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Functionalisation of cellulosic substrates by a facile solventless method of introducing carbamate groups

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ABSTRACT

A facile method for the introduction of carbamate groups in cellulosic substrates is described. Woven cellulosic fabrics were padded with non-alkali treatment solutions containing PEG 2000, urea, and LiCl and heated at elevated temperatures to obtain cellulose carbamate fabrics. The introduction of carbamate groups was confirmed with FTIR-ATR and NMR spectroscopy, and the treated fabrics exhibited nitrogen contents of 0.10–2.04% (DS 0.01–0.25). There was a reduction in the viscosity-average degree of polymerization (DP_v) of treated fabrics. However, the treatments did not significantly reduce mechanical properties (tensile strength, elongation at break and work of rupture) or thermal stability. The products were soluble in alkali solutions, but stable during storage at ambient conditions. Compared to the known carbamate processes reported in literature which can be applied only on wood pulp at the first state of fibre manufacture the advantages of this process are that not only this method can be employed on various cellulosic substrates at the latest state of the production but also the processing time can be reduced from hours to minutes. Moreover, the process is environmental friendly because it is a solventless procedure and employed less and non-toxic chemicals.

Symbols

η	Intrinsic viscosity (ml/g)
η_{rel}	Relative viscosity
N	Nitrogen content (%)

Abbreviations

RH	Relative Humidity (%)
PEG 2000	Polyethylene Glycol 2000
FeTNa	Ferric sodium tartrate
DP_v	Viscosity-average degree of polymerisation, determined by viscosity measurement of cellulose solution in FeTNa solvent
TGA	Thermogravimetric Analysis
DS	Degree of Substitution
FTIR–ATR	Fourier Transform Infrared Spectroscopy–Attenuated Total Reflectance
NMR	Nuclear Magnetic Resonance
AGU	Anhydroglucose Unit

1. Introduction

Cellulose is a natural linear polysaccharide, the most abundant renewable biopolymer with outstanding properties and a variety of useful applications (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998a). However, the disadvantages for processing of cellulose are that cellulose is not meltable and not soluble in common solvents. Its high crystallinity, strong inter- and intra-hydrogen bonding hinder the processability of cellulose (Bredereck & Hermanutz, 2005). To overcome these disadvantages, cellulose is modified by derivatisation so that it can be processed in common industrial processes, which greatly expands the applications of cellulosic materials (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998c).

Man-made cellulosics were developed about 100 years ago and have significantly influenced the modern world. The production of regenerated cellulosic materials is based mainly on the viscose process, where cellulose, mixed with CS_2, is dissolved in alkali and regenerated in acidic baths. The process is accompanied by the production of hazardous by-products including CS_2, H_2S and heavy metals (Bridgeford, 1991; Urbanowski, 1996). One alternative to the viscose process is the so-called carbamate process, where cellulose is heated at elevated temperatures with ammonia derivatives, such as urea, to form the alkali-soluble cellulose carbamate. The carbamate process is believed not to have significant environmental impact (Bridgeford, 1991). The first technical-scale process for

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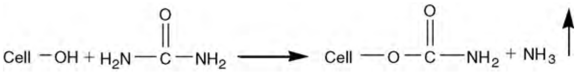


Scheme 1. Reaction of urea with cellulose (Segal & Eggerton, 1961).

the manufacture of regenerated cellulosic fibres with the carbamate process was established in the 1980s (Ekman et al., 1986). Since that time the carbamate process is still under extensive development and may play an important role in the future of regenerated cellulosics (Kotek, 2007).

Cellulose carbamate is an ester of cellulose and carbamic acid, conventionally prepared from the reaction of cellulose and urea which has been studied by Segal and co-worker (Scheme 1) (Segal & Eggerton, 1961). It is easily soluble in aqueous alkali solutions and conventional organic solvents (Ebeling & Fink, 2009). By dissolving carbamate the resulting solutions were spinnable in diluted acid or alkali solutions to yield fibres of cellulose carbamate or regenerated cellulose or the mixture of two. Therefore, the carbamate process does not require any use of special organic solvents and avoids many environmental problems (Huttunen, Turunen, Mandel, Eklund, & Ekman, 1982). The substance becomes an interesting alternative to petroleum-based polymers and can be processed to form fibres, foils, sponges, membranes and other products.

