Study on Molecular Weight Distribution of Cellulose by Using Rheological Methods

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Abstract: The degree of polymerization (DP) and the molecular weight distribution (MWD) play a special role in producing cellulose fiber by using the N-methyl morpholine N-oxide (NMMO) process. In this paper, rheological methods have been used to determine the MWD of cellulose. It is shown that the limiting compliance J_e^0 of cellulose samples increases strongly with the increasing broadness of MWD, and that the polydispersity index $\langle\tau_w\rangle/\langle\tau_n\rangle$ of the distribution of relaxation times can also well characterize the polydispersity of MWD of the cellulose samples. By using Tuminello's method, the cumulative weight distribution $C(M)$ can be calculated from the terminal modulus and the plateau modulus of the cellulose/NMMO solution via $1 - [G'(\omega)/G_N^0]^{1/5}$ ($G'(\omega)$ and G_N^0 are the storage modulus and the plateau modulus respectively).

Keywords: limiting compliance, molecular weight distribution, rheology

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1. Introduction

The increasing demands of an ecological character on the manufacture of manmade fibers from cellulose are leading to the interest in dissolving this polymer [1]. A process for making cellulose fibers using N-methylmorpholine-N-oxide (NMMO) has great advantages than conventional viscose process because the process are not polluting and can be recycled completely. This process provides clean environment for workers and substantially reduces the amount of wastewater and waste gases. Furthermore, the viscose process is very complicated and requires high energy-consumption. In view of production cost, the NMMO process is more economical and suitable than the viscose process. Moreover, the cellulose fibers obtained by the NMMO process are also superior to those from viscose rayon in view of their mechanical properties such as tensile strength and modulus.

There are some special requirements for cellulose when used as a raw material of fiber [2]. In addition to the degree of whiteness, ash content and especially α -cellulose content, the degree of polymerization (DP) and the molecular weight distribution (MWD) play a special role. Different kinds of cellulose will have very different spinnability and will result in different mechanical properties of the final fibers.

In general, the MWD of cellulose is determined by fraction method or by gel permeation chromatography (GPC). The fraction method is usually tedious and impractical for routine analysis. The GPC may be more practical, but it generally requires converting the cellulose sample into a derivative and then dissolving it in a certain organic solvent. The whole process will probably induce the cellulose chains to degradation. In addition, incomplete or non-uniform substitution may have some influences on the solubility of the cellulose sample. A recently discovered mixture solvent system of N-N-dimethylacetamide (DMAc) and lithium chloride (LiCl) for cellulose may be well used in GPC. However, due to the pre-activation of cellulose, the processes of swelling, stirring and dissolving should be carefully carried out and the conditions used in each step of the processes should depend on the various cellulose with different crystallinity and lignin contents. Thus, the GPC method is also complicated [3]. In this paper, we adopt some rheological methods for the same purpose, which not only can provide directly the processing parameters for spinning process of cellulose fibers, but also can offer much information about the raw materials. Through rheological technique and using the cellulose-NMMO solution system, the meaningful values of MW and MWD for various cellulose samples are obtained here.

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2. Experimental

2.1 Materials

2.1.1 N-methyl morpholine-N-oxide (NMMO)

Aqueous NMMO from BASF has initial water content of 50 % as determined by refractometry. A calibration curve of the index of refraction of aqueous NMMO solution as a function of water content was established beforehand in our laboratory.

2.1.2 Cellulose samples

Four cellulose samples got from Shanghai Chemical Fibre Co are used in this study. The standard cupriethylenediamine solution method is used for determining the intrinsic viscosity or DP of cellulose.

2.1.3 Additive

n-propyl gallate is used as an anti-oxidant for stabilizing the DP of cellulose during dissolving process.

2.2 Dissolution

The preparation of the cellulose solution was carried out as follows. 200 g of aqueous NMMO (water content 50 %) were put into a 250 ml spherical flask and 2 g of n-propyl gallate were added. The flask was then heated to 100°C under a vacuum of 15 mm Hg. When the water content of aqueous NMMO was reached 13 % as determined by refractometry, the distillation was then stopped. All cellulose solutions thereafter were made from this solvent. For example, 2,000 g of dried cellulose were added into 20,222 g of the above solvent. After half an hour of stirring at 90°C, a yellow transparent cellulose solution was formed. The solution was kept at 90°C in an oven for deaeration. After 3 hours the solution was absent of bubbles and insoluble particles, which was checked by putting a drop of solution on a preheated glass slide and observing it with a polarizing optical microscope.

