Preparation of Cationic Polyurethane and Its Application to Acrylic Fabrics

A. Atef El-Sayed, F. A. Kantouch, A. Kantouch

Textile Research Division, National Research Centre, Dokki, Cairo, Egypt

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ABSTRACT: The cationic aqueous polyurethane (CAPU) coatings were prepared by reacting isophoron diisocyanate with quaternized diethanolamine (DEA) and poly(ethylene glycol) of two different molecular weights (M_n = 600 and 1000 g/mol; $CAPU_{600}$ and $CAPU_{1000}$). The quaternization of DEA and the formation of cationic polyurethane were investigated by Fourier transform infrared analysis. The pilling resistance and the antimicrobial property of the coated acrylic fabric were also studied. Obtained results showed that the pilling resistance of the treated fabrics increased with the increase in the concentration of the used CAPU. The acrylic fabrics treated with $CAPU_{1000}$ shows higher value of pilling resistance, even at lower concentration in comparison with $CAPU_{600}$. The higher the curing temperature is, the higher the pilling resistance, fabric roughness, and yellowness of the treated acrylic fabrics are. The untreated fabric showed no antimicrobial property, while the treated fabrics with CAPU showed superior antimicrobial properties. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 777–783, 2011

Key words: cationic aqueous polyurethane; waterborne polyurethane acrylic fabrics; pilling; antimicrobial

INTRODUCTION

Polyacrylonitrile copolymer is widely used in manufacturing acrylic fibers. Acrylic fibers have some advantages such as high-tensile strength, good abrasion resistance, good insect resistance, and easy-dyeing,[1] which make these fibers popular in apparel and in out-door applications.

In spite of many superior properties of acrylic fibers, they have some poor features such as low-moisture absorption, poor antistatic properties, and high accessibility to pilling, which limit their usage without modification.

Addition of antibacterial functions on acrylic fibers has become a serious public concern in the recent years. Many research efforts have been spent on improving antimicrobial properties of the fibers.[2–4] Many biocides are small molecules that can easily leach out of the surface of fibers, especially in the process of washing, and therefore losing the active functions quickly. Improving durability of biocidal functions on acrylic polymers has been a challenge.

Aqueous polyurethane has been widely used in coating, because it has advantages in environmental pollution, fire safety, and soil resistance compared to solvent-based polyurethane.[5–7] As an important type of aqueous polyurethane, cationic aqueous polyurethane (CAPU) has attracted particular attention due to its unique properties such as dispersibility in water, excellent adhesion on many polymeric and glass substrates, and film-forming ability.[8–12] The physical properties of CAPU are greatly affected by the hard segment, soft segment, chain extender, and dispersing center.[13] The hard segment gives CAPU casting film superior tensile strength and hardness,[14–16] while the soft segment offers fine elasticity, abrasion resistance, flexibility, and weatherability.[17]

In this study, the CAPU emulsions were prepared by reacting isophoron diisocyanate with quaternized diethanolamine (DEA) and poly(ethylene glycol) (PEG) of two different molecular weights (M_n = 600 and 1000 g/mol). The cationic polyurethanes were characterized with Fourier transform infrared (FTIR), and the properties of the treated acrylic fabric were determined by different tests.

EXPERIMENTAL

Materials

PEG (Merck) (M_n = 600 and 1000 g/mol), used as the soft segment, was vacuum dried at 80°C for 3 h before use. Isophorone diisocyanate (IPDI; Fluka) was used as the hard segment, and

Correspondence to: A. A. El-Sayed (amratefelsayed@yahoo.com).

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dibutyltin dilaurate (DBTDL; Aldrich), was used as a catalyst. DEA (Fluka), methyl iodide (Aldrich), and methyl ethyl ketone (MEK) as solvent were used. White pure plain weave acrylic fabrics (T_g 82.6°C, T_c 479°C, and T_m 336.4°C), supplied from Misr Mehella for Spinning and Weaving, Mehalla El-Kobra, Egypt, were used. It is worth noting that the FTIR analysis of the untreated acrylic fibers is similar to that of acrylic fibers made from acrylonitrile, methyl acrylate, and itaconic acid comonomers. The fabrics were washed before treatment with a nonionic detergent (2 g/L) at 60°C for 45 min thoroughly rinsed and dried at room temperature.

