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AN INVESTIGATION OF THE STRUCTURAL CHARACTERISTICS OF MODIFIED CELLULOSE FROM ACACIA PULP

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ABSTRACT

In this paper, the structural characteristics of the modified celluloses from acacia pulp in Vietnam were investigated and compared to other pulps. The total crystalline index (TCI), the lateral order index (LOI) and the hydrogen bond intensity (HBI) were evaluated by the FTIR spectra. The size of crystallites was considered by XRD patterns. Peak separations were carried out using Gaussian deconvolution for the band at 3700 - 3000 cm^{-1} of the FTIR spectra and the XRD spectra. The results show that the TCI, LOI and HBI of modified acacia cellulose I are found to be around 1.09, 2.22 and 2.33, respectively, and the TCI, LOI, HBI of acacia cellulose II are found to be around 1.09, 1.51, 2.06, respectively. The crystalline size of modified acacia cellulose I is found to be as follows L(101) ~ 4.33 nm, L($10\bar{1}$) ~ 8.58 nm and L(002) ~ 4.80 nm, and that of cellulose II is found to be as follows: L(101) ~ 4.04 nm, L ($10\bar{1}$) ~ 3.55 nm and L(002) ~ 2.99 nm.

Keywords: structural characteristics, modified cellulose, acacia pulp.

1. INTRODUCTION

Cellulose, a natural polymer, is applied for making paper and preparing a lot of derivatives (such as nitrocellulose, methyl cellulose, cellulose acetate and etc.) [1]. In order to prepare the derivatives, cellulose is often purified and modified to increase its purity and reactivity. In making paper, pulps are cooked and bleached with brightness up to 89 %ISO. These pulps only have a content of alpha-cellulose of round 90 % weight and a content of lignin of less 0.5% weight. Because of that, these pulps have to continue purifying and modifying to increase more purity and reactivity. The reactivity of cellulose depends on the structural characteristics.

There are some reports on structural characteristics of modified cellulose from various origins [2 - 10]. Diana Ciolacu et al. investigated the structural characteristics of an initial cotton and the modified cotton by Fourier transform infra-red (FTIR) spectra and X-ray diffraction (XRD) spectra. The modification process was carried out as follows: the sample was extracted in a Soxhlet extractor with ethanol and benzene mixture for 8 hours, then boiled in 1 % NaOH solution for 6 hours, washed with distilled water, immersed in 1 % CH_3COOH, with distilled water [2]. They reported that the crystalline index of the initial cotton and the modified cotton were found to be 71.11 % and 18.11 % by XRD spectra, respectively. S. Y. Oh et al. analysed crystalline structure of modified cellulose from an initial cellulose with degree of polymerization of 850 units and 92 % alpha-cellulose. This initial cellulose was treated with NaOH solution of 5 %, 10 % and 15%, at 25 ^{o}C for 1 hour, then washed with distilled water up to pH 7 [3]. By FTIR method, they stated that the crystalline index LOI (A_{1430}/A_{897}) was evaluated to be around 2.3, 1.6 and 0.4 corresponding with NaOH solution of 5 %, 10 % and 15 %. Park et al. investigated the crystalline index of eight cellulose samples (> 93 % cellulose) by XRD method. By peak height, the crystalline index of these samples found to be from 78.0 to 95.2 % [4]. Matheus Poletto considered the structural characteristics of many types of cellulose (Eucalyptus, Pinus, Dipteryx, Mezilaurus, Curaua, Jute, Kenaf, Ramie, Sisal and Buriti). By FTIR spectra, the crystalline index of these samples were significantly different as follows: the TCIs were in range from 0.237 to 1.3, the LOIs were from 0.78 to 3.172, and the HBIs were from 1.119 to 2.241. By XRD method, the crystalline size L(002) of these samples were from 1.92 to 3.70 nm [5]. Karama E. B. treated the Alfa stems with solution of 1 % and 5 % NaOH for 6 hours at 60^{0}C, and then the characteristics of samples was investigated by means of scanning electron microscope (SEM), FTIR, XRD and thermogravimetric analysis (TGA). Microstructure analysis of the Alfa fibers by XRD revealed that the degree of crystallinity increased after alkali treatment and no structural transformation from cellulose I to cellulose II polymorph was observed [6]. Thus, the above researches show that the structural characteristics of cellulose have significantly difference because of their origin.

