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Rheological Method for Determining Molecular Weight and Molecular Weight Distribution

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1. Introduction

Gel permeation chromatography (GPC) method is a widely used and accepted method for measuring the *MW* and *MWD* for polymers. However, the method has its limitations. The key of this method is to find the suitable solvents to dissolve the polymer well. But cellulose can not be dissolved in most of the organic solvents because of the inter- and intra-hydrogen bonding of the cellulose chains. Lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc) can dissolve cellulose, but the dissolution process is very complicated, which includes pre-activation, solvent exchange, swelling and dissolution. Furthermore, more attention must be paid to each step, and cellulose has to be dissolved for 5-10 days according to the type of cellulose pulp [1-4]. Therefore, it is necessary to develop a simple and fast method which can get the *MW* and *MWD* of cellulose.

Wu [5] got the *MWD* from storage modulus G' and stress relaxation modulus $G(t)$ using approximations derived from the Doi-Edwards description of chain dynamics. Wu's method accurately predicted the *MWD* of polymers with narrow distribution. However, often, it led to a distorted shape of the *MWD* for the sample with bimodal distributions. Therefore, Tuminello [6-8] developed a theory based on a diluted assumption in 1986. His method rigorously applies only to linear polymers. Especially, it works better for linear polymers with $PI < 3.5$. According to his theory, the relative differential *MWD* of polymer can be determined well from dynamic modulus master curve.

Gu [9] applied the diluted assumption theory to the concentrated cellulose in *N*-methylemorpholine-*N*-oxide monohydrate (NMMO·H₂O) solution. He got relative differential *MWD* curves of three kinds of cellulose pulps from the dynamic data of cellulose/NMMO·H₂O solution in 2000. But the results were not compared with the results reported by GPC. In 2004, the relative differential *MWD* curves of four kinds of cellulose pulps were calculated on the basis of that method and the calculated results were compared with the non-calibrated GPC results by Zhang [10]. In their rheology experiments, the cellulose concentration in NMMO·H₂O solution was fixed (9%, wt), and the polydispersity index (*PDI*) of cellulose was not calculated.

In the present work, the effect of cellulose concentration in NMMO·H₂O solution on prediction of the *MW* and *MWD* of cellulose using the rheology-based method was

investigated. Furthermore, the calculation of the *PDI* of cellulose was developed. In addition, it also realized the conversion of the reciprocal of the frequency to the actual *MW* scale, obtaining *MWD* scale curve of cellulose [11,12].

2. Experimental

2.1 Materials

Pulp 1 was purchased from Sappi Saiccor (Durban, South Africa). Pulp 2 and 3 were supplied by Weyerhaeuser (Covington, Washington, USA). N-methylmorpholine-N-oxide (NMMO) aqueous solution from BASF (Ludwigshafen, Germany) had an initial water content of 50% (*wt*). N, N-dimethylacetamide (DMAc) was obtained from Fluka (Lausanne, Switzerland). LiCl was obtained from Yili Finer Chemical Ltd. (Shanghai, China). Polystyrene standard was purchased from Waters (Milford, Massachusetts, USA), with nominal *MWs* of 1.3×10^4 , 3.03×10^4 , 6.55×10^4 , 18.5×10^4 , 66.8×10^4 , and 101×10^4 .

2.1.1 Rheological measurement method

Preparation of cellulose/NMMO·H₂O solution. A mixture of cellulose pulp in 87% NMMO·H₂O (*wt*) was placed in a dissolving tank maintained at 100°C and stirred continually. The mixture gradually turned into a brown and clear homogeneous liquid. The solution with 12%, 11%, and 9% cellulose in NMMO·H₂O solution (*wt*) was obtained, respectively.

Rheological measurements. Rheological measurements were recorded on the RS1 rheometer [13] (Thermo Haake, Karlsruhe, Germany) in a frequency scanning mode of 0.2 to 620 (*rad s⁻¹*) with a cone plate (*Ti*, 35/1°). Dynamic rheological properties (storage modulus *G'* and loss modulus *G''*) were obtained in the linear viscoelastic region at the temperature of 75°C, 90°C, and 105°C, respectively. The data were analyzed with RheoSoft software (Thermo Haake).

