Synthesis and Characterization of Novel Biocidal Cyclodextrin Inclusion Complexes Grafted onto Polyamide-6 Fabric by a Redox Method

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ABSTRACT: The synthesis of immobilized β-cyclodextrin derivatives onto polyamide-6 fabric is presented. These novel fabrics were prepared by graft-copolymerization of glycidyl methacrylate (GMA) onto polyamide 6 fabric, using a chemical redox system $K_2S_2O_8/CuSO_4{\cdot}5H_2O$, followed by reaction of β-cyclodextrins (CD) or monochlorotriazinyl (MCT β-CD) with the GMA epoxy group. Some biocidal guests were complexed into CD cavity including *p*-hydroxy benzoic acid, $AgNO_3$–ethanolamine mixture, iodine, *N*,*N*-diethyltoluamide (DETA), citronella, jasmine, and sweet basil. Characterization of the novel fabrics was done by Fourier transform infrared spectroscopy (IR), electron scanning microscopy (SEM), and thermo gravimetric analysis (TGA). The biocidal activity of the grafted fabrics was tested against five strains of microorganisms. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2586–2593, 2006

Key words: PA-6; grafting; redox system; GMA; β-CD; MCT β-CD; CD inclusion compounds

INTRODUCTION

Some microorganisms are highly undesirable[1] since they are the cause of odors, skin irritation, and illness. The odor on clothing arises primarily as a result of bacteria and fungi that grow in the perspiration and on the skin cells that are in contact with the clothing. Bacteria, fungi are deposited on carpets through the normal traffic of people and animal. Food and beverages are often spilled on the carpet. Nylon surgical sutures incorporated into tissues and soaked with liquids that are potential culture media for bacteria may bring about lasting infection. Therefore, it is important that the nylon products should have antimicrobial activity.

The new modification of synthetic fibers surface by fixation of supramolecular compounds like β-cyclodextrin (CD) or monochlortriazinyl β-cyclodextrin (MCT β-CD), which contain some biocidal and reactive groups such as the triazinyl ring in addition to the presence of the chlorine atom, are very interesting.[2] Such host inner cavity CD compounds are able to form inclusion guest complexes with other chemical substances, and thus, the treated fibers containing CD groups will achieve new functional properties by selective inclusion of such compounds in the fixed CD cavities. Also, the complexed guest compounds may be released from the fibers at a special rate depending on the surrounding conditions. The inner CD cavity of molecules shows hydrophobic character, so that organic compounds containing nonpolar groups may be included in the CD cavity. As a result of this inclusion, the physicochemical properties of the included guest compounds are changed, i.e., the vapor pressure of the volatile substances is reduced and the stability of fibers sensitive to light and air is enhanced.[3,4] The CD complexes compounds may be volatile perfumed extracts, odorous human sweat, or specific active agents. This modification of the finishing process is important for the production of medical and upholstery textiles. Several articles and patents reported on relevant applications of CD in antimicrobial, insect-free, aroma finishing, and in textile dyeing through the formation of physical bonds to different fibers.[5–8]

Nowadays, cyclodextrins are used in pharmaceutical and cosmetic applications. Industrial applications[9] have also become possible owing to new improved cyclodextrins from industrial-production processes.

In the present work, glycidyl methacrylate (GMA) was used to graft PA. It is an interesting monomer because of the high reactivity of the epoxy group.

We proceeded by linking β-CD or MCT β-CD to polyamide-6 fabric grafted with GMA.

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A series of successive reactions were done to produce the new biocidal textiles. The modifications of the PA fabric were in the following order:

- Initiation of PA-6 fabrics using a chemical redox system of $K_2S_2O_8/CuSO_4{\cdot}5H_2O$ to create active sites onto the fabric.
- Graft polymerization of GMA monomer onto the PA actives sites to produce PA/GMA with different graft add.
- Chemical bonding of β-CD (or MCT β-CD) onto the grafted PA/GMA to produce PA/GMA/CD copolymers of different CD content.
- Formation of inclusion complexes into the CD cavity by introduction of guest molecules such as *p*-benzoic acid, $AgNO_3$–ethanolamine mixture, iodine, *N*,*N*-diethyltoluamide (DETA), citronella, jasmine, and sweet basil as biocidal antiseptic agents.
- Analysis of the produced biocidal fabric by infrared spectroscopy (IR), thermo gravimetric analysis (TGA), and electron scanning microscopy (SEM).
- The prepared fabrics were tested for antibacterial activity against five strains of bacteria.

