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Comparison of the resist effectiveness and leveling character of α-bromoacrylamide based and 2,4-dichloro-*s*-triazine based dye-resist agents for wool

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Abstract

Three dye-resists based on α-bromoacrylamide and three dye-resists based on dichlorotriazine were synthesized and their effectiveness and leveling properties were compared on wool. In general, the dichlorotriazine based dye-resist agents displayed higher resist effectiveness than their α-bromoacrylamide counterparts. However, the dye-resists based on α-bromoacrylamide exhibited better leveling properties than those based on dichlorotriazine. The resist effectiveness was significantly improved by increasing the number of sulphonate group in the dye-resist agents and the hydrophilic character of anionic dyes applied over them.

Keywords: Dye-resist agents; α-Bromoacrylamide; Dichlorotriazine; Resist effectiveness; Leveling property

1. Introduction

A resist process can be defined as one which modifies a textile fibre to absorb dye to a lesser extent or at a slower rate than untreated fibre [1].

A variety of chemicals have been designed and studied for imparting dye-resist effects on wool [2–8]. Among them, reactive dye-resist agents are preferred due to their easy handling and application [4].

Haarer and Höcker showed that dichlorotriazine based reactive dye-resist agents, due to their very high reactivity and low migration ability, reacted only with nucleophilic groups in the fibre periphery leaving the interior untreated [7]. Thus, treatment with dichlorotriazine based dye-resist agents might impair levelness and reproducibility. They have also suggested that to achieve better levelness and reproducibility, the reactive dichlorotriazine group could be substituted by less reactive groups such as the α-bromoacrylamide group [7].

Nevertheless, little work has been done on the resist effectiveness and leveling property of reactive dye-resist agents based on α-bromoacrylamide group.

This paper describes and compares dye-resist effectiveness and leveling property of α-bromoacrylamide and dichlorotriazine based reactive dye-resists.

2. Experimental

2.1. Preparation of reactive dye-resist agents

The molecular structures of reactive dye-resist agents synthesized in this study are shown in Fig. 1. They were characterized by ^{1}H NMR spectroscopy (Table 1).

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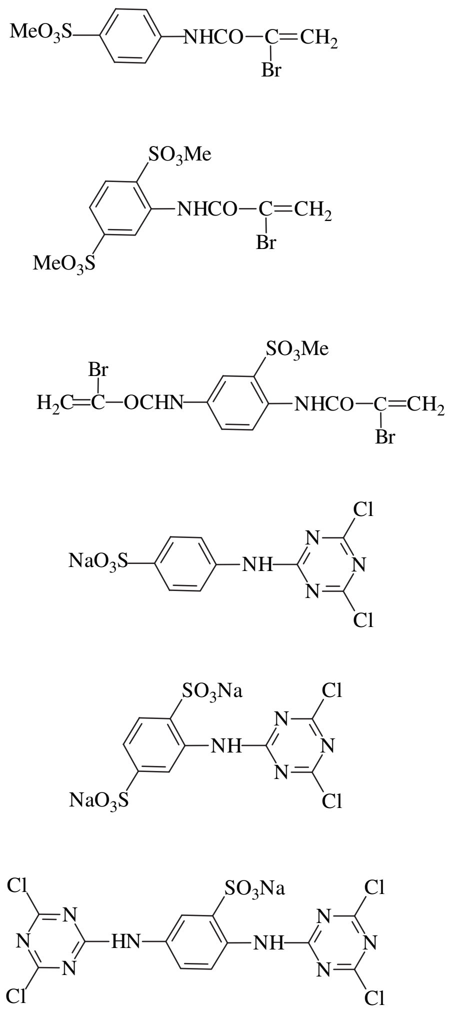


AB1S
4-(2-Bromo-acryloylamino)-benzenesulfonic acid sodium/potassium salt

AB2S
2-(2-Bromo-acryloylamino)-benzene-1,4-disulfonic acid disodium/potassium salt

AB2R
2,5-Bis-(2-bromo-acryloylamino)-benzenesulfonic acid sodium/potassium salt

DC1S
4-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-benzenesulfonic acid sodium salt

DC2S
2-(4,6-Dichloro-[1,3,5]triazine-2-ylamino)-benzene-1,4-disulfonic acid disodium salt

DC2R
2,5-Bis-(4,6-dichloro-[1,3,5]triazine-2-ylamino)-benzenesulfonic acid sodium salt

Fig. 1. The structures of reactive dye-resist agents synthesized in this study (Me = Na or K).