The acacia pulps have been made for making paper in industry. Some researches were carried out for modifying and preparing derivatives from these pulps [9 - 10]. However, the structure of the modified cellulose from this pulp has not been investigated. In this paper, the structural characteristics of the modified cellulose by cold caustic treatment from Vietnamese acacia pulp were considered and compared to others.

2. MATERIALS AND METHODS

2.1. Materials

The initial acacia pulp (AH-NL), which was collected from An Hoa Company, has a brightness of 89 % ISO, a content of alpha-cellulose of 90.86 % and a degree of polymerization of 878 units. A Canadian softwood cellulose (CND) with an alpha-cellulose of 93.10 % w., a polymerization degree of 889 units; and an Indonesian hardwood cellulose (INDO) with an alpha-cellulose of 94.42 % w., a polymerization degree of 870 units, which are used for manufacturing nitrocellulose, were collected from 95 company.

2.2. The method of modification

On basis of modification by cold caustic treatment according to S. Y. Oh [3], in this investigation the modification of acacia pulp was carried out as follows: the samples of 5 grams were immersed in 150 grams of NaOH solution of 7.5 % or 15 % w., at 20 ^{o}C and for 1 hour. Then, the solutions were diluted with distilled water, and the samples were filtered and washed with distilled water up to pH 7, and dried in oven, at 65 ^{o}C for 4 hours. The sample which was modified with NaOH solution of 7.5 % and 15 % is named AH-7.5 and AH-15, respectively.

2.3. Method of FTIR spectra

The samples were dried at temperature of 65 ^{o}C for 4 hours. Then, the samples were cooled down for 30 minutes at room temperature in desiccator. The measure of the samples were carried out at room temperature of 25 °C and the 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 in Military Technical Academy. A total of 32 cumulative scans were taken, with a resolution of 4 cm^{-1}, in the frequency range from 4000 to 450 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.

According to Buger-Lambert-Beer law, the intensity of peak depends on the nature of compound, a thick of cell and a concentration. In this case, the nature and concentration are the amount of crystalline or amorphous degree in a cellulose. So, when comparing a peak of the functional group in the crystalline domain with a peak of other functional group in the amorphous domain in each FTIR spectra, the characteristics of structure can be evaluated. The correlation of crystalline indices by FTIR with that of XRD was investigated [11]. This correlation is very high (R = 0.97). Nowadays, the scientists have been recognising and using the FTIR method for evaluating the characteristics of cellulosic structure [2 - 8, 11].

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 [2, 3, 5]:

$$TCI = \frac{A_{1372}}{A_{2900}} \tag{1}$$

The lateral order index (LOI) is determined by the absorbance ratio from 1430 cm^{-1} or 1420 cm^{-1} (A_{1430}) and 896 cm^{-1} (A_{896}) bands as follows [2, 3, 5]:

$$LOI = \frac{A_{1430}}{A_{896}} \tag{2}$$

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 [2, 5]:

$$HBI = \frac{A_{3350}}{A_{1318}} \tag{3}$$

2.4. XRD diffractograms

X-ray diffractograms were collected using a sample holder mounted on a PANalytical X'pert pro with monochromatic CuKα radiation (λ = 0.15406 nm) in Institute of Military Science and Technology. The generator was utilized at 40 kV and 40 mA, and the intensities were measured in the range of $5° < 2\theta < 40°$, 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 size (L), shown in Equation (5), was calculated using the Scherrer equation [5]:

$$L(nm) = \frac{K \times \lambda}{\beta \times \cos(\theta)} \tag{4}$$

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 the modified acacia cellulose

The structure of cellulose can be considered by FTIR method. The transformation of cellulose structure was related to shift and shape of the characteristic bands. The structural characteristics can be evaluated by intensity of these characteristic bands [2-5]. In order to investigate the structural characteristics of the modified acacia pulps, the FTIR spectra of these modified acacia pulps, the CND pulp and INDO pulp were recorded (Fig. 1).