EXPERIMENTAL

Materials

PA-6 fabric (warp 24 ends/cm, weft 36 picks/cm) was obtained from El Nasr Co. (El-Shorbagy). The GMA monomer (purity 98%) stabilized by 0.005% methylhydroquinone was supplied by Fluka Co. and used without further purification. β-Cyclodextrins or monochlorotriazinyl β-cyclodextrin were supplied from Wacker Gmbh, Munich, Germany. Potassium persulfate ($K_2S_2O_8$), copper sulfate ($CuSO_4{\cdot}5H_2O$), sodium chloride, and *N*,*N*′-dimethylformamide (DMF) were used as grade reagents.

Technical procedures

Fabric washing

PA-6 fabric was washed for 30 min, with a 2 g/L nonionic detergent solution at 45°C and air dried at room temperature.

Graft polymerization reaction

PA-6 fabric, 0.5 g, was immersed in 3% $K_2S_2O_8$ solution for 20 min at room temperature. The sample was then squeezed, thoroughly washed with water, and dried with a filter paper. The sample was then introduced into a stoppered flask containing 50 mL of the solution consisting of water, monomer, copper sulfate with the specified concentrations, and three drops of nonionic detergent as an emulsifier agent at 75°C for 1 h, at a liquor ratio 1:30. The sample was washed with warm and cold distilled water, extracted with acetone to remove any residual homopolymer, then dried, and the percentage GMA add-on onto PA-6 was calculated as follows:

$$\% \text{ GMA} = \frac{W - W_0}{W_0} \times 100$$

where W_0 and W represent the initial PA and PA/GMA grafted weights, respectively.

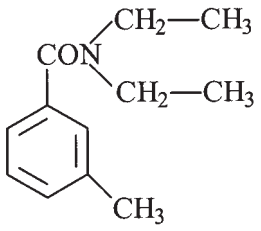
Immobilization of β-CD onto PA/GMA

The PA/GMA grafted sample, 1 g, W_1 was immersed into 100 mL of a solution consisting of (50% water/DMF) 2.2 g β-CD (or MCT β-CD), and 3% soduim hydroxide were added. The mixture was stirred at 80°C for the specific time. The final product was then washed with warm distilled water, dried, and weighed, W_2. The percentage of grafted β-CD was determined as follows:

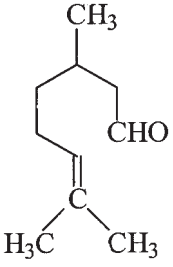
$$\% \text{ add on } \beta\text{-CD} = \frac{W_2 - W_1}{W_1} \times 100$$

Biocidal finishing of grafted PA/GMA fabrics with CD inclusion complexes

One gram of PA/GMA/β-CD grafted fabric was immersed in 25 mL of (50% ethanol–distilled water) containing 2% guest molecules, including *p*-hydroxy benzoic acid, $AgNO_3$–ethanolamine mixture, iodine, DETA, citronella, jasmine, or sweet basil. They were stored for 24 h in the dark at ambient temperature to form the inclusion complexes in the grafted CD molecules. They were then washed with cold distilled water, ethanol, air-dried, and the percentage increase in weight determined.



N,N-diethyl-m-toluamide
(DETA)



Citronella

Measurements

Infrared spectroscopy

The IR samples spectra were recorded on a Perkin–Elmer 781 Infrared Spectrophotometer.

Ultraviolet spectroscopy

UV spectra for the determination of aqueous benzoic acid concentrations were done with a Kontron Spectrophotometer

Thermal gravimetric analysis

Thermal gravimetric analysis TGA was carried out using a Perkin–Elmer 7 device.

The heating rate was adjusted at 10°C/min over a heating range of 50–650°C.

Scanning electron microscopy

SEM micrographs were done on JEOL Model JSM-T20 Instrument operating at 19 kV. Photos were prepared at a magnification range 500–1000×

Antimicrobial activity

The antimicrobial activity was determined by the diffusion disc method. A sample of the fabric was placed in a Petri dish containing solid bacterial medium (nutrient agar broth) or fungal medium (Doxs medium), which had been heavily seeded with a suspension of the tested organism. After inoculation, the sample was incubated at 37°C for 24–48 h. The diameter of the clear inhibition zone surrounding the sample was taken as a measure of the fabric inhibition action against the particular test organism.[10–13]

RESULTS AND DISCUSSION

Effect of cupric ions concentration on the GMA graft yield

The effect of various concentrations of copper sulfate on the percentage GMA graft yield is shown in Figure 1.

It is obvious that the percentage GMA graft yield increases gradually by increasing the Cu^{2+} ion concentration and reached about 198% at Cu^{2+} ion concentration of 0.15×10^{-2}m.M. By further increasing Cu^{2+} ion concentration beyond this limit, the graft yield was decreased and reached 120% at 0.25×10^{2}m.M. The increase in graft yield, due to the presence of Cu^{2+} ion, is referred to the accelerating effect of this ion on the decomposition of potassium persulfate (PPS).

