Antibacterial Finishing of Cotton Fabrics

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Abstract
Antibacterial properties have been given to the surface of a cotton fabric by a two-stage process of chemical modification. First, the fabric was treated with chloroacetyl chloride in THF using pyridine as a catalyst to incorporate chloroacetate groups. During the second stage, the chloroacetylated cotton was reacted with a potassium salt of a bioactive 1-naphthylacetic acid to prepare a cellulose-1-naphthylacetic acid adduct. The results of the FTIR ATR spectra confirmed the existence of a chemical linkage between 1-naphtylacetic acid and the cellulose chains. As a result of this modification, the cotton fabric surface becomes hydrophobic, and the fabric thermal stability is decreased. The hydrolysis in the heterogenous phase of adducts showed that the release of the bioactive compound is dependent on the pH values of the medium. An analysis of the antibacterial activity of one of the obtained adducts towards Escherichia coli was also performed.

Key words: *cotton fabric, functionalization, chloroacetate groups, bioactive carboxylic acid, antibacterial activity.*

Introduction

In recent years, great interest in the antibacterial finishing of fibres and fabrics for practical applications has been observed [1, 2]. Most textile materials currently used in hospitals and hotels are conducive to cross-infection or transmission of diseases caused by micro-organisms. Textiles for medical and hygienic use have become important areas in the textile industry. In general, antimicrobial properties can be imparted to textile materials by chemically or physically incorporating functional agents onto fibres or fabrics. The antimicrobial properties of such textile materials can be grouped into two categories, temporarily or durably functional fabrics. Temporary biocidal properties of fabrics are easy to achieve in finishing, but easy to lose in laundering. Durability has generally been accomplished by a common technology, a slow-releasing method. According to this method, sufficient antibacterial agents are incorporated into fibres or fabrics by means of a wet finishing process. The treated fabrics deactivate bacteria by slowly releasing the biocide from the materials. However, the antibacterial agents will vanish completely if they are impregnated in materials without covalent bond linkages. Some successful examples of chemically incorporated techniques have been noted.

Sun el at. [3, 4] obtained antimicrobial textile materials based on helamine chemistry. These materials have demonstrated biocidal properties against a wide range of pathogens, and are also non-toxic and environmentally friendly. In that approach, a dimethylol hydantoin derivative, dimethylol-5,5-dimethylhydanation, was used in chemical treatment of cellulose]], and subsequent chlorine bleaching can convert unreacted amide or imide bonds in the hydantoin.

Anti-microbial cellulosic fabrics were developed by means of the use of 1,2,3,4-butanetetracarboxylic acid and citric acid, together with subsequent oxygen bleaching. Carboxylic acids has been converted to peroxyacids by being reacted with hydrogen peroxide under acidic conditions, while carboxylic acid groups can be incorporated into cellulose fabrics. Polymeric materials containing such moieties were found to exhibit oxidative potentials, in particular antibacterial activities against Escherichia coli [5,6].

The present paper considers the possibilities of antibacterially finishing cotton woven fabrics by a two-stage chemical modification. In the first stage, the fabric is chloroacetylated with chloroacetyl chloride in THF, using pyridine as catalyst. In the second stage, the chloroacetylated cotton is treated with a bioactive carboxylic acid (1-naphthylacetic acid) in the form of potassium salt to obtain a cellulose-1-naphthylacetic acid adduct. Then, this adduct is hydrolysed in a heterogeneous phase to evaluate the release of the bioactive compound. Its activity towards Escherichia coli on the modified cotton fabric is then determined.

Experimental

Materials

Cotton fabric (from Uniotex) with a surface weight of about 140 g/m^2 was purified by treating it with a solution containing 1.5 g sodium carbonate in 1 dm^3 of water, followed by washing in distilled water and then in ethanol. Finally, 100% cotton fabric was dried and cut into rectangular 5×5cm pieces. Tetrahydrofurane (THF) (Aldrich) and dimethyl sulphoxide (DMSO) (Merck) were purified by distillation and then stored above Merck 4 A molecular sieves. Chloroacetyl chloride (Aldrich) was used without further purification. Pyridine (POCh) was refluxed over CaH_2 under a nitrogen atmosphere and then distilled. 1-naphtylacetic acid (Fluka) was used without further purification.

Potassium salt of 1-naphtylacetic acid was obtained by dissolving 9.3 g (0.05 mol) of the acid in 50 cm^3 of chloroform, which was then neutralised with 2.8 g (0.05) mol of KOH dissolved in 50 cm^3 of ethyl alcohol. The reaction product was precipitated by pouring the mixture into 600 cm^3 of dry acetone. After filtration, the salts were dried under reduced pressure at 50 ^{o}C to a constant weight.