2.1.1. Synthesis of α-bromoacrylamide based dye-resist agents

*2.1.1.1. 4-(2-Bromo-acryloylamino)-benzenesulfonic acid sodium/potassium salt (**AB1S**).* Sulfanilic acid (17.3 g, 0.1 mol) was suspended in water (100 ml) and the liquor was adjusted to neutral with slow addition of sodium carbonate to obtain a clear solution. The solution was subsequently cooled to below 5 °C, and α,β-dibromopropionyl chloride (30.7 g, 0.12 mol) was dropwisely added to the solution over 1 h period. The pH was maintained at 7.0 by simultaneous addition of sodium carbonate solution (10%, w/v). The solution was stirred for another 2 h at 0–5 °C and the reaction was monitored by HPLC. When the reaction was completed, the precipitate was filtered off and washed thoroughly with acetone (100 ml) to remove any excess α,β-dibromopropionyl chloride. The product [4-(2,3-dibromopropionylamino)-benzenesulfonic acid sodium salt] was dried to a constant weight.

4-(2,3-Dibromo-propionylamino)-benzenesulfonic acid sodium salt (20 g) was dissolved in 75 ml distilled water, which was adjusted to pH 12 by the addition of potassium hydroxide solution (10%, w/v) at 20 °C. After the reaction was completed (monitoring by HPLC), sodium chloride (5% w/v) and potassium chloride (5% w/v) were added to give a precipitate,

Table 1
Characterization data of reactive dye-resist agents

Agent	^{1}H NMR, (DMSO–d_6, δ ppm)	Yield (%)
AB1S	6.3(d, 1H, –CH$_2$=*cis* to –CBr–), 6.8(d, 1H, –CH$_2$=*trans* to –CBr–), 7.5(m, 4H, ArH), 10.3 (s, 1H, –NH–)	87.2
AB2S	6.3 (d, 1H, –CH$_2$=*cis* to –CBr–), 6.9(d, 1H, –CH$_2$=*trans* to –CBr–), 7.2–8.5(m, 3H, ArH); 11.2 (s, 1H, –NH–)	68.0
AB2R	6.3(m, 2H, –CH$_2$=*cis* to –CBr–), 6.9(m, 2H, –CH$_2$=*trans* to –CBr–), 7.2–8.5(m, 3H, ArH); 10.3 and 11.2(s, respectively 1H, –NH–)	82.6
DC1S	7.5(m, 5H, ArH), 11.2(s, 1H, –NH–)	86.0
DC2S	7.3–8.5(m, 3H, ArH), 11.2(s, 1H, –NH–)	37.3
DC2R	7.5–8.5(m, 3H, ArH), 10.7, 10.9 (s, respectively 1H, –NH–)	92.4

which was collected by filtration and washed with sodium chloride solution (20% w/v, 200 ml). The product [4-(2-bromo-acryloylamino)-benzenesulfonic acid sodium/potassium salt] was dried.

*2.1.1.2. 2-(2-Bromo-acryloylamino)-benzene-1,4-disulfonic acid disodium/potassium salt (**AB2S**).* To prepare **AB2S**, a similar reaction process with the preparation of **AB1S**, but replacing sulfanilic acid by 2-amino-benzene-1,4-disulfonic acid, was applied.

*2.1.1.3. 2,5-Bis-(2-bromo-acryloylamino)-benzenesulfonic acid sodium/potassium salt (**AB2R**).* To prepare **AB2R**, a similar reaction process with the preparation of AB1S, but replacing sulfanilic acid by 2,5-diaminobenzenesulfonic acid and use of 0.25 mol of α,β-dibromopropionyl chloride, is applied.

*2.1.2. Synthesis of 2,4-dichloro-s-triazine based dye-resist agents (**DC1S**, **DC2S** and **DC2R**)*

The method of Jeon et al. [8] was used for the synthesis of 2,4-dichloro-*s*-triazine based dye-resist agents (**DC1S**, **DC2S** and **DC2R**).

2.2. Application of reactive dye-resist agents

A 5 g wool sample was pre-treated with each reactive dye-resists at various concentrations (*x*: 1, 2, 4, 8, and 16% o.w.f.) by an exhaustion process using a liquor ratio of 20:1 in an Ahiba Nuance Laboratory IR Dyeing Machine.

The pretreatment bath was composed as follows:

> Albegal FFA (0.25 g/l) as wetting agent; dye-resist agents (*x*% o.w.f.); pH 4.5 buffer system (acetic acid/sodiumacetate buffer).

The process was started at 40 °C and run for 10 min, during which a pH of 4.5 was established and the dye-resist agents were added. Then the dyebath was raised to the boil over 60 min, held for 60 min at 100 °C and cooled over 10 min to 80 °C. Afterwards, samples were rinsed and dried at room temperature.

