AN INVESTIGATION OF THE STRUCTURAL CHARATERISTICS OF THE VIETNAMESE ACACIA PULP

Received 22-11-2016

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TÓM TẮT

KHẢO SÁT ĐẶC TRƯNG CẤU TRÚC CỦA BỘT GIẤY GỖ KEO VIỆT NAM

Đặc trưng cấu trúc là một trong những thông số quan trọng của vật liệu xenluloza. Các đặc trưng này ảnh hưởng đến điều kiện biến tính, khả năng phản ứng este hóa và chất lượng các sản phẩm từ xenuloza. Trong bài báo này, các đặc trưng cấu trúc bao gồm chỉ số tinh thể (TCI, LOI), chỉ số mật độ liên kết hydro (HBI), chỉ số bất đối xứng (a/b), của bột giấy gỗ keo đã được khảo sát bằng phương pháp phổ hồng ngoại và phương pháp nhiễu xạ tia X. Các đặc trưng cấu trúc của bột giấy gỗ keo này được so sánh, đánh giá với đặc trưng của một số loại bột gỗ nhập ngoại dùng trong sản xuất nitroxenluloza. Các kết quả khảo sát cho thấy, các đặc trưng cấu trúc của một số loại bột giấy gỗ keo không có nhiều sự khác biệt. Trong đó, chỉ số tinh thể tổng TCI khoảng 1.10÷1.14; chỉ số trật tự ngang LOI khoảng 1.90÷2.07; chỉ số mật độ liên kết hydro HBI khoảng 2.17÷2.49; chỉ số bất đối xứng a/b khoảng 0.25÷0.31. So với bột gỗ nhập ngoại, các chỉ số cấu trúc có những khác biệt nhất định. Đặc biệt, bột gỗ Canada có chỉ số LOI lớn hơn khá nhiều (2,906); chỉ số bất đối xứng a/b nhỏ hơn nhiều (0,21) so với bột giấy gỗ keo. Chỉ số tinh thể CI(XRD) và kích thước vùng tinh thể L(nm) của bột giấy gỗ keo và bột gỗ nhập ngoại cũng được đưa ra bằng phương pháp nhiễu xạ tia X.
***Keywords**: acacia pulp, cellulose, structural characteristics, crystallinity index.*

1. INTRODUTION

Cellulose is a natural polymer the unit of which is β-D-glucopyranose and has three hydroxyl groups at 2, 3, 6 positions [1]. The chains of cellulose bond each other by physical bonds such as hydrogen bonds and Van der Waals' bonds. Therein, the hydrogen bonds in cellulose materials can be intra-molecular or inter-molecular. The order of cellulosic chains can form crystalline domain or amorphous

domain. The structure of cellulose depends on origin and conditions of manufacturing. The structural characteristics of cellulose material are very important. These characteristics affect conditions of modification and reactivity of cellulose.

There were a lot of researches for structure of the various original celluloses [2-12]. Parida et al. (**2015**) investigated structure of cellulose fiber of Luffa cilindrica by Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectra at wavelength range 500÷4000 cm^{-1} and 300÷3000 cm^{-1}, respectively. The structures of this cellulose were detected by Raman spectroscopy and discussed. Its degree of crystallinity was determined from intensity of FTIR peaks by ratio I_{1454}/I_{893} and was found to be 74.12% [2]. Liu (**2013**) reported the progress in FTIR study of compositional, structural, physical attributes of developmental Cotton fibers. In this work, he chose the 956 cm^{-1} band of crystalline celluloses and the 1042 cm^{-1} band of amorphous celluloses. He indicated the crystallinity of immature cotton was less than 42% and the crystallinity of mature cotton was more than 42%. Katja Kavkler et al. (**2012**) applied FTIR and Raman spectroscopy to qualitative analysis in structural changes of cellulosic fibers (Cotton and Flax). He confirmed both methods are suitable for the analysis of structural changes in cellulosic fibers [3]. Ciolacu et al. (**2011**) investigated the structure and characterization of amorphous cellulose from Cotton and Spruce dissolving pulp. By X-ray method, crystalline index of Cotton cellulose and Spruce dissolving pulp was determined and found to be 71.11% and 65.47%, respectively. Based on FTIR method, IR crystalline index (A_{1430}/A_{893}), energy of hydrogen bond and asymmetric index of these both samples were evaluated [4].

