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Study on Nitrogen Content of Cellulose Carbamates by Fourier Transform Infrared Spectroscopy

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Cellulose carbamates were synthesized by using microcystalline cellulose and cellulose pulp as raw materials. The Fourier transform infrared (FTIR) spectra were recorded and used to determine the nitrogen content of cellulose carbamate. The accurate results of the nitrogen content can be obtained with the deconvolution method replacing the baseline method when the nitrogen content is not more than 4%.

INTRODUCTION

Cellulose is a natural polymer that can be degradable in the environment. The fibers made of the cellulose still occupy an important position among raw materials for the textile industry. Especially, the viscose that prevails in the manufacture of fibers from cellulose pulp yields high-quality and high-comfort fibers for garments[1]. However, the manufacturing process of the viscose inevitably produces emissions of hazardous CS_2 and H_2S and effluents containing sulphur compounds. So the efforts to find alternatives to the viscose technology are in progress. The cellulose carbamate (CC) is a better alternative that can turn the existing viscose plants to environment friendly facilities while maintaining high quality of the manufactured fibers and effective output of the installations.

Cellulose carbamate was first reported by Hill and Jacobsen[2]. Later the compound was studied by some authors[3–5]. Since the 80's, cellulose carbamate has been reported in numerous papers and patents[6–12]. However, the studies on the manufactures of cellulose carbamate prevail in these reports. The characterization and the studies on the properties of cellulose carbamate have been reported quite few[13]. It is worth mentioning that the nitrogen content is important for cellulose carbamate to be applied. So in the present work, a serials of cellulose carbamate were synthesized by using microcrystalline cellulose and cellulose pulp as raw materials. The nitrogen content of cellulose carbamate was quantiatively analyzed by Fourier Transform Infrared (FTIR) using deconvolution method. The results of the nitrogen content were in good agreement with those obtained by elemental analysis.

EXPERIMENTAL

Cellulose carbamate was synthesized in our laboratory using two different cellulose raw materials. One is the microcrystalline cellulose (MCC), produced by Shanghai Reagent Factory. The synthesis of cellulose carbamate using MCC was earlier reported[14]. The other raw material is cellulose pulp, a kind gift from Blue Peacock Chem. Fiber Co., Hangzhou. Cellulose pulp was preliminarily activated by 20% wt. aqueous sodium hydroxide. Then, the activated cellulose pulp was aged for a certain time at a selected temperature and mixed with saturated aqueous urea solution. The mixture was heated and the water in the solution was replaced with an organic solvent. And thereafter the cellulose was reacted with urea in the liquid phase to yield cellulose carbamate, which is separated from the liquid medium and washed with warm water.

Infrared spectra of cellulose carbamate were recorded in potassium bromide disk technique by a Nicolet MX-1 FTIR spectrophotometer at room temperature. A total of 27 scans were taken with a resolution of 2 cm^{-1} in all cases. Before determined by FTIR, the samples were dried in the vacuum oven at 60°C for one week. The nitrogen contents of the samples were determined by the elemental analysis equipment produced by Perkin-Elmer and listed in Table-1.

TABLE-1
THE RESULTS OF THE ELEMENTAL ANALYSIS FOR CELLULOSE CARBAMATE (CC)

Notation	Nitrogen content	Notation	Nitrogen content
CC01	1.55	CC20	1.44
CC02	1.92	CC21	1.52
CC03	2.14	CC22	2.03
CC04	2.45	CC23	2.41
CC05	2.88	CC24	2.73
CC06	3.13	CC25	3.16
CC07	3.66	CC26	3.64
CC08	3.85	CC27	3.87
CC09	4.33	CC28	4.22
CC10	4.51	CC29	4.83