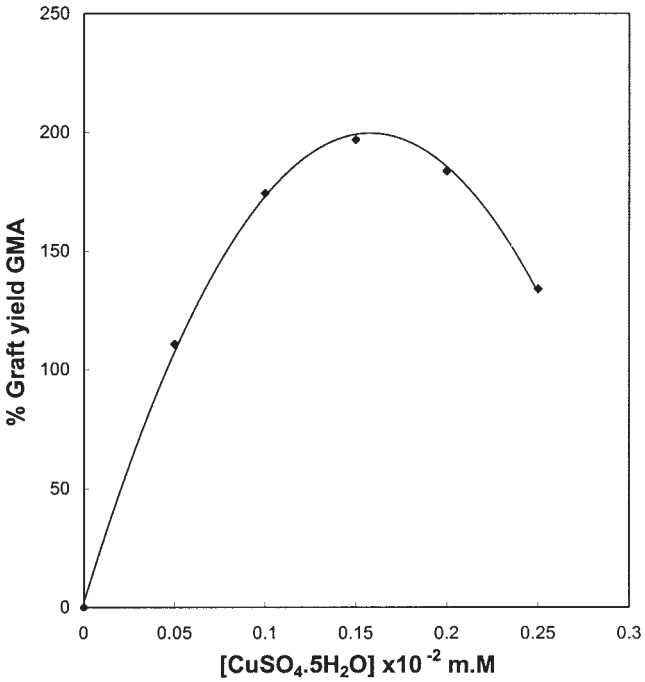


Figure 1 Yield of GMA grafting on PA fabrics: Effect of the $CuSO_4 \cdot 5H_2O$ concentration. Grafting conditions: GMA 0.36*M*, 3% $K_2S_2O_8$, temperature 75°C.

Effect of GMA concentration on the graft yield

The effect of GMA concentration on PA grafting is shown in Figure 2. It can be observed that the percentage GMA graft yield increases by increasing GMA concentration.

The percentage graft yield reached 190% at 0.3 m.M GMA. The grafting of GMA onto PA is shown in Scheme 1.

Influence of the reaction time on β-CD grafted onto PA/GMA fabric

The amount of fixed β-CD is dependent on both the percentage GMA graft yield onto PA fabric and the reaction time as shown in Figure 3.

It was found that β-CD graft yield increased by decreasing the percentage GMA onto the PA fabric, this effect being due to the β-CD supramolecular size molecules, which are anchored as side chains to the PA/GMA backbone chains. It seems that, as the graft yield of PA/GMA increases, there is some kind of steric hindrance occurring, which lead to the decrease of β-CD graft yield onto PA/GMA fabric.

The reaction of β-CD and MCT β-CD onto grafted PA/GMA fabric is shown in Scheme 2.

Thermal gravimetric analysis

The increased thermal stability of PA/GMA/β-CD and PA/MCT β-CD grafted fabrics have been mea-

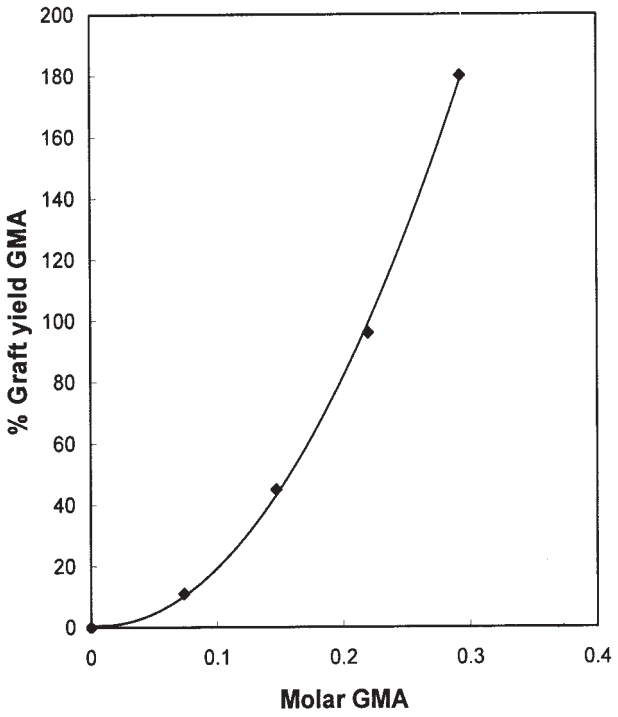


Figure 2 Effect of GMA concentration on the percentage graft yield of PA-6 fabric. Grafting conditions: [GMA]: 0.073, 0.147, 0.22, 0.293*M*, [$K_2S_2O_8$]: 3% (w/w) [$CuSO_4 \cdot 5H_2O$]: 0.15×10^{-2} m*M*, temp. 75°C, time 1 h.

