NON-LINEAR VISCOELASTIC BEHAVIOR OF NOVEL REGENERATED CELLULOSE FIBER IN DRY AND WET CONDITION

SHUAI ZHANG, WEN-CONG WANG,* FA-XUE LI* and JIAN-YONG YU**

College of Materials Science and Engineering, Shanghai 201620, China
**College of Textiles, Donghua University, Shanghai 201620, China*
***Modern Textile Institute, Donghua University, Shanghai 200051, China*

Received July 8, 2012

Viscoelastic models were employed to analyze the mechanical properties of novel regenerated cellulose fiber from NaOH complex solution. The stress-strain curves of the dry and wet fiber were fitted. The models were composed of a Maxwell element, linear spring and non-linear spring. The tested results indicate that the regenerated cellulose fibers exhibit better tensile properties in dry and wet condition than those of viscose rayon. It can be explained by the high molecular weight of novel regenerated cellulose fiber (~1.1×10^5), compared to that of viscose rayon (~5×10^4), as well as high degree of crystallinity (60~65% to 30~40%).

Keywords: non-linear, viscoelastic, cellulose fiber, orientation, wet condition

INTRODUCTION

Materials of biological origin contain natural polymers, and therefore they can be expected to exhibit viscoelastic behavior. For example, cellulose is of biological origin and consists of natural macromolecules.[1] The mechanical properties of cellulose fiber play a phenomenal role in the processability and in the quality of the final products. In our previous work, NaOH/thiourea/urea aqueous solvent was proved to be powerful in dissolving cellulose and the novel regenerated cellulose fiber has been successfully prepared by using the wet-spinning approach.[2-3]

Tensile properties are the most important characteristic of textile fiber, affecting the fiber strength and spinning performance and the properties of the final product. Moreover, cellulose or its regenerated fibers are viscoelastic and their mechanical behavior can be adjusted using mechanistic models consisting of elements such as Hook springs, Newton dashpots, unidirectional friction elements and inertional elements, which could simulate the mechanical behavior of the material under mechanical stress when correctly combined.[4-5] The Vangheluwe and the Zurek models have been used to describe the mechanical behavior of cotton yarns.

It is known that most hydrophilic fibers show poor wet mechanical behavior because of the moisture included in them. However, little has been reported in the literature on the mechanical model of the regenerated cellulose fiber, especially in wet condition. The tensile property of the fiber in wet condition is a very important performance parameter for the regenerated cellulose fiber. It would indeed influence the processing characteristics. In order to describe the mechanical properties of regenerated cellulose fibers in dry and wet condition, we have developed a non-linear viscoelastic model containing limited numbers of elements, which would be helpful for predicting the tensile properties of the fibers.

EXPERIMENTAL

Materials

Cellulose samples (cotton lint pulp, *DP* = 620) were supplied by Xinxiang Bailu Chemical Fiber Co. Ltd. (Henan, China). All the chemical reagents were of analytic grade and used as received.

Preparation of cellulose fiber

24 g cellulose pulps (the viscosity-average

molecular weight was of 1.1×10^4 g/mol) were dispersed into 400 g solvent (weight ratio of NaOH:thiourea:urea:H_2O equal to 8:6.5:8:77.5) precooled to -8 °C, followed by vigorous stirring for 3 min at room temperature. Thereafter, further stirring was conducted for 7 min at a temperature of -2 °C to 0 °C. The resulted cellulose solution was filtered through 400 pore meshes, and then degassed by centrifuging at 4600 rpm for 5 min at 10 °C.

A laboratory scale wet-spinning apparatus was used to prepare regenerated cellulose fiber, as schematically shown in Fig. 1. The cellulose solution was introduced into the cylinder at room temperature. A pressure of 0.1 MPa was applied to the spinning dope to extrude it into a coagulation bath using a spinneret of 12 orifices, the orifice diameter (d) was of 0.1 mm. The 10 wt% H_2SO_4/12.5 wt% Na_2SO_4 aqueous solution was selected as the coagulation bath. The temperature of the coagulation bath was preset for 20 °C. The apparent jet stretch ratio (the ratio of the take-up velocity to the dope extrusion velocity) was of 90%, the fibers were subsequently washed in boiling water and further drawn up, while the post-drawing ratio was adjusted to 120%. After spinning and washing thoroughly, the blend fibers were gradually dried by a heating roller (surface temperature 65-80 °C) and wound on a spool.

