

# Viscoelastic Behavior of AN-*g*-Casein Copolymer Concentrated Solution of Sodium Thiocyanate

QINGZHI DONG,<sup>1</sup> LIXIA GU<sup>2</sup>

<sup>1</sup> Petrochemical Institute, East China University of Science and Technology, Shanghai 201512, China

<sup>2</sup> Man-Made Fiber Research Institute and State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Dong Hua University, Shanghai 200051, China

Received 3 May 2001; accepted 13 September 2001

**ABSTRACT:** The viscoelastic behavior of sodium thiocyanate concentrated solution of graft copolymer of acrylonitrile onto casein (AN-*g*-casein) was investigated in detail by nitrogen pressure capillary rheometer. The experimental results show that the concentrated solution of AN-*g*-casein is a non-Newtonian fluid of shear thinning. The end correction increases with the increase of shear rate. In the course of practical spinning, the real shear stress only attributes about 35% to the apparent shear stress, which confirms the essentiality of end correction for the capillary extrusion of the concentrated solution of the graft copolymer. By using the Dewitt model, the Couette correction  $\xi$  and recoverable shear strain  $S_R$  were analyzed and separated. Quantitative function relation of  $\xi$  and  $S_R$  versus shear rate and temperature were deduced. It is a common equation within the range of experiment. In practical spinning process, the real viscoelastic parameters can be easily predicted by only a piece of flowing curve based on the common equation. Real elastic model  $G$  under any shear rate in the range of experiment was calculated. It was found that  $G$  increases with an increase of shear rate, which is opposite to the conclusion reported by Hayahara. The main reason for the error may be that Hayahara used the same Couette correction at a higher shear rate. Further, the die swell in the spinning process can be estimated efficiently. The theoretical base for the stability of AN-*g*-casein spinning technology was provided. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1721–1728, 2002; DOI 10.1002/app.10554

**Key words:** acrylonitrile; casein; graft copolymer; sodium thiocyanate; viscoelastic properties; shear; stress; swelling; rheology

## INTRODUCTION

Grafting provides a method of adding certain properties to a fiber without greatly disturbing the strength and other mechanical behavior of the fiber. Mitsuo has studied the grafting of casein with acrylonitrile (AN) in aqueous solution of zinc chloride, and further, the spinning of casein into a silk-like fiber named chinon,<sup>1</sup> which has better

elasticity than silk and cellulose triacetate fiber, and lower static electricity than nylon and poly(ethylene terephthalate) (PET) fiber.<sup>2</sup> It is surprising that little attention has been paid toward the grafting of AN onto casein in concentrated aqueous solution of sodium thiocyanate (NaSCN). Compared with the way zinc chloride aqueous solution acts, the NaSCN concentrated aqueous solution has higher solid levels in spinning solution and is more stable to process.

A capillary rheometer can be used to simulate the spinning conditions (shear rate:  $10^3$ – $10^4$  s<sup>-1</sup>; temperature: 40–80°C) to predict rheological be-

Correspondence to: Q. Dong (qzdong@online.sh.cn).

*Journal of Applied Polymer Science*, Vol. 84, 1721–1728 (2002)  
© 2002 Wiley Periodicals, Inc.

havior, such as shear stress, viscoelastic properties, and die swell. The end correction term  $e$  of viscoelastic polymer fluid is composed of entrance correction  $\xi$  and recoverable shear strain  $S_R$ . Historically, end correction has been determined maturely.<sup>3,4</sup> However, the problem of how to separate  $\xi$  and  $S_R$  from  $e$  has been reported little. Bagley<sup>5</sup> considered that recoverable shear strain increases with the increase of shear stress. When the shear stress approaches zero, the recoverable shear strain should tend to zero too. At that condition,  $e$  is only the contribution of the  $\xi$ , so the  $\xi$  in higher shear stress was replaced with  $\xi$  at the shear stress, tending to zero. Hayahara and Takao<sup>6</sup> used the  $\xi$  of sodium silicate solution, which shows Newtonian flow and has no recoverable shear strain, as the entrance correction term for the calculation of the recoverable shear strain. Therefore, the problem of how to separate  $\xi$  and  $S_R$  from  $e$  has not been really dealt with. In practical production, spinning is carried on in higher shear stress, so, how to analyze  $\xi$  and  $S_R$  is the key to analysis of the rheology and spinnability.

