Antibacterial Activity of Modified Polyamide Fibers

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ABSTRACT: Polyamide fibers were modified for the attainment of antibacterial activity using a graft copolymerization method. The fibers were grafted with monomers containing quaternary ammonium groups using sodium persulfate as initiator. Two monomers were used as vinyl monomers. The first monomer, called METAC, is methacryloyloxyethyl trimethylammonium chloride [$H_2C = C(CH_3)$-$CO_2CH_2CH_2N(CH_3)_3Cl$]. The second monomer, denoted CATAL, is a methacryloyloxyethyl dimethyldodecylammonium bromide [$H_2C = C(CH_3)CONHCH_2CH_2CH_2N$-$(CH_3)_2(C_{12}H_{25})Br$], kindly supplied by Catalyze (France). The graft copolymerization was confirmed by several methods such as elemental analysis and FTIR spectroscopy. The antibacterial activity of modified samples was investigated against *Staphylococcus aureus* using the antibacterial standard AFNOR test method XP G39–100. Polyamide fibers grafted with the second monomer exhibit high antibacterial activity against *S. aureus*, but the fibers grafted with the methacryloyloxyethyl trimethylammonium chloride did not. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 997–1000, 2005

Key words: antibacterial activity; quaternary ammonium; grafting; copolymerization; polyamide

INTRODUCTION

The modification of textiles to enable them to inactivate microorganisms is useful for a variety of applications. Medical products are perhaps the largest application. In health- related professions, protection from pathogens is a growing concern, and textiles with antimicrobial properties are desirable. Bacteria are responsible for significant infections and allergy problems. Less obvious applications for antimicrobial textiles include air filters, carpets, draperies, etc., particularly in environments where susceptible individuals live (e.g., sick, elderly). Prevention of odor and discoloration of the textile are significant, if less critical, reasons to use antimicrobials. Beside, consumers are showing increasing interest in antimicrobial products. The applications listed above are high-volume uses, and the resulting products become pervasive throughout the medical services and filtration industries, home furnishings, and apparel items.

To avoid contamination, some methods have been used to provide textiles with antibacterial functions such as finishing,[1,2] coating,[3,4] incorporation during spinning,[5–7] and grafting.[8–14]

We were interested in finding a convenient method that could be used to prepare polyamide fibers to which were covalently bonded antibacterial species. Thus, we choose graft copolymerization. In this study, we grafted vinyl monomers containing quaternary ammonium groups. They are used in therapeutics because of their disinfectant properties. These entities are responsible for imparting antibacterial activity. In fact, the quaternary ammonium group inhibits the growth of a wide variety of bacteria. There is no fixed theory. One of the theories is as follow. The quaternary ammonium group, having a polycationic nature, interacts with the negative charges on the cell wall of bacteria.[15,16] When the grafted polyamide fibers charged positively made contact with bacteria charged negatively, the quaternary ammonium cations on the grafted fibers were released and adsorbed on the cell surface. This results in the diffusion of the cations through the cell wall and the destruction of the bacteria.

The scope of the current work was to compare the activity of both monomers and then to investigate the effect of the structure of the monomer on antibacterial activity.

EXPERIMENTAL

Materials

A textured polyamide 6,6 yarn kindly provided by Nylstar was used in our studies. For antibacterial activity experiments, we needed intimate and repeatable

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contact between the sample and the medium contaminated with bacteria. Thus, the yarns were knitted using a flat machine. The used knitted structure has a good dimensional stability. Polyamide knitted fabrics were used after Soxhlet extraction in petrol ether (deoiling). They were then dried at room temperature to a constant weight. Two different monomers containing ammonium quaternary groups were used. The first one, METAC, is methacryloyloxyethyl trimethylammonium chloride [$H_2C = C(CH_3)CO_2CH_2CH_2N(CH_3)_3^+ Cl^-$] obtained from Aldrich. The second one, CATAL, is methacryloyloxyethyl dimethyldodecylammonium bromide [$H_2C = C(CH_3)CONHCH_2CH_2CH_2N(CH_3)_2(C_{12}H_{25})^+Br^-$], kindly supplied by Catalyze (Marseille, France). Both monomers were of pure grade and used without further treatments.

The initiator employed in this study was sodium persulfate (Aldrich), used without further purification.

Graft copolymerization

The optimum conditions for each graft copolymerization were investigated in detail in a previous paper.[17] Briefly, knitted fabric (0.5 g) was placed into a reactor equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a nitrogen supply. The grafting was carried out in a definite volume of bidistilled water containing the required amounts of monomer and initiator. Active centers on the polyamide were formed by treatment with sodium persulfate and bound with the monomer groups. After the grafting procedure, the knitted fabrics obtained were purified by extraction of unreacted monomers and homopolymers with boiled water. After extraction, the grafted fabrics (PA-*g*-METAC and PA-*g*-CATAL) were dried in an oven for 24 h at 30°C.