Reaction of cotton fabric with chloroacetyl chloride

The typical esterification procedure was as follows: the sample of cotton fabric 1.4 g (5 x 5 cm) was placed in 250 cm^3 round-bottom flasks equipped with a stirrer, and then 60 cm^3 THF and 1.0 cm^3 (13.4 mmol) pyridine were added. The mixture was cooled to 0°C, and 1.0 cm^3 (12.4 mmol) chloroacetyl chloride dissolved in 5 cm^3 THF was added dropwise. The reactions were carried out at 25 °C in a nitrogen atmosphere. After 24 h, the fabric samples were separated from the precipitated pyridine hydrochloride, carefully washed with water and ethanol to remove impurities, and then dried under reduced pressure at 40 °C to a constant weight.

Reaction of chloroacetylated cotton fabric with the potassium salt of 1-naphtylacetic acid

The sample chloroacetylated cellulose fabric with dimensions of 5×5 cm was placed in 250 cm^3 round-bottom flasks equipped with a magnetic stirrer, and 50 cm^3 of DMSO was added. Next, a solution of 1.2 g (18 mmol) of potassium salt of 1-naphtylacetic acid dissolved in 5 cm^3 DMSO was added. The reaction was performed at 30 °C with intense stirring for about 5 h. Once the reaction was terminated, the fabric sample was carefully washed with ethyl alcohol to remove unreacted potassium salt of 1-naphthylacetic acid, and then dried under reduced pressure at 60 °C to a constant weight.

Study of heterogenous hydrolysis of cellulose-1-naphthylacetic acid adduct

A 2×2 cm sample of cotton fabric containing the incorporated bioactive 1-naphthylacetic groups was placed in a conical flask with 100 cm^3 of aqueous NaOH solution (pH = 12 – 13) and heated at 35 °C in a water bath. At fixed intervals, solution specimens were taken from the liquid above the padded cotton fabric samples. The homogenous solution contained the released bioactive agent, which was quantitatively determined by UV spectroscopy at the absorption wavelength of 1-naphthylacetic acid (λ = 281 nm) using calibration curves (the aqueous solution of sodium hydroxide as a solvent). Tests were performed for the various pH values of the reaction environment.

Measurements

Infrared spectra of the samples were recorded in reflection mode using a Fourier-Transform Perkin Elmer 2000 FT-IR spectrometer (Beaconsfield, Buckinghamshire, England). An attenuated total reflection (ATR) unit was fitted with a KRS-5 crystal (45° entrance angle). Thirty scans were taken for each sample. A Hitachi S-4100 field emission scanning electron microscope (Tokyo, Japan) was used to observe the samples spattered with a 15nm thick gold-palladium layer. The instrument was operated at 5.0 kV. The water contact angle on the surface samples of the chemically modified cotton fabrics was measured using a sessile drop method at 25±0.1 °C using a DSA 10 Drop Shape Analysis System (Krüss, Hamburg, Germany). Two samples of each material were measured, and six measurements were carried out for each sample. The data presented are the means of twelve measurements (± standard deviation).

The thermogravimetric (TG) investigations were performed using a TGA-7 thermobalance of Perkin-Elmer in a nitrogen atmosphere (sample of about 5 mg, a heating rate of 15 °C min^{-1} within the temperature range of 25 to 600 °C).

A Japanese Industrial Standard (JIS L 1902:1998 'Testing method for antibacterial textiles') was used to assess the antibacterial efficiency of the cotton fabric with added naphthylacetic groups. The test method was performed using a gram-positive strain of Escherichia coli (ATCC 11229, American Type Culture Collection). The germs counted on the cotton fabric containing incorporated naphthylacetic groups and those on a reference sample were determined after a 24-hour incubation period. The antibacterial activity (quantitative test) was determined at the Microbiological Laboratory of the Institute of Chemical Fibres in Łódź.

Results and discussion

Cotton fabrics modified by chloroacetate groups with different degrees of substitution were synthesised in a heterogenous medium using the method followed for the bromoacetylation of polysaccharide [7, 8], according to the reaction presented by the scheme in Figure 1.