In this article, the end correction of AN-*g*-casein concentrated solution was analyzed by using a capillary rheometer with a series of capillaries of different length-to-radius ratios. Entrance correction and recoverable shear strain were analyzed and separated by using the Dewitt model. Furthermore, the quantitative function relations of  $\xi$  and  $S_R$  versus temperature and shear rate in the range of experiment were deduced. The real rheological parameters can be measured by using only one flow curve combining the common equation. The real elastic model ( $G$ ) can be valued according to the common equation of  $S_R$ , and then die swell ( $B$ ) is predicted. The theoretical basis of choosing spinning technology was provided.

## EXPERIMENTAL

### Preparation of Materials

Casein (chemical purity, Shanghai Chemical Reagent Co., Shanghai, China) was soaked 24 h in distilled water. Then the swollen casein was treated with a concentrated aqueous solution of NaSCN (chemical purity, Shanghai Chemical Reagent Co.) at 70°C for 30 min to obtain a casein solution. Monomer AN (99.5%, division 2 of Shanghai Petrochemical Co., Ltd., Shanghai, China) was purged to remove the hydroquinone and monomethyl ether hydroquinone inhibitors by using an inhibitor remover disposable column

(Aldrich Chemical). Azobisisobutyronitrile (AIBN; chemical purity, Aldrich Chemical) as an initiator was recrystallized two times.

A known concentration of casein solution was thermostated at the required temperature in a 500 mL four-necked flask equipped with a stainless steel stirrer under nitrogen atmosphere. After sufficient time, AN was added, followed by the initiator, AIBN. After a sufficient time interval, AN-*g*-casein concentrated solution of sodium thiocyanate was prepared.<sup>7</sup> The mass percentage of AN : casein in AN-*g*-casein is 76 : 24. According to Ou and Zhang,<sup>8</sup> the zero shear viscosity was measured by a ball viscometer,  $\eta_0 = 238$ . The concentration of sodium thiocyanate and graft copolymer was 44 and 12.8 wt %, respectively. AN-*g*-casein concentrated solution was deaerated at 80°C under vacuum of 750 mm Hg for 4 h and then filtered.

### Measurement of Rheology Behavior

Measurement was carried out by nitrogen pressure capillary rheometer. The capillary radius is 0.015 cm and the series of length-to-radius ratios ( $L/R$ ) are 3.01, 6.21, 12.36, 19.83, and 27.57. Experimental temperature measured from 40 to 80°C. The shear rate ranged from  $1.7 \times 10^3$  to  $4 \times 10^4$  s<sup>-1</sup>. The prepared concentrated solution was forced into capillary by nitrogen and the output rate was measured under various pressures, temperatures, and  $L/R$  ratios.

### Measurement of Die Swell

Tanner proposed a theory of die swell.<sup>9</sup> The relation of die-swelling ratio  $B_0$  at the exit of infinite length capillary and recoverable shear strain ( $S_R$ ) during the free extrude process was expressed as follows:

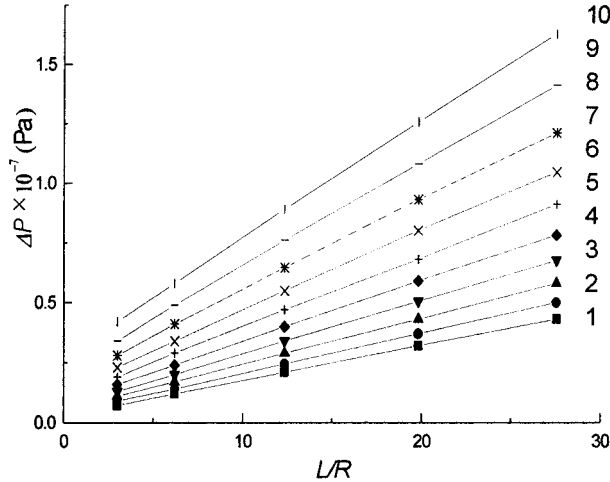
$$B_0 = \left( 1 + \frac{S_R^2}{2} \right)^{1/6} + 0.1 \quad (1)$$

Practical die swell at the exit of the capillary was measured by a microscope camera.

## RESULTS AND DISCUSSION

### End Correction for AN-*g*-Casein Concentrated Solution Flowing in the Capillary

The extra pressure drop, which was produced by the velocity profile adjusting at the entrance and the elastic energy storage in the viscoelastic fluid



**Figure 1** A series of pressure difference versus capillary length-to-radius ratio plots (each straight line corresponds to a constant shear rate).  $\dot{\gamma} \times 10^{-4} (\text{s}^{-1})$ : 1: 0.17; 2: 0.25; 3: 0.35; 4: 0.50; 5: 0.70; 6: 1.0; 7: 1.4; 8: 2.0; 9: 2.8; 10: 4.0.

flow, corresponds to elongating the capillary to a certain length. To obtain the real shear stress  $\sigma$ , Bagley<sup>3</sup> proposed a correction formula as:

$$\sigma = \Delta P R / 2(L + eR) \quad (2)$$

where  $e$  represents end correction term, and  $\Delta P$  represents the pressure difference.

