The efficiency of various carriers on the dyeing of an acrylic fibre

J P Kim* and S M Burkinshaw

Dept of Colour Chemistry and Dyeing, University of Leeds, Leeds LS2 9JT, UK

**Dept of Fiber and Polymer Science, College of Engineering, Seoul National University, Seoul 151-742, Korea*

The effects of various carriers on the reduction of the glass transition temperature (T_g) and the dyeing transition temperature (T_d) of an acrylic fibre in a cationic dyeing system have been investigated. Linear relationships were found between the concentration of carriers in the fibre and the reduction of the T_g and the T_d of the fibre. The efficiency of various carriers in reducing the T_g and the T_d, when compared in terms of the molar concentrations of the carriers in the fibre, was found to be similar, regardless of the carriers used.

INTRODUCTION

Carriers are thought to be adsorbed by man-made fibres through polar and non-polar forces of interaction, hydrogen bonding and hydrophobic interaction. Salvin postulated that carriers replace fibre–fibre interactions with more readily breakable fibre–carrier bonds [1]. This would permit easier movement of the polymer chain molecules and promote free volume availability in the fibre. The associated increase in segmental mobility of the polymer chains may then be expected to increase the rate of diffusion of dyes, and also to decrease the glass transition temperature (T_g) of the fibre [2]. Thus, the fundamental role of a carrier concerns the former's effects on the physical properties of the fibre, which are related to the segmental mobility of the polymer chains.

The molar efficiency of some hydrophobic carriers in Dacron has been examined by Schuler, who found out that, in both aqueous and non-aqueous dyebaths, an equimolar concentration of several carriers in polyester had a similar effect on dyeing rate and equilibrium uptake of disperse dyes [3]. Glentz *et al.* obtained analogous results [4].

However, more recently, Gur-Arieh *et al.* claimed that equimolar concentrations of various carriers in the fibre exerted different effects on dye uptake [5]. In addition, Ingamells *et al.* showed that carriers having similar association solubility parameters (δ_a) to those of acrylic and polyester will be the most effective carriers for these fibres [2,6].

The aims of the present work were to compare the molar efficiency of various carriers in the reduction of the T_g of an acrylic fibre and to investigate its relationship with the reduction of the dyeing transition temperature (T_d) in aqueous dyeing with a basic dye.

EXPERIMENTAL

Materials

A commercial sample of 0.33 tex (3 denier) Courtelle S staple yarn, supplied by Courtaulds Fibres plc, was used. The basic dye used in this work was Astrazon Green M (BAY, CI Basic Green 4). The yarn and the dye were scoured and purified as described elsewhere [7]. The chemicals used as carriers in the experiments were of laboratory grade, except *o*-phenylphenol which was of analytical grade.

Carrier treatment and T_g determination

Carrier treatments were carried out in 80 ml sealed stainless steel dye pots housed in a Rotadyer (John Jeffreys) laboratory dyeing machine. A sample of the yarn, 1 g, was treated in 50 ml aqueous dyebaths at various carrier concentrations as detailed previously [8]. The treatments were carried out for 90 min at 98°C; the treated fibre was then removed, and rinsed in distilled water and dried in an oven, both at 40°C.

The absorbance of the exhausted solution was measured using a Pye-Unicam PU 8600 UV/VIS spectrophotometer (Philips, UK). Subtraction of this residual carrier concentration from the original was taken as the amount adsorbed by the fibre.

Differential scanning calorimetry (DSC) of the carrier-treated fibre was carried out using a DuPont 1090 thermal analyser and the T_g of the fibre was determined using the DuPont General Analysis Program.

T_d determination

Aqueous dyebaths, 50 ml, containing 0.02 g CI Basic Green 4, 0.02 g acetic acid, 0.06 g sodium acetate and an appropriate quantity of a carrier were prepared in

stainless steel dye pots. The dyebath was adjusted to the required dyeing temperature, and after thermal equilibrium had been achieved a 1 g sample of the yarn was added to the dyebath and dyed for 30 min. The dyed sample was then removed, rinsed with water and acetone, and dried in an oven at 60°C. The dry dyed yarn, 0.02 g, was dissolved in DMF/acetic acid solution (80/20 by vol.) and the concentration of the dye in the fibre was measured by spectrometry as detailed elsewhere [7].

Figure 1 is a plot of dye concentration in the fibre as a function of dyeing temperature for each carrier concentration used. The T_d of the fibre, both in the presence and in the absence of the carrier, is the intercept on the abscissa of the line representing dye uptake of 1 g/kg per 1 degC increase in dyeing temperature.

