Novel Reactive Dyes and their Application onto Textile Substrates by Inkjet Printing

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Abstract

This paper describes the synthesis and evaluation of multifunctional reactive dyes based on dichloro-s-triazine reactive systems. The dyes were synthesised stepwise from specially synthesised dichloro-s-triazine dyes. The mono and di substituted modified dyes were synthesised by reacting one or both of the labile chlorine atom(s) in the parent dyes with "selected leaving group" under specific parameters of pH and temperature. Capillary electrophoresis was used to monitor both the course of the above reactions.

The new dyes were formulated into an ink and applied on to wool fabric through inkjet printing and fixed through batching at 65° C. The percent fixation of each dye has been calculated to determine the effects the modification has had on the fixation of the dye to the wool fabric; high fixation values were obtained for all modified dyes. These prints exhibited excellent colour fastness to light.

Introduction

In the later part of the 20th century, new types of colorants for the traditional applications onto textiles continued to be developed and introduced commercially but at a declining rate. It is clear that the colour manufacturing industries considered that a mature range of products existed for these conventional applications and adopted to transfer research emphasis towards process and product development, and the consolidation of existing product ranges. At the same time, during this period, research effort in organic colour chemistry developed in new directions, continued by the opportunities presented by the emergence of a range of novel applications techniques, demanding new types of colorants.

In recent years, digital inkjet printing applications on textiles have attracted increasing interest at both academic and industrial levels. As commercial inkjet reactive inks usually based on dyes with low-to-moderate fixation properties (generally monofunctional reactive dyes), so it is important to maximize dye fixation for technical, economic and environmental reasons.

At present, reactive dyes are becoming important in wool coloration due to environmental pressures on chrome and pre-metallised dyes despite their good wash fastness properties.

Moreover, inkjet printing provides a favourable method for wool printing because of the ability to produce economical short print runs and providing flexibility in print design.

This study describes the preparation of a specially modified reactive dyes based on replacing the leaving groups, formulation of modified dyes into inks, application of these inks onto wool substrate through inkjet printing and evaluation of fixation and light fastness.

Experimental

Synthesis of dichlorotriazine dye and modified dye

The synthesis of the magenta, yellow and blue dyes based on replacing the leaving group involved a one-step modification starting with the synthesis of the dichloro-s-triazine reactive dyes shown in Figure 1, followed by the substitution of the halogen on the triazine ring with other liable group(s) to produce both mono and di-substituted dyes, shown in Scheme 1 and Scheme 2.

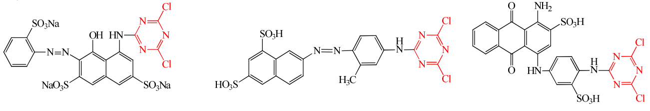
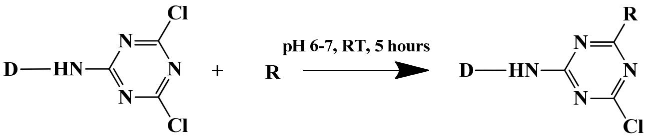
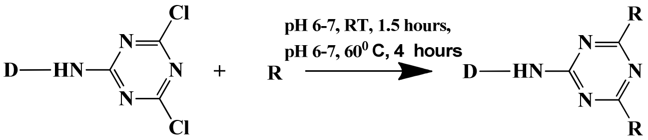

Magenta dichlorotriazine Dye
Yellow dichlorotriazine Dye
Blue dichlorotriazine Dye

Figure 1. *Fibre-reactive dyes based on dichloro-s-triazine*



Scheme 1. *Synthesis of mono substituted modified dye by replacing one labile chlorine atom by another leaving group*



Scheme 2. *Synthesis of di substituted modified dye by replacing both the labile chlorine atoms by another leaving group*

Application of the dyes to wool through Inkjet printing

The sequence of substrate preparation and ink jet printing can be summarised as follows: Fabric pretreatment; Ink-jet printing; Fixation; Washing off.

For pretreatment wool fabric was padded at 100% wet pick-up using a Werner Mathis HVF padder with the pretreatment solution, described in [1];following padding the fabric was dried at 70 °C using a Werner Mathis dryer.

Inkjet printing was carried out on *Hewlett-Packard (HP)* Deskjet 6940 thermal drop on demand Color Inkjet Printer with a single pass at a resolution of 600 dpi as a solid rectangle print pattern using the ink, formulated according to the recipe given in Table 1. Printed samples were allowed to air dry for 5 minutes and then batched for the appropriate times.

Table 1. Inkjet Printing Ink Recipe

Dye	4%
N-methylmorpholine N-oxide	30%
2- pyrrolidone	2%
Propan-2-ol	2.5%
Demonised Water	X

The printed samples were batched at 65 °C under moist conditions for 30, 60, 90, 120, and 150 minutes. The moist conditions were provided by interleaving the printed wool fabric with a moist cotton fabric padded with distilled water at a wet pick-up of 80%.

After batching for specific times the printed samples were washed according to the following three-step washing procedure:

- 5 min cold rinsing until no colour could be removed;
- 10 min hot washing at 85° C with the addition of 2 g/dm^3 Sandozin NIE and 5 g/dm^3 sodium bicarbonate;
- 10 min rinsing in running tap water

Analytical Techniques

Capillary Electrophoresis

Capillary electrophoresis (CE) is a technique which can be used to identify the components in a solution according to their different mobilities; mobility in the electric field depends on component size/mass-to-charge ratio.

