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Application of prepared waterborne polyurethane extended with chitosan to impart antibacterial properties to acrylic fabrics

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Abstract In this study, isophorone diisocyanate (IPDI), 2,2-bis (hydroxylmethyl)-propionic acid and polyethylene glycol (PEG) were employed to polymerize waterborne polyurethane. The polyurethane prepolymer was extended with chitosan of two different molecular weight (100,000 and 150,000), and used as finishing agent for acrylic fabrics. The antibacterial activity of the acrylic fabric treated with the polyurethane-chitosan solution was improved even after 15 washing times. Pretreatment of acrylic fabrics with hydrazine hydrate was found to improve the uptake of the polymer by the fabric. The effects of hydrazine and polyurethane treatments on some of the inherent properties of acrylic were assessed. The functional groups of polyurethane prepolymer as well as polyurethane extended with chitosan were confirmed with the analysis of the spectra of Fourier transform infrared spectroscopy (FT-IR).

1 Introduction

The increase in public knowledge and awareness of disease transmission and cross-infections caused by microorganisms, leads to the careful attention to the use of antimicrobial materials in many applications, such as the manufacturing of protective clothes for medical workers, underwear, sportswear and others health care products [1, 2].

On one hand, polyurethane (PU) copolymers demonstrate unique properties of both rubber and plastics. The unique properties of linear polyurethanes can be attributed to their specific micro-phase structure (hard-segment and soft-segment) [3]. Waterborne (emulsion in water) polyurethane coatings have gained more and more attention and speedy development. Therefore, it is expected to substitute the organic solvent soluble polyurethane coatings [4–17].

Moreover, chitosan is a natural polymer and a linear polysaccharide obtained from the *N*-deacetylation of chitin with a strong alkali [18, 19]. Chitosan structure is basically constituted of D-glucosamine units, and its content of *N*-acetyl–D-glucosamine is in the range of 0–50% [20, 21]. The most interesting property of chitosan is its high antimicrobial activity even at very low concentrations. Recently, many studies have been conducted to get use of the chitosan as a biomaterial and polyurethane through blending [22–24].

Among synthetic fibers, acrylic fibers seem to be an important fiber, because of their potential applications in the textile industry and other implants [25]. However, some minor textile performances (thermal stability, crease recovery, low moisture absorption and antimicrobial activity) need to be improved.

In the present study, waterborne polyurethane was prepared and reacted with chitosan as chain extender. The prepared polyurethane chitosan copolymer was studied as antimicrobial agent for acrylic fabrics. The treated acrylic fabrics are expected to be suitable in the manufacture of blankets and carpets in hospitals, as a result of its new antimicrobial properties.

2 Experimental

2.1 Materials

Carboxylic-containing acrylic fabrics, were supplied from Misr Mehella for Spinning and Weaving, Mehalla El-Kobra,

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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. These fabrics were washed before treatment with a non ionic detergent (2 g/l) at 60°C for 45 min then rinsed thoroughly in tap water and dried in the open air.

Isophorone diisocyanate (IPDI; Fluka), dibutyltin dilaurate (DBTDL; Aldrich), Hydrazine hydrate (HY; Merck), Triethylamine (TEA; Fluka) and 2, 2-bis (hydroxylmethyl)—propionic acid (DMPA, Aldrich) were used as received. Polyethylene glycol (PEG; Mn = 600), (Merck) was dried at 80°C under vacuum for 3 h.

Chitosans (CS) from a crab shell (Mallinckrodt) were used. The degree of deacetylation not less than 75% and their average molecular weight were (100,000 and 150,000). Cationic dyestuff (C.I. Basic Red 18).

2.2 Methods of preparation and treatments

2.2.1 *Preparation of waterborne polyurethane prepolymer*

IPDI, PEG and DMPA in a molar ratio of (4:1:1) and 0.1% DBTDL as a catalyst were charged in a three-necked flask equipped with mechanical stirrer, thermometer, reflux condenser and nitrogen inlet. The reaction was performed at 80°C for 4 h. The polyurethane prepolymer was left to cool until ambient temperature and diluted with appropriate amount of butanone. One mole TEA was added to ionize the carboxyl groups in DMPA. The chain extension step (copolymerization reaction) was carried out by dissolving one mmole chitosan in suitable amount of water containing 1% acetic acid; the chitosan solution was slowly dropped into polyurethane prepolymer with vigorous stirring. The polyurethane extended with chitosan of molecular weight 100,000 or 150,000 were designated as $\text{PUCH}_{100,000}$ and $\text{PUCH}_{150,000}$.