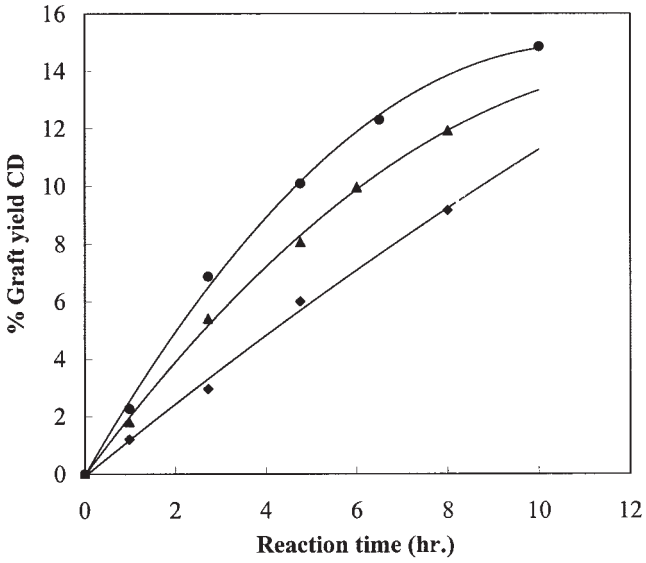


Figure 3 Effect of reaction time on the percentage of grafting of CD onto PA/GMA fabrics Grafting conditions: GMA (●)54%; (▲) 120%; (■) 188%), DMF/H_2O (v/v) 1:1, pH: 8, temp. 80°C, L.R. 1:100.

sured, confirmed, and compared with that of PA-6 fabric by TGA as a function of temperature (*T*) and the percentage weight loss, in the temperature range 50–650°C determined. Experimental results are given in Table I.

The decomposition temperatures of the control and grafted fabrics were obtained as follows:

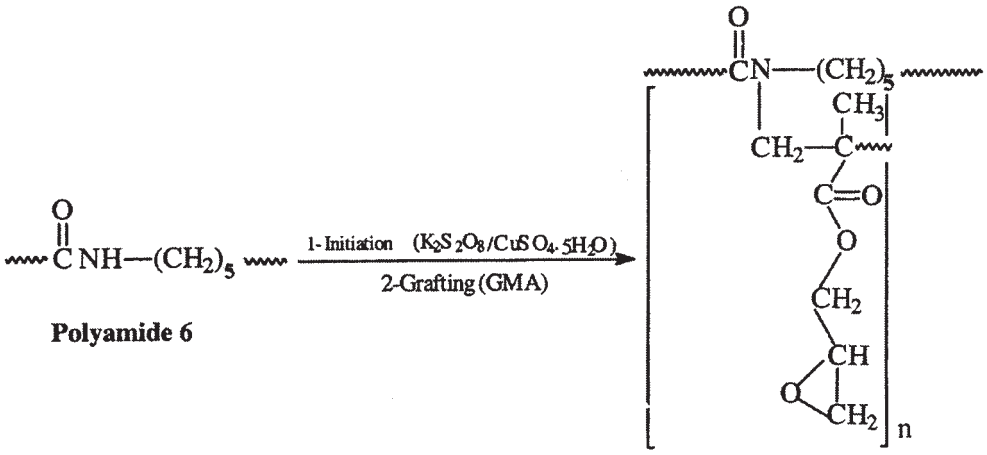
PA control: 520°C; PA/55.3% GMA/6.9% β-CD: 620°C; PA/109% GMA/3.3% MCT β-CD: 600°C.

It is clear from the previous data that grafting of PA, using the chemical redox initiation method, increases the decomposition temperature of PA fabric greatly, which was initially at 520°C. The grafting of GMA/β-CD to PA increases the decomposition temperature to 620°C and the grafting of PA by GMA/MCT β-CD increases the decomposition temperature to 600°C.