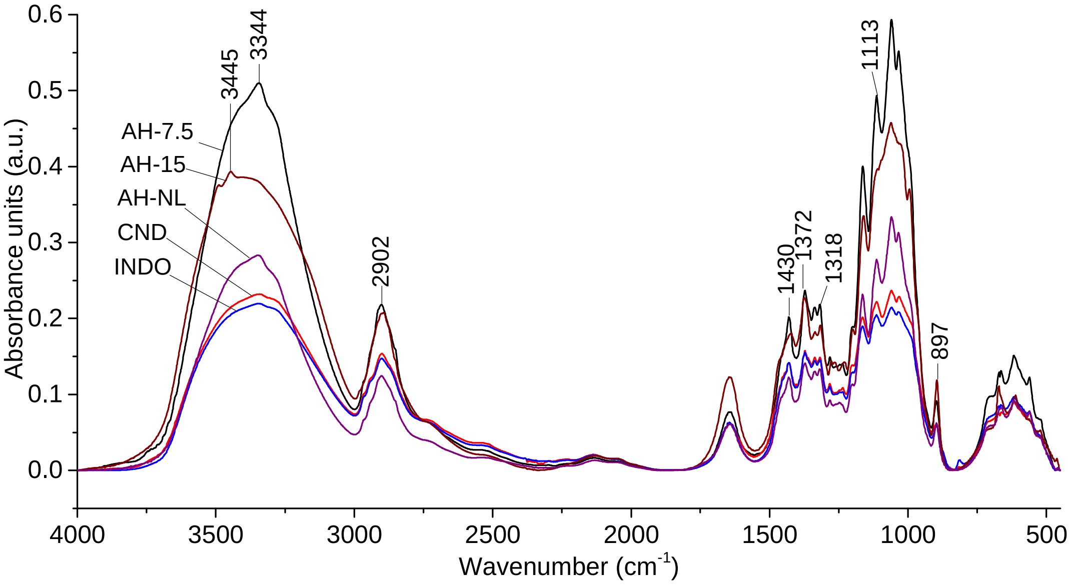


Figure 1. FTIR spectra of the cellulose samples

The FTIR spectra of the modified acacia celluloses have some similarities to the others and some differences from the others (Fig. 1). All characteristic peaks of AH-7.5 are similar to initial acacia pulp, CND pulp and INDO pulp as follows: the peak of OH at 3344 cm^{-1}, the peak of CH and CH_2 bonds in aliphatic methylene groups at 2900 cm^{-1}, the peak of CH_2 vibrations at 1430 cm^{-1}, the peak of COH, HCC vibrations at 1372 cm^{-1}, the peak of asymmetric vibrations of glucose rings at 1113 cm^{-1}, and the peaks of COC vibrations of glycoside bonds at 897 cm^{-1}. Corresponding to report of Nelson and O'Connor [12], these peaks show that AH-7.5 sample is cellulose I. Several characteristic peaks of structure of AH-15 are changed. Compared AH-15 with the initial pulp, the maximum absorbance of band at 3600 - 3000 cm^{-1} is shifted from 3350 cm^{-1} to 3445 cm^{-1}, and the absorbance of peak at 1430 cm^{-1} is shifted to 1423 cm^{-1}, and the absorbance of peak at 1111 cm^{-1} grows much weak. Besides, the peaks at 1372 cm^{-1}, 1318 cm^{-1} and 897 cm^{-1} are changed insignificantly. These peaks show that AH-15 sample is cellulose II. Thus, as initial acacia pulp, CND and INDO, the AH-7.5 sample is a cellulose I; on the contrary the AH-15 sample is a cellulose II.

In Fig. 1 the intensity of OH peaks and other peaks in the FTIR spectra of AH-7.5 and AH-15 samples increases in comparison with initial pulp that can be explained as follows: when immersing this pulp in alkaline medium the part of impurities (hemicellulose, residual lignin, etc.) can be dissolved; that leads to increase of cellulose purity; and change of cellulosic structure also can increase intensity of the peaks.

Based on the FTIR spectra of the samples, the structural characteristics were evaluated by Equation (1), (2) and (3). The results are shown in Table 1.

As shown in Table 1, the IR structural characteristics of modified acacia celluloses have some similar and some difference from the initial pulp, INDO pulp and CND pulp (the imported pulps). The TCIs of the modified acacia cellulose (AH-7.5 and AH-15) are similar to each other, and are slightly higher than that of the imported pulps. The LOI of the AH-7.5 sample is the same as the imported pulps. However, the LOI of the AH-15 sample is significantly lower than that of the others. The HBIs of the modified acacia pulps are higher than that of the imported pulps. Thus, these results show that the modified acacia cellulose I (AH-7.5) has a similar crystallinity to the imported pulps, but has a lower chain mobility than the imported pulps. Additionally, although the modified acacia cellulose II (AH-15) has a lower crystallinity than the imported pulps it still has a lower chain mobility than the imported pulps.

