

Antibacterial and Catalytic Properties of Textiles with Modified Surfaces

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Abstract

This paper presents methods for the surface modification of cotton woven fabric and polypropylene non-woven in order to make them antibacterial. In the case of cotton fabric, its surface was functionalised with chloroacetate groups by means of chloroacetyl chloride, using pyridine as a catalyst, followed by the quaternalisation of the chloroacetate groups with poly(4-vinylpyridine). In the second process polypropylene nonwoven was impregnated with a multimonomer containing vinyl groups, which were then changed into tertiary amine groups by the addition of diethylamine. These groups were quaternalised with propyl bromide. In the next method colloidal silver was incorporated into the nanolayers formed from polyelectrolytes on the polypropylene non-woven. Quantitative tests of bacteriological activity of the modified woven fabric and non-woven showed both bacteriostatic and bactericidal activities in relation to *Escherichia coli*. In addition, colloidal platinum was incorporated into previously deposited polyelectrolyte nanolayers in order to impart catalytic properties to fibers. The results obtained clearly show the catalytic action of such systems, the oxygen release from the hydrogen peroxide solution being an example.

Key words: antibacterial textiles, surface modification, multimonomers, catalysts.

Introduction

Over recent years one can observe increasing interest in the antibacterial finishing of fibers and textiles, which results from the possible practical utilisation of such fibers and textiles [1, 2]. Many textiles currently used in hospitals and hotels constitute a potential source of infection and disease caused by micro-organisms as a result of secondary infection. Medical and hygienic applications of textiles have become important areas in the textile industry. Antimicrobial properties can be imparted to textiles by physical or chemical treatment with appropriate agents. Textile materials with such properties are grouped into two categories, i.e. fabrics with unstable properties and those durably functionalised. Unstable bioactive properties can be easily obtained by finishing processes, but they are quickly lost during laundering. In this case antibacterial agents are incorporated into fibres or textile in the process of wet finishing. As a result of slow biocide release from such modified textiles, bacteria are completely destroyed. However, the antibacterial properties of textiles decay if the fabrics are impregnated with antibacterial agents only, with no covalent bonds between each other. Scientific literature on this subject provides some examples of the chemical addition of biocides to textiles. Sun and co-workers [3, 4] prepared textile materials based on helamine that show bioactive properties against a wide range of pathogenic micro-organisms, being also non-toxic and environmentally friendly. These materials were prepared with the use of a dimethyl derivative of hydantoin, such as dimethylol-5,5-dimethylhydantoin. This derivative was used for the chemi-

cal modification of cellulose, followed by the oxidising treatment with chlorine to obtain active hydantoin.

Antibacterial cellulose textiles were obtained with the use of 1,2,3,4-butanotetracarboxylic and citric acids, followed by oxidation with oxygen. Carboxylic acids were then converted to peroxide acids in a process with hydrogen peroxide. These acids were added to a cellulose woven fabric in an acidic medium. Polymeric materials containing such units show an oxidising potential as well as bacteriostatic and bactericidal activity against bacteria such as *Escherichia coli* [5, 6].

This paper presents possibilities of antibacterial modification of the surface of cotton fabric and polypropylene non-woven in a two-stage chemical process. In the first stage woven fabric was chloroacetylated with chloroacetyl chloride in THF, using pyridine as a catalyst. In the second stage the chloroacetylated cotton reacted with poly(4-vinylpyridine) to form a quaternary ammonium salt. Cotton fabric containing quaternary ammonium groups was tested for bacteriostatic and bactericidal activity against *Escherichia coli*.

The next object of study was a polypropylene non-woven containing nanolayers of polyelectrolytes deposited by the layer-by-layer technique, as described in previous papers [7, 8]. In order to find out whether the deposited layers, including those with added metals, can serve as catalysts of chemical reactions, a hydrogen peroxide solution was tested for decomposition under the influence of platinum deposited on the nonwoven.

Experimental

Materials

Cotton woven fabric (from Uniontext) with a surface weight of 140 g/m² was purified by treating it with a solution containing 1.5% sodium carbonate in 1 dm³ of water, followed by washing with distilled water and ethanol. After the purification treatment, 100% cotton fabric was dried and cut into 5 × 5 cm samples.

Polypropylene nonwoven with a surface weight of 27.9 g/m² and average filament diameter of 9.65 μm was prepared by the melt-blown method (Cenaro-Lodz, Poland).

Poly(4-vinylpyridine) (P4-VP) with M_n = 170 kDa and poly(allylamine hydrochloride) (PALL) with M_n = 70 kDa were obtained from Aldrich. Poly(acrylic acid) (PAA) and poly[2-(N,N-dimethylamino)ethyl methacrylate] (PDAMA) were prepared by radical polymerisation, as described in [7, 8].

