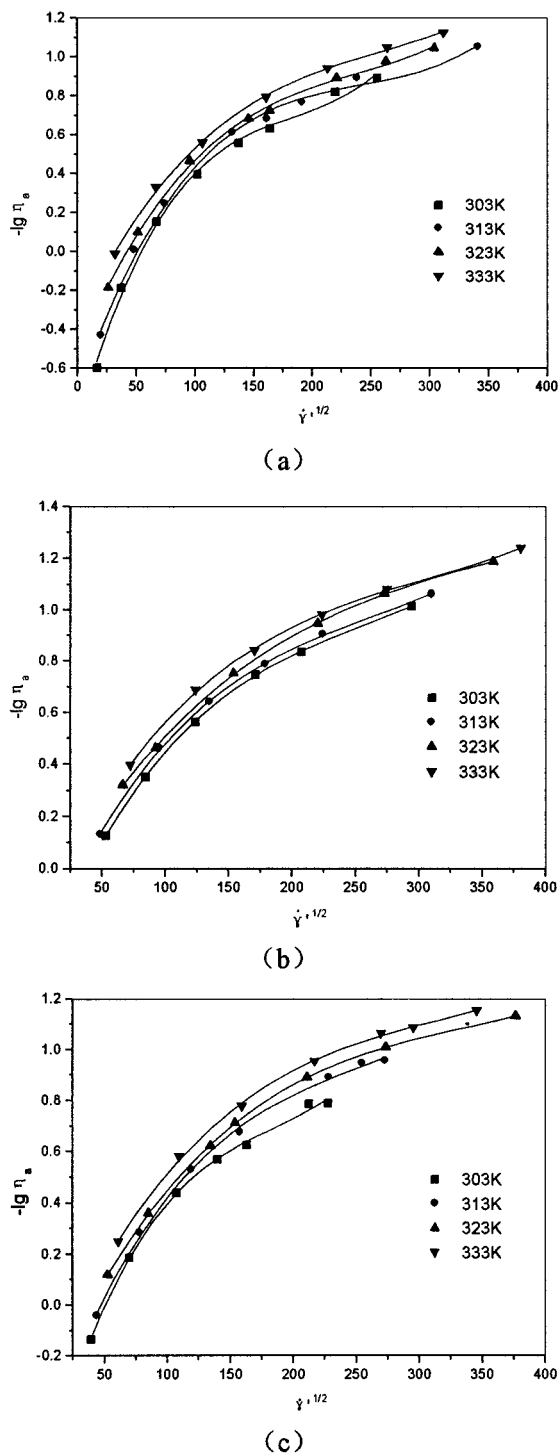
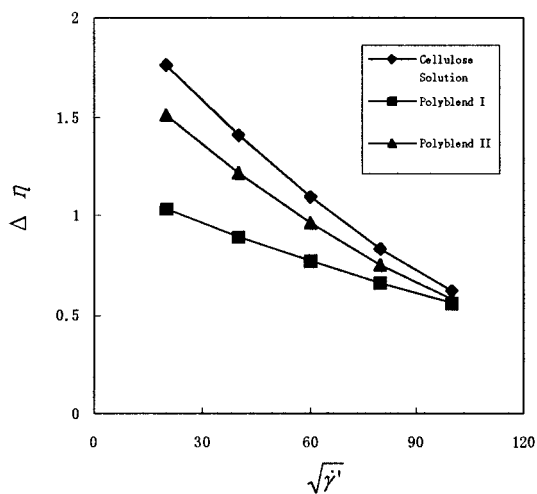