The effect of reaction conditions on the degree of substitution is summarised in Table 1. The extent of modification was controlled by the amount of chloroacetyl chloride used and the temperature. Based on the chlorine content in the fabric samples, the extent of fabric surface modification was assessed. Its value slightly increased when the chloroacetyl chloride to cotton fabric ratio was increased, as

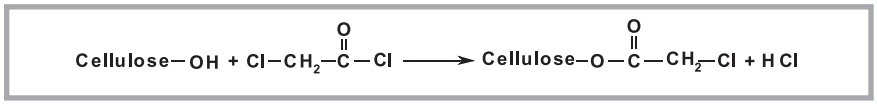

Figure 1. *Scheme of the reaction of cellulose modified with chloroacetate groups.*

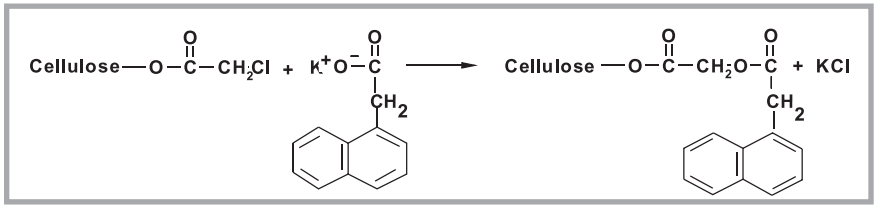

Figure 2. *Scheme of the coupling of bioactive carboxlic acid to cellulose functionalised with chloroacetate groups by using the potassium salt of 1-naphtylacetic acid.*

Table 1. *Effect of reaction conditions on the containing chloride for the esterification of the cotton fabric with chloroacetyl chloride.*

Sample	$ClCH_2COCl$ Cotton fabric, g/g	Temperature, °C	Cl, %
1	1.0	25	0.48
2	2.1	25	0.78
3	4.2	25	1.09
4	2.1	35	0.95
5	2.1	40	1.14

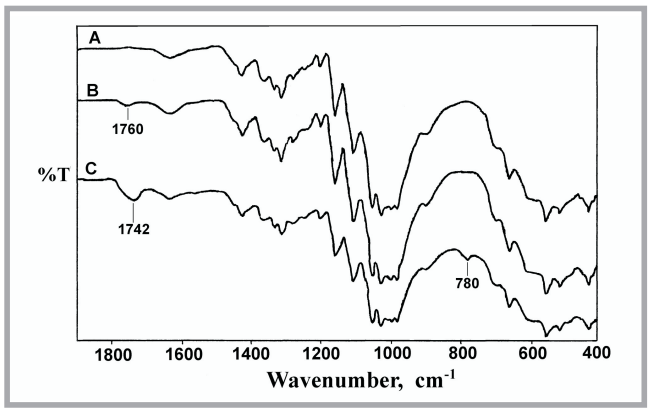

Figure 3. *FTIR spectra of unmodified cotton fabric (A), chloroacetylated cotton fabric (B), cotton fabric containing incorporated naphthylacetic groups (C).*

well as with the increase in temperature shown in Table 1.

The coupling of bioactive carboxylic acid to cotton fabrics functionalised with chloroacetate groups was achieved by using the potassium salt of 1-naphtylacetic acid according to the the reaction presented by the scheme in Figure 2.

Figure 3 (A-C) shows the FTIR ATR spectra of the unmodified cotton fabric (A), the chloroacetylated cotton fabric (B) and the cotton fabric with added naphthylacetic groups (C). Unlike the spectrum of the unmodified cotton fabric, the spectrum of the chloroacetylated fabric shows a new weak signal at 1760 cm^{-1} derived from the ester groups >C=O, while the spectrum of the cotton fabric containing 1-naphthylacetic groups incorporated on its surface reveals a higher intensity of the band of ester groups at 1742 cm^{-1} as well as a band at 780 cm^{-1}, which results from scissoring vibration bands >C=C< and C-H in the naphthyl ring [9, 10]. An analysis of the results of FTIR ATR spectroscopy confirmed the existence of the chemical linkage between cellulose chains and bioactive 1-naphtylacetic acid.

Representative scanning electron micrographs of the unmodified cotton fabric, the chloroacetylated cotton fabric and the cotton fabric with added naphthylacetic groups are shown in Figure 4. As can be seen, the surface of the elementary cotton fibres of the unmodified fabric (Figure 4A) is smoother and more homogeneous than that of the chemically modified fabric (Figure 4B, C). The surfaces of both modified fibres are rougher.