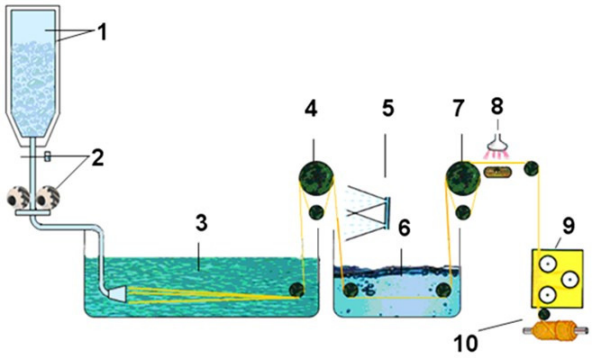

Figure 1: Scheme of multifilament spinning machine; 1 – a pressure extruder with a stainless cylinder having cooling jacket; 2 – gauging device; 3 – coagulation bath (12.5 wt% H_2SO_4/10 wt% Na_2SO_4 aqueous solution, 20 °C); 4 – Nelson-type roller; 5 – water spray device; 6 – washing bath (hot water, 70 °C); 7 – post-drawing roller; 8 – post-treatment device (finishing oil bath); 9 – heating roller; 10 – take-up device

Characterization and simulation

CP/MAS ^{13}C-NMR spectra were recorded on a Bruker MSL-300-type FT-NMR. The degree of breakdown of intramolecular hydrogen bonds (value X_{am}) at C(3)-hydroxyl groups in the glucopyranose unit was defined according to Kamide and co-workers and estimated using equations proposed in the literature,[6,7] that is, the relative amount of the higher field peaks $X_{am}(C_3)$ of the C(4) carbon peaks was estimated from eq. (1):

$$X_{am}(C_3)=I_h(C4)/\{I_1\ (C4)+I_h(C4)\} \quad (1)$$

where I_1 and I_h denote peaks under the peaks centered at 87.9 and 84 ppm, respectively, and the line shape was approximated as of the Lorenzian type.

The stress-strain experiments were made using a universal tensile tester (LLy-06, Laizhou Electron Instrument Co. Ltd., China). According to ASTM D3822-01, the fiber samples were conditioned for 24 h in standard atmosphere, before testing the dry mechanical properties of the fiber. However, the assessment of wet mechanical properties of the fiber, as well as the CP/MAS ^{13}C-NMR test under wet conditions, were carried out after the fiber were immersed in distilled water at 20 °C for 3 minutes.

The gauge length was of 20 mm and the tensile speed was of 5 mm/min, the pre-tensile forces of dry fiber and wet fiber were determined to be of 0.08 cN/dtex and 0.04 cN/dtex according to their linear densities, respectively. The tester gave stress, strain, tensile curve and their averages from sixty observations automatically. All the experiments were made under atmospheric conditions of 20 °C and relative humidity of 60%.

In order to get a good fit, a representative sampling of the measured tensile curves is needed. Meridith's method[8] was used in the analysis process, that is, extracting the representative curve from five measured curves in which their breaking strength, breaking elongation and yielding point are nearest to the averages of the yarn. The average of the five curves is considered to be the representative curve.

Next, the viscoelastic model equations were calculated using the iteration procedures included in the non-linear regression methods. Finally, we calculated the model's parameters. Fitting aptness can be assessed by comparing the coefficient estimation R^2. The higher the coefficient (near to 1), the better the obtained fit.

RESULTS AND DISCUSSION

Modeling the viscoelastic behavior of fiber may involve using simple multiple-element models or more generalized integrated forms. Simple models contain limited numbers of

elements combined in a certain set-up. The two-element combinations include Voigt, or Kelvin and Maxwell models. The three-element models include the so-called standard solid model and other variations. The four-element models comprise Burger's model and other options. In the linear viscoelastic region, these models contain a limited number of constants, determined through various designed and controlled experiments. The more generalized integrated form is used for a more complete description of the material response.[9]

Theoretical model for stress-strain curves of regenerated cellulose fiber in dry condition