Relative differential *MWD* curve and method of calculating *PDI*. Tuminello [6-8, 14] has a method of computing the relative differential *MWD* of linear polymer melts which is based on an analogy with polymer solutions. For the latter, it is well known that

$$G_{N,solution}^0 \approx \phi^2 G_{N,melt}^0 \quad (1)$$

Where ϕ is the volume fraction of the polymer. Tuminello assumes that the unrelaxed chains of a melt at any frequency (ω_i), are “diluted” by, but not entangled with, the relaxed (lower M_i) chains. He also assumes that each monodisperse fraction (M_i), has a single relaxation frequency (ω_i), below which it makes no contribution to the modulus – thus behaving as a step function. Hence, in Eq. (1), if one associates $G_{N,solution}^0$ with the storage modulus $G'(\omega_i)$, $G_{N,melt}^0$ with the rubbery plateau modulus G_N^0 , and ϕ with the mass fraction of unrelaxed chains of $M \geq M_i$, then

$$C(M) = 1 - [G'(\omega_i) / G_N^0]^{0.5} \quad (2)$$

where $C(M)$ is the mass fraction of relaxed chains, and

$$MWD = \frac{d(C(M))}{d(\log M)} \quad (3)$$

where M is the molecular weight.

It is well known for the relations

$$1/\omega \propto \eta_0 \propto M^{3.4} \quad (4)$$

where ω is the frequency of dynamic rheology data, η_0 is the zero-shear viscosity of dynamic rheology data, therefore, $\log(1/\omega)$ is proportional to $\log M$, then

$$MWD = \frac{d(C(M))}{d(\log(1/\omega))} \quad (5)$$

The above equations were employed in the calculation of the relative differential MWD curve of the cellulose pulps.

The relative differential MWD curve is a Weibull function which is the logarithm of the normal distribution function and is especially applied to measure the MWD of polymers. The Weibull function is given by [15, 16]:

$$Y = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma^2}(M - M_p)^2\right) \quad (6)$$

where Y is the relative content percent of MW , M is the molecular weight, σ is the standard deviation, and M_p is the peak MW on the MWD curve.

There is a correlation between the peak value of the ordinate (Y_{extre}) and the σ with respect to the logarithm normal distribution, as given by Eq.(6) [15, 16]:

$$Y_{extre} = \frac{1}{\sqrt{2\pi}\sigma} \quad (7)$$

Then the PDI value is calculated by Eq.(7) [15, 16]:

$$PDI = \exp(\sigma^2) \quad (8)$$

2.1.2 GPC measurements

Dissolution of cellulose in LiCl/DMAc. A 10mg sample of each of the three pulps was placed in a 10mL centrifuge tube, respectively. Then 5mL of distilled water was added to each tube. The mixtures were stirred for 5min and left overnight to pre-activate the cellulose. The samples were centrifuged at 4000rpm for 15min. The supernatant fluid was decanted and 5mL of DMAc was added, respectively. After stirring for 15min, the centrifugation and the decantation steps were repeated. The whole solvent exchange procedure was repeated five times. Finally, 1.25mL of 8% LiCl/DMAc (wt/vol) was added, stirred for 60s, and left for approximately one week to dissolve completely, with occasional gentle stirring. The dissolved cellulose solutions were diluted to 20ml with DMAc to give a

final cellulose concentration of 0.5mg/mL in 0.5% LiCl/DMAc (wt/vol). Then the solution was filtered through a 0.45µm membrane filter.