RESULTS AND DISCUSSION

Attempts were made to evaluate the efficiency with which carriers reduced the T_g of Courtelle S. When the T_g of the fibre was plotted against the concentration of each carrier in the bath used for the treatment, the difference in carrier efficiency was considerable. Figure 2 shows that 3 g/l of

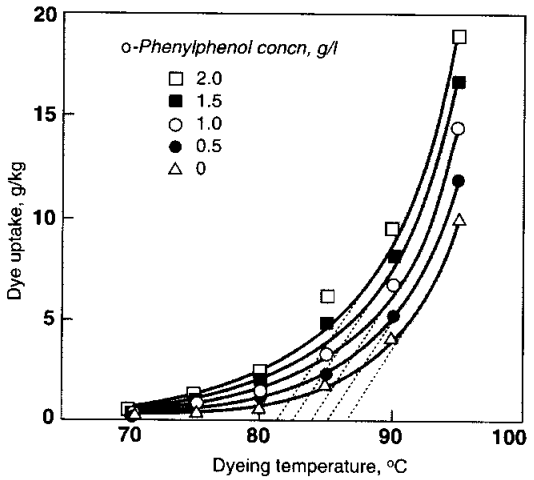

Figure 1 Effect of *o*-phenylphenol on the uptake of CI Basic Green 4 and determination of T_d of the fibre

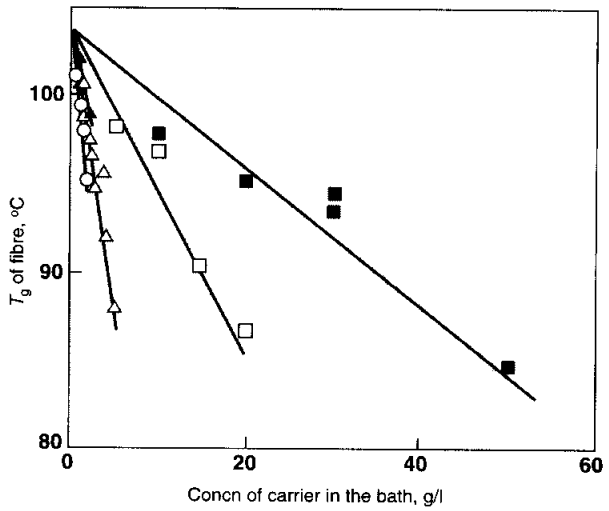

Figure 2 Effect of the carrier concentration in the bath on T_g of Courtelle S (for key see Figure 3)

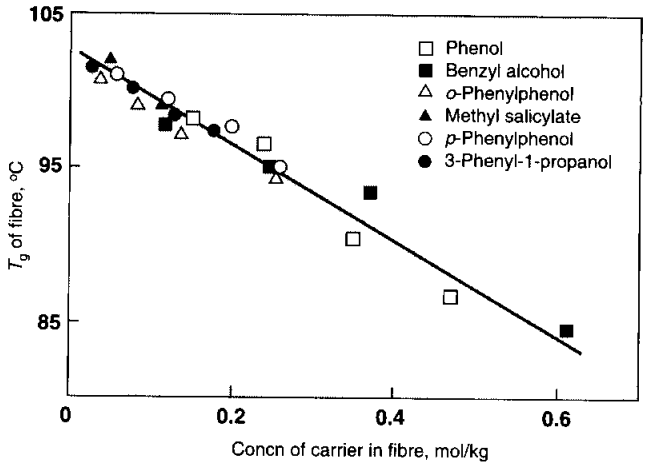

Figure 3 Effect of the carrier concentration in Courtelle S on T_g of the fibre

Table 1 Solubility parameters of polyacrylonitrile, carriers and water

Carrier	δ_t	δ_a	δ_d	Ref.
Polyacrylonitrile	12.8	8.3	9.3	11
o-Phenylphenol	11.1	4.4	10.2	12
p-Phenylphenol	11.2	4.5	10.2	
Methyl salycilate	10.6	7.2	7.8	13
Phenol	11.8	7.9	8.8	13
Benzyl alcohol	11.6	7.3	7.9	
3-Phenyl-1-propanol	10.4	6.6	7.9	13
Water	23.4	22.1	7.6	13

δ_t total solubility parameter
δ_a association solubility parameter
δ_d dispersion solubility parameters

o-phenylphenol reduced the T_g of Courtelle S by 10 degC, whilst 26 g/l of benzyl alcohol was required to achieve the same reduction. Clearly, at any given concentration, hydrophobic carriers, such as *o*- and *p*-phenylphenol are considerably more efficient than hydrophilic carriers, such as benzyl alcohol and phenol, for T_g reduction.