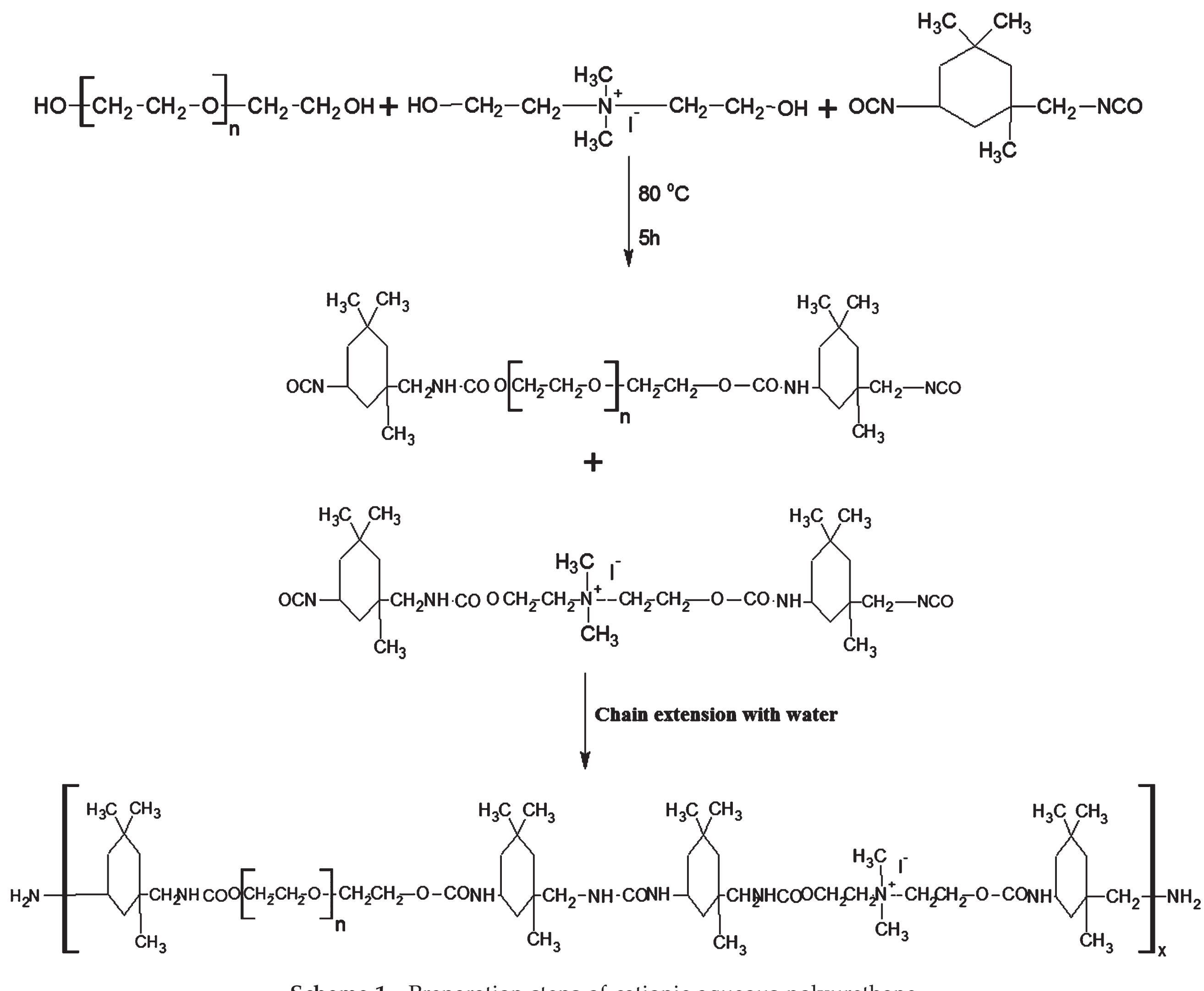
Quaternization of DEA

The quaternization reaction was conducted as follows: 2 mol of methyl iodide was added drop wise with continuous stirring to 1 mol diethanolamine (DEA) at 30°C for 3 h, and the reaction was left to complete over night at room temperature.