Beside using in a nonviscose rayon process, the carbamate was also employed in a variety uses such as in hygiene, healthcare and medical applications due to its pronounced microbiostatic properties (Zikeli & Endl, 2005; Laxen & Hassi, 2007), in absorbent nonwoven products thank to its high water absorbency (Schmidtbauer, 1998; Einzmann, Schmidtbauer, Schachtner, & Jary, 2005) and in the products for adsorption of heavy metals from the media containing heavy metals (Zikeli & Endl, 2005).

Cellulose carbamate can be formed by various synthesis routes. In conventional processes, cellulose carbamate was produced by reaction with urea in alkali medium and organic solvents such as xylene, toluene (Keunecke, 1998; Mamait & Eli, 2006; Fink, Pinnow, Fanter, & Kunze, 2008) with or without the presence of a catalyst (Struszczyk et al., 1997; Tsukamoto, Hiiro, & Fujii, 2008). The processes required long reaction time and high temperature. An alternative method to produce cellulose carbamate is that cellulose is treated with urea in a liquid ammonia solution (Huttunen et al., 1982; Wolf, 2001; Kaempf, Wolf, Seelig, 2003). In this case, ammonia brings the structural changes in cellulose and facilitates its reaction with urea. Because of the rigorous conditions and the consumption of the high amount of chemicals, the mentioned methods have limitations for technical application. Recently, several new methods for synthesising of cellulose carbamate including heating with microwave (Guo, Zhou, Song, & Zhang, 2009; Loth, 2002; Zhou et al., 2009), supercritical carbon dioxide ($scCO_2$) assisted impregnation (Yin, Xu, & Shen, 2006; Yin et al., 2007; Yin & Shen, 2007) and electron radiation (Iller, Mikolajczyk, Stupinska, & Starostka, 2003, Iller, Stupinska, & Starostka, 2007) were reported. The researchers have attempted to limit or eliminate the disadvantages of the cellulose treatment with alkali or ammonia solutions, reduce the chemical consumption and the prolonged reaction time for the whole processes.

Table 1
Concentration of each components (wt%) in the solution used for treatment.

Solution	PEG 2000	Urea	LiCl
1	20	50	30
2	30	50	20
3	20	60	20

In this paper, we describe a new approach of cellulose carbamate producing in very fast, reproducible, and controllable way. This provides a promising environmentally friendly route of cellulose carbamate preparation from different raw materials.

2. Experimental

2.1. Materials

Prior to use viscose fabrics (1,3 dtex, plain woven, 32 warps and 28 fills per cm and 150 g/m^2, Lenzing AG, Austria) were conditioned for 24 h in a standard atmosphere at 20 ± 2 °C and 65 ± 2% relative humidity (RH). Urea (99.7%), polyethylene glycol 2000 (PEG 2000) and lithium chloride (99%) were supplied by Roth (Austria) and used as received without further purification. Deionised water was used in all experiments.

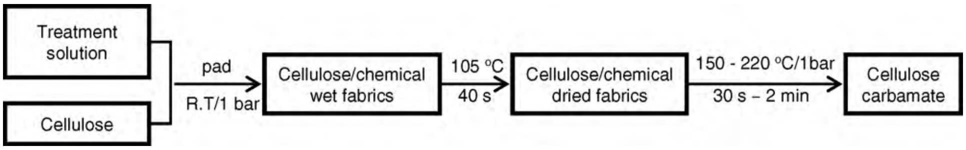
2.2. Preparation of treatment solutions

Treatment solutions were prepared with the concentrations according to Table 1. Chemicals were mixed together into a beaker at ambient temperature. The mixture was heated up to 100–110 °C and stirred with a magnetic stirrer until it was completely melted. An appropriate amount of deionised water was added into another beaker and warmed up to 60 °C. The melt was then poured slowly and carefully into warm water at approximately 60 °C under continuous stirring. The melt-to-water ratio was 2:1 (w/w). The prepared solutions were stable upon storage in a bottle at ambient temperature.

