Acid Dyeable and Printable Acrylic Fabrics Treated with Cationic Aqueous Polyurethane

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ABSTRACT: An acid dyeable acrylic fabric has been obtained by the pretreatment with cationic aqueous polyurethane, containing different amounts of quaternary nitrogen. Cationic polyurethane has the ability to interact with the carboxylic groups in the acrylic fabrics, as well as providing basic sites suitable for acid dyeing. The prepared polyurethane has been identified with FTIR, and the effect of the pretreatment conditions on the dyeability and printability of the fabrics has been investigated. The color strength values and the fastness properties of the dyed and printed samples, reveal the ionic interaction between the sulphonic groups in the acid dye molecules and the quaternary nitrogen on the fabrics. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2595–2601, 2011

Key words: cationic aqueous polyurethane; acrylic fabrics; acid dyeable and printable acrylic fabric

INTRODUCTION

Fibres made from acrylonitrile polymers and copolymers appeared on the textile market in 1949, manufactured by DuPont de Nemours at a unit for production of polyacrylonitrile fibres (Camden USA), with a capacity of approximately 3000 tons per year. According to modern industrial indexing of chemical fibres ISO/TC 38/SC-N1631, 1995, fibre materials whose polymer substrate contains more than 85 wt % acrylonitrile units are defined as polyacrylonitrile fibres and those containing 35–50 wt % acrylonitrile units are defined as modacrylic fibres. Acrylic, methacrylic, allyl, methallylsulfonic, itaconic, 2- acrylamide-2-methylpropanesulfonic, and *p*-styrenesulfonic acids are used as comonomers in amounts of approximately 2 wt % to give polyacrylonitrile fibres improved dyeability with cationic dyes.[1–3] Polyacrylonitrile fibres have been given the capability to be dyed with acid and direct dyes by incorporation of vinylpyridine[4] or *N*-vinylcaprolactame[5] units in the macromolecule of the fibre-forming polymer. Production of anionic dyeable acrylic fibres is rather more expansive than cationic dyeable one, so modification of acrylic fabrics to be anionic dyeable has been of prim importance, and so was investigated by many workers.[6–12]

Aqueous polyurethane has been widely used in coating because it has advantages in environmental pollution, fire safety, and soil resistance, compared with solvent-based polyurethane.[13–15] As an important type of aqueous polyurethane, the cationic aqueous polyurethane (CAPU), has attracted particular attention due to its unique properties, such as dispersibility in water, excellent adhesion to many polymeric and glass substrates and film-forming ability.[16–20]

In this study, cationic aqueous polyurethanes (CAPU) were prepared by reacting isophoron diisocyanate with quaternized diethanolamine and polyethylene glycol. It is expected that the cationic sites in the CAPU are able to react with the carboxyl groups in the acrylic fabrics, and the excess cationic sites will be available for interaction with acid dyes.

EXPERIMENTAL

Materials

Polyethylene glycol (PEG; Merck) (Mn = 600 g/mol), used as the soft segment, was vacuum dried at 80°C for 3 h before use.

Isophoron diisocyanate (IPDI; Fluka), was used as the hard segment; dibutyltin dilaurate (DBTDL; Aldrich), was used as a catalyst. Methyl ethyl ketone (MEK), was used as solvent. Diethanolamine (DEA; Fluka) and methyl iodide (Aldrich) were used as received.