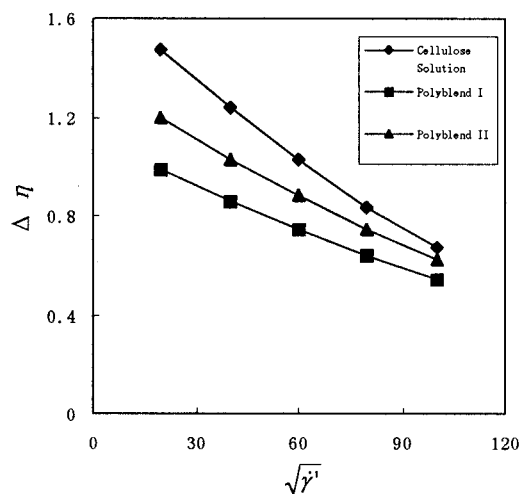
Figure 4 $-\lg \eta_a$ versus $\sqrt{\dot{\gamma}}$ of (a) cellulose solution, (b) Polyblend I, and (c) Polyblend II at different temperatures.

TABLE II
Results of the Cubic Polynomial Fitting of the Three Fluids at Different Temperatures

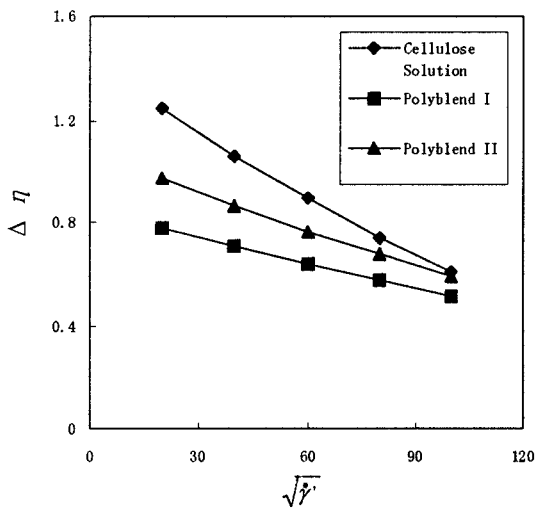
Fluid	Temperature (K)	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>r</i> ²
Cellulose solution	303	1.94E-07	-1.07E-04	0.0217	-0.895	0.99672
	313	9.18E-08	-6.66E-05	0.01724	-0.71861	0.99676
	323	7.48E-08	-5.34E-05	0.0145	-0.52326	0.99867
	333	5.33E-08	-4.14E-05	0.0125	-0.36182	0.99909
Polyblend I	303	4.92E-08	-3.80E-05	0.01172	-0.39729	0.99993
	313	4.51E-08	-3.57E-05	0.01122	-0.33403	0.99973
	323	1.76E-08	-1.95E-05	0.00852	-0.16884	0.99981
	333	2.97E-08	-2.73E-05	0.00984	-0.18093	0.99934
Polyblend II	303	1.55E-07	-8.59E-05	0.01827	-0.72831	0.99825
	313	6.13E-08	-4.67E-05	0.01373	-0.55022	0.9986
	323	2.87E-08	-2.89E-05	0.0108	-0.37332	0.9999
	333	3.22E-08	-3.05E-05	0.01094	-0.30835	0.9992



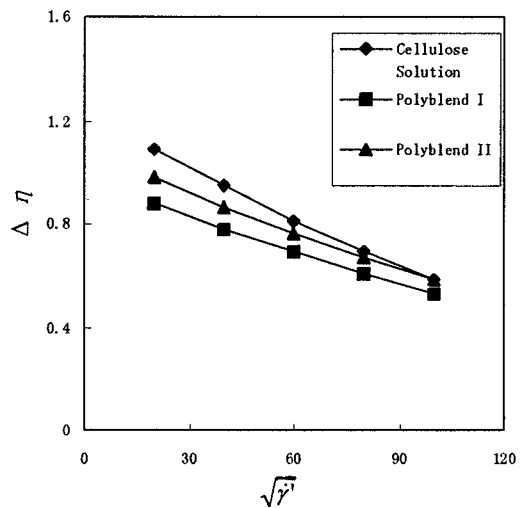
(a) 303K



(b) 313K



(c) 323K



(d) 333K

Figure 5 $\Delta\eta$ versus $\sqrt{\dot{\gamma}}$ curves of three fluids at different temperatures.