Preparation of cationic aqueous polyurethane

One mole of PEG, 1 mol of quaternary salt of DEA, and DBTDL (0.02% based on the total reaction mass) were introduced in a vacuum reactor to remove any moisture. This was followed by the addition of 4 mol of IPDI as a butanone solution. The reaction was carried out in a three-necked flask fitted with a reflux condenser, a mechanical stirrer, a thermometer, and a nitrogen gas inlet. The reaction mixture was stirred for 5 h at 75–80°C. At the end of reaction, water was added with vigorous stirring for complete emulsification. The mixture was heated to 80°C to remove MEK, yielding CAPU dispersions. The polymers prepared using PEG (M_n = 600 and 1000) were abbreviated as $CAPU_{600}$ and $CAPU_{1000}$, respectively.

The preparation steps of CAPU are shown in Scheme 1



Scheme 1 Preparation steps of cationic aqueous polyurethane.

Treatment of acrylic fabrics with polymer solution

The acrylic fabrics were subjected to a pad-cure method, using polymer solutions of different concentration (2, 4, 6, and 8%) using a SVETEMA laboratory padder. The padding pressure was adjusted to allow a pickup of 90% and padding speed was 3 m/min. The samples were dried at 80°C for 30 min and then cured at different temperatures (100–150°C) for 1 min in an electric oven. The samples were then washed at 50°C for 15 min, thoroughly rinsed, and finally air dried at ambient conditions.

Identification of CAPU

Infrared spectroscopy

The DEA and its quaternized form with methyl iodide as well as CAPU were analyzed by Fourier transform infrared (FTIR) (JASCO 6100 infrared spectrophotometer) at 25°C. The scanning range was 400–4000 cm^{-1}.

Characterization and analysis of the treated acrylic fabrics

Determination of the pilling resistance

The pilling resistance of untreated as well as treated acrylic samples was assessed according to ASTM 4966/4970 using Martindal Abrasion and Pilling Tester (M235-A, USA).

Antimicrobial activity

The antimicrobial activity was measured using the diffusion disc method.[18–20] The micro organisms used were *Bacillus substilis*, *Staphylococcus aureus*, *Escherichia coli*, and Pseudomonas aeruginosa. The method is summarized as follows:

A sterilized filter paper disc saturated with measured quantity of the sample is placed on a plate-containing solid bacterial medium, which has been heavily seeded with the spore suspension of the tested organism. After inoculation, the diameter of the clear inhibition zone surrounding the sample is taken as a measure of the inhibitory power of the samples against the particular test organism.

Yellowness index

Measurement of the yellowness index (YI) was carried out by using Hunter lab (The Color Management Company, USA). YI was determined according to ASTM method E313.

Roughness

Surface roughness of the untreated as well as the polymer-treated acrylic fabrics was measured according to JIS 94 Standard, using a Surface Roughness Measuring Instrument, SE 1700 α (Kosaka Laboratory, Japan).

Measurement of the acid content of the acrylic fabrics

Untreated acrylic fabrics as well as the polymer-treated fabrics were analyzed for the determination of their acid content. The fabrics was immersed in a standard sodium hydroxide solution of known concentration over night, and then the excess hydroxide was back titrated with standard HCl.[21]

Scanning electron microscopy

Untreated as well as treated acrylic fabric was mounted on aluminum stubs, sputter coated with gold in a 150 Å sputter (coated Edwards), and examined by Jeol (JXA-840A) Electron Probe Microanalysis (Japan) with magnification range of 35–10,000.