Figure 1 shows a series of pressure difference versus length-to-radius ratio plots in the flow of AN-g-casein concentrated solution. The shear rate range  $1.7 \times 10^3$  to  $4 \times 10^4 \text{ s}^{-1}$  is covered and the  $L/R$  value ranges from 3.01 to 27.57. Within experimental error, these plots are linear.

On the grounds of Bagley's correction, eq. 2, shear stress  $\sigma$ , and end correction term  $e$  can be calculated and obtained by using the slope and intercept of the lines from Figure 1; then the apparent viscosity  $\eta_a$  can be calculated as:

$$\eta_a = \sigma / \dot{\gamma} \quad (3)$$

The values of real shear stress  $\sigma$ , end correction term  $e$ , and apparent viscosity  $\eta_a$  in different shear rates are presented in Table I. From Table I, the end correction term increases and apparent viscosity  $\eta_a$  decreases, whereas shear rate increases, which confirms the shear-thinning property of AN-g-casein concentrated solution. Generally, in actual wet spinning technology, fiber extrusion is at lower  $L/R$  of orifices and higher at shear rate. For example, when shear rate is  $4 \times 10^4 \text{ s}^{-1}$  and  $L/R$  is 3.01, the real shear stress

only attributes 35.3% to the apparent shear stress in the same condition, which demonstrated that the correction of shear stress is quite essential. Similar behavior was observed in the concentrated solution of poly(vinyl alcohol) (PVA) by Zhang et al.<sup>10</sup>

### Analysis and Separation of End Correction in Capillary Flow of AN-g-Casein Concentrated Solution

Philippoff and Gaskins proposed that the end correction of viscoelastic polymer fluid includes the contributions of entrance effect and recoverable shear strain in shear flow,<sup>4</sup> where

$$e = \xi + \frac{1}{2} S_R = \xi + \frac{1}{2} \frac{\sigma}{G} \quad (4)$$

and where  $G$  is the shear elasticity modulus;  $\xi$  is the correction of loss energy in entrance for adjusting velocity profile, which is designated Couette correction; and  $S_R$  is the recoverable shear strain (equal to normal stress difference), which is designated the Philippoff-Gaskins correction.

The Maxwell method proceeds from the point of view of a relaxing solid and uses a simple superposition of relaxation and elastic effects. In a strained liquid, where the medium is in motion, this might seem to be an important consideration. Allowance for this is made by modifying a reference configuration system, designated the Dewitt model, which is to be interpreted as a description of that configuration to which the fluid would return on release of the stresses. By using the Jaumann differential equation, a modified Maxwell model can be obtained<sup>11</sup>, designated the Dewitt model as follows:

**Table I** Values of Real Shear Stress  $\sigma$ , End Correction Term  $e$ , and Apparent Viscosity  $\eta_a$  in Different Shear Rates (80°C)

$\dot{\gamma} (\times 10^{-3}/\text{s}^{-1})$	$\sigma (\times 10^{-5}/\text{Pa})$	$e$	$\eta_a/\text{Pas}$
1.7	0.730	2.03	42.9
2.5	0.838	2.33	33.5
3.5	0.961	2.66	27.5
5.0	1.11	2.95	22.2
7.0	1.27	3.31	18.1
10.0	1.45	3.69	14.5
14.0	1.65	4.16	11.8
20.0	1.89	4.62	9.45
28.0	2.17	5.05	7.75
40.0	2.46	5.61	6.15

$$\sigma_{ij} + \tau \left( \frac{D\sigma_{ij}}{Dt} \right) = 2\eta \varepsilon_{ij} \quad (5)$$

where the Jaumann differential of second-order tensor can be defined as:

$$\frac{D\sigma_{ij}}{Dt} = \left( \frac{\partial \sigma_{ij}}{\partial t} \right) + V^K \left( \frac{\partial \sigma_{ij}}{\partial X^k} \right) + w_{iK} \sigma_{jK} + W_{jK} \sigma_{iK} \quad (6)$$

and where  $(\partial \sigma_{ij} / \partial t)$  is the time partial derivative of the stress of the components in the  $ij$  coordinate system;  $V^K(\partial \sigma_{ij} / \partial X^k)$  is the partial derivative of stress versus the coordinate system; and  $w_{iK} \sigma_{jK}$ ,  $W_{jK} \sigma_{iK}$  are the rotation tensors of the components.