GPC analysis. The *MWDs* for the three cellulose pulps were determined by GPC in a liquid chromatography (Waters1525) with a refractive index detector (Waters 2410). The mobile phase of 0.5% LiCl/DMAc (wt/vol) was pumped into the system at a flow rate of 1ml/min. Columns were Waters styragel HR 3, 4, and 5 (300mm × 7.8mm) preceded by a guard column. The system was operated at 50°C controlled by a column heater (Waters column temperature system). Injection volume was 200µL. Run time was 45min. A linear calibration curve was constructed with polystyrene standards directly dissolved in 0.5 % LiCl/DMAc (wt/vol). Data acquisition and *MWD* calculations were performed using Breeze software (Waters, Milford, MA, USA). Furthermore, the GPC data were calibrated using the Eawkins and Maddock calibration equation, as follows [1, 2]:

$$\log M_1 = \log M_2 + \frac{2}{3} \log \frac{(\kappa_\theta)_2}{(\kappa_\theta)_1} \quad (9)$$

where subscript 1 and 2 represent the unknown sample and the standard sample, respectively. Here, they are the cellulose and the polystyrene. K_θ values [1] of cellulose and polystyrene are 0.528 and 0.081 in the 0.5% LiCl/DMAc (wt/vol) system, respectively.

3. Results and discussion

3.1 Effect of cellulose concentration in NMMO·H₂O solution on the rheology-based results

Fig.1a, 1b, and 1c show G' and G'' master curves of the pulp 1 at various cellulose concentrations in NMMO·H₂O solutions according to the time-temperature superposition theory [13]. In terms of the Tuminello diluted assumption theory [6-8, 14], these curves are converted to relative differential *MWD* curves of the pulp 1 at different cellulose concentrations in NMMO·H₂O solutions shown in Fig.2a. Using the same procedure, relative differential *MWD* curves of the pulp 2 and 3 are obtained at various cellulose concentrations in NMMO·H₂O solutions and presented in Fig.2b and 2c, respectively. Meanwhile, the calculated $\log (1/\omega_p)$, σ and *PDI* values of the three pulps are given in Table 1.

Fig.2a, 2b, and 2c show that the relative differential *MWD* curves almost overlap with each other when the cellulose concentrations are 12% and 11%, respectively. However, when the cellulose concentration is 9%, the relative differential *MWD* curves shift slightly to the left.

The data in Table 1 clearly indicate that $\log (1/\omega_p)$ are higher and *PDI* decrease with increasing concentration. However, the relative deviation of the cellulose concentration between 9% and 11% is up to 16%, and the relative deviation of the cellulose concentration between 11% and 12% is less than 0.9%. Obviously, the calculated $\log (1/\omega_p)$ and *PDI* are approximately equal when the cellulose concentrations are 12% and 11%.

This phenomenon originates from the relaxation time (τ) of molecular chains and the steady-state recoverable compliance (J_e^0) in a polymer solution. With increasing concentration, the polymer chains are more strongly entangled with each other and get more and more

