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ScienceDirect

Dyes and Pigments 74 (2007) 215–222

DYES and PIGMENTS

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Anionic colouration of acrylic fibre. Part II: Printing with reactive, acid and direct dyes

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Received 16 August 2005; received in revised form 17 December 2005; accepted 22 January 2006
Available online 24 March 2006

Abstract

Modified acrylic fibre was obtained and printed with vinyl sulphone (CI Reactive Blue 238), chlorotriazine (CI Reactive Red 24), α-bromoacrylamide (CI Reactive Red 84), CI Acid Green 25 and CI Direct Blue 78. Two thickening agents namely sodium alginate and Meypro gum were used in the printing paste formulation. Compared with the prints obtained from modified acrylics, those of blank samples appeared almost colourless. Atmospheric steaming at 100 °C for 20–30 min achieved the fixation of the prints and the maximum colour strength was obtained at pH 4–5. The fixation of the dye molecules with the modified acrylic fibres was investigated to show mainly ionic and covalent bonds for the case of reactive dyes, whereas for acid and direct dyes it was mainly due to ionic bonds. The colour strength and the extent of dye fixation of the prints obtained using sodium alginate as the thickening agent was generally better than those obtained using Meypro gum. The prints displayed excellent to good fastness properties.

Keywords: Modified acrylic fibre; Amidoxime; Printing; Acid dye; Direct dye; Reactive dye

1. Introduction

Conventionally, acrylic fibres, which spun from a copolymer of acrylonitrile containing 1–15 wt.% of several vinyl comonomers containing carboxylate or sulfonate groups, are printed with cationic dyes [1–3]. Anionic dyes namely reactive, acid and direct dyes are not usually used for acrylic colouration as these dyes suffer from being not substantive for the fibres as a result of the repulsive effects that occur between the anionic groups present in the fibres and those present in the dye molecules.

Therefore, anionic dyes except acid dyes are usually used for the colouration of cellulosic fibres with the aid of exhausting agents (NaCl or Na_2SO_4). Also, acid, direct and reactive dyes could be used for the colouration of cationic cotton fibres in either neutral (the case of acid and direct dyes) or neutral to alkaline mediums (the case of reactive dyes) [4–6]. Also, anionic colouration of proteinic fibres is being conducted in acid medium to render the fibres protonated at their amino groups and thus leading to ion–ion attractive interactions between the sluphonic groups present in the dye molecules and the fibres [7]. These problems have been realized by rendering the surface of acrylic fibres with amino and/or quaternary amino groups so as not only to produce antimicrobial fibres [8–10] but also to enhance its anionic dyeability [11]. It is considered that widening the scope of acrylic colouration using different classes of dyes would facilitate the technical production of different colours of the fibre alone or its blends with other natural fibres. To the best of our knowledge, however, there is no report as yet that has appeared on printing acrylic fibres with conventional anionic dyes.

In the previous part of this work [11], which presented an efficient and mild pretreatment of acrylic fibre that rendered the fabric anionic dyeable with acid dyes, it was found that the presence of amidoxime groups in the pretreated fibres produced fibres with less crystalline and more hydrophilic and

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0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.01.036

acted as a positive sites for acid dyes during the dyeing process. As a part of our ongoing interest in exploring the viability of the pretreated acrylic fibres toward anionic dyes, we wish to report in this work the printability of the pretreated acrylic fibres with reactive, acid and direct dyes. Two print paste formulations were thoroughly compared throughout the work. The effect of pH in terms of formic acid contents of the print paste, and the steaming time on the colour strength obtained for the acrylic prints and their overall fastness properties were also investigated.

2. Experimental

2.1. Materials

2.1.1. Acrylic fibre

Plain 1/1 woven acrylic fibre was used (43 × 38 threads/inch, metric count 16, weft and warp and 562 den), which was kindly supplied by Misr El-Mehalla Co. (Egypt). The fabric was soaped with 2 g/l non-ionic detergent (Hostapal CV, from Clariant – Egypt) at 60 °C for 30 min, thoroughly rinsed and air dried.

2.1.2. Dyestuffs and chemicals

The dyes used in this work were CI Acid Green 25 (AG25), CI Direct Blue 78 (DB78), CI Reactive Red 84 (RR84), CI Reactive Blue 238 (RB238) and CI Reactive Red 24 (RR24). These dyes (Fig. 1) were kindly supplied by Ciba and Ismadye Egypt and were used as received.