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

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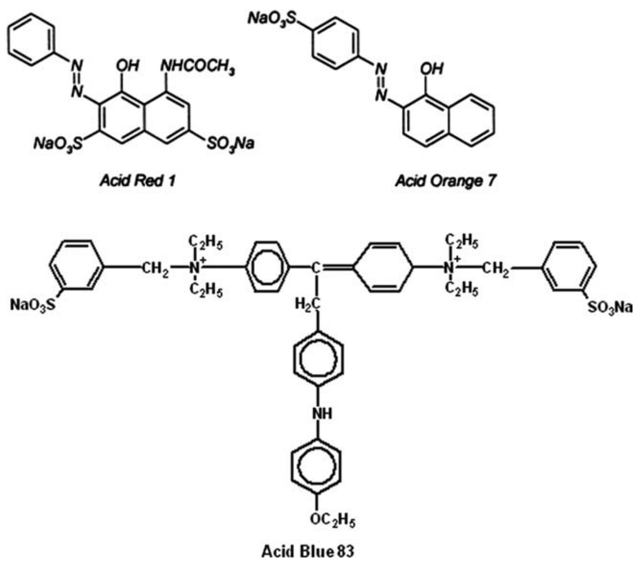


Figure 1 The chemical formula of the used acid dyes.

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 fabric was washed before treatment with a nonionic detergent (2 g/l) at 60°C for 45 min, thoroughly rinsed and dried at room temperature.

Meypro Gum NP-16 (Meyhall, Switzerland), a plant- seed gum ether was used as thickening agent.

The dyes used were Acid Orange (CI Acid Orange 7), Acid Fast Red (CI acid Red 1), and Polar Cyanine 6b (CI Acid Blue 83). The chemical structures of these dyes are shown in Figure 1. These dyes were supplied by Bayer, Ismadye, and Clariant, respectively and were used as received.

The other chemicals were all of analytical grade and used without further purification.

Quaternisation of diethanolamine

Two moles of methyl iodide were added drop wise with continuous stirring to one mole diethanolamine at 5°C until complete addition. The temperature was raised to 30 for 3 h and the reaction was left to complete over night at room temperature. Any unreacted methyl iodide was removed by vacuum distillation.

Preparation of cationic aqueous polyurethane (CAPU)

Polyethylene glycol, the quaternary salt of diethanolamine and DBTDL (0.02% based on the total reaction mass) are introduced in a vacuum reactor to remove any moisture. This was followed by addition of IPDI as butanone solution. Table I shows the molar ratio of glycol to the quaternised diethanolamine used in the polyurethane preparation. 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 water was added with vigorous stirring for emulsification. The mixture was heated to 80°C to remove MEK, yielding CAPU dispersion. The preparation steps of CAPU are shown in Scheme 1.

Treatment of acrylic fabrics with CAPU

The acrylic fabrics were treated with CAPU solutions of concentration (4%) using the exhaustion technique; the liquor ratio was 1 : 50, at different temperatures (60–100°C) and for different periods of time (10–60 min), the samples were then thoroughly washed at 50°C for 15 min, and finally air dried at ambient conditions.