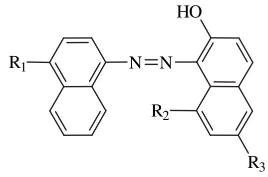
2.3. Determination of mass gain

The degree of fixation of the reactive dye-resist agents examined in this work was assessed as dry mass gains, calculated from oven-dry masses determined before and after the treatment. The wool samples were dried to a constant mass in a circulating oven at 95 °C.

2.4. Dyeing of wool fabric

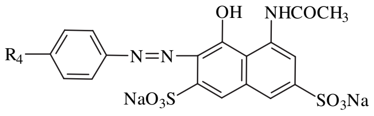
The resist effectiveness of reactive dye-resist agents on wool was evaluated with the dyes listed in Fig. 2. These dyes were applied to wool at dye concentrations shown 1/1 standard depth on untreated wool. In order to simulate commercial resist dyeing, competition dyeing used by Bell et al. [6] was carried out with a 3:1 ratio of untreated to treated wool, using a liquor ratio of 20:1.

Dye Group-1



C.I. Acid Red 88 (Dye-1) $R_1 = SO_3Na$ $R_2 = H$ $R_3 = H$
C.I. Acid Red 44 (Dye-2) $R_1 = H$ $R_2 = SO_3Na$ $R_3 = SO_3Na$
C.I. Acid Red 18 (Dye-3) $R_1 = SO_3Na$ $R_2 = SO_3Na$ $R_3 = SO_3Na$

Dye Group-2



C.I. Acid Red 1 (Dye-4) $R_4 = H$
C.I. Acid Red 138 (Dye-5) $R_4 = C_{12}H_{25}$

Fig. 2. Structures of dyes used in this study.

The process was started at 40 °C and run for 10 min, during which a pH of 4.5 was stabilized and the acid dyes were added.

The dyebath was composed as follows:

> Albegal FFA (0.25 g/l); Glauber's salt (5% o.m.f.); Dye.

Then the dyebath was raised to the boil over 30 min, held for 40 min at 100 °C and cooled over 10 min to 80 °C. Afterwards, samples were rinsed and dried at room temperature.

2.5. Evaluation of dye-resist effectiveness

The extent of resist effectiveness was quantified by using the following equation with *K*/*S* values of the dyed fabric obtained on a Macbeth Color-Eye 3000 reflectance spectrophotometer at the wavelength of maximum absorption. The percentage resist was then calculated as follows:

$$\%\text{Resist} = [(K/S_{\text{untreated}}) - (K/S_{\text{treated}})]/(K/S_{\text{untreated}}) \times 100$$

2.6. Leveling test of reactive dye-resist agent

A pretreatment bath as explained in Section 2.2 with each reactive dye-resists at the concentration to obtain 40% dye-resist effectiveness was prepared. A 2.5 g wool sample was treated from the start to 70 °C, then, another 2.5 g sample was put in the same bath and treated together as described in Section 2.2. The treated samples were dyed as explained in Section 2.4 and resist effectiveness of each samples was evaluated. The less the difference of %resist between sample treated from 40 °C and sample treated from 70 °C, the better leveling property.

3. Results and discussion

3.1. Resist effectiveness against dye

For **Dye Group-1** (Dye-1, Dye-2 and Dye-3), a series of acid dyes having different numbers of sulphonate groups were selected. The resist effectiveness of dye-resists to Dye-3 is shown in Fig. 3. When the uptake of **AB1S** is low, negative resist effect (assist effect) to acid dyeing is obtained. When the resist agents are applied at the boiling temperature, wool fibre will be damaged. This will lower the dye diffusion barrier effect and assist dye uptake. The assist effect is obtained at the treatment of wool in blank bath (%resist = −27%). Also, if this assist effect is greater than the resist effect at low weight gain, overall negative resist effect will be observed.

Fig. 4 shows the resist effectiveness of wool treated with each resist agent to **Dye Group-1** at 3% weight gain. Generally, dichlorotriazine based resist agents have better resist effect than α-bromoacrylamide based ones. It is known that dichlorotriazinyl group is more reactive than α-bromoacrylamide group and can react with wool fibre bifunctionally. Church et al. [9,10] reported cross-links between α-bromoacrylamide compounds and peptide chains within wool are unlikely to occur. Therefore it is presumed that dichlorotriazine based agents will deactivate the dye binding sites on fibre surface more effectively than α-bromoacrylamide derivatives, resulting better resist effectiveness.