Meypro gum NP-16, a non-ionic chemically modified Guar endosperm derivative, kindly supplied by Meyhall Chemical AG Switzerland, was used. Sodium alginate of medium viscosity, hydroxylamine hydrochloride, ammonium acetate, ammonium sulphate, formic acid, urea and DMF were laboratory reagent grade chemicals.

2.2. Pretreatment and printing

2.2.1. Pretreatment

Following our previously described method [11], a known weight of acrylic fibre was pretreated with hydroxylamine hydrochloride (10 g/l) using aqueous solutions of ammonium acetate (20 g/l) at a liquor-to-goods ratio of 50:1 at 85 °C for 1 h. The pretreated samples were thoroughly rinsed with water and air dried.

2.2.2. Printing

The printing pastes were prepared as follows:

Dye, 20 g/l
Urea, 50 g/l
Water, X
Sodium alginate (SA), 50 g/l or Meypro gum (MG), 100 g/l
Ammonium sulphate solution (50%), 60 g/l
Formic acid (85%), variables (0, 5, 10, 15, 20 g/l)

where X is the amount of water in gram used for 1 l paste.

The aforementioned printing pastes were applied to untreated and treated acrylic fibres according to conventional flat screen-printing method [12]. Fixation of the prints was made by drying at room temperature followed by steaming for different time intervals (0–40 min) using atmospheric type steamer at 100 °C.

2.2.3. Washing method

The prints made from all dyes were rinsed with hot water, cold water and soaped with 2 g/l non-ionic detergent at 60 °C for 30 min, thoroughly rinsed and air dried. Only a proportion of the total reactive dye present on the substrate reacts to form covalent linkages, whilst the remaining dye is attached by ionic bonds and by van der Waals forces. Therefore, in order to determine the extent of dye fixation, the prints that had been soaped as mentioned above were further extracted with aqueous solution of 50% DMF [13,14] at boil for 15 min and then rinsed with water and air dried.

2.3. Measurements and analyses

2.3.1. Colour strength

The relative colour strength (K/S) of printed fabrics was measured by the light reflectance technique using the Kubelka–Munk equation Eq. (1) [15]. The reflectance (R) of printed fabrics was measured on a Reflectance Model Ics-Texicon spectrophotometer.

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

2.3.2. Dye fixation

The extent of reactive dye fixation ($\%F$) was determined by a method used by several researchers [16–20] using Eq. (2). This method assumes, at least at the concentration of dyes employed, that K/S values are proportional to concentration of dye on fibre.

$$\%F = \frac{K/S_{\text{after DMF}}}{K/S_{\text{after soaping}}} \times 100 \tag{2}$$

2.3.3. Fastness testing

Fastness testing for the printed samples was tested according to ISO standard methods. The specific tests were: ISO 105-X12 (1987), colour fastness to rubbing; ISO 105-C02 (1989), colour fastness to washing; and ISO 105-E04 (1989), colour fastness to perspiration.

3. Results and discussion

The viable modification method of acrylic fibres [11], which relies on a partial conversion of some of the nitrile groups present in the macromolecules of the fibres into amidoxime groups, has prompted us to explore the printability of the modified fibres with reactive, acid and direct dyes.

