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β-Cyclodextrin as retarding reagent in polyacrylonitrile dyeing

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Abstract

β-Cyclodextrin was tested as a dye complexing agent – as a dye retardant in the dyeing of PAN fibres with cationic dyes. Significant improvement of colour uniformity and some improvements in colour depth were observed when PAN fibres were dyed in the presence of β-cyclodextrin as compared to dyeing in the presence of a commercial retardant.

Keywords: Polyacrylonitrile; Dyeing; Cationic dyes; Cyclodextrin; Complexation

1. Introduction

Cyclodextrins (CD) are macrocyclic compounds built from glucopyranose units linked by α-(1,4)-glycosidic bonds [1,2]. The structure of β-cyclodextrin is shown schematically in Fig. 1.

CD can be obtained by enzymatic degradation of starch; in this process compounds with 6–12 glucopyranose units per ring are produced. Depending on the enzyme and the way in which the reaction is controlled, the main product is α, β or γ-cyclodextrin (6, 7 and 8 glucopyranose units, respectively). CD are of circular, conical conformation and height of about 800 pm; the inner diameter of the cavity varies from 500 to 800 pm [2,3]. Commercially, the most interesting is β-cyclodextrin (β-CD), because of its simple production, availability, cavity diameter and price. It is the most widely used and constitutes at least 95% of all produced and consumed CDs [4]. The inner diameter of the β-CD cavity varies from 600 to 680 pm (Fig. 2) [5,6] and can accommodate aromatic compounds such as volatile molecules and drugs.

Cyclodextrins can form inclusion complexes with a large number of organic molecules, a property that enables them to be used in a variety of different textile applications [2,7–10]. As cyclodextrins can incorporate different dyes into their cavity, they should be able to act as retarders in a dyeing process.

Cationic dyes [11] have very low migration power on polyacrylonitrile (PAN) fibres due to their high substantivity and rapid uptake over small temperature range above the T_g of the fibre. Colour levelness can be improved by the use of different retarding reagents. In this work, β-cyclodextrin was investigated as a retarding agent in the dyeing of PAN fibres with cationic dyes. The retarding effect of β-cyclodextrin was compared to that of a commercial product.

2. Experimental

A commercial sample of Maxilon Blue GRL from Ciba (C.I. Basic Blue 41) was used without purification (Fig. 3).

β-Cyclodextrin was supplied by Fluka and the commercial retarding reagent *Tinegal MR New* (*N*-tetraalkyl ammonium methyl sulphate) was obtained from Ciba. Stock solutions of 2.5 g of *Tinegal MR New* in 100 ml of distilled water were prepared at room temperature.

Plain fabric made out of anionic copolymeric acrilan fibres (Solutia Inc.) with the saturation value of 1.4 was used for dyeing. The fabric weight was 126 g/m^2; the warp thread density was 18 threads/cm and the weft thread density was 13 threads/cm.

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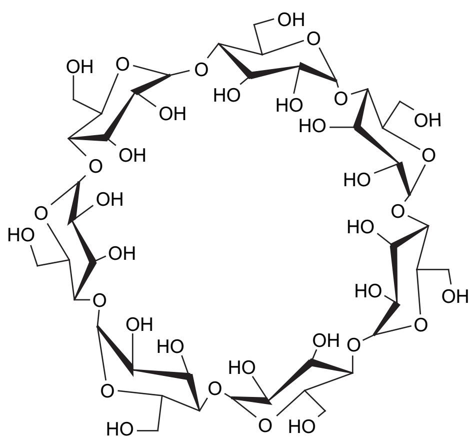

Fig. 1. Schematic structure of β-cyclodextrin.

PAN fibres were dyed in a laboratory-scale *Roaches Pyrotcec-S* dyeing machine, the capacity of the dyeing tubes were 200 cm^3. The concentration of the dye, β-cyclodextrin and commercial retarding agent in the dyeing bath was varied as shown in Table 1.

Dyeing was carried out using a liquor-to-goods ratio of 20:1, pH value was adjusted to 4 with the addition of CH_3COOH (30%) and CH_3COONa (Fig. 4). The standard dyeing procedure (60 min at 95 °C), which is recommended by Ciba, was modified by reducing the dyeing time or the temperature; dyeing for a shorter time was carried out at 95 °C for 40 min and dyeing at a lower temperature was carried out for 60 min at 85 °C. The dyed PAN fabrics were rinsed in cold water for 5 min and dried at room temperature.