2.2.2 *Treatment with hydrazine*

Acrylic fabrics were immersed in aqueous solution containing 10–30 g/l hydrazine hydrate for 20 min at 80°C, liquor ratio 1:25. The samples were then thoroughly washed in warm and cold water and air-dried.

2.2.3 *Treatment of acrylic fabrics with polymer solution*

The acrylic fabrics pretreated with hydrazine hydrate as well as untreated fabric were immersed in the polymer solution of 6% concentration and squeezed between two stainless steel rollers (pad-cure method), using SVETEMA laboratory padder. The padding pressure was adjusted to allow a pick up of 90%; padding speed was 3 m/min. The samples were dried at 80°C for 30 min and then cured at 150°C for 1 min in an electric oven.

2.2.4 *Dyeing of acrylic fabrics*

Acrylic fabrics were dyed using dyestuff (C.I. Basic Red 18). Accurately weighed and pasted dye with small amount of water was prepared. This paste was then dissolved in water at 100°C and then filtered. The dye bath was adjusted to pH 4.5 using acetic acid and heated at 90°C, for varying periods of time (15–150 min). The dyed samples were then thoroughly washed in warm and cold water and air-dried.

2.2.5 *Analytical methods*

2.2.5.1 Infrared spectroscopy (FTIR-ATR) The chemical structure of the chitosan, polyurethane prepolymer and polyurethane extended with chitosan were analyzed in a JASCO 6100 infrared spectrophotometer, provided with Fourier transform analysis (FTIR).

2.2.5.2 Colour value The colour value is Referring to the amount of dye absorbed by the fabrics, and determined by spectral reflectance measurements of the dyed fabrics. The colour values of the dyed fabrics were carried out using a recording filter Spectrophotometer Hunter lab (The Colour Management Company, USA). The colour value expressed as K/S of the dyed samples was determined by applying the Kubelka–Munk [26] equation.

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_o)^2}{2R_o}$$

where R: is the decimal fraction of the reflectance of the dyed substrate. R_o: is the decimal fraction of the reflectance of the undyed substrate S: is the scattering coefficient K: is the absorption coefficient

2.2.5.3 Yellowness index The yellowness index is the measure of the tendency of plastics to turn yellow upon long-term exposure to light. Measurement of the yellowness index was carried out by using Hunter lab (The Colour Management Company, USA). Yellowness Index (YI) was determined using ASTM method E (313).

2.2.5.4 Colour washing fastness The colour fastness to washing was determined according to ISO 106-Coz (1993) using a Launder meter. The soaped specimens (5 × 5 cm) were sewed between two pieces of wool and acrylic fabrics. Evaluation of the washing fastness was given using the Grey Scale reference for colour change.

2.2.5.5 Antibacterial washing fastness In order to simulate the washing program for acrylic fabrics in automatic washing machines. The following procedure for estimating the antibacterial washing fastness was adopted. The specimens were immersed into an aqueous solution containing 5 g/l nonionic detergent and 2 g/l sodium carbonate, liquor ratio of 1:50 at 40°C. The test was run for 15 min. The samples were then removed, rinsed twice in 100 ml of water with occasional stirring and hand squeezing.

2.2.5.6 Moisture regain The moisture regain is the parameter to evaluate the moisture present in a material, expressed as a percentage of the moisture-free weight, as determined under definite prescribed conditions.

The measurement of the moisture regain of the acrylic sample was performed according to ASTM Standard 2654-76. [27]. The moisture regain of the samples were calculated according to:

$$\text{Moisture regain } \% = \frac{W_1 - W_2}{W_2} \times 100$$

where W_1: Weight of sample after saturation in the standard humidity atmosphere. W_2: Constant weight of dried sample.

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

2.2.5.8 Antimicrobial activity The antimicrobial activity was measured using diffusion disc method [28–30], the micro organisms used were *Bacillus substilis*, *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. The method is summarized as follow:

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.

2.2.5.9 Molecular weight distribution The molecular weight and molecular weight distributions of the polyurethane prepolymer and polyurethane copolymerized with chitosan were obtained by Agilent Gel Permeation Chromatography (GPC), using a Waters peristaltic pump HPLC (flow rate of DMF was 1 ml/min), and a Waters 410 refraction index detector.