Acacia pulp is produced for making paper in Vietnam. This pulp has been applied for producing nitrocellulose [5] and for other derivatives. However, the structure of this pulp has not still been reported. So, the problems of nitrocellulose quality and conditions of its production have not been explained clearly. Thus, in this work the structure of Vietnamese acacia pulp is investigated.

2. MATERIALS AND METHODS

2.1. Materials

The samples of Vietnamese acacia pulp (signed like that AH-83, AH-84, AH-85, AH-86, AH-87, AH-88 and AH-89), which were chosen for this investigation, were produced in An Hoa factory. These samples have some initial characteristics in Table 1.

The Indonesian pulp (Indo) and Canadian pulp (CND), which were imported for producing nitrocellulose, were collected from Chemical Company 95. The characteristics of these both samples are shown in Table 1.

Table 1. Some initial characteristics of the Vietnamese acacia pulps and the imported pulps

No.	Samples	Brightness, %ISO	Alpha-cellulose, %	Degree of polymerization	Lignin, %	Ash, %
1	AH-83	83	89.29	856	0.41	0.25
2	AH-84	84	88.93	860	0.40	0.24

3	AH-85	85	89.12	875	0.34	0.28
4	AH-86	86	90.98	855	0.35	0.23
5	AH-87	87	90.03	842	0.30	0.26
6	AH-88	88	89.94	862	0.28	0.31
7	AH-89	89	90.86	878	0.29	0.24
8	Indo	-	94.42	870	0.26	0.25
9	CND	-	93.10	889	0.27	0.30

2.2. Methods

2.2.1. Method of FTIR spectra

The samples were dried at temperature of 65^0C for 2 hours. Then, the samples were cooled down for 30 minutes at room temperature in desiccator. The measure of the samples were carried out in a room with temperature of 25^0C and relative humidity of 35%. Pellets of 2 mg of the samples were prepared by mixing with 200 mg of spectroscopic grade KBr.

FTIR spectra of the samples were recorded on a Perkin Elmer Spectrum 400. A total of 32 cumulative scans were taken, with a resolution of 4 cm^{-1}, in the frequency range from 4000 to 400 cm^{-1}. The absorbance of the bands was determined from ACDLABS software. The baseline of the spectrums were chosen at auto baseline method/end to end and draw/below spectrum.

The total crystalline index (TCI) is determined by the absorbance ratio from 1372 cm^{-1} (A_{1372}) and 2900 cm^{-1} (A_{2900}) bands as follows [4]:

$$TCI = \frac{A_{1372}}{A_{2900}} \qquad (1)$$

The lateral order index (LOI) is determined by the absorbance ratio from 1430 cm^{-1} (A_{1430}) and 896 cm^{-1} (A_{896}) bands as follows [4]:

$$LOI = \frac{A_{1430}}{A_{896}} \qquad (2)$$

The hydrogen bond intensity (HBI) is determined by the absorbance ratio from 3350 cm^{-1} (A_{3350}) and 1318 cm^{-1} (A_{1318}) bands as follows [4]:

$$HBI = \frac{A_{3350}}{A_{1318}} \qquad (3)$$

The asymmetric index (a/b) is the ratio between segment widths at half height of the hydroxyl absorbance band at around 3350 cm^{-1}.

2.2.2. Method of XRD spectra

X-ray diffractograms were collected using a sample holder mounted on a PW_3050-60 X-ray equipment with monochromatic CuKα radiation (λ = 0.15406 nm). The generator was utilized at 40 kV and 40 mA, and the intensities were measured in the range of 5° < 2θ < 40°, typically with scan steps of 0.1° at 1 s/step (6° /min). Peak separations were carried out using Gaussian deconvolution. After deconvolution, it is possible to calculate and compare several parameters.

