

THERMAL PROPERTIES OF CELLULOSE CARBAMATE

B. Łaszkiwicz and B. Domasik

TECHNICAL UNIVERSITY OF ŁÓDŹ, 90-924 ŁÓDŹ, POLAND

(Received June 14, 1988)

The thermal properties of cellulose carbamate with various nitrogen content are discussed. Thermal analysis was performed in air and under nitrogen atmosphere. The increase in the nitrogen content in cellulose carbamate brings about only a shift of the maximum decomposition rate towards lower temperatures. It can be concluded that cellulose carbamate heated to 320 °C is readily dehydrated and cross-linked, which results in the formation of aromatic structure.

Cellulose carbamate is prepared by treating cellulose with urea [1] at a temperature above the melting point of urea, i.e. 132.7°. Urea, after melting in air is decomposed evolving isocyanic acid which readily reacts with cellulose [2].

The IR spectra of cellulose carbamate show a wide absorption band at 1715 cm^{-1} corresponding to the carbonyl group [3]. In an alkaline system, the carbamation of cellulose proceeds relatively rapidly [4] with a simultaneous drop in the polymerization degree of cellulose [5]. The reaction of cellulose carbamation with urea takes place within the intracellular regions of the cellulose treated with a liquid ammonia solution of urea [6]. In this case, ammonia brings about structural changes in cellulose, facilitating its reaction with urea. The cellulose activation in liquid ammonia with simultaneous saturation of cellulose with urea results, after subsequent evaporation of ammonia and heating of the cellulose—urea mixture at 135–160°, in forming a cellulose carbamate which is soluble in dilute sodium hydroxide solution. Among the catalysts for the carbamation process are alkaline metal carbamates soluble cellulose carbamate can also be obtained from fir or beech cellulose previously mercerized with 17–19% NaOH [7] in the presence of activators [8].

Experimental

Fir cellulose containing 94% of α -cellulose was first activated by mercerization with an aqueous 19% NaOH solution at 55° for 30 min. The mercerization was

carried out by the mash method at a cellulose to lye ratio of 1 : 15 (by wt.). The mercerizing lye contained 1% of urea as activator.

The alkal cellulose obtained was separated from the excess lye by pressing and then neutralized with 10% H_2SO_4 . Sodium sulphate was then washed out with water. The cellulose so prepared was treated with a solution containing urea in an amount equal to the cellulose mass. After that the sample was dried. It contained also 1% of Na_2CO_3 as catalyst for the carbamation process. The treated cellulose was dried at 60° and then reheated at 130° and 160° in air for 1–5 h. The cellulose carbamate obtained was purified from unreacted urea and by-products with hot water. After drying the chemical composition of the product was determined. The nitrogen content was determined by the Kjeldahl method and carbon and hydrogen contents by the micro-method of Pregl.

Thermal analysis was performed with an OD-102 derivatograph (MOM, Hungary) in air using 100 mg samples and 5 deg/min heating rate, and with a TGF-1 thermobalance (Perkin-Elmer), using an UU-1 programmer, under nitrogen atmosphere. In the second case 5 mg samples placed in an aluminium container were used. IR spectrophotometric examinations were carried out with a Specord 71 spectrophotometer, using KBr pellets.

Results and discussion

The thermal curves of cellulose carbamate prepared at 135° for 5 h is shown in Fig. 1. The degree of substitution of this carbamate was $DS=92$ and the nitrogen content 6.4%. It results from the TG and DTA curves that the highest decomposition rate of cellulose carbamate in air is shown within the temperature range $250\text{--}300^\circ$ with the maximum at 280° . The decomposition begins at 180° and is completed at 550° . The character of the DTA curve points to the existence of three separate thermal decomposition processes in the cellulose carbamate under investigation. In order to explain the changes in chemical composition of cellulose carbamate, the heating in the derivatograph was performed at various temperatures: 150, 220, 250 and 320° . These temperatures are marked with points A, B, C and D, respectively in the DTA curve (Fig. 1).