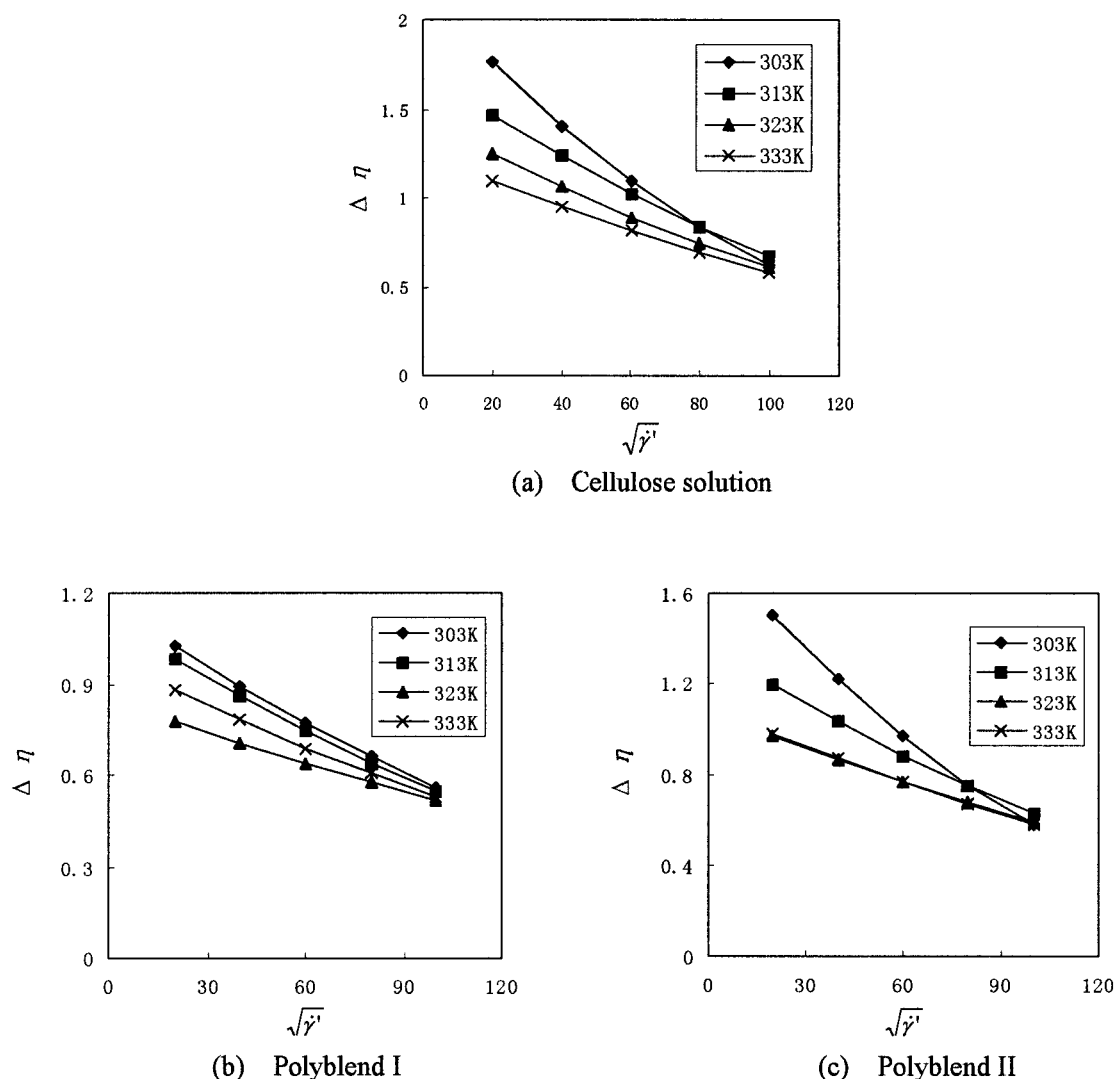


Figure 6 Effect of temperature on structural viscosity index of the three fluids.

exerted on the solution, the physical networks are dissociated and macromolecular chains are oriented. Thus, the viscosity decreases with increase in the shear rate.