RESULTS AND DISCUSSION

FTIR analysis of CAPU

Comparing the FTIR spectra of DEA (A) and its quaternized form (B) are given in Figure 1. A new intense peak at 1640 cm^{-1} is observed as a result of the quaternization process of the nitrogen atom in

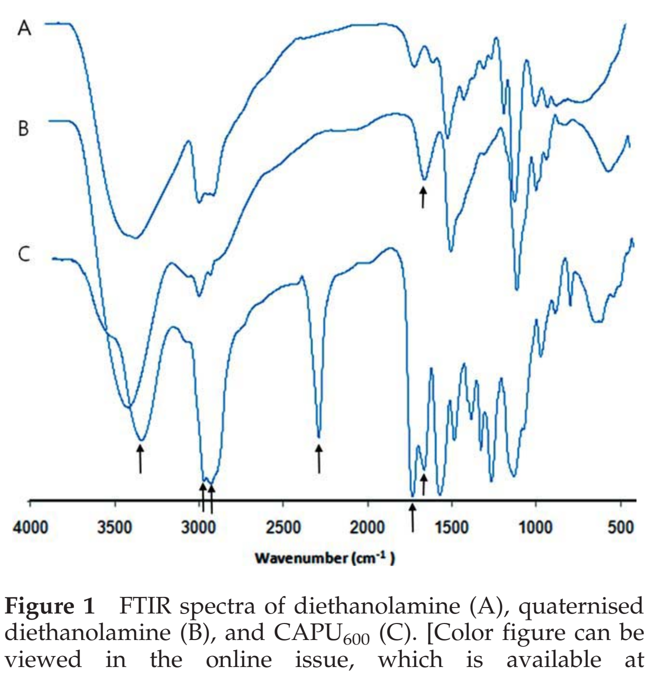


Figure 1 FTIR spectra of diethanolamine (A), quaternised diethanolamine (B), and CAPU$_{600}$ (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Effect of Concentration of CAPU on the Pilling Resistance of Acrylic Fabrics (Curing Temperature : 140°C, Curing Time : 1 min)

Treatment	Concentration of CAPU solution (%)	Increase in fabric weight (%)	Acid content (meq/100 g fabric)	Pilling factor
Untreated acrylic fabrics	–	–	27.8	1
$CAPU_{600}$	2	1.42	22.5	2
	4	3.31	15.9	4–5
	6	5.10	11	5
	8	6.7	6.1	5
$CAPU_{1000}$	2	1.22	23.9	3–4
	4	3.10	17.2	4–5
	6	5.00	11.7	5
	8	6.3	8.1	5

Pilling factor : 1 = bad, 2 = fair, 3 = good, 4 = very good, and 5 = excellent.

DEA. The FTIR analysis of $CAPU_{600}$ (C) shows the NH peak of urethane at 3319 cm^{-1}. The absorption peaks of CH_2 (symmetric and asymmetric) occurred at 2949 and 2910 cm^{-1}. The absorption peak at 2266 cm^{-1} is designated for the isocyanate group (NCO) of the unextended $CAPU_{600}$. Further, the absorption peak for CO appearing at 1709 cm^{-1} with its broad nature indicates that this group is involved in hydrogen bonding. The polyurethane cationomers show a strong peak at 1640 cm^{-1}, which is specifically due to the quaternization of DEA.

Effect of CAPU concentration on the pilling resistance of the treated acrylic fabrics

Pilling is an operation of forming small balls on the surface of the fabrics called pills. These pills are made up of fibers that appear on the surface of the fabric. They impart an undesirable appearance to the garment. Pilling takes place as a result of migration of loose fibers from the interior of the fabric to the surface.[22] The pilling resistance of the treated fabrics increased with an increase in the concentration of the CAPU, as shown in Table I. This result emphasizes the ability of CAPU to form an outer surface coating on acrylic fibers; therefore, the fibers are becoming fixed in place, more resistant to external forces, and do not glide against each other. Thus, the fabric would become more resistant to pilling. It is also found that $CAPU_{1000}$ shows enhancement in pilling resistance (pilling factor 3–4) even at lower concentration in comparison with $CAPU_{600}$. The increase in fabric weight with an increase in the polymer solution concentration may be due to the interaction between the carboxylic groups in acrylic fibers and the positively charged quaternary nitrogen in CAPU (in the same way of reaction of cationic dyes with acrylic fabrics). The decrease in the acid content of the fabrics with an increase in polymer concentration also emphasizes the neutralization of the carboxylic groups in acrylic fibers and the positively charged quaternary nitrogen in CAPU.