3 Results and discussion

3.1 Synthesis and identification

Table 1 shows the data obtained from the GPC analysis of the pure waterborne polyurethane and polyurethane extended with chitosan (Mn 100,000 and 150,000). The copolymerization reaction between polyurethane prepolymer and chitosan, leads to noticeable increase in the molecular weight.

Figure 1 shows FTIR spectroscopic analyses of the synthesized waterborne PU. (a) is the FTIR spectrum for the chitosan (Mn 100,000), (b) is polyurethane prepolymer before the chain-extending reaction and (c) is polyurethane extended with chitosan. From Fig. 1b, there is an absorption peak for –C–O–C– soft linkage at 1103 cm^{-1} Also, there are absorption peaks at 3327, 1730, 1530, and 1450 cm^{-1} corresponding to functional groups of –NH–, –C=O, –COO–, and –CNH, respectively, also we can see that the absorption peak of NCO at 2250–2270 cm^{-1} is very prominent before the chain-extending reaction, but this peak disappeared in the polyurethane product after the chain-extending reaction (Fig. 1c). These prove the formation of urethane groups in the waterborne PU. The chain extending reaction is expected to be through the formation of urea linkage (Fig. 2) as a result of the reaction between the terminal isocyanate in the polyurethane prepolymer and the amino group in the chitosan; considering the higher reactivity of NH_2 in comparison with the OH groups of chitosan or with water [31]. Figure 1c shows an additional intense absorption band at 1643 cm^{-1} corresponding to NH of urea.

3.2 Effect of hydrazination on the amount of PUCH uptake

Studying the effect of pretreatment of acrylic fabric with hydrazine hydrate solutions of different concentrations (10–30 g/l), on the amount of PUCH uptake, shows that the % uptake of $\text{PUCH}_{100,000}$ or $\text{PUCH}_{150,000}$ by the acrylic fabric were increased, with the increase in the concentration of hydrazine hydrate solution (Table 2). That could be attributed to the reaction of hydrazine with the acrylonitrile group

Table 1 Average molecular weight of the waterborne polyurethane

Sample	M_n	M_w
Polyurethane prepolymer	1.05×10^4	1.14×10^4
Polyurethane extended with chitosan (Mn 100,000	1.1×10^5	3.9×10^5
Polyurethane extended with chitosan (Mn 150,000	1.53×10^5	5.35×10^5

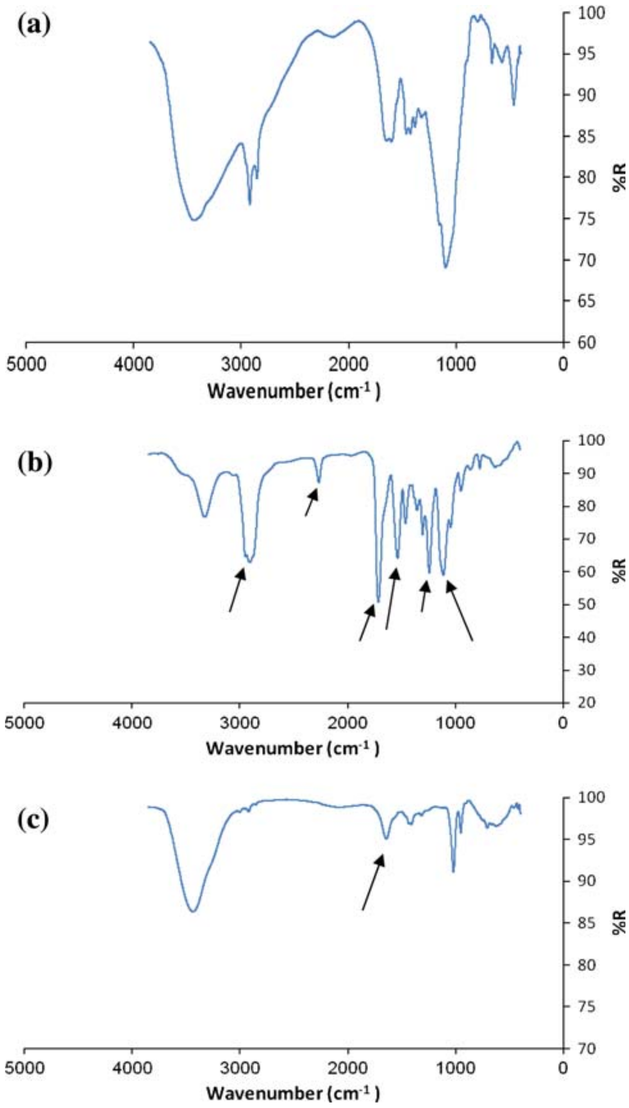


Fig. 1 **a** The FTIR spectrum for the chitosan (Mn 100,000). **b** The FTIR spectrum for the polyurethane prepolymer. **c** The FTIR spectrum for the polyurethane extended with chitosan

