Antimicrobial Finishing of Regular and Modified Nylon-6 Fabrics

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ABSTRACT: A simple, efficient, and practically applicable functional approach for improvement antimicrobial properties of nylon-6 fabrics and increase the washing durability of biofunctions was developed. This finishing approach is based on grafting of the fabrics with methacrylic acid (MAA) to create additional carboxylic groups in nylon-6 macromolecules, followed by subsequent reaction with dimethylalklbenzyl ammonium chloride (DMABAC) solution under alkaline conditions. The carboxylic groups react with cationic agent through ionic interaction, which led to the immobilization of QAS on nylon-6 fabrics. This immobilization was proofed through determination of nitrogen content, applying scanning electron microscopy (SEM), and FTIR microscopy. The effect of treatment conditions on salt uptake (SUT) on nylon-6 fabrics and reaction efficiency (RE) was investigated. The antimicrobial assessment of regular and grafted with PMAA nylon-6 fabrics treated with DMABAC revealed that both types of fabrics are characterized before washing, by quite strong biocide effect on *Bacillus mycoides*, *Escherichia coli* and *Candida albicans*. The role of grafting nylon-6 fabrics before treatment with salt on durability of antimicrobial functions seems to be more significant as the samples were repeatedly washed. Even after Laundring 10 times the grafted samples could still provide 80%, 100%, and 87.5% microbial reduction against *B. mycoides*, *E. coli* and *C. albicans*, respectively, in contrast with 42.6%, 65.6%, and 42.5% in case of regular nylon-6 fabrics. J Appl Polym Sci 110: 738–746, 2008

Key words: regular nylon-6 fabric; grafted nylon-6 fabric; grafting; MAA; PMAA; antimicrobial treatment; QAS; SEM; FTIR; salt uptake; reaction efficiency; inhibition zone of growth; antimicrobial properties

INTRODUCTION

In health-related professions, protection from pathogens is a growing concern, and textiles with antimicrobial properties are desirable. Nylon-6 fabrics are of considerable use in the textile industry. Accordingly, modification of the surface of this fiber to give it antimicrobial properties is very important task for a wide range of industrial applications, including clothing, bedding, and interior materials.

The manufacture of bioactive polyamide fibers can be accomplished by the addition of bactericides to polyamide chips before fiber formulation.[1] However, this technique suffers from several problems, including difficulties associated with spinning the fibers and with sustained antimicrobial activity. In addition, the agents may be washed away during the laundering of the garments. More promising and widely used method for imparting antimicrobial activity to polyamide fibers is the preliminary modification of ready-made articles via reaction in polyamide chain or by grafting of ionogenic and nonionogenic monomers, with the objective of increasing the content or creating on the fibers new functional groups, which are able to react with biocides.[2–21] This method was used for immobilization of chitosan,[11] grafting antimicrobial agents such as appropriate antibiotics or anesthetic,[8,9,12–16] protoporphyrin IX and zinc protoporphyrin,[17,18] *N*-halamine structures,[20,21] and monomers containing quaternary ammonium groups,[22] on nylon-6 fabrics.

One of the effective ways of obtaining antimicrobial fibers and textiles is modifying man-made fibers with quaternary ammonium compounds. Immobilization of these compounds on polyamide fibers and fabrics is based on reaction with carboxylic end groups in polymer macromolecule. Cetylpyridinium chloride (CPC) and benzyl-dimethylhexadecyl ammonium chloride (BDHAC) were employed by Son and Sun[10] in the chemical finishing of nylon-6 fabrics for imparting antimicrobial properties. The authors have reported that the functions on the treated fabrics were reduced to certain level after 10 Launder-Ometer washes, and that the fabrics treated with the abovementioned salts could still provide more than 60% bacterial reduction against *E. Coli*. It is well known that, polyamide fibers have limited carboxylic end groups. Therefore, increase in both antimicrobial

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activity and durability of antimicrobial functions necessitates the creation of additional carboxylic groups in polyamide macromolecule.

In light of the abovementioned, the present work, aims at developing a simple and practically applicable functional approach for improvement antimicrobial properties of nylon-6 fabrics and increase the washing durability of biofunctions. Finishing approach is based on grafting of the fabrics with methacrylic acid (MAA) to create additional carboxylic groups in nylon-6 macromolecules followed by subsequent reaction with dimethylalkylbenzyl ammonium chloride (DMABAC) under alkaline conditions. For comparison, regular nylon-6 fabrics were also treated with the same quaternary ammonium salt under the same conditions. Moreover, some related finishing conditions are discussed. Characterization of the finished fabrics was carried out through determination of both carboxylic and nitrogen contents and applying scanning electron microscopy (SEM) and FTIR spectroscopy. The growth inhibition of the microorganisms on the surface of finished fabrics and the durability of antimicrobial functions were also examined.

