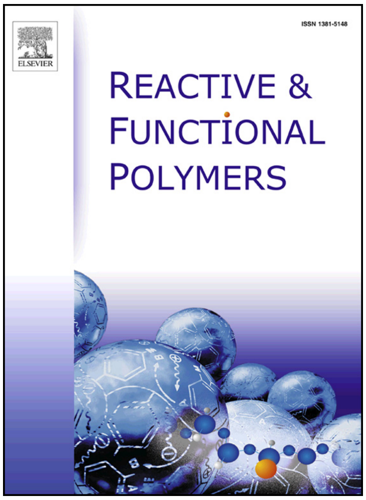


Imidazolium salts grafted on cotton fibres for long-term antimicrobial activity

Boris Izmaylov, Diana Di Gioia, Galy Markova, Irene Aloisio, Martino Colonna, Valery Vasnev

PII: S1381-5148(15)00002-4
DOI: http://dx.doi.org/10.1016/j.reactfunctpolym.2014.12.007
Reference: REACT 3480

To appear in: *Reactive & Functional Polymers*

Received Date: 10 October 2014
Revised Date: 27 December 2014
Accepted Date: 30 December 2014

Please cite this article as: B. Izmaylov, D. Di Gioia, G. Markova, I. Aloisio, M. Colonna, V. Vasnev, Imidazolium salts grafted on cotton fibres for long-term antimicrobial activity, *Reactive & Functional Polymers* (2015), doi: http://dx.doi.org/10.1016/j.reactfunctpolym.2014.12.007

Imidazolium salts grafted on cotton fibres for long-term antimicrobial activity

Boris Izmaylov,[a] Diana Di Gioia,[b] Galy Markova,[a] Irene Aloisio,[b] Martino Colonna,[c,*] Valery Vasnev[a]

[a] A.N.Nesmeynov Institute of Organoelement Compounds RAS, Str.Vavilov, 28. 119991 Moscow, Russia

[b]Dipartimento di Scienze Agrarie, viale Fanin 42, 40127 Bologna (Italy)

[c] Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Via Terracini 28, 40131 Bologna, Italy.

Corresponding author: Martino Colonna. Email martino.colonna@unibo.it; Tel +390512090331

Abstract

New antimicrobial (AM) coatings based on imidazolium salts have been prepared linking the imidazolium salts to the cotton fabric using siloxane oligomers as coupling agents. Three different imidazolium salts, linked to the siloxane oligomers connected to the cotton fabric either with ionic or covalent linkages, have been used. FTIR analysis shows that the imidazolium salts are linked to the cotton fabric. All the coatings prepared have high antimicrobial activity at both concentrations tested (3% and 10% wt) and against a Gram positive and a Gram negative bacterium. The AM activity is mainly retained after 4 cycles of washing.

Keywords: antimicrobial activity; imidazolium salt; cotton fibers; siloxane oligomers; surface grafting.

1. Introduction

It is well known [1-3] that polymeric materials are subjected to the influence of microorganisms such as microscopic mushrooms, actinomycetes or bacteria. The prevention of microbial attack on textiles has become increasingly important to consumers and textiles producers. Therefore, interests in antimicrobial fabric finishing have steadily increased over the last few years. The major classes of antimicrobial (AM) agents for textiles include organometallics, phenols, quaternary ammonium salt and organosilicones [1-7]. These finishes should have several important features: in particular should be durable and have selective activity toward undesirable organisms. In addition, antimicrobial agents must be safe for humans.

An interesting way to impart AM properties to polymeric materials consists in the grafting onto the surface of the polymeric material or of the natural fabric of polyorganosiloxanes coatings linked to biocides, such as for example 1,6 di(guanidinhydrochloride)hexane groups [8], oligomers on the basis of γ-aminopropyltriethoxysilane and bisphenols [9] and aminomethylenphosphonic ligands [10].

Imidazolium salts have proved to be very active as microbicidal agents [11,12]. The effect of substituents of the imidazolium moiety on the antibacterial activity of imidazolium salts has been reported in the literature [12]. In particular, imidazolium salts bearing long alkyl chains (with 15-18 methylene groups) can more easily interact with the cell membrane of bacteria causing loss of permeability with consequent cell death and therefore present the strongest bactericidal properties [12]. Imidazolium salts derivative are also widely used as "green" ionic solvents since they permit to avoid the use of toxic solvents. Moreover, imidazolium salts are thermally stable at temperatures that can be as high as 350 °C, depending on the type on counter-ion used [13]. Imidazolium salt derivatives have also been used in the last few years in several biological and material science applications and represent a very interesting class of functional polymers for advanced applications. For example, a review [14] reports that polyimidazoles can be used as oxygen transport membranes [15] or as scaffold for biomimetic applications [16]. Imidazolium ionomers can also be used to create polyelectrolyte brushes [17], coat metal nanoparticles [18] and produce oriented liquid crystals [19]. Imidazolium derivatives have been used in most applications as additives blended with the polymer matrix [20,21]. However, the chemical structure of imidazolium groups permits their easy modification and the insertion on the imidazolium ring of reactive groups (e.g. carboxylic acid esters and hydroxylic groups), permitting their grafting on polymer backbones. We have reported [22] the synthesis and the study of AM properties of imidazolium telechelic poly(butylene terephthalate) (PBT) with ionic moieties selectively located as chain ends. Imidazolium ionomers have proved to possess good AM properties [22] with a 97.5% reduction of viable cells of *Staphylococcus aureus* and a 48.5% of *Escherichia coli* in 24 hours. Moreover, we have prepared imidazolium ionomers of PBT [23] with imidazolium groups not only covalently linked to the polymer backbone but also linked with ionic aggregation. All the imidazolium ionomers prepared presented a high AM activity that was significantly retained also after washing at 60 °C for 6 days. Imidazolium salts have also been grafted onto a poly(fluoroethylenepropylene) to impart AM activity [24].

Imidazolium salts can be easily modified with groups (carboxylic acids and esters and hydroxyl groups) able to react with oligosiloxane polymers that can form covalent linkages with the surface of cotton fabrics. For this reason, we have performed a study on the preparation of oligorganosiloxanes coatings containing imidazolium groups linked covalently or ionically to oligorganosiloxanes. In this paper we report the synthesis of the oligorganosiloxanes coatings linked both to imidazolium salts and to cotton fabrics, as well as the AM properties of the coatings obtained also after 4 washing cycles at 60 °C.

2. Experimental

2.1 Materials

Potassium hydroxide, imidazole, 1-methylimidazole, sodium *p*-toluenesulfonate, 1-bromohexadecane, 6-chlorohexanol, 3-sulfobenzoic acid sodium salt, dimethyl-5-sulfoisophthalate sodium salt (all from Aldrich Chemicals) were high purity products and were not purified before use. Tetradecaethoxyhexasiloxane from Pentasilikon (Russia) was used without preliminary purification.

