Dyeing of polypropylene with some azo disperse dyes of basic character via chlorination route

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Polypropylene fabric, after chlorination by sodium hypochlorite under an optimized condition, was dyed separately with twelve azo disperse dyes of basic character in both alkaline and acidic medium. The higher affinity of these dyes to chlorinated polypropylene than to unmodified polypropylene has been observed in both acidic and alkaline medium with a few exceptions. The possible mechanism of higher affinity of such dyes to chlorinated polypropylene is shown and explained. The influence of dye structure and substituent groups on dye uptake and fastness properties is discussed on the basis of inductive effect, electrostatic interactions, steric cause, etc. It is observed that these dyes with electron donating groups as substituents when applied in acid medium give higher dye uptake and improved fastness properties with a few exceptions for other structural interactions including steric cause.

Keywords: Azo disperse dyes, Dyeing, Polypropylene

1 Introduction

Besides mass coloration to limiting shades, coloration of polypropylene even after modification has remained a problem for decades. Disperse dyes only give tints to unmodified polypropylene fibre. Application of disperse dyes of different structures and properties on unmodified polypropylene fibre has been reported. However, in most of the cases, it was found that the saturation values were very low on unmodified polypropylene. Many approaches of dyeing polypropylene by modification have also been reported. Agster reported the chlorination of polypropylene for affinity of basic and few disperse dyes in 1975. Such modification was also reported in a Japanese patent. In our earlier work, we have standardized the process of chlorination of polypropylene and studied the effect of application of few basic dyes of different structures on chlorinated polypropylene. The effect of substituents on the fading behaviour of disperse dyes on polypropylene was studied by Ahmed and Mallet. The fading behaviour of different dyes on modified polypropylene was also studied by Shah and Jain. In the present work, the possibility of dyeing polypropylene, after chlorination, with few azo disperse dyes of basic character has been explored and the effect of the dye structure and substituent groups on dye uptake and fastness properties has been investigated. The results of dye uptake and fastness properties are explained on the basis of inductive effect, electrostatic interaction, steric effect, etc of these dyes.

2 Materials and Methods

2.1 Fabric

100% polypropylene fabric (3/1 twill; 1.1 g/cm²; 1.15 mm thick; warp 2/14s; weft 7s; 28 picks/in. and 40 ends/in) supplied by M/s Neomer Ltd, India, was used after thorough scouring by boiling with aq. solution of 1 g/L nonionic detergent (Lissapol-NX) for 30 min. followed by washing and drying.

2.2 Chemicals and Dyes

20 g/L stock solutions of LR grade NaOCl and HCl were used. All the azo disperse dyes enlisted below, except dye no. 2, were prepared in the laboratory in pure form (by solvent extraction) and ground (milled) to fine particle in crucible for use: (1) 4-aminoazobenzene, (2) 4-(dimethylamino)azobenzene, (3) 4-methyl-4'-(dimethylamino)azobenzene, (4) 4-amino-4'-methylazobenzene, (5) 4-amino-4'-nitroazobenzene, (6) 8-hydroxy-5-(4-methylphenyl)-quinoline, (7) 8-hydroxy-5-(4-nitrophenyl)-quinoline, (8) 4-amino-3'-chloroazobenzene, (9)
4-amino-2'-methoxy-5'-nitroazobenzene, (10) 8-hydroxy-5-phenylazoquinoline, (11) 4', 4'-bis(4-aminophenylazo)biphenyl, and (12) 4'-amino-3''-chloro-1, 4-bis(phenylazo)benzene.

2.3 Chlorination

Chlorination of polypropylene fabric was carried out under the optimized conditions on a laboratory scale by dipping the fabric piece in diluted NaOCl solution (available chlorine, 10 g/L), keeping the material-to-liquor ratio at 1:40 for 45 min at pH 4.5 (adjusted by HCl). The treated fabric was then washed thoroughly and dried at ambient temperature.

The extent of chlorination of polypropylene was measured by stepnows method.

2.4 Disperse Dyeing

Disperse dyeing of both unmodified polypropylene and chlorinated polypropylene fabrics was carried out in acid medium at 100°C and 110°C following the usual procedure in a laboratory model HT-HP beaker dyeing machine. The same dyeings were also carried out in alkaline medium following the procedure used for application of basic dyes to chlorinated polypropylene to see whether chlorinated polypropylene can react with disperse dyes of basic character like basic dyes. The dyeing conditions in acid and alkaline medium are given below:

Aqueous acid both
(HT-HP beaker dyeing machine)
Dye, 4% (owf)
Setamol ws, 1 g/L (Dispersing agent)
Acetic acid, 1-0.5% (to adjust pH, 4-4.5)
Material-to-liquor ratio, 1:40
Time, 1.5 h
Temperature, 100°C and 110°C

Aqueous alkali bath
(Open bath beaker dyeing machine)
Dye, 4% (owf)
Setamol ws, 1 g/L (Dispersing agent)
Na₂CO₃, After 45 min (to adjust pH, 10-11)
Material-to-liquor ratio, 1:40
Time, 1.5 h
Temperature at boil, 100°C

After dyeing, the dyed fabric samples were washed, soaped (Lux soap powder) for 15 min at 65-70°C, rinsed, washed and dried.