2.3. Preparation of cellulose carbamate

Scheme 2 illustrates the route of cellulose carbamate fabrics preparation. Conditioned viscose fabrics were padded through a padder containing the treatment solutions of PEG 2000, urea and LiCl (Table 1). Padding was carried out at room temperature under the pressure of 1 bar, and at 1 m/min speed of the rollers. The padded fabrics containing about 26–33 wt% of urea were then dried inside a stenter at 105 °C for 40 s. After drying, the fabrics were further cured in a hot-press instrument (Kannegiesser HKZ, Kannegiesser GmbH & Co., Germany) under the pressure of 1 bar and at various controlled temperatures (150–190–220 °C) and times (30 s to 2 min). The reaction occurred inside the hot-press accompanied by NH_3 liberation.

The reaction products were then washed thoroughly with tap water to remove water-soluble contents until the washing liquor were colourless and line-dried in open air. The white to brownish cellulose carbamate fabrics were obtained by changing the reaction time, and temperature. All experiments were done in two repetitions.



Scheme 2. The treatment procedure to form cellulose carbamate.

2.4. Characterisation

The intrinsic viscosity of cellulose and cellulose carbamate was determined at 20 ± 1 °C in ferric sodium tartarate (FeTNa) solvent (0.3 M $FeCl_3 \cdot 6H_2O$, 0.98 M Tartaric acid, and 5.36 M NaOH) prepared in the laboratory, using an Ubbelohde viscometer and calculated by equation (DIN 54270):

$$\eta = \frac{(\eta_{\text{rel}} - 1)/c}{1 + k \times (\eta_{\text{rel}} - 1)} \tag{1}$$

where η (ml/g) is the intrinsic viscosity, c (g/ml) is the concentration of cellulose and cellulose carbamate in the solution, $k = 0.339$ and η_{rel} is relative viscosity calculated according to the equation below:

$$\eta_{\text{rel}} = \frac{t}{t_o} \tag{2}$$

where t and t_o (s) are the efflux time of the solution and solvent, respectively. The viscosity-average degree of polymerization (DP_v) was calculated from the intrinsic viscosity η by the following equation (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998b).

$$\eta = 4.85 \times DP_v^{0.61} \tag{3}$$

The nitrogen content of cellulose carbamate was determined using DUMAS method with a nitrogen analyzer (Rapid N III, Elementar Analysensystem GmbH, Germany). The values of nitrogen content were used to calculate degree of substitution (DS) of hydroxyl groups on cellulose by carbamate groups following the equation:

$$DS = \frac{162 \times N}{14 \times 100 - 43 \times N} \tag{4}$$

where N (%) is the nitrogen content of modified cellulose determined by elemental analysis, 162 is the molecular weight of the anhydroglucose unit (AGU), 14 is the molecular mass of nitrogen atom and 43 is the net increment in the AGU for every substituted carbamate group.

FTIR–ATR experiments were performed using a Brucker Vector 22 spectrometer (Brucker Analytik GmbH, Germany) with ATR diamond crystal, 4 cm^{-1} resolution and collecting 32 scans. The spectra manipulations were carried out with baseline correction and min-max normalisation. The liquid ^{13}C NMR spectra of cellulose carbamate were recorded on a spectroscopy Brucker Avance 400 (carried out at University of Jena, Germany). The sample concentration was ca. 5 wt% in DMSO-d_6 with LiCl solution. The sample solution was stirred for ca. 4 h at 60 °C and the spectrum was acquired at 70 °C, collecting 62,725 scans.

Mechanical properties including tensile strength, elongation at break and work of rupture of untreated cellulose and cellulose carbamate samples were measured using a Zwick/Roell Z010 instrument (Zwick Roell, Germany) following DIN EN ISO 13934-1 standard. The specimens were the raveled strips with 50 mm width. The gauge length was 150 mm, the rate of extension was 100 mm/min and 2 N pre-load was applied. Thermogravimetric analysis (TGA) was conducted in a thermal analysis instrument (STA PT 1600, Linseis, Germany) with alumina crucibles in a heating range from 40 to 500 °C, under air atmosphere and the heating rate was 20 °C/min.