The fabric used was composed by 100% cotton with a surface density of 120 g/m^2, a number of threads per 10 cm of 332 for the base and of 270 for weft. The fiber is a mixture of cellulose triacetate and ethyl cellulose with a ratio of 1/4 as measured by XPS analysis.

2.2 Imidazolium salts synthesis

1-Hexadecylimidazole: Potassium hydroxide, 16.830 g (0.300 mol), was added to a solution containing 13.600 g (0.200 mol) of imidazole in 500 mL of dimethyl sulfoxide (DMSO), then the mixture was stirred for 30 min at 70°C and 1-bromohexadecane (64.120 g, 0.210 mol) was added drop-wise under vigorous stirring. After 6 h, the mixture was cooled at room temperature and 100 mL of water were added in order to allow the precipitation of the N-alkylimidazole. The precipitate was filtered out and washed by suspension in 2 L of distilled water. The washing procedure was repeated twice. The final product was dried in an oven under reduced pressure (yield > 95%).

*1-Hexadecyl-3-(6-hydroxyhexyl)imidazolium chloride (Im-C6OHCl)***:** 6-chlorohexanol (16.590 g, 0.121 mol), was added drop-wise under vigorous stirring to a solution containing 1-hexadecylimidazole (32.250 g, 0.100 mol) dissolved in 25 mL of anhydrous toluene. The solution was stirred for 3 days at reflux temperature. The solvent was then distilled off under reduced pressure. The residue was washed twice by suspension in 500 mL of ethyl acetate and dried under reduced pressure (yield > 95%).

3-Sulfobenzoic acid 1-hexadecyl-3-methyl imidazolium salt (Im-SBA) synthesis: 1-hexadecyl-3-methyl imidazolium bromide (5.00 g, 0.0129 mol) was dissolved in 65 mL of dichloromethane (DCM) and added to a solution of sulfobenzoic acid sodium salt (3.18 g, 0.0142 mol) dissolved in 50 mL of water in a separating funnel. The content of the funnel was vigorously shaken for 5 min until no precipitate was present in the resulting two-phase mixture. The organic layer was separated and a silver nitrate test was performed to verify the complete exchange of the bromide counter-ion. If the exchange was not complete, the organic layer was exchanged with a new water solution containing the sulfobenzoic acid salt. The organic layer was separated, dried over magnesium sulfate and the solvent removed under reduced pressure. The yellow solid was washed twice with ethyl acetate (100 mL each time). The product was dried under vacuum (yield =95%).

1-hexadecyl-3-methyl imidazolium bromide synthesis: 1-methylimidazole (8.21 g, 0.100 mol) and 1-bromohexadecane (32.1 g, 0.105 mol) were dissolved in 100 mL of toluene. The solution was put under vigorous stirring and refluxed for 6 hours. The solvent was removed under reduced pressure and the solid was washed twice with ethyl acetate (200 mL each time) and dried under vacuum. (Yield=99%)

Dimethyl-5-sulfoisophthalate 1-hexadecyl-3-methyl imidazolium salt (Im-DMSIP) synthesis: 1-hexadecyl-3-methyl imidazolium bromide (10.0 g, 0.0258 mol) was dissolved in 130 mL of dichloromethane (DCM) and added to a solution of dimethyl-5-sulfoisophthalate sodium salt (8.02 g, 0.0271 mol) dissolved in 400 mL of water in a separating funnel. The content of the funnel was vigorously shaken for 5 min until no precipitate was present in the resulting two-phase mixture. The organic layer was separated and a silver nitrate test was performed to verify the complete exchange of the bromide counter-ion. If the exchange was not complete, the organic layer was exchanged with a new water solution containing the dimethyl-5-sulfoisophthalate sodium salt. The organic layer was separated, dried over magnesium sulfate and the solvent removed under reduced pressure. The yellow solid was washed twice with ethyl acetate (200 mL each time). The product was dried under vacuum (yield= 95%).

2.3 Oligosiloxane synthesis

Oligo(aminopropylsiloxane) (oligomer **1**) was synthesized by hydrolytic polycondensation from 3-aminopropyltriethoxysilane as reported in Figure 1.

28.3 mL (0.129 mol) of 3-aminopropyltriethoxysilane dissolved in 88.5 mL of dried ethanol was mixed with 2.097 mL (0.116 mol) of water. The resulting mixture was heated at reflux for 20 hours, cooled to room temperature. Ethanol was then distilled on a rotary evaporator and oligomer **1** was obtained with a yield of 18.7 g (93.5%). The length of the siloxane chains was determined by ^{1}H-NMR.

NMR-^{1}H spectrum (in $CDCl_3$, ppm.): 0,62 m 20H, 10 $SiC\underline{H}_2$; 1,23 m. 36 H, 12 $C\underline{H}_3$; 1,54 m. 20H, 10 CH_2; 2,21 bs 20H,10$N\underline{H}_2$; 2,70 m. 20H, 10$NC\underline{H}_2$; 3 78 m 24H, 12$OC\underline{H}_2$.

2.4 Preparation of coatings.

Cotton samples coated with oligosiloxane containing Im-C6OHCl have been prepared in one-step according to the following procedure:

The cotton sample was kept in ethanol for 20 minutes, heated for 20 minutes at 140 °C, cooled in a closed bottle and weighted. Tetradecaethoxyhexasiloxane (0.0160 g; $1.85 \cdot 10^{-5}$ mol) and Im-C6OHCl (0.0479 g; $1.116 \cdot 10^{-4}$ mol) were dissolved in 5 mL of ethanol.

3% wt sample: 7 mL of ethanol were added to 0.457 g of the solution containing tetradecaethoxyhexasiloxane and Im-C6OHCl. The cotton sample (0.241 g) was immersed in this solution for 1 minute, air dried for 5 minutes and then heated for 1 hour at 80 ^{0}C. The operation was repeated for 8 times until the solution was completely adsorbed by the cotton.

10% wt sample: 23 mL of ethanol were added to 1.522 g of the solution containing tetradecaethoxyhexasiloxane and Im-C6OHCl. The cotton sample (0.242 g) was immersed in this solution for 1 minute, air dried for 5 minutes and then heated for 1 hour at 80 ^{0}C. The operation was repeated for 24 times until the solution was completely adsorbed by the cotton.

The samples have been washed immersing them in water for 1 minute after the last treatment with the solution containing the ionomer. The amount of coating present on the fiber was determined after drying the sample for 1 h at 80 °C from the difference in weight between the coated cotton fabric sample and the native one.