2.3 Rheological measurements

The viscoelastic measurements were made on a DSR-200 Dynamic Stress Rheometer (Rheometrics Co., USA) in frequency scanning mode and creep recovery mode. Parallel and circular plates (25 mm diameter and 1 mm interval distance) were used. After making sure that all tests are in the linear viscoelastic region, the measurements were then made at certain amplitude of strain. Frequency scanning was made from 0.1 to 200 (radian/s) and the measurements were carried out at 70, 90 and 110°C.

3. Results

3.1 Dynamic Modulus Spectra

The dynamic moduli G' and G'' were automatically determined and recorded by the instrument. To ensure

linear viscoelastic behavior, the torque trace during sinusoidal oscillation was also examined for confirming its sinusoidal waveform. In order to avoid crystallization of cellulose the lowest temperature used was 70°C, and in order to avoid thermal decomposition of solvent and cellulose the highest temperature used was 110°C. The master curves for G' and G'' at the reference temperature of 90°C for samples 1[#] to 4[#] were obtained via superimposition method using 'Rhuos software' (Figures 1-4). The viscosity $\eta^*(\omega)$ was obtained as well according to its relation with the storage modulus G' and the loss modulus G'' (equation (1)), the curves of the viscosity for the four samples are shown in Fig. 5

$$\eta^*(\omega) = \frac{\sqrt{(G')^2 + (G'')^2}}{\omega} \quad (1)$$

Fig.1 Dynamic frequency sweep for sample1[#]

Fig.2 Dynamic frequency sweep for sample2[#]

Fig.3 Dynamic frequency sweep for sample3[#]

Fig.4 Dynamic frequency sweep for sample4[#]

Fig.5 Comparison of complex viscosity for four samples

Table 1. The DP and η_0 of four samples

Sample	1 [#]	2 [#]	3 [#]	4 [#]
$\overline{DP}$	480	710	680	200
η_0 (Pa·s)	1460	2970	2750	120

The viscosity at zero shear rate can be approximately determined from the viscosity at the lowest frequency used (cf. Fig. 5) by using Cox-Merz rule and the results for the four cellulose samples are listed in Table 1. The DP of cellulose listed also in Table 1 is determined by the standard cupriethylenediamine solution method. Therefore, a relationship between DP and the viscosity at zero shear rate can be established as follows

$$\eta_0 = 0.00017(\overline{DP})^{2.55} \quad (2)$$

The MWD of the four samples can be evaluated from the value of the shear rate at which the non-Newtonian flowing begins [4]. The higher the value of this shear rate, the narrower is the MWD of cellulose. Thus, samples 1[#] and 4[#] have narrower MWD, while 2[#] and 3[#] have broader MWD, as shown in Fig. 5.

3.2 The limiting compliance J_e^0 and the distribution of the relaxation times

The limiting compliance J_e^0 depends not only on the

species used, but also on the MWD of the species, or the polydispersity index as a first approximation. The value of J_e^0 for sample 1[#] can be obtained from the creep and recovery test, and the result is shown in Figure 6. The values of J for the four samples are listed in Table 2. Although the limiting compliance is not a simple function of the polydispersity and will depend upon the overall shape of the MWD curve, it increases strongly with the increasing broadness of the MWD. Thus, from Table 2 it can be seen that sample 3[#] has the broadest MWD, sample 2[#] is the next, then follows sample 1[#], and sample 4[#] has the narrowest MWD.