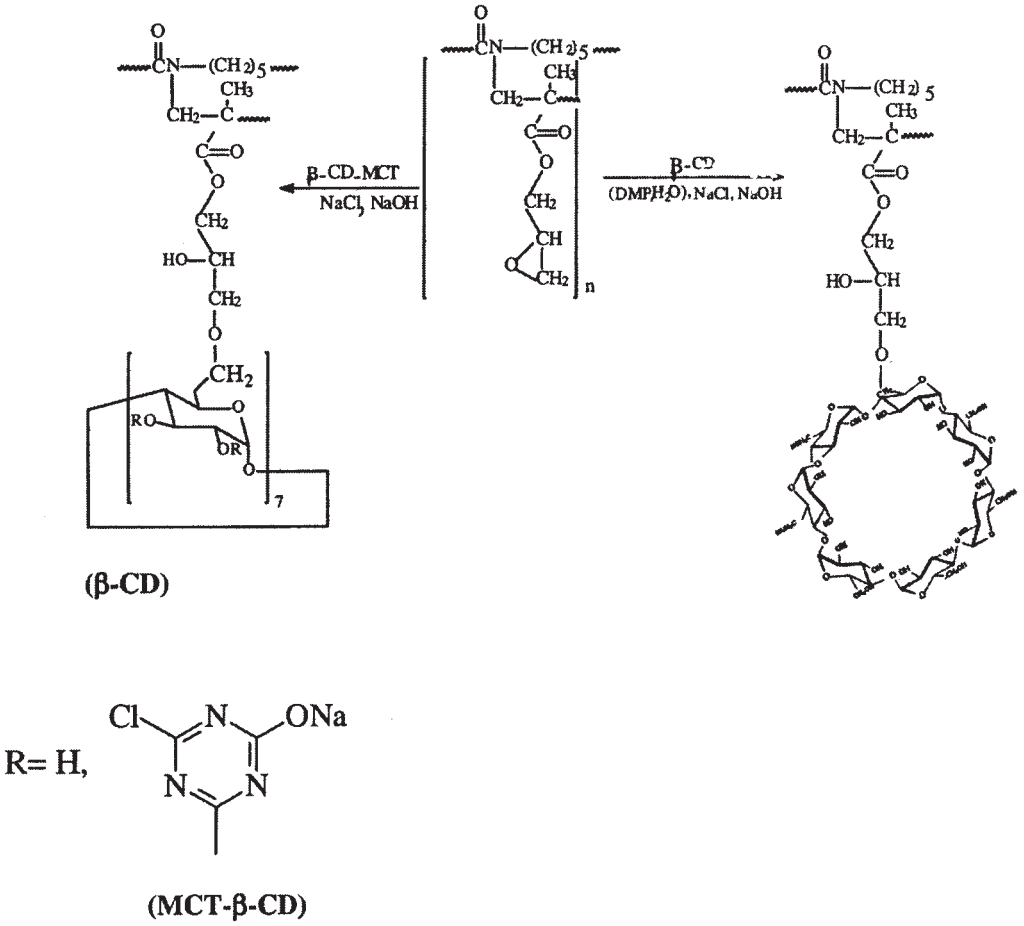
Infrared spectroscopy

The infrared spectra of the control and the grafted fabrics : PA-6 fabric (a), PA/GMA (b), PA/GMA β-CD (c) have been investigated and are compared in Figure 4.

The spectrum for PA-6 shows an absorbance band that can be attributed to the amide group (1654–1542 cm^{-1}), and to NH_2 group (3303 cm^{-1}), N—H stretching at (3081 cm^{-1}), C—H stretching at (2928–2859



Scheme 1



Scheme 2

cm^{-1}). The spectrum of PA/GMA fabric compared with that of PA, shows an additional absorbance band that can be attributed to the ester carbonyl group (1737–1611 cm^{-1}), and the epoxide group is characterized by the bands 1168 cm^{-1} shoulder and 905–842 cm^{-1}.

The immobilization of β-CD onto PA/GMA fabric is confirmed by the spectrum of PA/GMA β-CD that shows a significant decrease of the epoxide signals mentioned earlier and the deformation vibrations of OH groups and hydrogen bond overtone at 749–444 cm^{-1}.

TABLE I
TGA, Effect of Temperature on the Weight Loss of PA and Grafted Fabrics PA/GMAI β-CD and PA/GMA/MCT β-CD

Samples	Temperature (°C)	Weight loss (%)
Blank PA	287.5	3.3
	440	89.1
	560	99.8
PA/59.3% GMA/6.9% β-CD	283.8	14.7
	342.5	38.5
	650	98.8
PA/109% GMA/3.3% MCT-β CD	249.6	4.2
	328.7	44.1
	500	76.6
	631.6	99.7

Scanning electron microscopy

The SEM photographs of ungrafted PA-6 are shown in Figure 5.

The PA/GMA graft is clear in Figure 5(b), also the supra molecular size of round CD graft as side chain on the PA/GMA backbone chains is detected in Figure 5(c).