Tetrahydrofuran (THF) (Aldrich) and dimethylsulfoxide (DMSO) (Merck) were purified by distillation and stored over Merck 4 Å molecular sieves. Chloroacetyl chloride (Aldrich) was used without additional purification. Pyridine (POCh) was heated to boiling point under nitrogen over CaH₂ and distilled.

Reaction between cotton fabric and chloroacetyl chloride (Figure 1)

A typical esterification procedure was as follows: a 5 × 5 cm cotton fabric sample (1.4 g) was placed in a 250 ml round-bottomed flask equipped with a stirrer. Then 60 ml of THF and 1.0 ml (13.4 mmol) of

pyridine were added. The mixture was cooled to 0 °C and 1.0 ml (12.4 mmol) of chloroacetyl chloride dissolved in 5 ml of THF was added. The reaction was carried out under nitrogen. After 24 hours the fabric samples were separated from the precipitated pyridine hydrochloride, thoroughly washed with water and ethanol to remove impurities and then dried under vacuum at a temperature of 40 °C to a constant weight. The chlorine content in the sample was 1.09% by wt.

Reaction between chloroacetylated cotton fabric

and poly(4-vinylpyridine) (Figure 2)

A 5 × 5 cm sample of chloroacetylated cellulose fabric was immersed in an ethanol solution of P4-VP with a concentration of 10⁻² base mol/L at 20 °C for 2 hours, then washed thoroughly with ethanol and dried under vacuum at 60 °C to a constant weight.

Synthesis of multimonomer (multiacrylate) (Figure 3)

Multiacrylate (MA) was prepared by the esterification of poly(2-hydroxyethyl methacrylate) with acrylate chloride. The process was carried out under the optimum conditions described in our previous paper [9]. The MA obtained contained pendant acrylate groups of 99.3 mol%, with an Mn = 28,230 g/mol.

Deposition of a layer of quaternary ammonium salt on polypropylene nonwoven (Figure 4)

A typical procedure was as follows: a 5 × 5 cm sample of polypropylene nonwoven was impregnated with the multimonomer by dipping the material in a solution of MA with a concentration of 10⁻² base mol/l dissolved in THF at 20 °C for 2 hours. Then the sample was dried to a constant weight and irradiated with UV on both sides for 1 min. The content of MA was 4% by wt. The addition of diethylamine to the vinyl groups of MA was performed by immersing the nonwoven sample with deposited, and by some degree cross-linked, multimonomer into a 40% solution of diethylamine in ethanol for 2 hours at 40 °C and then thoroughly washed with ethanol and dried in air. The tertiary amine groups formed in the layer of multimonomer were quaternised by dipping the nonwoven sample into a 50% solution of 1-propylbromide in THF for 2 hours at a temperature of 30 °C, which was then thoroughly washed with THF and dried under vacuum at a temperature of 40 °C to a constant weight.

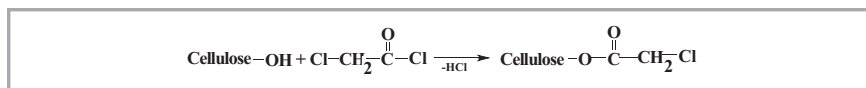


Figure 1. Reaction of cellulose modified with chloroacetate groups.

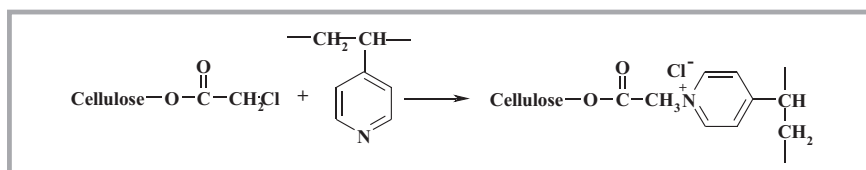


Figure 2. Reaction of quaternisation of chloroacetate groups formed on cellulose with poly(4-vinylpyridine).

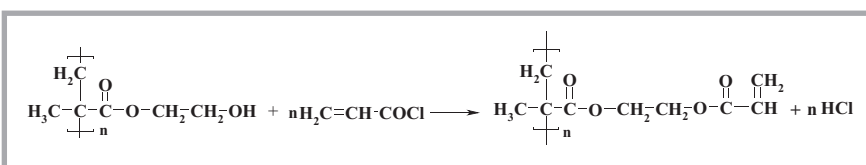


Figure 3. Reaction of multiacrylate formation.