The relations between the apparent viscosity and the shear rate are similar for all three systems. (cf. Fig. 3) It is of 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 expensive. So, from the angle of the shear rate, one can select the initial stage of the apparent viscosity platform to spin.

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

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

The 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 physico-crosslinking sites in the cellulose solution. These crosslinking sites may counteract the orientation of macromolecules during the spinning process and thus affect the fiber quality. Reducing the structural viscosity index can weaken the structuralizing tendency of the spinning solution and, therefore, improve the spinnability.

Figure 4 displays the $-\lg \eta_a - \sqrt{\dot{\gamma}'}$ curves of the cellulose solution and Polyblends I and II at different temperatures. Because all three fluids are shear-thinning fluids, their $\Delta\eta$ are always greater than 0. $\Delta\eta$, at a certain shear rate, can be regarded as the slope of the tangent at that shear rate point. Suppose that $y = -\lg \eta_a$ and $x = \sqrt{\dot{\gamma}'}$; then, one can fit the above $-\lg \eta_a - \sqrt{\dot{\gamma}'}$ curves with a cubic polynomial as follows:

$$y = ax^3 + bx^2 + cx + d \quad (5)$$

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

By deducing eq. (5), one can get

$$\frac{dy}{dx} = 3ax^2 + 2bx + c \quad (6)$$

then

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

Hence, the $\Delta\eta$ at a certain point $\sqrt{\dot{\gamma}'}$ can be calculated. Figure 5 illustrates the $\Delta\eta$ - $\sqrt{\dot{\gamma}'}$ curves of the three fluids at different temperatures. In Polyblends I and II, O-CMCh microparticles disperse uniformly within the system, obstruct the entanglement of the cellulose macromolecule chains, and, to a certain extent, decrease the intermolecular force. Therefore, the instant quasi-network structure is partially destroyed. The addition of O-CMCh reduces the $\Delta\eta$ of the fluid. Because Polyblend I has a better O-CMCh dispersion degree, it shows the lowest $\Delta\eta$ among the three fluids.

$\Delta\eta$ is also affected by the temperature. (cf. Fig. 6) For the cellulose solution, $\Delta\eta$ decreases with increase of the temperature. For Polyblends I and II, however, $\Delta\eta$ shows a minimum value. In Figure 6(c), which represents Polyblend II, $\Delta\eta$ at 323 and 333 K are almost the same, while Polyblend I gives the lowest $\Delta\eta$ at 323 K [cf. Fig. 6(b)]. So, 323 K could be regarded as the most fitting temperature for polyblend spinning from the angle of $\Delta\eta$.

CONCLUSIONS

A cellulose solution was characterized as a power-law fluid. When an O-CMCh water solution or DMAc emulsion was added to the cellulose solution, the power-law curve was preserved. The power-law in-

dices (n) of all three fluids, the cellulose solution and Polyblends I and II, increase along with the temperature. Polyblend I displays an n close to but a little higher than that of the cellulose solution, while Polyblend II shows a higher power index than that of the other two fluids. The apparent viscosity (η_a) of all three fluids are close to each other and decrease along with an increase in temperature. Polyblends I and II display a lower structural viscosity index ($\Delta\eta$) than that of the cellulose solution. Moreover, this phenomenon is very obvious in Polyblend I, in which the O-CMCh microparticles show a better dispersion than that of Polyblend II. The cellulose solution's $\Delta\eta$ decreases with an enhancing temperature, while the $\Delta\eta$'s of both Polyblends I and II show similar minimum values at about 323 K.

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