Fig.6 The creep and recovery test for sample 1[#]

Table 2. The limiting compliance J_e^0 and the distribution of relaxation times of four samples

Sample	1 [#]	2 [#]	3 [#]	4 [#]
J_e^0 (Pa ⁻¹)	0.0042	0.0573	0.0687	0.0038
$\langle\tau_w\rangle/\langle\tau_N\rangle$	50.4	687	824	45.6

Another important parameter of rheological characterization of polymer studied here is $\langle\tau_w\rangle/\langle\tau_N\rangle$, called 'polydispersity index of relaxation times', which characterizes the broadness of the distribution of relaxation times [5]. The value of $\langle\tau_w\rangle/\langle\tau_N\rangle$ can be calculated from the following equation

$$\frac{\langle\tau_w\rangle}{\langle\tau_N\rangle} = \frac{\int \tau^2 H(\tau) d \ln \tau}{\int \tau H(\tau) d \ln \tau} \bigg/ \frac{\int \tau H(\tau) d \ln \tau}{\int H(\tau) d \ln \tau} = J_e^0 G_N^0 \quad (3)$$

where G_N^0 is the plateau modulus and $H(\tau)$ is the distribution function of relaxation times. When the chains are fully entangled, the storage modulus G' will have a limiting maximum value in the terminal zone (in high frequency zone), called plateau modulus. For a given macromolecular species, the plateau modulus G_N^0 is a characteristic parameter of polymer species and does not depend upon molecular weight (MW) if the MW is greater than a certain critical value [5]. As shown in

Figures 1-4, the storage modulus of sample 3[#] or 4[#] has not reached the plateau modulus within the measurement frequency range used, but the storage modulus G' of sample 1[#] or 2[#] has nearly reached the plateau modulus. Thus, as an estimation, we can suppose that the plateau modulus of cellulose is approximately equal to 1.2×10^4 Pa. This value is also supported by our experimental results on the other cellulose solutions, which are not reported here. Thus, the values of $\langle \tau_w \rangle / \langle \tau_N \rangle$ for the four samples can be obtained, as listed in Table 2. Thus, we can also use the value of $\langle \tau_w \rangle / \langle \tau_N \rangle$, instead of J_e^0 , to characterize the broadness of the MWD of cellulose.

3.3 The relative MWD

3.3.1 Tuminello's method [6-9]

W. H. Tuminello has provided a method for calculating the relative MWD function $W(M)$ of linear polymeric melts based on an analogy with polymer solutions. It is well known that

$$G_{N,solution}^0 \equiv \phi^2 G_{N,melt}^0 \quad (4)$$

where ϕ is the volume fraction of polymer in solution. W. H. Tuminello assumed that the unrelaxed chains of the melt at any frequency, ω , are "diluted" by the already relaxed chains of the melt, which do not entangle with the unrelaxed chains. He also assumed that each monodisperse fraction of MW, M_i , corresponds to a single relaxation frequency ω_i and all chains of MW less than M_i are thoroughly "relaxed" at frequency ω_i and make no contribution to the plateau modulus at all. Hence, in equation (4), one may use the storage modulus $G'(\omega_i)$ instead of $G_{N,solution}^0$, the plateau modulus G_N^0 instead of $G_{N,melt}^0$, then, the weight fraction W_u of the unrelaxed chains of $M \geq M_i$ can be calculated as follows

$$W_u = \left[G'(\omega_i) / G_N^0 \right]^{0.5} \quad (5)$$

where the value of $\left[G'(\omega_i) / G_N^0 \right]^{0.5}$ is also defined as the reduced modulus elsewhere. We also know that [10]

$$1/\omega = KM^\alpha \quad (6)$$

where α is equal to 3.4 for flexible polymers and may be a little different from 3.4 for semi-rigid cellulose. Equations (7) and (8) then transform the reduced modulus into the weight fraction and the relaxation frequency into the corresponding MW, respectively, which leads to the determination of the cumulative MWD (CMWD) or the cumulative weight fraction $C(M)$ of chains up to a specified M . Thus, we have

$$C(M) = 1 - W_u = 1 - \left[G'(\omega_i) / G_N^0 \right]^{0.5} \quad (7)$$

and

$$W(M) = \frac{d\{C(M)\}}{d\{\log(M)\}} \quad (8)$$

where $W(M)$ is the differential function of $C(M)$ with respect to logarithm scale of M .

Using this method, Tuminello obtained good results compared with GPC. Although Tuminello's method is generally used for simple linear polymeric melt and solution, this theory that the cumulative weight fraction, $C(M)$, is equal to $1 - \left[G'(\omega) / G_N^0 \right]^{0.5}$ should still hold for the case of the concentrated cellulose/NMMO solution, where the relaxed macromolecular chains and the small molecules both play a role of the solvent. It is well known that the effect of the relaxed low MW compatible chains on the elastic parameters are mainly topological, i.e., the nature of the "dilution solvent" is not important here and has little effect on the shape of the distribution of the relaxation times [4]. On the contrary, the effects of the "dilution solvent" on the viscosity will be twofold i.e., a topological effect and a dynamic effect based on the mobility of molecules. Here only the elastic parameters G' and G_N^0 are used for Tuminello's method, and hence this method is considered as successful.