of acrylic fabric and converting it into semi-nitrile terminated with amino group [32, 33] as follow (Scheme 1):

The increment of amino groups to the fiber surface is believed to be the reason behind the increase in the uptake (gm polymer/100 gm fabric) of PUCH$_{100,000}$ or PUCH$_{150,000}$, as it act as a favorable site for the ionic interaction with the carboxylic groups in the PU backbone chain.

3.3 Yellowness index, roughness and moisture regain

The effect of treatment of acrylic fabrics with hydrazine hydrate, chitosan, polyurethane prepolymer or PUCH on some of its inherent properties. Results of this investigation are summarized in Table 3. Data of this Table show that the yellowness index is greatly affected by treatment with hydrazine (16.11–28.58) in comparison with the untreated fabrics (3.29), while treatment with polyurethane prepolymer or PUCH show no remarkable effect on yellowness index of the acrylic fabrics. Only CH$_{150,000}$ or PU CH$_{150,000}$ give increase in the surface roughness of the treated fabrics, but however stile in acceptable limit. Either treatment with polyurethane prepolymer or PUCH show appreciable decrease in moisture regain of acrylic fabrics relative to the untreated one.

3.4 Effect of pretreatment with hydrazine then polyurethane on dyeability

The effect of treatment of acrylic fabrics with hydrazine hydrate of different concentrations, followed by treatment with waterborne polyurethane on its dyeability was studied (Figs. 3, 4, 5). The dyeability of acrylic fabrics treated either with PUCH$_{100,000}$ or PUCH$_{150,000}$, were increased in comparison with the untreated fabrics. This is due to the contribution of the carboxylic groups in the polyurethane backbone, with the carboxylic groups existed in the acrylic chains in the uptake of dye molecules. Pretreatment of acrylic fabrics with hydrazine hydrate, was found to have adverse effect on dyeability as a result of increasing the basic nature of the fabric. The aforementioned conclusion is also confirmed by the data obtained form the colour fastness study (Table 4), which shows that the washing fastness rates of the dyed pretreated acrylic fabrics with cationic dyes, was improved with all treatments as compared with untreated one.

3.5 Effect of treatment on antibacterial activity

Table 5 shows the effect of the different treatments of acrylic fabric on its antimicrobial activity against four strains of bacteria. The treated samples with CH$_{100,000}$, CH$_{150,000}$, PUCH$_{100,000}$ or PUCH$_{150,000}$ show remarkable enhancement in the antibacterial activity, in comparison with the untreated acrylic sample. In general the antibacterial activity was found to increases with the increasing in the molecular weight of chitosan, which could be understood on the bases of the effective cationic amino groups in the chitosan macro chins. The cationic amino group of chitosan would in turn, reduce bacterial metabolism by the adsorption and stacking of chitosan chains on the bacterial cell wall, and by blocking DNA transcription. This process would thereby enhance the antimicrobial property of the treated fabric [34]. The aforementioned mechanism could be used to explain the increase in antibacterial activity with increasing in the molecular weight of chitosan (i.e., higher molecular weight, means larger number of amino groups). Data of Table 4 also shows that there is no washing