Table 1. The structural characteristics of modified cellulose from acacia pulp and the imported pulps.

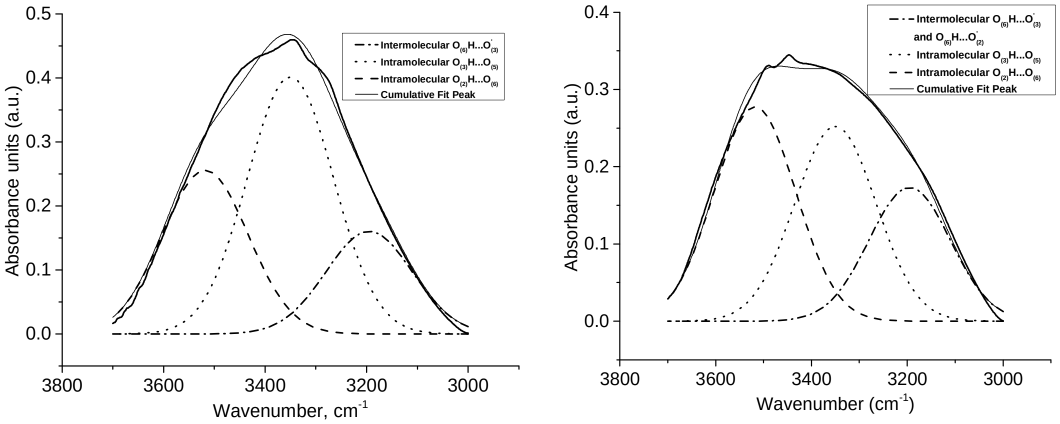
No.	The samples	IR structural characteristics		
		TCI	LOI	HBI
1	AH-NL	1.14	2.01	2.49
2	AH-7.5	1.09	2.22	2.33
3	AH-15	1.09	1.51	2.06
4	INDO	1.05	2.41	1.51
5	CND	1.03	2.33	1.56

3.2. The hydrogen bond of modified cellulose

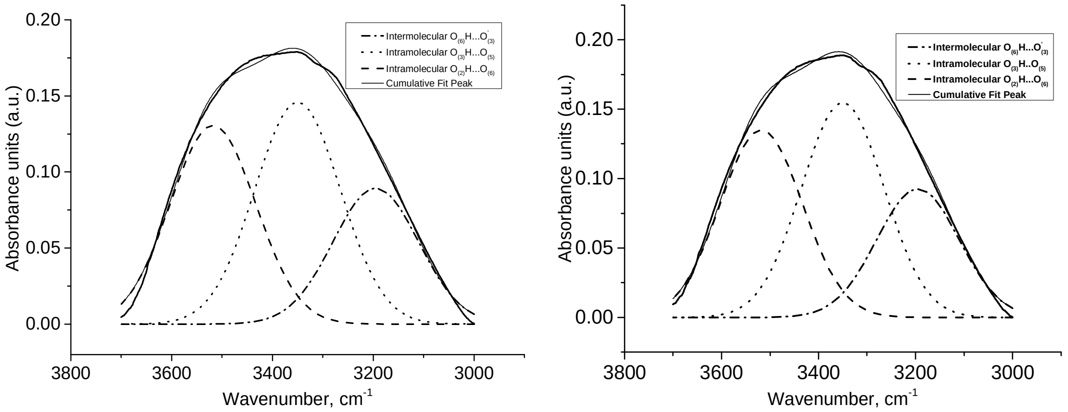
When modifying cellulose in alkaline medium the changes of structure were also caused by the splitting and formation of new inter-molecular and intra-molecular hydrogen bonds. In cellulose I, there are two intra-molecular hydrogen bonds $O_{(6)}H...O_{(2)}$ and $O_{(3)}H...O_{(5)}$, and the one inter-molecular hydrogen bonds $O_{(6)}H...O'_{(3)}$ at 3518 cm^{-1}, 3350 cm^{-1} and 3195 cm^{-1}, respectively. In cellulose II, there are also three hydrogen bonds similar to the cellulose I, additionally an inter-molecular hydrogen bond $O_{(2)}H...O'_{(2)}$ or $O_{(6)}H...O'_{(3)}$. In this investigation, the FTIR spectra of three cellulosic samples at 3700 - 3000 cm^{-1} were resolved by Gaussian function into three bands. The results are shown in Figure 2 and in Table 2.