Dyeing of pretreated acrylic fabrics

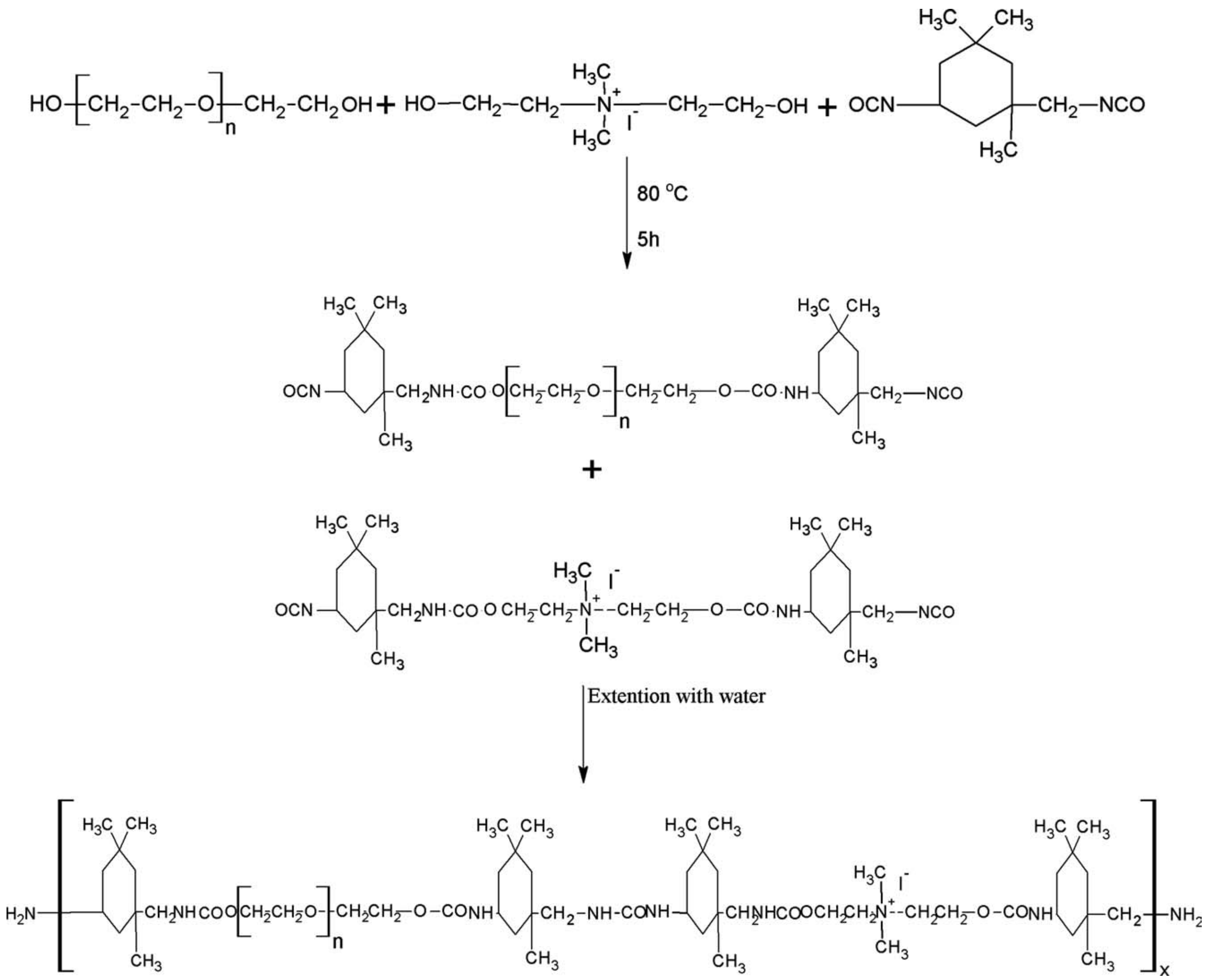
The dyeing of acrylic fabrics were conducted in accordance to the traditional exhaustion dyeing procedure. Dye bath[5] was prepared using acid dyes (Acid Orange, Acid Fast Red and Polar Cyanine 6b) of concentration of 2% shade. The pH of the dyeing bath was varied from pH 1 to 5. The liquor ratio was kept at 1 : 50. The treated acrylic fabrics were introduced into the dyeing bath at initial dyeing temperature (50°C) and the dyeing process was continued for 15 min. The bath temperature was raised to 70°C in 5–10 min and gradually to 100°C during 60 min to allow maximum reaction with the dyes. The fabrics were then thoroughly rinsed with distilled water several times and squeezed. The rate of dye exhaustion from the bath was followed using Jenway 6405 UV/Vis Spectrophotometer.

Printing of pretreated acrylic fabrics

The printing paste was prepared according to the recipe shown in Table II. The thickener (Meypro Gum) was soaked in a small amount of water and kept overnight at room temperature. The dye was mixed with urea and pasted with some water. The dye paste was diluted with hot water (60°C) while stirring to homogenize the dye solution. The latter

TABLE I
Polymer Composition and Code

Polymer code	Molar ratio of N^+/glycol	Molar ratio of OH : NCO
CAPU1	1	1 : 2
CAPU2	3	
CAPU3	7	



Scheme 1 Preparation steps of the cationic aqueous polyurethane.

was then poured on the thickener suspension, and the whole mixture was thoroughly stirred while adding the wetting agent and ammonium sulphate solution and citric acid. The total mass of the whole paste was then adjusted to 1 kg by addition of water (Table II).

