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Average molecular weight and molecular weight distribution of the Vietnamese acacia pulps

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Abstract

The average molecular weight (MW) and the molecular weight distribution (MWD) of the several acacia pulps produced from wood of acacia tree in Vietnam were investigated. These chosen pulps had the various brightness were produced by Kraft method and bleaching. The MW was determined by viscosity of the pulps in copper-ammonium complex. The MWD was determined by fractional method which was carried out by dissolving pulp in the various phosphoric acids from 73.3 to 83 % in weight. The results show that these pulps have an average degree of polymerization (DP) in the range from 842 to 878. Additionally, the fraction of pulps with DP lower than 200 units is about 15 percent. The fractionations have the most percentage in the range from 600 to 1050 units. And, there are differences of MW and MWD of pulps from various brightness.

Keywords. Acacia pulp, average molecular weight, molecular weight distribution.

1. INTRODUCTION

The MW and the MWD of cellulose are very important characteristics. These characteristics have an effect on physical properties, structure and reactivity of cellulose. The MW and MWD depend strongly on the type of wood, climate conditions, the method of production, etc. [1]. Thus, the various origin of cellulose causes the difference of MW and MWD. Additionally, cellulose difficultly dissolves in the common organic solvents and the water [1, 7]. In the case, there are not much solvent dissolving cellulose for analysis of MW and MWD.

There are many researches for MW and MWD of various celluloses [1, 3-9]. Jose M. Perena [3] analyzed MWD of a purified cellulose pulp by fractionation where the pulp was dissolved in cadoxene and the solution was diluted with water 1:1 by volume. As non-solvent, the mixture water/propanol (1:3) was used. In that work, the pulp is split into 14 fractionations which have M_n from 19,000 to 453,000 and the percentage of each fractional weight from 3.05 to 13.4 %. G. M. Guzman [4] also analyzed MWD of cellulose by fractionation in cadoxen solutions. Hereby, either hydrophilic cotton or bleached bi-sulphite of eucalyptus pulp is fractionated. This result of fractionation is analyzed by Schulz and Beell method. Timo Leskinen [5] carried out determination of MWDs in native and pretreated wood from pine sawdust, pin EMAL lignin and CF1 cellulose by size-exclusion chromatography (SEC). K. Bernhard and W. Oppermann [6] determined molar mass distributions of eucalyptus pulp by analytical ultracentrifugation. The MW of the pulp concentrates in the range approximately 100,000 g/mol.

Recently, the authors refined and applied the Vietnamese acacia pulp for producing nitrocellulose in Vietnam [2]. In that paper, the MW and MWD of the acacia pulps have not been investigated. In this research, the MW and MWD of the Vietnamese acacia pulps will be investigated.

2. MATERIALS AND METHODS

2.1. Materials

The acacia pulps which are investigated have the various brightness of 83, 85, 87 and 89% ISO (named such as AH-83, AH-85, AH-87 and AH-89, respectively) for producing papers in An Hoa factory. These pulps were produced by Kraft method and were bleached in four stages consisting of the first stage O_2 (bleached by oxygen in alkaline medium), the second stage DHT (bleached by

chlorine dioxide), the third stage EOP (bleached by hydrogen peroxide in low alkaline medium) and the fourth stage D2 (bleached by chlorine dioxide at low temperature). The content of lignin of these samples is shown in table 1.

Table 1: The content of lignin of the samples

Samples	AH-83	AH-85	AH-87	AH-89
Lignin, %	0.35	0.30	0.27	0.25

2.2. Methods

2.2.1. The MW of cellulose

The MW of cellulose is determined by viscosity of cellulose solution when cellulose is dissolved in copper-ammonium complex corresponding to GOST 9105-74 [10]. The viscosity is measured by Ostwald viscometer. The constant of this viscometer is 0.03 mm^2/s^2 at temperature of 20 ^oC. The concentration of cellulose solution is prepared in order to calculate specific viscosity (η_{sp}) from 0.1 to 0.3 [10].

The specific viscosity of cellulose is calculated by equation (1):

$$\eta_{sp} = \frac{t - t_0}{t_0} \quad (1)$$

The intrinsic viscosity of cellulose is calculated by equation (2) (Schulz – Blaschke):

$$\eta = \frac{\eta_{sp}}{C.\ 1 + k'.\eta_{sp}} \quad (2)$$

Where: k' = 0.29 for copper-ammonium complex.