The crystalline index CI(XRD) was calculated by Equation (6) which was the empirical method proposed by Segal et al. [6], which is:

$$CI(XRD) = \frac{I_{002} - I_{Am}}{I_{002}} \times 100 \qquad (6)$$

Where I_{002} is the maximum intensity of the (002) lattice diffraction; and I_{Am} is the diffraction intensity of the amorphous band at $18.35 \div 19.50^0$.

The crystalline size (L), shown in Equation (7), was calculated using the Scherrer equation:

$$L(nm) = \frac{K \times \lambda}{\beta \times \cos(\theta)} \qquad (7)$$

Where K is a constant of value 0.94; λ is the X-ray wavelength (0.15406 nm); β is the half-height width of the diffraction band (radian); and θ is the Bragg angle corresponding to the (101), ($10\bar{1}$) and (002) plane.

3. RESULTS AND DISCUSSION

3.1. The structural characteristics of Vietnamese acacia pulps by FTIR method

FTIR spectra is often used to determine a presence of functional groups in organic or inorganic materials. However, when recording FTIR spectra of a polymer in solid state, the physical interaction of functional groups causes a shift of bands and a change of absorbance intensity of bands. So, these both changes can exhibit information of structure in polymeric material. For cellulose materials, the chains can interact each other to form crystalline domains or amorphous domains by physical bonds such as hydrogen bond and Van der Waals' bond. Because of these bonds, the bands of FTIR spectra of cellulose are shifted and absorbance intensity of bands are changed. As researches of many authors by FTIR method, there are the characteristic bands of cellulose structure [2-12]. In this work, for investigation of structural characteristics, FTIR spectra of seven samples of Vietnamese acacia pulp were recorded. The results are shown in Figure 1.

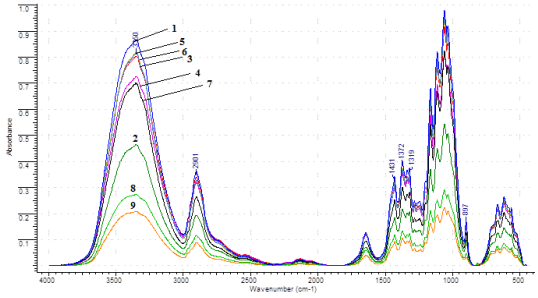


Figure 1. FTIR spectra of the Vietnamese acacia pulps and the imported pulps: 1 – AH-83; 2 – AH-84; 3 – AH-85; 4 – AH-86; 5 – AH-87; 6 – AH-88; 7 – AH-89; 8 – Indo; 9 – CND;

FTIR spectra of these samples (Figure 1) have the characteristic bands of cellulose such as a strong band at around 3350 cm^{-1} is assigned to OH stretching mode, a band at around 2900 cm^{-1} is of CH and CH_2 groups, a band at around 1430 cm^{-1} is of CH_2 vibrations, HCH and OCH in-plane blending, a band at around 1372 cm^{-1} is of COH and HCC vibrations of cellulose and hemicellulose, a band at 1318 cm^{-1} is of COH and HCC vibrations, a band at 896 cm^{-1} is of COC vibrations of glycoside bonds. Besides, there are some bands of a little impurity such as a band at 1700 cm^{-1} of lignin. Based on the spectra of the samples in Figure 1, the absorbance of above bands were determined. These results are shown in Table 2.