Cotton samples coated with oligosiloxane containing Im-SBA were prepared in two-steps according to the following procedure:

The cotton sample was kept in ethanol for 20 minutes, heated for 20 minutes at 140 °C, cooled in a closed bottle and weighted. Oligomer **1** (0.0024 g for 3% wt, 0.0084 g for 10% wt) was dissolved in 2 mL of ethanol and the cotton sample was immersed in the resulting solution for 10 minutes, removed and air-dried. This operation was repeated several times until the complete exhaustion of the solution. The sample was then heated for 1 hour at 80 °C. Im-SBA (0.0046 g for 3% wt, 0.0165 g for 10% wt) was then dissolved in 2 mL of ethanol and the cotton sample coated with oligomer **1** was immersed in the obtained ionomer solution (that had a oligosiloxane/ionomer molar ratio of 1/6) for 1 minute, removed, air dried for 5 minutes and heated for 1 hour at 80 °C. This operation was repeated several times until the complete exhaustion of the solution. The samples have been washed immersing them in water for 1 minute after the last treatment with the solution containing the ionomer. The amount of coating present on the fiber was determined after drying the sample for 1h at 80 °C from the difference in weight between the coated cotton fabric sample and the native one.

Cotton samples coated with oligosiloxane containing Im-DMSIP were prepared in two-steps according to the following procedure:

The cotton sample was kept in ethanol for 20 minutes, heated for 20 minutes at 140 °C, cooled in a closed bottle and weighted. Oligomer **1** (0.0022 g for 3% wt, 0.0081 g for 10% wt) was dissolved in 2 mL of ethanol and the cotton sample was immersed in the resulting solution for 10 minutes, removed and air-dried. This operation was repeated several times until the complete exhaustion of the solution. The sample was then heated for 1 hour at 80 °C. Im-DMSIP (0.0052 g for 3% wt, 0.0188 g for 10% wt) was then dissolved in ethanol and the cotton sample coated with oligomer **1** was immersed in the obtained ionomer solution (that had a oligosiloxane/ionomer molar ratio of 1/6) for 1 minute, removed, air dried for 5 minutes and heated for 1 hour at 80 °C. This operation was repeated several times until the complete exhaustion of the solution. The amount of coating present on the fiber was determined from the difference in weight between the coated cotton fabric sample and the native one.

Cotton samples coated with oligosiloxane containing Im-DMSIP were prepared in one-step according to the following procedure:

The cotton sample was kept in ethanol for 20 minutes, heated for 20 minutes at 140 °C, cooled in a closed bottle and weighted. Im-DMSIP (0.01742 g) and oligomer **1** (0,0079 g) (with an oligosiloxane/ionomer molar ratio of 1/6) were dissolved in 5 mL ethanol and the obtained solutions were mixed. The cotton samples were then immersed in the resulting solution for 1 minute, removed, air dried for 5 minutes and heated for 1 hour at 80 ^{0}C. This operation was repeated several times until the complete exhaustion of the solution. The amount of coating present on the fiber was determined from the difference in weight between the coated cotton fabric sample and the native one.

2.5 Experimental techniques

2.5.1 NMR

^{1}H-NMR spectra were recorded using a Varian Mercury 400 spectrometer (chemical shifts are downfield from TMS), using $CDCl_3$ as solvent.

2.5.2 FTIR

FTIR spectra were measured on a Fourier transform infrared spectrometer VERTEX 70v (BRUKER, Germany) with a resolution of 4 cm^{-1} in the mode of Attenuated Total Internal

Reflection (ATR) using a set-top box Glady (PIKE). FTIR spectra were corrected using the instrument software to account the dependence of the depth of radiation penetration into the sample from the wavelength.

2.5.3 Antimicrobial tests

The AM activity was assessed by evaluating the survival of bacterial cells exposed to coated and uncoated fabric samples. Two microorganisms were used: a Gram negative bacterium, Escherichia coli ATCC11105, and a Gram positive one, *Staphylococcus aureus* ATCC 6538p. Bacteria were grown aerobically in nutrient broth (Oxoid, Basingstoke, UK) for 16 h at 37 °C. The bacterial culture thus obtained was centrifuged at 7000 rpm for 10 min, washed in sterile phosphate buffer solution (PBS) and re-suspended in the same buffer in order to obtain a cell suspension of 10^6–10^7 colony-forming units per milliliter (CFU/mL). Pieces of each test cotton specimen with a fixed surface area of 4 cm^2 were transferred into capped 2 mL tubes containing 0.2 mL of the PBS cell suspension previously prepared. The tubes were capped, placed in a shaker (Sheldon Manufacturing Inc SI4-2), gently shaken at 30 rpm at 37 °C for 24 h. For each specimen, 6 samples were prepared: 3 of them were processed after 10 min of incubation (to check initial bacterial concentration) and the other 3 at the end of the incubation. In order to count viable bacterial cells 1.8 mL of PBS was added to the tube (thus obtaining a 10^{-1} dilution) which was then serially diluted and 0.1 mL plated on Plate Count Agar. After incubation of the plates at 37 °C for 24 h, the number of colonies, corresponding to the number of viable cells, was counted (CFU/mL). The percentage of reduction of viable cells was determined, after averaging the triplicate counts, through a modification of the equation suggested by Lala et al. [25] as follows:

$R\% = (B - A) / B \times 100$

where R% = Percentage of reduction of viable cells, A = average number of viable bacterial cells obtained after a 24 h exposure to the functionalized fabric, and B = average number of viable bacterial cells at the 24 h incubation with the uncoated fabric.

At a later stage fabric samples have been washed in hot water to check the retention of the AM activity after washing. The fabric samples have been inserted in 10 mL tubes filled with sterile water and immersed in a water bath equipped with a stirrer at 60 °C for 1 h. Washing has been repeated 4 times under shaking and then AM activity has been checked using the procedure described above.

3. Results and Discussion

Imidazolium salts must be modified with reactive groups in order to react with oligosiloxane coatings. For this reason imidazolium has been modified with the insertion of hydroxyl groups (Im-C6OHCl). Moreover, imidazolium groups have been linked by ionic aggregation to groups containing reactive moieties able to react with siloxane groups (Im-SBA and Im-DMSIP). Two types of reactive end-groups have been used for this purpose: carboxylic acid and methyl ester groups. All the imidazolium groups used present a long alkyl chain (with 16 carbon atoms) that is well known to impart antibacterial properties to the imidazolium salt [12]. The synthesis of the imidazolium salts have been performed with the insertion of the C16 alkyl chain followed in the case of ionomer **1** by the insertion of and hydroxyhexyl group and in the case of ionomer **2** and **3** by the exchange reaction with sulfobenzoic acid and of sulfonated dimethyl isophthalate respectively (Figure 2).