All of the samples were conditioned for 24 h in the standard atmosphere at 20 ± 2 °C and 65 ± 2% RH prior to tests. The viscose fabrics treated with H_2O were used as the control samples.

3. Results and discussion

3.1. Synthesis of cellulose carbamate

The effects of temperature, time and concentration of the individual components in the treatment solutions on nitrogen content and degree of substitution of modified cellulose were investigated. The nitrogen content of the cellulose carbamate samples increased from 0.10 to 2.04% corresponding to relative low DS from 0.01 to 0.25 as the reaction time increased from 30 s to 2 min and the temperature raised from 150 to 220 °C as illustrated in Fig. 1 and Table 2. When the treatment time increased from 30 s to 2 min, at 150 °C nitrogen content changed slightly from 0.10 to 0.23%, compared to that at 190 and 220 °C nitrogen content increases considerably from 0.45 to 1.17% and from 1.19 to 2.04%, respectively. Therefore, the temperature has a significant influence on the carbamate process and temperature above 190 °C is favouring the esterification of cellulose. It may be explained by the fact that at the lower temperature

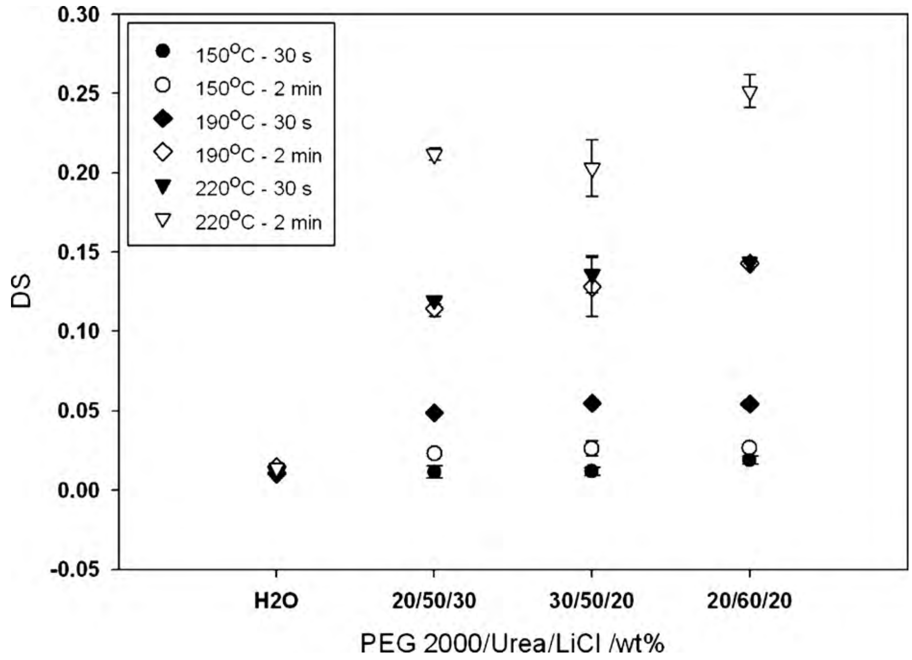


Fig. 1. Degree of substitution (DS) of modified cellulose as a function of curing temperature and time as well as the components in the treatment solutions.

Table 2
Nitrogen content, degree of polymerization and mechanical properties of fabrics treated under different conditions.