The chemical compositions of cellulose carbamate for particular temperatures are given in Table 1. It is clear from these data that the composition of cellulose carbamate rapidly changes when heated to temperatures above 220° . Even below this temperature some changes in the composition take place, mainly in the range $150\text{--}220^\circ$. On the other hand, above this range of temperature, an increase in carbon and nitrogen contents is observed, which may suggest that dehydration takes place in the heated cellulose carbamate as well as its crosslinking with the

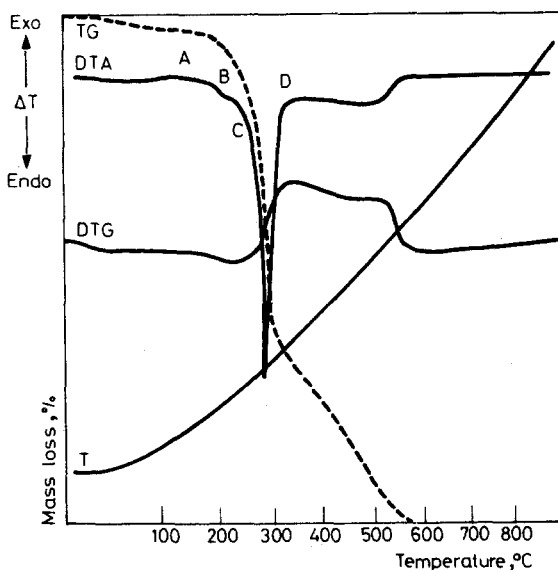


Fig. 1 TG and DTA curves of cellulose carbamate with DS = 92

Table 1 Composition of cellulose carbamate heated at various temperatures

Sample	End temp. of heating, °C	Content of elements, %		
		C	H	N
1	100	39.63	6.07	6.41
2	150	39.92	5.54	6.16
3	220	43.57	5.29	3.90
4	250	52.06	4.53	4.21
5	320	65.21	3.04	6.98

Content of elements in cellulose: C = 44.23% and H = 6.10%.

participation of carbamino groups. In order to confirm this observation IR spectral examinations were performed on cellulose carbamate samples heated to definite temperatures. It results from the spectrograms (Fig. 2) that some chemical changes take place already at 250°, which are accompanied by the disappearance of carbamino group having two characteristic bands at 1715 cm^{-1} and 1600 cm^{-1} (curve b). When the heating temperature is 320°, a clear aromatization of cellulose carbamate is observed (curve c) and it is shown by the disappearance of absorption bands and the black colour of decomposed cellulose carbamate. Thus, the results of spectrophotometric examinations confirm the fact that within 250–320° dehydration of cellulose carbamate takes place if the latter is heated in air.

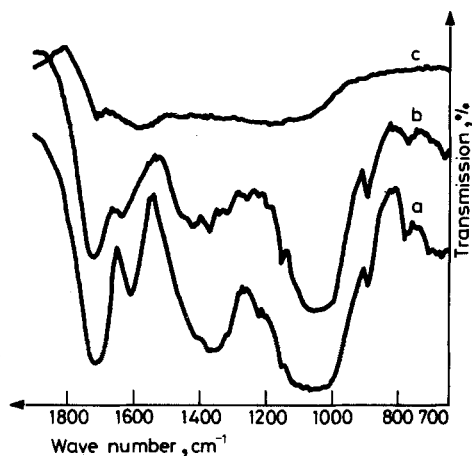


Fig. 2 IR spectra of cellulose carbamate (a), cellulose carbamate heated to 250 °C (b) and cellulose carbamate heated to 320 °C (c)

In order to obtain further thermal characteristics of cellulose carbamate, the TG and DTG examinations were also carried out in nitrogen atmosphere. The DTG data obtained and given in Fig. 3 show that as the nitrogen content increases the maximum of decomposition rate of cellulose carbamate shifts towards lower temperatures (curves 2–5) as compared with the temperature of maximum decomposition rate of cellulose (curve 1). Also, the peak height at the maximum