Effect of curing temperature on the pilling resistance of the treated acrylic fabrics

Adopting padding technique, acrylic fabric was treated with $CAPU_{600}$ or $CAPU_{1000}$ and cured at different temperatures. Results of these treatments are illustrated in Table II. The untreated acrylic fabric showed severe pill formation, which could be attributed to the presence of loose fibers of different fineness and low-surface smoothness.

The addition of $CAPU_{600}$ or $CAPU_{1000}$ leads to improvement in the pilling resistance of the treated samples. This can be due to increased fixation of the loose fibers through formation of an outer surface coating on the acrylic fibers. This makes the treated fabrics more resistant to the outside forces, because the fibers do not glide against each other. Thus, the fabric would become more pilling resistant.[22] This outer surface coating on the acrylic fibers has been confirmed by SEM (Fig. 2), which shows the formation of a polyurethane layer on the fiber surface. Table II also shows that the higher the curing temperature is, the higher the pilling resistance of the acrylic fabrics is. This result might be because when the curing temperature increases, the polyurethane cast over the fibers becomes more fixed by the heat, and thus the fibers lose the freedom of relative mobility. Moreover, at a higher temperature, the reaction between the quaternary nitrogen in polyurethane and the carboxylic groups in the acrylic fiber would be facilitated, resulting in better adhesion. Table II

TABLE II
Effect of the Curing Temperature on the Pilling Resistance of the Treated Acrylic Fabrics (CAPU Concentration: 4%, Curing Time: 1 min)

Treatment	Curing temperature (°C)	Pilling factor
Untreated acrylic fabrics	–	1
$CAPU_{600}$	100	2–3
	110	3
	120	3
	130	4
	140	4–5
	150	4–5
$CAPU_{1000}$	100	3
	110	3
	120	4
	130	4
	140	4–5
	150	5