PEG/urea/LiCl (wt%)	DP_v	Nitrogen content (wt%)	Breaking force (N)	Break elongation (%)	Work of rupture (N.m)
150 °C, 30 s					
Water	383 ± (74)[a]	0.10 ± 0.01	565 ± 6	33.4 ± 0.6	9.36 ± 0.11
20/50/30	412 ± 10	0.10 ± 0.03	521 ± 1	27.8 ± 0.6	7.46 ± 0.12
30/50/20	386 ± 36	0.10 ± 0.02	550 ± 20	29.5 ± 1.0	8.38 ± 0.61
20/60/20	361 ± 23	0.16 ± 0.02	561 ± 12	31.9 ± 1.3	8.95 ± 0.43
150 °C, 2 min					
Water	322 ± 10	0.10 ± 0.00	529 ± 31	32.9 ± 1.3	8.50 ± 0.59
20/50/30	335 ± 39	0.20 ± 0.02	559 ± 6	32.2 ± 0.0	8.98 ± 0.07
30/50/20	367 ± 55	0.23 ± 0.04	528 ± 49	32.5 ± 0.8	8.36 ± 1.33
20/60/20	357 ± 55	0.23 ± 0.01	558 ± 1	34.2 ± 0.9	9.00 ± 0.09
190 °C, 30 s					
Water	412 ± 13	0.09 ± 0.02	527 ± 51	33.0 ± 2.0	8.41 ± 1.34
20/50/30	394 ± 11	0.42 ± 0.00	547 ± 7	31.9 ± 1.0	8.69 ± 0.37
30/50/20	385 ± 21	0.47 ± 0.00	547 ± 4	32.0 ± 0.0	8.70 ± 0.12
20/60/20	332 ± 1	0.46 ± 0.00	566 ± 13	31.0 ± 0.3	9.04 ± 0.12
190 °C, 2 min					
Water	398 ± 7	0.13 ± 0.01	518 ± 16	31.4 ± 0.0	8.07 ± 0.38
20/50/30	327 ± 64	0.96 ± 0.04	571 ± 7	35.3 ± 0.1	9.45 ± 0.01
30/50/20	314 ± 9	1.07 ± 0.15	552 ± 37	34.7 ± 0.7	8.96 ± 0.85
20/60/20	350 ± 3	1.19 ± 0.01	524 ± 9	33.8 ± 0.0	8.18 ± 0.20
220 °C, 30 s					
Water	361 ± 45	0.11 ± 0.01	560 ± 26	33.8 ± 0.9	9.26 ± 0.70
20/50/30	330 ± 48	1.00 ± 0.02	552 ± 8	32.9 ± 1.3	8.95 ± 0.04
30/50/20	354 ± 8	1.13 ± 0.09	552 ± 17	33.4 ± 0.3	8.89 ± 0.37
20/60/20	353 ± 30	1.20 ± 0.01	550 ± 7	31.2 ± 0.3	8.74 ± 0.14
220 °C, 2 min					
Water	316 ± 17	0.12 ± 0.01	546 ± 7	32.4 ± 0.3	8.70 ± 0.18
20/50/30	266 ± 10	1.73 ± 0.03	514 ± 6	31.9 ± 0.4	7.76 ± 0.22
30/50/20	278 ± 1	1.67 ± 0.14	538 ± 13	32.5 ± 0.4	8.25 ± 0.37
20/60/20	257 ± 9	2.04 ± 0.08	521 ± 13	31.1 ± 1.6	7.76 ± 0.39

[a] Standard deviation.

no reaction occurred or the reaction took place only on the surface of the cellulose fabrics. In addition, the cellulose carbamate reaction (Scheme 1) was affected by curing time. The longer the treatment time was, the higher the nitrogen content was achieved. The longer time of heat transfer from surface to internal phase of cellulose fabrics, the more urea can react with cellulose and improve degree of substitution.

However, higher temperature and prolonged reaction time may result in the pyrolysis of cellulose, cellulose carbamate and render the aromatic formation from urea as well as the creation of the other by-products. Fig. 2 shows the fragmentation of viscose fibres when applied temperature was higher than 245 °C.

Treated viscose fabrics with nitrogen content of 2.04% can be dissolved in aqueous NaOH solution at ambient temperature within 10 min to obtain ca. 2 wt% cellulose solution. Fig. 3 shows the cellulose carbamate fabrics in alkali solutions with various concentrations. It reveals that the carbamate functional groups are uniformly distributed on the modified cellulose. The substitution of the hydroxyl groups in urea treated cellulose reduces the density of hydrogen bonds and as a result, the obtained cellulose carbamates display good solubility in aqueous alkali solution even at ambient temperature (Nada & El-sakkhawy, 2000).

