
Studies of dyeing woolpolyester fiber blend with reactive disperse dyes

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The present thesis is concerned with the synthesis of novel reactive-disperse dyes containing different reactive groups and their application on wool, polyester and wool/polyester blend fabrics. Temporarily anionic sulphatoethylsulphone reactive disperse dyes were found to be considerable in dyeing wool/polyester fiber blend; selected bifunctional and polyfunctional reactive systems are considered to be good determinants for high potential reactive-disperse dyes for wool, polyester and wool/polyester blend fibers. Different combinations of the temporarily anionic sulphatoethylsulphone (SES) group with an additional temporarily anionic (SES) group or monochlorotriazine (MCT) group are examined. The factors affecting the dyeability of wool, polyester and wool/polyester blend fibers using bifunctional (SES), bifunctional (SES/MCT) and polyfunctional bis(SES)/MCT reactive-disperse dyes are thoroughly investigated. Within the framework of this approach, the original work presented in this thesis comprises two parts. The results obtained are summarized as follows.

CHAPTER 2 Neutral dyeing of wool and wool/polyester blend fabrics using sulphatoethylsulphone reactive-disperse dyes

A novel bifunctional reactive-disperse dye 1, containing two temporarily anionic sulphatoethylsulphone groups was synthesized and applied to wool, polyester and wool/polyester blend fabrics. The dyeing properties were evaluated and compared with those of the monofunctional sulphatoethylsulphone reactive-disperse dye 2. The dyeings were conducted at various pH, dyeing time and dye concentration.

Bifunctional reactive disperse dye 1

Monofunctional reactive-disperse dye 2

- Bifunctional dye 1, containing two SES groups, showed greater exhaustion and total fixation efficiency than the monofunctional SES dye 2 over the pH range studied. Maximum exhaustion and total fixation efficiency were achieved at neutral pH 7. This is mainly attributed to higher β -elimination reaction of the two temporarily anionic SES groups to generate the nonionic reactive bis-VS derivatives form as well as higher nucleophilicity of the nucleophilic sites in wool fabric under neutral condition.
- At low pH, the β -elimination of the SES group to form the VS dye as well as the nucleophilicity of the nucleophilic sites in wool fabric is likely to be limited. However both dyes 1 and 2 possess only a relatively high exhaustion values at low pH presumably due to the electrostatic interaction between the unconverted temporarily anionic SES groups in the dye molecules and the protonated amino groups on the wool fabric under acidic dyeing condition. Therefore the most appropriate pH for both reactive disperse dyes 1 and 2 is pH 7; this is confirmed by

the higher fixation efficiency on wool dyeings. • At neutral pH, a proper hydrophobic interaction between the hydrophobic nonionic VS derivatives of both dyes and the hydrophobic polyester fabric is performed. In other words, the formation of nonionic VS derivatives of both dyes under neutral condition increases not only the hydrophobic interaction between the dyes and hydrophobic polyester fabric, but also maximize the nucleophilic interactions between the VS reactive groups and the nucleophilic sites on wool fabric. • The dyeing rates of the bifunctional dye 1 are higher through the whole dyeing procedure than those of monofunctional dye 2. Interestingly, the exhaustion of dyes 1 and 2 tends to equilibrate after 45 min, but this equilibrium is disturbed in the case of dye 1 as the bis-VS reactive system reacts with the fibre leading to further dye fixation up to the end of dyeing time (90 min). This indicates that the structure-reactivity of the nonionic bis-VS reactive system of dye 1 not only imparts high substantivity but also effectively exhibit high fixation efficiency if compared with the monofunctional VS reactive group of dye 2. • The exhaustion values on polyester and wool/polyester blend reached a maximum at 100 °C for 45 min. and did not show any further change in the exhaustion values at the last 15 min. of dyeing. Moreover the exhaustion values of both dyes dye 1 and 2 on wool/polyester blend fabric were found to be between those on wool and those on polyester. • The bifunctional dye 1 gave greater fixation efficiencies, even at high dye concentrations. Dye 2 gave less dye fixation over the range of dye concentrations studied. This implies that the structure-reactivity of dye 1 aids dye exhaustion by being effectively fixed. Its bis VS derivative may cause further build-up via nonionic dye-dye interaction as mentioned previously. However, the build-up of the monofunctional dye 2 seems to be limited due to not only the unique VS reaction, but also the HES group in dye 2 may react in solution with its free VS group to form an oligomeric dye which could lower the dye 2 exhaustion as mentioned above, resulting in a lower exhaustion and fixation yield. • Also the bifunctional dye 1 gave greater exhaustion values on polyester and wool/polyester blend fabrics, even at high dye concentrations and dye 2 gave less dye exhaustion over the range of dye concentrations studied. This implies that the formation of bis-nonionic VS derivatives of dye 1 under neutral condition increases not only the hydrophobic interaction between the dye and hydrophobic polyester fabric, but also maximise the nucleophilic interactions between the VS reactive groups and the nucleophilic sites on wool fabric. • The colour of the dyed fabrics was assessed by tristimulus colorimetry. It can be seen that the chroma and hue values of the dyed wool, polyester and wool/polyester blend fabrics in consideration with the un-dyed (blank) samples are approximately similar. This indicates that the shades of blend dyeings are of approximately colours to those of wool and polyester. • The fastness to washing, rubbing and perspiration of all samples dyed with dyes 1 and 2 were excellent to very good irrespective to the fabric used. The bifunctional dye 1 showed better fastness results than the monofunctional dye 2. Also, for each dyed fabric the light fastness using both dyes 1 and 2 was the same. This seems reasonable as the dyes under investigation have approximately the same chromophoric system. • The neutral dyeing of such model of bifunctional temporarily anionic SES reactive disperse dye 1 could improve the build-up and wet fastness properties, contributing to sustainable and eco-friendly

