

# Modeling the Stress-Relaxation Behavior of Wool Fibers

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**ABSTRACT:** The stress-relaxation behavior of wool fibers after a pretreatment with a chemical solution is particularly important for evaluating the efficiency of the pretreatment. In this study, three viscoelastic models, including the Maxwell, two Maxwell unit, and modified two Maxwell unit models, were established first. To verify the feasibility of the models, stress-relaxation experiments for wool fibers were performed. The wool fibers were pretreated with a sodium bisulfite solution (1 and 3%) at various temperatures (293, 298, 303, 308, 313, and 318 K). Then, the experimental values were fitted to the three models to obtain the rate constants of relaxation. The activation energy of the wool fibers was calculated with the Arrhenius equation. The results showed

that the modified two Maxwell unit model provided the best fit for the experimental data of the wool fibers. The stress-relaxation process of the wool fibers could be divided into two stages, a rapid stage followed by a slow stage. The rapid relaxation of stress was attributed to the weak bonds in the wool fibers, and the following slow relaxation stage was attributed to strong bonds. The Arrhenius equation could describe the stress-relaxation process of the wool fibers very well. Furthermore, the activation energy decreased in the presence of sodium bisulfite. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2078–2084, 2008

**Key words:** fibers; relaxation; modeling; activation energy

## INTRODUCTION

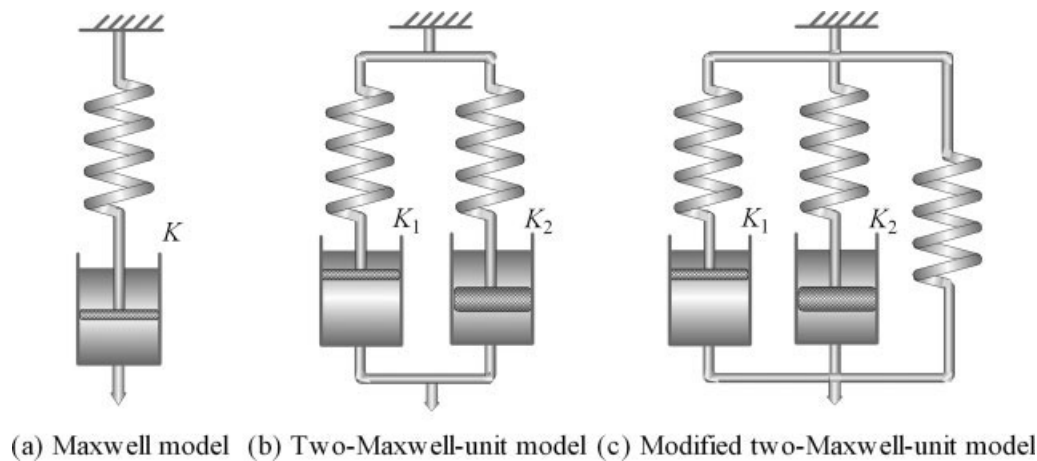
The stretching slenderization of wool fibers is a novel technique for improving the fineness of wool fibers.<sup>1</sup> Our previous studies have demonstrated that the chemical mechanism of the technique is the breakage and reconstruction of some chemical bonds, especially hydrogen bonds and disulfide bonds in wool fibers.<sup>2,3</sup> Therefore, wool fibers should be pretreated with chemical reagents before the stretching slenderization process to weaken the chemical crosslinks and make the breakage of crosslinks easy. The efficiency of the pretreatment might be characterized by the stress-relaxation behavior of the wool fibers after the pretreatment. Only when the relaxation rate is high enough can the wool fibers be stretched smoothly with little damage to the fibers.

The stress-relaxation behavior of wool fibers has been studied by many researchers.<sup>4–11</sup> The relaxation is attributed to the breaking of various chemical crosslinks on extension, and their re-formation may occur with the passage of time. Based on the time-scale, these bonds are categorized into three groups: (1) weak bonds having relaxation times below 0.1 min, including hydrogen bonds, salt linkages, and

van der Waals and electrostatic forces; (2) bonds of intermediate strength having relaxation times between 0.1 and 10 min, which are due to the disengagement of bonds between the matrix and filament components; and (3) strong bonds having relaxation times above 10 min, which consist of covalent crosslinks, mainly disulfide bonds.<sup>6</sup> The intensity and rate of relaxation depend on many conditions such as the chemical agent, concentration of the agent, temperature, humidity, and strain history.<sup>11</sup> In addition, a low crystalline content, poor fibril orientation, and packing tend to result in great viscoelastic effects in wool.