According to the practical spinning condition, through mathematics treatment, an equation can be obtained in a simple shear, as follows:

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} + \tau \dot{\gamma} \begin{bmatrix} -\sigma_{12} & (\sigma_{11} - \sigma_{22})/2 & 0 \\ (\sigma_{11} - \sigma_{22})/2 & \sigma_{12} & 0 \\ 0 & 0 & 0 \end{bmatrix} = 2\eta \begin{bmatrix} 0 & \dot{\gamma}/2 & 0 \\ \dot{\gamma}/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (7)$$

where

$$S_R = \tau \dot{\gamma} \quad (8)$$

The recoverable shear strain can be deduced according to eqs. 7 and 8.<sup>12</sup> The end correction  $e$  in the capillary flow can be separated into two parts: the Couette correction  $\xi$  and Philippoff-Gaskins correction  $S_R$ . Table II shows the  $\xi$  and  $S_R$  of AN-g-casein concentrated solution at different shear rates in 80°C. It can be seen that the  $\xi$  and  $S_R$  increase separately with shear rate.

### Common Equation of $\xi$ and $S_R$ versus Shear Rate and Temperature

The plots of  $\lg \xi$  against  $\lg \dot{\gamma}$  at different temperatures are shown in Figure 2, from which it can be observed that  $\xi$  increases with the increase of shear rate in the same temperature, whereas  $\xi$  decreases with the temperature at the same shear rate.  $\lg \xi$  appears in a linear function of  $\lg \dot{\gamma}$ , so the

**Table II Values of Couette Correction  $\xi$  and Recoverable Shear Strain  $S_R$  of AN-g-casein Concentration Solution at Different Shear Rates (80°C)**

$\dot{\gamma}$ ( $10^3 \text{s}^{-1}$ )	$\xi$	$S_R$
1.7	0.965	2.13
2.5	1.10	2.46
3.5	1.28	2.77
5.0	1.40	3.11
7.0	1.57	3.48
10.0	1.73	3.93
14.0	1.97	4.38
20.0	2.16	4.92
28.0	2.32	5.45
40.0	2.54	6.14

quantitative function relation can be described in a power law form, as follows:

$$\xi(\dot{\gamma}, T) = K' \dot{\gamma}^{n'} \quad (9)$$

Therefore, relation 9 becomes a common equation according to the experimental data in Figure 2:

$$\lg \xi [\dot{\gamma}, T(^{\circ}\text{K})] = (3.194 - 0.0116T) + (-0.388 + 0.0019T) \lg \dot{\gamma} \quad (10)$$

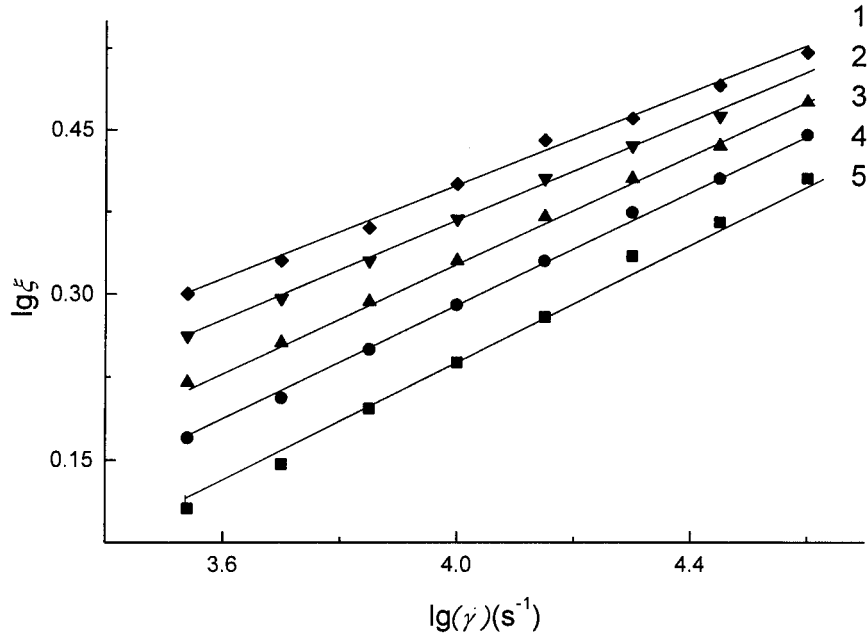
Within the range of experiment, the higher the shear rate is, the bigger the deformation of the pseudonetwork structure and the higher the required energy for adjusting velocity profile. The  $\xi$  of AN-g-casein concentrated solution varies according to eq. 10.