Characterization

Elemental analysis

The monomers used METAC and CATAL for grafting contain chlorine (Cl) or bromine (Br), respectively, elements absents from the structure of polyamide. Thus, we made an elemental analysis of these elements. The analyses were achieved in a CNRS laboratory (Vernaison). The obtained results (%Cl or %Br) were expressed in grams per 100 g of grafted fiber and used to determine the number of moles of grafted monomer (N).

$$N = \%\ \text{Element}/M_{\text{element}} \quad (1)$$

where N = number of moles of monomer (METAC or CATAL) per 100 g of grafted fibers, % element = %Cl or %Br (elemental analysis), and M_{element} = molar mass of Cl or Br.

TABLE I
Optimum Conditions of Grafting[17]

Parameters	
Monomer concentration (mol/l)	1,8
Initiator concentration (mol/l)	2.10^{-2}
Temperature (°C)	90
Time reaction (min)	120

FTIR spectroscopy

The FTIR spectra were recorded for ungrafted and grafted polyamide 6,6 using a microscope connected to Nexus FTIR spectrometer (Nicolet).

Antibacterial assessment

Antibacterial properties of the fabrics were assessed using a direct method (standard XP G 39–010).[18] It consists of the placement of fabric samples (a disc of 3.8 mm diameter) onto an agar support inoculated with tested bacteria. After the required incubation time (24 h), the dimensions of inhibition zones around the fabrics were measured. Then, each sample was placed in a flask containing a nutrient medium. The suspension was diluted several times and was spread on an agar plate made of nutrient agar for 48 h. The number of viable cells was calculated by counting the number of the colonies formed on the plate. The test provides a quantitative evaluation of the residual bacterial activity of the sample. Each experiment was repeated at least three times. The given results were an average of the three experiments.

Briefly, the antibacterial activity is estimated first by a millimeter measurement of the diameter of the zone of inhibition and second by a quantification of the number of viable bacteria, N, after contact.

The bacteria used in this study were *Staphylococcus aureus* (ATCC 6538). These stains came from the Institut Pasteur (Lille). Cultured cell suspensions contain about 10^6–10^8 colony forming units (CFU)/mL.

RESULTS AND DISCUSSION

Graft copolymerization

Graft copolymerization of monomers containing quaternary ammonium groups onto knitted polyamide fibers was carried out under various conditions (monomer concentration, initiator concentration, temperature) using sodium persulfate as initiator.

The grafting percentage G was calculated by using the formula

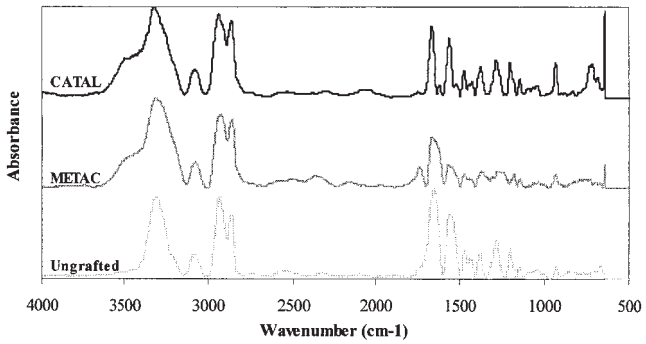

Figure 1 IR spectra of the original fabric and the grafted fabric.

$$G = [W_f - W_i / W_i] \times 100 \quad (2)$$

where W_i and W_f are the weights of the polyamide knitted fabrics before and after graft polymerization.

In our previous paper[17] we showed that the grafting percentage increased with increasing monomer concentration, initiator concentration, and temperature and then decreased. These results indicate that with an excess of monomer or initiator or at a higher temperature than the appropriate one, the reactions that are competitive with the grafting like homopolymerization probably take place in the solution.

By looking for the optimum conditions (monomer concentration, initiator concentration, temperature, and reaction time), we reach a grafting percentage of around 22% for both monomers. The optimum conditions of METAC grafting are shown in Table I. These samples were tested for antibacterial activity.

Characterization

The elemental analyses performed on grafted fabrics confirm that grafting occurs on polyamide. In fact, 0.186 mol METAC and 0.138 mol CATAL were found on grafted fibers (eq. 1).

The FTIR spectra of ungrafted and grafted fibers are given in Figure 1. The spectrum of fibers grafted with METAC shows a peak of interest at 1730 cm^{-1} characteristic of the stretching vibration of the COOR group present in the METAC species. Moreover, the spectrum of fibers grafted with CATAL has an absorption peak at 1622 cm^{-1}, characteristic of the stretching vibration of the C = O group present in the CATAL species. These facts confirm the chemical grafting of METAC and CATAL units onto the polyamide 6,6 fibers.