Colour measurement of the dyed samples was carried out using a Data Color SF 600 Plus spectrophotometer using Pulsed Xenon illuminant, and dual beam d/8° optical geometry. MC90 dual beam spectrometer with dual 128 pixel custom diode array was used. Textile substrates were measured in two layers. The depth of each dyeing was evaluated by measurements of *K*/*S* value; the colour uniformity was evaluated by means of the standard deviation of the mean of the *K*/*S* values.

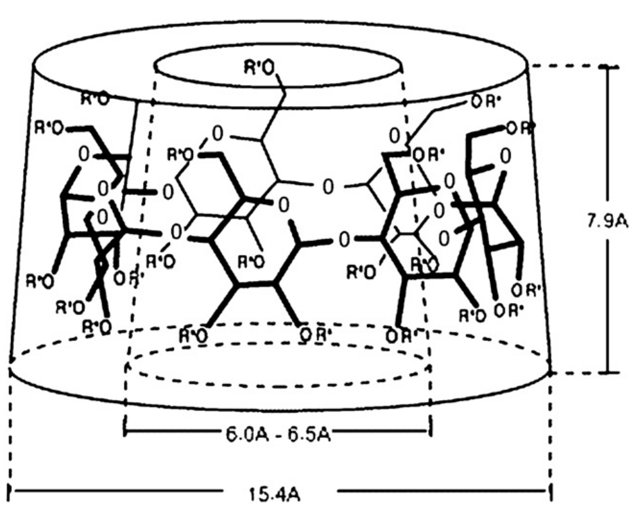

Fig. 2. Conical structure of β-cyclodextrin.

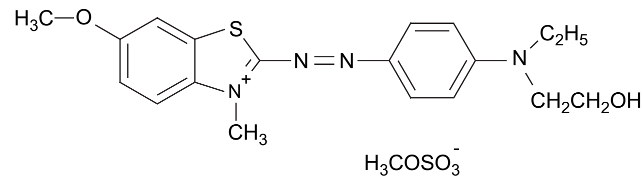

Fig. 3. Structure of C.I. Basic Blue 41.

Five measurements were carried out at five different positions for each specimen.

After dyeing, the amount of residual dye in the dyeing bath was measured using UV/vis spectroscopy. For these purposes, a Varian Carry 50 spectrophotometer was used; the absorbances (λ_{max}) were measured at the wavelength of 616 nm. The reference solution was water containing all chemicals used in dyeing procedures except dye. The λ_{max} values were the same for dyeing solutions containing β-CD or commercial retarding reagent.

3. Results and discussion

3.1. Colour depth and colour uniformity measurements

Fig. 5 shows the *K*/*S* values of PAN fabrics which had been dyed using the standard procedure in solutions with different dye concentrations and with different concentrations of β-CD and the commercial retardant. It is evident that higher *K*/*S* values were obtained when β-CD had been used as retarding agent.

The colour uniformity of the dyeings was evaluated from the standard deviation of the mean *K*/*S* values (Fig. 6). Significant improvement in colour uniformity was observed when β-CD had been used, especially when higher concentrations (2 and 3%) of β-CD were employed.

Table 1
Concentration of dye and retarders – β-cyclodextrin and commercial retarding agent in the dyeing bath

Sample	Dye (C.I Basic Blue 41) [%]	Retarder (β-CD) [%]
S 01	0.01	1
S 02	0.50	1
S 03	1.00	1
S 04	0.01	2
S 05	0.50	2
S 06	1.00	2
S 07	0.01	3
S 08	0.50	3
S 09	1.00	3
Sample	Dye (C.I Basic Blue 41) [%]	Commercial retarder [%]
S 10	0.01	1
S 11	0.50	1
S 12	1.00	1
S 13	0.01	2
S 14	0.50	2
S 15	1.00	2
S 16	0.01	3
S 17	0.50	3
S 18	1.00	3

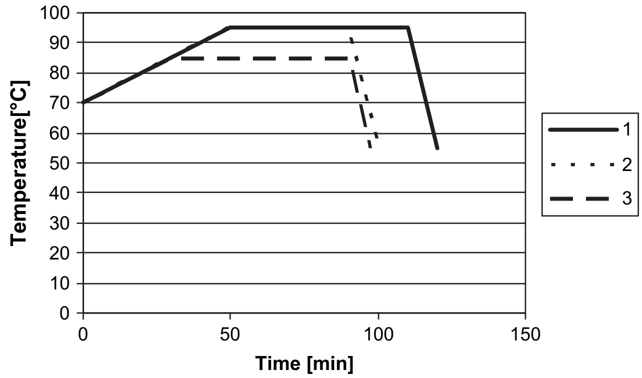

Fig. 4. 1. Standard dyeing procedure: $T = 95$ °C; $t = 60$ min, 2. reduced time of dyeing: $T = 95$ °C; $t = 40$ min, and 3. reduced temperature of dyeing: $T = 85$ °C; $t = 60$ min.

