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Biodegradability of cellulose fabric modified by imidazolidinone

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Abstract

The influence of modifying cellulose by imidazolidinone on its biodegradability was studied using the soil burial test and enzymatic hydrolysis. The degree of biodegradation was determined on the basis of scanning electron micrographs, tensile strength, degree of polymerization, polymer solubility measurements, and infrared spectroscopic analyses (FT-IR). The results show that the incorporation of 1,3-dimethyl-4,5-dihydroxyethylene urea into the structure of cellulose highly decreased the biodegradability of cellulose macromolecules. This was confirmed by the smaller morphological changes, lower decrease of breaking strength and lower polymer solubility determined for the modified cellulose. FT-IR spectra analysis also revealed that during the biodegradation period much greater structural damage was caused in the case of unmodified than of modified cellulose, and that the intensity of the bands at 1640 and 1548 belonging to the Amides I and II bonds resulting from the presence of protein produced by microbial growth.

Keywords: Cellulose; Modification; Easy-care finishing; Imidazolidinone; Biodegradation; Soil burial test; Breaking strength; Wettability; Scanning electron microscopy; FT-IR spectroscopy

1. Introduction

In chemical finishing of textiles, easy-care finishing of cellulose fibres is of great technological importance (Schindler & Hauser, 2004; Sharpe & Mallinson, 2003). In this process, an appropriate crosslinking agent, which is able to penetrate into the fibres and react with the hydroxyl groups of cellulose, is used to crosslink the cellulose macromolecules in the disordered amorphous regions. This reduces the swelling and the shrinkage of cellulose fibres, and improves their crease-recovery and crease-resistant properties.

Much research work has been focused on the study of the influence of easy-care and durable press finishing on textile properties in wear and care. In these studies, different mechanical, physical and chemical properties of fabrics, such as tensile strength, pilling, wet and dry crease recovery angles, rigidity, dimensional stability, fastness of dyed fabrics or yellowing of whites, are observed before and after treatment (Abidi, Hequet, Turner, & Sari-Sarraf, 2005; Jiang, Meng, & Qing, 2005; Katovic, Vukusic, & Grgac, 2005; Purwar & Joshi, 2005; Qiu & Yang, 2005; Schramm & Rinderer, 2006). But there is no information about the influence of the applied finish on the biodegradation of cellulose fibres.

The biodegradation of cellulose has been extensively studied over recent decades (Allen, Auer, & Pailthorpe, 1995; Desai & Pandey, 1971; Itävaara, Siika-aho, & Viikari, 1999; Montegut, Indicor, & Koestler, 1991; Park, Kang, & Im, 2004; Salerno-Kochan & Szostak-Kotowa, 2001). In these articles, it is well documented that cotton fibres, which are mainly composed of cellulose, are highly susceptible to microbial degradation. Microorganisms that cause the hydrolytic and oxidative degradation of cellulose are found among fungal and bacterial genera, which are present in air, water and soil. The most active fungi belong to the genera *Chaetomium* sp., *Fusarium* sp., *Myrothecium* sp., *Memnoniella* sp., *Stachybotrys* sp., *Verticillium* sp., *Alternaria* sp., *Trichoderma* sp., *Penicillium* sp. and *Aspergillus* sp.,

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whereas, the most active bacteria species are *Cytohaga* sp., *Cellulomonas* sp., *Cellvibrio* sp., *Bacillus* sp., *Clostridium* sp. and *Sporocytophaga* sp. (Szostak-Kotowa, 2004). Fungi and bacteria degrade cotton fabric in two different modes. Fungi attack fibres from the inside towards the outer layer of fibres, whereas the contamination of fibres starts at cracks on the surface of the fibres or at the cut-off ends of the fibres. Contrary to fungi, the degradation of cotton fibres by bacteria proceeds from the fibre surface towards the inner parts of the fibres. In the process of cellulose degradation bacteria are of lesser importance in comparison to fungi, due to their need for a higher percentage of moisture, which requires the fabric to be saturated throughout the whole process of degradation (Clarke, 1997).

Cellulose biodegradation results in depolymerization of cellulose macromolecules, which is reflected in decreased molecular weight and strength, increased solubility and changed crystallinity. Although biodegradable textile fibres are classed as environment-friendly material, the biodegradation process which occurs when the textile product is still in use could cause serious functional, aesthetic and hygienic problems because of textile deterioration, staining, discoloration and odour. These problems are of special importance when the preservation and conservation of historic textiles are considered.

The purpose of this study was to investigate the influence of easy-care finishing on the biodegradation of cellulose fibres. In this process cellulose fibres are chemically modified with a non-formaldehyde-containing finish based on imidazolidinone. The biodegradability of cellulose fibres was measured by the soil burial test and enzymatic hydrolysis. Structural changes after different periods of biodegradation were determined from electron microscopic and spectroscopic analyses, and tensile strength, degree of polymerisation, crystallinity and polymer solubility measurements.

2. Experimental

2.1. Materials

Plane-wave 100% cotton fabric with a mass of 162 g/m^2 was used in the experiments. In pre-treatment processes the fabric was bleached in an H_2O_2 bath, mercerised in NaOH solution and neutralised with diluted CH_3COOH solution.

The finish 1,3-dimethyl-4,5-dihydroxyethylene urea (DMeDHEU) was used for cellulose modification (CHT, Tübingen). It is a non-formaldehyde containing product based on imidazolidinone. The fabric was finished with 80 g/l DMeDHEU with the pad-dry-cure method, including full immersion at 20 °C, wet pick-up of 80% at 20 °C, drying at 100 °C and curing at 150 °C for 5 min. The cross-linking reaction of the finish with the cellulose hydroxyl groups was catalysed with 15 g/l hydrated magnesium chloride (Aldrich).