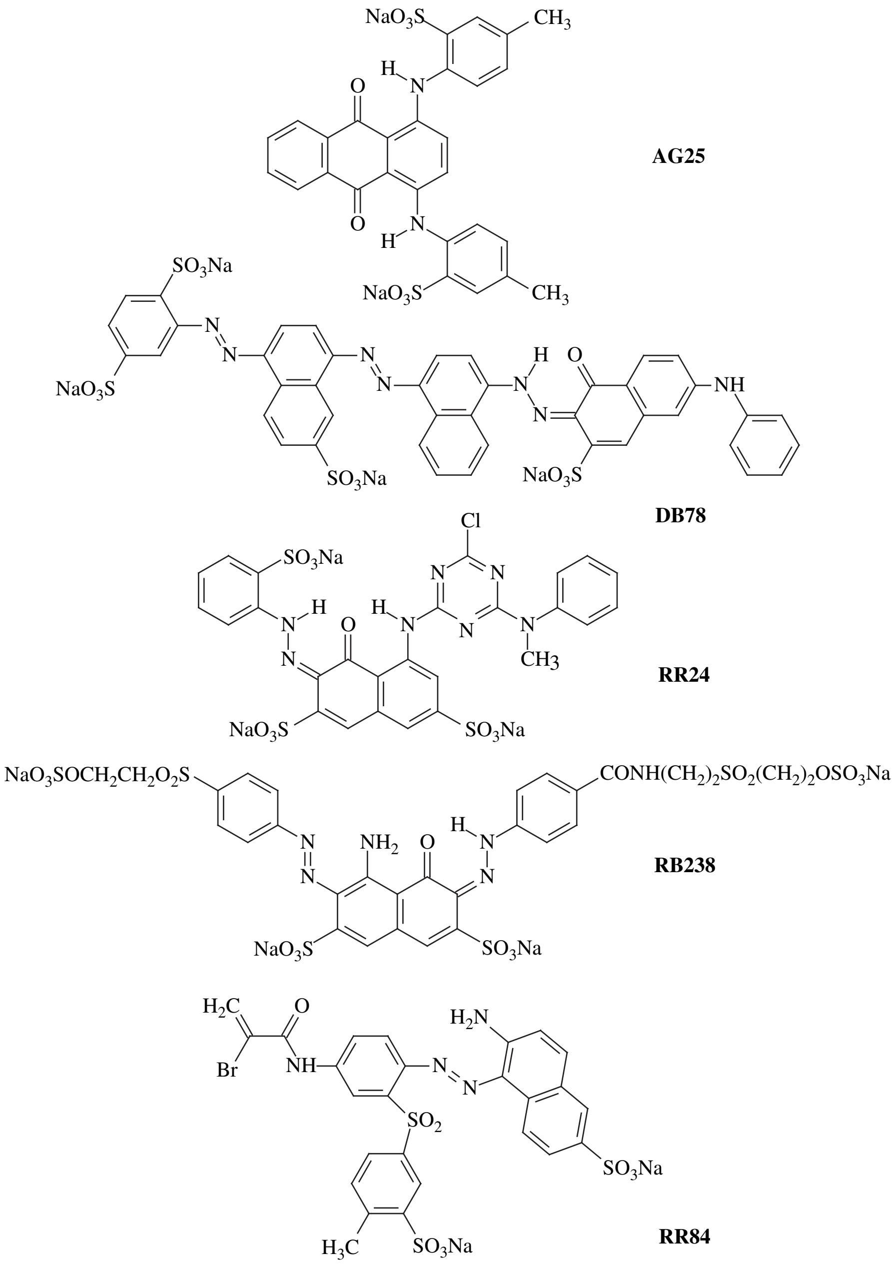


Fig. 1. Anionic dyes used.

Different classes of dyes used in this work were selected based on their structural differences in molecular size, the content of sulphonic groups, and the difference in the reactive center. To explore the printability of the modified acrylic fibres with these dyes, two print pastes based on SA and MG and different factors that may affect the colour strength of the prints obtained are investigated.

3.1. Effect of formic acid concentration

Print pastes mixed with different amounts of formic acid (0–20 g/l), which correspond to different pH values (neat pH 7–8 to pH 3.2), were assisted based on the colour strength values of the prints obtained after 30 min fixation time at 100 °C.

Fig. 2 shows the effect of formic acid concentration on *K*/*S* values of the prints obtained from reactive dyes. Irrespective of the dye structure used, it is clear that *K*/*S* value increases as the concentration of formic acid increased up to certain level (ca. 5 and 10 g/l of formic acid for the prints made from SA and MG (pH 4–5 in both cases), respectively), after which point the plot starts to decline.

This result indicates that the printability is better in acidic medium (pH 4–5) than neat neutral pH (0 g/l formic acid). These findings confirm the fact that these reactive dyes behaved in a manner like other anionic dyes in their adsorption behaviour toward proteinic fibres in which the extent of dye