The stress-strain relationship of regenerated cellulose fiber (CF) is illustrated in Fig. 2. It can be found that the shape of the CF curve is a reversed S form, which can be classed as a typical stress-strain relationship of fiber. It can be characterized by three approximate regions, called the elastic region (linear region), yield region and reinforcement region. The stress-strain curve intersects the stress axis with an intercept that is equal to the pre-tension. This means that there should be a constant term in the model equation describing the curve. The straight line at lower elongation indicates that there exists a linear component in the model equation. Then slowly increasing of the stress with the increment of elongation in the yield region reveals the exponential relationship between the stress and elongation. The fast rise of stress in the reinforcement region demonstrates that the curve should be an equation of a higher degree. So a non-linear model that consists of a linear spring, a Maxwell element and a non-linear spring in parallel was proposed to investigate the stress-strain change trends of CF. As depicted in Fig. 3, the linear spring in the model is used to describe the Hookean region in the tensile curve at lower strain, the Maxwell element to illustrate the viscoelasticity, and the non-linear spring to characterize the non-linear mechanical properties of CF.

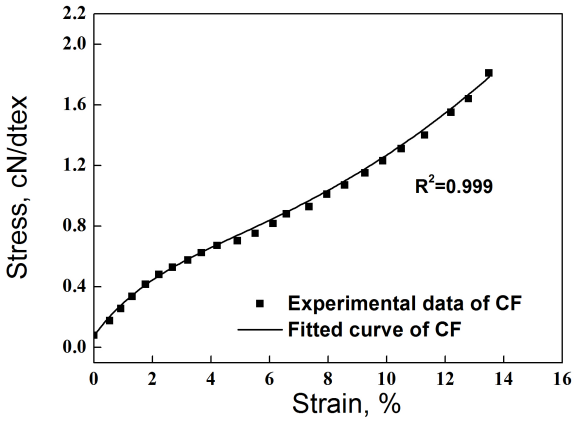

Figure 2: Experimental data and the fitted curve of regenerated cellulose fiber in dry condition

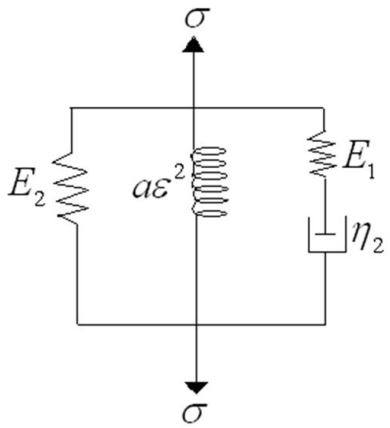

Figure 3: Non-linear viscoelasticity models for regenerated cellulose fiber in dry condition

In the proposed model for CF, a Maxwell element, a linear spring and a non-linear spring are placed in parallel. The Maxwell element consists of a linear spring and a Newton dashpot in series, where the spring of modulus E_1 is assumed to follow Hook's law and the dashpot is assumed to be filled with a Newtonian fluid of viscosity η_1. If the stress of the Maxwell element is σ_1 and its strain is ε_1, the differential equation describing its stress-strain behavior is given by:

$$\frac{d\varepsilon_1}{dt} = \frac{1}{E_1}\frac{d\sigma}{dt} + \frac{\sigma_1}{\eta_1} \quad (2)$$

for the linear spring of modulus E_2 in parallel with the Maxwell element, the stress-strain relationship is given by:

$$\sigma_2 = E_2\varepsilon_2 \quad (3)$$

where σ_2 and ε_2 are stress and strain of the linear spring. For the non-linear spring, we assume that the corresponding equation is quadratic:

$$\sigma_3 = a\varepsilon_3^2 \quad (4)$$

where σ_3 and ε_3 are stress and strain of the non-linear spring and a is the spring constant of the non-linear spring. Total stress σ of the yarn must equal the sum of the stresses in the Maxwell element, linear spring and non-linear spring, so that:

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3 \quad (5)$$

The total strain ε of the model is the same as that in Maxwell element, linear spring or non-linear spring. That is:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \quad (6)$$