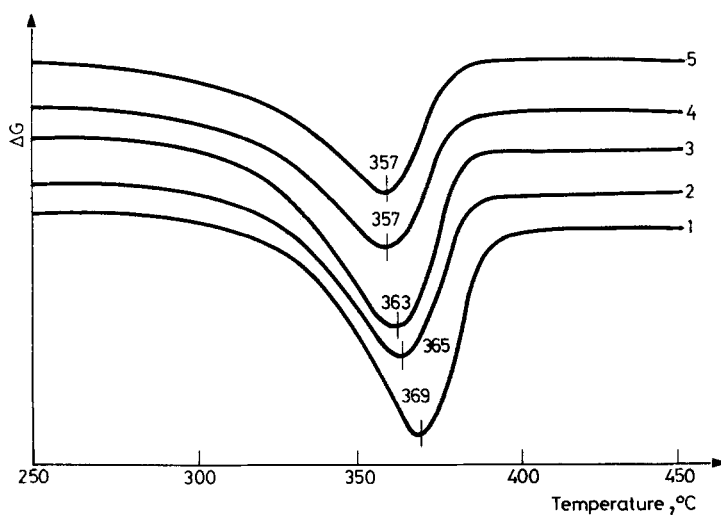


Fig. 3 DTG curves of cellulose (curve 1) and cellulose carbamate (curves 2–5) with various nitrogen content (see Table 2)

decomposition rate of cellulose carbamate, expressed as ΔG , decreases with increasing nitrogen content in the samples (Table 2), which is particularly clearly seen when the decomposition rate is given in terms of the so called specific decomposition rate calculated per weight unit. The nitrogen content in the modified cellulose increases with carbamation time. Generally, the decomposition energy

Table 2 DTG data of cellulose carbamate

Sample	N ₂ content %	DTG peak temperature, °C	Sample mass, mg	ΔG of sample		Specific mass loss rate $\frac{\Delta G}{m}$	Carbamina- tion time, h
2	1.00	365	4.60	66	14.34	1	
3	2.17	363	5.50	73	13.27	2	
4	5.85	357	4.87	54	11.09	3	
5	7.02	357	4.92	50	10.16	5	

of cellulose carbamate decreases with increasing nitrogen content and is considerably lower than that of unmodified cellulose. The removal of lye from cellulose after mercerization and before the urea treatment brings about a great water consumption and an increased number of laboratory operations. Therefore, it was decided to examine whether the preparation of cellulose carbamate is possible under conditions where urea is introduced into the mercerized cellulose neutralized with sulphuric acid, i.e. containing sodium sulphate. A cellulose batch containing 100% by wt. of urea was heated at 160° in air and samples of the modified product were taken at 1 h intervals. It was found that the nitrogen content in the product increased with increasing time of heating of cellulose with urea (Table 3). At the

Table 3 DTG data of cellulose carbamate synthesised from cellulose containing sodium sulphate

Heating time, h	N ₂ content, %	Polymeri- zation degree	DTG peak temperature, °C		ΔG of sample		Mass of sample, mg	Specific mass loss, $\frac{\Delta G}{m}$
			Peak I	Peak II	Peak I	Peak II		
			1	0.34	659	364.5		
2	0.79	632	364.0	—	94	—	5.83	16.12
3	2.56	565	363.0	—	104	—	7.03	14.79
4	3.93	473	358.5	310.3	70	30	6.83	10.68
5	4.74	405	357.0	313.0	59	30	6.13	9.62