The ionomer containing oligosiloxane coatings (**SC**) have been prepared by reaction of siloxane oligomers containing ethoxy groups with the OH groups present on the cotton surface. The oligosiloxanes have been synthesized by hydrolytic polycondensation from 3-aminopropyltriethoxysilane and from tetraethoxysilane. The structures of the oligosiloxanes used are reported in Figure 3. The type of functional groups used has been chosen accordingly to the type of reactive group on the imidazolium salt. In particular, the oligosiloxane with the amino group (**5**) was used for imidazolium salts containing carboxylic acid and ester groups. The number of repeating units of siloxane oligomers has been measured by ^{1}H-NMR.

Two different approaches have been used for the grafting of the imidazolium salt on the surface of cotton: the one-step reaction of the imidazolium with the cotton and with the oligosiloxane and the two-steps reaction in which the oligosiloxane is first reacted with the cotton and then with the imidazolium salt.

Two concentrations of the imidazolium salt on the cotton fiber have been used: 3% and 10% weight gain of the cotton substrate. The reason of these two concentrations is related to previous work [8-10] in this field that generally employs a concentration of AM coating on the cotton fabric between 3 and 10% wt. The amount of imidazolium was measured weighting the cotton sample before and after reaction with imidazolium salts.

Coating **SC-1** with **ionomer 1** was prepared in one-step reaction according to Scheme 1.

Coatings **SC-2** with **ionomer 2** was prepared in two steps procedure according to Scheme 2.

Coatings SC-**3** with **ionomer 3** was prepared in a two-steps reaction according to Scheme 3. In the first step cotton was functionalized with oligo(aminopropylsiloxane) and then reacted with Im-DMSIP while Coating **SC-4** (Scheme 4) was prepared in one-step.

Contact angle analysis showed that all coatings are fully hydrophilic with a contact angle of 0. IR spectra of surface diffuse scattering were taken for the initial cotton sample and for the samples with the coatings. The IR spectra (Figure 4) indicate the formation of oligosiloxane coatings due to the presence of the band at 1560-1567 cm^{-1}, characteristic of the imidazole ring in all samples. A band in the range of 1726-1742 cm^{-1}, corresponding to the ester bond, can be observed in samples **SC-3** and **SC-4.** For the sample **SC-2** (10%) it is possible to observe a band at 1596 cm^{-1}, corresponding to the amide bond and small humps are also present around 1590 cm^{-1} in **SC-3** and **SC-4** FTIR spectra. Due to the small amount of imidazolium used, the FTIR technique is not able to provide quantitative measurements of the groups formed during the reactions between the imidazolium salt, the siloxane oligomer and the surface and therefore the formation of non-covalent linkages (e-g- ionic interactions) between the amino groups of the cotton with the carboxylic acid cannot be excluded.

Antimicrobial tests

The AM activity of the cotton samples has been tested against *E. coli* and *S. aureus*. The percentage of reduction viable cells has been calculated referring to the uncoated cotton sample (as reported in detail in the experimental section) (Table 1).

The results obtained show a very high activity of imidazolium salts linked to the cotton surface that are able to completely reduce the amount of viable cells after 24 h of incubation. All the different imidazolium salts and the approaches used have given a 99.8-100 % reduction of viable cells.
The amount of imidazolium salts does not have any effect on AM activity since 3% and 10% (wt%) both showed a comparable AM activity.
In order to determine the persistence of the AM activity upon washing, the AM test has also been performed after 4 washing cycles at 60 °C with the samples with 3% wt of imidazolium (Table 2).

All the coatings maintain a high AM activity after 4 cycles of washing at 60 °C. In particular, **SC-2** and **SC-3** retain almost completely the AM activity differently from SC-1, which shows a slight reduction of the activity. The fact that in **SC-2** and **SC-3** the imidazolium salts is not covalently linked to the cotton fabric does not have any detrimental effect on the AM activity after washing, indicating that the washing treatment is not able to break the ionic linkage that connect the imidazolium salt to the siloxane oligomer bound to the cotton fabric. The lower AM activity of **SC-1** after washing compared to **SC-2** and **SC-3** indicates that the two-steps method is able to impart a longer lasting AM activity with respect to the one-step method. Another possibility of the decreased AM activity of the **SC-1** sample after washing can be attributed to the hydrolytic removal of Im-C6OHCl during washing.

4. Conclusions

New AM coatings based on imidazolium salts have been prepared. The imidazolium salts have been linked to the cotton fabric using siloxane oligomers as coupling agents. Three different imidazolium salts have been used. In one case the imidazolium was covalently linked to the siloxane while in the other 3 cases the link between the imidazolium and the cotton is made by ionic interactions. FTIR analysis shows that the imidazolium salts are linked to the cotton fabric.

The coatings prepared all have high AM activity at both concentration tested (3% and 10%). The AM activity is mainly retained after 4 cycles of washing especially for the samples prepared using a two-steps procedure that involves first the reaction of the siloxane oligomer with the cotton fabric followed in a second step by reaction of the amide group of the siloxane with the ester group of the derivatized imidazolium salt.

Imidazolium based coatings represent a very promising class of coating for cotton fabric with durable AM activity.

5. References

[1] Y.-A. Son, B.-S. Kim, K. Ravikumar, S.-G- Lee, Imparting durable antimicrobial properties to cotton fabrics using quaternary ammonium salts through 4-aminobenezenesulfonic acid-chloro-triazine adduct, Europ. Polym. J. 42 (2006) 3059-3067.

[2] F. Zhang, D. Zhang, Y. Chen, The antimicrobial activity of the cotton fabric grafted with an amino-terminated hyperbranched polymer. Cellulose 16 (2009) 281-288.

[3] X. Wang, C. Wang, The antibacterial finish of cotton via sols containing quaternary ammonium salts, J. Sol-Gel Sci. Tech. 50 (2009) 15-21.

[4] A. Hou, M. Zhou, X. Wang, Preparation and characterization of durable antibacterial cellulose biomaterials modified with triazine derivatives. Carbohyd. Polym. 75 (2009) 328-332.

[5] E.S. Bang, E.S. Lee, S.I. Kim, Y.H. Yu, S.E. Bae, Durable antimicrobial finish of cotton fabrics, J. Appl. Polym. Sci. 106 (2007) 938-943.

[6] D. Gupta, A. Haile, Multifunctional properties of cotton fabrics treated with chitosan and carboxymethyl chitosan, Carbohyd. Polym. 69 (2007) 164-171.

[7] G. Totaro, L. Cruciani, M. Vannini, G. Mazzola, D. Di Gioia, A. Celli, L. Sisti, Synthesis of castor oil-derived polyesters with antimicrobial activity, Eur. Polym. J. 56 (2014) 174-184.