Equations (2)-(6) provide a system of equations relating time, stress and strain of the proposed model. If the fiber is stretched at a constant rate of extension, $\varepsilon = \mathrm{k}t$, where k is a constant, and the initial condition $\sigma(0) = 0$, the solution of equations (2)-(6) is given by:

$$\sigma_{\mathrm{CF}} = E_2\varepsilon + \mathrm{a}\varepsilon^2 + \eta_1\mathrm{k}(1 - e^{-\frac{E_1\varepsilon}{\eta_1\mathrm{k}}}) \quad (7)$$

Considering the effect of the pre-tension (a_0 = 0.08 cN/dtex, following ISO 2062), a correction has to be made, since the strain of the fiber at this pre-tension is zero. Equation (7) needs to be revised as:

$$\sigma_{\mathrm{CF}} = \sigma_0 + E_2\varepsilon + \mathrm{a}\varepsilon^2 + \eta_1\mathrm{k}(1 - e^{-\frac{E_1\varepsilon}{\eta_1\mathrm{k}}}) \quad (8)$$

where σ_0 is the pre-tension of the fiber. For practical use, Equation (8) can be written as:

$$\sigma_{\mathrm{CF}} = \sigma_0 + \mathrm{A}\varepsilon + \mathrm{B}\varepsilon^2 + \mathrm{C}(1 - e^{-\mathrm{D}\varepsilon}) \quad (9)$$

where $\mathrm{A} = \mathrm{E}_2, \mathrm{B} = b, \mathrm{C} = \eta_1\mathrm{k}$ and $\mathrm{D} = \mathrm{E}_1/\eta_1\mathrm{k}$.

In the wet spinning methods, molecular chains can not be fully drawn due to the low diffusion of solvent into the coagulants, which results in inferior mechanical properties of the regenerated cellulose fiber.[10] Some extended molecular chains bear the load and exhibit a high slope. With the increment of the elongation, the extended molecular chains begin to breakdown and the unextended chains are straightened under the external force. It is in accordance with the smaller slope in the yield region of the curve. In the reinforcement region, however, the latter extended chains are stretched and show a fast rise of stress in this region.

Theoretical model for stress-strain curves of regenerated cellulose fiber in wet condition

Generally, tensile strength and elongation of fiber decrease with wetting. In contrast, the tensile strength and elongation of natural cellulose fiber increase with wetting.[11] The unique tensile properties of cotton fiber are caused by the formation of a stable structure and relaxation of an internal stress concentration with wetting.[12-14]

However, the tensile strength of viscose rayon decreases sharply with wetting. The tensile strength of polymer materials mainly depends on defects and internal stress concentration in the material, particularly on the number of chain ends in the amorphous region.[15-16] The orientation of the amorphous cellulose chains in dry rayon is mobile, because shrinkage is very high and crystallinity is very low (30-50%). The amorphous cellulose chains are packed loosely and elongate easily in dry rayon. Rayon has low molecular weight and many chain ends. If wet rayon is strained, the probability of fracture at chain ends is high. This is the most important reason why the tensile strength of the wet rayon is much lower than that of dry rayon.[17-18] On the other hand, the decrease of the orientation degree caused by the swelling is also responsible for the drop of tensile strength.

Fig. 4 shows the stress-strain experiment data for wet fiber, which exhibits a different trend, compared to dry fiber. Both trends can be described by a linear spring and Maxwell element, which is the same as the model used in Fig. 3. The two elements refer to the linear region and viscoelastic region of fiber behavior during the tensile process, respectively. The model for the tensile properties of wet fiber can be simulated by the following equation:

$$\sigma = \sigma_0 + \mathrm{E}_1\varepsilon + \eta\mathrm{k}(1 - e^{-\frac{\mathrm{E}_2\varepsilon}{\eta\mathrm{k}}}) \quad (10)$$

Substituting the pre-tensile forces σ_0 by 0.04 cN/dtex and according to the experimental fitting, the model for wet fiber is calculated:

$$\sigma_{\text{CF-wet}} = 0.04 + 0.0403\varepsilon + 0.8578(1 - e^{-0.0736\varepsilon}) \quad (11)$$

The fitted curve can be found in Fig. 4 and R^2 of the fitted model equals 0.999. It indicates that the proposed model is suitable for the simulation of the stress-strain behavior of regenerated cellulose fiber in wet condition.