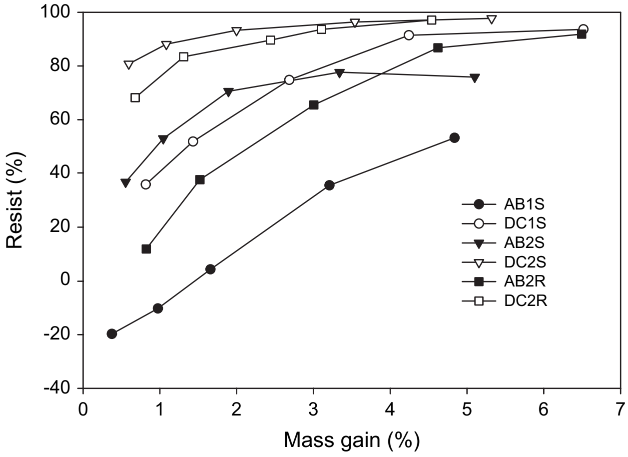


Fig. 3. Resist effectiveness of resist-treated wool to C.I. Acid Red 18 (Dye-3).

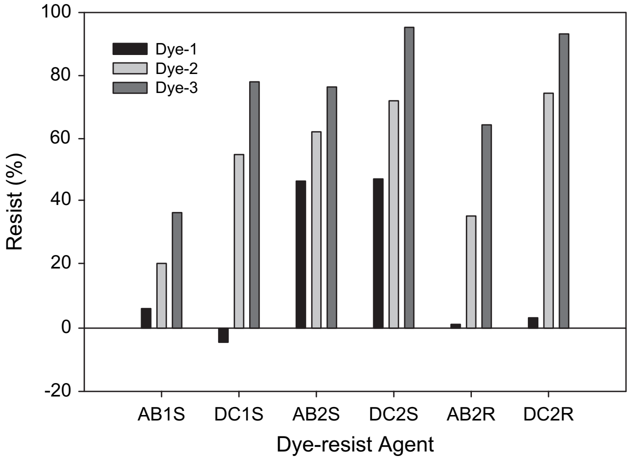


Fig. 4. Resist effectiveness of resist-treated wool to Dye Group-1 at 3% mass gain.

The resist effectiveness of the six reactive dye-resist agents varies greatly. Their resist effectiveness changes with the types of acid dyes used. The higher the number of ionic charges of acid dyes, the better the resist effectiveness (Dye-1 < Dye-2 < Dye-3).

A dye-resist effect can be achieved when the interaction between dye and fibre is efficiently prevented. This may be achieved in three different ways:

(a) electrostatic repulsion between dye molecules and wool fibre;
(b) hindrance of dye diffusion into wool fibre;
(c) deactivation of reactive dye binding sites.

Dye-1 (C.I. Acid Red 88, the monosulphonate dye) is poorly resisted since the ionic repulsion between the dye anions and the sulphone groups of dye-resists is weak, compared to the hydrophobic forces responsible for dye uptake on wool. Dye-3 (C.I. Acid Red 18, the trisulphonate dye) is strongly resisted due to the stronger ionic repulsion between dye anions of higher charge and dye-resist-treated wool.

Fig. 5 shows the resist effectiveness of wool treated with each resist agent to **Dye Group-2** at 3% mass gain. For **Dye Group-2** (Dye-4 and Dye-5), two acid dyes having different hydrophobic character were selected. The more hydrophobic Dye-5 had, as expected, greater affinity for wool resulting lower resist effectiveness than more hydrophilic Dye-4 as shown in Fig. 5.

In general, resist agents with two sulfonate groups (**AB2S**, **DC2S**) show better resist effectiveness than those with one sulfonate group (**AB1S**, **DC1S**) due to their increased ionic repulsion with anionic dyes.

Resist agents with two reactive groups (**AB2R**, **DC2R**) have higher resist effectiveness than those with one reactive group (**AB1S**, **DC1S**), since they can deactivate more numbers of amine dyeing sites in wool.

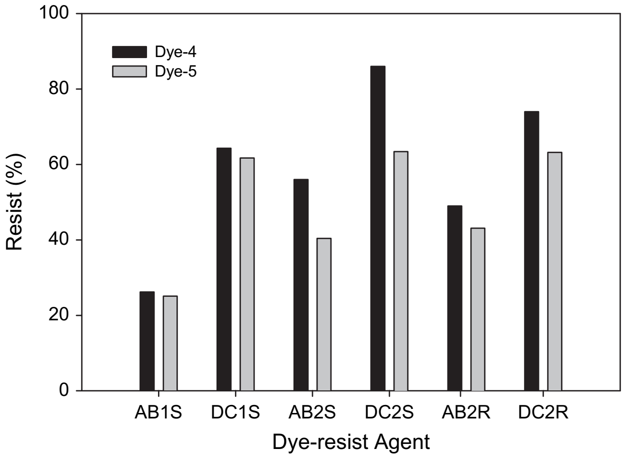


Fig. 5. Resist effectiveness of resist-treated wool to Dye Group-2 at 3% mass gain.