[8] B.A. Izmailov, V.M. Gorchakova, Defense of textile materials from biodeterioration and moisture, Non-woven materials 1 (2008) 10-12.

[9] N.A. Karmishina, E.N. Rodlovskaya, B.A. Izmailov, V.A. Vasnev, M.I., Buzin Synthesis and Fungicidal Properties of New Bisphenol-Containing Oligoorganosiloxanes, Russian J. Appl. Chem. 85 (2012) 675–678.

[10] B.A. Izmailov, Synthesis and properties of fibrous sorbents with imparted nano-dimensional organosiloxanes the polymeric coverings containing aminomethylenphosphonic ligands, The Bulletin of the Moscow state textile university (2010) 55-58.

[11] W. Hilmes, F. Mueller, T. Neil, H. Schramm, (Goldschmidt AG TH) Eur. Pat. 0796557 (1997).

[12] D. Demberelnyamba, K. Ki-Sub, P. Seung-Yeob, L. Huen, K. Chang-Jin, Y. Ick-Dong, Synthesis and antimicrobial properties of imidazolium and pyrrolidinonium salts, Bioorg. Med. Chem. 12 (2004) 853-857.

[13] S. Sowmiah, V. Srinivasadesikan, M.-C. Tseng, Y.-H. Chu, On the Chemical Stabilities of Ionic Liquids, Molecules 14 (2009) 3780-3813.

[14] E. Anderson, T.E. Long, Imidazole- and imidazolium-containing polymers for biology and material science applications, Polymer 51 (2010) 2447-2454.

[15] N. Preethi, H. Shinohara, H. Nishide, Reversible oxygen-binding and facilitated oxygen transport in membranes of polyvinylimidazole complexed with cobalt-phthalocyanine, React. Funct. Polym. 66 (2006) 851-855.

[16] N. Le Poul, M. Campion, B. Douziech, Y. Rondelez, L. Le Clainche, O. Reinaud, Y. Le Mest, Monocopper center embedded in a biomimetic cavity: From supramolecular control of copper coordination to redox regulation, J. Am. Chem. Soc. 129 (2007) 8801-8810.

[17] B. Yu, F. Zhou, H. Hu, C. Wang, W. Liu, Synthesis and properties of polymer brushes bearing ionic liquid moieties, Electroch. Acta 53 (2007) 487-494.

[18] S.-G. Lee, Functionalized Imidazolium Salts for Task- Specific Ionic Liquids and their Applications, Chem. Comm. (2006) 1049-1063.

[19] D. Batra, D.N.T Hay, M.A. Firestone, Formation of a Biomimetic Liquid-Crystalline Hydrogel by Self-Assembly and Polymerization of an Ionic Liquid, Chem. Mater. 19 (2007) 4423-4431.

[20] M. Scott, M. Rahman, C. Brazel, Application of ionic liquids as low-volatility plasticizers for PMMA, Eur. Polym. J. 39 (2003) 1947-1953.

[21] A. Dias, S. Marceneiro, M. Braga, J. Coelho, A. Ferreira, P. Simões, H. Veiga, L. Tomé, I. Marrucho, J. Esperança, A. Matias, C. Duarte, L. Rebelo, H. de Sousa, Phosphonium-based ionic liquids as modifiers for biomedical grade poly(vinyl chloride), Acta Biomater. 3 (2012) 1366-1379.

[22] M. Colonna, C. Berti, E. Binassi, M. Fiorini, S. Sullalti, F. Acquasanta, M. Vannini, D. Di Gioia, I. Aloisio, S. Karanam, D.J. Brunelle, Synthesis and characterization of imidazolium telechelic poly (butylene terephthalate) for antimicrobial applications, React. Funct. Polym. 72 (2012) 133-141.

[23] M. Colonna, C. Berti, E. Binassi, M. Fiorini, S. Sullalti, F. Acquasanta, M. Vannini, D. Di Gioia, I. Aloisio, Imidazolium poly (butylene terephthalate) ionomers with long-term antimicrobial activity, Polymer 53 (2012) 1823-1830.

[24] L. Sisti, L. Cruciani, G. Totaro, M. Vannini, C. Berti, C., I. Aloisio, D. Di Gioia, Antibacterial coatings on poly (fluoroethylenepropylene) films via grafting of 3-hexadecyl-1-vinylimidazolium bromide, Prog. Org. Coat. 73 (2012) 257-263.

[25] N.L. Lala, R. Ramaseshan, L. Bojun, S. Sundarrajan, R.S. Barhate, L. Ying-Jun, S. Ramakrishn, Fabrication of nanofibers with antimicrobial functionality used as filters: protection against bacterial contaminants, Biotechnol. Bioeng. 97 (2007) 1357–1365.

Figure Captions

Figure 1: Oligo(aminopropylsiloxane) synthesis.

Figure 2: Chemical structures of Im-C6OHCl (**1**), Im-SBA (**2**), Im-DMSIP (**3**) ionomers.

Figure 3: Chemical structures of tetradecaethoxyhexasiloxane (**4**), oligo(aminopropylsiloxane) (n=10) (oligomer I) (**5**) siloxane oligomers.

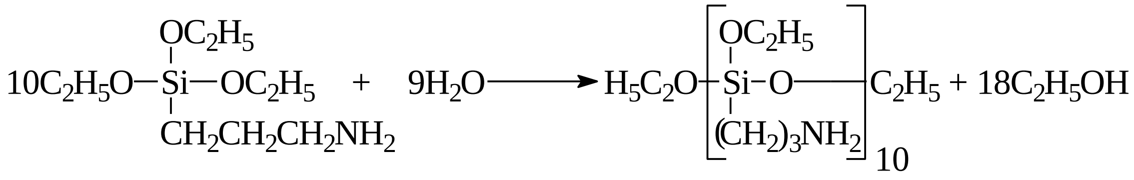
Figure 4: FTIR spectra of the modified and un-modified cotton.

Scheme 1: Functionalization of cotton with Im-C6OHCl in one-step.

Scheme 2: Functionalization of cotton with Im-SBA in two-steps with a first reaction of cotton with the oligosiloxane and subsequent reaction with Im-SBA.