EXPERIMENTAL

Materials

Nylon-6 fabrics used throughout this study were in the form of filament woven fabric cloth made from filament yarns (warp 42 ends/cm, weft 36 picks/cm). They were kindly supplied by El-Nasr (Shourbagy) Co., Cairo, Egypt. The fabrics were scoured at 80°C for 45 min with solution containing 2 g/L nonionic detergent, washed with cooled water, squeezed, and finally air dried.

Chemicals

MAA of pure grade was freshly distilled before using.

Potassium persulphate ($K_2S_2O_8$), copper sulfate ($CuSO_4 \cdot 5H_2O$), sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$), are analytical grade chemicals.

Dimethylalklbenzyl ammonium chloride (DMABAC), (alkyl = C_{10}–C_{12}), used in this work was in the form of 50% aqueous solution, and was kindly supplied by NIIPAV, Volgodonck, Russia.

Microorganisms

Bacillus mycoides (*B. mycoides*) (Gram positive bacterium), *Escherichia coli* (*E. coli*) (Gram negative bacterium), and *Candida albicans* (*C. albicans*) (nonfilamentous fungus) were used for estimation of antimicrobial potency of control and treated samples. Microorganisms were obtained from the culture collection of the Department of Microbial Chemistry, Division of Genetic Engineering and Biotechnology, National Research Centre of Egypt.

Culture medium

Modified nutrient agar medium was used and is composed of the following ingredients (g/L): peptone (10.0), beef extract (5.0), NaCl (5.0), and agar (20.0). The pH was adjusted to 6.8. This medium was sterilized for 20 min at 121°C under pressure.[23]

Methods

Grafting of nylon-6 fabrics with MAA

Nylon-6 fabrics samples were treated with 2% aqueous solution of ($K_2S_2O_8$) at room temperature. The samples were then removed, washed thoroughly with distilled water, squeezed and dried at room temperature. The samples retained some persulphate which was determined iodometrically. Pretreated samples were introduced into stoppered Erlenmeyer flask containing water, MAA, and copper sulfate. The flask was stoppered, kept in water thermostat at prescribed temperature and shaken occasionally during the reaction period. After an elapsed time, the reaction mixture was filtered and the residue was washed with water, dried in an oven at 105°C for 2 h. The dried sample was then repeatedly Soxhlet extracted with methanol to remove the homopolymer, dried again as previously indicated and weighed. The percentage of grafted polymer was calculated as follows:

$$\%\,\text{Graft yield} = \frac{P - P_o}{P_o} \times 100$$

where P is the weight of grafted sample, and P_o is the dry weight of ungrafted sample.

Fixation of DMABAC on regular and grafted nylon-6 fabrics

The treatment of regular and grafted nylon-6 fabrics with DMABAC was carried out using a high temperature high pressure laboratory dyeing machine. Required amounts of DMABAC solutions were placed in stainless-steel bowls, nylon-6 samples were immersed in the solutions, and the sealed bowls were rotated in a closed bath containing ethylene glycol at the desired temperature. The material-to-liquor ratio (M : L) was 1 : 50. The bath temperature increased at rate of 2°C/min. After the predetermined durations, the samples were removed from the bath, rinsed repeatedly with distilled water and allowed to dry in the open air.

TABLE I
Carboxylic and Nitrogen Contents in Nylon-6 and Nylon-6-*gr*-PMAA Before and After Treatment with DMABAC

Fabric	Carboxylic content (determined) mg/g. fabrics	Nitrogen content (%)	
		Determined	Calculated
Nylon-6	7.5	12.38	12.39
Nylon-6- Treated with DMABAC[a]	–	12.56	–
Nylon-6-gr-PMAA (8%)	45.0	11.77	11.70
Nylon-6-gr-PMAA (8%) Treated with DMABAC[a]	–	12.14	–
Nylon-6-gr-PMAA (15%)	66.0	––	–
Nylon-6-gr-PMAA 20%)	84.0	–	–

Treatment conditions: [DMABAC], 1.55%; pH, 11; Temperature, 90°C; Reaction time, 90 min.; Material: Liquor Ratio (M : L), 1 : 50.
[a] Subject to Launder Ometer washing test using AATCC standard method (61–1989) 10 cycles.

The initial and final concentrations of DMABAC solutions were determined by spectrophotometer at λ_{max} = 208 nm.

The salt exhaustion on the fabrics (E, %) was calculated according to the following equation: E (%) = $[C_1 - C_2/C_1] \times 100$, where C_1 and C_2 are the concentrations (g/L) of QAS solutions before and after treatments, respectively.

The salt uptake on nylon-6 fabrics (SUT) was calculated as follows:

SUT (mg/g fabric) = $[V(C_1 - C_2)/W]$, where C_1 and C_2 are the concentrations (g/L) of QAS solutions before and after treatments, respectively, V is the volume of QAS solutions (cm^3) used in treatment, and W is the weight of nylon-6 fabric.