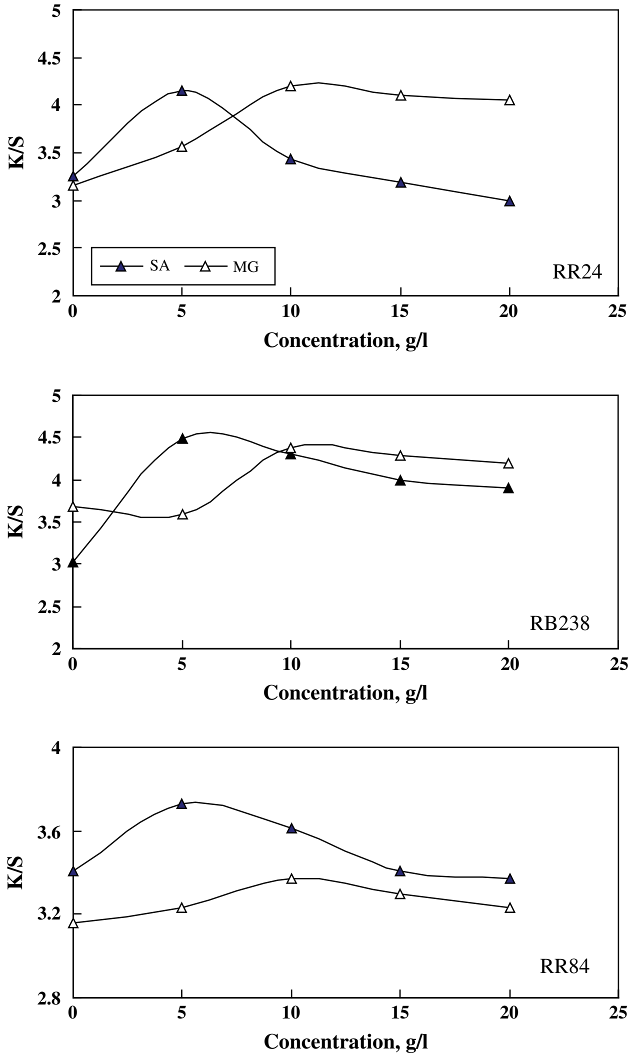


Fig. 2. Colour strength of soaped and DMF washed printed fabrics using different reactive dyes as a function of formic acid concentration in the print paste.

adsorption mirrored the extent of protonation of the terminal amino groups in these fibres. It is an equilibrium process of protonation and deprotonation as depicted in Scheme 1 and therefore, the protonation of the amino groups will increase with the increasing concentration of formic acid, i.e. decreasing the pH of the print paste. Also, this result further confirms our previous findings of dyeing modified acrylic fibres with acid dyes [11].

On the other hand, the decline behaviour in the printability of the fibres as the concentration of formic acid increased over the certain levels indicated above is a direct consequence of the pH effect on the thickener used. Since MG is a non-ionic thickener and SA is an anionic thickener due its content of carboxylate anions, the latter was more affected by increasing the acidity due to gel formation [21] than the former.

Furthermore, printing modified acrylic fibres with acid and direct dyes using both thickeners under different conditions of pHs reveal a similar behaviour like the case of reactive dyes mentioned above. As shown in Fig. 3, the printability of AG25 increases as the concentration of formic acid increased up to certain level (ca. 5 and 10 g/l of formic acid for the prints made from SA and MG (pH 4–5 in both cases), respectively). However, in the case of DB87 although similar in printing behaviour like AG25, it was rather more sensitive toward increasing the concentration of formic acid more than ca. 5 g/l formic acid. The similarity of molecular size of AG25 with those of reactive dyes used has led to the same level of formic acid concentration. However, DB78 with its big molecular size has become more amenable to make aggregation and more entrapped in the print paste as the acidity increased above the level indicated.

3.2. *Effect of steaming time*

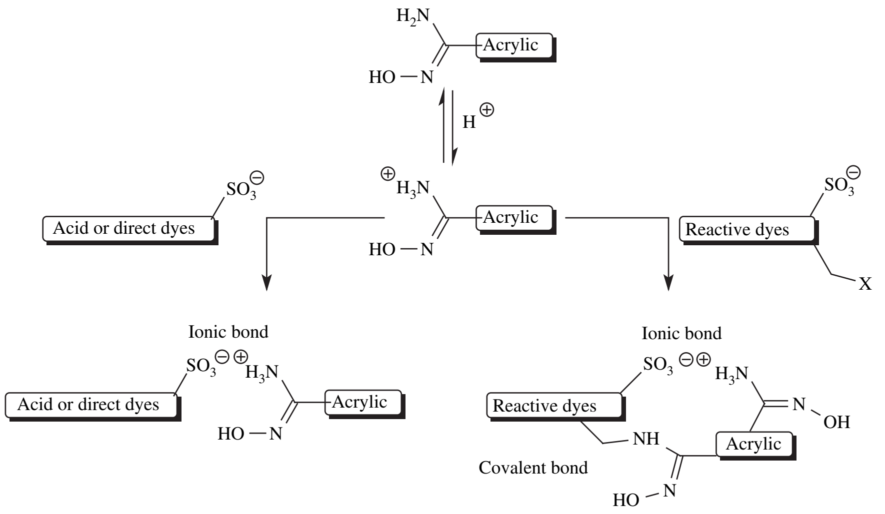
It is known that steaming causes the dye to penetrate into the fibre and to become fixed. Fixation allows the dye molecules and fibre molecules to interact and achieve the lowest energy level. Steaming of reactive dye prints is a process involving dye penetration and chemical reaction. Therefore, it was important to study this factor and shed light on its effect on the printability of the modified acrylic fibres with different anionic dyes.