2.5 Measurement of Depth of Shade

Depth of shade, i.e. dye uptake was measured on the dyed sample by determining the K/S value by Kubelka-Munk equation measuring reflectance at wavelength of maximum absorbance using Beckman DK-2A reflectance spectrophotometer.

2.6 Fastness Tests

Light fastness tests were done using SDL microscale light fastness tester with MBTF standard fading bulb. Wash fastness tests were done in Atlas Launder-o-meter as per ISO-IV recommendation. Dry-rubbing fastness tests were done as per IS: 766-1956 using Shirley electronic crockmeter.

3 Results and Discussion

3.1 Disperse Dyeing of Unmodified and Chlorinated Polypropylene Fabric in Acid Medium

The K/S values of unmodified and chlorinated polypropylene fabrics disperse dyed in acid and alkaline medium are given in Table 1. It is observed that the K/S values of unmodified and chlorinated polypropylene disperse dyed with dyes 5-9 and 11 in acid medium at 100°C have almost insignificant difference. Therefore, we may assume almost no dependence of the uptake of above dyes on chlorination of polypropylene. While in case of dye 1-4, 10 and 12, the K/S value increases significantly on chlorination of polypropylene. Looking at the dye structure, it may be noted that dyes 5 and 7-9 have an electron withdrawing group (positive inductive effect of -NO₂, -Cl and -OCH₃ groups) while the dyes 1-4 have an electron donating group (negative inductive effect of -CH₃, -NH₂ and -N(CH₃)₂ groups). Dye 6 probably causes steric hindrance in diffusing to isotactic polypropylene fibre. Also, the higher basicity due to both -CH₃ group and hydroxy quinoline structure may cause more solubility, restricting the dye to be absorbed to polypropylene. But dye 10, differing from dye 6 by an -CH₃ group only, shows increase in K/S value when the PP fabric is dyed after chlorination. It may be inferred from this that the inductive effects and basicity are much predominant here over the steric causes.

Interestingly, dye 12 having two groups of opposing inductive effect, shows good increase in K/S value when PP fabric is dyed after chlorination. Also, increase in dyeing temperature from 100°C to 110°C shows some improvement in dye uptake on chlorinated PP except in case of dye 7. Disperse dyeing of polypropylene at more than 110°C was not studied as the softening temperature of polypropylene is 125-130°C.

3.2 Disperse Dyeing of Unmodified and Chlorinated Polypropylene Fabric in Alkaline Medium and Comparison with that in Acid Medium

It is reported in earlier work that basic dyes form covalent bonds with chlorinated polypropylene when dyed in alkaline medium, like reactive dyes. Therefore, the disperse dyes of basic
Table I—K/S values of disperse dyed unmodified and chlorinated PP fabric dyed in different baths

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Dye structure</th>
<th>K/S value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Unmodified (control) PP fabric</td>
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<tr>
<td></td>
<td></td>
<td>Acid bath (100°C)</td>
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<tr>
<td>1</td>
<td><img src="image1.png" alt="Structure" /></td>
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<tr>
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<td><img src="image5.png" alt="Structure" /></td>
<td>2.14</td>
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<tr>
<td>6</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>3.19</td>
</tr>
<tr>
<td>7</td>
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</tr>
<tr>
<td>8</td>
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</tr>
<tr>
<td>9</td>
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<td>2.84</td>
</tr>
<tr>
<td>10</td>
<td><img src="image10.png" alt="Structure" /></td>
<td>7.89</td>
</tr>
<tr>
<td>11</td>
<td><img src="image11.png" alt="Structure" /></td>
<td>2.96</td>
</tr>
<tr>
<td>12</td>
<td><img src="image12.png" alt="Structure" /></td>
<td>3.17</td>
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</table>

character with different substituents were applied on unmodified and chlorinated polypropylene fabric in alkaline medium also and the results in terms of K/S value are given in Table I. In alkaline dyeing, dyes 5-9 and 12 give lower K/S values for chlorinated polypropylene than for unmodified polypropylene. While dyes 1-4, 7 and 10 show considerable increase in K/S value for chlorinated polypropylene. Among these six dyes, both dye 1 and dye 10 have unsubstituted benzene ring (lower molecular weight, small size and less or no substitution) and the dye 1 has basic character due to −NH₂ group and dye 10 has basic character with quinoline structure and in addition it has also an −OH group. Between dye 7 and dye 10, the former has an additional −NO₂ group (electron withdrawing) which reduces quinolinic basic character in dye 7.