dyeing process for wool/polyester blend fabrics. Moreover, time and cost-saving is also another advantage of one-bath dyeing of wool-polyester blend fabric with such models of temporarily anionic reactive disperse dyes if compared the conventional anionic/nonionic dye combinations for dyeing wool/polyester blend fabric.

CHAPTER 3 Neutral dyeing of wool and wool/polyester blend fabrics using sulphatoethylsulphone/monochlorotriazine reactive-disperse dyes

Further to our approaches using sulphatoethylsulphone based reactive disperse dyes for dyeing wool, polyester and wool/polyester blend fibers, this part study the synthesis and application of reactive-disperse dyes having sulphatoethylsulphone reactive group combined with monochlorotriazine reactive group. The dyeing behavior of polyfunctional bis(VS)/MCT 3 was evaluated and compared with those of the bifunctional VS/MCT reactive disperse dye 4. In this regard, a series of dyeings were conducted at various pH, and dye concentration.

polyfunctional reactive disperse dye 3

Heterobifunctional reactive-disperse dye 4

The polyfunctional dye 3 shows remarkably high fixation properties over the pH range studied; approximately 15–20% higher fixation efficiencies were obtained than with the bifunctional dye 4. This is not surprising as dye 3 has three functional groups in the dye molecule. The formation of the nonionic polyfunctional bis-VS/MCT derivative increased the substantivity of dye 3 towards wool fabric and, therefore enhanced the extent of reaction with the nucleophilic sites in wool fabric, while the reaction of the bifunctional VS/MCT derivative of dye 4 was likely to be limited due to its bifunctional reaction. A further advantage, the nonionic character of the bis-VS/MCT reactive system of dye 3 seems to assist further build-up on wool fabric under neutral conditions as there is no repulsive effect between the nonionic fixed dye in the fabric and the nonionic dye in solution. Maximum exhaustion and total fixation efficiency were achieved at neutral pH 7. In the case of monochlorotriazine/sulphatoethyl-sulphone reactive-disperse dyes, the monochlorotriazine group accounts for the fixation below pH 4 as elimination of bisulphate from the β -sulphatoethylsulphone group to give the vinylsulphone group at low pH region (≤ 4) is almost absent. Therefore the most appropriate pH for both reactive-disperse dyes 3 and 4 is pH 7; this is confirmed by the higher fixation efficiency on wool dyeings.

