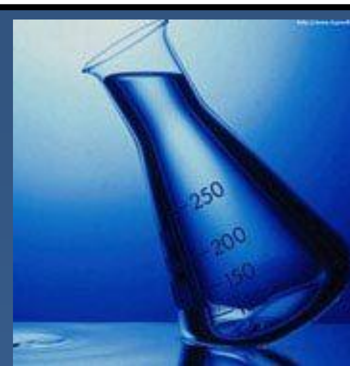

Improving Optical Brightness Of Cellulosic Textiles with β-Cyclodextrin

By: Morgane Le Fur & Graça M.B. Soares

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Abstract

Cyclodextrins are known to form noncovalent inclusion complexes with various fluorescent dye molecules in aqueous solution. This interaction can result in an increase in fluorescence of the compound that can modify the properties of the materials where they are applied.

In this study the effect of combined application of fluorescent whitening agents and hydroxypropyl-β-cyclodextrin to cotton fabrics was investigated. For this purpose, 4,4´-diamino-2,2´-stilbendissulfonic acid, an important precursor for the synthesis of fluorescent whitening agents and C.I. Fluorescent Brightener 252 dye, a derivative of stilbene dissulfonic acid widely used as optical brightener for textiles, were chosen as model compounds. All samples were characterized by infrared spectroscopy and differential scanning calorimetry.

The evaluation of fabric performance showed that addition of 0.75% hydroxypropyl-β-cyclodextrin increased the whitening effect by 15%, and caused a slight improvement in terms of light fastness. The washing fastness remained unchanged.

Introduction

β-cyclodextrins, especially in their more water-soluble derivative forms, are versatile complexing agents. They have been used to functionalize textile substrates, operating as a controlled release agents for water-insoluble substances such as flavorings or natural extracts, and in cosmetic textiles production. Their contribution to the kinetics of dyeing modeling has also been explored with promising results for different types of dyes (Savarino, et al., 1999, Savarino, et al., 2000; Buschmann et al., 2001; Szejtli, 2003; Savarino, et al., 2004, Savarino, et al., 2006 ; Carpignano et al.,2010; Martins, et al., 2008; Bereck, 2010; Soares et al., 2010; Bhaskara-Amrit et al., 2011; Lu et al., 2011).

Their ability to complex fluorescent substances was established for different types of compounds, often resulting in increased efficiency and photo stability of the fluorescence effect produced by complexes formed (Syamala et al., 1980; Lui et al., 2001; Liu et al., 2002; Szuster et al., 2004; Arunkumar et al., 2005; Soares et al., 2010).

The present paper aims to describe results obtained from the study of conjugated application of hydroxypropyl-β-cyclodextrin with stilbene fabric brighteners on cotton optical bleaching properties.

Methodology

A. Materials

Cotton fabric (Jersey, 100% cotton) was obtained from Lameirinho (Portugal); caustic soda, hydrogen peroxide, acetic acid and sodium carbonate were purchased from Merck ;

Hydroxypropyl-β-cyclodextrin was purchased from Wacker Chemie (Spain); 4,4´-diamino-2,2´-stilbendissulfonic acid (DDA) (Fig. 1) was kindly provided by Radim Hrdina, University of Parduce, Czech Republic; C.I. Fluorescent Brightener 252 dye (BHT) (Fig. 2) was supplied by Huntsman (Portugal).

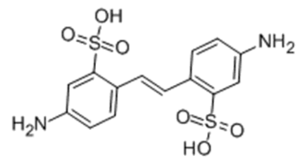

Figure 1- 4, 4´-diamino-2, 2´-stilbendissulfonic acid

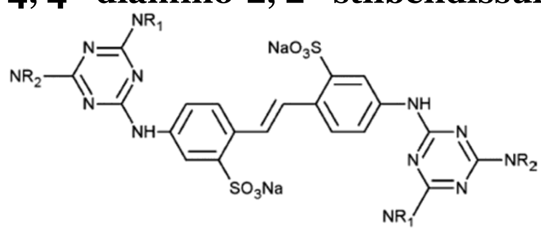

Figure 2- C.I. Fluorescent Brightener 252 dye

B. *Methods*

1) *Encapsulation studies*

The Job's plot was done from UV spectral data according to the continuous variation method (Hirose, 2007)

2) *Application process*

The samples (5 g) of previously bleached cotton were treated using gradient exhaustion process (1:20 liquor ratio). Fabric auxiliar products and BHT (0.75% o.w.f) were introduced at the beginning of the process to a bath with pH ajusted to 8 with Na_2CO_3. The temperature was increased from 30ºC to 90ºC (4ºC/min) and mantained for 30 min. After that, the temperature was lowered to 30ºC (4ºC/min), the hydroxypropyl-β-cyclodextrin (0 to 10%) was added and the process was allowed to run for a further 15 min. Subsequently, samples were removed from the bath, washed under running tap water and dried.