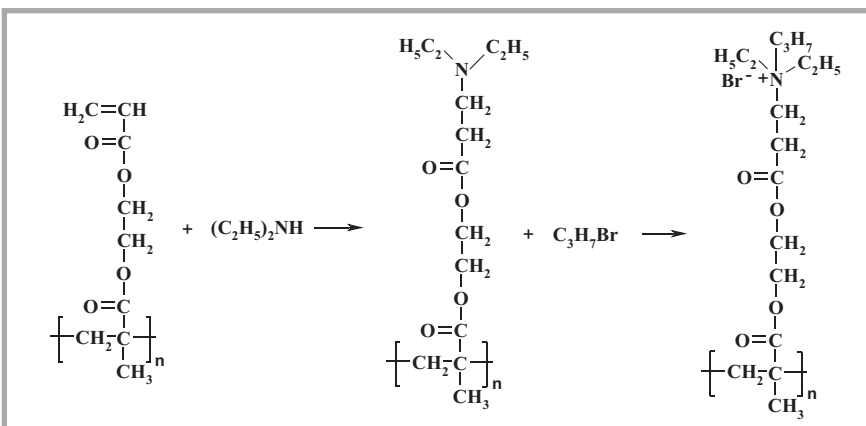


Figure 4. Reaction of the addition of diethylamine to vinyl groups and quaternisation of tertiary amine groups with 1-propylbromide.

Deposition of colloidal silver on polypropylene nonwoven

Colloidal silver was deposited on polypropylene nonwoven with previously deposited nanolayers of polyelectrolytes: poly(acrylic acid), poly(allylamine hydrochloride) and poly[2-(N,N-dimethylamino)ethyl methacrylate], by the method described in previous papers [7, 8]. Several methods of silver deposition were used:

A. Silver sol was prepared as in [10].

To 100 ml of AgNO₃ solution heated to 95 °C with a concentration of 10⁻² mol/l, 3 ml of 0.24 M sodium citrate solution was added. The resultant sol was left to cool down.

Using a "Mütek" electric charge meter, it was found that the sol had a negative charge. It was titrated with poly(allylamine hydrochloride) solution

with a concentration of 10⁻³ mol/l to neutralise the charge. The charge per 1 l of sol calculated was 4.1 × 10⁻³ Q/l.

This solution was used to impregnate polypropylene nonwoven containing deposited layers of the composition given in Table 1.

B. Silver sol, NANOSILVER SM15 from Amepox [11], diluted four times with water (the concentration of dry solid was 3.77%), was deposited on polypropylene nonwoven containing layers of the composition given in Table 1. The nonwoven was dipped in this solution, and after 10 min. it was washed with water and dried in air.

C. Polypropylene nonwoven containing deposited nanolayers (Table 1) was impregnated with a 0.1 M AgNO₃ solution, rinsed and reduced with a 0.24 M solution of sodium citrate.

Measurements of bacteriologic activity

Determination of the bacteriostatic and bactericidal activity of the modified cotton fabric and polypropylene nonwoven was carried out on the basis of the Japanese standard: JIS L 1902:1998. The tests were performed with the use of bacterial strains *Escherichia coli* (ATCC 11229 – derived from the American Type Culture Collection). The bacteria were counted on the sample surface and compared with those on an unmodified sample after a 24 h incubation period.

The microbiological quantitative tests were carried out at our Microbiology Laboratory (Institute of Biopolymers and Chemical Fibers, Łódź, Poland).

From the data given in **Table 1**, we can conclude that that silver deposited on polypropylene nonwoven imparts bacteriostatic properties to this material (samples 1 - 4). The most effective method of deposition is the process of direct silver deposition in the layer of modified nonwoven (method C, sample 4), consisting in the saturation of this layer with silver salt, followed by its reduction to metallic silver. Relatively less effective are the methods of depositing colloidal silver on the top layer of modified nonwoven. The incorporation of tertiary amine groups alone into the external nanolayer brings about some, though insignificant, bacteriostatic activity (samples 5 and 6).

All in all, the formation of quaternary ammonium groups on the surface of polypropylene nonwoven as well as on cotton fabric (samples 7 and 9) has turned out to be a very effective method of imparting bacteriostatic properties.

Decomposition of hydrogen peroxide solution by platinum deposited on nonwoven

Samples of polypropylene nonwoven with deposited platinum were prepared as described previously [12]. Polyelectrolyte layers were deposited as previously stated [7, 8]. After grafting with

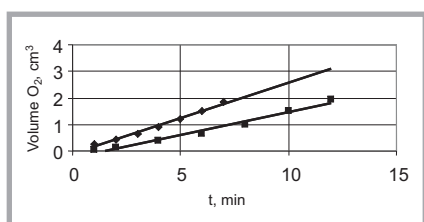


Figure 5. Decomposition of hydrogen peroxide solution by the sample containing platinum deposited in the form of sol: ◆ 30%; and ■ – 15% H_2O_2 .