The aim of this study was to investigate the influence of a pretreatment with a sodium bisulfite solution on the microstructure of wool fibers through the modeling of the stress-relaxation behavior of wool fibers after the pretreatment. For this purpose, three viscoelastic models containing various elements to characterize the stress-relaxation behavior of wool fibers were established first. To verify the feasibility of the models, stress-relaxation experiments with wool fibers were performed. The wool fibers were pretreated with sodium bisulfite solutions (1 and 3%) at various temperatures (293, 298, 303, 308, 313, and 318 K). Then, the experimental values of the fractional stress change,  $\sigma/\sigma_0$  (where  $\sigma$  is the stress at time  $t$  and  $\sigma_0$  is the initial stress), as a function of time  $t$  were fitted to the three models to obtain the rate constants of relaxation. Furthermore, the activation energy of the wool fibers during stress

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**Figure 1** Viscoelastic models for the stress relaxation of wool fibers.

relaxation was calculated with the Arrhenius equation. Finally, the effect of the concentration on the stress-relaxation process of the fibers was analyzed.

## MODELING

### Viscoelastic model of stress relaxation

The Maxwell model, which consists of a spring and dashpot in series, is the first model to characterize the phenomenon of stress relaxation,<sup>12</sup> as illustrated in Figure 1(a). The equation of stress relaxation can be expressed as follows:

$$\frac{\sigma}{\sigma_0} = e^{-\frac{t}{\tau_1}} = e^{-K_1 t} \quad (1)$$

where  $\sigma_0$  is the initial stress and  $\tau_1$  is the relaxation time, that is, the time at which the stress of the Maxwell element is equal to 36.8% of  $\sigma_0$ .  $K_1 = 1/\tau_1$  is the rate constant for relaxation processes. The larger the value of  $K_1$  is, the faster the stress in the fiber relaxes, and this demonstrates that more crosslinks in the fibers are broken by the chemical solution during the pretreatment process. Therefore, the influence of the pretreatment process might be characterized by the rate parameter  $K_1$ .

However, most textile fibers do not relax with a single relaxation time as predicted by the Maxwell model. One effective method of introducing a range of relaxation times into the problem is to construct models consisting of a number of Maxwell elements connected in parallel, that is, the generalized Maxwell model.<sup>13</sup> Manich and coworkers<sup>14,15</sup> used a three-unit generalized Maxwell model, which consists of a set of three Maxwell units and a spring connected in parallel, to study the stress relaxation of leather and polyamide 6.6 yarns. Figure 1(b) illustrates the two Maxwell unit model, in which the strain is the same in each of the connected Maxwell

units and the total stress is given by the sum of the stresses experienced by each unit. Therefore, the two Maxwell unit model is written as follows:

$$\dot{\epsilon} = \frac{\dot{\sigma}_1}{E_1} + \frac{\sigma_1}{\eta_1} = \frac{\dot{\sigma}_2}{E_2} + \frac{\sigma_2}{\eta_2} \quad (2)$$

where  $\dot{\epsilon}$  is equal to  $d\epsilon/dt$ .  $E_1$  and  $E_2$  are the elastic modulus of two springs, respectively, and  $\eta_1$  and  $\eta_2$  are the coefficient of viscosity of dashpots, respectively.