Considering the changes in the modified fabric surface, it should be expected that they would be reflected by changes in the properties of fabric surface such as wettability. As has been found, the condition of fibre or fabric surface can be examined by measuring the wetting angle. The contact angles of untreated cotton fabric and chemically modified cotton fabrics are presented in Table 2. It was not possible to measure the angle contact for the sample A untreated cotton fabric. The drop immediately after placing it on these surfaces was absorbed by the fabric's fibres. Such behaviour by the water drops may result from the hydrophilicity of these samples, and additionally from the capillary effect connected with the fabric structure. Despite having the same fabric structure as that of the unmodified sample, sample B (chloroacetylated cotton fabric, 1.09 %Cl) and sample C (cotton fabric with added 1-naphtylacetic groups) show higher contact angle values, indicating that the chemical modification has significantly changed their surface properties from hydrophilic to hydrophobic.

Figure 5 shows thermograms of the unmodified cotton fabric (curve A), chloroacetylated cotton fabric (curve B) and cotton fabric containing incorporated naphthylacetic groups on its surface (curve C). The decompositions of the three samples under examination show a similar character. Initially, up to a temperature of about 70 °C, a weight loss of about 2% is observed, which can result from the evaporation of residual water and volatile impurities.

Table 3 includes the values of temperatures at which samples lose their weight from 5% to 50% as determined from the TG curves. Both the TG curves and the thermal stability indices show that the unmodified cotton fabric has a higher thermal stability than those of cotton fabrics modified by the two-stage process. The lowest thermal stability is shown by the chloroacetylated cotton fabric, which

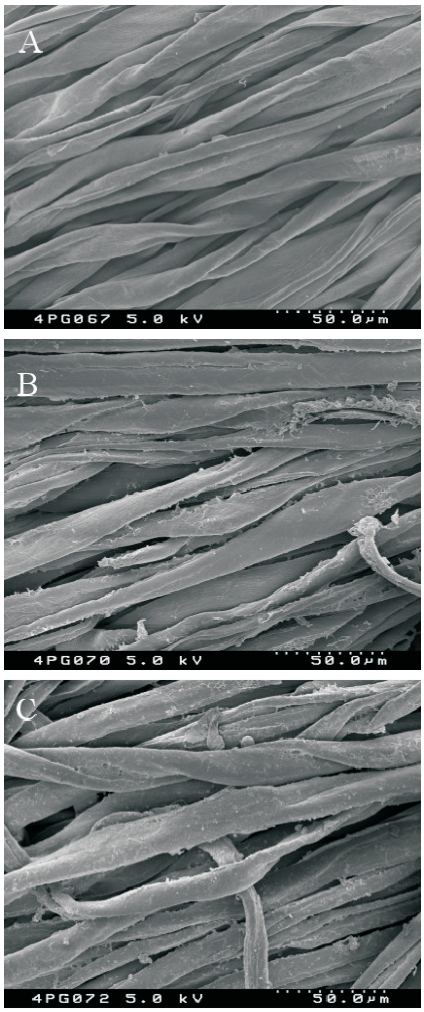

Figure 4. *SEM photographs of the surfaces of unmodified cotton fabric (A), chloroacetylated cotton fabric (B), cotton fabric containing incorporated naphthylacetic groups (C); (900×).*

Table 3. *Thermal stability indices of untreated and modification of cotton fabric.*

Sample	Thermal stability indices	
	T_5	T_{50}
A	321	395
B	254	380
C	304	375

T_5, T_{50} – temperature of 5 and 50% mass loss of the sample.

is probably connected with the weakest bond C-Cl, which has already decomposed at about 240 °C, resulting in an appreciable weight losses.

An analysis of heterogenous hydrolysis of the cellulose-1-naphthylacetic acid adduct at various solution pH values was also performed. Analysing the curves shown in Figure 6, it is seen that the release of the bioactive compound from the cellulose-1-naphthylacetic acid adduct formed on the fabric surface depends on

the pH value of the medium. The higher is the pH of the solution, the higher the rate of the bioactive compound release. This is consistent with the results obtained by Arranz et al. [11] for the poly(vinyl alcohol)-1-naphthylacetic acid adduct.

The efficacy of the antibacterial activity of the cellulose-1-naphthylacetic acid derivative produced was also analysed. Table 4 presents the results of bioactivity of cotton fabric containing the incorporated naphthylacetic groups. The data was compared to those of the cotton sample used as reference material. Tests of the cellulose-1-naphthylacetic acid adduct confirm not only the inhibition of bacteria growth, but also its total destruction. The high values of bacteriostatic and bactericidal activities indicate the efficiency of the adduct produced.