Reaction efficiency (RE) of treatment of nylon-6 fabrics with QAS solutions (RE%) was calculated as follows: RE (%) = $[A/B] \times 100$, where A is the salt uptake on nylon-6 sample (mg/g fabric), and B is the amount of salt equivalent to the carboxylic content (mg/g fabric) in nylon-6 fabric before treatment.

Analysis

Antimicrobial potency by diffusion was quantified by measurement in millimeters of the width of the zone of growth inhibition around the sample according to AATCC standard test method.[24]

Carboxylic content was determined according to the method described in.[25]

A JEOL-Model JSM T20 scanning electron microscope (SEM) operating at 19 kV was used to obtain photomicrographs of fibers surfaces.

The chemical structure was determined using the Fourier transformation infrared (FTIR) spectrometer, model NEXUS 670, NICOLET USA. The measurements were carried in spectral range from 4000 to 400 cm^{-1} by using resolution 4 cm^{-1} KBr disc technique was applied.

Nitrogen content was determined by Duma method using Vario Elementar.

RESULTS AND DISCUSSION

Regular and grafted with polymethacrylic acid nylon-6 fabrics were treated with DMABAC aqueous solution at a temperature higher than the T_g of the polymer. It was observed that, an increase in weight, due to the salt uptake on nylon-6 fabrics, took place. However, the salt uptake was always higher in the case of grafted nylon-6 fabrics, irrespective of the reaction condition used; a point which signifies the role of grafting nylon-6 samples with MAA prior to reaction with quaternary ammonium salt. A part of this salt uptake still existed even after several extractions of the samples with water which is the solvent of the salt. It is well-known that, nylon polymers have two different ends, amino and carboxylic groups. The carboxylic groups are able to react with cationic functional agents under basic conditions at which these groups can form carboxylate anions.[10] Such an ionic interaction can lead to the immobilization of DMABAC on nylon-6 fabrics. To prove this, characterization of the so modified fabrics was carried out through determination of nitrogen and carboxylic contents, and applying SEM, and FTIR microscopy.

The effect of treatment of regular and modified nylon-6 fabrics with DMABAC on nitrogen content is shown in Table I. As it is evident, this treatment brings about an increase in nitrogen content in nylon-6 fabrics. However, a significant increase could be achieved in case of grafted fabrics. For instance, an increase of 0.37% in nitrogen content was obtained after treatment of modified fabrics with quaternary ammonium salt. This contrasts with an increase of 0.20% in nitrogen content in case of regular nylon-6 fabrics. It was observed that, this increase in nitrogen content still existed even after the nylon-6 fabrics have been subjected to Launder-Ometer