For a stress-relaxation experiment,  $\dot{\epsilon} = 0$ . Then

$$\begin{aligned} \sigma &= \sigma_1 + \sigma_2 = \sigma_{01}e^{-K_1 t} + \sigma_{02}e^{-K_2 t} \\ \frac{\sigma}{\sigma_0} &= \frac{\sigma_{01}}{\sigma_{01} + \sigma_{02}} e^{-K_1 t} + \frac{\sigma_{02}}{\sigma_{01} + \sigma_{02}} e^{-K_2 t} \\ &= A_1 e^{-K_1 t} + A_2 e^{-K_2 t} \end{aligned} \quad (3)$$

where  $\sigma_0 = \sigma_{01} + \sigma_{02}$ ,  $\sigma_{01}$  and  $\sigma_{02}$  are the initial stress in two Maxwell units, respectively,  $A_1$  and  $A_2$  are constants without dimensions, and  $A_1 + A_2 = 1$ .  $K_1$  and  $K_2$  are two rate constants. For convenience, the value of  $K_1$  is assumed to be larger than that of  $K_2$ . Accordingly, the parameters  $A_1$  and  $K_1$  might be related to the fast relaxation process, which usually occurs at the beginning of the stress relaxation. Because the weak bonds including hydrogen bonds, salt linkages, and electrostatic forces have a short relaxation time,<sup>6</sup> the parameter  $K_1$  may express the relaxation rate of these bonds, and the parameter  $A_1$  might show the proportion of stress relaxation. Furthermore, the parameters  $A_2$  and  $K_2$  might be related to the relaxation of strong bonds, including disulfide bonds.

With the increase of time to infinity, the stress in eq. (3) goes to zero, which is not applicable to the majority of textile fibers. The pretreatment of wool fibers before stretching slenderization should not break all of the crosslinks in the fibers. Therefore, the stress in the fibers might not approach zero.

Accordingly, a Hookean spring should be introduced into the model in parallel, and this is called the modified two Maxwell unit model, as shown in Figure 1(c). The following equation of stress relaxation can then be obtained:

$$\begin{aligned} \sigma &= \sigma_1 + \sigma_2 + \sigma_3 = \sigma_{01}e^{-K_1t} + \sigma_{02}e^{-K_2t} + \sigma_{03} \\ \frac{\sigma}{\sigma_0} &= \frac{\sigma_{01}}{\sigma_{01} + \sigma_{02} + \sigma_{03}}e^{-K_1t} + \frac{\sigma_{02}}{\sigma_{01} + \sigma_{02} + \sigma_{03}}e^{-K_2t} \\ &+ \frac{\sigma_{03}}{\sigma_{01} + \sigma_{02} + \sigma_{03}} = A_1e^{-K_1t} + A_2e^{-K_2t} + A_3 \quad (4) \end{aligned}$$

where  $\sigma_{03}$  is the initial stress in the third Maxwell unit,  $\sigma_0 = \sigma_{01} + \sigma_{02} + \sigma_{03}$ ,  $A_3 = \sigma_{03}/(\sigma_{01} + \sigma_{02} + \sigma_{03})$ ,  $A_1 + A_2 + A_3 = 1$ , and  $K_1 > K_2$ .

Therefore, three viscoelastic models [eqs. (1), (3), and (4)] might be used to characterize the stress-relaxation behaviors of wool fibers. The stress-relaxation ( $\sigma/\sigma_0$ ) data collected for wool fibers under various environmental conditions can be fitted with the three equations to obtain the relaxation rates.

#### Activation energy model of stress relaxation

The computation of the rates of relaxation as a function of temperature enables the estimation of the activation energies for the intermolecular forces participating in the viscoelastic properties of wool fibers. Nowadays, the influence of temperature on the rates of chemical reactions is usually interpreted in terms of the Arrhenius equation. According to this equation, the rate constant ( $K$ ) is the product of a pre-exponential factor ( $K'$ ) and an exponential factor:<sup>16</sup>

$$K = K'e^{-\frac{E_a}{RT}} \quad (5)$$

where  $T$  is the temperature,  $R$  is the gas constant, and  $E_a$  is the activation energy. Equation (5) can be rewritten as

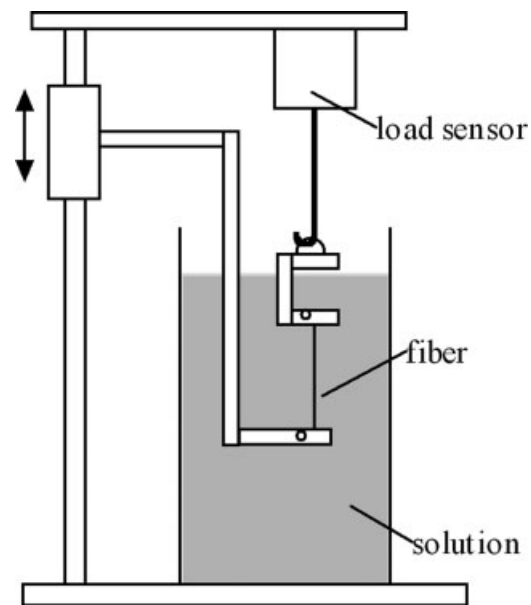
$$\ln K - \ln K' = -\frac{E_a}{R} \frac{1}{T} \quad (6)$$