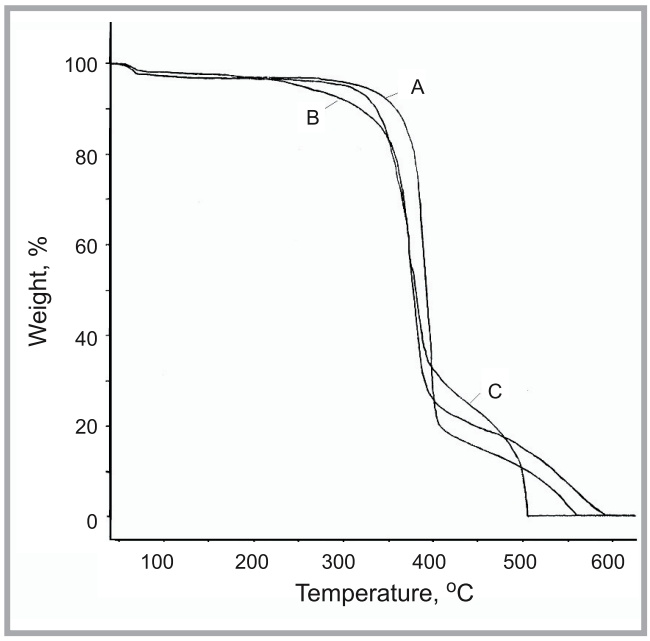

Figure 5. *TG curves of unmodified cotton fabric (A), chloroacetylated cotton fabric (B), cotton fabric containing incorporated naphthylacetic groups (C).*

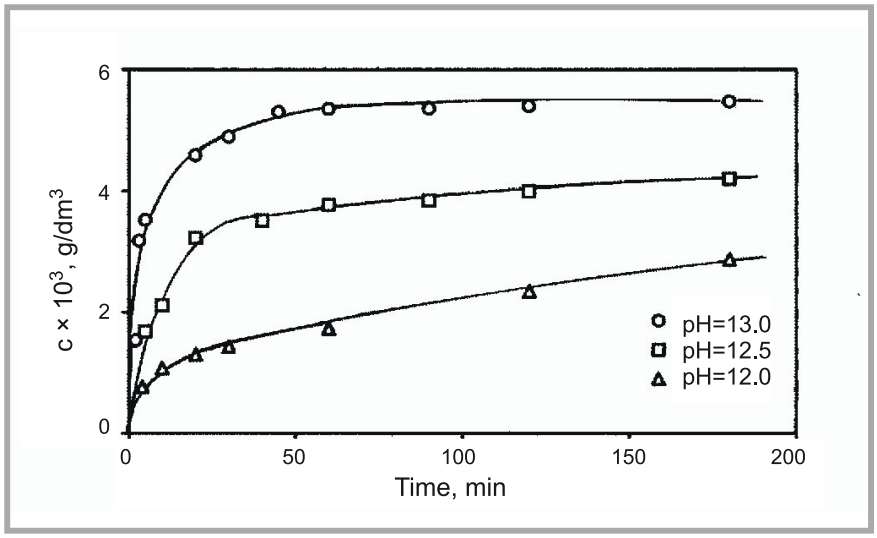

Figure 6. *The release of the bioactive compound from the cellulose-1-naphthylacetic acid adduct formed on the surface of cotton fabric, versus the pH of the reaction medium.*

Table 2. *Results of contact angles for of untreated and chemical modification of cotton fabric.*

Sample	A	B	C
Contact angle, degress	-	110 ± 3.8	122 ± 4

Table 4. *Bioactivity tests for modified cotton fabric towards Escherichia coli.*

Sample symbol	Time, h	Total bacteria number,CFU	Bacteriostatic activity	Bactericidal activity	Antibacterial activity [12]
Cotton standard	0	$6.4x10^4$	-	-	-
Cotton standard	24	$1.2x10^8$	-	-	-
Tested sample	24	$2.6x10^1$	6.7	3.4	strong

Conclusions

As the result of the esterification of the cotton fabric's surface with chloroacetyl chloride, using pyridine as catalysts and THF, a cotton fabric with chloroacetate groups was produced. The presence of chloroacetate groups was used to obtain an adduct with bioactive carboxylic acid during the reaction with potassium salt. On the basis of the results of the adduct's heterogenous hydrolysis, it was stated that the rate of biocide release depends on the pH value of the reaction environment. Quantitative tests of the bacteriological activity of cotton fabric containing incorporated naphthylacetic groups show highly bacteriostatic and bactericidal activities against *Escherichia coli*.

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