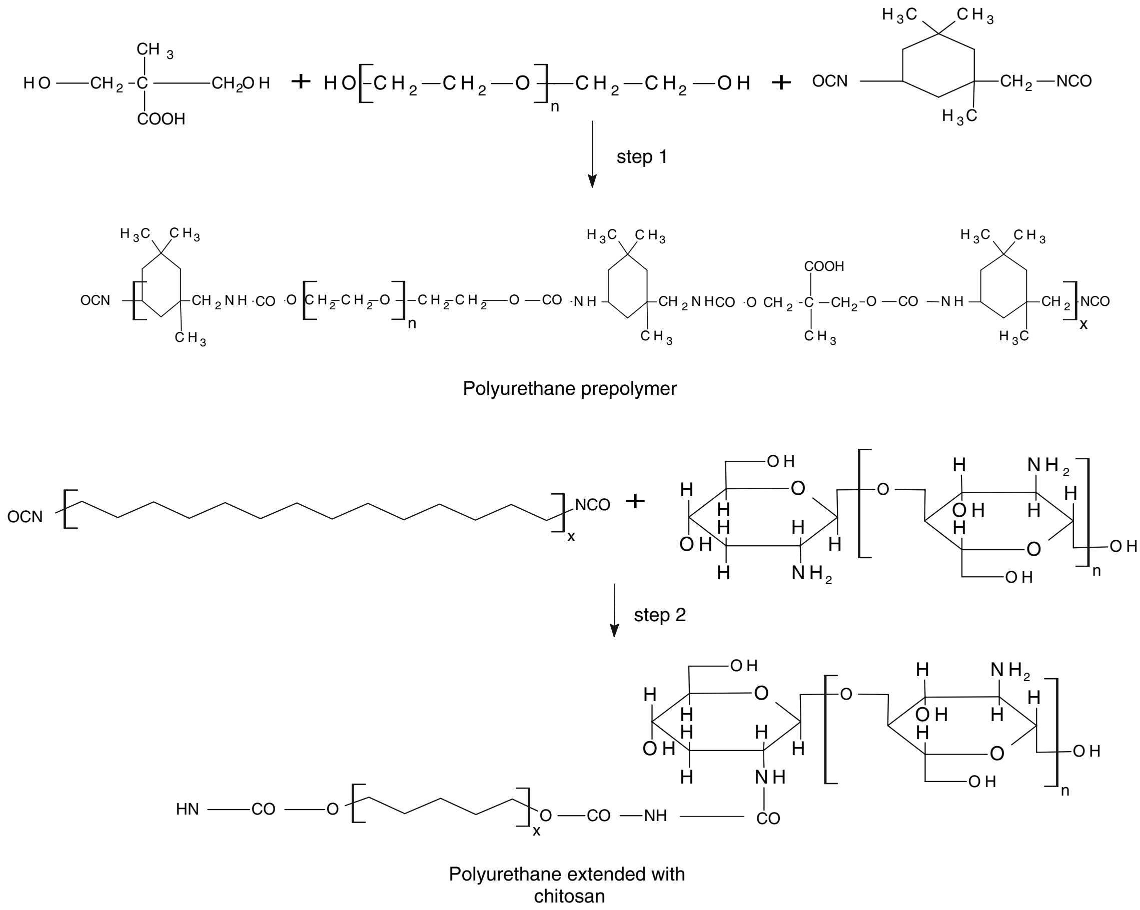
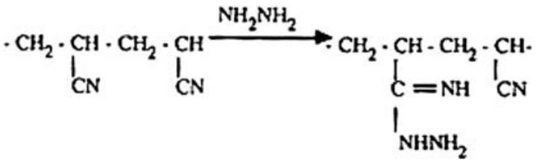


Fig. 2 Schematic representation of the polyurethane prepolymerization reaction (*step 1*), then chain extension (copolymerization) with chitosan (*step 2*)

Table 2 Effect of pretreatment of acrylic fabric with hydrazine hydrate solutions on the uptake (gm polymer/100 gm fabric) of $PUCH_{100,000}$ or $PUCH_{150,000}$ by acrylic fabrics

Conc. of hydrazine hydrate solution (g/l)	The uptake of $PUCH_{100,000}$ (gm polymer/100 gm fabric)	The uptake of $PUCH_{150,000}$ (gm polymer/100 gm fabric)
10	2.9	2.6
20	3.8	3.7
30	4.2	4.0



$$-CH_2-\underset{CN}{CH}-CH_2-\underset{CN}{CH}\xrightarrow{NH_2NH_2}-CH_2-\underset{\underset{NHNH_2}{C=NH}}{CH}-CH_2-\underset{CN}{CH}-$$

Scheme 1 The reaction between acrylic fabrics and hydrazine

fastness of the acrylic fabrics treated with $CH_{100,000}$ or $CH_{150,000}$, which indicates the absence of linkage between chitosan macro chains and acrylic fabric at the adopted curing conditions. On the other hand, acrylic fabrics treated with either $PUCH_{100,000}$ or $PUCH_{150,000}$ seems to be not affected by washing, and the antimicrobial activity remains unchanged after 15 washing cycles. The washing durability indicates the permanency of treatment, which could be explained as a result of ionic interaction between the carboxylic groups of polyurethane (Scheme 1) and the created amino groups on acrylic fabric (Scheme 1), which could also converted into amid linkage at the curing condition.

