

Partially Carbamate Reaction of Cellulose with Urea

The reaction of cellulose with urea and substituted ureas has been studied by Segal¹ and Nuessle.² Some cellulose carbamate derivatives of aromatic amines³ were investigated to prepare in relation to facts that the treated cotton cellulose with urea at 120°C in alkaline condition was favorable to dye.^{4,5} The treatments of cellulose with urea are believed to be significant in the sense of improving fiber and cotton cloth, and so a precise curing condition should be considered to get an optimum on the cellulose carbamate reactions. The conventional curing procedures on heating to an elevated temperature had been applied to the cellulose materials, which were pretreated to soak in an aqueous padding solution of urea and dried at 116°C. The effects of the curing conditions such as temperature, time, and weight ratio of urea to cellulose on the carbamate reactions are not able to examine adequately in the curing manner since the reaction may occur at the drying stage of the samples padded. Therefore, the carbamate reactions of microcrystalline cellulose curing with urea in the state of a dry solid mixture were discussed with reference to the relation between a nitrogen content and an intensity ratio of absorption band in infrared spectra.

EXPERIMENTAL

Various samples were prepared by the following procedures. Dried mixture of solid both predetermined weight ratio of microcrystalline cellulose (Avicel, Asahi Kasei Co.) and urea (Wako Pure Chemical Co.) were heated to cure in a glass vessel immersed in a silicone oil bath at a controlled temperature of 110, 135, 160, or 185°C for 1–15 h without catalyst. These samples were thoroughly washed with boiling water more than five times until the washings were no longer colored, then finally washed with methyl alcohol, and dried under reduced pressure. The samples' color turned slightly grayish brown. Nitrogen contents of the samples prepared were determined by the apparatus of Nitrogen-Nalyzer Coleman model 29. Infrared spectra were recorded in potassium bromide disk technique by JASCO AP-2 spectrometer. The intensity of maxima in infrared absorption band was determined by the baseline method.

RESULTS AND DISCUSSION

Infrared spectra of cellulose and the cured sample were shown in Figure 1. Both lines are almost the same except for the absorption band around 1710 cm^{-1} in the cured sample. The spectrum of cellulose cured without urea on heating at 160°C was identical to that of the original cellulose absence of the band at 1710 cm^{-1} . This band appeared in cellulose treated with urea, which had been found by Segal,¹ was assigned to carbonyl stretching on the basis of urethanes examined by Bellamy (6). A similar band was also obtained in partly urethanized polyvinyl alcohol (7, 8), which was provided to treat with urea in the medium of dimethyl formamide (DMF) at 150°C, according to the procedure described by Sakurada (9).

The absorption band at 1710 cm^{-1} gradually diminished with the treatments of the media pH more than 12 at 85°C for 7 h, and then the spectrum came to the same as that of cellulose, as shown in Figure 2. These may be attributable to the carbamate groups on the cellulose to be subjected to alkalysis, while the band at 1620 cm^{-1} appeared in cellulose itself did not vary in an intensity with such treatments.

To investigate the cellulose carbamate reaction further both an absorption intensity ratio of the band at 1710 cm^{-1} to the band at 1620 cm^{-1} and the nitrogen content of treated cellulose were investigated on various curing conditions such as temperature, time, and weight ratio of urea to cellulose, as shown in Figures 3(a), 3(b), and 3(c), respectively. The absorption intensity ratio had a maximum on the curing temperature around 160°C, and was a little high on the curing time 3–6 hr, although the nitrogen content increased with the curing temperature and curing time. While both the intensity ratio and nitrogen content were decreasing slightly as the weight ratio of urea to cellulose is increasing from 0.4 to 4.0.