2.2. Methods

2.2.1. Thin-layer wicking measurements

The wettability of the finished and untreated cotton samples was determined with the use of thin-layer wicking method, which was proposed by Van Oss et al. (1992) and further elaborated by Chibowski and Gonzales-Caballero (1993). According to this method, the rate of the liquid penetration (wicking) into the porous solid can be described with the general form of Washburn equation for the horizontal capillary:

$$\frac{x^2}{t} = \frac{R}{2\eta}\Delta G \tag{1}$$

where x is the penetrated distance, R is the effective radius of porous solid, t is the penetration time of the distance x, η is the liquid viscosity and ΔG is the free energy change, accompanying the liquid penetration process. As it can be seen from Eq. (1) the liquid penetration rate, which is proportional to ΔG, represents a quantitative measure of the solid wettability.

In the wetting experiment, a dry cotton fabric sample was used as a porous solid and water as a wicking liquid. The fabric sample was placed in a horizontal position between two glass plates, which were in contact with a wicking liquid. An edge of the glass plate was equipped with a ruler, which enabled the determination of the water penetration distance at different penetration time. The measurements of the rate of water penetration through the fabric sample were carried out at 20 ± 1 °C. For every untreated and finished fabric sample at least 10 measurements were made. The average value of x^2/t was obtained graphically from the slope of the plot of t versus x^2.

2.2.2. Soil burial test

Determination of the resistance of finished and unfinished cotton fabrics to the action of soil microflora was carried out by the soil burial test, according to the ISO 11721-1:2001 and ISO 11721:2003 standards. In this standard process, the container was filled with commercial grade compost. The water content of the soil was 60 ± 5% of its maximum moisture retention capacity. It was held constant during the experiment by spraying with water. The pH of the soil was between 4.0 and 7.5. Cotton fabric samples were buried in the soil for periods of 3, 6, 9 and 12 days. After the defined incubation time, the samples were removed from the test soil, lightly rinsed with running tap water and immersed in 70% ethanol for 30 min before air drying.

2.2.3. Enzymatic hydrolysis

Finished and unfinished cotton samples 25 mg in weight were separately treated in 8 ml of acetate buffer, which contained 100 CU (cellulase units) of cellulase. The mixture was incubated at 44 °C for 24 h. After that time, the cotton sample was removed from the mixture, which was afterwards filtered through a micropore membrane (0.4 μm).

In the filtrate, the amount of total organic carbon (TOC) was measured.

2.2.4. Scanning electron microscopy (SEM)

A microscopic evaluation of morphological changes occurring during the biodegradation of finished and unfinished cotton samples after 6 and 12 days of fibre exposure to the soil microflora was carried out using a JEOL JSM 6060 LV scanning electron microscope, where samples were coated with a thin layer of gold before observation.

2.2.5. Colour measurements

The reflectance values of finished and unfinished cotton samples after different periods of burial time were measured at 5 different points on each sample with a Datacolor Spectraflash SF 600 Spectrophotometer using CIE D65 and the CIE 1964 10° observation. From the reflectance values the corresponding CIE $L^*a^*b^*$ coordinates were calculated at λ_{max} and the colour difference, ΔE^*, between two samples was calculated according to the equation (Berger-Schunn, 1994):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

where an unburied sample was chosen as the standard and the buried sample as the trial.

2.2.6. Breaking strength

Breaking strength was measured with an Instron 5567 dynamometer in accordance with SIST ISO 5081:1996. The relative reduction in breaking strength, q_{red}, of the buried cotton samples compared with the unburied ones was calculated from the mean value of the breaking strength of ten specimens, using the following relationship:

$$q_{red,t} = \frac{F_t}{F_{t0}} \quad (3)$$

where $q_{red,t}$ is the loss of breaking strength of the buried cotton sample after burial time t, F_t is the breaking strength of the buried cotton sample after burial time t, and F_{t0} is the breaking strength of the unburied cotton sample. Before testing, the samples were conditioned at 65 ± 2% relative humidity and 20 ± 1 °C for 24 h.

2.2.7. Degree of polymerisation (DP)

The DP of the cellulose samples dissolved in Cuoxam, a solution of cupric hydroxide in aqueous ammonia $[Cu(NH_3)_4](OH)_2$, was determined viscosimetrically using an Oswald shear dilution viscometer.

2.2.8. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra were obtained on a Brucker IFS 66/S spectrophotometer, equipped with an attenuated total reflection (ATR) cell (SpectraTech) with a Ge crystal ($n = 4.0$). The spectra were recorded over the range 4000–600 cm^{-1}, with a resolution of 4 cm^{-1} and averaged over 128 spectra. Before the measurement, the studied samples were dried for 5 h at 100 °C.

3. Results and discussion

The reaction modifying of cellulose fibres by DMeDHEU is shown in Fig. 1. According to the crosslinking mechanism, covalent bonds are formed between hydroxyl groups of DMeDHEU and cellulose molecules, in the condensation reaction in the curing stage of the finishing process (Schindler & Hauser, 2004). Since the finish molecules are small enough to enter the fibres, it was assumed that the crosslinking reaction occurs in amorphous regions of fibres. The formation of new intermolecular bonds which hold the macromolecular chains together results in a decrease in cellulose chain mobility. This restricts the amount of space between the molecules which control the entry of water. Therefore, cellulose fibres modified by DMeDHEU are less hydrophilic than untreated ones and do not swell as much on wetting. This is confirmed by the results of the wetting experiment presented in Fig. 2, from which it is clearly seen that the rate of water penetration into the finished cotton sample ($x^2/t = 0{,}15$ cm^2/s) is more than four times lower in comparison to that obtained for the untreated sample ($x^2/t = 0.64$ cm^2/s). The lower the rate of water penetration, the lower the sample wettability.