4 Conclusions

The chain extension reaction between the waterborne polyurethane and chitosan was carried out and confirmed by GPC and FT-IR analysis, (the disappearance of the absorption peak of NCO at 2250–2270 cm^{-1} before the

Table 3 Effect of treatment of acrylic with hydrazine hydrate, chitosan, polyurethane prepolymer or PUCH on some of the inherent properties of acrylic fabrics

Treatment	Yellowness index	Roughness (μm)	Moisture regain %
Untreated acrylic fabric	3.29	17.6	1.8
Chitosan (Mn100,000)[a]	4.14	19.3	1.9
Chitosan (Mn150,000)[a]	4.40	21.7	2.2
Polyurethane prepolymer[b]	4.73	18.5	1.1
Hydrazine solution (10 g/l)	16.11	17.8	1.8
Hydrazine solution (20 g/l)	20.37	17.3	2.0
Hydrazine solution (30 g/l)	28.58	17.6	2.2
Hydrazine solution (10 g/l) and $PUCH_{100,000}$	19.49	21.2	1.4
Hydrazine solution (20 g/l) and $PUCH_{100,000}$	22.19	21.5	1.22
Hydrazine solution (30 g/l) and $PUCH_{100,000}$	31.97	21.3	0.9
Hydrazine solution (10 g/l) and $PUCH_{150,000}$	20.11	22.6	1.7
Hydrazine solution (20 g/l) and $PUCH_{150,000}$	22.50	22.9	1.1
Hydrazine solution (30 g/l) and $PUCH_{150,000}$	33.32	22.3	1.3

[a] Chitosan solution of concentration 0.01 mol/100 ml water and 2% acetic acid

[b] 6% polyurethane prepolymer solution

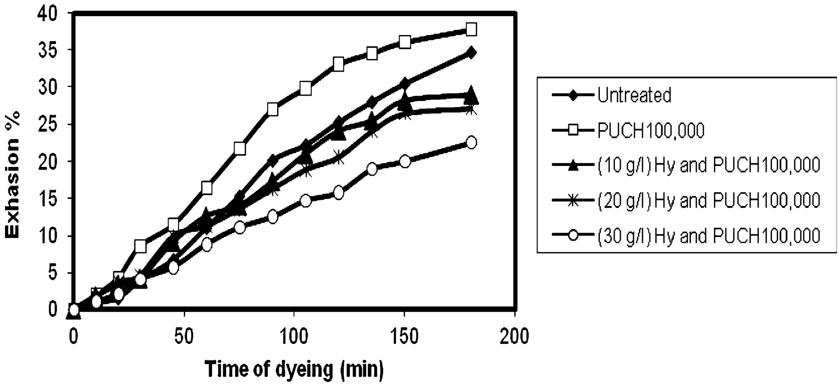


Fig. 3 Effect of treatment with hydrazine and $PUCH_{100,000}$ on dyeability of acrylic fabric with basic red dye

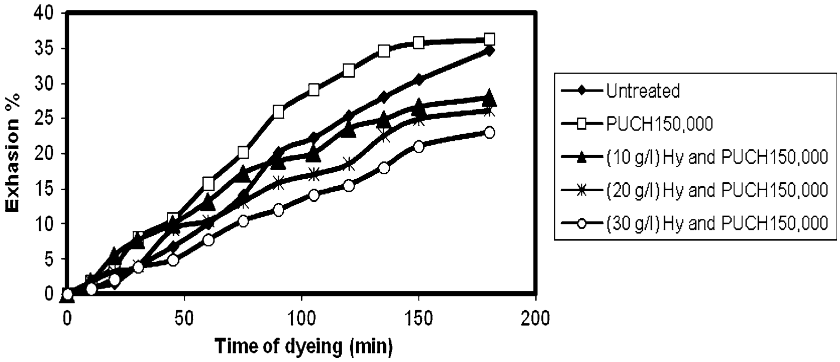


Fig. 4 Effect of treatment with hydrazine and $PUCH_{150,000}$ on dyeability of acrylic fabric with basic red dye