Mechanical properties and structure of regenerated cellulose fiber in wet condition

The mechanical properties of the fiber in dry and wet condition are summarized and listed in Table 1. Wet fiber possesses better wet mechanical properties than those of viscose rayon (the stress drops by 50% and strain rises by 30%). However, as the novel regenerated fibers have high molecular weight and high crystallinity

(60-65%), namely few chain ends, if wet fibers are strained, the probability of fracture at the molecular chain ends is very low.

The spectral shape in the NMR spectra of regenerated cellulose fiber in dry state is different from that of cellulose in wet state (Fig. 5). This tendency is most distinct for C4 carbon peak region, suggesting that there are several molecular packing (or ordering) states in the molecules. C4 carbon peak region might reflect the possibility of the formation of O3···O5' intramolecular hydrogen bonds.[19] The low magnetic field envelope in the C4 carbon peak can be assigned to cellobiose units having fewer intramolecular hydrongen bonds. When measured in wet state, the peak separation as a whole for all samples becomes better than that for dry state. For example, each two sharp peak components at 107 and 105.1 ppm for C1 carbon peak region, 88.7 87.5 and 86.2 ppm for C4 carbon peak region, 74.7 and 73.5 ppm for C2,3,5 carbon peak region, and 62.7 and 61.3 ppm C6 carbon peak region are clearly detectable. The whole spectral shape for C4 carbon peak region of the new fiber in wet state is relatively sharper than that of others. X_{am}(C3) for all samples increases more or less by wetting. This indicates that O3···O5' intramolecular hydrogen bond in the regenerated cellulose fiber apparently decreases for wet state.

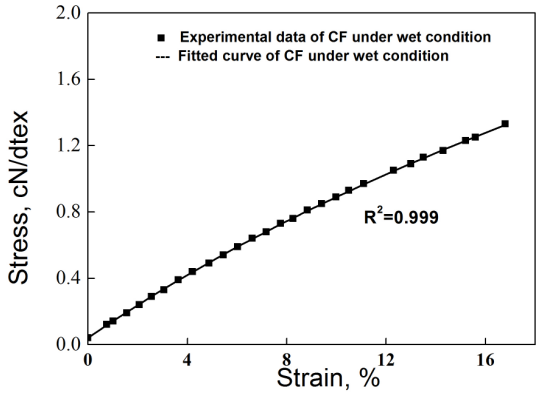

Figure 4: Experimental data and the fitted curve of regenerated cellulose fiber in wet condition