The influence of cellulose modification on its biodegradability was determined visually, by scanning electron microscopy, from the results for the loss of breaking strength, the degree of polymerisation, TOC and the crystallinity measurements, as well as on the basis of FT-IR spectroscopic analysis. These results show that the incorporation of DMeDHEU into the cellulose structure greatly decreases the biodegradability of the fibre. Inspection of

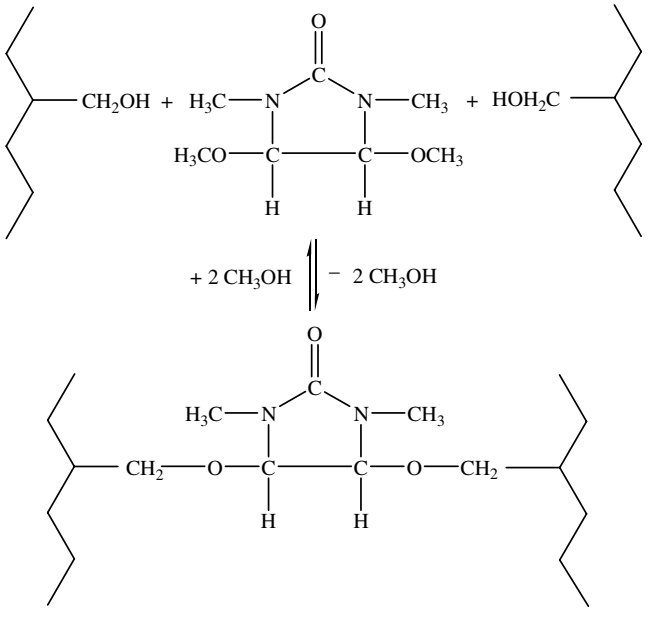

Fig. 1. Crosslinking of cellulose with DMeDHEU.

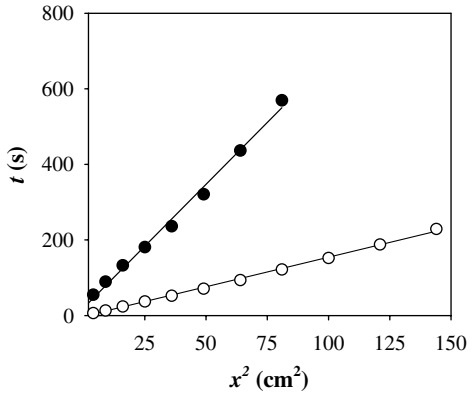

Fig. 2. Penetration rate of water into the cotton sample. Sample: -○-○- untreated, -●-●- finished with DMeDHEU. Slope of the plot: -○-○- 1.56, -●-●- 6.54.

samples removed from the test soil after different incubation times, showed that the progress of the rotting process, caused by microorganisms in the soil, is much more intensive for the untreated than for the finished sample. After 12 days of burial, the untreated sample was degraded to such an extent that it fell to pieces (Fig. 3). Since fibre rotting is accompanied by a colour change of the sample surface, the colour difference determined after different periods of burial can also represent a measure of sample biodegradability. Accordingly, the lower colour differences obtained for the finished samples proved that these samples degraded slower in comparison with the untreated ones (Fig. 4).

Furthermore, scanning electron micrographs (Fig. 5) revealed a great difference in morphological changes in the two buried cotton samples, due to the decomposition action of the soil microflora. It can be seen that the biodegradation process is much faster for the untreated than for the finished cellulose. In the initial stage of the experiment, the surface of both cotton fabrics was very smooth, whereas, the development of superficial cracks in the case of the untreated fibres could be observed after 6 days of soil burial. The intensity of this morphological damage increased with increasing soil burial time, where serious disintegration and defibrillation of the untreated fibres could be observed after 12 days of soil burial to such an extent that individual macrofibrils could be seen. In contrast to the untreated fibres, the surface of the DMeDHEU treated cotton fibres was mainly smooth even after 6 days exposure to soil microflora, whereas development of localized surface cracks in the direction of the fibre axis could be observed after 12 days of soil burial.

The breaking strength, which is an important mechanical property of a fabric, is directly influenced by the degree of sample degradation. In the case of untreated cotton samples, the breaking strength rapidly decreased with increasing time of burial (Fig. 6), and reached the value of 0.002 after 9 days of incubation. The results also show that the loss of breaking strength was directly related to the rupture of the $(1 \rightarrow 4)$ glycosidic bonds of cellulose macromolecules, resulting in a marked decrease of DP from 1923 for an unburied sample to 1551 for a sample buried 12 days (Fig. 6). In the case of finished samples, the reduction of breaking strength was lower than of the untreated ones, under the same conditions. Contrary to the untreated sample, the relationship between the breaking strength to the DP of the finished sample cannot be discussed, since this sample is not soluble in Cuoxam.

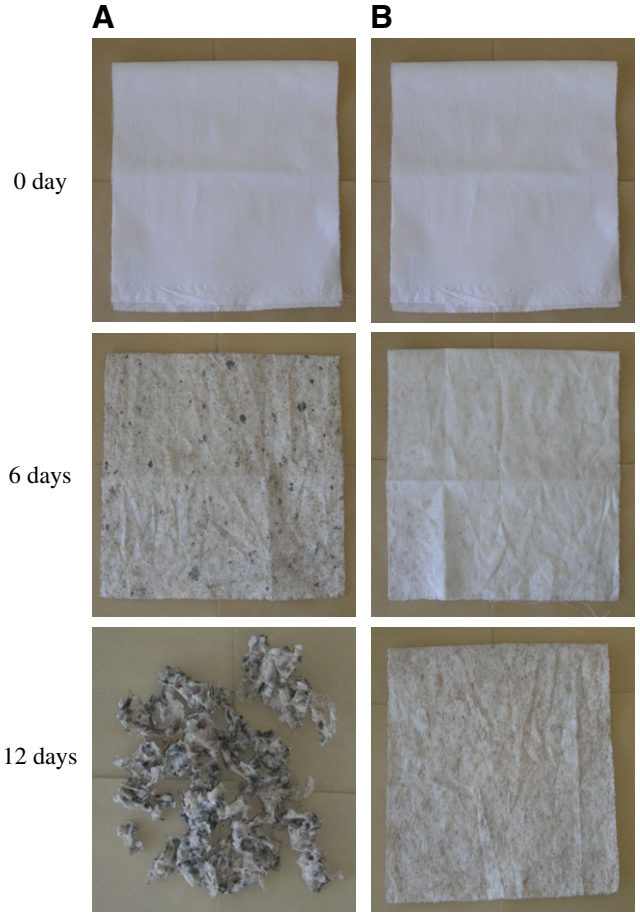

Fig. 3. Photos of unfinished (A) and finished (B) cotton samples after 0, 6 and 12 days of soil burial.