C. *Analysis*

Fourier Transformed Infrared (FTIR) spectra were recorded on an ATR FTIR Avatar 360 spectrophotometer.

DSC analyses were performed with a differential scanning calorimeter DSC-822^e instrument (Mettler Toledo). Melting point and heat of fusion calibration were carried out with indium. A heating rate of 10ºC min^{-1} from 25 to 400ºC was used. Standard aluminum sample pans (PerkinElmer) were used. An empty pan was used as the reference standard. Analyses were performed under a nitrogen purge and triple runs were carried out for each sample. The weight of each sample was kept constant (4.1 ±0.1 mg).

Fastness tests were performed according standard tests (ISO 105-B02; ISO 105-C06/A1S; BS EN ISO 105F10)

Results and Discussion

A. Inclusion complex study

The encapsulation of stilbene compounds by hydroxypropyl-β-cyclodextrin was evaluated by continuous variation method at pH 8. The results obtained confirm complex formation under the specified experimental conditions.

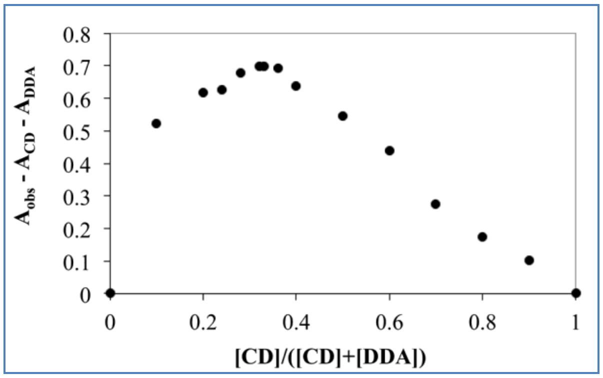

Figure 3- Determination of the stoichiometry of the DDA- hydroxypropyl-β-cyclodextrin complexes by the Job´s method.

The Job's method provided 2:1 stoichiometry for the inclusion complex between hydroxypropyl-β-cyclodextrin and DDA (Fig. 3) (Hebeish at al., 2001; Olson, et al., 2011).

B. Sample characterization

A comparative analysis of FTIR spectra of standard and treated materials is shown in Fig. 4. Only slight spectral differences were observed. Untreated material exhibited O–H stretching absorption at 3270 cm^{-1}, C–H stretching absorption at 2890 cm^{-1}, C–H wagging 1425 cm^{-1} and C–O–C stretching absorption at 1157 and 1005 cm^{-1}.

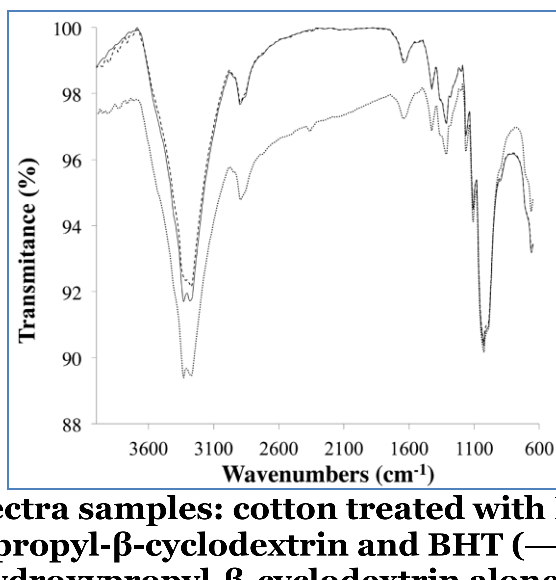

Figure 4- FTIR spectra samples: cotton treated with BHT (....), cotton treated with hydroxypropyl-β-cyclodextrin and BHT (—) and cotton treated with hydroxypropyl-β-cyclodextrin alone (----)

These absorptions are consistent with those of a typical cellulose backbone (Chung et al., 2004; Xue at al., 2008). The strong absorption at 3330 cm^{-1} due to N-H stretching of secondary amines corroborates the presence of BHT (see chemical structures presented in Fig. 1 and Fig. 2) in both types of treated samples. The peak at 1634 cm^{-1} corresponds to the bending mode of the absorbed water.

The thermogram of untreated cotton shows one endothermic peak, initiated at 349.18ºC and finished at 397.99 ºC associated with decomposition processes, which may occur within the fabric during heating (Fig. 5).