All the printing pastes were applied to the fabrics using the flat-screen printing technique. The printed samples were then subjected to thermo fixation at 150°C for 2 min. The printed samples were then washed with water to remove the thickener and any unfixed dye.

Identification of CAPU and characterization of the treated acrylic fabrics

The diethanolamine 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 $cm^{-1.}$

The polymer treated acrylic fabrics were analyzed for the determination of the quaternary nitrogen content.[21] The color intensity measurements were conducted adopting the spectral reflectance measurements, using a recording spectrophotometer.

The color intensity, expressed in terms of K/S values, was determined according to Kubelka-Munk equation.[22]

TABLE II
Printing Paste Composition

	Normal technique
Constituent	Weight in g
Acid dye	20
Urea	50
Thickener	100
citric acid	5
Ammonium sulphate solution (1 : 2)	60
Water	X
Total	1000

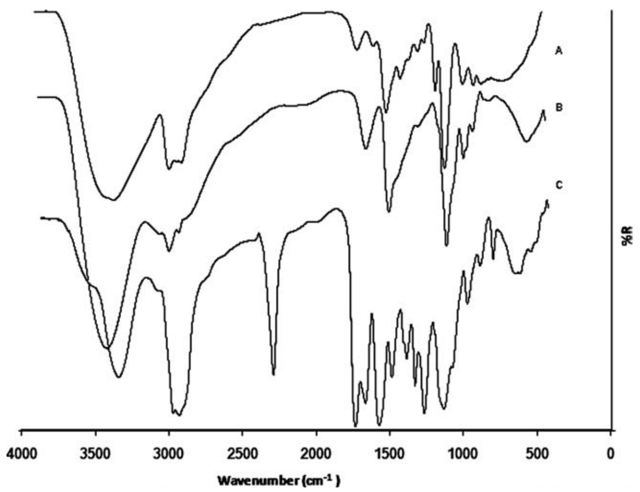


Figure 2 FTIR spectra of diethanolamine (A), quaternized diethanolamine (B), and CAPU600 (C).

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

Where S is the scattering coefficient, K is the absorption coefficient, and R is the reflectance.

Fastness properties of the dyed samples were measured according to ISO standard test methods; washing fastness (ISO 105-C02, 1989), rubbing fastness (ISO 105-X12, 1987), and perspiration fastness (ISO 105-E04, 1989).

RESULTS AND DISCUSSION

FTIR analysis of CAPU

Figure 2 shows the FTIR spectra of diethanolamine (A) and its quaternized form (B). It can be seen, that formation of a new intense peak appeared at 1617 cm^{-1} as a result of the quaternization process of the nitrogen atom of diethanolamine. The FTIR analysis of CAPU [Fig. 2(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} was designated for the isocyanate group (NCO) of the unextended $CAPU_{600}$. Further the absorption peak for CO appeared at 1709 cm^{-1}; its broad nature indicates that this group is involved in hydrogen bonding. The polyurethane cationomer shows a strong peak at 1640 cm^{-1}, which is specifically due to quaternization of diethanolamine.

Effect of treatment conditions of acrylic fabrics with CAPU on its dyeability

Untreated acrylic fabric (control sample), showed no affinity to the used acid dyes (Acid Orange, Acid Fast Red, and Polar Cyanine 6b). This is due to the absence of any cationic sites in the used acrylic fabrics.