It is believed that carriers function by plasticising the compact structure of fibres. Since plasticisation is reflected in the reduction of fibre T_g, which in turn is related to the concentration of the plasticiser present, the observed reduction in the T_g of Courtelle S must be related to the molar concentration of the carrier within the fibre. Figure 3 shows that the relationship between T_g reduction in Courtelle S and the molar concentration of carriers in the fibre was linear. This observation is in agreement with those obtained by Thorton (plasticisation of Acrilan filament by phenol) [9], and by Fujino *et al.* (decrease in T_g of polyester fibre with increasing concentration of plasticisers within the fibre) [10].

When the reduction of the T_g of Courtelle S was compared in terms of the molar concentration of carriers in the fibre, there was little efficiency difference among the carriers used (Figure 3).

Table 1 presents the various solubility parameters of the

carriers quoted in the literature, together with those of water and acrylic fibre [11–13]. For *p*-phenylphenol and 3-phenyl-1-propanol, values of δ_t were calculated using Small's method [14], those of δ_d were taken from figures quoted for biphenyl and isopropylbenzene respectively, and those of δ_a were calculated using Eqn 1:

$$\delta_t = (\delta_a^2 + \delta_d^2)^{0.5} \quad (1)$$

Any possible dependence between the solubility parameters of the carriers and T_g reduction in Courtelle S should be apparent from the values quoted in Table 1. In fact, when the solubility parameters of the six carriers used in this work were compared with the extent of T_g reduction brought about by each carrier (from Figure 3), no correlation could be found. As Table 1 shows, the δ_a values of *o*- and *p*-phenylphenol were considerably lower than those of acrylic fibre and the other carriers used. According to the theory proposed by Ingamells *et al.*, these two carriers should be the least efficient, whereas there was little difference in terms of T_g reduction for all six carriers used. Moreover, although the solubility parameters of water are so widely different to those for acrylic fibre, Rosenbaum found that water reduced the T_g of acrylic fibres by between 30 and 35 degC [15]. Indeed, it is known that water is an excellent plasticiser for various fibres [16].

Ingamells [17] and Gur-Arieh *et al.* [18] determined the glass transition temperature of acrylic fibre in an aqueous solution of carriers, although the plasticising effect of water was not considered. Because carriers are dissolved in water and a considerable quantity of water is adsorbed by the fibre, then the solubility parameter of a water/carrier mixture is really the important criterion, rather than that of the carrier alone. The effective solubility parameters (total, association and dispersion solubility parameters) of a mixture (δ_m) of components 1 and 2, with volume fractions V_1 and V_2 respectively, can be estimated from the Scott and Magat formula [19,20] (Eqn 2):

$$\delta_m = \delta_1 V_1 + \delta_2 V_2 \quad (2)$$

where δ_1 and δ_2 are the solubility parameters of the pure components.

According Eqn 2, solubility parameters calculated for aqueous carrier solutions will give almost identical values for any carrier, because of the relatively low concentration of carrier present in the large volume of water typically used for such treatments. Consequently, if the solubility parameter of the carrier/water mixture is the key factor in determining the efficiency of carrier action, then the actual carrier used is relatively unimportant (Figure 4). Many workers have observed that equimolar concentrations of various carriers in polyester fibres produced a similar plasticising effect [1,4,21–23].

Solubility parameters can be applied most satisfactorily to non-electrolytes and non-polar substances. Therefore, as Ibe has stated, they are not suitable for inclusion in a model that describes the dyeing of acrylic fibres, which involves electrolytes (cationic dyes), a highly polar solvent (water) and a polar substrate [24]. The solubility parameter concept has had its principal success in explaining miscibility and dissolution of non-polar polymers, since it neglects such factors as solvation, crystallinity and entropy of solution [13].

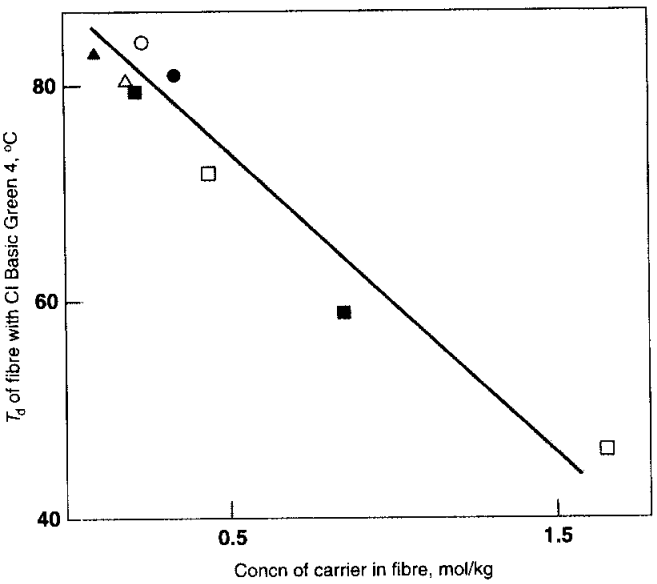

Figure 4 Effect of the carrier concentration in Courtelle S on T_d of the fibre with CI Basic Green 4 (for key see Figure 3)