Fig. 7 shows the *K*/*S* values of PAN fabrics that had been dyed for 40 min, using different dye concentrations and different concentrations of the two retarding agents (β-CD and the commercial reagent). It is clear that either the same or higher *K*/*S* values were obtained when β-CD had been used as retardant.

Reducing the time of dyeing did not have a negative effect on colour uniformity (Fig. 8) as the standard deviation of the mean *K*/*S* values of PAN dyed fibres for 40 min using β-CD was either the same or even higher than when the conventional retarding agent had been used.

Reduction of the dyeing temperature from 95 °C to 85 °C did not influence the colour depth of PAN fibres which had been dyed in the presence of either β-CD or the commercial retarding agent (Fig. 9 as compared to Fig. 5). Using β-CD in the dyeing baths still give better results than did the commercial retarding reagent.

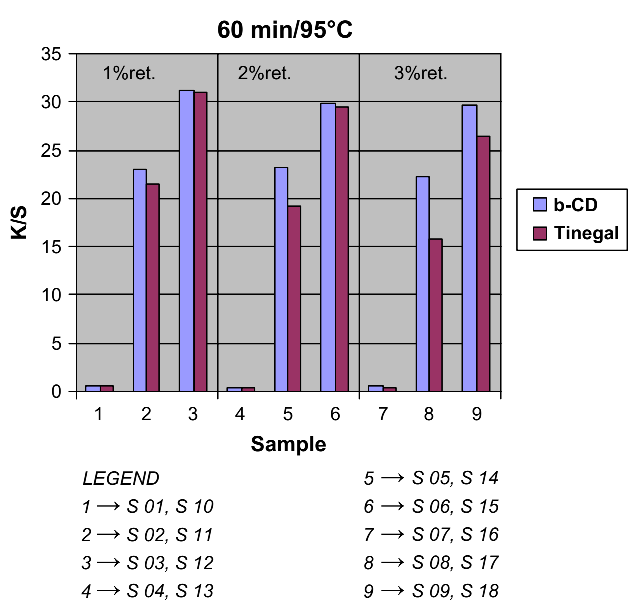

Fig. 5. *K*/*S* values of PAN fabrics dyed with different concentrations of dye and retarding reagents – β-CD and commercial reagent (dyeing procedure: 60 min at 95 °C).

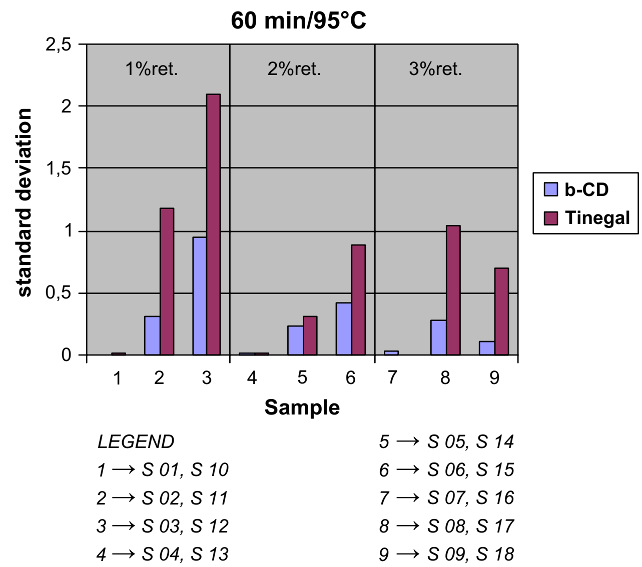

Fig. 6. Standard deviation of the mean *K*/*S* values of PAN fabrics dyed with different concentrations of dye and retarding reagents – β-CD and commercial reagent (dyeing procedure: 60 min at 95 °C).