chain-extending reaction and the appearance of absorption band at 1643 cm^{-1} corresponding to NH of urea). The uptake of $PUCH_{100,000}$ or $PUCH_{150,000}$ by the acrylic fabric pretreated with hydrazine were increased, with the increase in the concentration of hydrazine hydrate solution (from 2.9 and 2.6 to 4.25 and 4). In general, the whole treatments show no effect on the inherent properties of the treated acrylic fabric in comparison with untreated one. The dyeability of acrylic fabrics treated either with $PUCH_{100,000}$ or $PUCH_{150,000}$,(K/S is 12.89 &12.27), is higher than the untreated fabrics (K/S 11). This is due to the contribution of the carboxylic groups in the polyurethane backbone,

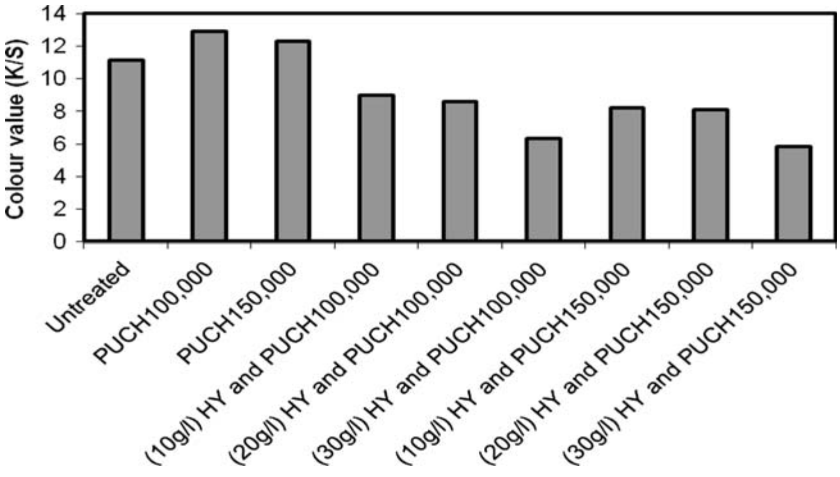


Fig. 5 Effect of treatment with hydrazine and waterborne polyurethane on the colour value of the basic red dye on acrylic fabric

Table 4 Fastness properties of dyed pretreated acrylic fabrics

Samples	Washing fastness		
	Alteration[a]	Staining of wool	Staining of acrylic
Untreated	4	3–4	4
Chitosan (Mn100000)	4	4–5	4–5
Chitosan (Mn150000)	4	4–5	4–5
Polyurethane prepolymer	5	5	4–5
Hydrazine solution (10 g/l) and PUCH100,000	5	5	5
Hydrazine solution (20 g/l) and PUCH100,000	4–5	4	4–5
Hydrazine solution (30 g/l) and PUCH100,000	4–5	4–5	5
Hydrazine solution (10 g/l) and PUCH150,000	5	5	5
Hydrazine solution (20 g/l) and PUCH150,000	4–5	4–55	5
Hydrazine solution (30 g/l) and PUCH150,000	4–5	4–5	5

[a] It is the act of changing in colour of dyed fabric after washing

Table 5 The antibacterial activity of acrylic fabrics treated with chitosan or PUCH before and after washing

Treatment of acrylic fabrics	Inhibition zone diameter (mm/1 cm sample)			
	Escherichia coli (G+)	Bacillus substilis (G+)	Pseudomonas aeruginosa (G−)	Staphylococcus aureus (G−)
Untreated	0.0	0.0	0.0	0.0
$CH_{100,000}$	13	10	9	11
$CH_{150,000}$	15	10	5	11
HY and $PUCH_{100,000}$	23	17	12	19
HY and $PUCH_{150,000}$	25	20	16	21
After washing for 15 washing times				
$CH_{100,000}$	0.0	0.0	0.0	0.0
$CH_{150,000}$	3	0.0	0.0	0.0
HY and $PUCH_{100,000}$	20	14	7	15
HY and $PUCH_{150,000}$	21	20	11	16

with the carboxylic groups existed in the acrylic chains in the uptake of dye molecules. The antibacterial activity were in the rank of $PUCH_{150,000} > PUCH_{100,000}$ and both $PUCH_{100,000}$ or $PUCH_{150,000}$ seams to be not affected by washing, and the antibacterial activity remains unchanged after 15 washing cycles.

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