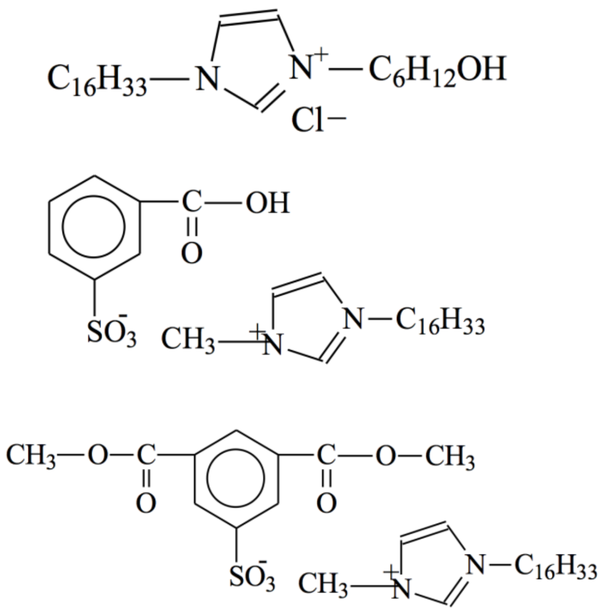
Scheme 3: Functionalization of cotton with Im-DMSIP in two-steps with a first reaction of cotton with the oligosiloxane and subsequent reaction with Im-DMSIP.

Scheme 4: Functionalization of cotton with Im-DMSIP in one-step.



$$10C_2H_5O-\underset{CH_2CH_2CH_2NH_2}{\overset{OC_2H_5}{Si}}-OC_2H_5 + 9H_2O \longrightarrow H_5C_2O\left[\underset{(CH_2)_3NH_2}{\overset{OC_2H_5}{Si}}-O\right]_{10}C_2H_5 + 18C_2H_5OH$$

Figure 1: Oligo(aminopropylsiloxane) synthesis.



Im-C6OHCl (**1**)

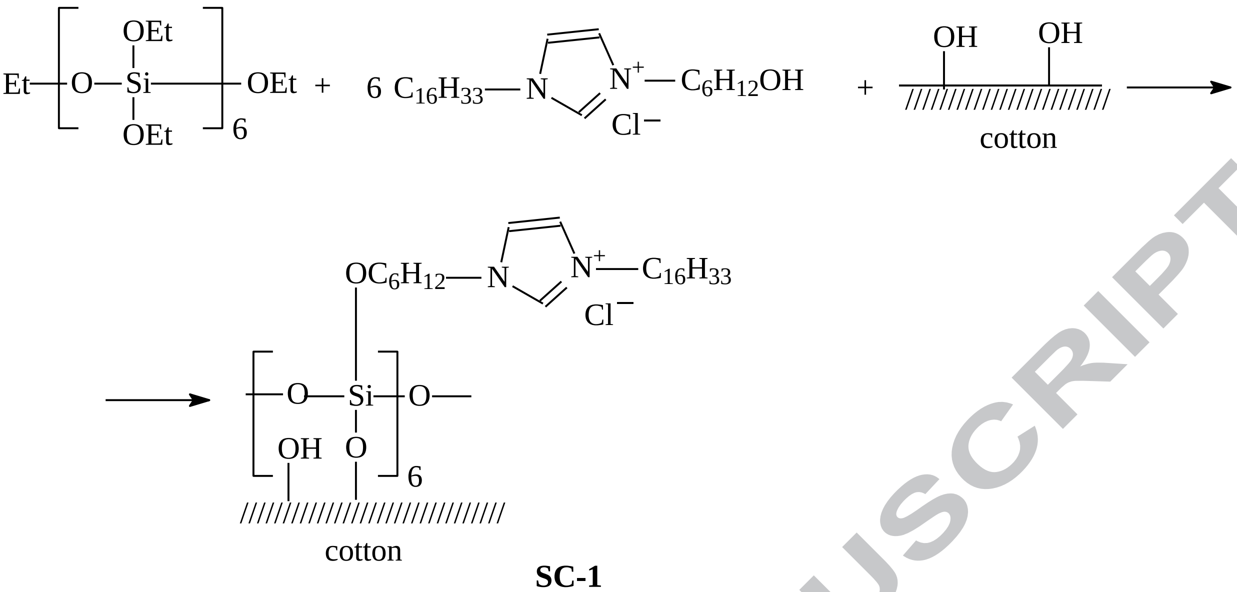
Im-SBA (**2**)

Im-DMSIP (**3**)

Figure 2: Chemical structures of Im-C6OHCl (**1**), Im-SBA (**2**), Im-DMSIP (**3**) ionomers.

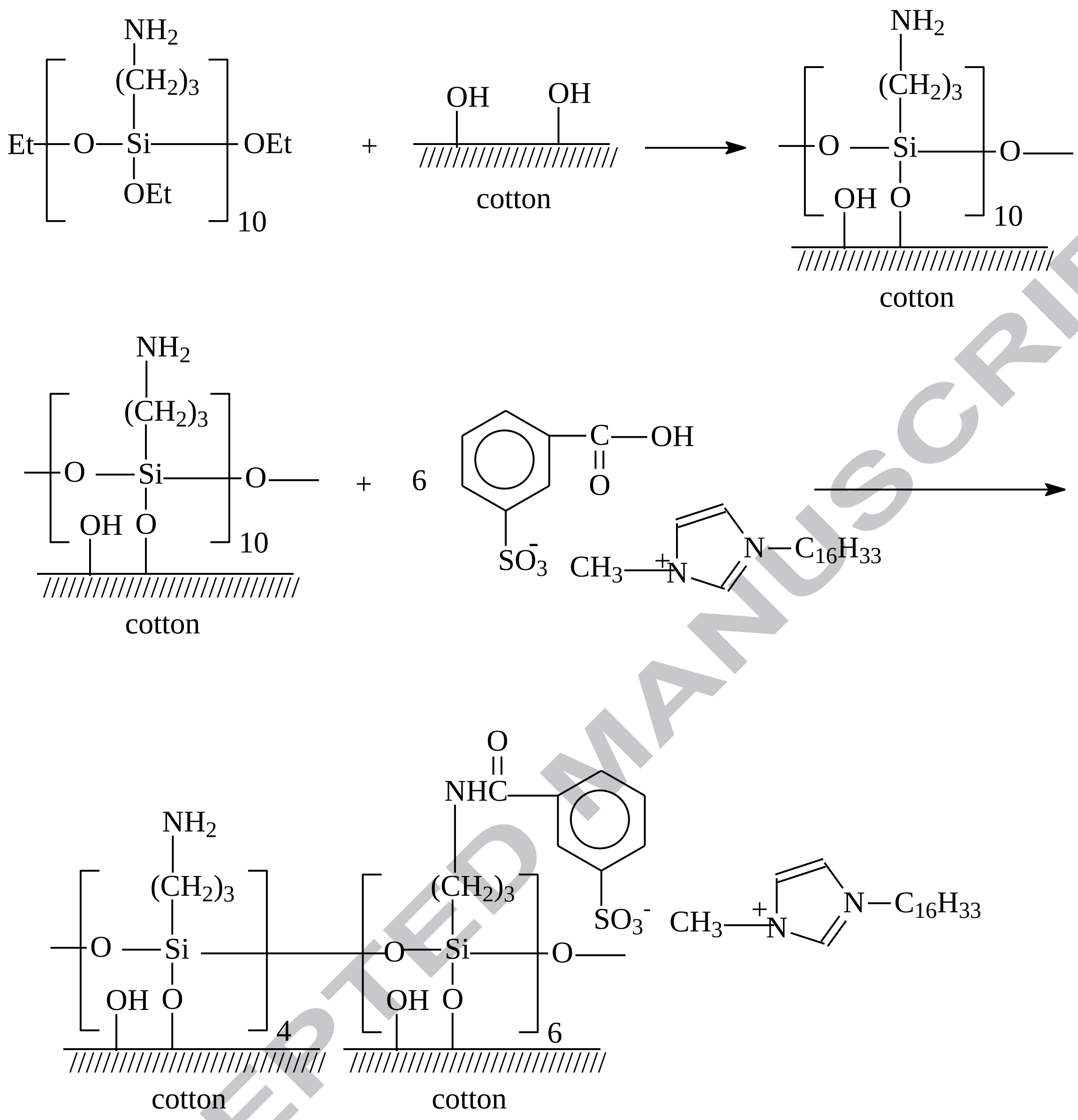
(4) (5)