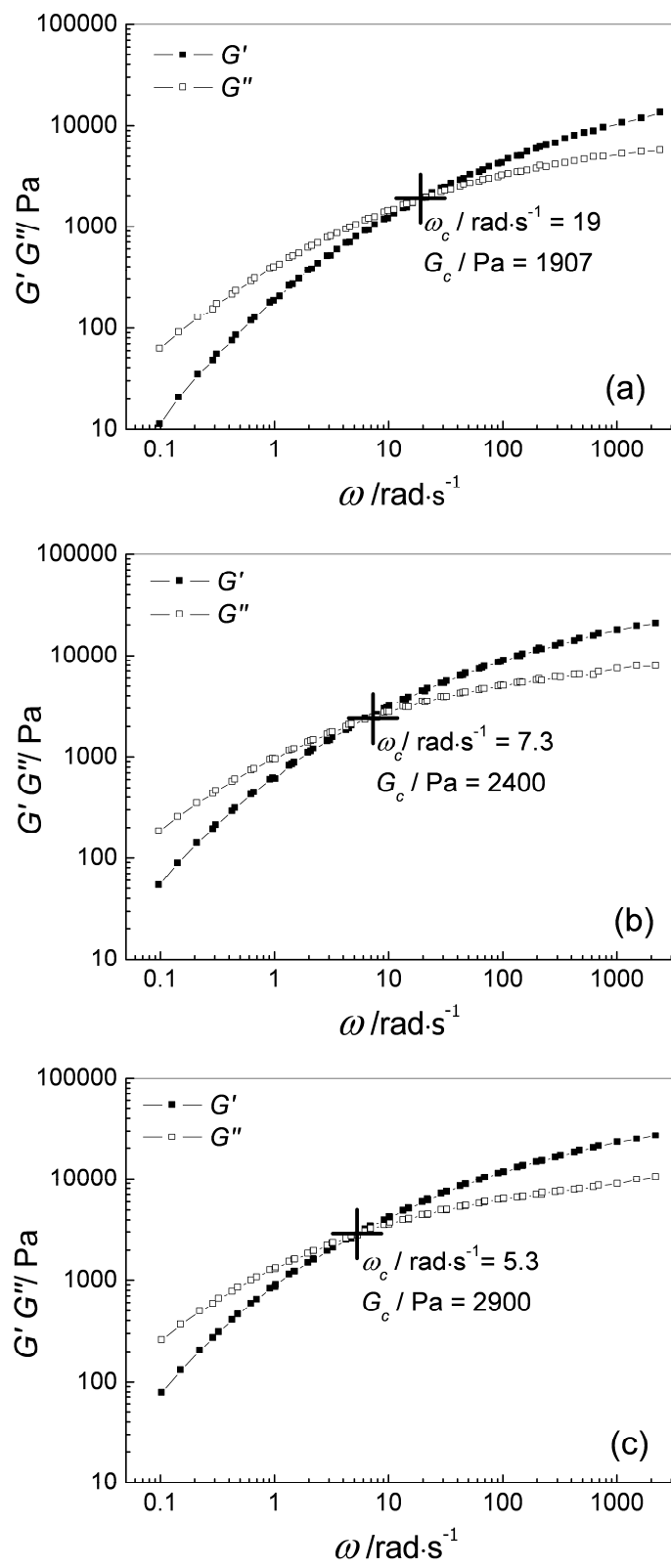


Fig. 1. Master curves of the pulp1 at different cellulose concentrations in NMMO-H₂O solutions: (a) 9%, (b) 11%, and (c) 12%.