Equation (6) shows that  $\ln K$  and the reciprocal of the temperature ( $1/T$ ) approximately satisfy the linear relationship if the stress relaxation of wool fibers can be characterized by the Arrhenius equation.

## EXPERIMENTAL

### Materials

All the fibers used were Merino wool (Shanghai Sanmao Enterprise Group Co., Ltd., Shanghai, China), which was cleaned by extraction in ether and in cold ethanol. It was assumed that the fibers were circular in cross section, and they were measured along a 20-mm length of fiber with an optical microscope. Those fibers whose diameter varied along their length by more than 10% were discarded.



**Figure 2** Diagram of the experimental apparatus for stress relaxation.

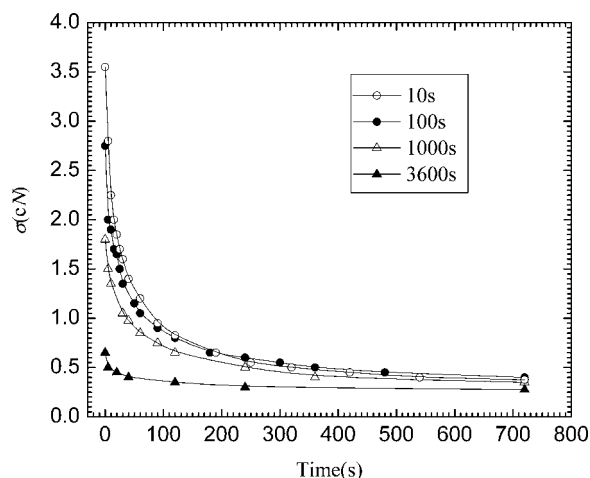
### Experiments

The stress-relaxation experiments were carried out in a fiber tensile testing machine with a liquid cell container (Fig. 2) for single wool fibers after pretreatment with water or sodium bisulfite solutions of different concentrations (1 and 3%) at various temperatures (293, 298, 303, 308, 313, and 318 K) for 100 s. The gauge length of the fiber was 20 mm. Then, the fiber was extended 30% at a strain rate of 20 mm/min in the corresponding solution. Thereafter, the strain was kept constant, and the stress decay was monitored for up to 3 h. During the stress-relaxation test, the wool fiber was immersed in the treatment solution for the entire time. The experiments were repeated 10 times. However, only the curve that could represent the average properties of the sample was selected and plotted in the figures. From the load–time graph, the values of  $\sigma/\sigma_0$  as a function of time  $t$  could be plotted. In the experiments, the pretreatment time had an apparent influence on the stress-relaxation behaviors of wool fibers. Therefore, relaxation experiments with wool fibers with a 1% sodium bisulfite solution at 303 K for various pretreatment times (10, 100, 1000, and 3600 s) were also performed.

## RESULTS AND DISCUSSION

### Effect of the pretreatment time

Relaxation results for stress  $\sigma$  against time  $t$  for wool fibers in a 1% sodium bisulfite solution at 303 K for various pretreatment times (10, 100, 1000, and 3600 s) are shown in Figure 3. With the passage of



**Figure 3** Stress relaxation of the wool fibers in a 1% sodium bisulfite solution at 303 K with various pretreatment times.

time, the stress of the wool fiber decreases rapidly until an equilibrium stress is reached. The longer the pretreatment time is, the lower  $\sigma_0$  and the equilibrium stress are. With an increase in the pretreatment time, the sodium bisulfite solution breaks more and more crosslinks in the wool fibers, mainly disulfide bonds. As a result, the wool fiber relaxes quickly and can be stretched with low stress. From this point of view, the pretreatment times for all of the stress-relaxation experiments should be identical. Therefore, the identical pretreatment time in this study was chosen to be 100 s.