The curves of  $\lg S_R$  against  $\lg \dot{\gamma}$  at different temperatures are plotted in Figure 3. With the increase of shear rate, the recoverable shear strain increases in the range of experiment. However, the recoverable shear strain decreases with the increase of temperature, which is similar to the effects of temperature on melt-spinning.<sup>13</sup>

In the same way, the common equation  $S_R(\dot{\gamma}, T)$  can be deduced according to the data of Figure 3:

$$\lg S_R [\dot{\gamma}, T(^{\circ}\text{K})] = (3.22 - 0.0111T) + (-0.449 + 0.00219T) \lg \dot{\gamma} \quad (11)$$

The function relation of  $\xi$  and  $S_R$  against  $\dot{\gamma}$  and  $T$  in the capillary flow of AN-g-casein solution are defined in the two quantity equations, which are significant to analyze the rheology behavior of



**Figure 2** lg–lg plots of Couette correction against shear rate at various temperatures ( $T/^\circ\text{C}$ ): 1, 40; 2, 50; 3, 60; 4, 70; 5, 80.

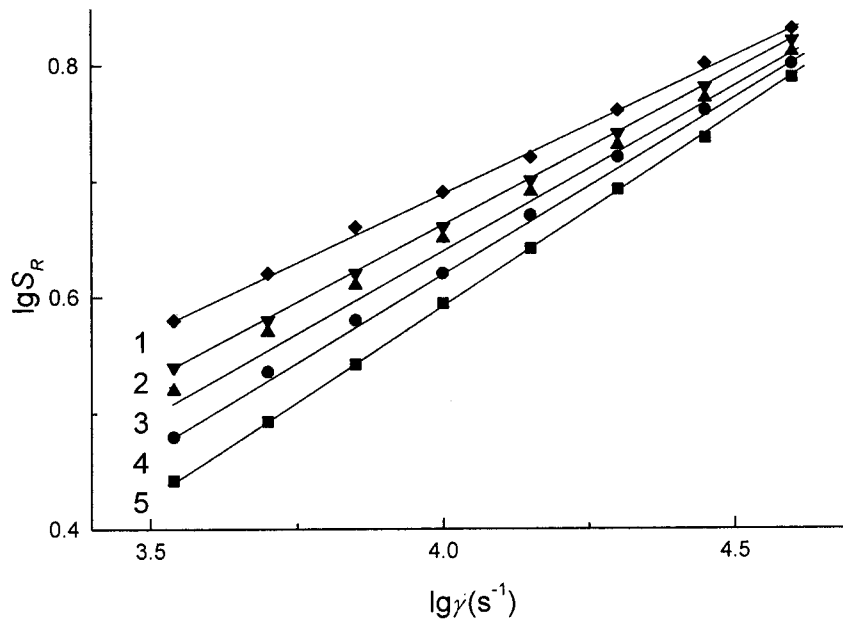
AN-g-casein concentrated solution, and find the original causes for the melt disruption to adjust the parameters for practical spinning technology.

**Efficient Simple Measurement and Correction of Rheological Parameters of AN-g-Casein Concentrated Solution**

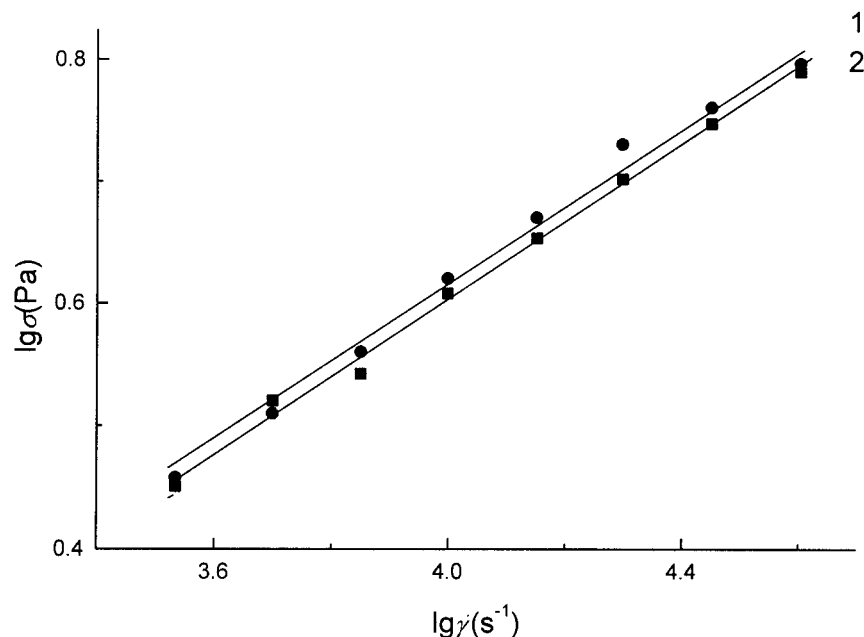
In reality, much work is needed for measurement and correction of rheological parameters using a