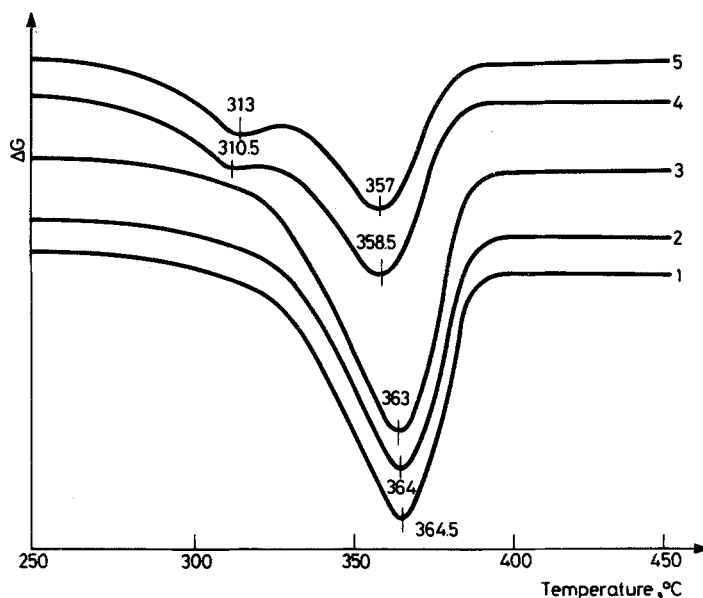


Fig. 4 DTG curves of cellulose carbamate with various nitrogen content (see Table 3)

same time the degree of polymerization of the-modified cellulose decreased. Thermal studies showed (Fig. 4) that the decomposition rate of cellulose carbamate containing less than 3.93% of nitrogen is characterized by the same relationship as in the case of carbamate prepared without sodium sulphate present in the cellulose. On the other hand, samples of carbamate containing 3.93% N_2 and 4.74% N_2 reveal differences shown by the TG curves which contain an additional peak with maximum of decomposition rate at 310.5 and 313.0°, respectively. This would suggest two different processes of thermal decomposition in these samples. One may assume that the first peak with the maximum decomposition rate at 357.0° and 358.5° (curves 4 and 5) (Fig. 4) corresponds to the hydration of cellulose carbamate and partly to deamination, but the second peak, with the maximum decomposition rate at 310.5° (curve 4) and 313.0° (curve 5), corresponds probably to the decomposition of carbamate with simultaneous cross-linking. To obtain more detailed information on the thermal properties of cellulose carbamate prepared under various conditions, a product obtained in a strongly alkaline system was also examined. In this case, solid urea was added to alkalicellulose with the degree of lye pressing off being 2.6. Having been thoroughly mixed, alkalicellulose and urea were heated to 160° (Table 4). It was found, in this case, that the time of treatment with urea considerably affected the nitrogen content in the cellulose carbamate obtained. In addition, a significant decrease in the polymerization degree of cellulose was

Table 4 DTG data of cellulose carbamate synthesised in strongly alkaline medium

Heating time, h	N ₂ content, %	Polymerization degree	DTG peak temperature, °C	Mass of sample, mg	ΔG of sample	Specific mass loss rate, $\frac{\Delta G}{m}$
1	0.49	266	362.0	5.43	64	11.77
2	0.75	168	359.0	6.39	68	10.64
3	2.80	129	357.0	5.95	59	9.95
4	7.34	126	358.0	5.08	51	10.04
5	8.12	120	355.0	5.73	58	10.12

observed, namely—after heating for 5 the polymerization degree was 120 while its value for the initial cellulose was 680. The samples of this carbamate were readily soluble in dilute NaOH solution but produced solutions with a low viscosity. Thermogravimetric curves for these carbamate samples (Fig. 5) were characterized by a single peak only with the maximum decomposition rate being within the range 355–362° independently of the nitrogen content of the sample. The increase in the nitrogen content in carbamate brings about only a shift of the maximum decomposition rate towards lower temperatures.