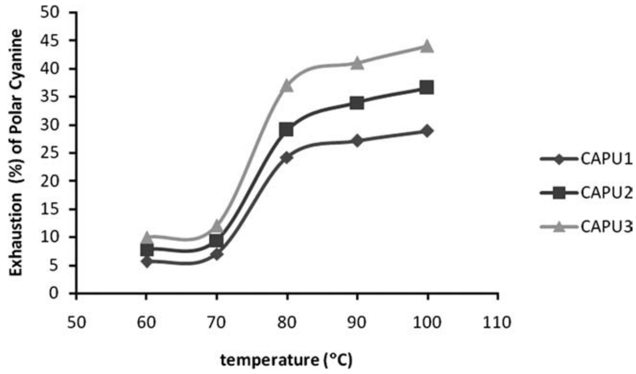
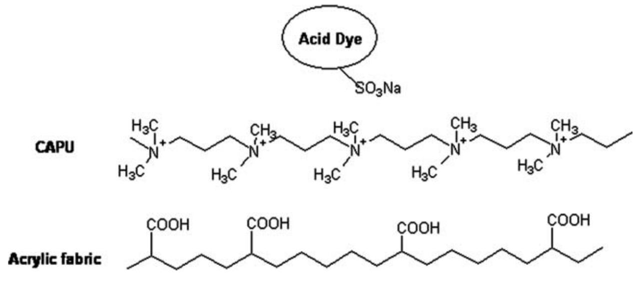


Figure 3 Effect of the temperature of treatment of acrylic fabrics with CAPU on the dyeability of acrylic fabrics with acid Polar Cyanine. (CAPU 4%, L.R. 1 : 50 and time of treatment 60 min). (Dyeing conditions are 2% shade, pH, 90°C and for 60 min).

Figure 3 shows the effect of the treatment temperature of the acrylic fabrics with CAPU on the rate of exhaustion of acid Polar Cyanine by these treated acrylic fabrics. The interaction between CAPU and the acrylic fabrics is through ionic bonding between the quaternary nitrogen of CAPU and the carboxylic groups of acrylic fabrics, whereas the remaining quaternary nitrogen represents favorable sites for interaction with acid dyes (Scheme 2). Figure 3 shows that, the exhaustion % of Polar Cyanine dye by the fabric is in the order of CAPU3 > CAPU2 > CAPU1, due to the increase in the number of N^+ available for the dye.

Figure 3 also shows that the exhaustion (%) increases rapidly at temperature above 70°C and reaches its maximum level at about 80–90°C, which is around the glass-transition temperature (T_g) of the acrylic fiber. Above the T_g of the fiber, at which the polymer chain segmental movement occurs, the free volume within the polymer chain increases, and allows more CAPU molecules to migrate easily into the interior of the fiber, resulting in a higher pick up of the polymer by the fiber. Again, the CAPU is responsible for the dyeability with acid dye; an



Scheme 2 The expected interaction between the acrylic fabrics, CAPU and the dye molecule.

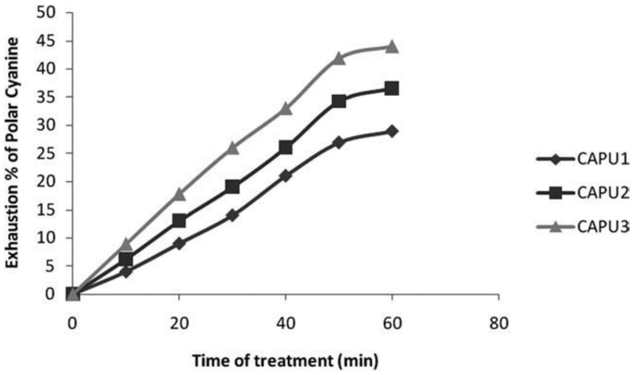


Figure 4 Effect of the treatment time of acrylic fabrics with CAPU on its dyeability with acid Polar Cyanine. (CAPU 4%, L.R. 1 : 50 and temp. of treatment 90°C). (Dyeing conditions are 2% shade, pH 2, temp. 90°C for 60 min).

optimal temperature of 90°C has been chosen to avoid any undesirable side reactions in the fiber.