Fig. 4 shows the effect of steaming time on the colour strength of the substrate printed with different reactive dyes. It is clear that the colour strength of the printed fabrics increases with increasing time of steaming up to 20 min above which point the plot shows least shade variation between 20 and 40 min. Similarly, printing behaviour of AG25 and DB78 (Fig. 5) as a function of steaming time reveals the increases in *K*/*S* values of the prints as the steaming time increased up to ca. 30 min above which a marginal increase is observed.

3.3. *Dye type, thickener type and comparative dye fixation*

It was desirable to select hot and warm type reactive dyes to reflect their reactivity difference on the extent of their fixation under the printing condition. Therefore, monochlorotriazine reactive dye (RR24, hot type), vinyl sulphone reactive dye (RB238, warm type) and α-bromoacrylamido reactive dye (RR84, warm type) were selected.

It has been reported that the optimum pH of reactive dye fixation onto nylon fibre is 4 [17–19]. Therefore, it is of no surprise to get better fixation of the reactive dyes used in this work at pH 4–5 with the modified acrylic fibre, which contains amidoxime groups (Scheme 1). Similar to the case of nylon fibre, it is expected that the reaction between the reactive dyes used in this study and the modified acrylic fibre will occur by the nucleophilic amino group attacking the electrophilic reactive group of the dye. The protonation of the amino groups is an equilibrium process; under low pH conditions, the equilibrium (Scheme 1) can be expected to be largely toward the protonated side. However, even under low pH conditions it can be proffered that at a given instant of time, a nucleophilic (unprotonated) amino group can exist.



Scheme 1. Acid, direct and reactive dye bonds with modified acrylic fibres. Where X= Br (sub.) or -CBr=CH_2 (add.) for RR84, Cl (sub.) for RR24 and -CH=CH_2 (add.) for RB238.

Consequently, under low pH conditions the anionic dye can be considered to be attracted strongly toward the protonated amino group in the fibre and, within this relatively enclosed micro-environment, an unprotonated amino group attacks the reactive group of the adsorbed dye molecule resulting in dye–fibre reaction. Such a mechanism would account for the observation that dye–fibre fixation was observed at acidic pH value.

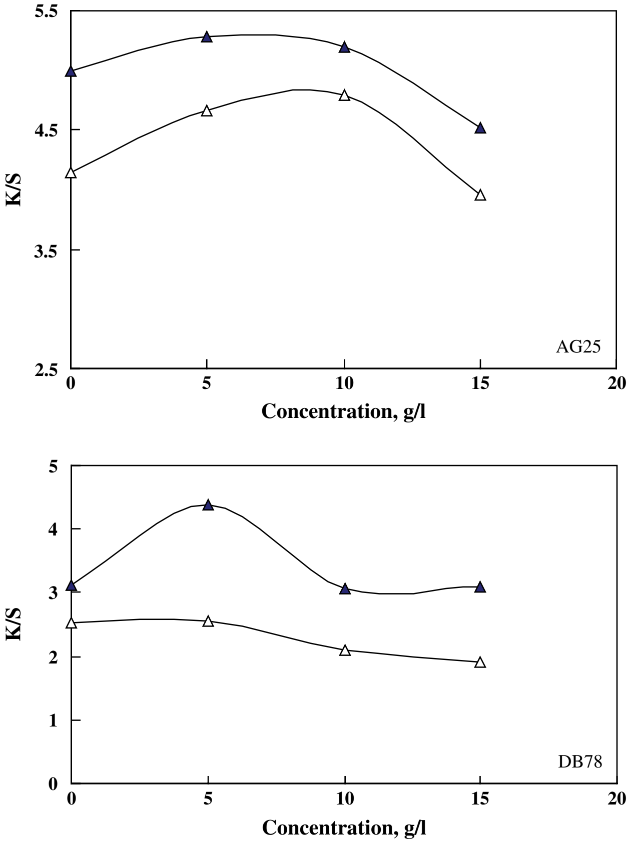


Fig. 3. Colour strength of soaped printed fabrics using acid and direct dyes as a function of formic acid concentration in the print paste; for key see Fig. 2.