Table 1. Results of bacteriological activity tests; * - Polypropylene nonwoven containing a deposited layer of multimonomer + $(Et)_2NH + C_3H_7Br$. ** - Chloroacetylated cotton fabric + Poly(4-vinylpyridine).

No	Deposited layers	Method of Ag deposition	Number of bacteria, cfu/sample	Bacteriostatic activity
0	PP standard	0	$1,43 \times 10^9$	0
1	PKA;PALL;PKA;PDAMA	A	$4,27 \times 10^2$	6,5
2	PKA, PALL	A	<20	>6,9
3	PKA;PALL;PKA;PDAMA;PKA	B	$4,64 \times 10^3$	5,5
4	PKA, PDAMA	C	<20	>6,9
5	PKA;PALL;PKA;PDAMA	0	$2,6 \times 10^7$	1,7
6	PKA, PDAMA	0	$5,84 \times 10^6$	2,4
7	PP/MM*	0	<20	>6,9
8	Cotton standard	0	$1,69 \times 10^8$	0
9	Modified cotton fabric**	0	<20	>6,9

acrylic acid, the nonwovens were immersed in aqueous solutions of appropriate electrolytes, PAA and PDAMA, with a concentration of 10^{-2} mol/l. Prior to each operation, the samples were rinsed with distilled water.

Preparation of platinum sol

46 ml of a 0.1% solution of chloroplatinic acid was neutralised to pH 8 with K_2CO_3 . The solution was heated to boiling point and several drops of freshly prepared 1% tannin solution were added and left for cooling. The resultant dark green sol showed a negative charge. The titration with a 10^{-2} mol/l solution of poly(allylamine hydrochloride) showed that the concentration of charges was $3,4 \times 10^{-3}$ C/l.

Method A

Samples of the nonwoven prepared were dipped into platinum sol, rinsed, and dried in air. Specimens with a weight of about 2 mg were cut from the prepared nonwoven and placed in an eudiometer filled with 30% or 15% H_2O_2 . The decomposition of the hydrogen peroxide solution was tested by measuring the volume of liberating oxygen with time. The results are given in **Figure 5**.

Method B

The next sample was prepared as described above, which was then saturated with a solution of chloroplatinic acid with a concentration of 2×10^{-3} mol/l and neutralised with potassium carbonate to pH = 8 ($0,0449g H_2PtCl_6 \times H_2O$ in 50 ml of water). The saturated sample was then immersed into a 1% solution of gallic acid to reduce it. The sample was heated for about 30 min. at a temperature of about $50^\circ C$, and dried in air.

The decomposition of 30% hydrogen peroxide solution by this sample is shown in **Figure 6**.

As is seen, this decomposition is faster than that in the case of the respective sample with deposited platinum sol.

The decomposition in the initial phase satisfies the straight line equation, i.e. $Y = ax + b$.

The values of a and b and the standard deviation, R^2 , for the experiments performed are listed in **Table 2**.

Conclusions

The results obtained confirm the possibility of using the methods described herein for modification of the surfaces of cotton fabric and polypropylene nonwoven in order to impart antibacterial properties to them. The most effective with respect to antibacterial activity against *Escherichia coli* are the modifications leading to the formation of quaternary ammonium salts

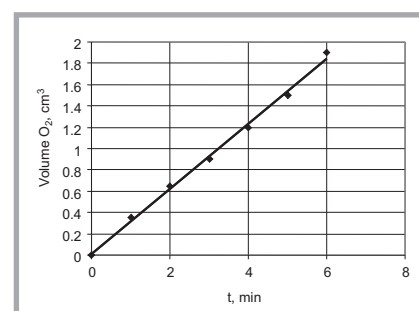


Figure 6. Decomposition of 30% hydrogen peroxide solution by the sample containing platinum produced by reduction in the nanolayer.

Table 2. Values of the constants in the linear equation.

Method	% H_2O_2	a	b	R^2
A	15	0,17	-0,23	0,976
A	30	0,27	-0,09	0,989
B	30	0,31	+0,01	0,997

on the surface of the fabrics under discussion, as well as colloidal silver incorporated into nanolayers formed from polyelectrolyte complexes deposited on polypropylene nonwoven.

The addition of tertiary amine groups to the external nanolayer is relatively insufficient for antibacterial action.

It was found that the reduction of silver salt incorporated previously into the top layer is a very effective method of metallic silver deposition. Relatively less effective is the method of silver deposition from previously formed sol.

In addition, it was shown that a polypropylene nonwoven surface modified with metallic platinum shows catalytic properties in the reaction of hydrogen peroxide decomposition. The catalytic action of platinum is also confirmed by the previous observation of the increased thermal resistance of modified polypropylene fibres [12].



Acknowledgment

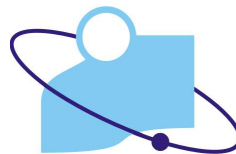
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