Reducing the dyeing temperature did not improve colour uniformity (Fig. 10) when compared to the colour uniformity achieved using the standard procedure (Fig. 6). The standard deviation of the mean *K*/*S* values of PAN fabrics dyed at 85 °C for 60 min in the presence of β-CD was lower than those obtained for fabrics which had been dyed at 85 °C for 60 min in the presence of commercial retarding agent. Thus, dyeing in the presence of β-CD improved colour levelness.

3.2. UV/vis spectroscopy

It is well known that β-CD forms complexes with various small molecules. The formation of β-CD/dye complex at elevated temperature was studied using UV/vis spectroscopy. For this purpose the absorbance of water solutions containing

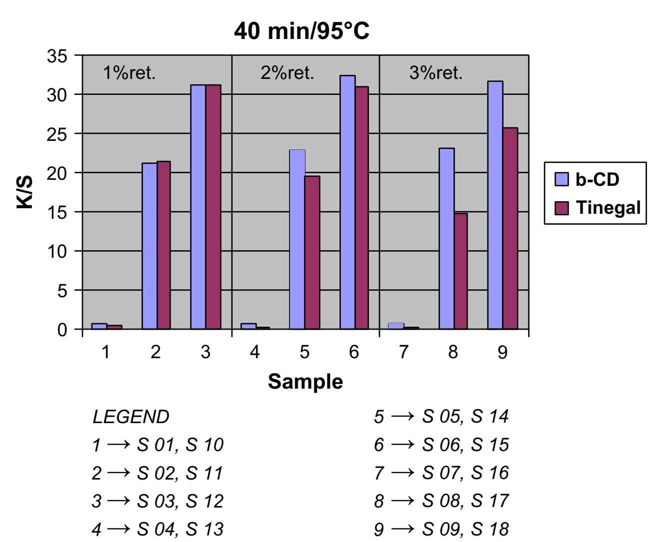

Fig. 7. *K*/*S* values of PAN fabrics dyed with different concentrations of dye and retarding reagents – β-CD and commercial reagent (dyeing procedure: 40 min at 95 °C).

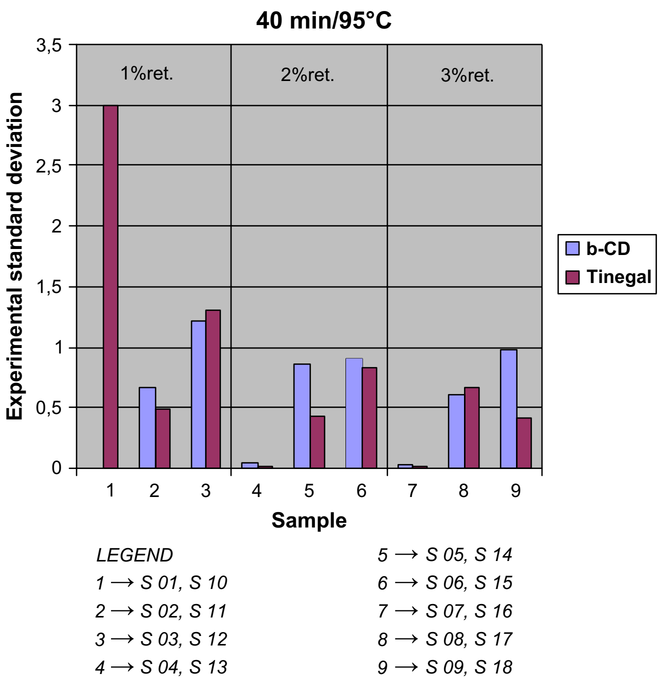

Fig. 8. Standard deviation of the mean *K/S* values of PAN fabrics dyed with different concentrations of dye and retarding reagents – β-CD and commercial reagent (dyeing procedure: 40 min at 95 °C).