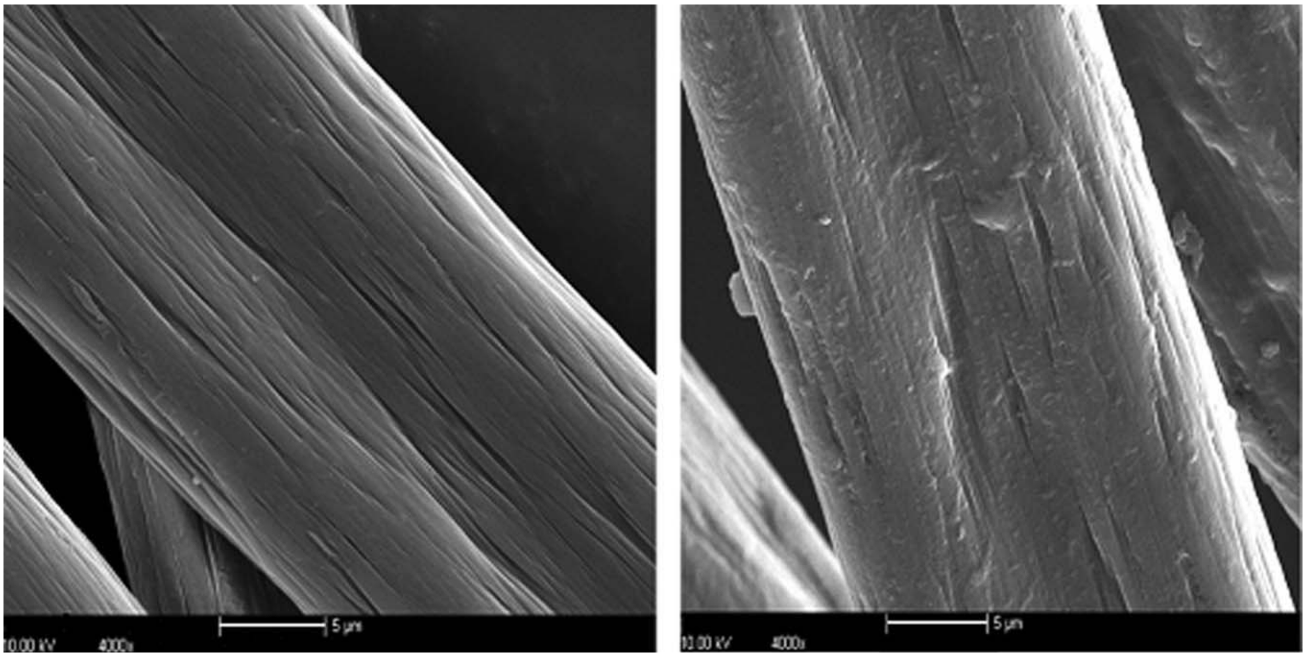


Figure 2 SEM images of the untreated acrylic fabric (A) and treated with $CAPU_{600}$ (B) ($CAPU_{600}$ concentration : 4%, curing temperature : 140, curing time : 1 min).

also gives the evidence that the molecular weight of the PEG molecule (the soft segment in the polyurethane chain) has an effect on the pilling resistance of the treated fabric. The higher the molecular weight of PEG is, the less the pilling is. The reason for this effect is that when the molecular weight of CAPU increases, the molecular chain becomes longer, and there is more chance for it to link with the fiber, and the fabric structure becomes more stable, so that there is less gliding mobility between fibers, that is, the fabric would become more pilling resistant.[23] Therefore, the $CAPU_{1000}$ gave the fabric the best pilling resistance.

Effect of the curing temperature on YI and roughness of the treated fabrics

The effect of treatment of acrylic fabrics with CAPU at various temperatures on its YI and roughness was studied. Results of this investigation are represented by Figures 3 and 4. As seen from Figure 3, the roughness of the treated fabrics is worse than that of the untreated one, and the roughness of the fabric increases with curing temperature. This result is most probably due to the formation of an uneven layer of tough membrane on the surface of the fabric through the combination of the CAPU with fiber. However, it is hard to explain the origin of an

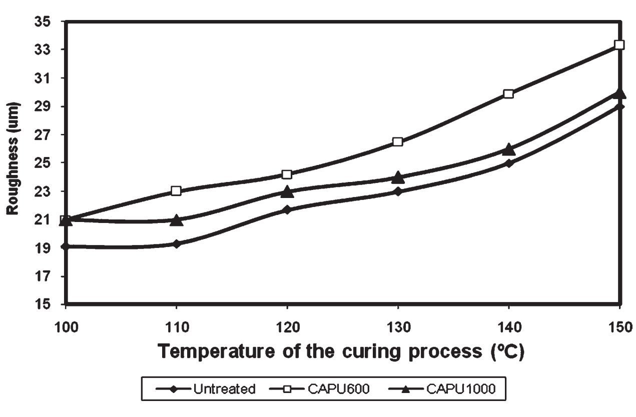


Figure 3 Effect of the curing temperature on the roughness of the treated fabrics (CAPU concentration : 6%, curing time : 1 min. The roughness of raw acrylic fabric is 17.1).