Fig. 6 shows a comparative *K*/*S* and extent of dye fixation (%*F*) of blank and modified printed fabrics. Needless to say that the blank sample has negligible *K*/*S* after soaping and zero values after DMF extraction as a consequence of the absence of nucleophilic groups in the fibres before modification. Additionally, similar DMF treatment of the prints obtained from acid and direct dyes (data not shown) has led to almost colourless samples to confirm the suitability of this treatment to determine the extent of reactive dye fixation for the prints obtained from reactive dyes.

As a function of thickener type and irrespective of the reactive dye used, it is generally observed that the extent of dye fixation values was better in the case of using SA than those of MG. These results can be rationalized based on dye reactivity toward the substrate as well as dye/thickener compatibility. SA is a polysaccharide containing hydroxyl groups, but the reaction between alginate and dye is limited by mutual anion repulsion of the alginate's carboxyl groups and the dye's sulphonic acid groups. The repulsion additionally promotes migration of the dye from the thickener into the fabric during steaming [22]. On the other hand MG is a non-ionic polysaccharide and as a consequence the repulsive effect between the dye molecules and MG is smaller than in the case of SA, which in turn leads to a slower dye migration from the paste to the fibre and thus producing prints with lower values of %*F*.

As a function of reactive dye type, it is clear from Fig. 6 that the %*F* values are in the order RR24 ≈ RB238 > RR84. This order may be attributed to the difference in the number of sulphonic groups, reactivity and dye diffusibility. Judging from the number of sulphonic groups, it is anticipated that RR24 and RB238 would be comparable to each other with regard to dye fixation and both will produce better %*F* values than that of RR84. This is a direct consequence of increasing

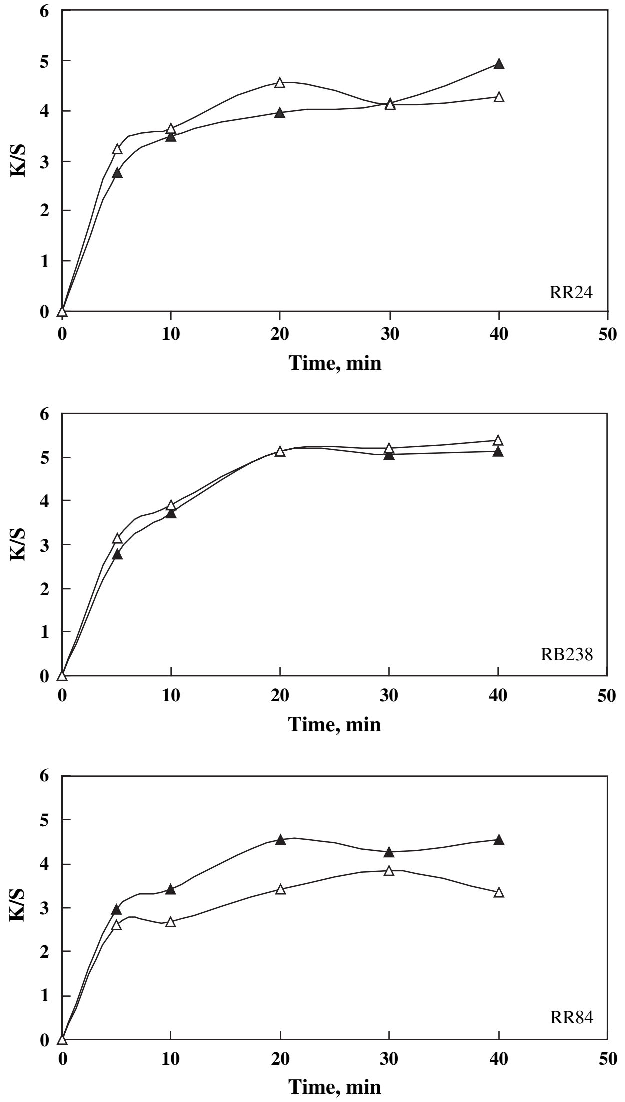


Fig. 4. Colour strength of soaped and DMF washed printed fabrics using different reactive dyes as a function of steaming time at 100 °C; for key see Fig. 2.