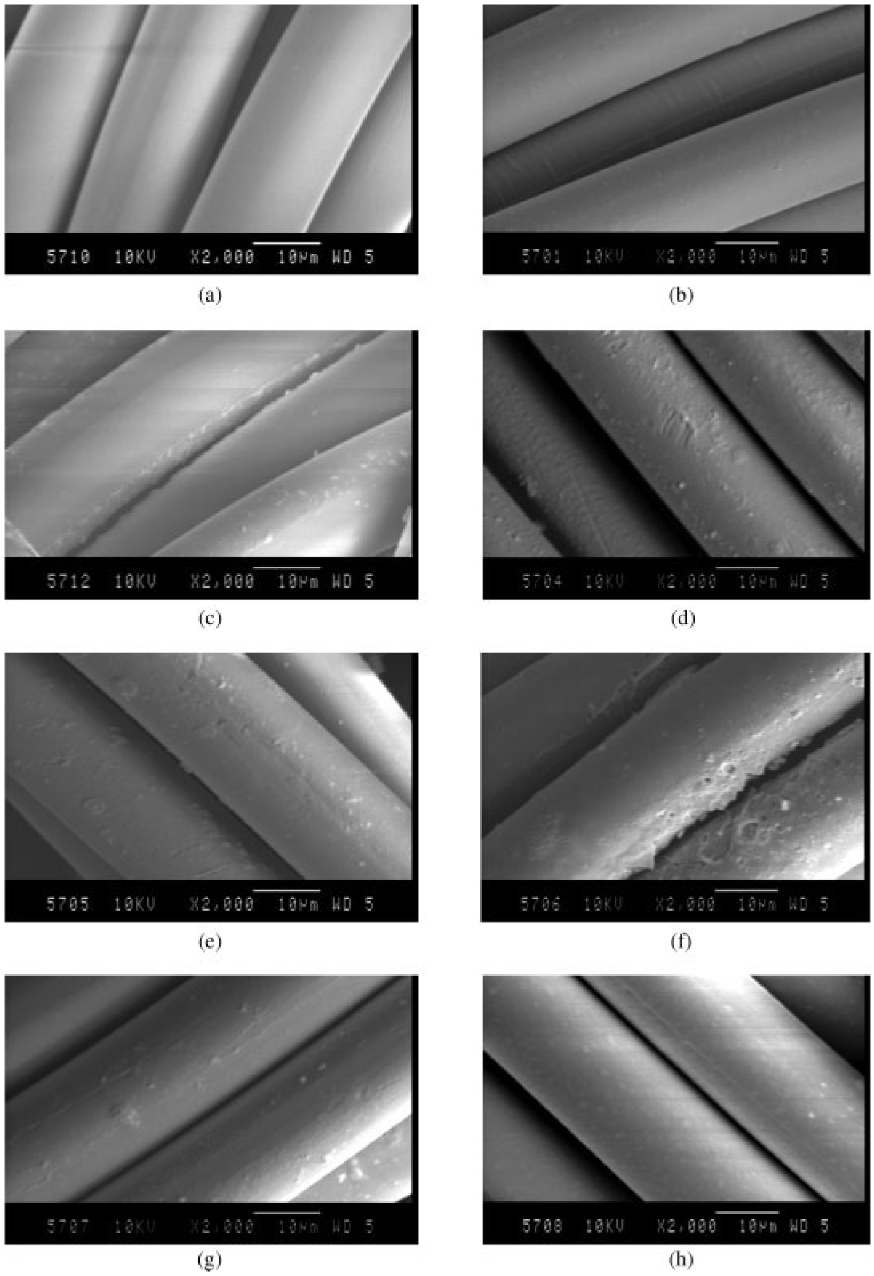


Figure 1 Scanning electron micrographs for regular Nylon-6 and Nylon-6 fabrics grafted with PMAA and treated with DMABAC (×2000). (a) Nylon-6, (b) Nylon-6 treated with DMABAC, (c) Nylon-6-*gr*-MAA 8%, (d) Nylon-6-*gr*-MAA 8% treated with DMABAC, (e) Nylon-6-*gr*-MAA 15%, (f) Nylon-6-*gr*-MAA 15% treated with DMABAC, (g) Nylon-6-*gr*-MAA 20%, (h) Nylon-6-*gr*-MAA 20% treated with DMABAC.

washing using AATCC standard method (61–1989). This, indeed, provides proof of immobilization of DMABAC onto to the investigated fabrics.

The fabric topography

Figure 1 presents scanning electron micrographs corresponding to regular, grafted with PMAA and treated with DMABAC nylon-6 fabrics. It is seen from the SEM results that, regular nylon-6 surface has a smooth and relatively homogeneous appearance [Fig. 1(a)]. After grafting PMAA onto the nylon-6 fabrics, surface has gained a roughness, the density of which increased by increasing the percentage of the grafted polymer up to 20% [Fig. 1(c,e,g)]. The treatment with DMABAC led to formation of a layer on the surface of all investigated samples [Fig. 1(b,d,f,h)]. The density of this layer increases gradually with increasing the graft level from 8 to 20%. This gives another proof of the ionic interaction between carboxylic groups and QAS, which led to the immobilization of the salt on nylon-6 fabrics.