The average DP of cellulose is calculated by Mark – Kun – Houwink:

$$[\eta] = k.MW^a = k''.DP^a \quad (3)$$

Where: k'' = 5×10^{-4} for copper-ammonium complex and a =1.

Based on equations (2) and (3), the average DP of cellulose is calculated by equation (4) [10]:

$$DP = \frac{2000.\eta_{sp}}{C.(1 + 0{,}29.\eta_{sp})} \quad (4)$$

Where: DP - Average DP of cellulose;
C - Concentration of cellulose, g/l.

2.2.2. The MWD of cellulose

The fractionation of cellulose is determined by dissolving cellulose in phosphoric acid at temperature 20±0.1 ^oC. This method is based on the different dissolubility of cellulose in the various concentration of phosphoric acid. The fractionations of cellulose corresponding to DP are shown in table 2 [10].

Table 2: The solutions of phosphoric acid for fractionation of cellulose

Fractionations	I	II	III	IV	V	VI	VII	VIII	IX	X
Limits of DP	10	60	120	200	300	420	600	800	1050	1200
Concentrations of H_3PO_4, %	73.3	75	76	77	78	79	80	81	82	83
Solution of 73,3% H_3PO_4, ml	10	10	10	10	10	10 (5)	10 (5)	10 (5)	10 (5)	10 (5)
Solution of 82% H_3PO_4, ml	-	2.3	4.2	6.95	11	17.9 (9)	31.6 (15.8)	-	-	-
Solution of 86% H_3PO_4, ml	-	-	-	-	-	-	-	14.1 (7.1)	19.9 (10)	29.7 (14.9)

A curve of integration is expressed by following equation (5):

$$w\ \%\ = f\ DP \quad (5)$$

Where: w (%) – percent of cumulative sum of each fractionation, %; DP – degree of polymerization of fractionation.

A curve of MWD of cellulose is based on differentiating the following equation (6):

$$\frac{dw}{d(LogMW)} \approx \frac{\Delta w\ \%}{\Delta\ LogMW} = f\ DP \quad (6)$$

3. RESULTS AND DISCUSSION

3.1. The MW of the acacia pulps

The MW of cellulose is an important parameter of cellulose. It affects swelling, dissolubility of cellulose in the solvents, its structure and other properties. In this work, the viscosity method was used for investigating its MW. The MWs of the acacia pulps with various brightness such as 83, 85, 87, 89 %ISO were

determined. Additionally, these MWs were compared with some types of cellulose. The results are shown in table 3.

Table 3: The data of MW of the acacia pulps

No.	The samples	C, g/l	η_{sp}	DP	MW
1	AH-83	0.510	0.233	856	138,700
2	AH-85	0.495	0.251	875	141,700
3	AH-87	0.512	0.254	842	136,400
4	AH-89	0.545	0.267	878	142,200
5	Unbleached Kraft pulp of acacia	-	-	1,400÷2,500	-
6	Mechanic treated hardwood pulp [9]	-	-	998	-
7	Purified cotton [1]	-	-	800÷1,500	-
8	Purified cellulose of wood [1]	-	-	800÷1,100	-

As shown in table 3, the MW of the acacia pulps is in the range from 136.400 to 142.200 (DP from 842 to 878, respectively). The brightness of the samples has not a much effect on MW. And, the MW of the pulps seems not depending on brightness. In principle, MW of pulp depends on brightness because of the various conditions of bleaching. In this case, the MW of pulps depends on some other factors such as age of tree, its growing conditions [1]. So, in this case it is concluded that the brightness has a not much effect on MW of these pulps. Compared to unbleached Kraft pulp of acacia, the MW of these pulps are decreased quite much. Besides, compared to the purified cotton and the purified cellulose of wood, the MW of these pulps are similar.

In general, the pulps produced in factories for making paper have brightness from 76 to 89 % ISO, however, the higher brightness of pulp the lower content of lignin (table 1). Thus, for preparing its derivatives, the high brightness pulps are chosen.