The analysis was carried out on a Beckman P /ACE MDQ with P /ACE station software. The voltage power applied was 20 kV and the buffer employed was 10 mM potassium dihydrogen phosphate at pH 9.0 adjusted using 1 M sodium hydroxide.

UV/VIS Spectrometer

The percent fixation was determined using a Perkin Elmer Lambda 40 UV–vis Spectrophotometer (UK) in order to calculate dye concentration in the various wash-off solutions.

After printing, the first sample was washed off immediately to obtain the total amount of the dye printed on the fabric and the solution was diluted to 100 cm^3. The remaining samples were used for batching followed by washing to obtain the amount of the hydrolysed and unreacted dye after the fixation process; the washing solutions were diluted to the same volume of 100 cm^3 individually. The absorbance of the printed dye solution A_0 and absorbance of the wash-off solution A_i at the wavelength of maximum absorption λ_{max} were used to obtain the percent fixation (%F) according to equation (1);

$$\%F = \frac{A0-Ai}{A0} * 100 \qquad (1)$$

Results and discussion

Dye Synthesis

The electropherograms from the CE analysis show the progression of the synthesis reactions (Figure 2 and Figure 3). Dichlorotriazine dyes (Magenta, Yellow and Blue) has an increased molecular weight compared to their dye Chromophores but no additional sulphonate groups that would increase the negative charge; therefore dichlorotriazine dyes elutes faster than their chromophores, Figure 2.

After the modification, the negative charge to mass ratio of the modified dyes increases compared to their parent dichlorotriazine dyes, therefore the migration time of the modified dyes increases.

Moreover, the percent area of the modified dyes were 100% which indicates that there was no residues in the final products, Figure 3.

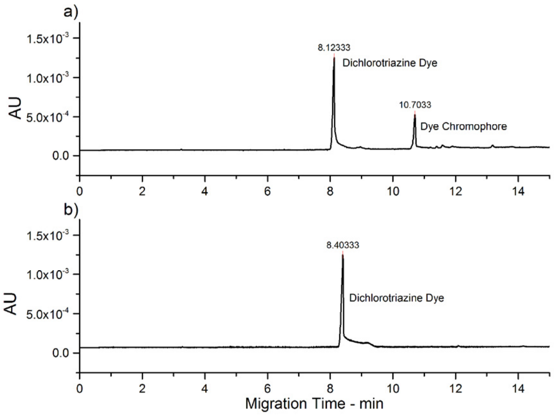


Figure 2. CE electropherograms showing (a) progression of reaction of dye chromophore with triazine reactive group (b) completion of reaction to yield dichlorotriazie dye

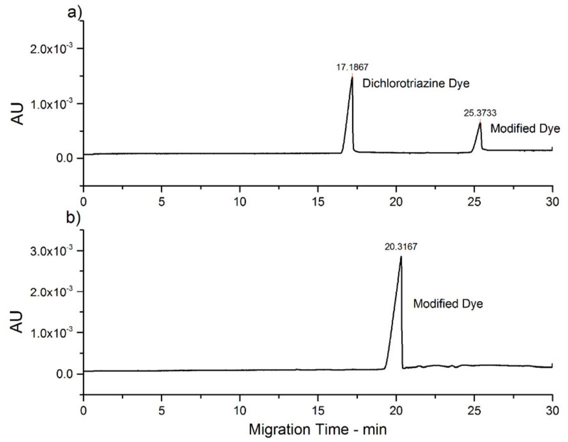


Figure 3. CE electropherograms showing (a) progression of reaction of dichlorotriazine dye with other labile group (b) completion of reaction to yield modified dye

% Fixation of Inks containing modified dyes

Significant improvement in the extent of covalent dye fixation (%F) was observed when the modified magenta, yellow & blue dyes were applied by a print (Ink-jet)–batch technique. The highest level of percent fixation observed with inks based on dichlorotriazine dyes were 82.9% for magenta, 80.1% for yellow and 79.8% for blue. Whereas, for modified dye based inks they were 89.0% for magenta, 84.8% for yellow and 91.4% for blue[2].

Light Fastness Test

Light fastness was carried out using a QSun 1000 Xenon test chamber with irradiance of 0.65 W/m^2 at a temperature of 45° C. The printed samples were tested to Blue Wool reference number 5 and 6. All of the dyes used in this work pass grade 6.

In general, the parent dye-based inks were either the same grade or 0.5 grade lower when compared with the modified dye ink prints for light fastness test.

Conclusions

The research has shown that reactive dyes can be modified by the incorporation of other labile atoms onto the dichlorotriazine reactive group of the dye. The modified dyes, when inkjet printed onto the wool, are able to reactive with the fibre and show good fixation results. Moreover, all the samples printed with modified dye based inks showed excellent light fastness.

Acknowledgements

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References

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Author Biography

Saira Faisal received her BE (2001) and MEngg (2007) in textile engineering from the NED University of Engineering and Technology Pakistan. Currently she is doing PhD at University of Leeds. Her work has focused on reactive dyes for inkjet printing

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