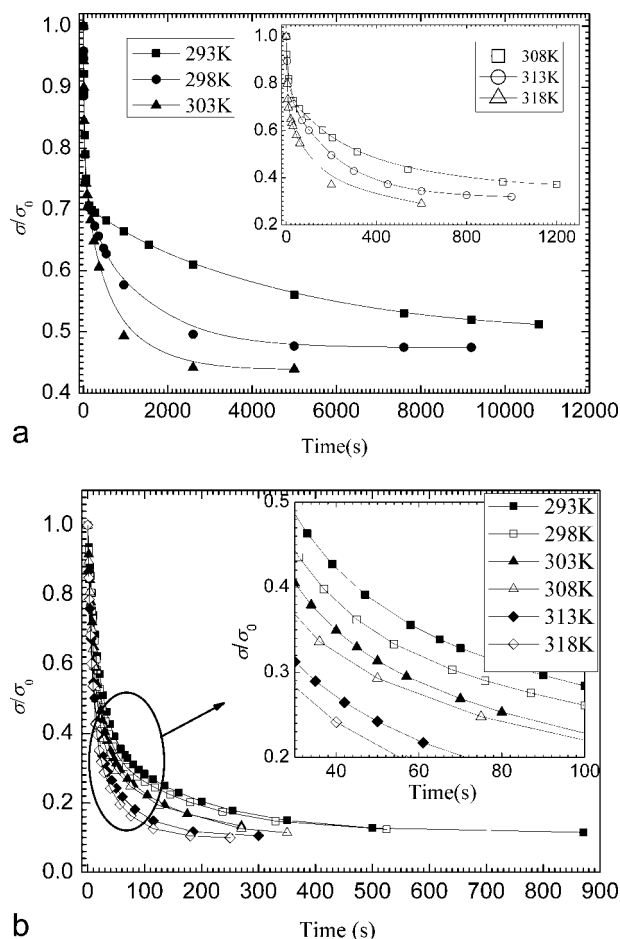
### Relaxation model of wool fibers

Plots of normalized stress  $\sigma/\sigma_0$  against time  $t$  for wool fibers after pretreatment with water and a 1% sodium bisulfite solution at various temperatures is given in Figure 4. The rate of relaxation in the sodium bisulfite solution is apparently quicker than that in water. Furthermore, the equilibrium stress in the sodium bisulfite solution is evidently lower than that in water. This may contribute to the fact that the sodium bisulfite solution breaks some of the disulfide crosslinks in the wool fibers, whereas water breaks only some of the hydrogen bonds.<sup>3</sup> In addition, the temperature has a significant effect on the stress-relaxation process. The higher the temperature is, the lower the stress at the same time is.

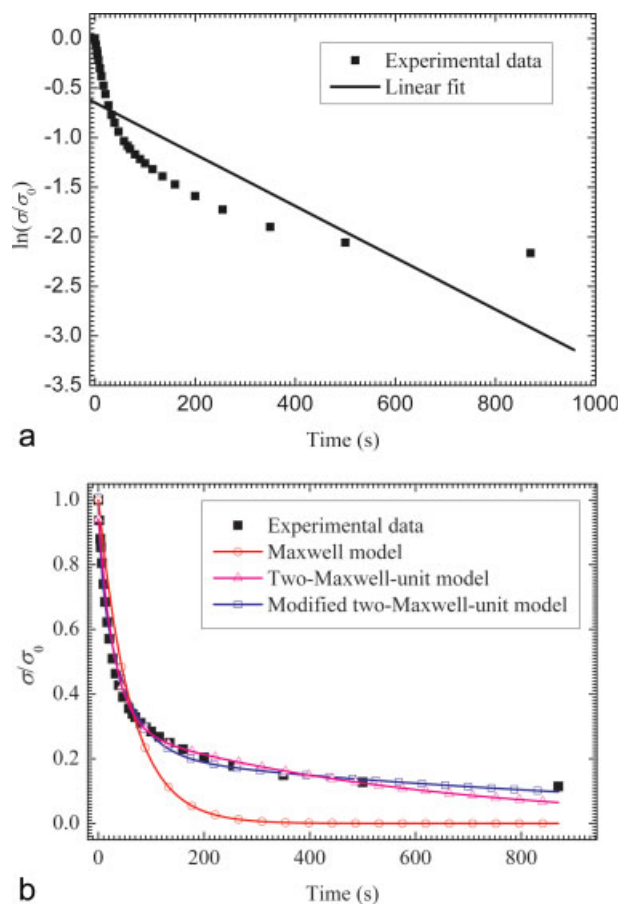
To choose the appropriate model for describing the stress-relaxation process of wool fibers, the experimental values of  $\sigma/\sigma_0$  against time  $t$  in a 1% sodium bisulfite solution at 293 K were fitted to the various models as shown in Figure 5. The values of  $\sigma/\sigma_0$  were first expressed with the natural logarithm against time  $t$  as illustrated in Figure 5(a). It is evident that eq. (1) predicts linear plots of  $\ln \sigma/\sigma_0$  against time  $t$ . However, the plot of the experimental