Based on the resolution of hydrogen-bonded OH stretching of the samples, the percentage of types of the hydrogen bonds is calculated (Table 2).

The percentage of types of the hydrogen bonds of modified acacia celluloses has much difference from the initial pulp and the imported pulps. The amount of inter-molecular hydrogen bond in modified acacia cellulose I (AH-7.5) and cellulose II (AH-15) is about 4 % and 9 % higher than that of the initial pulps, respectively. In contrast to inter-molecular hydrogen bond, the amount of intra-molecular bond $O_{(3)}H…O_{(5)}$ in modified acacia cellulose I (AH-7.5) and cellulose II (AH-15) is about 4 % and 18 % lower than that of the initial pulps. When immersing cellulose in alkaline medium the hydrogen bonds in cellulose are split because the cellulose is not reacted to form a new compound and only strongly swelled. After washing cellulose clean from alkaline solution, the direction of hydrogen atom in OH group can be changed due to having three options of the hydrogen atom in space. Thus, when modifying in alkaline medium, there are the transformation of intra-molecular bond $O_{(3)}H\ldots O_{(5)}$ to inter-molecular hydrogen bond and intra-molecular bond $O_{(6)}H\ldots O_{(2)}$.



(a) AH-7.5 (b) AH-15



(c) INDO (d) CND

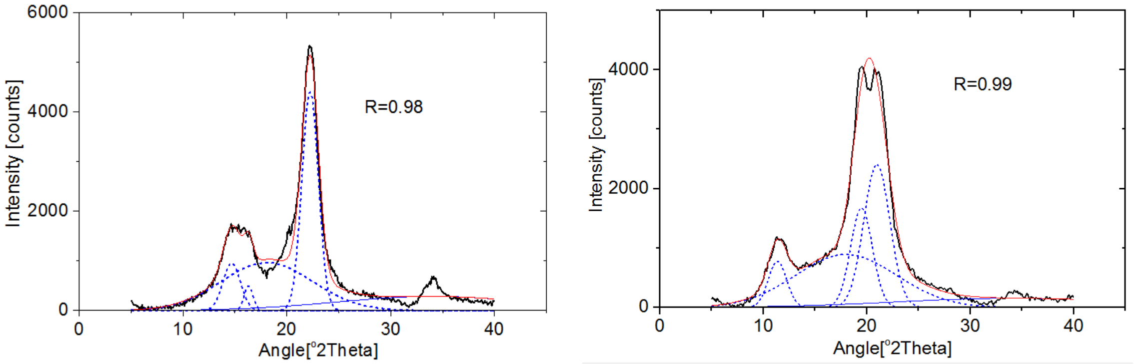
Figure 2. Resolution of hydrogen-bonded OH stretching for modified acacia pulps AH-7.5 (a) and AH-15 (b), INDO pulp, and CND pulp.

Table 2. The amount of the hydrogen bonding types of the several celluloses.

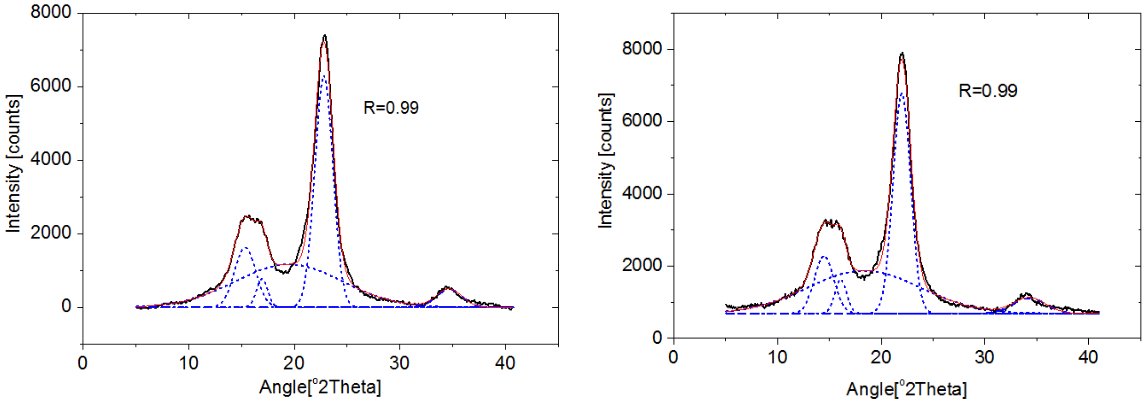
No.	The Samples	Inter-molecular hydrogen bonds, %	Intra-molecular hydrogen bonds, %	
		$O_{(6)}H\ldots O'_{(3)}$ and $O_{(2)}H\ldots O'_{(2)}$	$O_{(3)}H\ldots O_{(5)}$	$O_{(6)}H\ldots O_{(2)}$
1	AH-NL	15.85	53.70	30.45
2	AH-7.5	19.63	49.12	31.25
3	AH-15	24.65	35.87	39.48
4	INDO	24.43	39.85	35.72
5	CND	24.23	40.47	35.30