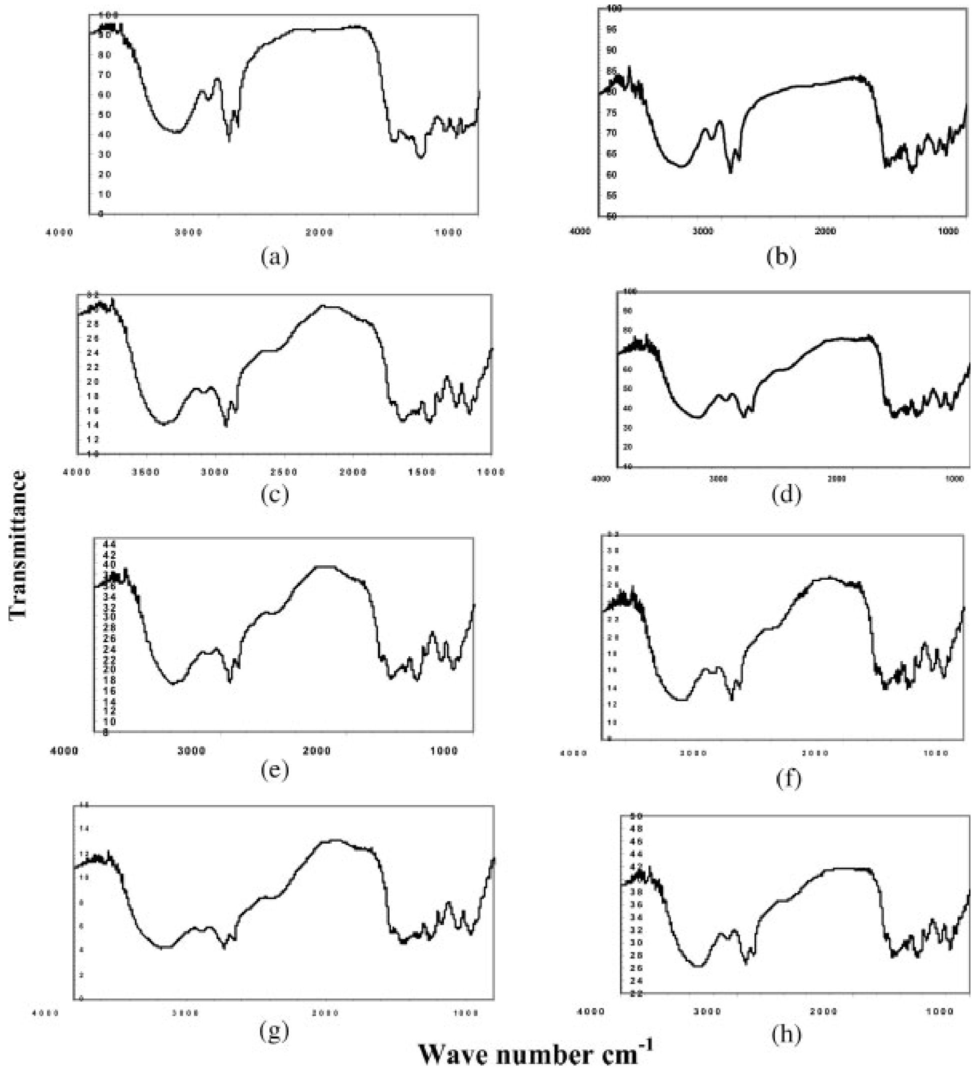


Figure 2 FTIR for regular Nylon-6 and Nylon-6 fabrics grafted with PMAA and Treated with DMABAC. (a) Nylon-6, (b) Nylon-6 treated with DMABAC, (c) Nylon-6-*gr*-MAA 8%, (d) Nylon-6-*gr*-MAA 8% treated with DMABAC, (e) Nylon-6-*gr*-MAA 15%, (f) Nylon-6-*gr*-MAA 15% treated with DMABAC, (g) Nylon-6-*gr*-MAA 20%, (h) Nylon-6-*gr*-MAA 20% treated with DMABAC.

FTIR spectrum

Figure 2 shows the FTIR spectra of regular and grafted nylon-6 fabrics before [Fig. 2(a)] and after [Fig. 2(b)] treatment with DMABAC. On the basis of the obtained spectra, one can conclude the following:

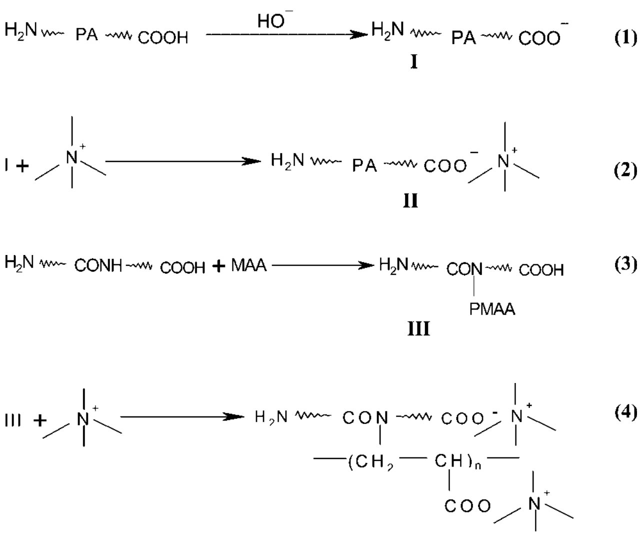
1. The FTIR spectrum of regular nylon-6 fabrics shows absorptions at 1662–1531, 3083, and 2920–2852 cm^{-1}, which are typical to those of C=O in CONH, NH_2, NH stretching and CH stretching respectively.
2. The spectrum of grafted nylon-6 with PMAA fabrics shows an additional absorption band at 1708 cm^{-1} that can be attributed to C=O in COOH of MAA. The presence of this band verifies that the grafting of MAA to nylon-6 fabrics has occurred as expected.
3. The absorption corresponding to NH group at 3080 cm^{-1} has gradually weakened with the increase of grafting. This leads to the suggestion that the grafting reaction happened on the nitrogen atoms of nylon-6 molecules.
4. A new band at 1548 cm^{-1} is observed in the spectrum on nylon-6 fabrics grafted with PMAA, which can correspond to the carboxylic ions of the new bond nylon-6-*gr*-PMAA-DMABAC. The presence of this band can support the ionic character of the new band formed due the addition of DMABAC to regular and modified nylon-6 fabrics.