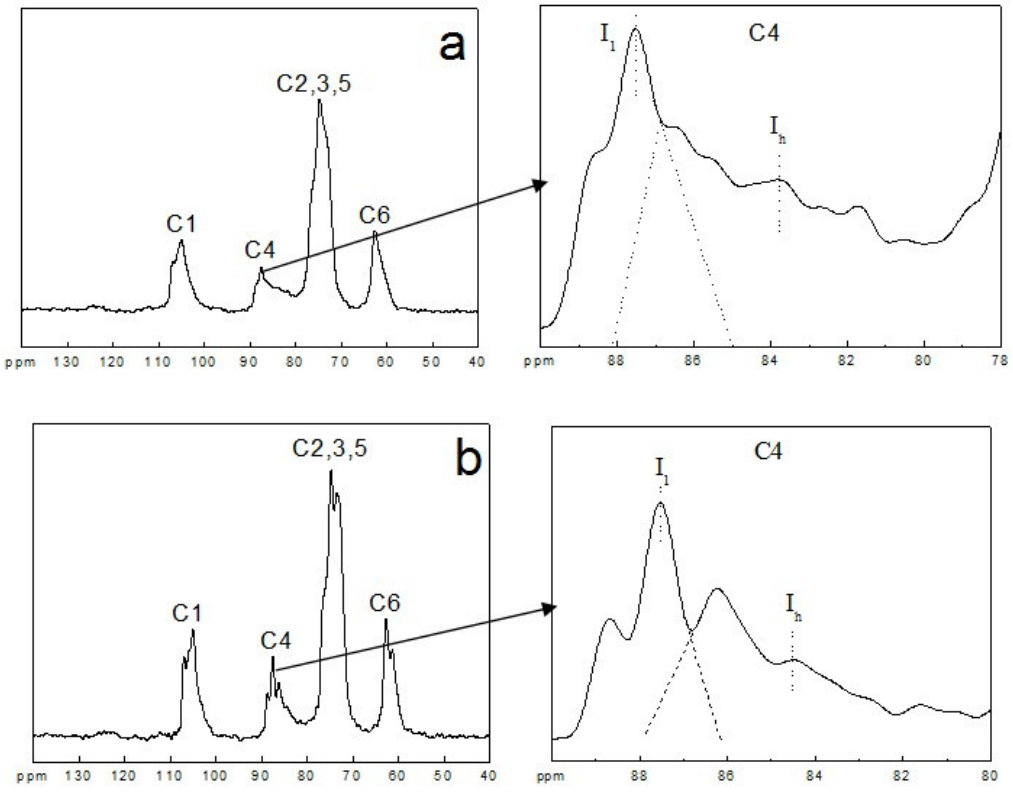

Figure 5: CP/MAS ^{13}C-NMR spectra of regenerated cellulose fiber in (a) dry and (b) wet state

Table 1
Mechanical properties of novel regenerated cellulose fiber (CF) in dry and wet condition

Sample	Stress (cN/dtex)		Strain (%)	
	Dry	Wet	Dry	Wet
CF	1.81	1.33	13.5	16.8

CONCLUSION

The viscoelastic models used for fitting stress-strain curves of dry and wet regenerated cellulose fiber give good results. Bearing in mind the very high values of coefficient ratios R^2, it can be found from the fitted curves that the tensile property of the dry fibers prepared is better than that of the wetted ones. It can be explained by the weakened intramolecular hydrogen bonds in wet state. In addition, the novel regenerated cellulose fibers show better mechanical properties than viscose rayon in both dry and wet condition, which can be attributed to the high molecular weight and high degree of crystallinity of the novel fibers.

ACKNOWLEDGMENTS: This work was supported by the National Science Foundation for Post-doctoral Scientists of China (Grant No. 2012M511012).

REFERENCES

[1] E. L. Hirst, *Nature*, **568**, 157 (1946).
[2] S. Zhang, F. X. Li, J. Y. Yu and Y. L. Hsieh, *Carbohyd. Polym.*, **81**, 668 (2010).
[3] S. Zhang, F. X. Li and J. Y. Yu, *Cellulose Chem. Technol.*, **43**, 393 (2009).
[4] A. M. Manich, M. H. Ussman and A. Barella, *Text. Res. J.*, **325**, 69 (1999).
[5] A. M. Manich, P. N. Marino, M. D. De Castellar, M. Saldivia and R. Sauri, *J. Appl. Polym. Sci.*, **2062**, 76 (2000).
[6] T. Yamashiki, T. Matsui, M. Saitoh and K. Okajima, *British Polym. J.*, **73**, 22 (1990).
[7] K. Kamide, K. Okajima and K. Kowsaka, *Polym. J.*, **71**, 24 (1992).
[8] R. Meredith, *J. Text. Inst.*, **107**, 36 (1945).
[9] C. Zhong, *Text. Res. J.*, **461**, 65 (1995).
[10] K. P. Seung and J. F. Richard, *Polymer*, **10087**, 42 (2001).
[11] W. Tsuji, *Bull. Inst. Chem. Res.*, **69**, 49 (1971).
[12] K. Nakamura, T. Hatakeyama and H. Hatakeyama, *Text. Res. J.*, **607**, 51 (1981).
[13] K. Nakamura, T. Hatakeyama and H. Hatakeyama, *Text. Res. J.*, **682**, 53 (1983).
[14] H. Hatakeyama, T. Hatakeyama and K. Nakamura, *J. Appl. Polym. Sci.*, **979**, 37 (1983).
[15] H. H. Kausch and K. L. DeVries, *Int. J. Fracture*, **727**, 11 (1975).
[16] V. I. Vettegren, I. I. Novak and K. J. Friedland, *Int. J. Fracture*, **789**, 11 (1975).
[17] H. Miyake, Y. Otoh, Y. Ohkoshi and M. Nagura, *Polym. J.*, **29**, 32 (2000).
[18] G. Odian, in "Principles of Polymerization", 4th edition, John Wiley & Sons, Inc, New York, 2004.
[19] K. Kamide, K. Okajima, T. Matsui and K. Kowsaka, *Polym. J.*, **857**, 16 (1984).