data for  $\ln \sigma/\sigma_0$  against time  $t$  is not precisely linear. Therefore, the Maxwell model cannot adequately explain the relaxation behavior of wool fibers. Then, the experimental results are expressed with linear coordinates as shown in Figure 5(b). The values of the pre-exponential and exponential terms in eqs. (1), (3), and (4) were estimated with a nonlinear least-squares fitter with the Levenberg–Marquardt algorithm on Origin version 7.5 (Microcal Software, Inc., Northampton, MA). Such estimated values are given in Table I. The statistical correlation parameter  $R^2$  is also included in the tables.

The results in Figure 5(b) also show that the Maxwell model cannot describe satisfactorily the variations of  $\sigma/\sigma_0$  against time  $t$ . However, the two Maxwell unit and modified two Maxwell unit models produce a better fit with the experimental data. The results indicate that the relaxation of wool fibers might include two or more relaxation mechanisms. Each relaxation mechanism has a corresponding relaxation rate. Because the equilibrium stress cannot be reduced to zero, the modified two Maxwell unit model containing two distinct rates of relaxation



**Figure 4** Stress relaxation of the wool fibers in (a) water and (b) a 1% sodium bisulfite solution.



**Figure 5** Fitted relaxation results for the wool fibers in a 1% sodium bisulfite solution at 293 K with (a) natural logarithm coordinates and (b) linear coordinates. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

might be regarded as the best model to describe the relaxation of wool fibers. Therefore, the relaxation processes of wool fibers may be treated as fast and slow stages; that is, the first rapid relaxation of stress may be attributed to the weak bonds in the wool fibers, including hydrogen bonds, salt linkages, and van der Waals and electrostatic forces, and the following slow relaxation stage may be attributed to strong bonds including covalent crosslinks, mainly disulfide bonds. The results in Table I also support this point of view. The fast rate of relaxation is  $0.054 \text{ s}^{-1}$ , so the corresponding relaxation time is approximately 18.5 s, which may contribute to the weak or

intermediate-strength bonds.<sup>6</sup> The slow rate of relaxation is  $0.0062 \text{ s}^{-1}$ , and the relaxation time is 161.3 s, which is related to the relaxation of strong bonds. The presence of a sodium bisulfite solution may shorten the relaxation time slightly.

Therefore, the relaxation data of wool fibers in water and 1 and 3% sodium bisulfite solutions at various temperatures were fitted to the modified two Maxwell unit model. The estimated results are shown in Table II. With an increase in the temperature, the relaxation rates increase gradually. Furthermore, the relaxation rates in sodium bisulfite solutions are apparently higher than that in water. However, the values of  $A_3$ , related to the equilibrium stress, are evidently lower in the sodium bisulfite solutions than that in water. Accordingly, the stress in the wool fiber cannot relax to a low value if it is treated only with water. However, sodium bisulfite can control the stress-relaxation process to a desired level.

#### Activation energy of wool fibers

An Arrhenius plot of the temperature dependence of the rate constant is shown in Figure 6. The temperature dependence of the rate constant data was treated with eq. (6). It seems that the rate  $\ln K$  depends linearly on  $1/T$ . The linear fitting plot is also shown in the figure.