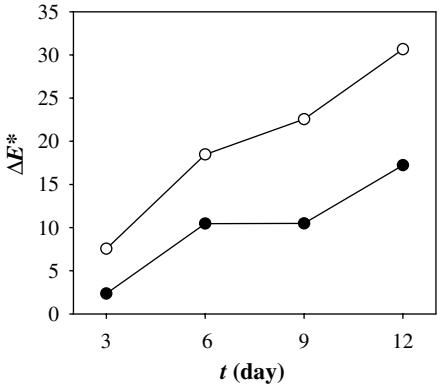

Fig. 4. Colour difference, ΔE^*, between unburied cotton sample and samples buried for different periods of time, t. Sample: -○-○- untreated, -●-●- finished with DMeDHEU.

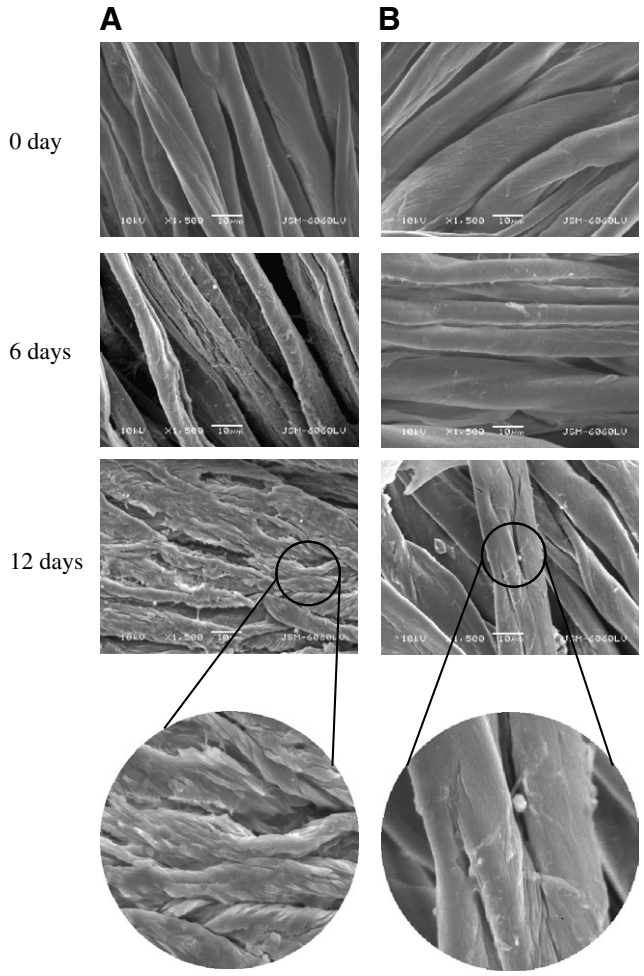

Fig. 5. Scanning electron micrographs of untreated (A) and finished (B) cotton samples after 0, 6 and 12 days of soil burial.

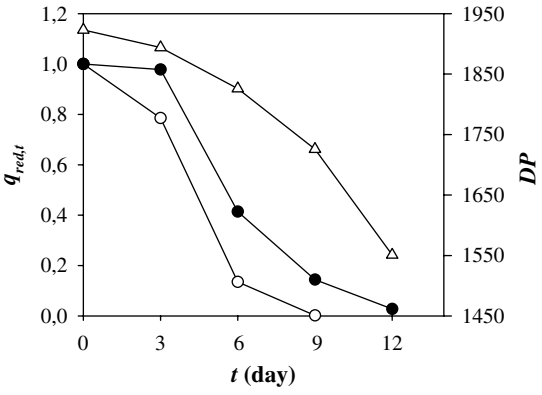

Fig. 6. Plots of the loss of breaking strength, $q_{red,t}$, and DP of cotton samples versus the burial time, t. $q_{red,t}$: -○-○- untreated sample, -●-●- sample finished with DMeDHEU. DP: -△-△- unfinished sample.

In Fig. 7, the results for enzymatic degradation of cotton samples are shown. In this process, the enzyme cellulase causes hydrolysis of the $(1 \rightarrow 4)$ glycosidic bonds of cellulose molecules, resulting in the formation of soluble oligosaccharides, which are quantified by the TOC value.

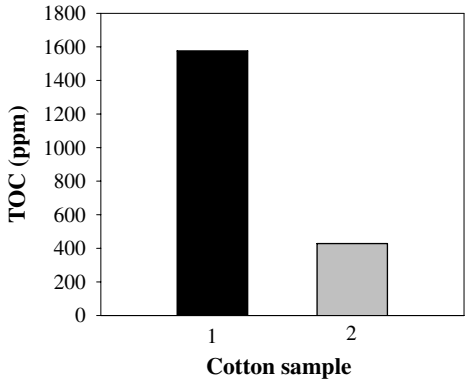

Fig. 7. TOC (total organic carbon) of water-soluble compounds produced by enzymatic hydrolysis of cotton samples for 24 h at 44 °C and pH 4.7. Sample: 1 – untreated, 2 – finished with DMeDHEU.

The higher TOC, the higher the concentration of oligosaccharide solution. The results of the measurements showed that for the untreated sample the TOC value was more than 3.5 times higher than for the finished one, indicating that the former is much more biodegradable by cellulase than the latter. These results could be explained by an increase in the regulation of arrangement of amorphous regions in the cellulose structure after incorporation of DMeDHEU molecules. The crosslinks between DMeDHEU and hydroxyl groups of cellulose molecules seem to prevent the enzyme from entering the amorphous regions and catalysing the biodegradation process.