The relation between the time of treatment of acrylic fabrics with CAPU solution and its dyeability with Polar Cyanine was also studied; the data obtained are presented in Figure 4. The pick up of CAPU by the fibre, and therefore the dyeability was found to increases with the increase in treatment time. Saturation was reached after 50 min, and no appreciable increase in dyeing up to 60 min.

Effect of dye type on the percentage exhaustion of the treated acrylic fabrics

Table III represents the relation between the (N^+) content (meq/100 g fabric) in the fibres and the exhaustion of different types of acid dyes. Again, with all types of dye used the percentage exhaustion increases with the increasing in the (N^+) content; as the quaternary nitrogen represents the favourable sites for interaction with acid dyes. Also, for all types of treatment, the exhaustion of the used dyes was found to be in the order of Acid Orange > Polar Cyanine 6b > Acid Fast Red. This could be attributed to the number of sulphonic groups in the dye, as well as its structural formula and reactivity.[23] The aforementioned order of dye exhaustion may be explained by the presence of different van der Waals attraction forces between the dye molecules and the cationised acrylic fabrics. This may be the reason of relatively higher color value of Polar Cyanine 6b as compared with Acid Fast Red. Although both days have the same number of sulphonic groups but different van der Waals attraction forces, resulting from their different chemical structure.

TABLE III
Relation Between the (N^+) Content of the Fibres and the Exhaustion of Different Types of Acid Dyes

Type of polyurethane used in treatment of acrylic fabrics	Dye type	(N^+) content (meq/100 gm fabric)	Exhaustion (%)
Untreated acrylic fabrics	Acid orange	0	0
Untreated acrylic fabrics	Polar cyanine 6b	0	0
Untreated acrylic fabrics	Fast acid red	0	0
CAPU1	Acid orange	5.65	41.6
CAPU2		8.23	47.3
CAPU3		11.74	60.55
CAPU1	Polar cyanine 6b	5.65	29.9
CAPU2		8.23	36.5
CAPU3		11.74	44.61
CAPU1	Fast acid red	5.65	26.53
CAPU2		8.23	31.3
CAPU3		11.74	37.1

(CAPU 4%, L.R. 1 : 50 and temp. of treatment 90°C for 60 min. Dyeing conditions are 2% shade, pH 2, temp. 90°C for 60 min).

TABLE IV
Fastness Properties of the Dyed Acrylic Fabrics Pretreated with CAPU

Dye type	Type of polyurethane used in treatment of acrylic fabrics	K/S	Washing fastness		Rubbing fastness		Perspiration fastness			
							Acidic		Alkaline	
			Alt.	St.	Dry	Wet	Alt.	St.	Alt.	St.
Acid orange	CAPU1	3.4	3–4	3–4	4–5	3–4	5	5	5	5
	CAPU2	4.1	2	3	4	3	4–5	4–5	4–5	4–5
	CAPU3	5.8	1–2	2	4	2–3	3–4	3–4	3–4	3–4
Polar cyanine 6b	CAPU1	2.5	4–5	4–5	4–5	3	4–5	4–5	4–5	4–5
	CAPU2	3.1	4	3–4	4–5	2–3	4	4	4	4
	CAPU3	3.8	3–4	3–4	4	2–3	3–4	3–4	3–4	3–4
Fast acid red	CAPU1	1.3	4	4	3–4	3	4	4	4	4
	CAPU2	1.8	2–3	2–3	2–3	2–3	3–4	3–4	3–4	3–4
	CAPU3	2.4	2	1–2	2	2	3	3	3	3

(CAPU 4%, L.R. 1 : 50 and temp. of treatment 90°C for 60 min. Dyeing conditions are 2% shade, pH 2, temp. 90°C for 60 min).
Alt. = Alteration, St. = Staining.