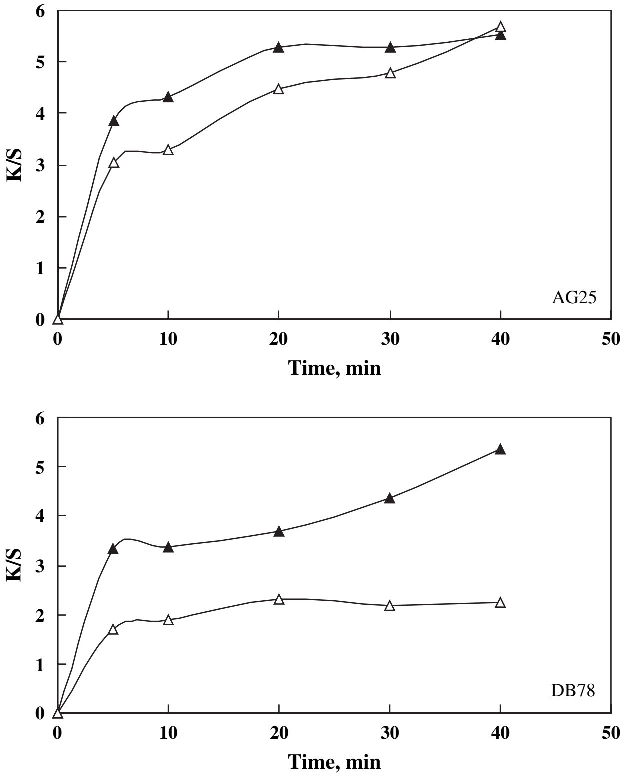


Fig. 5. Colour strength of soaped printed fabrics using acid and direct dyes as a function of steaming time at 100 °C; for key see Fig. 2.

the migration effect from the print paste toward the modified fabrics.

Furthermore, the hydrazone nature of RR24 and RRB238 would make these dyes in better coplanarity relative to RR84 and thus might facilitate their diffusibility more than RR84. It is worth noting that although RB238 is bi-functional vinyl sulphone reactive dye, it gives about the same fixation like monochlorotriazine RR24, this is attributed mainly to the difference in the extent of dye hydrolysis and the mode of dye fixation. RR24 as a hot fibre reactive dye (80 °C) and RB238 as a warm fibre reactive dye (60 °C) are reacting

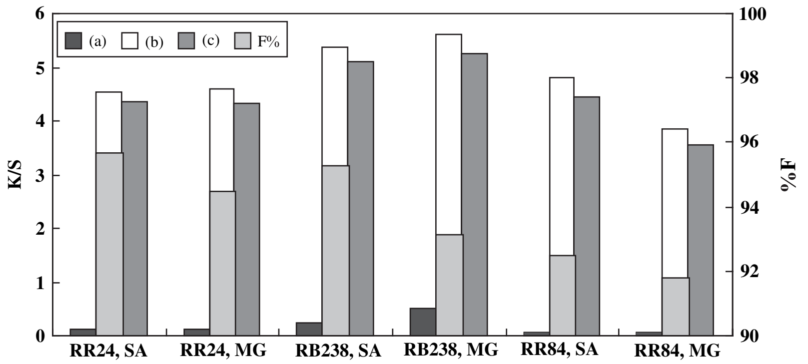


Fig. 6. Comparative colour strength and extent of dye fixation of blank (a; after soaping) and modified printed fabrics (b; after soaping, *C*; after soaping and DMF) using different reactive dyes; *K*/*S* values for (b) and (c) are the average values obtained from the readings at 20, 30 and 40 min steaming after soaping (data not shown) and after soaping and DMF (data shown in Fig. 4), respectively; %*F* values are their average extent of dye fixation.