Determination of the inclusion capacity

The capacity of the different fabrics to retain benzoic acid was determined to evaluate the availability of the cyclodextrin cavities grafted onto PA-6. For example, a sample containing 7.69 wt % of CD and a control PA-6 reference sample (without any graft) were soaked, during 12 h, in a 1% benzoic acid solution to complex all the CD cavities. From the concentration of the residual solution, and by difference with the control

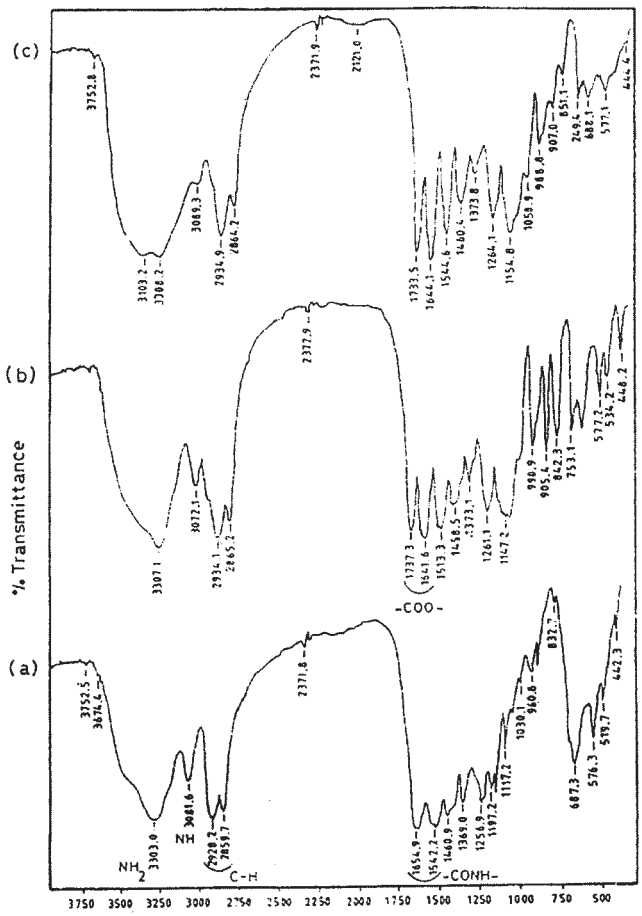


Figure 4 PA Infra red spectra of (a) blank PA-6, (b) PA-6/120% grafted GMA, (c) PA-6/120% GMA/11% CD.

sample, the amount of complexed CD cavities was determined, assuming the formation of 1:1 CD: benzoic acid inclusion complex. In that case, the percentage weight of complex CD was 5.2%. This means that only about two thirds of the grafted CD is actually available for inclusion, probably because of steric hindrance.

Kinetics of release

A grafted sample and a control PA-6, previously saturated with benzoic acid were then washed and dried, immersed in pure water and the concentration of benzoic acid released in the solution was followed as a function of time, as was measured spectrophotometrically in the UV range.

For the control PA-6 fabric containing no GMA or CD, benzoic acid is completely and rapidly released in less than 1 day whereas for the CD grafted sample, the concentration slowly increases and is far from the maximum value even after 50 days. Thus, the kinetics of release is controlled by the association complex and should depend on the stability of the latter. This gives to the CD grafted sample, a prolonged antibacterial activity in the case of benzoic acid.

Preliminary experiment shows that, in the same way, CD grafted fabrics, impregnated with volatile