A relation between the intensity ratio and the nitrogen contents is shown in Figure 4. An approximately linear relationship was obtained up to 1.25% in nitrogen content except for samples cured at 185°C for more than 6 h, in which may exist unknown water-insoluble nitrogen components

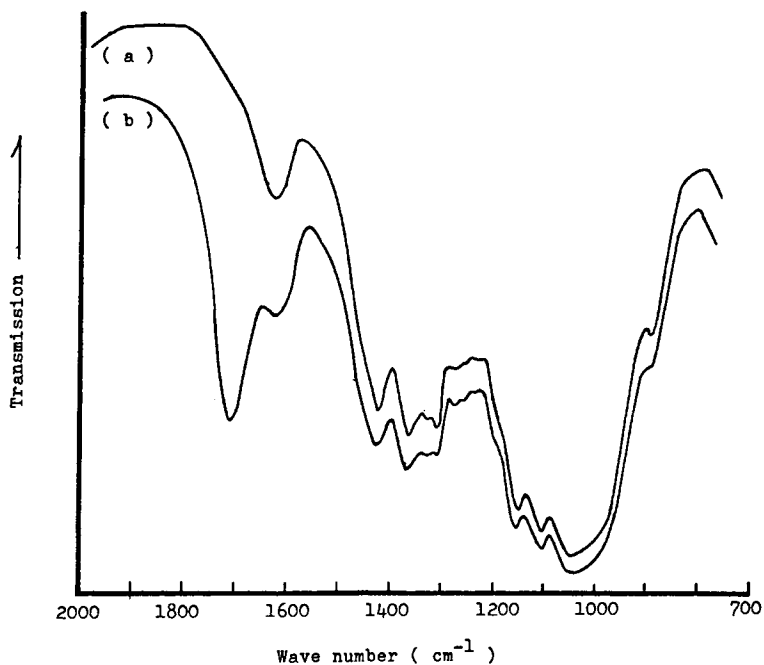


Fig. 1. Infrared spectra of (a) cellulose and (b) treated cellulose cured with urea at 160°C for 3 h.

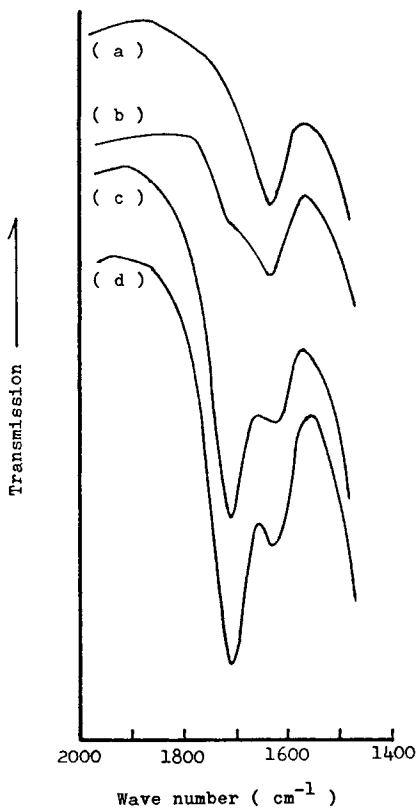


Fig. 2. Changes of the absorption band at 1710 cm⁻¹ on cured cellulose with treatment of acidic alkaline media at 85°C for 7 h: (a) 2N NaOH; (b) pH 13.5; (c) pH 12; and (d) 2N HCl.