Important information about the differences in the biodegradability of untreated and finished cellulose samples can be provided by the infrared spectral analysis. An inspection of the ATR spectra (Fig. 8) revealed that the incorporation of molecules of DMeDHEU into the cellulose structure caused important spectral changes in the 1800–1500 cm^{-1} region. For the finished cellulose, rather week but characteristic bands due to C=O and C–N stretching vibration of DMeDHEU appeared at 1760, 1700 and 1260 cm^{-1} (Socrates, 2001). Additional evidence of DMeDHEU incorporation into cellulose structure was obtained from inspection of C=O stretching band which blue shifted from 1680 to 1700 cm^{-1}. The reason for the band shift was attributed to the environmental change occurred when DMeDHEU reacted with cellulose macromolecules. To prove that the band shift of C=O was really caused by the DMeDHEU incorporation into the cellulose structure, the ATR spectrum of the DMeDHEU in *n*-butanol after the catalysed crosslinking was measured (Fig. 9). The broad absorption band at 1645 cm^{-1}, which is characteristic of the HOH bending vibrations of adsorbed water molecules (Hofstetter, Hinterstoisser, & Salmn, 2006; Kondo, 1997; Łojewska, Miśkowiec, Łojewski, & Proniewicz, 2005) and therefore very sensitive to the relative humidity (Fig. 10), occurred in the spectrum of untreated cellulose, whereas it was partly overlapped by the C=O stretching band at 1700 cm^{-1} in the case of finished cellulose. The frequencies of bands belonging to cellulose

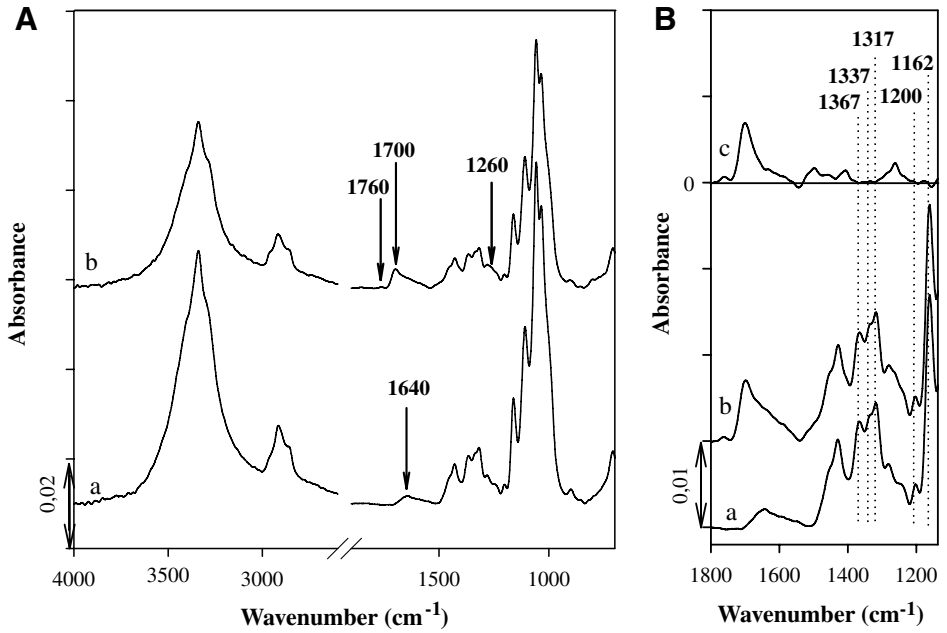

Fig. 8. Measured infrared ATR spectra (A) and spectra normalized to the integral absorbance of the CH band at 2917 cm^{-1} (B) of the untreated (a) and DMeDHEU finished cellulose fibres (b) and their difference (c).

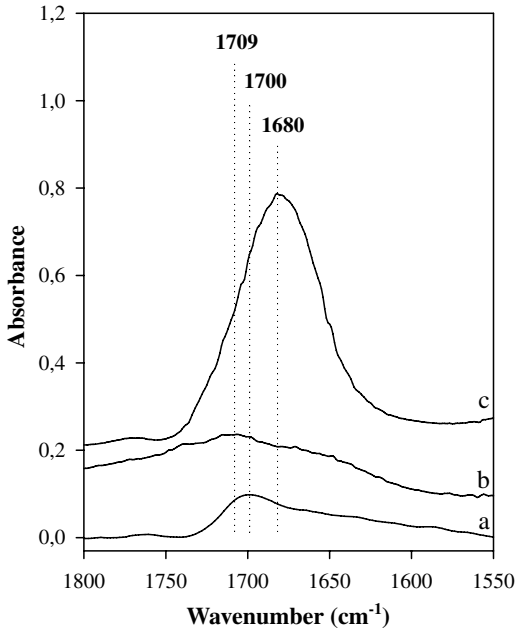

Fig. 9. Measured ATR spectra of cellulose treated with DMeDHEU (a), DMeDHEU crosslinked with *n*-butanol (b) and DMeDHEU film (c) in the region of 1800–1550 cm^{-1}.

macromolecules, which occur in the region 1500–800 cm^{-1} (Hulleman, van Hazendonk, & van Dam, 1994; Kačurá-ková & Wilson, 2001; Langkilde & Svantesson, 1995) remained unchanged after finishing.

When the spectra were normalized relative to the integral absorbance of the CH band (2917 cm^{-1}) (Fig. 8B), which was assumed to be insensitive to the introduction of DMeDHEU, it was observed that the presence of the finish did not change the intensity of the CH bending (1367 cm^{-1}), OH rocking (1337 cm^{-1}), CH_2 wagging (1317 cm^{-1}), OH bending (1200 cm^{-1}) and COC antisymmetric stretching (1162 cm^{-1}) bands. This finding was successfully used in further spectral interpretation, where the integral absorbance of the band at 1200 cm^{-1}, which was also determined to be insensitive to changes in molecular environment (Hulleman et al., 1994), and therefore to structural changes during biodegradation, was used for normalisation of cellulose spectra before and after biodegradation.