Table 2. The result of the FTIR absorbance bands of the samples and the imported pulps

No.	Samples	A_{3350}	A_{2900}	A_{1430}	A_{1372}	A_{1318}	A_{896}
1	AH-83	0.867	0.360	0.341	0.401	0.374	0.170
2	AH-84	0.464	0.194	0.185	0.218	0.206	0.097
3	AH-85	0.805	0.340	0.320	0.375	0.35	0.159

4	AH-86	0.726	0.319	0.307	0.357	0.334	0.149
5	AH-87	0.819	0.328	0.319	0.375	0.351	0.154
6	AH-88	0.816	0.327	0.313	0.370	0.347	0.157
7	AH-89	0.700	0.264	0.253	0.301	0.281	0.126
8	Indo	0.273	0.116	0.119	0.134	0.124	0.047
9	CND	0.207	0.088	0.093	0.106	0.098	0.032

As shown in Table 2, the bands are characterized for cellulose structure as follows:

The band at around 1430 cm^{-1} is associated with the amount of the crystalline structure of the cellulose, while the band at 896 cm^{-1} is assigned to the amorphous region in cellulose [6]. The ratio between these two bands was defined as an empirical crystalline index proposed by Nelson and O'Connor [7] as a lateral order index (LOI). The ratio between the bands at 1372 and 2900 cm^{-1}, also proposed by Nelson and O'Connor to be the total crystalline index (TCI), was used to evaluate the infrared crystalline ratio. Considering the chain mobility, the hydrogen bond intensity (HBI) of cellulose is closely related to the crystalline system and the degree of intermolecular regularity. The ratio between the absorbance bands at 3400 and 1318 cm^{-1} was used to study the HBI of cellulose fibers [6].

From the data of the absorbance bands in Table 2, the structural characteristics of the samples were calculated by the Equations (1), (2), (3), (4) and (5). The results are shown in Table 3.

Table 3. IR crystallinity indexes (TCI, LOI), hydrogen bond intensity (HBI) and asymmetric index (a/b) of the Vietnamese acacia pulps and the imported pulps

No.	Samples	TCI	LOI	HBI	a/b
1	AH-83	1.114	2.006	2.318	0.29
2	AH-84	1.124	1.907	2.252	0.29
3	AH-85	1.103	2.013	2.300	0.26
4	AH-86	1.119	2.060	2.174	0.25
5	AH-87	1.143	2.071	2.333	0.30
6	AH-88	1.131	1.994	2.352	0.31
7	AH-89	1.140	2.008	2.491	0.31
8	Indo	1.155	2.532	2.202	0.24
9	CND	1.205	2.906	2.112	0.21

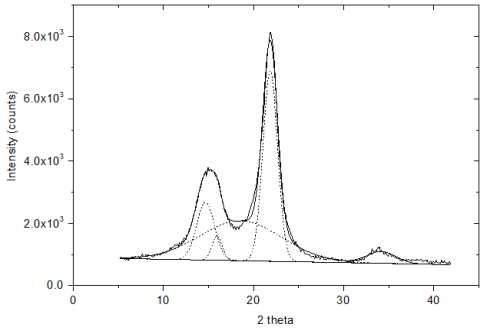
The TCI and LOI of Vietnamese acacia pulps (Table 3) have not much difference and are in the range from 1.10 to 1.14 and from 1.90 to 2.07, respectively. These can be explained by two reasons as follows: In order to stable quality, the age of acacia trees for producing pulp is the same (about five years) when they are collected. Additionally, the condition of bleaching has a slight effect on cellulose structure. Compared to the imported pulps, these indexes of the acacia pulps are lower, especially much lower than LOI of Canadian pulp (2,906). These LOIs show that the percentage of crystallite of the acacia pulps is lower than that of the imported pulps.

