Chinese Chemical Letters Vol. 12, No. 4, pp. 365 – 368, 2001

Deconvolution Method for Determination of the Nitrogen Content in Cellulose Carbamates

Guang Mei CHEN*, Yi Ping HUANG

Department of Chemistry, Anhui University, Hefei 230039

Abstract: Cellulose carbamates (CC) were synthesized with microcrystalline cellulose as raw materials. The Fourier transform infrared spectra of CC with different nitrogen content were recorded. The accurate results of the nitrogen content for CC can be obtained by using the deconvolution method when the nitrogen content is less than 3.5%. The relationship between the nitrogen content and the absorption intensity ratio of the corresponding separated absorption peaks in FTIR spectra has been expressed by an equation precisely.

Keywords: Cellulose carbamates, nitrogen content, deconvolution method, baseline method.

Cellulose carbamate (CC) is a derivative of cellulose. It can be turned into synthetic fiber in high quality with the existing viscose facilities[1]. CC was first reported by Hill and Jacobsen[2]. Since the 80's, numerous papers and patents about study on CC have been reported[3-9]. The studies on the synthesis of CC and the manufactures of fibers prevailed in these reports. But there were quite few reports about the characterization and the properties of CC[10]. Elemental analysis and FTIR measurements for a serious synthetic CC are reported in this paper. The nitrogen content of CC was obtained by FTIR deconvolution method in a relatively wide range and they were in good agreement with those obtained by elemental analysis.

The microcrystalline cellulose, which was produced by Shanghai Reagent Factory, was preliminarily activated by 0.1mol/L aqueous sodium hydroxide solution. Then the activated cellulose was aged for a certain time at a selected temperature and reacted with urea in organic solvent. Eventually, CC is separated from the liquid medium, washed with warm water and dried in vacuum oven at 60°C for one week.

The nitrogen contents of CC samples determined by the elemental analysis were listed in **Table 1.** FTIR measurements for the all CC samples were carried out by a Bruker FTIR spectrophotometer at room temperature. A total of 27 scans were taken with a resolution of 2 cm^{-1}. Infrared spectra of some CC samples were shown in F**igure 1.** It is almost the same as the spectrum of cellulose, but a strong peak appeared at 1718 cm^{-1}. Nozawa[10] and Segal[11] have also verified this result. One can find that the ratio of absorption intensity of the band at 1718 cm^{-1} to the band at 1628 cm^{-1} increases with the increasing of the nitrogen content of CC. This phenomenon implies that the quantitative relationship exists between the nitrogen content and the absorption intensity

Table 1 The results of the elemental analysis for CC

Notation	Nitrogen content %	Notation	Nitrogen content %	Notation	Nitrogen content %
CC01	0.29	CC07	1.42	CC13	3.13
CC02	0.41	CC08	1.55	CC14	3.66
CC03	0.65	CC09	1.92	CC15	3.85
CC04	0.88	CC10	2.14	CC16	4.33
CC05	1.01	CC11	2.45	CC17	4.51
CC06	1.26	CC12	2.88	CC18	5.07

Figure 1 The FTIR spectra of CC

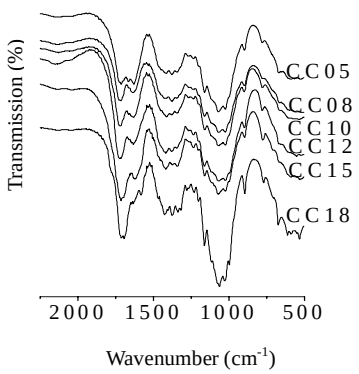
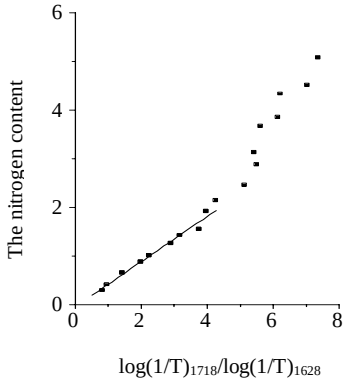


Figure 2 The nitrogen contents as a function of the absorption intensity ratios



ratio in IR. According to the baseline method, the ratio of absorption intensities can be expressed by $\log(1/T)_{1718}/\log(1/T)_{1628}$. The ratios of the all samples are listed in **Table 2.** When the nitrogen content of CC is less than 1.5%, the linear relationship between the ratios and the nitrogen contents of CC (N%) exists and the N% can be expressed by equation (1):

$$N\% = 0.43\log(1/T)_{1718}/\log(1/T)_{1628} \quad (1)$$

Because the absorption band of the carbonyl group is very strong, it is overlapped with the bands at 1718cm^{-1} and 1628cm^{-1} (**Figure 1**). Obviously, it can commit the errors if the baseline method is used to determine the absorption intensity of the two bands directly. In order to obtain the more accurate absorption intensity, the deconvolution method for the infrared spectra is recommended in this work. The deconvolved result of the CC05 sample in the range 1550 cm^{-1} ~ 1800 cm^{-1} is shown in **Figure 3.** In this range, the infrared spectrum of CC05 sample can be divided into two absorption bands 1720 cm^{-1} (a) and 1630 cm^{-1} (b), respectively. The deconvolved spectrum of the two peaks is in good agreement with the observed spectrum (see **Figure 3**). The ratios of A_{1720}/A_{1630} were listed in **Table 2**. The relation between the area ratio A_{1720} to A_{1630} and the nitrogen content can be expressed by equation (2):

$$N\% = 1.97A_{1720}/A_{1630} + 0.43 \quad (2)$$

$A_{1720:}$ area of the peak at 1720 cm^{-1}; $A_{1630:}$ area of the peak at 1630 cm^{-1}