An inspection of the measured ATR spectra of cotton samples after 12 days of burial (Fig. 11) revealed that microbial biodegradation lead to structural changes in untreated and finished cellulose. To provide a clear view of the changes appearing during the biodegradation process, the difference ATR spectra, obtained by subtracting the spectrum of unburied cellulose from the buried one were examined. In Fig. 12A, negative band absorptions occur at 3340 cm^{-1} due to OH stretching, at 2918 and 2853 cm^{-1} due to CH and CH_2 stretching and at 1456, 1429, 1370, 1336, 1318, 1280, 1160, 1105, 1053 and 1029 cm^{-1} due to C–C and C–O stretching vibrations, skeletal vibrations and ring vibrations in the cellulose fingerprint region as a result of the decreased intensities of these bands after biodegradation. Hulleman et al. (1994) suggested that the decrease of band intensities in the region 1500–900 cm^{-1} may be attributed to a decrease in cellulose crystallinity. This finding is in agreement with that obtained by Nelson et al. (Nelson & O'Connor, 1964, p. 1337), where the intensity of bands at 1429, 1370, 1335, and 1315 cm^{-1} (which were assumed to be very sensitive to changes in cellulose crystallinity and lattice type) decreased with decreasing crystallinity. Examination of

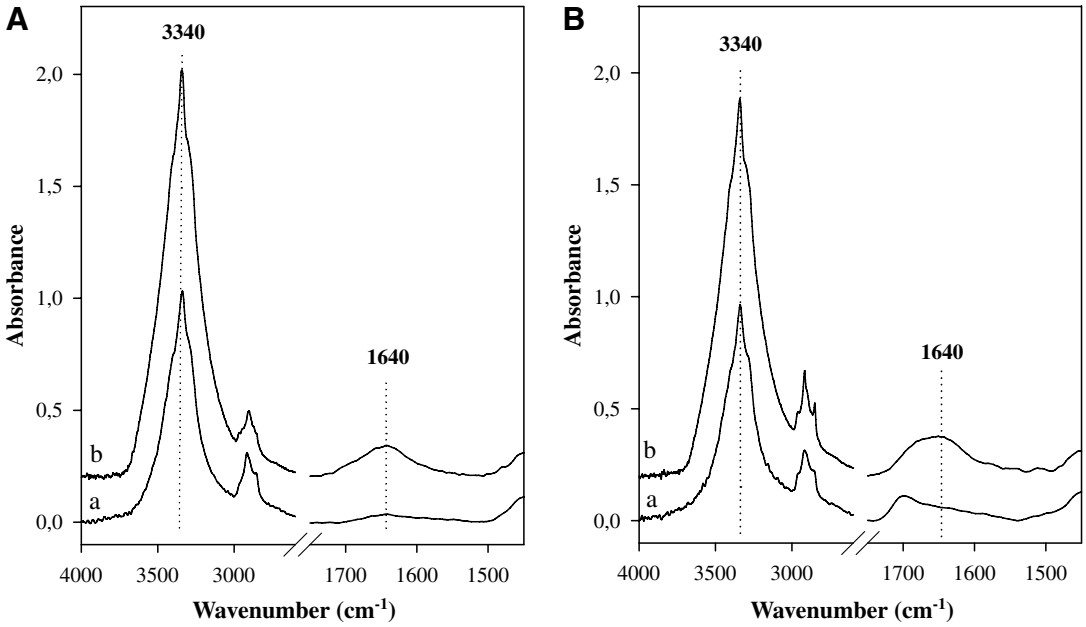

Fig. 10. Measured infrared ATR spectra of untreated (A) and finished (B) cellulose. a – dry sample (dried for 7 h at 100 °C), b – wet sample (conditioned at 95 ± 2% relative humidity for 24 h). Spectral normalization was based on the integral absorbance of the CH bending at 1372 cm^{-1}.

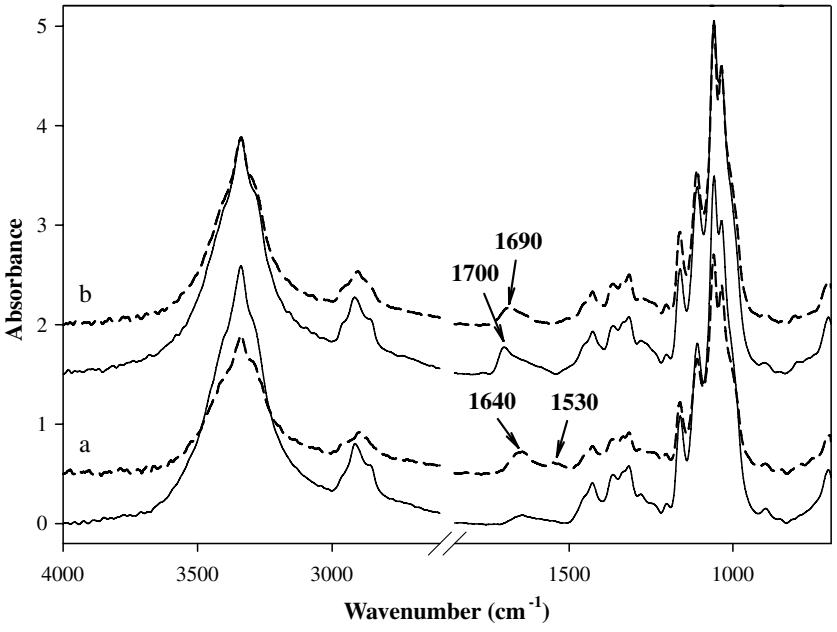

Fig. 11. Measured infrared ATR spectrum of untreated (a) and finished (b) cotton samples before (—) and after (---) 12 days of burial.

these bands in Fig. 12A showed that the fall in their intensity was much higher in the case of untreated cellulose in comparison with finished cellulose. This phenomenon may indicate that, although a decrease in cellulose crystallinity was observed for both buried samples, it was much higher for untreated than for finished sample. As suggested by Fengel (Fengel, 1992, p. 287), additional useful information about structural changes could be provided by inspection of the intensity change of the OH stretching (3340 cm^{-1}) band, whose intensity decreases with decreasing cellulose crystallinity. Accordingly, the decrease of this band in Fig. 12A, which was more than twice as high for unfinished as for finished sample, proved that during the biodegradation process the microorganisms present in soil caused much greater structural damage to the untreated cellulose than to the DMeDHEU modified cellulose. Furthermore, the difference ATR spectrum of the finished cellulose presented in Fig.12B clearly shows that degradation of DMeDHEU also took place during 12 days of burial, accompanied by a decrease of the bands at 1760, 1700 and 1260 cm^{-1}, which are characteristic of the finish. The band at 1700 cm^{-1} is red shifted to 1690 cm^{-1}.