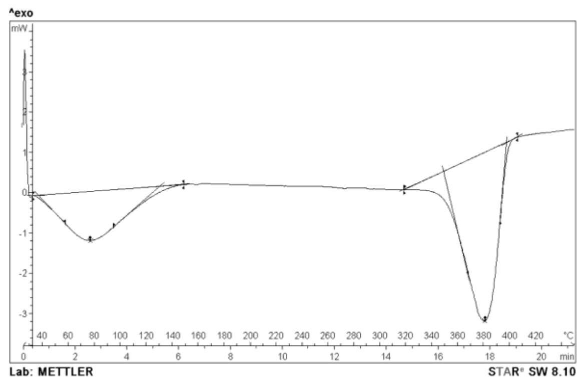

Figure 5- DSC plot of standard cotton

The DSC curves of the modified material with hydroxypropyl-β-cyclodextrin and hydroxypropyl-β-cyclodextrin plus optical brightener were compared (Fig. 6). For the cotton treated with hydroxypropyl-β-cyclodextrin and BHT the enthotermic peak initiated at 330.83ºC, finished at 376.51ºC. For cotton finished with hydroxypropyl-β-cyclodextrin the enthotermic peak initiated at 332.87ºC and finished at 377.40ºC. Futhermore, the differences in enthalpy values suggest that the treatment not influences the crystallinity of cotton fibers (☐H = -143,06J/g and -145,51J/g respectively) (Macsim at al., 2011).

The treated cotton samples also contained endothermic peaks at 85.51ºC and 83.94ºC, which is probably associated with the melting of hydroxypropyl-β-cyclodextrin, BHT and possibly some water from cellulose polymer chains.

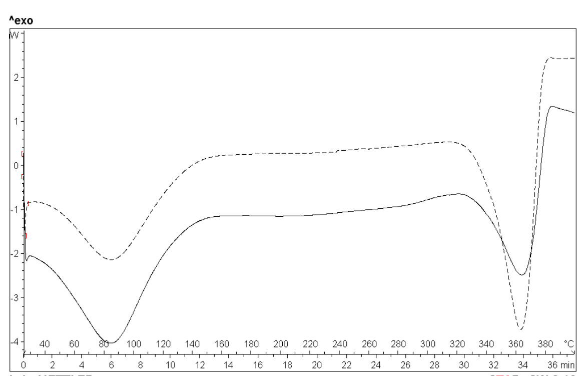

Figure 6- DSC plots of cotton with hydroxypropyl-β-cyclodextrin and BHT () & cotton with hydroxypropyl-β-cyclodextrin (---)

***C.** Effect of CD in the optical bleaching of cotton*

The application process of BHT and CD was optimised by, changing parameters such pH, temperature and CD at different stages of process. Best application conditions are described under Methodology.

Fig. 7 shows the reflectance curves of different samples analysed. The bleaching effect of the HBT is noted when comparing the reflectance of the samples treated with the standard cotton. However, the presence of hydroxypropyl-β-cyclodextrin increases the reflectance value from 111.3 to 129.6.

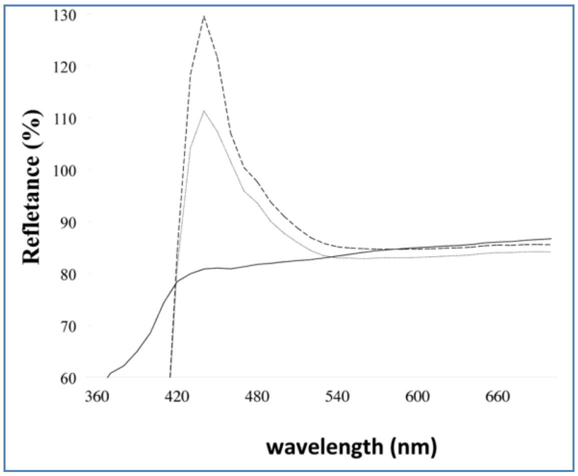

Figure 7- Refletance curves of standard cotton (—), cotton treated with BHT (....) & cotton treated with hydroxypropyl-β-cyclodextrin and BHT (---)

These results obtained are in agreement with the literature concerning the effect of the encapsulation on the photochemical behavior of fluorescent molecules. The reasons for this behavior are related to the effect of encapsulation on the geometric isomerization of these compounds (Syamala et al., 1980). Furthermore, it is known that organic compounds like fabric optical brighteners have a tendency to aggregate, which induces multichromophoric interactions that alter the quenching of the photoluminescence. In principle, these problems can also be attenuated by encapsulation strategies that isolate the individual molecule and prevent self-aggregation or similar interactions with the chemical environment Lui et al., 2002). In keeping with this suggestion, in earlier work we have verified the increase in fluorescence of encapsulated Rhodamine B (Martins et al., 2008).

The performance of materials in terms of fastness properties was evaluated. The fastness testes showed that the washing fastness did not change (4-5) and the colourfastness to light increased slightly from 3-4 to 6.

Conclusion

From this study it can be concluded that the application of hydroxypropyl-β-cyclodextrin with optical brightener increased the fluorescent effect on cotton fabric by about 15%.

The results obtained from continuous variation absorption method, DSC and FTIR studies showed host–guest interactions between stilbene derivatives and hydroxypropyl-β-cyclodextrin.

The fastness performance of fabrics was not influenced whereas the light fastness improved slightly.

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