RESULTS AND DISCUSSION

The infrared spectra of cellulose carbamate (CC) samples were shown in Fig. 1. We observed that all of the absorption bands except for the absorption band about 1720 cm^{-1} for the cured samples are almost same to the bands of cellulose. Segal[5] and Nozawa[13] have also verified this result. At the same time, the absorption intensity ratio of the band at 1718 cm^{-1} to the band at 1628 cm^{-1} increases with the increasing of the nitrogen content of cellulose carbamate. This phenomenon implies that the quantitative relation may exist between the absorption intensity ratio and the nitrogen content for cellulose carbamate. However, the absorption intensity of the carbonyl group is very strong, which results in the overlapping part between the 1718 cm^{-1} band and the 1628 cm^{-1}

band, as shown in Fig. 1. It is obviously that the values of the intensity maximum in infrared absorption band determined directly by the baseline method exist error to some degree. In order to obtain the more accurate absorption intensity, the deconvolution method for the infrared spectra is recommended in this work. The result of the deconvolution for the CC05 in the range 1550 cm^{-1} ~ 1800 cm^{-1} is shown in Fig. 2. In this range, the infrared spectrum of CC05 can be divided into two absorption bands that peak at about 1720 cm^{-1} (a) and 1630 cm^{-1} (b), respectively. The deconvolved spectrum of the two peaks is good corresponding with the observed spectrum. In Fig. 2, the areas of the peak *a* and the peak *b* are marked as A_{1720} and A_{1630} and listed in Table-2. The A_{1720} and A_{1630} of the other samples are also listed in Table-2. The relation between the area ratio of A_{1720} to A_{1630} and the nitrogen content (N%) is shown in Fig. 3 and its regression equation is followed:

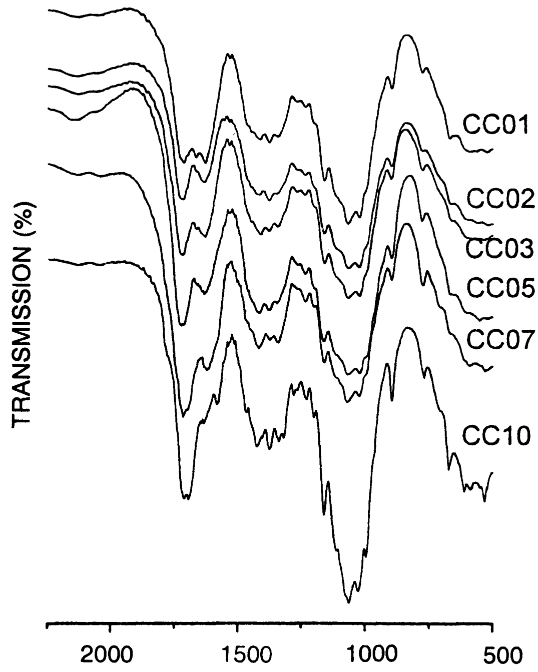

Fig. 1. The FTIR spectra of cellulose carbamate with different nitrogen content.

$$N\% = 1.9413\ A_{1720}/A_{1630} + 0.4637 \qquad (1)$$

From Fig. 3, we find that the relationship between the ratio A_{1720}/A_{1630} and the nitrogen content is linear (correlation coefficient equal to 0.998) when the nitrogen content is less than 4%. Beyond 4%, the relation between the ratio

A_{1720}/A_{1630} and the nitrogen content can not meet the above equation. The increment of the ratio A_{1720}/A_{1630} is more than that of the nitrogen content, as shown in Fig. 3. In fact, from Fig. 1, we can find that the absorption of the carbonyl group at 1718 cm^{-1} is very strong and conceals the absorption of 1628 cm^{-1} band for the higher nitrogen content samples. Such a result brings about the bigger error of the deconvolution method. So the accurate results can not be obtained by the deconvolution method.