On the basis of the aforementioned results, it can be suggested with a high probability that, addition of QAS can proceed according to the following reactions:

TABLE II
Effect of pH, [DMABAC], and Reaction Time on Salt uptake (SUT) and Reaction Efficiency (RE)

	Nylon-6		Nylon-6-*gr*-PMAA (8%)		Nylon-6-*gr*-PMAA (15%)		Nylon-6-*gr*-PMAA (20%)	
	SUT (mg/g fabric)	R.E (%)	SUT (mg/g fabric)	RE (%)	SUT (mg/g fabric)	RE (%)	SUT (mg/g fabric)	RE (%)
pH[a]								
4	5.0	9.8	15.0	4.9	19.0	4.3	25.0	4.21
7	12.0	23.5	50.0	16.4	75.0	16.8	99.0	17.0
11	51.0	100	90.0	29.6	110.0	24.7	121.0	21.3
[DMABAC](%)[b]								
0.15	24.3	47.6	32.5	10.6	40.9	9.9	54.0	9.5
0.25	36.9	72.4	48.0	15.8	56.8	12.7	76.0	13.4
0.60	46.0	90.2	68.0	22.4	76.0	17.0	98.0	17.3
1.28	48.0	94.1	74.9	24.6	90.0	20.2	110	19.4
1.55	51.0	100	90.0	29.6	110.0	24.7	121	21.3
Reaction Time (min)[c]								
10	12.8	25.1	20.0	6.6	28.7	6.4	35.8	6.3
20	26.1	51.2	41.7	13.7	69.0	15.5	86.0	15.2
30	38.6	75.7	61.1	20.1	84.0	18.8	100.5	17.7
40	47.4	92.9	71.8	23.6	92.0	20.7	107	19.0
50	50.0	98.0	80.0	26.3	100	22.4	114	20.0
60	51.0	100	90.0	29.6	110	24.7	121	21.3

[a] [DMABAC], 1.55%; Temperature, 90°C; Reaction Time, 60 min; M : L, 1 : 50.
[b] pH, 11%; Temperature, 90°C; Time, 60 min.; M : L, 1 : 50.
[c] [DMABAC], 1.55%; Temperature, 90°C; pH, 11; M : L, 1 : 50.



The effect of treatment conditions such as pH, concentration of DMABAC, reaction time and temperature on salt uptake on nylon-6 fabrics and reaction efficiency was investigated to discover the optimal conditions for antimicrobial finishing of regular and modified fabrics.

Effect of pH

The effect of adsorption of DMABAC on regular and grafted nylon-6 fabrics under different pH values was studied. The results of the salt uptake on the fabrics and reaction efficiency are listed in Table II. As predicted, acidic treatment conditions did not result in significant salt uptake on the fabrics, irrespective of the type of nylon-6 fabrics used. The higher pH solution led to a higher salt uptake and higher reaction efficiency since the QAS is more attractive to the relatively charged carboxylate groups under the basic conditions.[10] Because of the ionic interactions, the DMABAC was quickly absorbed onto and then diffused into the fabrics. Such a result further reveals that, the promoted interactions between the fabrics and the functional agents can be achieved by varying the pH values of the finishing solutions.

The data in Table II also revealed that, under any pH value, the salt uptake on the nylon-6 fabrics is always higher than that on the regular samples. Under any pH value, the salt uptake on the grafted nylon-6 fabrics are always higher than that on the regular samples. The increased carboxylic content in grafted fabrics (Table I) could lead to increased exhaustion of the QAS by the sample and to increased diffusion of the salt into the polymer under the basic conditions. This could increase ionic bonds formed inside the fabrics and would improve both of antimicrobial and the wash fastness properties. Indeed, antimicrobial tests of the treated fabrics have already demonstrated this trend (Table IV).

Effect of DMABAC concentration

The effect of DMABAC concentration on the salt uptake on the nylon-6 fabrics and finishing efficiency

TABLE III
Effect of Reaction Temperature on Salt Uptake (SUT) and Reaction Efficiency (RE)

	Nylon-6						Nylon-6-*gr* PMAA (8%)					
	70°C		80°C		90°C		70°C		80°C		90°C	
Reaction Time (min)	SUT mg/g fabric	RE (%)	SUT mg/g fabric	RE (%)	SUT mg/g fabric	RE (%)	SUT mg/g fabric	RE (%)	SUT mg/g fabric	RE (%)	SUT mg/g fabric	RE (%)
10	5.5	10.8	3.7	14.3	12.8	25.0	9.9	3.3	14.0	4.6	20.0	6.6
20	10.0	19.7	15.0	29.4	26.1	51.2	25.0	8.2	30.0	9.9	41.7	13.7
30	17.0	33.3	24.0	47.1	38.6	75.7	31.0	10.2	41.0	13.5	61.1	20.1
40	21.0	41.2	34.8	68.2	47.4	92.9	39.0	12.8	45.0	14.8	71.8	23.6
50	29.0	56.9	45.0	88.2	50.0	98.0	43.0	14.1	62.0	20.4	80.0	26.3
60	35.0	68.6	47.0	92.2	51.0	100.0	50.0	16.4	74.8	24.6	90.0	29.6