series of capillaries. Therefore, the correction way using only one flow curve is put forward. The Bagley correction formula of shear stress can be referred to in another way, as follows.<sup>3</sup>

$$\sigma = \sigma_a \frac{1}{1 + R/L \left[ \xi + \frac{1}{2} S_R \right]} \tag{12}$$



**Figure 3** lg–lg plots of recoverable shear strain against shear rate at various temperatures ( $T/^\circ\text{C}$ ): 1, 40; 2, 50; 3, 60; 4, 70; 5, 80.



**Figure 4** Flow curves for AN-g-casein concentrated solution, obtained by using different correction methods (80°C): 1, method of this article (by one flow curve,  $L/R$ : 3.01); 2, method of Bagley (by a series of capillaries).

When the spinning technology is given,  $\sigma_a$  can be calculated after the Rabinowitsh correction.  $\xi$  and  $S_R$  can be valued by a common equation. Therefore, real shear stress  $\sigma$  can be deduced by only one flow curve according to eq. 12.

Figure 4 shows the two correction results: one is obtained from the way of the common equation, and the other is obtained from a series of capillaries with different  $L/R$ . It is evident that the results of the two ways are almost identical. The way of the common equation only needs one flow curve, which makes the experiment easy. The similar results of the two ways prove that it is reasonable to use the Dewitt model to deal with the rheology parameter so as to separate recoverable shear strain  $S_R$  and Couette correction  $\xi$ , and the common equation is true to the AN-g-casein concentrated solution.

#### Real Elastic Model $G$

After obtaining the real shear stress and recoverable shear strain by analysis and separation of end correction, the elastic model  $G$  was evaluated according to the formula, as follows:

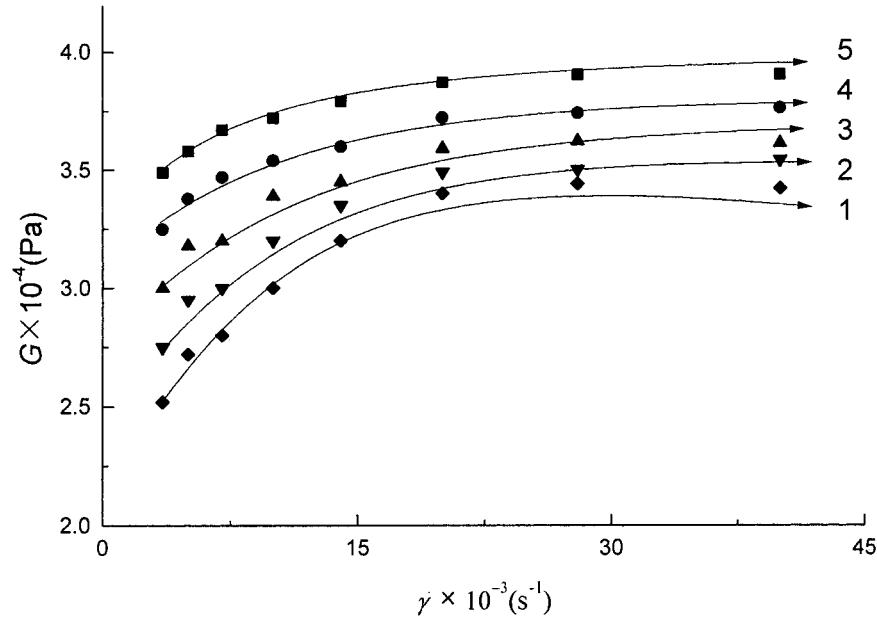
$$G = \sigma/S_R \quad (13)$$

Bagley took the Couette correction by extrapolation of the plots of  $(2\xi + S_R)$  versus  $\sigma$  to the limit of  $\sigma = 0$

as the Couette correction in higher shear stress. Hayahama used the  $S_R$  of sodium silicate solution at low shear stress as a substitute of  $S_R$ . Here, the elastic model  $G$  of AN-g-casein concentrated solution in steady-state flow was calculated according to eq. 13 to predict the elastic behavior. The value of  $G$  shows the elastic model at each real point of the shear stress in Figure 5. The elastic model increases with an increase of shear rate. Hayahara reported that the elastic model decreases with an increase of the shear stress. The main reason for this error is because the same  $\xi$  is used in higher shear rate. Really, the elastic model is no longer a constant under higher shear rate.