Figure 3: Chemical structures of tetradecaethoxyhexasiloxane (**4**), oligo(aminopropylsiloxane) (n=10) (oligomer I) (**5**) siloxane oligomers.



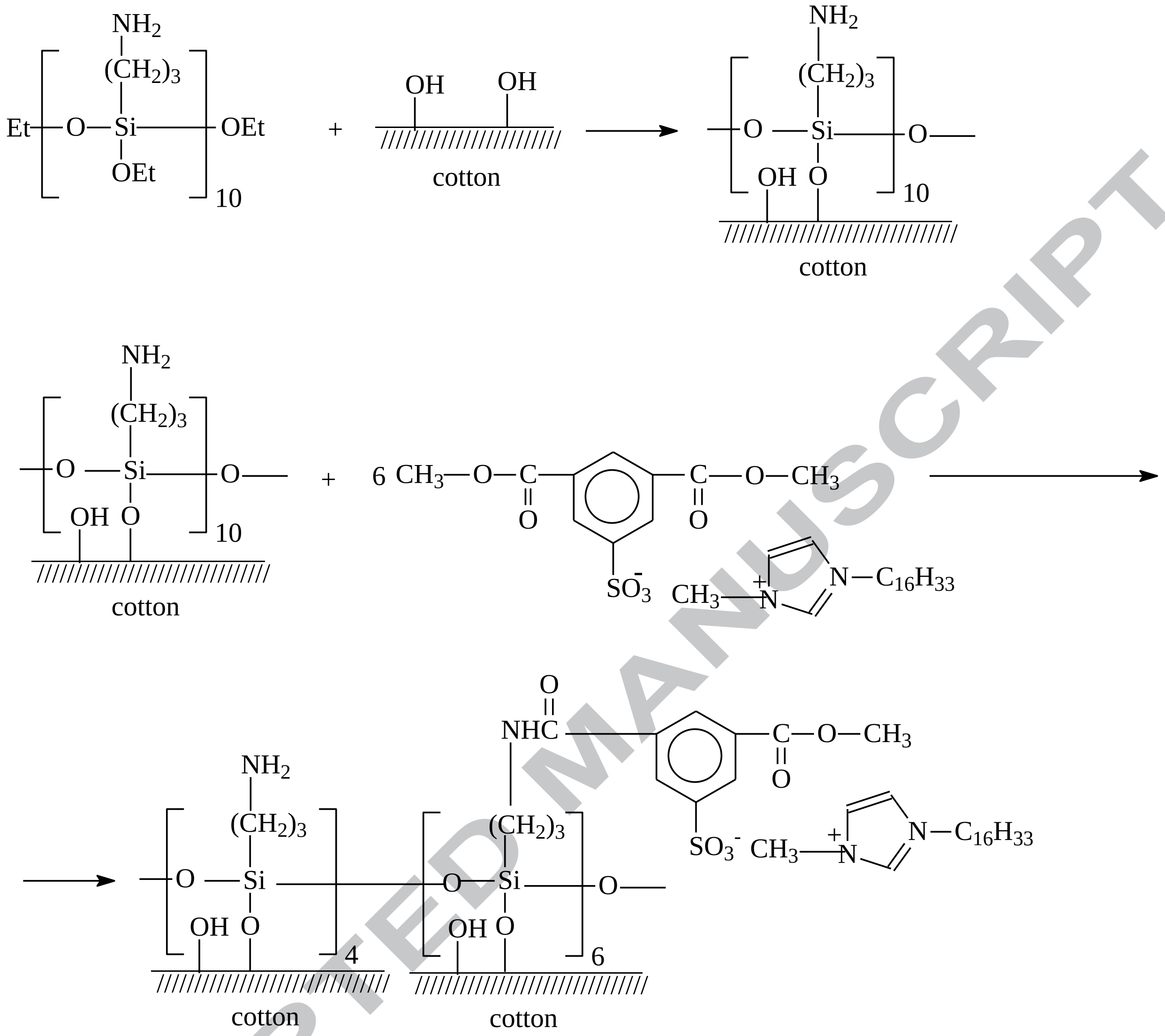
SC-1

Scheme 1: Functionalization of cotton with Im-C6OHCl in one-step.