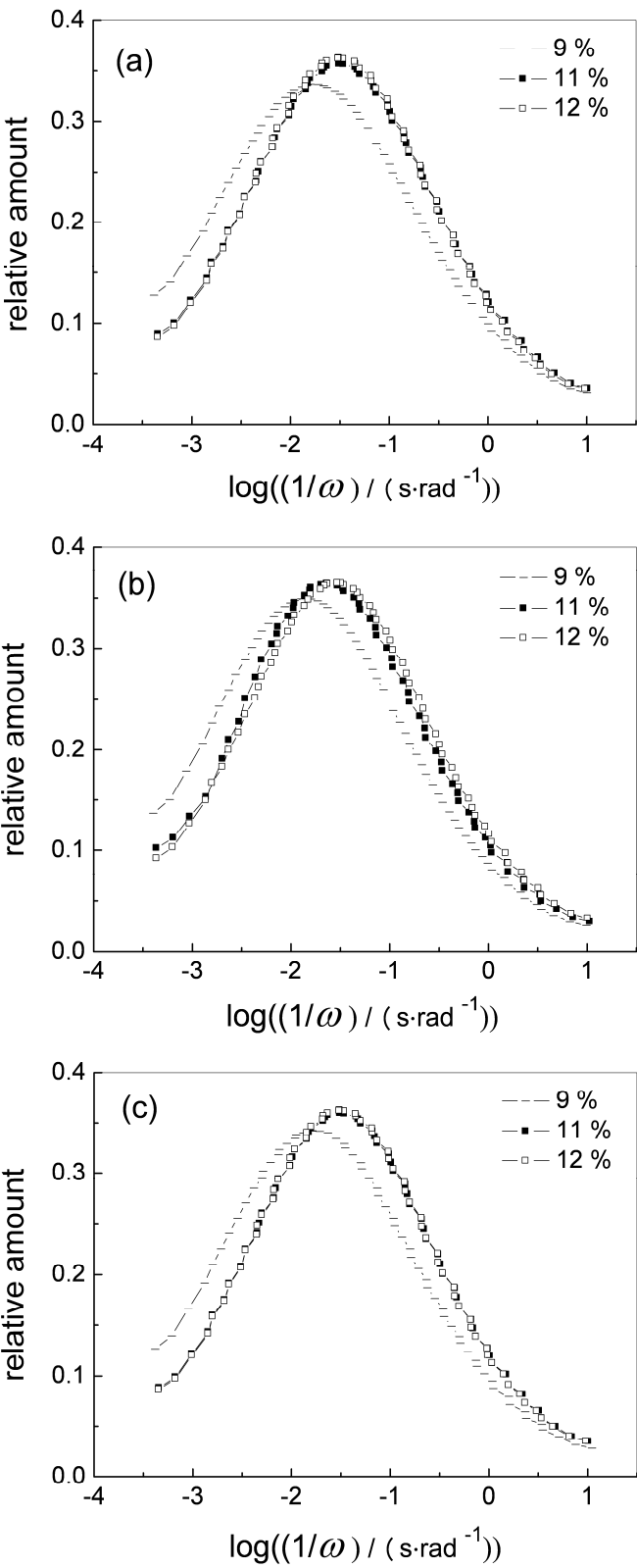


Fig. 2. Relative differential *MWD* curves of the three pulps at different cellulose concentrations in NMMO-H₂O solutions: (a) pulp 1, (b) pulp 2, and (c) pulp3.

| Samples | | Pulp1 | Pulp 2 | Pulp 3 |
|----------------------|---------------------|---------|---------|---------|
| Concentration (12 %) | $\log (1/\omega_p)$ | -1.5024 | -1.5296 | -1.4888 |
| | σ | 1.1091 | 1.0956 | 1.1036 |
| | PDI | 3.4217 | 3.3211 | 3.3850 |
| Concentration (11 %) | $\log (1/\omega_p)$ | -1.5099 | -1.5437 | -1.4982 |
| | σ | 1.1118 | 1.0986 | 1.1069 |
| | PDI | 3.4424 | 3.3429 | 3.4046 |
| Concentration (9 %) | $\log (1/\omega_p)$ | -1.7982 | -1.8398 | -1.7635 |
| | σ | 1.1853 | 1.1410 | 1.1650 |
| | PDI | 4.0753 | 3.6759 | 3.8854 |

Table 1. Logarithm of relative molecular weight $\log ((1/\omega_p)/(s\ rad^{-1}))$, standard deviation σ , and polydispersity index PDI of the three pulps calculated by the rheology-based method with different concentrations.

difficult to relax the entanglement network, leading to a longer τ . Meanwhile, with increasing concentration, the polymer solution shows a decreasing J_e^0 because the entangled polymers do not fully and freely stretch with rearranging configurationally.

However, when the polymer concentration reaches a certain value, τ and J_e^0 of the polymer solution will tend towards equilibrium because the gyration radius, the end-to-end distance, and the “degree” of mutual entanglement of the chains will reach critical points, respectively [17].

It is well known that the τ is a function of MW of the polymer [17, 18], and J_e^0 is correlated with PDI of the polymer [17, 18]. Therefore, MW and PDI of the polymer move towards stabilization with the polymer concentration reaches a critical point. Accordingly, in the rheology-based method, a high enough concentration of cellulose in NMMO·H₂O solution has to be used in order to obtain reliable and stable data.