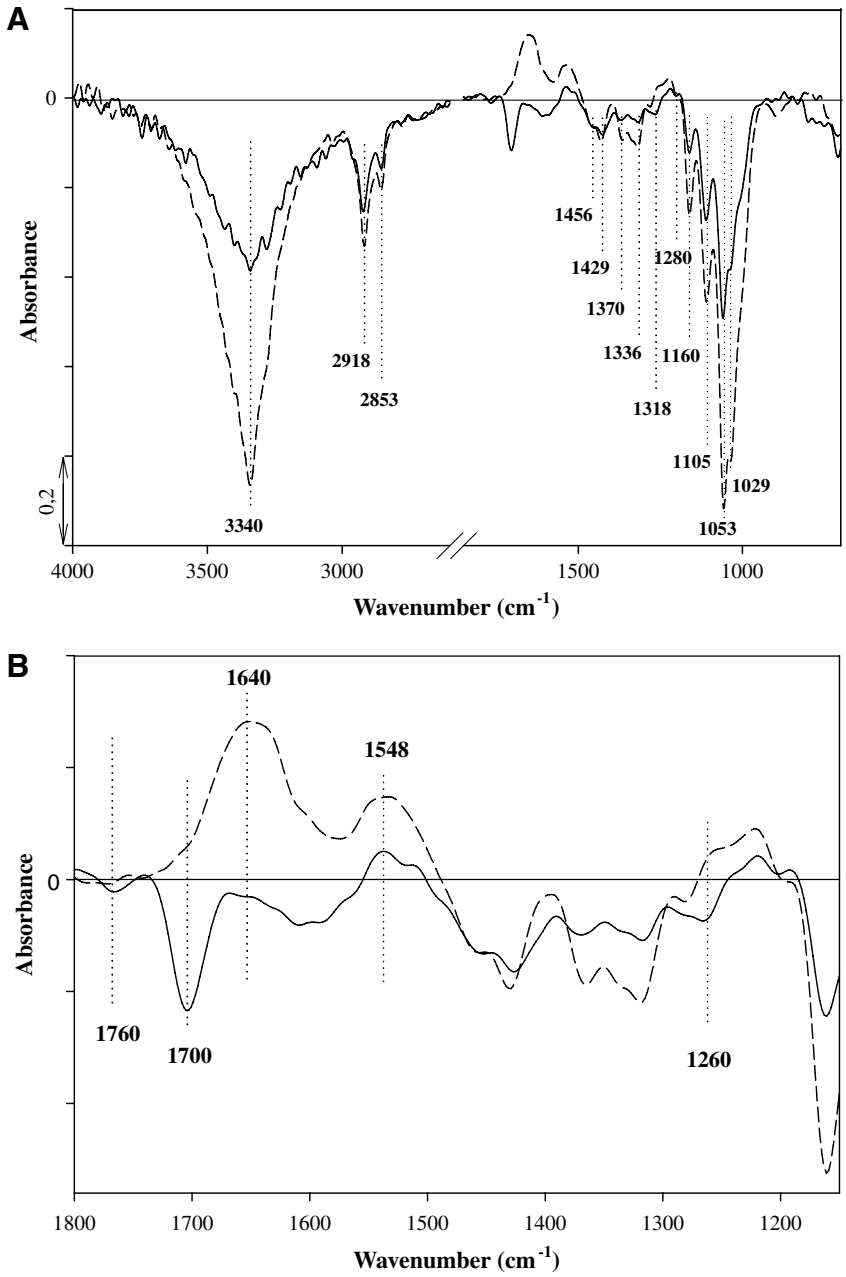

Fig. 12. (A) Difference ATR spectra obtained by subtracting the spectrum of unburied cellulose from the buried one. — finished cellulose, --- untreated cellulose. (B) Difference ATR spectra obtained by subtracting the spectrum of unburied cellulose from the buried one in the region of 1800–1100 cm^{-1}. — finished cellulose, --- untreated cellulose.

Simultaneously, a very weak broad band appears at 1548 cm^{-1}. There is no intensity change of the band at 1640 cm^{-1} in the spectrum of finished cellulose. On the contrary, the intensity of the last two bands significantly increased in the spectrum of untreated cellulose after 12 days of biodegradation. This indicates that very important structural changes appear in the spectral region from 1700 to 1500 cm^{-1}, reflected in the intensity change of bands at 1640 and 1548 cm^{-1}.

In discussing the structural changes caused by the biodegradation process, it is assumed that during burial the enzymes produced by various bacteria and fungi in soil catalyse the hydrolytic degradation of cellulose macromolecules, where the breaking of $(1 \rightarrow 4)$ glycosidic bonds results in the formation of aldehyde groups, as well as the oxidative degradation of cellulose, where the opening of the β-D-glucopyranose rings results in the formation of carboxylic and aldehyde groups (Clarke, 1997). Consequently, the intensity of carbonyl and carboxyl bands could represent a reasonable measure of the degree of cellulose degradation. In the literature, these bands are located in the region from 1750 to 1617 cm^{-1} (Socrates, 2001). According to Chung, Lee, and Choe (2004), the presence of carboxylic groups in the structure of degraded cellulose