3.3.2 Applications in cellulose/NMMO solutions

In Figure 7, the original data $\left[G'(\omega) / G_N^0 \right]^{0.5}$ of sample 1[#] are represented by black squares and fitted by an S-shaped curve via using Microal Origin 5.0 software. Its corresponding differential curve is shown in Figure 8.

Fig. 7 Square root of the reduced modulus $\left(G' / G_N^0 \right)^{0.5}$ vs ω

Fig.8 Differential relative MWD plot for sample 1[#]

Because the monodisperse cellulose can not be obtained in our laboratory, we can not get the exact value of the constant K. However, we know that

$$\log(1/\omega) = \log K + \alpha \log M \quad (9)$$

This means that $\log(1/\omega)$ represents a relative logarithm-scaled MW and the region of high value of $\log(1/\omega)$, i.e., low frequency region or the right side of the curves in Figure 9, corresponds to the high MW composition of the system, and vice versa.

The instrument limits the range of the scanning frequency used and the measurement temperature range also limits the whole frequency range of the master curve in order to avoid crystallization and decomposition of the system. However, it is already very clearly shown in Figure 9 that samples 1[#] and 4[#] have narrower MWD and sample 4[#] has the lowest average molecular weight as compared with others. Of these four samples, the MWD of sample 3[#] is relatively broader, and sample 2[#] has a high MW tail particularly. Here, sample 1[#] is of cotton linter, samples 2[#] and 3[#] are of wood pulps, and sample 4[#] of rayon fibers. Hence, the above results are confident because wood pulps naturally have a broader MWD and a high average MW tail, while cotton linters has narrow MWD and rayon fibers has narrow MWD and low average MW [3].

Fig.9 Differential relative MWD plot for different cellulose samples

4. Conclusion

In the nature, there are many kinds of cellulose, e.g., from various woods and linters. Solutions prepared from different cellulose will have very different behavior in spinning process and fibers finally obtained will have

very different properties also. The linear viscoelastic properties are the basic rheological characterization of the polymer systems and can be used to relate them to the macromolecular structure. By using rheological methods, the values of J_e^0 and $\langle\tau_w\rangle/\langle\tau_N\rangle$ for the four cellulose samples are obtained, as listed in Table 2. It is shown that the distribution of relaxation times is closely related to the MWD. From the value of $\langle\tau_w\rangle/\langle\tau_N\rangle$, one can obtain the broadness of the MWD of the cellulose samples, which is consistent with criterion via J_e^0 . Moreover, based on the linear viscoelastic behavior of a linear polymeric system and by using Tuminello's method, the reduced modulus, the cumulative weight fraction, and the MWD function of the cellulose samples can be well determined with a reasonable accuracy. Therefore, cellulose from different raw materials can be well compared and the optimal cellulose for preparing fibers via NMMO process can be selected.

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References

1. D. Loubinoux, and S. Chaunis, *Text. Res. J.*, **57**, 61 (1987).
2. I. P. Baksheev, and P. A. Butyagin, *Fibre Chemistry*, **29**, 221 (1997).
3. A. A. Silva and M. L. Laver, *Tappi J.*, **80**, 173 (1997).
4. C. D. Han, *"Rheology in Polymer Processing"*, Academic Press, New York, p.60 (1976).
5. J. Piau, and J. Agassant, *"Rheology for Polymer Melt Processing"*, Elsevier Science B.V.: New York, p.95 (1996).
6. W.H. Tuminello, *Polym. Eng. Sci.*, **26**, 1339(1986).
7. W.H. Tuminello, *Polym Eng Sci.*, **29**, 645 (1989).
8. C. Carrot, and J. Guillet, *J. Rheo.*, **41**, 1203 (1997).
9. C. Lavallee, and A. Berker, *J. Rheo.*, **41**, 851 (1997).
10. D. Ferry, *"Viscoelasticity Properties of Polymers"*, 3rd Ed., Wiley, New York, p.224 (1980)