3.2 Prediction of MW scale and MWD of cellulose using the rheology-based method

Methodology. Definition of the Rouse terminal relaxation time is well known as follows [14].

$$\tau_1 = \frac{6\eta_0 M}{\pi^2 \rho R T} = 1/\omega_{char}$$

(10)

where ρ is the density, η_0 the zero-shear viscosity, R the universal gas constant, M the molecular weight, T the temperature. ω_{char} is the 79th percentile point of the zero shear normalized flow curve and normally symbolized as $\omega_{.79}$. The $\omega_{.79}$ is the gradually-changed frequency from Newtonian to non-Newtonian behavior for a liquid of polymer solution, with which the apparent viscosity of the polymer solution decreases and the untangling effect is stronger than the entangling effect among molecular chains.

According to the Rouse terminal relaxation time theory [14], a polymer solution always has a corresponding characteristic relaxation frequency (ω_{char}). Here, the ω_{char} is the $\omega_{.79}$ corresponding to the point of maximum curvature of the flow curve. Therefore the calculated M is believed to be the peak MW (M_p). M_p indicates the maximum probability of

molecular weight on the curve of *MWD*. In addition, it can be believed that the maximum probability of molecular weight begins to untangle, which would lead to a decreasing apparent viscosity of the polymer solution.

Accordingly, the peak *MW* scale is obtained by $M_p = M = \pi^2 \rho RT / (6\eta_0 \omega_{.79})$ and the *MWD* scale curve is obtained with shifting the abscissa ($\log M_p - \log (1/\omega_p)$) units. Here, the M_p and $(1/\omega_p)$ indicate the peak *MW* on the *MWD* scale curve and the relative *MWD* curve, respectively.

For the 79th percentile point of the normalized flow curve, the Vinogradov extrapolation leads to [14]:

$$\omega_{.79} = 0.3365 m_0^2 / m_1 \quad (11)$$

where m_0 and m_1 are respectively the intercept and the slope on the curve of stress versus viscosity at the low frequency of the dynamic data. In the current paper, the m_0 and m_1 are obtained in the frequency range from 0.2 to 2 ($\text{rad} \cdot \text{s}^{-1}$).

Results. Fig.2a, 2b, and 2c respectively represent relative *MWD* curves of the three pulps at various cellulose concentrations in NMMO-H₂O solutions. Choosing a concentration of 12%, these relative *MWD* curves are converted to the *MWD* scale curves of the three pulps shown in Fig.3, using the above-mentioned method. Furthermore, in terms of the *MWD* scale curve, $\log M_p$, σ , and *PDI* of the three pulps are calculated and given in Table 2. From Fig.3 and Table 2, it can be found that the relation of peak *MW* is pulp 3 > pulp 1 > pulp 2. For the *MWD* of the three pulps, pulp 1 appears the broadest, next is pulp 3, and then pulp 2.

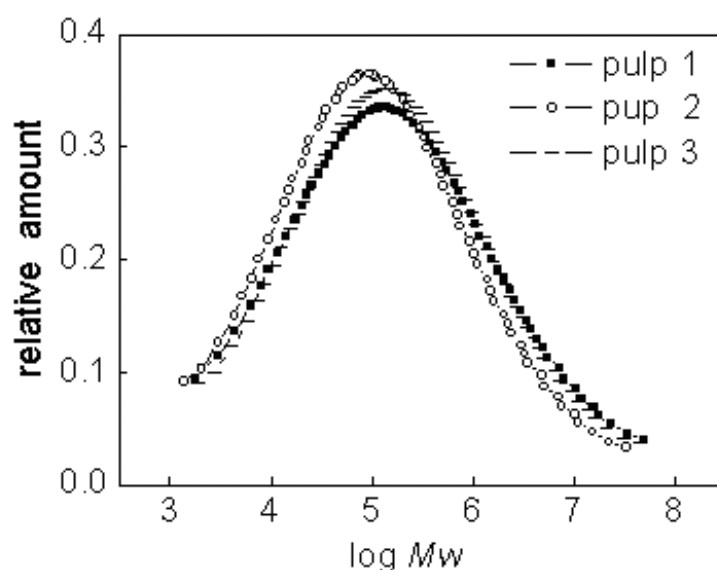


Fig. 3. *MW* scale curves of the three pulps by the rheology-based method with 12% cellulose concentration in NMMO-H₂O solution.