The HBIs of these acacia pulps are in the range from 2.17 to 2.49. These HBIs show that the chain mobility and degree of intermolecular regularity of these acacia pulps are remarkable difference and are equivalent to that of the imported pulps. The index of asymmetry (a/b) characterizes the uniformity of the cellulosic samples. The values tending to 1.0 indicate the most uniform samples. The asymmetric

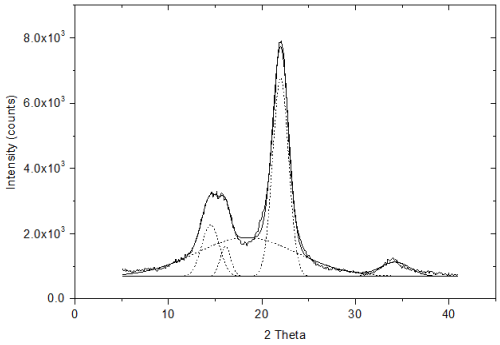
index of these acacia pulps is significantly higher than that of imported pulps. Both these indexes also confirm that the crystal of cellulose in the imported pulps has lower regularity than that in the acacia pulps.

3.2. The structural characteristics of Vietnamese acacia pulp by XRD method

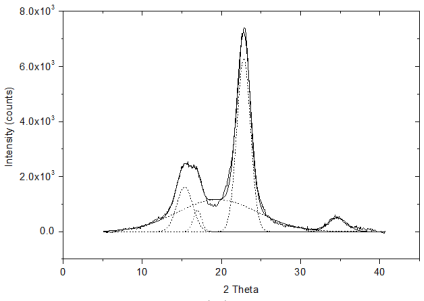
XRD spectra exhibits several important parameters of cellulosic structure. It can use to calculate the crystalline ratio of cellulose and the average size of crystalline domains. Based on the results of above IR index of An Hoa pulps, it can be chosen one of the An Hoa pulps for this investigation. So, in order to investigate these parameters of the acacia pulp and compare to imported pulps, we collected the XRD spectra of the samples as follows: AH-88, Indo, and CND. The results are shown in Figure 2.



(a)



(b)



(c)

Figure 2. XRD spectra of three pulps as follows: (a) Vietnamese acacia pulp AH-88; (b) Indonesian pulp; (c) Canadian pulp.

In Figure 2 (a), (b) and (c), the characteristic bands the three pulps have a little shift as follows: The diffraction bands of crystallites are in range 14.50 ÷ 15.35^0 of 101 plane, 16.1÷16.95^0 of $10\bar{1}$ plane, 21.85÷22.80^0 of 002 plane and at 34.17÷34.66^0 of 004 plane. The amorphous bands of these samples are in range 18.35 ÷ 19.50^0. Based on equation (6) and (7), crystalline index and the average size of the crystalline domain were calculated and shown in Table 4.

Table 4. The crystalline indexes CI(XRD) and the average size of the crystalline domain

No.	The samples	CI(XRD), %	The average size of the crystalline domains, nm		
			L(101)	L($10\bar{1}$)	L(002)
1	AH-88	83.02	3.71	6.54	4.67
2	Indo	86.09	3.88	6.54	4.48
3	CND	89.42	3.68	6.55	4.44

The crystalline index of AH-88 sample (83.02%) is smaller than that of the imported pulps (86.09% and 89.42%). This is similar to the result by FTIR method, however, the CI(XRD) exhibits a clearer ratio of cellulosic crystallite. In addition, the average size of the crystalline domain of AH-88 sample is

different to that of imported pulps as follows: While the average size of $10\bar{1}$ plane is the same, the average size of 101 plane of AH-88 is smaller than that of Indo and is a little larger than that of CND. Especially, the average size of 002 plane of AH-88 is larger than that of the both.

4. CONCLUSION

The Vietnamese acacia pulps have the structural characteristics as follows: The TCIs and LOIs are in the range from 1.10 to 1.14 and from 1.90 to 2.07, respectively. The HBIs of these acacia pulps are in the range from 2.17 to 2.49. The asymmetric index of them is in the range from 0.25 to 0.31. The crystalline index CI(XRD) of Vietnamese acacia pulps is around 83%. The average size of the crystalline domains of 101 plane, $10\bar{1}$ plane and 002 plane evaluate to be 3.71, 6.54 and 4.67, respectively. Compared to imported pulps, the crystallnity of Vietnamese acacia pulps is less than that of the imported pulps. However, the average size of the crystalline domains of these pulps is larger than that of the imported pulps.

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