#### Die Swell of AN-g-Casein Concentrated Solution in the Extruding Process

Tanner presented a die-swell theory similar to eq. 1,<sup>9</sup> in which some assumptions were made, as follows: (a) the flow is isothermal and incompressible; (b) the die is very long ( $L/R \rightarrow \infty$ ); (c) inertial effects in flow may be ignored; and (d) gravity, other body force, and surface tension forces are ignored. Figure 6 shows the die-swell ratio  $B_0$  calculated by using the Tanner theory and real-experiment die-swell  $B_e$  was investigated by using a microscope camera at 50°C. It can be seen that  $B_0$  and  $B_e$  increase with the increase of shear

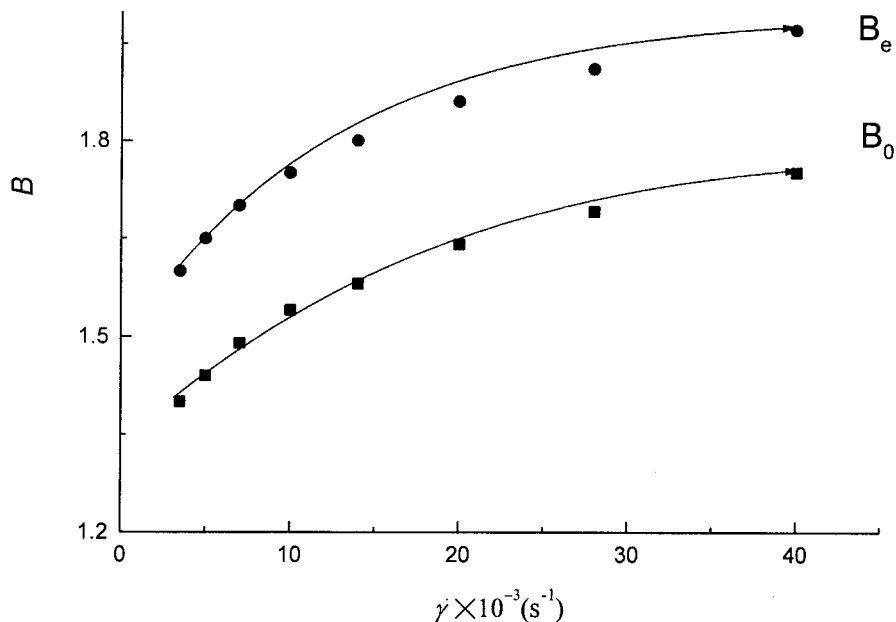


**Figure 5** A series of real elastic modulus versus shear rate plots (each curve corresponds to a constant temperature): 1, 40°C; 2, 50°C; 3, 60°C; 4, 70°C; 5, 80°C.

rate.  $B_e$  is always higher than  $B_0$  in the shear rate range of experiment, and the error may be caused by the assumptions in Tanner die-swell theory.

As shear rate at  $2 \times 10^4 \text{ s}^{-1}$  approaches real spinning condition, the curve of  $B_e/B_0$  versus different  $L/R$  was obtained, as shown in Figure 7.  $B_e/B_0$  tends to 1 with the increase of  $L/R$ , which

means that the real die swell by experiments in higher  $R/L$  is more agreeable with the die swell, as predicted by Tanner theory. It proves that the method of  $\xi$  and  $S_R$  being separated and corrected by using the Dewitt model is reasonable. Therefore, the real die swell of the AN-g-casein concentrated solution in the spinning process can be



**Figure 6** Die-swell ratio  $B_0$  by Tanner theory and real die-swell ratio  $B_e$  by experiment versus shear rate plots (50°C,  $L/R$ : 12.36).