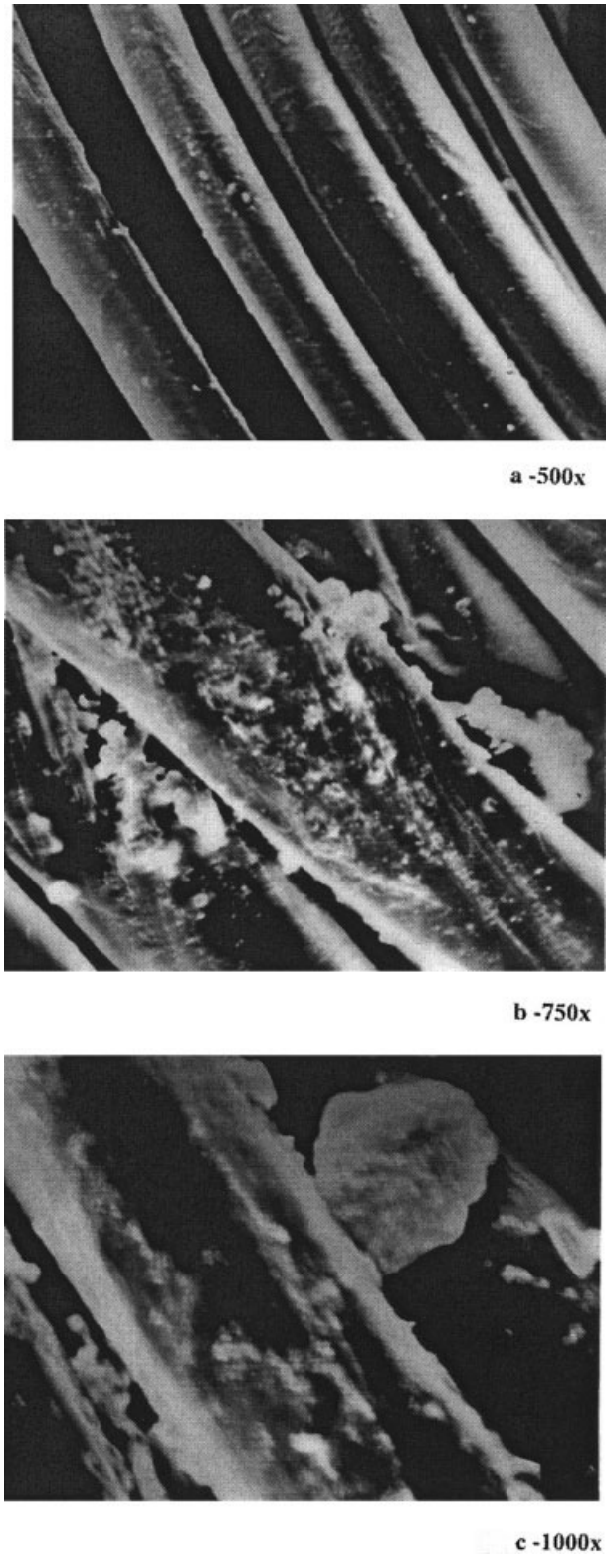


Figure 5 ESM (a) untreated PA-6 fabric (b) grafted PA/GMA (c) PA-6/120% grafted GMA/11% CD.

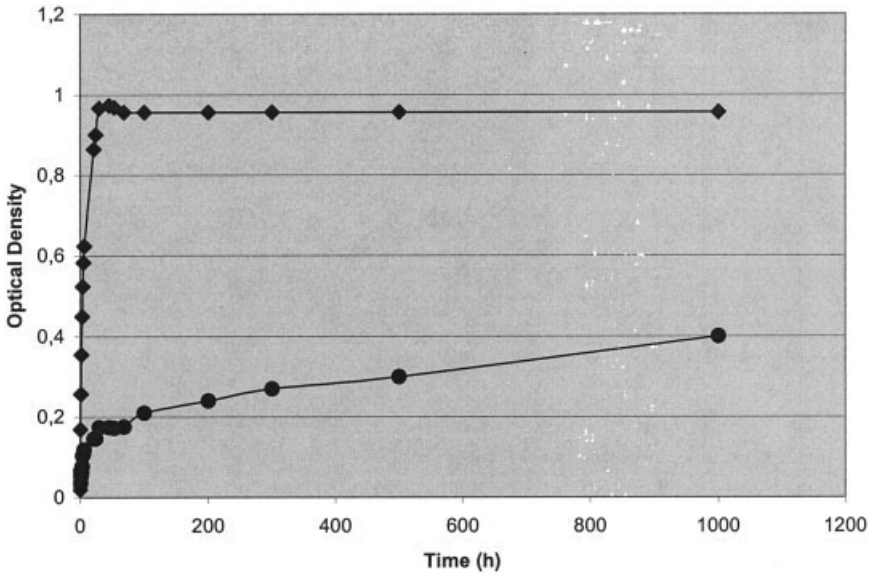


Figure 6 Kinetics of release of benzoic acid by: (▲) Reference PA-6; (●) Sample PA-6 with 59.85% GMA and 7.69% CD.

perfumed extracts, keep their fragrance during long times.

Effect of PA/GMA/β-CD grafted inclusion guests on microorganisms

The following chemicals and volatile perfumed extracts were used as inclusion complex guests into the β-CD moiety of the grafted PA/GMA/β-CD grafted fabric: Iodine, $AgNO_3$, *p*-hydroxy benzoic acid, DETA, and volatile perfumed extracts such as sweet basil, citronella, and jasmine. All the earlier mentioned fabrics containing β-CD and the guest compounds gave very good inhibition zone ranging from 12 to 32 mm/mg fabric with *Staphylococcus albus* microorganism compared with that of nil for the control PA-6 (Table II).