| Samples | Pulp 1 | Pulp 2 | Pulp 3 |
|------------|--------|--------|--------|
| $\log M_p$ | 5.12 | 4.96 | 5.14 |
| σ | 1.109 | 1.096 | 1.104 |
| PDI | 3.42 | 3.32 | 3.38 |

Table 2. Logarithm of molecular weight scale $\log M_p$, standard deviation σ , and polydispersity index PDI values of the three pulps calculated by the rheology-based method with 12% cellulose concentration in NMMO-H₂O solution.

3.3 Comparison of the results from the rheology-based method and the GPC method

Because of the lack of commercial cellulose standards with a narrow distribution, the narrow distribution polystyrenes standards are employed to measure MW and MWD of cellulose. The MWD curves of the three pulps measured by the GPC method are illustrated in Fig.4. Meanwhile, the calibrated GPC data are listed in Table 3.

Comparing the data of Table 2 with those of Table 3, one can observe that $\log M_p$ calculated by the rheology-based method is nearly equal to $\log M_p'$ determined by the GPC method. Therefore, it is feasible and reasonable that the calculated M with Eq. (10) is regarded as the peak MW (M_p) on the MWD curve. Consequently, the reciprocal of the frequency is converted to the MW scale in the rheology-based method.

The results of Table 3 show that PDI' of the three pulps is pulp 1 > pulp 3 > pulp 2, which are consistent with the results from the rheology-based method. Moreover, more information can also be obtained from Fig.4 by the GPC method than that from Fig.3 by the rheology-based method. For example, pulp 1 shows a symmetrical distribution, and moderate MW components are dominating. Pulp 3 shows a slightly asymmetrical distribution, moderate MW components are the major composition, and it has a little lower MW . For pulp 2, it is asymmetrical and slightly protuberant in the lower MW region, which indicates the presence of a higher low MW content. However, such useful information can not be reflected from the MWD scale curves obtained by the rheology-based method directly. It shows that further modification is still needed for the application of the rheology-based method.

| Samples | Pulp 1 | Pulp 2 | Pulp 3 |
|-----------------|---------------------|---------------------|---------------------|
| $\log Mp'$ | 5.133 | 5.071 | 5.157 |
| \overline{Mw} | 16.07×10^4 | 12.83×10^4 | 15.59×10^4 |
| \overline{Mn} | 3.989×10^4 | 3.878×10^4 | 4.355×10^4 |
| PDI' | 4.030 | 3.309 | 3.581 |

Table 3. Logarithm of molecular weight $\log Mp'$, mass-average molecular weight \overline{Mw} , number-average molecular weight \overline{Mn} , and polydispersity index PDI' of the three pulps measured by the GPC method.