Also, when **AB2S** is compared with **AB2R** and **DC2S** with **DC2R**, resist agent with the more sulfonate groups (**AB2S** and **DC2S**) obtained better resist effectiveness than those with the more reactive groups (**AB2R** and **DC2R**). Therefore, for a reactive dye-resist agent to be more effective, it should rather have more sulfonate groups than more reactive groups.

3.2. Leveling character

The results of leveling test of reactive dye-resist agents for Dye-2 are shown in Fig. 6. Resist agents showing smaller difference in %resist between (a) and (b) have higher leveling property. Fig. 6 shows that resist agents based on α-bromoacrylamide have better leveling property than those based on dichlorotriazine. Also, leveling property of resist agents decreased as the number of sulfonate group and reactive group increased.

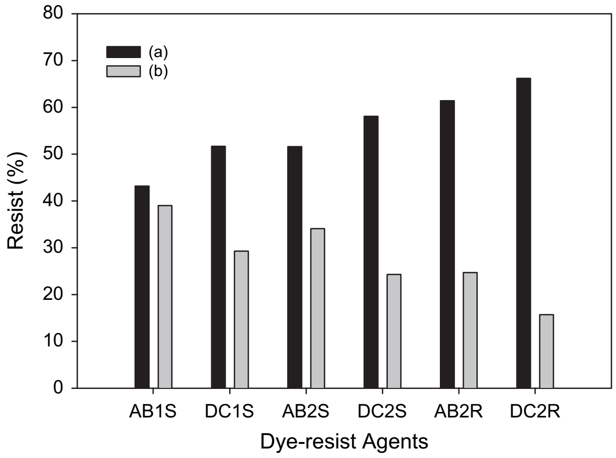


Fig. 6. Leveling character of dye-resist agents for C.I. Acid Red 44 (Dye-2). (a) Sample treated from 40 °C, and (b) sample treated from 70 °C.

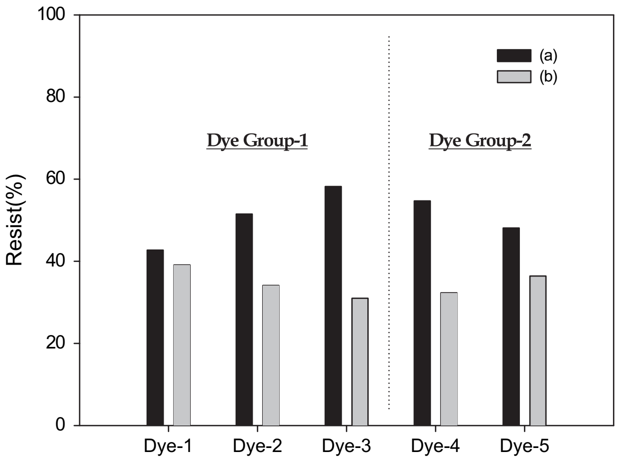


Fig. 7. Leveling character to the type of dye of resist-treated wool with **AB2S**. (a) Sample treated from 40 °C, (b) sample treated from 70 °C.

Fig. 7 shows the leveling property of resist-treated wool with **AB2S**. Dye with the more hydrophobic character (Dye-1 > Dye-2 > Dye-3, Dye-4 < Dye-5) show better leveling property than dye with the more hydrophilic character.

Similar results were obtained for the other resist agents.

4. Conclusions

The dichlorotriazine based reactive dye-resists showed a better resist effectiveness than α-bromoacrylamide based ones. However, dye-resists based on α-bromoacrylamide achieved better leveling properties than those based on dichlorotriazine.

Resist effectiveness of reactive dye-resist agents increased with the number of sulfonate group and reactive group in the molecule.

The hydrophilic/hydrophilic character of anionic dye significantly influences resist effectiveness. An increase in the number of ionic groups in acid dyes leads to better electrostatic repulsion of reactive resist-treated wool and thus improves the resist effectiveness.

In order to achieve good dye-resist effects, dyes with more sulphonated groups and less hydrophobic character and resist agent with more sulfonate groups coupled with more reactive groups have to be selected.

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