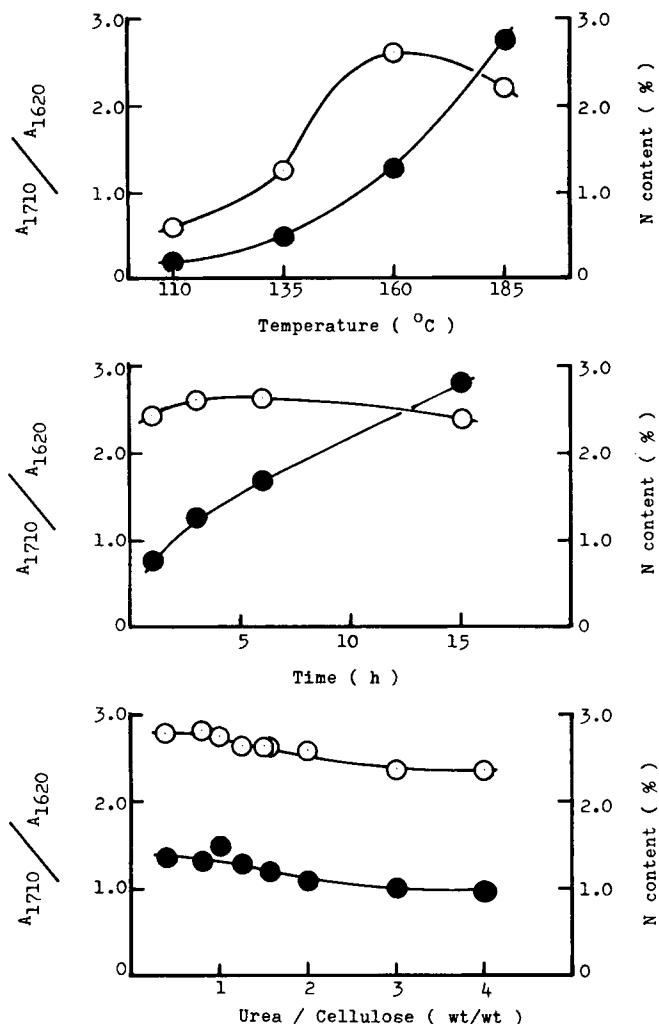


Fig. 3. (O) Absorption intensity ratio and (●) nitrogen content of the treated cellulose in the various curing conditions: (a) curing temperature, urea/cellulose = 1.5, 3 h; (b) curing time, urea/cellulose = 1.5, 160°C; (c) weight ratio of urea to cellulose, 3 h, 160°C

to bind. From the above facts, the optimum in the cellulose carbamation will be found in the curing condition at 160°C for 3 hr.

The original cellulose did not have the nitrogen components at all within the accuracy of the analysis. Therefore, a maximum nitrogen content of 1.25% in cured cellulose at optimum was estimated to a degree of the urethanization corresponded to 0.15 substitution for unit pyranose ring in whole cellulose, that is, corresponded to one substitution in six or seven pyranose rings. The maximum amount of the nitrogen content obtained is slightly lower than that in cured cotton yarn by Segal.¹ It is supposed to be due to the fact that the reaction took place merely on the surface of crystalline particles of cellulose, which has little amorphous regions. The crystallinity of cellulose was estimated to at most 79% in natural cotton (10), and more than 95% in microcrystalline cellulose, which was determined by an x-ray diffraction technique according to Hermans procedure.¹¹

The absorption intensity ratio of the treated cellulose prepared in the various curing conditions is summarized in Table I. The carbamate reaction was affected little by adding the catalysts such as $ZnCl_2$ or $CuCl_2$ to the curing system. It also became slightly lower in the pretreated cellulose with acidic or alkaline media, rather lower in the presence of the medium DMF. No reaction had taken place in the alkaline medium. This may also be supported properly by the facts obtained in Figure 2. Moreover, the effects of such a catalyst as chloride, phosphate, carbonate, sulfate and acetate