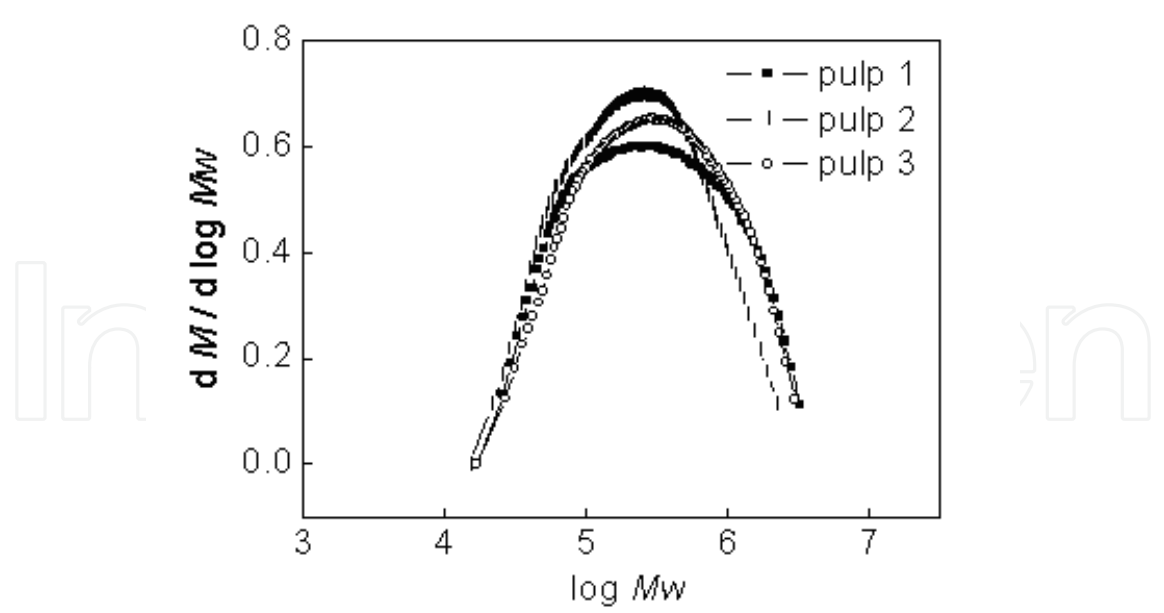


Fig. 4. MWD curves of the three pulps by the GPC method.

In the present work, the data obtained by the GPC method are relative values because of the use of polystyrenes standards, nevertheless the GPC method is an effective way for observing the differences of *MW* and *MWD* of cellulose. The relative data can not reflect the real *MW* characteristics of cellulose, so the data from GPC can not be used to calibrate the results from the rheology-based method. Even so, the comparison of the results from the two methods shows that it may be feasible to compare the *MW* and *MWD* of cellulose by the rheology-based method.

4. Conclusions

Prediction of *MW* scale and *MWD* of cellulose by means of a rheology-based method was developed. With this method, insignificant effect of cellulose concentration on predicting *MW* and *MWD* of cellulose was found using a rheology-based method when the cellulose concentration in the NMMO·H₂O solution is high enough. Furthermore, a method of calculating *PDI* of cellulose was established according to the Wesslan function which is the logarithm of the normal distribution function. For the cellulose/NMMO·H₂O solution, the cellulose *MW* values calculated by the Rouse terminal relaxation time can be considered as the peak *MW* on the *MWD* curves of cellulose. Consequently, the reciprocal of the frequency is converted to the *MW* scale, obtaining *MWD* scale curves of cellulose.

Meanwhile, the results obtained by the rheology-based method were compared with those measured by the GPC method. All obtained results from the two methods are only relative values. The comparison shows that the calculated peak *MW* are approximately equal, the calculated *PDI* have the same trends, but the shapes of the *MWD* curves do not match. GPC method is advantageous to depict finer characteristics of the *MWD* of cellulose. In spite of that, the rheology-based method is simple and fast. Therefore it is a useful and easy way to analyze the *MW* scale and *MWD* of cellulose in the fiber industry.

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Materials are important to mankind because of the benefits that can be derived from the manipulation of their properties, for example electrical conductivity, dielectric constant, magnetization, optical transmittance, strength and toughness. Materials science is a broad field and can be considered to be an interdisciplinary area. Included within it are the studies of the structure and properties of any material, the creation of new types of materials, and the manipulation of a material's properties to suit the needs of a specific application. The contributors of the chapters in this book have various areas of expertise. therefore this book is interdisciplinary and is written for readers with backgrounds in physical science. The book consists of fourteen chapters that have been divided into four sections. Section one includes five chapters on advanced materials and processing. Section two includes two chapters on bio-materials which deal with the preparation and modification of new types of bio-materials. Section three consists of three chapters on nanomaterials, specifically the study of carbon nanotubes, nano-machining, and nanoparticles. Section four includes four chapters on optical materials.

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