The segmental mobility of polymeric chains increases abruptly when the glass transition temperature of the fibre is reached. The diffusion of cationic dyes into acrylic fibres is also controlled by the segmental mobility, so the physical change of the fibre structure caused either by the temperature rise or by the presence of carriers in the fibre will be directly reflected in the dyeing kinetics. The rate of uptake of basic dyes onto Courtelle S was found to increase sharply over a relatively narrow temperature range. Many workers have referred to the inflection point of such rate-of-dyeing plots as the 'dyeing transition temperature' (T_d) [25–29].

The T_d of Courtelle S was determined as shown in Figure 1; in a carrier-free dyebath it was located at 86.5°C, lower than the T_g of Courtelle S at 0% RH (104°C) by some 17.5 degC, indicating very good plasticisation of the fibre by the water molecules. Rosenbaum has attributed the strong plasticisation power of the water on acrylic fibres to its high dielectric constant, which reduces the molecular rigidity of the fibre-forming polymer chains by decreasing the repulsion forces operating between the adjacent nitrile dipoles within the chains [15].

When the T_d of Courtelle S dyed with CI Basic Green 4 was plotted against the molar concentration of various carriers, all the data seemed to fall in one straight line, indicating little difference in the efficiency of each carrier in reducing the T_d value (Figure 4). As previously discussed, the predominant factor in the diffusion of cationic dyes within an acrylic fibre is the segmental mobility of the fibre-forming polymer chains, and equimolar concentrations of various carriers gave similar

reductions in the T_g of Courtelle S. Therefore, it was expected that equimolar concentrations of various carriers in Courtelle S would also give a similar reduction in T_d, as shown in Figure 4.

It has been reported that, because carriers are generally of smaller molecular size than disperse dyes, they are adsorbed onto polyester fibre at a lower temperatures [30,31]. Gulrajani *et al.* observed that the T_d of Dacron dyed with disperse dyes was higher than the T_g of the fibre measured in the dyebath [32]. These authors claimed that the difference between the T_d and the T_g depended on the structure, size and shape of the dye molecule used, and on the nature of the dye–polymer interactions. The T_d of Courtelle S dyed with cationic dyes was expected to be higher than the T_g of the fibre in the dyebath owing to the large size and bulky nature of the dye molecules together with the strong dye–fibre interactions involved.

A linear relationship between T_d and T_g has been reported [25,33]. Gur-Arieh *et al.* showed that the decrease in the T_d with basic dyes paralleled the decrease in the T_g of an acrylic fibre when measured under dyebath conditions [33]. Regrettably, the T_g of Courtelle S under dyebath conditions was not measured in this study, so a direct comparison between the T_d and the T_g values under these conditions could not be made. However, the T_g of carrier-treated Courtelle S was plotted against the T_d of the fibre dyed with CI Basic Green 4 in the presence of various carriers. As Figure 5 shows, the relationship between the two values could be represented by a straight line of slope 1. Therefore the extent of the T_g reduction and the plasticisation effect of water molecules within the fibre is fully reflected by the decrease in T_d at 0% RH.

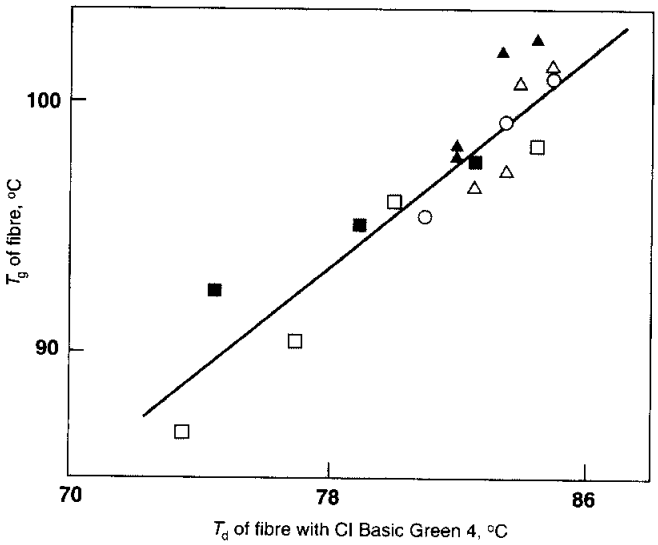

Figure 5 Relationship between T_g of Courtelle S and T_d of the fibre with CI Basic Green 4 (for key see Figure 3)