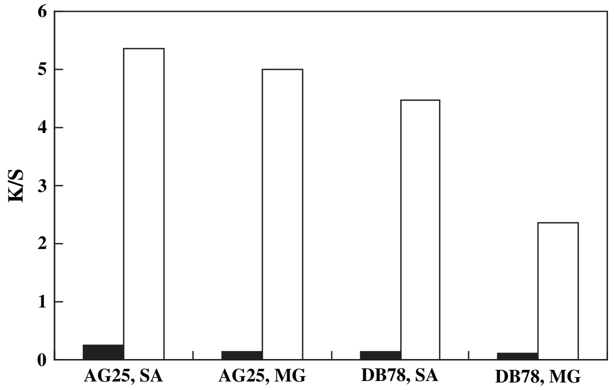


Fig. 7. Comparative colour strength of blank and modified printed fabrics using acid and direct dyes; for key see Fig. 6; *K*/*S* values are the average values obtained from the readings at 20, 30 and 40 min steaming after soaping (data shown in Fig. 5).

through nucleophilic substitution (sub.) and nucleophilic addition (add.) with amino groups present in the modified fibre as depicted in Scheme 1. Therefore, it is anticipated that RR24 would rather withstand the high temperature of fixation more than RB238 and thus leading to lower hydrolysis of the former than the latter in which it is compensated by its bifunctionality to result more or less the same value of %*F*.

α-Bromoacrylamido reactive dye (RR84) on the other hand has been reported to have the same reactivity as vinyl sulphone reactive dyes, i.e. warm fibre reactive dye (60 °C) and can react by both ways, i.e. nucleophilic substitution and nucleophilic addition [23,24]. Since this dye is not coplanar like the other dyes mentioned above and a warm type fibre reactive dye, it is anticipated to give the lowest fixation values as explained above.

Also, Fig. 7 shows comparative *K*/*S* values of blank and modified printed fabrics with AG25 and DB78. As mentioned above *K*/*S* values of the prints made with both dyes using SA and MG were improved than the blank samples and the values of *K*/*S* of the prints obtained irrespective of the dye type were better in case of SA than those of MG for the same reasons elaborated above emphasizing again the ionic nature of fixation between the dye molecules and the substrate (Scheme 1).

With regard to the dye type, it is clear from Fig. 7 that AG25 is better than DB78. This is expected, as the molecular size of DB78 is larger than AG25, which hampers the dye from being well diffused and makes it more entrapped in the print paste leading to a lower *K*/*S* values.

3.4. Fastness properties

Table 1 shows the fastness tests of washing, rubbing and perspiration of samples that had been printed with reactive, acid and direct dyes. Reactive and acid dye prints were made following the conditions of 5 and 10 g/l formic acid for the print paste formulations made from SA and MG, respectively. The steaming of the prints made from acid and reactive dyes was at 100 °C for 30 and 20 min, respectively.

Direct dye prints were made following the conditions of 5 g/l formic acid for 30 min steaming at 100 °C for the print paste formulations made from both SA and MG. As shown in Table 1, the fastnesses are excellent to good indicating the existence of strong bonds between the dye molecules and the fabrics (ionic and covalent bonds for reactive and ionic bonds for acid and direct dyes) and the best results obtained were from those prints made from SA.

4. Conclusions

Modified acrylic fibres could be printed with various reactive, acid and direct dyes. Due to its large size, the direct dye used in this work gave the worst results. Coplanarity and small molecular size of the dye molecules together with dye/thickener compatibility seem to be crucial factors for better dye–fibre build up. The optimum pH for printing was in the range of 4–5. Sodium alginate as thickening agent was better than Meypro gum owing to its repulsive ionicity with anionic dyes. The prints displayed excellent to good fastness properties. Future work is under way to further explore the colouration of this substrate.

Table 1
Fastness properties of printed pretreated acrylic fibres

Dye	Thickener	Rubbing		Washing				Perspiration[a]							
								Alkaline				Acidic			
		Dry	Wet	*A*	PN	*C*	*W*	*A*	PN	*C*	*W*	*A*	PN	*C*	*W*
AG25	SA	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
	MG	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
DB78	SA	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
	MG	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4	4	4–5	4–5	4–5	4–5	4–5
RR24	SA	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
	MG	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
RB238	SA	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
	MG	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4	4–5	4–5	4–5	4–5	4–5	4–5
RR84	SA	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
	MG	4–5	3–4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5

[a] *A*: change in colour; PN: staining on acrylic; *C*: staining on cotton; *W*: staining on wool.

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