TABLE V
Fastness Properties of the Printed Acrylic Fabrics Pretreated with CAPU

Dye type	Type of polyurethane used in treatment of acrylic fabrics	K/S	Washing fastness		Rubbing fastness		Perspiration fastness			
							Acidic		Alkaline	
			Alt.	St.	Dry	Wet	Alt.	St.	Alt.	St.
Acid orange	CAPU1	6.7	4	4	3–4	3–4	3	3	3	3
	CAPU2	6.9	4	4	3–4	3–4	3	3	3	3
	CAPU3	8.5	3–4	3–4	3	3	2–3	2–3	2–3	2–3
Polar cyanine 6b	CAPU1	4.29	4–5	4–5	4	3–4	3	3	3	3
	CAPU2	5.4	4	4	3–4	3	3	3	3	3
	CAPU3	6.3	3	3	3	2–3	3	3	3	3
Fast acid red	CAPU1	2.3	4–5	4–5	4	4	4	4	4	4
	CAPU2	2.7	4	4	4	4	3–4	3–4	3–4	3–4
	CAPU3	3.2	3–4	3–4	3	3	3	3	3	3

Alt. = Alteration, St. = Staining.

Fastness properties of the dyed acrylic fabrics

As presented in Table IV, the fastness properties of the treated samples toward washing, rubbing, and perspiration were affected by the type of the CAPU used and or the type of dye. Data of Table IV show that, as the number of sulphonic groups in the dye molecules increases, the fastness properties of the treated samples increase. Therefore both Polar Cyanine 6b and Acid Fast red show superior fastness in comparison with Acid Orange. It has been also observed that, the increase of dye exhaustion and the fastness properties of dyes are in opposite direction. This behavior may be due to higher increase in swellability of the CAPU with the increase in the number of polar sites in the polymer backbone, which may affect the stability of the reacted dye with basic sites in the polymer

Effect of CAPU type on the printability of acrylic fabric with acid dyes

As printing is a surface treatment of the fabrics, therefore it's expected to give good results with the acrylic fabric treated with CAPU. Table V shows the color strength (K/S) and the fastness properties of the printed acrylic fabrics. The high (K/S) values indicate the great affinity of the dyes to the treated fabrics. Also the printed samples show excellent fastness properties. The difference between color strength of the dyed and printed fabrics can be explained on the bases of the high amount of color fixed on the fabric and or the method of fixation of the dye. The dye fixation of the dyed fabric taking place under the action of the heat of dying bath (90°C), while the fixation of the printed fabric has been done by thermo fixation (150°C, 2 min). This means that, thermo fixation in this case is better than exhaustion at 90°C for both reactions of the CAPU and dye stuff at 150°C.

CONCLUSION

The FTIR analysis confirms the presence of quaternary nitrogen in the prepared polyurethane. The interaction between CAPU and the acrylic fabrics is through ionic bonding between the quaternary nitrogen of CAPU and the carboxylic groups of acrylic fabrics, whereas the remaining quaternary nitrogen represents favorable sites for interaction with acid dyes. The exhaustion % of Polar Cyanine dye by the fabric is in the order of CAPU3 > CAPU2 > CAPU1, due to the increase in the number of N^+ available for the dye. The exhaustion (%) increases rapidly at temperature above 70°C and reaches its maximum level at about 80–90°C, which is around the glass-transition temperature (T_g) of the acrylic fiber. The pick up of CAPU by the fibre, and therefore the dyeability was found to increases with the increase in treatment time. Saturation was reached after 50 min. The exhaustion of the used dyes was found to be in the order of Acid Orange > Polar Cyanine 6b > Acid Fast Red. This could be attributed to the number of sulphonic groups in the dye. As the number of sulphonic groups in the dye molecules increases, the fastness properties of the treated samples increase. The printed samples show high (K/S) values as well as excellent fastness properties in comparison with the dyed samples.

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