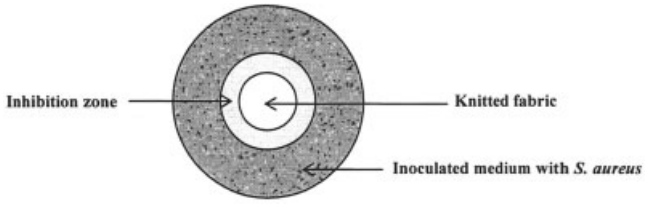

Figure 2 Inhibition zone around the sample.

TABLE II
Antibacterial Activity by Contact of Knitted Fabrics Grafted by the Monomers

	Length of the zone with inhibited bacterial growth (mm)	
	Reference sample	Grafted sample
METAC	0	0
CATAL	0	2

Antibacterial activity

The antibacterial activity of the grafted polyamide knitted fabrics against *S. aureus*, Gram-positive bacteria, was investigated. Both samples, PA-*g*-METAC and PA-*g*-CATAL, have almost the same polymer add-on.

Several cases can arise for measurements:

Colonies develop around the fabric and a check of the effectiveness by a numeration of the colonies is required.

A zone of inhibition appears around the fabric: the product has an effectiveness by diffusion.

The more significant the zone of inhibition is, the more active the product is by diffusion.

The first step is the test by contact, allowing us to check whether there is activity by migration of biocide molecules in the contaminated medium. The activity by diffusion is quantified by the measurement in millimeters of the width of the zone of inhibition around the sample (Fig. 2).

The results of the PA-*g*-METAC and PA-*g*-CATAL fabrics are collected in Table II. The contact time was 24 h.

Data indicate that the PA-*g*-METAC fabrics were inactive against *S. aureus*. To the contrary, fabrics bounded with CATAL were active against *S. aureus*. In fact, the inhibition zone for the PA-*g*-CATAL is significant (2 mm), whereas it is null for the PA-*g*-METAC.

TABLE III
Estimation of Viable Bacterial Cells (CFU/surface)

	Reference sample		Grafted sample	
	N_0	N	N_0	N
METAC	1.5×10^3	1.8×10^3	1.5×10^3	1.8×10^3
CATAL	10^6	$> 10^6$	10^6	0

N_0: number of bacteria deposited initially
N: number of viable bacteria found after contact

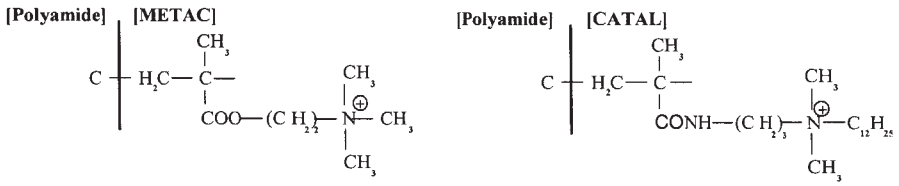

Figure 3 Grafted fibers with both monomers.

The reference sample (neat polyamide) shows in both cases a null inhibition zone. The compounds brought by CATAL on the knitted fabric have an effectiveness by diffusion.

After the incubation period of 24 h, the fabrics, tested previously, were placed in a nutrient suspension to quantify their effectiveness by numeration of the viable bacteria. The results are presented in Table III.

As expected, for the PA-*g*-METAC fabrics and the reference samples, no reduction of bacteria is noticed but a slight proliferation. On the contrary, the PA-*g*-CATAL fabrics exhibit high effectiveness by destroying all bacterial cells.

For the PA-*g*-CATAL fabrics, the presence of a zone that inhibits bacterial growth and the absence of germs after numeration show that grafting CATAL provide polyamide with antibacterial activity against *S. aureus*. However, grafting METAC on polyamide is ineffective.

A hypothetical explanation of these results concerns the length of the alkyl radicals in the monomers. The structure of the grafted fibers is reported in Figure 3. The N atom has a valency of five; three of the substituent radicals are alkyl radicals and the fourth is an anion (Cl^- or Br^-). One of the alkyl radical in CATAL contains 12C whereas all alkyl radicals in METAC are methyl (1C). It could be reasonably deduced that the antibacterial effects are linked to the presence of a long chain since the grafting percentage is almost the same for both fibers.

CONCLUSIONS

This work examined the antibacterial activity of modified textiles. The antibacterial textiles were prepared by grafting quaternary ammonium compounds. Thanks to this method, the antibacterial functionality was covalently bonded to the textile material (vinyl monomers). Two monomers were used: METAC and CATAL on polyamide knitted fabrics. The PA-*g*-METAC were inactive against *S. aureus*, whereas the PA-*g*-CATAL exhibited high antibacterial activity against *S. aureus*.

The process investigated in this study for the attachment of active sites in textiles should be useful for a variety of applications other than antibacterial action.

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