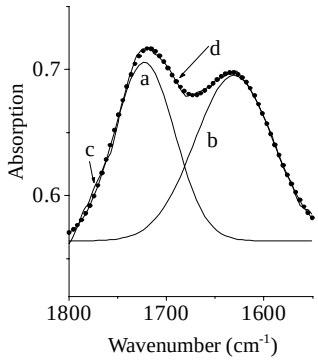
Table 2 The absorption intensity ratio and the area ratio of the bands of CC in IR

Notation	The FTIR results		Notation	The FTIR results	
	The absorption ratios [a]	The area ratios [b]		The absorption ratios [a]	The area ratios [b]
CC01	0.82	0.03	CC10	4.25	0.87
CC02	0.96	0.05	CC11	5.13	0.97
CC03	1.42	0.10	CC12	5.49	1.17
CC04	1.98	0.22	CC13	5.42	1.34
CC05	2.23	0.28	CC14	5.60	1.72
CC06	2.89	0.41	CC15	6.13	2.31
CC07	3.17	0.49	CC16	6.21	3.08
CC08	3.74	0.63	CC17	7.02	4.35
CC09	3.96	0.76	CC18	7.36	4.97

[a] $Log(1/T)_{1718}/log(1/T)_{1628}$, obtained by the baseline method;
[b] A_{1720}/A_{1630}, obtained by the deconvolution method

The linear relationship of N% and A_{1720}/A_{1630} was shown in **Figure 4.** When the nitrogen content is less than 3.5%, the relationship between the ratio A_{1718}/A_{1628} and the nitrogen content is in linearity (the correlation coefficient R = 0.998). The N% exceeded 3.5%, the linearity of relationship between the area ratio and N% was not consistent, as shown in **Figure 4**. **Figure 1** has shown that the absorption of the carbonyl group at 1718 cm^{-1} is very strong and conceals the absorption of 1628 cm^{-1} band wholly for the higher nitrogen content samples. The difference of the absorption intensity between the two peaks is so remarkable that the big errors can be occurred even with the deconvolution method.

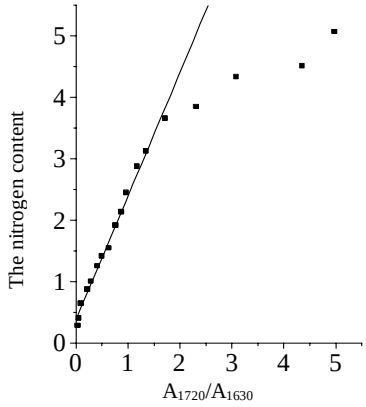
Figure 3 The deconvolved result of CC05 in the range 1550 cm^{-1}~1800 cm^{-1}



a: absorption peak at 1720cm^{-1} b: absorption peak at 1630 cm^{-1}
c: (⋯⋯) the deconvolved spectrum d: (——) the observed spectrum

In conclusion, the nitrogen content in the CC can be quantitatively determined by FTIR. When the nitrogen content is less than 3.5%, the accurate result of the nitrogen content for CC can be obtained by using the deconvolution method.

Figure 4 The nitrogen content as a function of the area ratio



References

1. A. Urbanowski, *Chem. Fibers Int.*,**1996**, *46* (4), 260.
2. J. W. Hill, R. A. Jacobsen, *USP* 2 134 825.
3. G. M. Chen, B. B. Li, Y. P. Huang, *Fine Chem.* (in Chinese), **2000,** *17* (6), 356.
4. T. R. Zimina, G. A. Petropavlovskii, *Zh Prikl Khim* (S-Peterburg) (in Russian), **1998**, *71* (5), 856.
5. W. Makschin, H. Schleicher, *et al*., Ger Pat DE 4 407 906.
6. Ekman, *et al*., *Cellulose Structure, Modification and Hydrolysis*, John Wiley and Sons, Inc., New York, **1986**, 67.
7. H. Struszczyk, P. Starostka, *et al.*, Pol Pat PL 160 863.
8. H. Struszczyk, D. Wawro, P. Starostka, *Chem. Vlakna*., **1991**, *41*, 59.
9. F. Hermanutz, W. Oppermann, Ger Pat DE 19 635 707.
10. H. Nozawa, *J. Appl. Polym. Sci*., **1981**, *26*, 2103.
11. L. Segal, F. V. Eggerton, *Text. Res. J.*, **1961**, *31*, 460.

Received 5 September, 2000