However, the concentration of urea in the treatment solution did not affect substantially the formation of cellulose carbamate. In this context we suggested that LiCl is used as a swelling agent (Heinze & Koschella, 2005) and PEG 2000 acts as a co-solvent for urea or a softening agent. The swelling and softening agents can improve the accessibility, the penetration into the highly ordered regions and also split bonds between cellulose chains, disrupting its supramolecular structure (Fidale, Ruiz, Heinze, & Seoud, 2008). These effects probably accompanied the increase in the number of active sites in cellulose and provided the possibility for agents to react with cellulose. As a result, the penetration and diffusion of urea into cellulose matrices were facilitated and the reaction

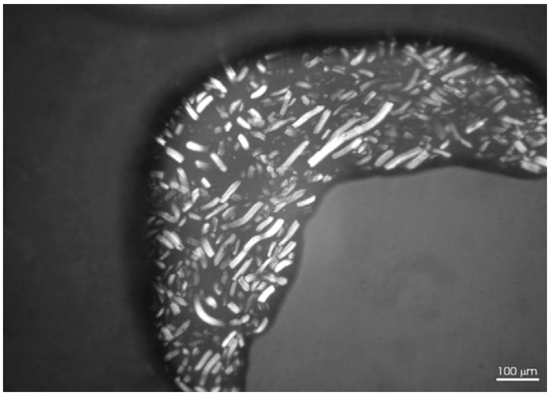


Fig. 2. Microscopy image of viscose fibres after heating up to 250 °C with the mixture of PEG 2000/Urea/LiCl.

Fig. 3. Cellulose carbamate fabrics (ca. 0.5 g) in aqueous sodium hydroxide solutions (ca. 50 ml) with various concentrations (6) 0.5 M, (7) 1.5 M, (8) 2.5 M, (9) 3.5 M and (10) 5.0 M.

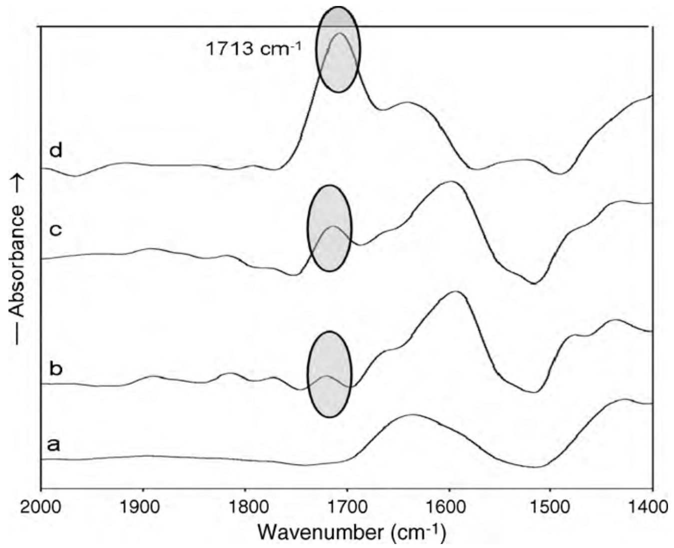


Fig. 4. Infrared spectra of (a) cellulose and cellulose carbamates with various nitrogen content: (b) N = 0.16%, (c) N = 0.46% and (d) N = 1.20%.

occurred immediately when elevated temperature applied, even if cellulose was not activated with alkali solution before treatment. These effects also enhanced the reaction rate and reduced time required for the esterification.

The determination of DP_v of partially functionalised cellulose or low DS cellulose carbamate was performed by conventional techniques, assuming that the splitting-off of the substitutents would not cause any major chain degradation (Klemm et al., 1998b). DP_v of cellulose and cellulose carbamate in FeTNa solvent provides the important information that the treated fabrics do not undergo significant degradation at the temperature lower than 220 °C under the treatment conditions applied. At the temperature as high as 220 °C simultaneous drop in DP_v of cellulose was observed. DP_v changes from ca. 400 for untreated cellulose to 260 for cellulose derivatives as shown in Table 2.