Through linear fitting, the activation energy values associated with the fast and slow relaxations were calculated to understand the various factors affecting the stress-relaxation behavior of wool fibers. The activation energies calculated in this study with the rates of relaxation for wool fibers under various conditions are given in Table III.

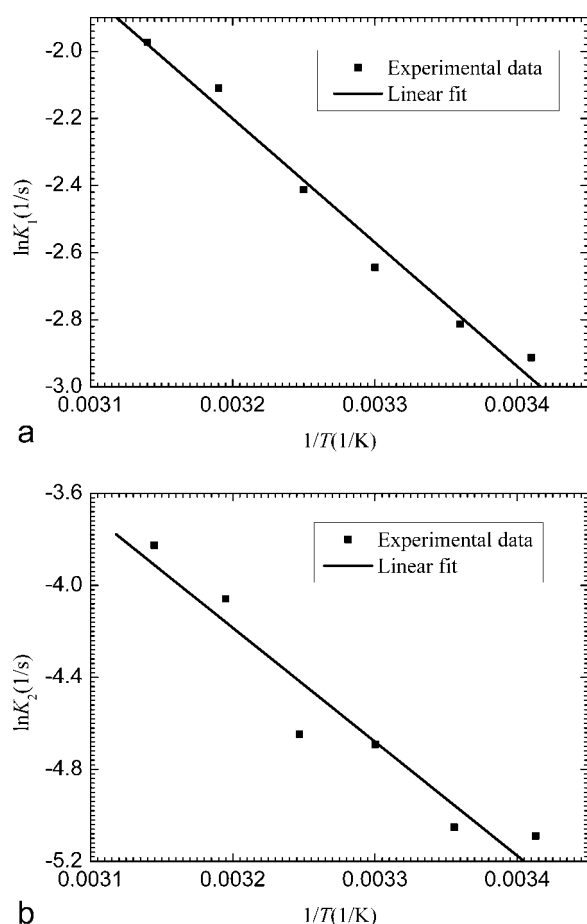
In general, the activation energy calculated from the rate constant  $K_1$  is approximately 15 kJ/mol lower than that obtained from  $K_2$ . The stress-relaxation activation energy is the energy required for stress-induced segmental motion. The results indicate that the slow relaxation stage due to the strong bonds needs more energy than the rapid relaxation stage corresponding to the weak bonds. The two activation energy values for wool fibers in water are  $68.0 \pm 9.7$  and  $83.2 \pm 5.7$  kJ/mol, respectively. In a 1% sodium bisulfite solution, the calculated activation energy values are  $32.8 \pm 2.6$  and  $47.5 \pm 6.6$  kJ/

**TABLE I**  
Estimated Relaxation Parameters of the Wool Fibers in a 1% Sodium Bisulfite Solution at 293 K

Model	$A_1$	$K_1 \times 10^2 \text{ (s}^{-1}\text{)}$	$A_2$	$K_2 \times 10^3 \text{ (s}^{-1}\text{)}$	$A_3$	$R^2$
Maxwell	1	$1.7 \pm 0.1$				0.8000
Two Maxwell unit	$0.67 \pm 0.01$	$4.6 \pm 0.2$	0.33	$1.9 \pm 0.2$		0.9818
Modified two Maxwell unit	$0.58 \pm 0.01$	$5.4 \pm 0.1$	$0.31 \pm 0.01$	$6.2 \pm 0.1$	0.11	0.9956