3.4. The size of crystalline domains of the modified celluloses

The order of the cellulose chains forms the crystalline domains and amorphous domains. The size of these crystalline domains depends on the type of wood, conditions of modification and affects the properties and reactivity of the cellulose. In this paper, the size of these crystalline domains of the modified cellulose I and the modified cellulose II from an acacia pulp was investigated by XRD method. The XRD spectra of the modified acacia celluloses are resolved by a Gaussian function. The results are shown in Figure 3 and Table 3.



(a) AH-7.5 (b) AH-15



(c) CND (d) INDO

Figure 3. The resolution of XRD spectra of the several celluloses: (a) – cellulose I (AH-7.5); (b) – cellulose II (AH-15); (c) – CND; (d) – INDO.

The Figure 3 shows that the diffractive bands of the AH-7.5 sample differ from the diffractive bands of AH-15 sample. The AH-7.5 sample has the characteristic bands as follows: 14.68^0 of 101 plane, 16.31^0 of $10\bar{1}$ plane, 22.24^0 of 002 plane and 34.11^0 of 004 plane. These diffractive bands confirm a cellulose I of AH-7.5 sample modified from the acacia pulp. Additionally, the AH-15 sample has the characteristic bands of diffraction as follows: 11.37^0 of 101 plane, 19.48^0 of $10\bar{1}$ plane, 20.97^0 of 002 plane and at 34.32^0 of 004 plane. These diffractive bands confirm a cellulose II of AH-715 sample modified from the acacia pulp.

Table 3. The size of crystalline domains of the modified acacia celluloses.

No.	The samples	The average size of the crystalline domains, nm		
		L(101)	$L(10\bar{1})$	L(002)
1	AH-NL	3.71	6.54	4.67
2	AH-7.5	4.33	8.58	4.80
3	AH-15	4.04	3.55	2.99
4	INDO	3.88	6.54	4.48
5	CND	3.68	6.55	4.44

As shown in Table 3, the size of crystalline domains of the modified acacia celluloses have some differences from the others. The AH-7.5 sample, which is a cellulose I, has the larger size of crystalline domain than that of the initial pulp and the others. Especially, the size of $L(10\bar{1})$ increases significantly. This can be explained that when modifying cellulose in this concentration although the transformation of cellulose isn't occurred the part of hemicellulose and amorphous cellulose in cellulose is dissolved and then the crystalline domains are restructured. The size of AH-15 sample is much lower than that of the others because the form of crystalline in cellulose II unit differs from that of cellulose I and the molecular direction of cellulose II rotates an angle in comparison with that of cellulose I. Therein, the size of L(101) almost remain stable, but the size of $L(10\bar{1})$ and L(002) goes down.

4. CONCLUSION

The modified acacia celluloses from acacia pulp in Vietnam have some different characteristics from the Canadian softwood cellulose, the Indonesian hardwood cellulose and the initial acacia pulp. As the initial acacia pulp, CND and INDO, the AH-7.5 sample is a cellulose I, and the AH-15 sample is a cellulose II. The cellulose I of modified acacia has a TCI of 1.09, a LOI of 2.22 and a HBI of 2.33, and the cellulose II of modified acacia has a TCI of 1.09, a LOI of 1.51 and HBI of 2.06. The crystalline size of modified acacia cellulose I is about 4.33 nm of L(101) plane, 8.58 nm of $L(10\bar{1})$ plane and 4.80 nm of L(002) plane, and that of cellulose II is about 4.04 nm of L(101) plane, 3.55 nm of $L\ (10\bar{1})$ plane and 2.99 nm of L(002) plane.

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