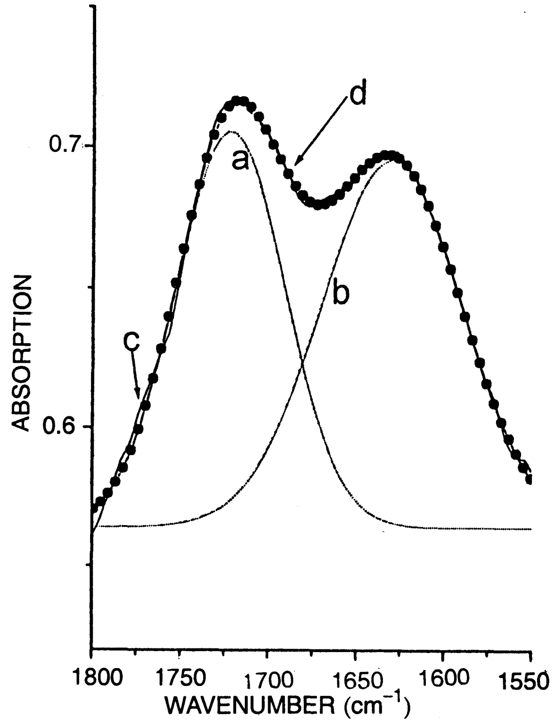

Fig. 2. The deconvolved result of CC05 in the range 1550 cm^{-1} ~ 1800 cm^{-1}. *a* and *b*: the separated absorption peaks; *c*: the deconvolved spectrum; *d*: the observed spectrum.

On the other hand, the deconvolution method was used to analyze the samples manufactured from the cellulose pulp. The results are listed Table-3. The absorption area ratio A_{1720}/A_{1630} and the nitrogen content are also shown in Fig. 3. The result similar to that of the cellulose carbamate from MCC can be obtained. So equation (1) is fit to the samples either from MCC or from cellulose pulp.

So as a conclusion, it can be said that the nitrogen content in the cellulose carbamate can be quantitatively determined by FTIR. When the nitrogen content is less than 4%, the accurate result of the nitrogen content for CC both from MCC and from cellulose pulp can be obtained by using the deconvolution method.

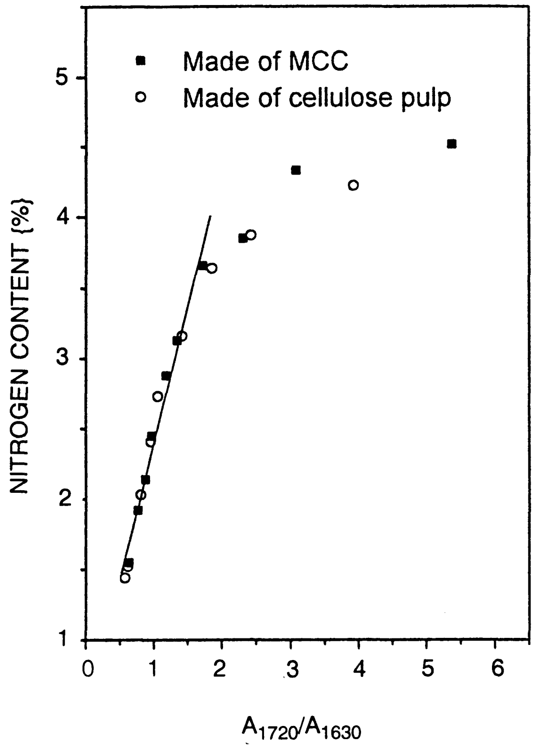

Fig. 3. Relation between nitrogen content and absorption area ratio in the treated.cellulose.

TABLE-2
THE FTIR RESULTS OF CELLULOSE CARBAMATE (CC) MANUFACTURED FROM MICROCRYSTALLINE CELLULOSE

Notation	A_{1720}	A_{1630}	A_{1720}/A_{1630}
CC01	4.799	7.630	0.629
CC02	8.597	11.303	0.761
CC03	11.049	12.661	0.873
CC04	7.443	7.715	0.965
CC05	10.819	9.216	1.174
CC06	12.473	9.295	1.342
CC07	14.538	8.645	1.717
CC08	12.775	5.527	2.311
CC09	13.096	4.250	3.082
CC10	14.682	2.735	5.369

TABLE-3
THE FTIR RESULTS OF CELLULOSE CARBAMATE (CC) MANUFACTURED FROM CELLULOSE PULP

Notation	A_{1720}	A_{1630}	A_{1720}/A_{1630}
CC20	10.773	18.736	0.575
CC21	9.826	15.900	0.618
CC22	9.802	12.176	0.805
CC23	10.352	10.908	0.949
CC24	11.814	11.219	1.053
CC25	13.229	9.349	1.415
CC26	12.616	6.823	1.849
CC27	13.683	5.642	2.425
CC28	14.458	2.563	3.924
CC29	14.208	2.429	5.849

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