Dyeing of wool, polyester and wool/polyester blend fabrics using dyes 3 and 4 indicate that the pH was influencing factor on dye exhaustion, adding support to the use of polyfunctional bis-VS/MCT dye 3 for dyeing blend, particularly at neutral pH. The difference in exhaustion values on wool and polyester are quite wide at $\text{pH} \leq 4$. The exhaustion value on polyester fabrics increased with pH increasing, this is clearly obvious in the case of dye 3 compared to dye 4. Due to the higher content of VS groups of dye 3 than dye 4, the substantivity of dye 3 on polyester decreases at lower pH. Accordingly the application of dyes should involve higher pH. These results make the dye 3 more suitable than the corresponding dye 4 for dyeing polyester due to its bis-VS derivatives. The exhaustion values of dye 4 obtained at lower pH was slightly higher than dye 3, however exhaustion values of dye 3 was marginally increased by the increase of pH, illustrating the advantage of bis-VS/MCT dye to the polyester fabric at neutral pH. As the pH increased the gap between the exhaustion values of wool and polyester fabrics is narrowed, resulting in the same tone on both fabrics is

successfully obtained. • The polyfunctional dye 3 gave greater fixation efficiencies, even at high dye concentrations. Dye 4 gave less dye fixation over the range of dye concentrations studied. This implies that the structure-reactivity of dye 3 aids dye exhaustion by being effectively fixed. The bis-VS/MCT derivative of dye 3 may cause further build-up via nonionic dye-dye interaction. However, the build-up of the bifunctional dye 4 seems to be limited due to bifunctional reaction of VS/MCT reactive system, resulting in a lower exhaustion and fixation yield. • The colour of the dyed fabrics was assessed by tristimulus colorimetry. It can be seen that the chroma and hue values of the dyed wool, polyester and wool/polyester blend fabrics in consideration with the un-dyed (blank) samples are approximately similar. This indicates that the shades of blend dyeings are of approximately colours to those of wool and polyester. • The fastness to washing, rubbing and perspiration of all samples dyed with dyes 3 and 4 were excellent to very good irrespective to the fabric used. The polyfunctional dye 3 showed better fastness results than the bifunctional dye 4. Also, for each dyed fabric the light fastness using both dyes 3 and 4 was the same. This seems reasonable as the dyes under investigation have approximately the same chromophoric system. The present thesis is concerned with the synthesis of novel reactive-disperse dyes containing different reactive groups and their application on wool, polyester and wool/polyester blend fabrics. Temporarily anionic sulphatoethylsulphone reactive-disperse dyes was found to be considerable in dyeing wool/polyester fiber blend; selected bifunctional and polyfunctional reactive systems are considered to be a good determinants for high potential reactive-disperse dyes for wool, polyester and wool/polyester blend fibers. Different combinations of the temporarily anionic sulphatoethylsulphone (SES) group with an additional temporarily anionic (SES) group or monochlorotriazine (MCT) group are examined. The factors affecting the dyeability of wool, polyester and wool/polyester blend fibers using bifunctional (SES), bifunctional (SES/MCT) and polyfunctional bis(SES)/MCT reactive-disperse dyes are thoroughly investigated. Within the framework of this approach, the original work presented in this thesis comprises two parts. The results obtained are summarized as follows.

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Monofunctional reactive-disperse dye 2 • Bifunctional dye 1, containing two SES groups, showed greater exhaustion and total fixation efficiency than the monofunctional SES dye 2 over the pH range studied. Maximum exhaustion and total fixation efficiency were achieved at neutral pH 7. This is mainly attributed to higher β -elimination reaction of the two temporarily anionic SES groups to generate the nonionic reactive bis-VS derivatives form as well as higher nucleophilicity of the -nucleophilic sites in wool fabric under neutral condition. • At low pH, the β elimination of the SES group to form the VS dye as well as the nucleophilicity of the nucleophilic sites in wool fabric is likely to be limited. However both dyes 1 and 2

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• The neutral dyeing of such model of bifunctional temporarily anionic SES reactive disperse dye 1 could improve the build-up and wet fastness properties, contributing to sustainable and eco-friendly dyeing process for wool/polyester blend fabrics. Moreover, time and cost-saving is also another advantage of one-bath dyeing of wool-polyester blend fabric with such models of temporarily anionic reactive disperse dyes if compared the conventional anionic/nonionic dye combinations for dyeing wool/polyester blend fabric.

CHAPTER 3

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