In dyes 2-4 there is methyl substitution either at nitrogen or in the benzene ring and this methyl substitution increases the basic character of the electron lone pair on nitrogen by the electron donating inductive effect (positive) of methyl group. So, as the basicity of nitrogeneous lone pair increases, the more attraction of these dyes towards chlorinated polypropylene is expected.

Of the bis-azo dyes 11 and 12, dye 11 is linear unsubstituted whereas dye 12 is chlorine substituted and also has one benzene ring and one −NH₂ group less in comparison with dye 11, i.e. dye 12 has less molecular weight. The dye 12 shows no improvement in depth of shade after chlorination while higher molecular weight but linear bis-azo dye 11 gives slight improvement but not appreciable depth of shade. IR spectra for only chlorinated polypropylene and dyed chlorina-
ted polypropylene in alkaline medium (dyed with disperse dyes of basic character, C.I. Solvent Yellow-2) did not show any evidence of bond formation unlike in case of application of basic dyes to chlorinated polypropylene. However, Table 1 shows that most of the basic character disperse dyes, specially those having electron donating group (negative inductive effect) and no other effects like steric hindrance, higher aqueous solubility due to higher basicity, etc. show more dye uptake both in acid and alkaline bath when dyed after chlorination. Dyes 7 and 12, however, show reverse result for dyeings in acid and alkaline medium. This may be due to some unknown effect related with pH and/or structural peculiarities in alkaline medium.

The possible mechanism of interaction between chlorinated polypropylene and one basic character disperse dye (C.I. Solvent Yellow-2) through electrostatic attraction and negative inductive effect, generating higher affinity for chlorinated polypropylene, is shown in Fig. 1.

3.3 Fastness Properties

Table 2 shows that dyes 1, 3, 6 and 10 have overall good fastness properties. However, for dye 6, the dye uptake is not acceptable. Dyes 1, 3, 4 and 6 show good light fastness (6-7). Dyes 7 and 10 give increased depth of shade on chlorinated polypropylene but have moderate light fastness (4-5). Dye 4 has poor fastness to drycleaning and dry-rubbing and dye 7 has poor rubbing fastness. Relating these findings with the structural constitution of the dyes needs further indepth study. Ahmed and Mallet, however, found that the fading of some azo dyes and pigments on polypropylene occurs usually by photoreduction rather than photooxidation in polypropylene by a mechanism entailing abstraction of tertiary hydrogen of the polypropylene molecule. As per their findings, the relative fading rate increases with increase in Hammet constant of the substituent (measure of decrease in electron density at azo link).

Light fastness results of these dyes on chlorinated polypropylene show that the electron withdrawing groups like $NO_2$, $Cl$ and $OCH_3$ with positive inductive effect and higher Hammet constant value cause more quick light fading. Light fastness of bisazo dyes (Dyes 11 and 12) has been found to be poor in this case. Wash fastness of all the dyes is moderate to good and acceptable. Fastness to drycleaning is also moderate to good for these dyes on chlorinated poly-

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Light</th>
<th>Wash</th>
<th>Drycleaning</th>
<th>Dry rubbing</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Loss of depth</td>
<td>Stain on PP</td>
<td>Loss of depth</td>
<td>Stain on PP</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>3-4</td>
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<td>3</td>
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<td>3</td>
<td>3-4</td>
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<td>6</td>
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<td>2-3</td>
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<td>7</td>
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<td>12</td>
<td>2-3</td>
<td>3-4</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>
propylene. The rubbing fastness of all the dyes, except
dyes 4 and 7, on chlorinated polypropylene is also
good.

4 Conclusions

4.1 Some of the azo disperse dyes with basic character
show increased depth of shade and good fastness on
chlorinated PP but no covalent bond formation occ-
urs unlike in fixing of basic dyes to chlorinated poly-
propylene by covalent bond formation as reported in
earlier work.14,17,19,20.

4.2 The disperse dyes studied exhibit more affinity
to chlorinated polypropylene than to unmodified poly-
propylene and the extent of increase in dye affinity
depends on the nature of substituents in the dyes
and also on the medium of application (acid or alkaline).
Electron withdrawing groups like – NO₂, – OCH₃
and – Cl (positive inductive effect) do not favour
higher dye uptake and also show lower light fastness,
while the disperse dyes of basic character with elec-
tron donating groups as substituents (with negative
inductive effect) applied in acid medium give good
results showing increased dye uptake and improved
fastness performances with a few exceptions for other
structural interactions, steric causes, etc. Further im-
proved results are obtained in acid medium at slightly
higher temperature (110°C) for application of these
dyes to chlorinated polypropylene.

4.3 Dye 1 (4-aminoazobenzene), dye 3 [4-methyl-
4-(dimethylamino)azobenzene] and dye 10 (8-hydr-
oxys-5-phenylazoquinoline) show acceptable depth
of shade with overall good fastness on chlorinated poly-
propylene.

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