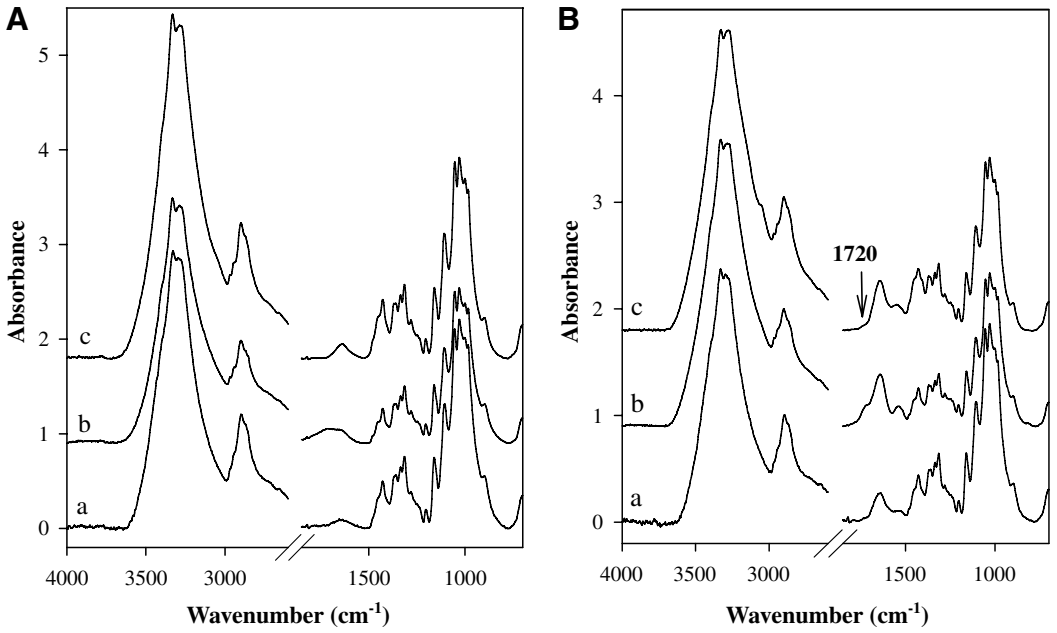

Fig. 13. ATR spectra untreated cellulose before (A) and after 12 days of burial (B). a – untreated sample, b – sample treated with HCL vapour, c – sample treated with NH_3 vapour.

can be proved after fabric is exposed to HCl vapour for a few minutes. In an HCl atmosphere, the protonation of carboxylate groups results in the rise of the absorption band at 1720 cm^{-1}, which disappears again when the fabric is exposed to the NH_3 vapour (Fig. 13).

In addition, a detailed analysis of the spectra showed that the significant increase of the band at 1640 cm^{-1}, obtained for the untreated cotton samples buried 12 days, was not caused by the increase of adsorbed water onto the degraded cellulose. The difference ATR spectra in Fig. 14, obtained by subtracting the spectrum of dry cellulose from wet, show a decrease in intensity of the bands at 1640 and 3340 cm^{-1}. This indicates that the ability to adsorb water decreases after the period of biodegradation for the unfinished and finished cellulose. This phenomenon is contrary to that obtained for unburied samples where the increase of relative humidity simultaneously causes increase in the bands at 3340 and 1640 cm^{-1}. Therefore, the reason for

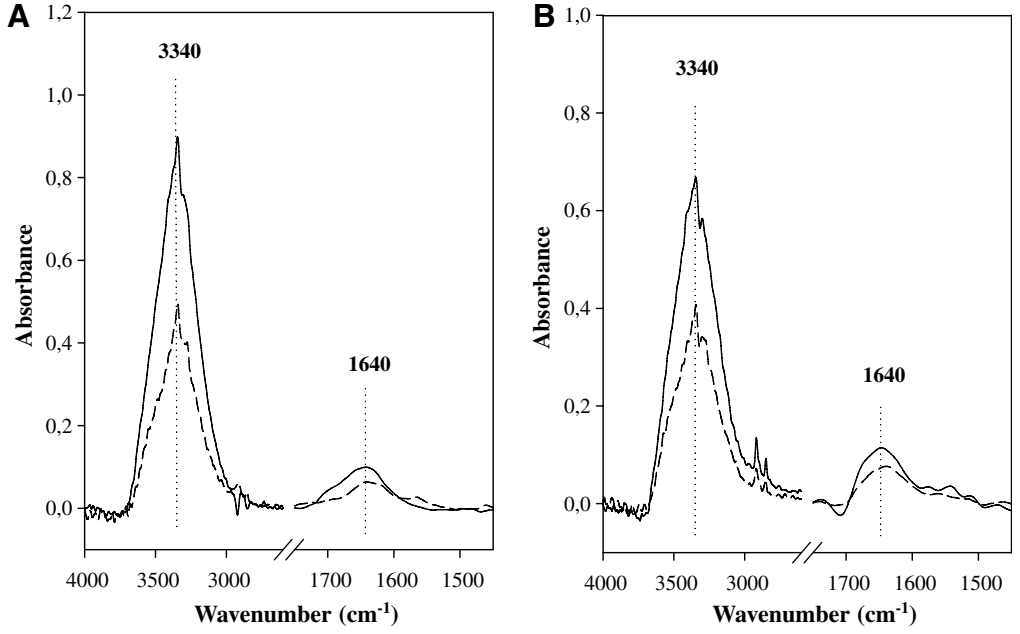

Fig. 14. Difference ATR spectra obtained by subtracting the spectrum of the dry cellulose from the wet one. (A) Untreated cellulose and (B) finished cellulose. — unburied sample, --- buried sample.

the increase of the band at 1640 cm^{-1}, which occurs as a result of the biodegradation process, should be attributed to other structural changes.

Further inspection of the bands at 1640 and 1548 cm^{-1} also shows that their position and shape are not representative of the spectral absorption of the aldehyde or carboxylic functional groups which are produced in the cellulose biodegradation process. They seem to be more related to the amides I and II (Socrates, 2001; Vince et al., 2006). Their appearance in the cellulose structure could be explained by the presence of secondary polyamides due to the proteins which are produced during the growth of microorganisms on the fibres, and could be adsorbed on the degradable cellulose macromolecules. Accordingly, greater microbial growth results in greater biodegradation, as well as in a larger increase of the bands at 1640 and 1548 cm^{-1}. These results are in agreement with the vibrational spectra of bacteria grown on a culture media (Socrates, 2001).

4. Conclusions

In the finishing process, modification of the cellulose macromolecules is carried out using DMeDHEU. The incorporation of the finish into the cellulose structure does not only result in the improvement of the fibre properties in wear and care, but also decreases their biodegradability. In the DMeDHEU modified cotton fibres the formation of covalent bonds between hydroxyl groups of the finish and of the cellulose molecules strengthens the less ordered amorphous regions, which results in a decrease of fibre swelling. Consequently, the finished cotton sample is more hydrophobic and thus less wettable in comparison to the unfinished one. These properties are probably those most responsible for retarding the biodegradation process in the samples studied, since the increase in macromolecular arrangement and the decreased amount of moisture in the finished fibres impair the conditions for growth of microorganisms.

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