CONCLUSION

The carriers used in this study, when compared in terms of their molar concentrations in Courtelle S, showed similar efficiencies in reducing the glass transition temperature and the dyeing transition temperature of the fibre. Thus when the same amount of carriers were used in aqueous dyebaths, within their solubility limits, higher amounts of more hydrophobic carriers were adsorbed by the fibre, resulting greater reductions in dyeing temperature and dyeing time. Hydrophobic carriers are usually less soluble in water, limiting the amounts that can be adsorbed by the fibre. Consequently, when evaluating the efficiency of a carrier in a dyebath, the solubility of the carrier and the partition of the carrier between the fibre and the dyebath should be considered together.

REFERENCES

1. V S Salvin, *Amer. Dyestuff Rep.*, **49** (1960) 600.
2. W C Ingamells, R H Peters and S R Thorton, *J. Appl. Polymer Sci.*, **17** (1973) 3733.
3. M J Schuler, *Text. Res. J.*, **27** (1957) 352.
4. O Glentz, V Beckmann and W Wunder, *J.S.D.C.*, **75** (1959) 141.
5. Z Gur-Arieh, W Ingamells and R H Peters, *J. Appl. Polymer Sci.*, **20** (1976) 41.
6. W C Ingamells and W C Thomas, *Text. Chem. Colorist*, **16** (3) (1984) 55.
7. J P Kim and S M Burkinshaw, *J. Appl. Polymer Sci.*, **49** (1993) 1647.
8. J P Kim, PhD thesis, University of Leeds (1990).
9. S R Thorton, PhD thesis, UMIST (1971).
10. G M Fujino and A T Walter, *Text. Res. J.*, **29** (1959) 211.
11. J L Cardon, *Encyclopedia of polymer science and technology* (New York: Interscience, 1966) 833.
12. A Urbanick, *Text. Chem. Colorist*, **15** (3) (1983) 36.
13. C M Hansen and A Beerbower, *Kirk-Othmer encyclopedia of chemical technology*, 2nd Edn, Supplement Vol. (New York: John Wiley, 1971) 889.
14. C M Hansen and K Skarup, *J. Paint Tech.*, **39** (1967) 511.
15. S Rosenbaum, *J. Appl. Polymer Sci.*, **9** (1965) 2071.
16. T M A Hossian, T Iijima and Z Morita, *J. Polymer Sci.*, Part B, **5** (1967) 1069.
17. W C Ingamells, *J.S.D.C.*, **96** (1980) 466.
18. Z Gur-Arieh, W C Ingamells and R H Peters, *J.S.D.C.*, **92** (1976) 332.
19. R L Scott and M Margat, *J. Polymer Sci.*, **4** (1949) 555.
20. M Margat, *J. Chem. Phys.*, **46** (1949) 344.
21. F Feichtmayer and A Wurz, *J.S.D.C.*, **77** (1961) 626.
22. J Rubin and R D Andrew, *Polymer Eng. Sci.*, **8** (1968) 302.
23. E A Duffy and E S Oslon, *J. Appl. Polymer Sci.*, **16** (1972) 1539.
24. E C Ibe, *J. Appl. Polymer Sci.*, **14** (1970) 837.
25. R H Peters, *Diffusion in polymers*, Ed Crank and Park (London: Academic Press, 1968).
26. A Takoaka and M Aki, *Sen-i Gakkaishi*, **21** (1965) 437.
27. T H Guion, T M A Hossain, R McGregor and J R Thagard, *J.S.D.C.*, **89** (1973) 409.
28. A Takoaka and J Seki, *Sen-i Gakkaishi*, **20** (1964) 671.
29. A Takaoka and J Seki, *Sen-i Gakkaishi*, **21** (1965) 437.
30. G A F Roberts and R K Salanki, *J.S.D.C.*, **95** (1979) 437.
31. G A F Roberts and R K Salanki, *J.S.D.C.*, **95** (1979) 226.
32. M L Gulrajani and R K Saxena, *J.S.D.C.*, **95** (1979) 330.
33. Z Gur-Arieh and W Ingamells, *J.S.D.C.*, **90** (1974) 12.