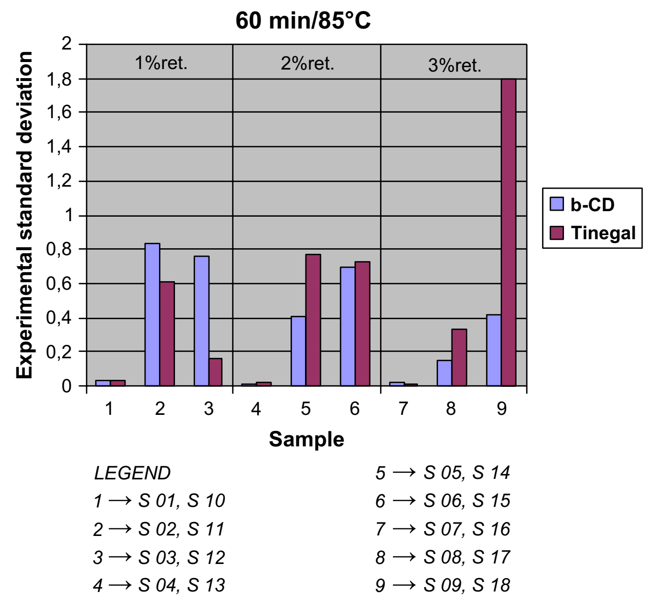

Fig. 10. Standard deviation of the mean *K/S* values of PAN fabrics dyed with different concentrations of dye and retarding reagents – β-CD and commercial reagent (dyeing procedure: 60 min at 85 °C).

different concentrations of dye with and without the addition of β-CD was measured. Temperature and time wise the standard dyeing procedure was simulated. After the simulation of dyeing, the solutions containing dye and β-CD showed significantly lower absorbance when compared to solutions containing only dye (Table 2).

The addition of β-CD to the dyeing bath significantly increases the bath exhaustion and thus reduces the absorbance of the residual dyeing bath, compared to the bath containing dye and commercial retarding reagent. This phenomenon can be explained by the formation of a complex between β-CD and the dye. The complex formation is not static but rather a dynamic equilibrium process and the dye can be released during the dyeing procedure.

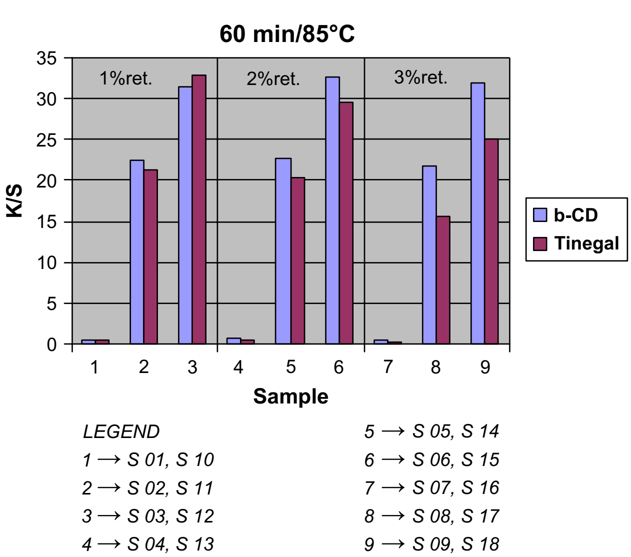

Fig. 9. *K/S* values of PAN fabrics dyed with different concentrations of dye and retarding reagents – β-CD and commercial reagent (dyeing procedure: 60 min at 85 °C).

4. Conclusions

Quality dyeing was obtained and the values of bath exhaustion were significantly improved when β-CD was used as a retarding reagent compared to the cationic retarding reagent based on quaternary ammonium compound.

Significant improvement of colour levelness and some improvements in colour depth have been found when PAN fibres were dyed in the presence of β-cyclodextrin compared to dyeing in the presence of commercial retarding reagent. These improvements are more significant when higher concentrations of the dye and β-cyclodextrin were used. Reducing the time of dyeing from 60 to 40 min and reducing the dyeing temperature for 10 °C had no influence on colour depth of the dyed PAN fibres using either β-CD or commercial retarding reagent.

Table 2
Absorbance of water solutions containing different quantities of cationic dye with and without the addition of β-CD

Concentration of dye [mg/l]	Absorbance of the dye solution + β-CD	Absorbance of the dye solution
0.175	0.039	0.036
0.2	0.045	0.058
0.225	0.045	0.080
0.25	0.046	0.092
0.275	0.052	0.094

Our current research work shows that in a water solution a complex between β-CD and the dye is formed at elevated temperatures. The β-CD/dye complex with the increased molecular weight does not diffuse within the fibre and has low substantivity for the textile substrate. Because the complex formation is a dynamic equilibrium process, the dye can easily be released and adsorbed on the textile substrate during the dyeing procedure. This indicates that the mechanism of retarding when using β-CD is through the formation of a dye/β-CD complex. This complex would slow down the rapid uptake of the dye.

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