In the case of *Candida salivarius*, a very strong pathogenic fungus, the grafted fabrics containing in the CD cavity, sweet basil citronella, DETA, or I_2 all were very effective and gave the following inhibition zones of 30, 18, 17, and 18 mm, respectively, whereas $AgNO_3$, *p*-hydroxy benzoic acid, Jasmine, and the control were ineffective against this fungus. In this respect, it is interesting to note also that $AgNO_3$–ethanolamine complex mixture was used for treatment of burns and infected wounds and has a greater germicidal activity than sulfadiazine–Ag complex.[14,15]

The fabric containing I_2 guest in the CD cavity gave a highly biocidal action against all the microorganisms used and inhibition zones ranging from 18 to 35 mm were obtained. Grafted PA fabrics also including I_2, DETA, and citronella in the β-CD cavity gave good inhibition zones of 35, 13, and 15 mm against *Escherichia coli*. Iodine and jasmine guests showed inhibition zones of 27 and 14 mm in case of *Bacillus subtilis* (Table II).

The introduction of CMT β-CD group, anchored to PA/GMA graft, shows a highly effective biocidal ef-

TABLE II
Effect of PA/GMA/β-CD Including Different Chemicals and Volatile Perfumed Extracts (as Inclusion Guests) on the Biocidal Activity of Microorganisms

Microorganisms	Gram reaction	Inhibition zone diameter (mm/mg sample) measured after 72 h.							
		I	II	III	IV	V	VI	VII	VIII
Staphylococcus albus	G^+	0.0	32_R	12	14	15	15	15	15
Candida albicans	Fungus	0.0	18	0.0	0.0	17	30	18	0.0
Escherichia coli	G^-	0.0	35	0.0	0.0	13	0.0	15	0.0
Bacillus subtilis	G^-	0.0	27	0.0	0.0	0.0	0.0	0.0	14
Streptococcus salivarius	G^+	0.0	25_R	0.0	0.0	0.0	0.0	00	0.0

(R), Repelling action on bacterial growth; (I), PA/42.3% GMA/7.3% β-CD, (blank)); (II), PA/42.3% GMA/7.3% β-CD/9.1% I_2, (III), PA/42.3% GMA/7.3% β-CD/0.7% AgNO3; (IV), PA/42.3% GMA/7.3% β-CD/1.82% *p*-benzoic acid; (V), PA/42.3% GMA/7.3% β-CD/0.53% DETA; (VI), PA/55.32% GMA/7% β-CD/2.29% sweet basil; (VII), PA/55.32% GMA/7% β-CD/4.27% citronella; (VIII), PA/55.32% GMA/7% β-CD/0.52% Jasmine.

TABLE III
Effect of PA/GMA/CMT–BCD Grafts Including Different Chemicals (as Inclusion Guests) on the Biocidal Activity of Microorganisms

Microorganisms	Gram reaction	Inhibition zone diameter (mm/mg sample)						
		I		II		III		IV
		24 h	72 h	24 h	72 h	24 h	72 h	72 h
Staphylococcus albus	G^+	19_R	12_R	15	15	0.0	0.0	35_R
Candida albicans	Fungus	0.0	15_R	0.0	20_R	0.0	0.0	15_R
Escherichia coli	G^-	17_R	16_R	14	12_R	15_R	15	35
Bacillus subtilis	G^+	0.0	0.0	15	15	0.0	0.0	25
Streptococcus salivarius	G^+	30_R	30_R	0.0	15	0.0	12	40_R

(R), Repelling action on bacterial growth; (I), PA/109% GMA/3.3% CMT-β CD, (Blank); (II), PA/109% GMA/3.3% CMT-β CD/0.28% DETA; (III), PA/109% GMA/3.3% CMT-β CD/2.2% *p*-hydroxy benzoic acid; (IV), PA/113.3% GMA/2.5% CMT-β-CD/17% iodine.

fect due to the presence of the triazinyl group attached to the CD moiety against all tested microorganisms with the exception of *B. subtilis* (Table III).

The inclusion of DETA as a guest in the CMT β-CD moiety gave nearly the same effect as that of the control, but it was more effective than the control on *B. subtilis.* The sample IV, containing iodine (Table III) as guest molecule, into the CMT β-CD shows highly effective biocidal action against all the bacteria used and the inhibition zones (mm) were as follows:

35R (*Staphylococcus albus*),15R (*Candida albicans*), 35 (*Escherichia coli*), 25 (*Bacillus subtilis*), and 40R (*Streptococcus salivarius*).

CONCLUSIONS

This work has shown that the grafting of CD onto PA is feasible, using a redox reaction and GMA as an intermediate. The resulting grafted samples keep to a large extent, the complex ability of CD and are able to slowly release active complex substances over long periods of time. The biocidal activity of the treated fabrics with various guests has been demonstrated.

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