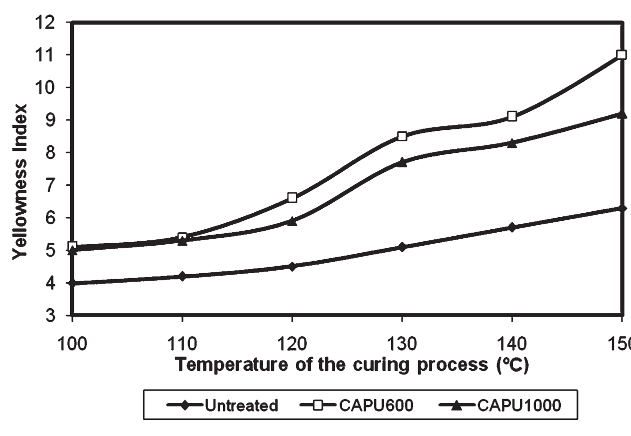


Figure 4 Effect of the curing temperature on the yellowness index (YI) of the treated fabrics (CAPU concentration : 6%, curing time : 1 min. The YI of raw acrylic fabric is 3.4).

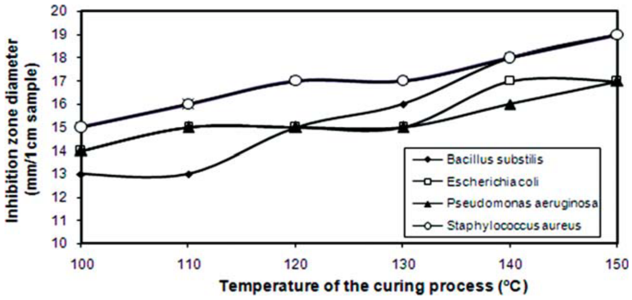


Figure 5 Effect of curing temperature on the antimicrobial property of acrylic fabrics ($CAPU_{600}$ concentration : 4%, curing time : 1 min, inhibition zone diameter of raw acrylic fabric : 0).

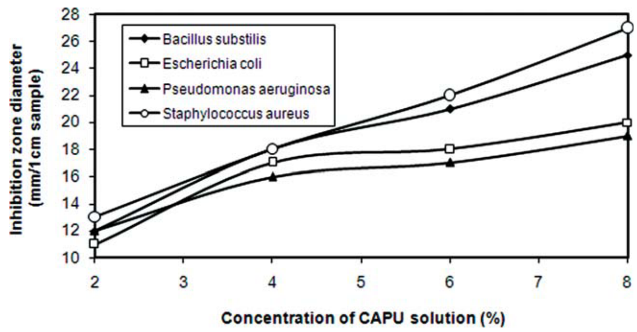


Figure 6 Effect of polymer concentration on the antimicrobial property of acrylic fabrics (polymer used is $CAPU_{600}$, curing temperature : 140°C, curing time : 1 min, inhibition zone diameter of raw acrylic fabric : 0).

increase in roughness with curing temperature. It is also obvious that the higher the molecular weight of PEG is, the lower is the roughness of the treated fabric. The reason for this effect is that the molecular chain of the prepared polyurethane forms more elastic and softer film on the fabric surface with an increase in the molecular weight of PEG. As shown in Figure 4, the treated fabrics with CAPU turned yellow more than the untreated fabrics, and the degree of yellowing increased with curing temperature. This result could be understood on the bases of the thermal stability of the fibers and the CAPU. It is also worthwhile to note that the higher the molecular weight of PEG is, the degree of yellowing decreases. This result reflects the higher thermal stability of $CAPU_{1000}$ in comparison with $CAPU_{600}$, which is in accordance with literature.[23]

Effect of the curing temperature on the antimicrobial property of the treated fabrics

The effect of curing temperature on the antimicrobial property of the treated fabric is shown in Figure 5. The untreated fabric shows no antimicrobial property, whereas the fabrics treated with CAPU show superior antimicrobial properties. This difference is presumably because of the presence of positively charged quaternary ammonium ions in the polymer chains that would reduce bacterial metabolism by the adsorption and stacking of polymer chains on the bacterial cell wall and by blocking DNA transcription by CAPU. This process would thereby enhance the antimicrobial property of the treated fabric.[24] Figure 5 also shows that the higher the curing temperature is, the higher is the antimicrobial resistance of the acrylic fabrics. This result might be because, at higher temperature, the reaction between the quaternary nitrogen in polyurethane and the carboxylic groups in the acrylic fiber would be facilitated, resulting in better adhesion, and, consequently, the polyurethane cast over the fibers becomes more fixed. Therefore, even after washing, high amount of the quaternary nitrogen can be present for killing bacteria. However, the size of the PEG molecule had little influence on the antimicrobial properties of the treated fabrics.