3.2. The MWD of the acacia pulps

The behaviors of cellulose depend strongly not only on MW but also on MWD. Especially, it has an effect on the behaviors of structural phase of cellulose. In this work, for investigation of MWD of the acacia pulps we carried out 10 fractionations of the pulps from 10 to 1200 units (as table 2). Then, the data was calculated by equation (5). The results are shown in table 4.

Table 4: The data of cumulative percent of weight in the fractionations of four pulp types

Limits of DP	Cumulative percent of weight (%)			
	AH-89	AH-87	AH-85	AH-83
10	5.13	3.45	4.52	4.66
60	8.92	6.96	7.87	8.57
120	12.08	10.38	14.56	13.23
200	14.09	12.83	15.98	15.69
300	16.43	14.62	17.02	17.35
420	20.44	16.68	21.87	18.54
600	28.12	20.57	30.12	27.33
800	63.22	58.96	63.10	64.21
1050	82.31	80.78	81.01	81.87
1200	89.29	90.98	88.29	87.90

On the basis of the data in table 4 and calculation by equation (6), the curve of the integral weight distribution and the curve of the differential weight distribution of the pulps are shown in figures 1 and 2.

As shown in table 4 and Fig. 1, the DP of the acacia pulps are in the large range (from about 10 units to more 1200 units). In the curves of differential in Fig. 2, the two range of DP which concentrate large percentage of pulp are from 10 to 200 units and from 600 to 1050 units. Especially, the fractionations of 600÷1050 DP are from 50 to

60 % pulp. Additionally, there is not much different from MWD of the various pulps. It is also not showing a law of effect of brightness on MWD of the pulps.

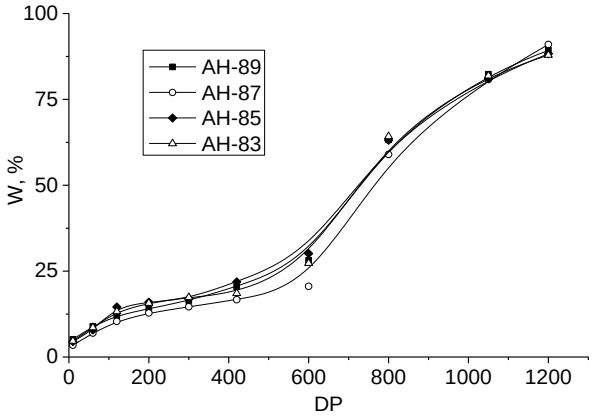

Figure 1: The curves of integral weight distribution of the four acacia pulps

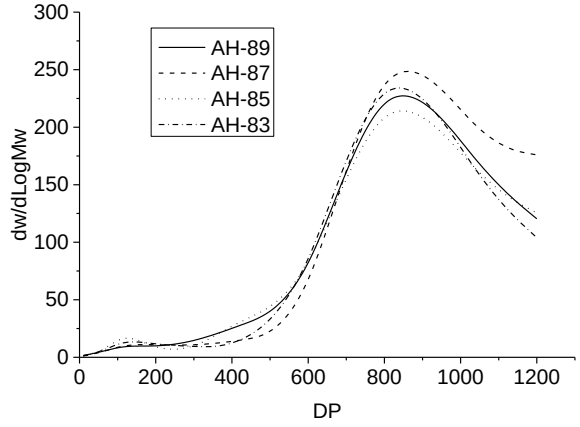

Figure 2: The curves of differential weight distribution of the four acacia pulps

Compared with dissolving pulp, it is shown that the percentage of the fractionations of above 200 units (alpha-cellulose) is quite low (about 85 % pulp). It is explained that it is keeping a content of residue hemicellulose (fractionations of lower 200 units) to improving the physico-mechanical properties of pulp for making paper. However, the content of alpha-cellulose of dissolving pulp is above 92 % [2]. Thus, when preparing derivatives of cellulose (such as nitrate cellulose, acetate cellulose, etc.) from these pulps, we have to purifying and modifying them.

4. CONCLUSION

The acacia pulps which are produced in Vietnam have the average DP in the range from 842 to 878. Additionally, the fractionations of pulp in which the DP is lower than 200 units is about 15 percent. The fractionations have the most percentage in the range from 600 to 1050 units. And, there are different MW and MWD of pulps from various brightness. These results are based on researching structure, properties and reactivity of the acacia pulp and modifying these pulps for producing types of nitrocellulose in the future.

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