3.2. FTIR–ATR and NMR spectroscopy

The samples obtained were confirmed as cellulose carbamate by FTIR–ATR and liquid-state ^{13}C NMR spectroscopy. Fig. 4 shows the FTIR–ATR spectra of the untreated and treated cellulose fabrics with various nitrogen contents in the 2000–1400 cm^{-1} region. In comparison with the spectrum obtained from the untreated cellulose, it can be seen that the treated ones have an obvious new absorption peak at 1713 cm^{-1} which was assigned to the stretching vibration of the carbonyl (C═O) in the base of urethane (Segal & Eggerton, 1961). The intensity of the absorption band at 1713 cm^{-1} gradually increases with an increase of nitrogen content of cellulose carbamates. Furthermore, the broad adsorption of unsubstituted cellulose at 1648 cm^{-1} is caused by an O–H deformation vibration and this absorption was shifted to lower wavenumber band (1593 cm^{-1}) in the spectra obtained from cellulose carbamate. It is known that the absorption wavelength is influenced by neighbouring groups and which could be attributed to a carbonyl vibration (Mormann & Michel, 2002). This indicates that urea has reacted with cellulose to form cellulose carbamate.

Fig. 5 represents the ^{13}C NMR spectrum of cellulose carbamate with the nitrogen content of 2.04%. This provides additional information about the cellulose and its derivatives structures. The chemical shifts of carbon could be assigned to 102.8 ppm for C-1, 79.7 ppm for C-4, 73.0–75.6 ppm for C-2, C-3 and C-5, and 60.5 ppm for C-6, for the absorption of the glucose monomer from the original cellulose. Except these chemical shifts in untreated cellulose, the cellulose carbamate sample displayed a remarkable signal at 157.3 ppm typical of the carbonyl carbon of the carbamate function group. Moreover, there is a small peak at 63.3 ppm and the C-1 signal is not split. According to recent ^{13}C NMR findings, no functionisation occurred at C-2 and the reaction of hydroxy groups by carbamate groups took place at C-6 position of the AGU (Heinze, Koschella, Kull, Klohr, & Koch, 2000; Kotek, 2007). Additional experiments are required to prove this assumption. The NMR spectrum supported that the introduction of carbamate group into cellulose backbone was successful during the course of the reaction, which was in good agreement with FTIR–ATR results.