Reaction Conditions: [DMABAC], 1.55%; pH, 11; M : L, 1 : 50.

is shown in Table II. It is clear that the increase in QAS concentrations from 0.15% to 1.55% is accompanied by a substantial enhancement in the salt uptake on the fabrics and reaction efficiency. It must be noted, however, that at low salt concentrations from 0.15% to 0.60% the salt uptake and reaction efficiency continue to increase with increasing DMABAC concentration. Further increase in salt concentrations i.e., 1.28% and 1.55% has a little effect on the salt uptake especially in the case of regular nylon-6 fabrics. It was also found that, the salt uptake is affected by the amount of grafted PMAA onto nylon-6 fabrics. It can be seen from Table II that, at any salt concentration the regular nylon-6 fabrics have only a slight quantity of the QAS added. This is due to the fact that these fabrics contain only very small quantities of carboxylic end groups (Table I). Therefore, the grafted fabrics containing numerous carboxylic groups tend to combine QAS much more effectively. Moreover, reaction efficiency decreases by increasing the amount of grafted PMAA on the fabrics. Vainburg et al.[26] have declared that a stable antimicrobial effect on cellulosic textile materials is obtained at a low QAS content: 4–6 mg of preparation per gram of fabrics. On the basis of the abovementioned one can conclude that a graft yield of PMAA of 8% is quiet enough for imparting high biological activity to nylon-6 fabrics.

Effect of reaction time

The majority of the polymer structure is crystalline, which is tightly packed and difficult to penetrate for the salts. Thus, the treatment time is quite critical to the exhaustion of DMABAC on nylon-6 fabrics. The effect of the treatment time on the salt uptake and reaction efficiency is listed in Table II. It can be seen that, the salt uptake and reaction efficiency increase steadily with an increase in reaction time. Moreover, at a shorter treatment time (40 min) there is a significant increase in salt uptake and reaction efficiency (Table II). As the treatment time increased, the diffusion of DMABAC on the nylon-6 fabrics could be improved significantly, resulting in high salt uptake and reaction efficiency. However, further increasing in the reaction time has a little effect on the aforementioned properties, especially when a nylon-6 fabric with lower carboxylic content is used.

Effect of reaction temperature

The effect of reaction temperature at different treatment time on the DMABAC uptake on nylon-6 fabrics and reaction efficiency was also investigated. The obtained results (Table III) show that, irrespective of the type of treated nylon-6 fabrics, the salt uptake and reaction efficiency were increased as the temperature increased from 70 to 90°C. At a lower treatment temperature, a longer reaction time is needed to achieve a higher salt uptake on the fabrics. The increase in both salt uptake and reaction efficiency was more significant in the temperature range around the T_g of the nylon-6 fabrics. At 90°C the exhaustion of DMABAC reached its higher rates under the chosen conditions. The results obtained show the same trend but the values are much greater in the case of nylon-6-*gr* PMAA (8%) fabrics. The favorable effect of temperature on salt uptake and reaction efficiency could probably be associated with: (a) enhancement in nylon-6 fabrics swellability; (b) increased mobility of the DMABAC molecules; (c) higher rate of salt diffusion from the reaction medium to the nylon-6 fabrics; and (d) increased interactions between the fabrics and the functional agent. The net effect of these factors would be expected to lead to higher salt uptake.

Antimicrobial assessment

The antimicrobial activity of regular nylon-6 and nylon-6 grafted with PMAA fabrics treated with DMABAC against Gram-positive bacteria *B. mycoides*,

TABLE IV
Effect of [DMABAC] and Reaction Time on Antimicrobial Activity of Nylon-6 Fabrics

	Nylon-6 fabrics												Nylon-6-*gr*-PMAA (8%) fabrics											
	Inhibition zone of growth (mm) in case of:												Inhibition zone of growth (mm) in case of:											
	B. mycoides				*E. coli*				*C. albicans*				*B. mycoides*				*E. coli*				*C. albicans*			
Factor	w.w.	1*	5*	10*	w.w.	1*	5*	10*	w.w.	1*	5*	10*	w.w.	1*	5*	10*	w.w.	1*	5*	10*	w.w.	1*	5*	10*
[DMABAC][a]																								
1 0.79	33	19	17	16	42	24	24	24	34	18	17	16	29	19	17	15	42	24	23	23	34	19	16	15
2 1.55	39	23	18	17	38	28	25	25	40	22	18	17	35	32	28	28	34	34	34	34	32	32	28	28
Reaction Time (min)[b]																								
1 10	37	19	17	16	39	24	24	21	35	18	16	15	52	26	25	25	49	32	25	26	45	24	24	24
2 60	39	23	18	17	38	28	25	25	40	22	18	17	35	32	28	28	34	34	34	34	32	32	28	28

W.W.: without washing.
* After 1, 5, and 10 times Laurder-Ometer washing.
[a] pH, 11; Reaction time, 60 min; Reaction Temperature, 90°C; M : L, 1 : 50.
[b] [DMABAC], 1.55%; pH, 11; Reaction Temperature, 90°C; M : L, 1 : 50.