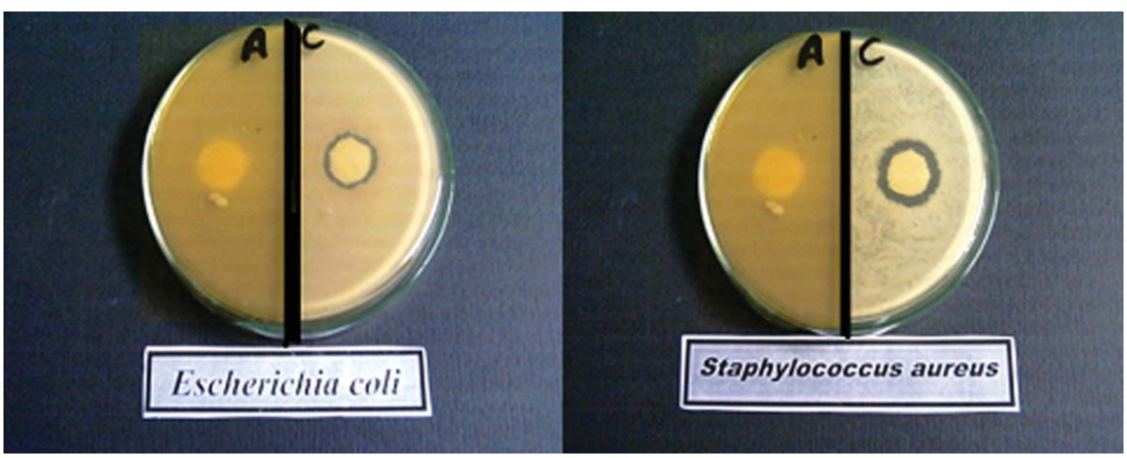


Figure 7 The photographs of the bacteria inhibition zone for the untreated acrylic fabric (A) and treated with $CAPU_{600}$ (C) ($CAPU_{600}$ concentration : 4%, curing temperature : 140°C, curing time : 1 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of CAPU concentration on the antimicrobial property of the treated acrylic fabrics

Figure 6 shows that the antimicrobial property increases with the increase in the concentration of the polymer solution. This result could be attributed to the increase in the number of quaternary nitrogen present on the fiber surface, which is the main factor in killing bacteria and selected photographs of the obtained results are shown in Figure 7.

CONCLUSIONS

The CAPU coatings were prepared by reacting isophoron diisocyanate with quaternized DEA and PEG of two different molecular weights ($M_n = 600$ and 1000 g/mol). The obtained results are summarized in the following:

Comparing the FTIR spectra of DEA and its quaternized form, a new intense peak appeared at 1617 cm^{-1} as a result of the quaternization process of the nitrogen atom in DEA. The polyurethane cationomer showed a strong peak at 1640 cm^{-1}, which is specifically due to the quaternization of DEA.

Acrylic fabrics treated with CAPU showed very low-pill formation when compared with untreated fabrics. The pilling resistance was increased with increase in the concentration of the CAPU and the molecular weight of PEG ($CAPU_{1000} > CAPU_{600}$).

The decrease in the acid content of the acrylic fabrics with an increase in polymer concentration indicates the interaction between carboxylic groups in acrylic fibers and the positively charged quaternary nitrogen in CAPU.

The higher the curing temperature is, the higher is the pilling resistance of the acrylic fabrics.

The untreated fabric has no antimicrobial property, while the fabrics treated with CAPU show superior antimicrobial properties. The size of the PEG molecule has little influence on the antimicrobial properties of the treated fabrics. The increasing concentration of the polymer solution increases the antimicrobial property of the treated acrylic fabrics. This result could be attributed to the increase in the number of quaternary nitrogen present on the fiber surface, which is the main factor in killing bacteria.

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