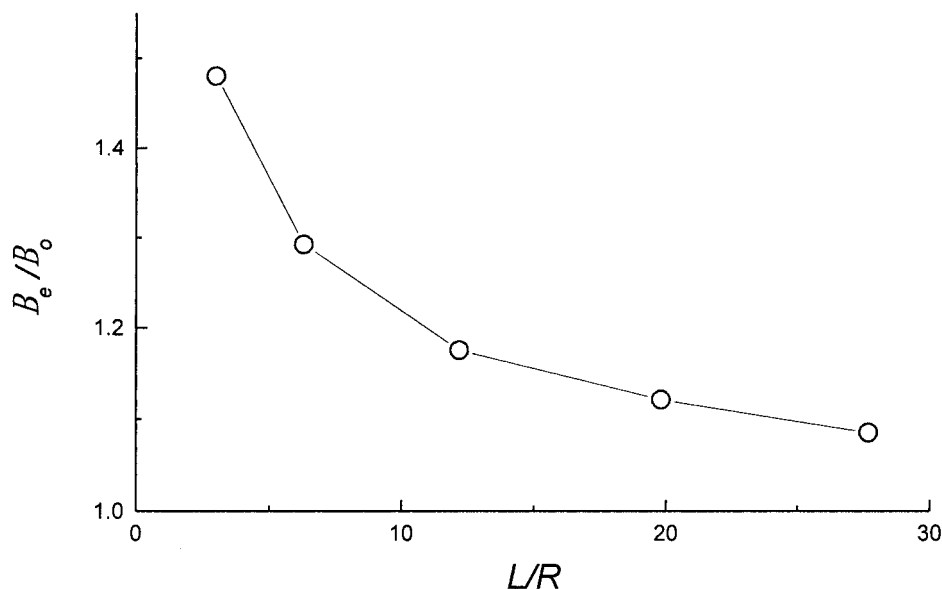


Figure 7 The curve of  $B_e/B_0$  versus  $L/R$  (shear rate:  $2 \times 10^4 \text{ s}^{-1}$ ).

predicted only by using one flow curve, according to the error of  $B_e$  and  $B_0$  in Figure 6. Further, the theoretic basis of stabilizing the wet spinning technology was given and the spinning condition can be chosen.

## CONCLUSIONS

1. The rheological behavior of AN-g-casein concentrated solution is investigated. The result shows the AN-g-casein concentrated solution is a kind of non-Newtonian fluid of shear thinning.

2. Within the experimental error range, the end correction term increases with the increase of shear rate. Under the real spinning process, real shear stress only attributed about 35% to the apparent shear stress, which confirmed the essentiality of correction for rheology parameter in capillary flow.

3. The Couette correction and recoverable shear strain were analyzed and separated by using the Dewitt model. The quantitative functional relations of Couette correction and recoverable shear strain versus temperature and shear rate were deduced in the extrusion process of AN-g-casein concentrated solution. During practical spinning, using the quantitative functional relations, the rheological parameter can be obtained by only one flow curve.

4. By obtaining the real elastic model  $G$ , which fits any shear rate in the range of experiment, the  $G$  increases with the increase of shear rate, which is opposite to the conclusion reported by Haya-

hara and Takao.<sup>6</sup> It may be explained that Haya-hara used the same Couette correction at a higher shear rate.

5. By using the method in this article, die swell can be evaluated efficiently. Furthermore, the theoretical basis for the stability of the wet spinning technology of AN-g-casein concentrated solution was provided.

## REFERENCES

- Mitsuo, Y. *Modern Chem (Jpn)* 1990, 10, 23–31.
- Ishii, K.; Oka, S. *Sen-I Gakkaishi* 1983, 39 (11), T479–T484.
- Bagley, E. B. *J Appl Phys* 1957, 28, 624–627.
- Philippoff, W.; Gaskins, F. H. *Trans Soc Rheol* 1958, 2, 263.
- Bagley, E. B. *Trans Soc Rheol* 1961, 5, 355.
- Hayahara, T.; Takao, S. *J Appl Polym Sci* 1968, 12, 1755–1763.
- Dong, Q. *J. Chin Text Univ* 2000, 26 (3), 1–4.
- Ou, G.; Zhang D. *Experiments of Polymer Materials Science and Engineering*; East China University of Science and Technology: Shanghai, 1997; pp 141–144.
- Tanner, R. L. *J Polym Sci, Part A: Polym Chem* 1970, 8, 2067.
- Zhang, J.; Gao X.; Dong, J. *Man-Made Fiber* 1981, 1, 1–8.
- Han, C. D. *Rheology in Polymer Processing*; Academic Press: New York, Academic Press, 1976; p 37.
- Dewitt, T. W. *J Appl Phys* 1955, 26, 889.
- Ziabicki, A. *Fundamentals of Fiber Formation*; Wiley-Interscience: New York, 1976; p 158.