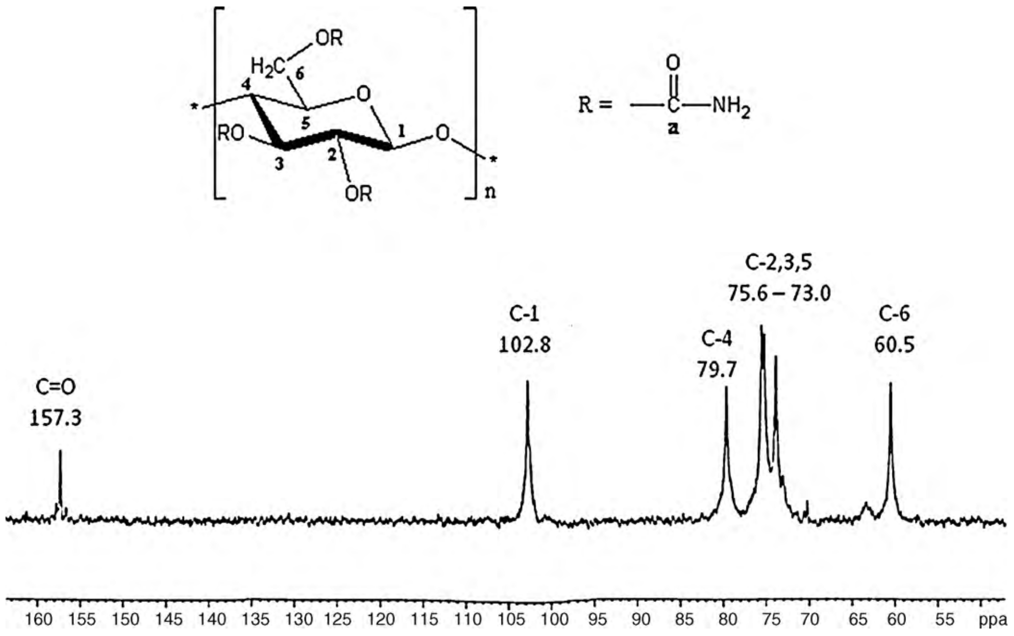


Fig. 5. ^{13}C NMR spectrum of cellulose carbamate in DMSO-d_6/LiCl at 70 °C (N = 2.04%, DS = 0.25).

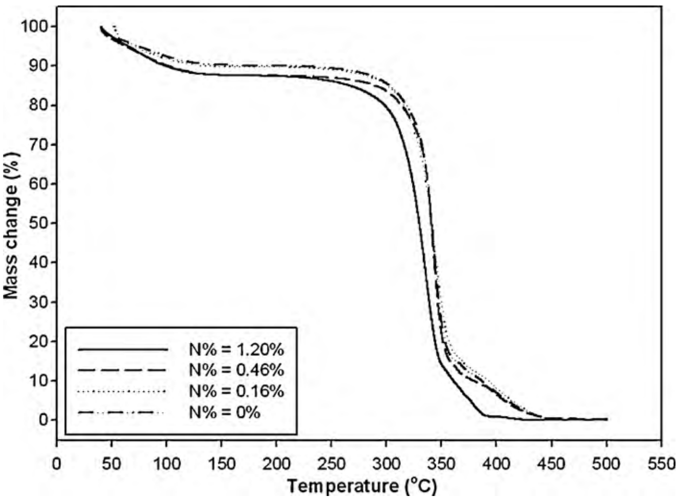


Fig. 6. Thermogravimetric diagrams of cellulose and cellulose carbamates with various nitrogen contents.

3.3. Thermal and mechanical properties

Thermogravimetric analysis was used to study the thermal behaviour of cellulose and its derivatives. TGA curves for untreated cellulose and cellulose carbamates with various nitrogen contents are shown in Fig. 6. After the initial loss of moisture and the desorption of gases at ca. 100–120 °C, a major decomposition for both cellulose and cellulose carbamate was observed in temperature range 338–378 °C. No distinct differences among untreated cellulose and low nitrogen content carbamates were noticed. However, the onset decomposition temperature of cellulose carbamate with higher nitrogen content was lower than that of untreated cellulose. This can be explained by the degradation of cellulose during the carbamation process and the increase in the amorphous or disorder regions in the cellulose chains which are decomposed by thermal treatment faster than the crystalline parts (Nada & El-sakkhawy, 2000). The thermal stability remains acceptable in spite of the elevated temperature during the course of esterification. On the other hand, the percentage of residual mass are 0% after the washed samples were heated up to 500 °C. It indicates that there is no LiCl or inorganic residue remaining inside the treated and washed fabrics.

Moreover, no significant changes after the treatment of cellulose even at high temperature in other physical properties such as tensile strength, elongation at break and work of rupture from cellulose and cellulose carbamate were observed (Table 2).

4. Conclusions

Conditions of chemical modification of viscose fabrics with urea at elevated temperature using the treatment solutions containing PEG 2000 as a softening agent and LiCl as a swelling agent were established. Cellulose carbamate was successfully synthesised on fabrics, which was confirmed by FTIR–ATR and ^{13}C NMR spectroscopy. The nitrogen content changed from 0.01 to 2.04% which corresponds to relative low DS in the range of 0.01–0.25. The nitrogen content can be varied by adjusting esterfication temperature and time. This method provides the advantages for reduction the consumption of chemicals and time for the cellulose esterification and to obtain homogenous treatment. We believe that it can be applied on various raw cellulosic materials such as fibres, yarn, or fabrics depending on the available equipment (Vo, Tatárová, Manian, Široká, & Bechtold, 2010).

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