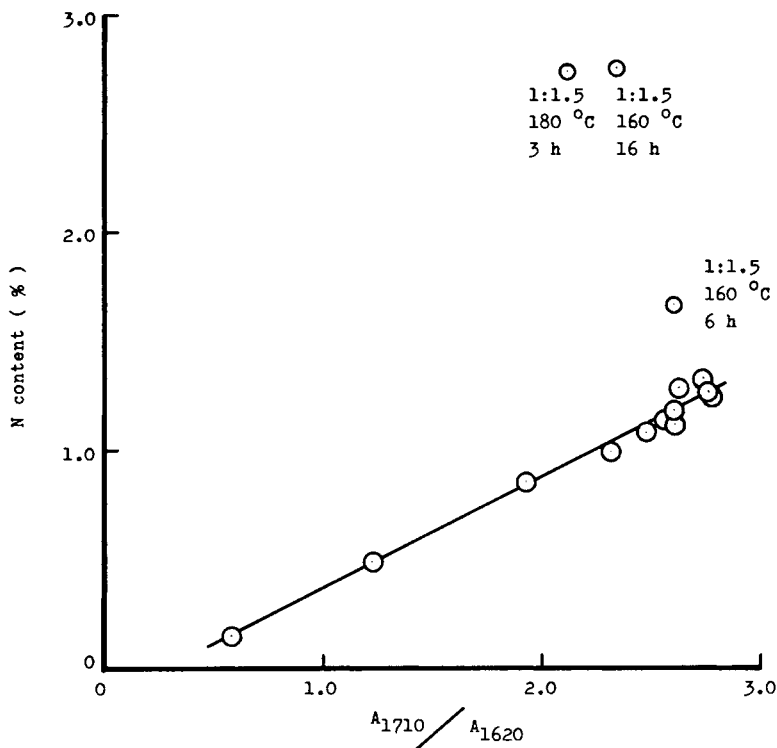


Fig. 4. Relation between nitrogen content and absorption intensity ratio in the treated cellulose.

of sodium and potassium, and sodium cyanate on the carbamate reactions of cellulose with urea were investigated. A prominent carbamate reaction on cellulose hardly was obtained in such a curing system.

The cellulose carbamate and its derivatives with reactant of the dialdehydes such as dialdehyde starch, glutaraldehyde, and glyoxal had been able to immobilize enzymes trypsin and α -amylase easily (12). The facts suggest that these materials may be available to release slowly and to bind bioactive substances as an auxiliary agent to the drugs.

TABLE I
Absorption Intensity Ratio of Modified Cellulose Cured in Various Conditions

Weight ratio of urea to cellulose (w)	Catalyst	Curing condition		Absorption intensity ratio (A_{1710}/A_{1620})
		Temperature (°C)	Time (h)	
2.0 ^a	None	160	7	2.43
2.0	None	160	7	2.24
1.5	None	160	3	2.58
2.0	None	160	3	2.50
1.6	ZnCl ₂ ^c	160	3	2.56
2.0	CuCl ₂ ^c	160	3	2.51
1.2 ^d	None	150	7	0.93
4.0 ^e	None	100	9	0.00

^a Cellulose was pretreated with 10 wt % HCl solution and washed.

^b Cellulose was pretreated with 15 wt % NaOH solution and washed.

^c Quantity of catalyst is 6 wt % for cellulose.

^d Cured in the medium of dimethyl formamide.

^e Cured in the medium of 5 wt % NaOH.

References

1. L. Segal and F. V. Eggerton, *Text. Res. J.*, **31**, 460 (1961).
2. A. C. Nuessle, *Text. Res. J.*, **31**, 990 (1961).
3. A. Hebeish, A. I. Waly, N. Y. Abou-Zeid, and E. A. El-Alfy, *Text. Res. J.*, **48**, 468 (1968).
4. A. C. Nuessle, *Am. Dyestuff Rep.*, **53**, 26 (1964).
5. U. Baumgarte, *Melliland Textilber*, **46** 851 (1965).
6. L. J. Bellamy *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, p. 222.
7. A. Paquin, *Z. Naturforsch.*, **1**, 518 (1948).
8. F. Mashio, K. Watanabe, T. Morii, and T. Iida, *Report of Poval Committee*, No. 39, Kyoto, Japan (June, 1961).
9. I. Sakurada, A. Nakajima, and K. Shibatani, *J. Polym. Sci. Part A-2*, 3545 (1964).
10. L. Segal, *Text. Res. J.*, **20**, 786 (1959).
11. P. H. Hermans, and A. Weidinger, *J. Appl. Phys.*, **19**, 491 (1948).
12. Y. Nozawa, M. Hasegawa, and F. Higashide, *Kobunshi Ronbunshu*, **38**, 39 (1981).

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