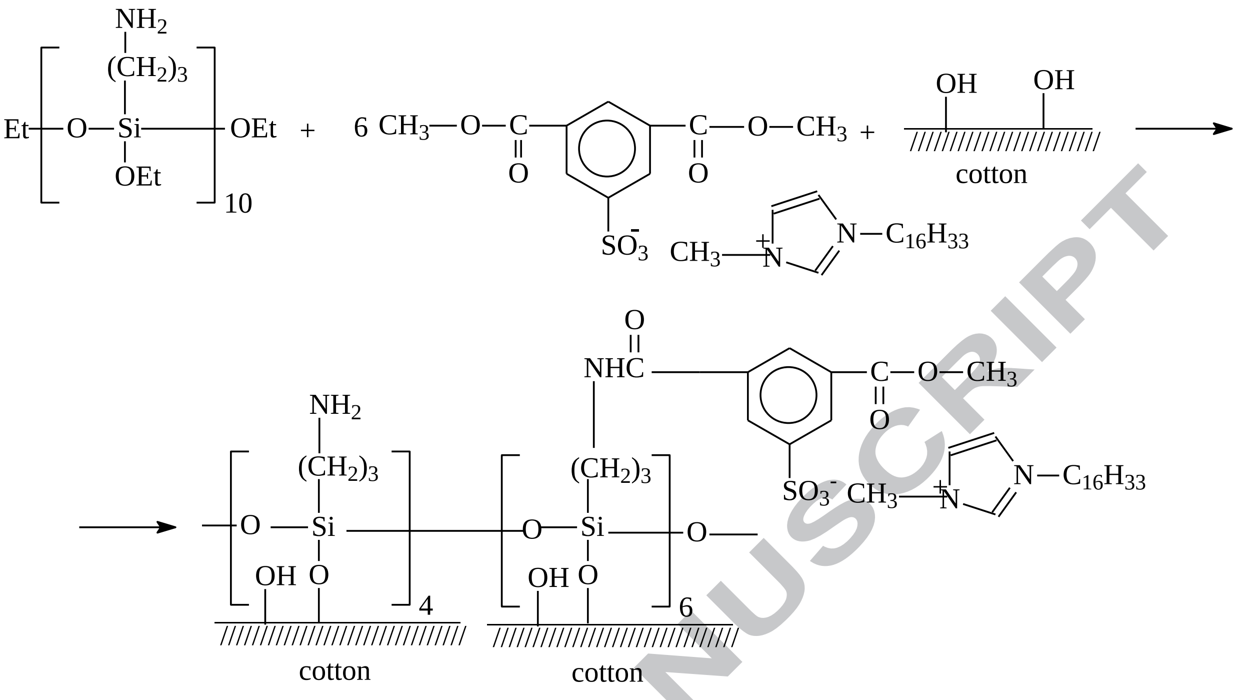
SC-2

Scheme 2: Functionalization of cotton with Im-SBA in two-steps with a first reaction of cotton with the oligosiloxane and subsequent reaction with Im-SBA.



SC-3

Scheme 3: Functionalization of cotton with Im-DMSIP in two-steps with a first reaction of cotton with the oligosiloxane and subsequent reaction with Im-DMSIP.



SC-4

Scheme 4: Functionalization of cotton with Im-DMSIP in one-step.

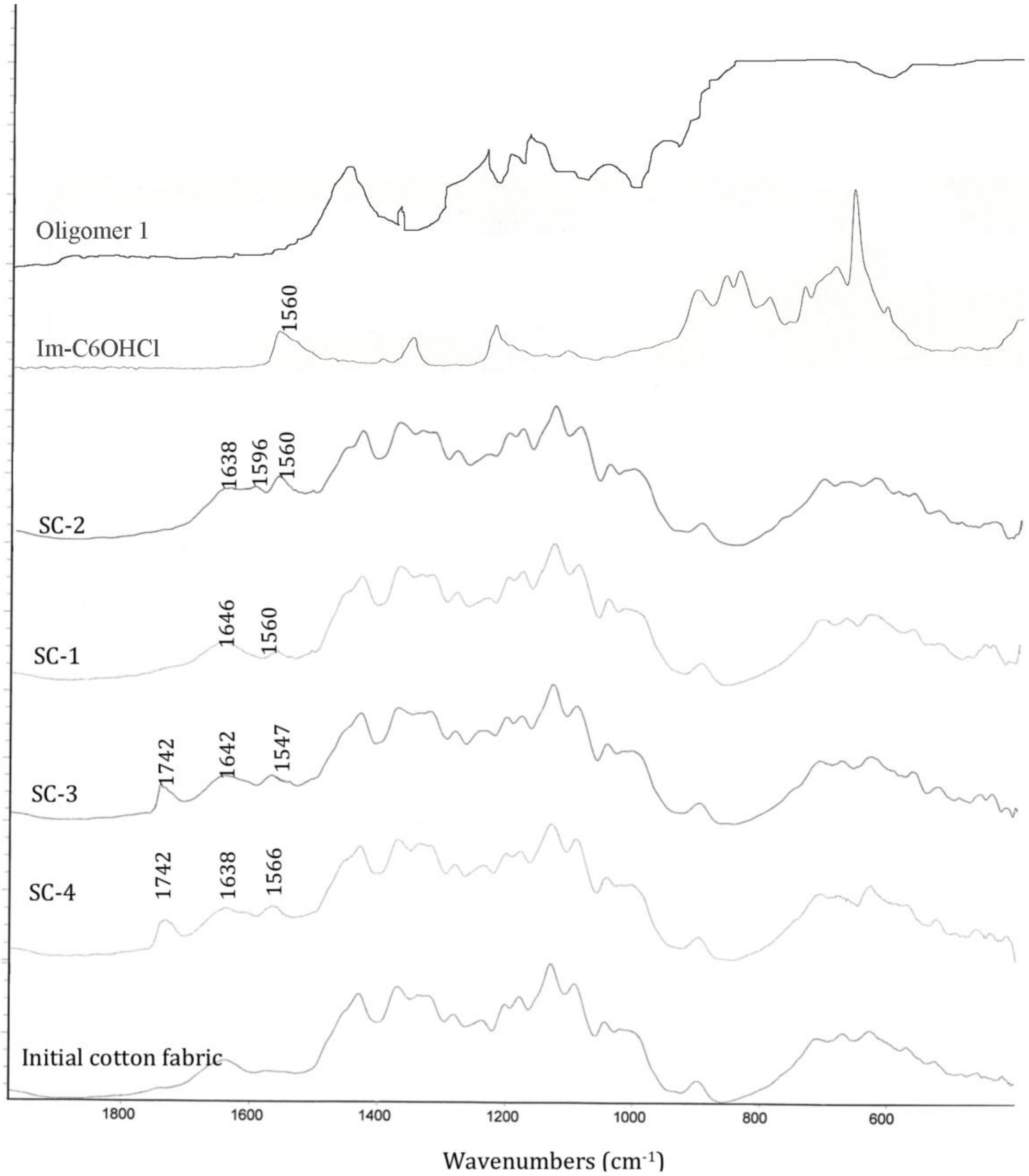


Figure 4: FTIR spectra of the modified and un-modified cotton.

Table 1: antimicrobial activity of the cotton samples treated with imidazolium salts.

		Percentage of reduction of viable cells	
Type of coating	Amount of imidazolium (wt%)	*E. coli*	*S. aureus*
SC-1	3%	100.00	100.00
SC-1	10%	100.00	100.00
SC-2	3%	99.82	100.00
SC-2	10%	100.00	100.00
SC-3	3%	99.85	100.00
SC-3	10%	100.00	100.00
SC-4	10%	100.00	100.00

Table 2: antimicrobial activity of the fibers with 3% wt of imidazolium salts after 4 cycles of washing at 60 °C.

Type of coating	Percentage of reduction of viable cells	
	E. coli	*S. aureus*
SC-1	88.2	60.0
SC-2	97.4	87.0
SC-3	93.6	98.8