Gram-negative bacteria *E. coli* and nonfilamentous fungus *C. albicans* was investigated. The activity by diffusion is quantified by the measurement in millimeters of the width of the zone of inhibition around the sample. Table IV indicates the antimicrobial activity of regular and modified nylon-6 fabrics treated with DMABAC under different conditions. It is seen from the data listed in this table that, both types of fabrics are characterized, before washing, by quite strong biocide effects on *B. mycoides*, *E. coli*, and *C. albicans*. This was demonstrated by quite large zones of stunted microorganism growth irrespective of the treatment conditions used.

The role of grafting nylon-6 fabrics with MAA before treatment with DMABAC on the antimicrobial activity seems to be more significant as the samples were laundered repeatedly in launder-Ometer. It was found that, the bioactivity of the substrates treated under different DMABAC concentrations and different reaction times became significantly different (Table V). The desorption of the salt from the finished samples treated with a solution containing low (0.79%) salt concentration occurred progressively as the number of washes increased. The same holds true when the treatment process was carried out for 10 min. Under these conditions both regular and grafted nylon-6 fabrics has lost about 50% its antimicrobial activity after 10 Lauender-Ometer washes. On the other hand, it was found that, further increase in both salt concentration in the finishing solution (up a 1.55%) and reaction time during treatment of regular nylon-6 fabrics seems to display little effect on bacterial and fungal reduction against *B. mycoides* and *C. albicans* after 10 washes, respectively. However, the same fabric treated and washed under the abovementioned conditions could still provide more than 65% bacterial reduction against *E.coli*. In contrast, in case of grafted samples, the antimicrobial functions were unchanged or were slightly reduced to certain level. After 10 launder-Ometer washes, the grafted nylon-6 fabrics treated with the concentration of 1.55% could still provide 80%, 100%, and 87.5% microbial reduction against *B.mycoides*, *E.coli*, and *C.albicans*, respectively. This again verifies the feasibility of increasing the carboxylic content in nylon-6 fabrics before its antimicrobial

TABLE V
Effect of [DMABAC] and Reaction Time on Microbial Reduction

	Nylon-6 fabrics									Nylon-6-*gr*-PMAA (8%) fabrics								
	Microbial Reduction (%) In case of:									Microbial Reduction (%) In case of:								
	B. mycoides			*E. coli*			*C. albicans*			*B. mycoides*			*E. coli*			*C. albicans*		
Factor	1*	5*	10*	1*	5*	10*	1*	5*	10*	1*	5*	10*	1*	5*	10*	1*	5*	10*
[DMABAC][a]																		
1 0.79	57.6	51.5	48.5	57.1	57.1	57.1	52.9	50.0	47.1	65.5	58.6	51.7	57.1	54.8	54.8	55.9	47.1	44.1
2 1.55	59.0	46.2	43.6	73.3	65.8	65.8	55.0	45.0	42.5	91.4	80.0	80.0	100.0	100.0	100.0	100.0	87.5	87.5
Reaction Time (min)[b]																		
1 10	51.3	45.9	43.2	61.5	61.5	53.8	51.4	45.7	42.9	50.0	48.1	48.1	65.3	59.2	53.1	53.3	53.3	53.3
2 60	59.0	46.2	43.6	73.3	65.8	65.8	55.0	45.0	42.5	91.4	80.0	80.0	100.0	100.0	100.0	100.0	87.5	87.5

* After 1, 5, and 10 times Laurder-Ometer washing.
[a] pH, 11; Reaction time, 60 min; Reaction Temperature, 90°C; M : L, 1 : 50.
[b] [DMABAC], 1.55%; pH, 11; Reaction Temperature, 90°C; M : L, 1 : 50.

finishing: These results also show that, regardless of the finishing concentrations used in the study, the existence of DMABAC salt on nylon-6 fabrics will still provide antimicrobial activities. The antimicrobial activities can be explained by the fact that the cationic amino groups of regular nylon-6 and nylon-6 grafted with PMAA fabrics treated with DMABAC probably bind to anionic groups of these microorganisms, resulting in growth inhibition.[27]

CONCLUSIONS

A simple, efficient, and practically applicable functional finishing approach for the improvement antimicrobial properties of nylon-6 fabrics and increase the durability of biofunctions was developed. This finishing approach is based on grafting of fabrics with MAA to create additional carboxylic groups in nylon-6 macromolecules, followed by subsequent reaction with DMABAC under alkaline conditions. The optimum reaction conditions were determined. Characterization of the finished fabrics was carried out. The growth inhibition of *B.mycoides*, *E.coli*, and *C. albicans* on the surface of the finished fabrics and the durability of antimicrobial functions were also determined.

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