**TABLE II**  
**Estimated Relaxation Values of the Wool Fibers Under Various Experimental Conditions**

Experimental conditions		Relaxation parameters					
Solution	Temperature (K)	$A_1$	$K_1 \times 10^2$ (s <sup>-1</sup> )	$A_2$	$K_2 \times 10^3$ (s <sup>-1</sup> )	$A_3$	$R^2$
Water	293	0.2919	3.104	0.2118	0.240	0.4963	0.9883
	298	0.2684	5.400	0.2569	0.960	0.4747	0.9522
	303	0.2244	6.920	0.3364	1.900	0.4392	0.9895
	308	0.2407	11.873	0.3968	3.140	0.3625	0.9940
	313	0.2312	13.443	0.4541	4.600	0.3147	0.9859
1% sodium bisulfite solution	318	0.2899	26.000	0.4224	8.160	0.2877	0.9740
	293	0.5754	5.432	0.3112	6.160	0.1134	0.9956
	298	0.6100	6.001	0.2757	6.400	0.1143	0.9961
	303	0.5941	7.109	0.2977	9.170	0.1082	0.9985
	308	0.6018	8.959	0.2945	9.590	0.1037	0.9991
3% sodium bisulfite solution	313	0.5707	12.127	0.3258	17.290	0.1035	0.9993
	318	0.5648	13.908	0.3369	21.800	0.0983	0.9985
	293	0.5071	8.297	0.3997	9.720	0.0932	0.9963
	298	0.6094	8.582	0.2845	14.650	0.1061	0.9966
	303	0.5826	13.511	0.3128	17.450	0.1046	0.9988
3% sodium bisulfite solution	308	0.6007	12.171	0.3021	23.100	0.0972	0.9987
	313	0.5586	15.153	0.3525	32.060	0.0889	0.9885
	318	0.6198	19.521	0.3084	39.840	0.0718	0.9933



**Figure 6** Arrhenius plots of (a)  $K_1$  and (b)  $K_2$  for the wool fibers in a 1% sodium bisulfite solution.

mol, respectively. The values of the activation energy in the sodium bisulfite solution are evidently lower than that of water. The sodium bisulfite, as the disulfide-bond-breaking reagent, makes the relaxation of the wool fibers easy. Therefore, the stress-relaxation processes might be significantly influenced by the variation of the solution concentration. The effect of the solution concentration on the stress-relaxation process of wool fibers is shown in Figure 7. The higher the concentration is, the higher the rate of stress relaxation is and the lower the equilibrium stress is. In other words, the number of broken disulfide bonds increases with the solution concentration. In view of the integrality of the wool microstructure, the concentration of the solution should not be too high in practical processing.

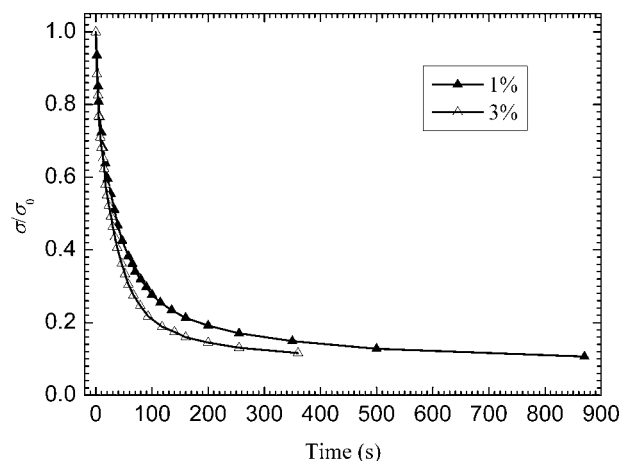
## CONCLUSIONS

The stress-relaxation behavior of wool fibers after a pretreatment with a sodium bisulfite solution at

**TABLE III**  
**Activation Energy Values of the Wool Fibers in Water and Sodium Bisulfite Solutions**

Solution	$E_{a1}$ (kJ/mol)	$E_{a2}$ (kJ/mol)
Water	$68.0 \pm 9.7$	$83.2 \pm 5.7$
1% sodium bisulfite solution	$32.8 \pm 2.6$	$47.5 \pm 6.6$
3% sodium bisulfite solution	$26.6 \pm 4.8$	$42.6 \pm 1.9$

$E_{a1}$  and  $E_{a2}$  are the activation energy values associated with the rapid and slow relaxations.



**Figure 7** Stress relaxation of wool fibers in 1 and 3% sodium bisulfite solutions at 293 K.

various temperatures has been studied. The results show that the modified two Maxwell unit model provides the best fit for the experimental data of the wool fibers. The stress-relaxation process of the wool fibers can be divided into two stages: a fast stage followed by a slow stage. The Arrhenius equation can describe the stress-relaxation process of the wool fibers very well, and the activation energy of the fast

stage is markedly larger than that of the slow stage. It is evident from the results that the activation energy decreases in the presence of a chemical reagent. In addition, the rate of stress relaxation increases with the concentration of the solution.

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