It can be concluded from the thermogravimetric examinations that cellulose carbamate is decomposed at a lower temperature than the cellulose. In addition, the maximum decomposition rate is affected by the nitrogen content. The increase in

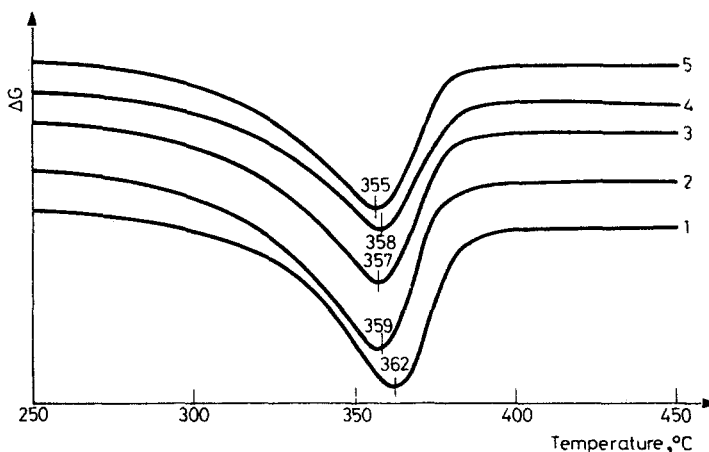


Fig. 5 DTG curves of cellulose carbamate synthesised in a strong alkaline medium with various nitrogen content (see Table 4)

the nitrogen content brings about a shift of the maximum decomposition rate towards lower temperatures. Cellulose carbamate heated to 320° is readily dehydrated and cross-linked, which results in the formation of aromatic structure.

References

- 1 C. E. Reddmann, F. C. Riesenfeld and F. S. Ia Viola, *Ind. Eng. Chem.*, 50 (1958) 633.
- 2 L. Segal and F. V. Eggerton, *Text. Res. J.*, 31 (1961) 460.
- 3 Y. Hozawa and F. Higashide, *J. Appl. Polym. Sci.*, 26 (1981) 2103.
- 4 A. Hebeish, A. Waly, N. Y. Abou-Zied and E. A. El-Alfy, *Text. Res. J.*, 43 (1978) 468.
- 5 B. Łaszkiwicz and B. Domasik, *J. Appl. Polym. Symp.*, in press.
- 6 K. Ekman, V. Eklund, J. Fors, J. I. Huttunen, J. F. Selin and O. T. Turunen, *Carbamate Cellulose*, Chapter 7 in *Cellulose: Structure, Modification and Hydrolysis*, Eds R. A. Young, R. M. Rowel by J. Wiley and Sons, Inc., New York 1986.
- 7 B. Łaszkiwicz and B. Domasik, *Polish Chem. Soc. Symp.*, Łódź 1988.
- 8 B. Łaszkiwicz and P. Wcisło, *Third Chemical Congress of North America*, Toronto 1988, Canada.

Zusammenfassung — Es werden die thermischen Eigenschaften von Zellulosekarbamat mit unterschiedlichem Stickstoffgehalt beschrieben. Die Thermoanalyse wurde in Luft- und in Stickstoffatmosphäre durchgeführt. Der Anstieg des Stickstoffgehaltes in Zellulosekarbamaten bringt eine Verschiebung der maximalen Zersetzungsgeschwindigkeit in Richtung niedrigerer Temperaturen mit sich. Erhitzt man Zellulosekarbamat bei 320 °C, wird es leicht dehydratiert und querverkettet, es bildet sich letztendlich eine aromatische Struktur.

Резюме — Обсуждены термические свойства карбамат-целлюлозы с различным содержанием азота. Термический анализ был проведен в атмосфере воздуха и азота. Увеличение содержания азота в карбамат-целлюлозе вызывает только незначительный сдвиг максимума разложения в сторону более низких температур. Сделано заключение, что нагретая при 320 °C карбамат-целлюлоза легко дегидратируется и происходит сшивание звеньев, что приводит к образованию ароматической структуры.