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An Investigation Into the Possibility of Using Cyclodextrin in Crease Resistant Finish

Abstract
Cyclodextrins (CDs) can form molecular complexes with a very wide range of compounds thanks to their hydrophobic internal cavity. This feature enables them to be incorporated into fabrics, to entrap and mask a very wide range of solid, liquid and gaseous odours. One well-known disadvantage of classical crease-resistant finish is that the treated fabrics emit formaldehyde, and there are several approaches to preventing or decreasing the volume of formaldehyde emitted. In this study we evaluate the possibility of using CDs for this purpose. We assumed that formaldehyde would settle within the cavity of the CD, and that the cross-linking occurring between CDs and the cross-linking agent would the increase the crease-resistance property. However, the presence of CDs in crease-resistant finish did not show the expected results.

Key words: *cyclodextrins, crease resistant, formaldehyde, wrinkle recovery angle, cross-linking.*

Introduction

The most commonly used approach to improve crease resistance has been to introduce crosslinks between individual fibre chains by means of crosslinking agents. These are usually small molecules containing several functional groups capable of reacting with some active groups in the polymer, such as hydroxyl groups. N-methylol reagents such as dimethyloldihydroxylethyleneurea (DMDHEU) have long been used as durable press finishes producing crease-resistant fabrics. The usage of DMDHEU as a cross-linking agent has known disadvantages, such as a decrease in the tensile properties of the textile, and the treated fabric emitting formaldehyde during use. Formaldehyde, a known human carcinogen, is a colourless and strong-smelling gas that can cause a response from the immune system upon exposure. Acute exposure is highly irritating to the eyes, nose, and throat, and subsequent exposure may cause severe allergic reactions of the skin, eyes, and respiratory tract [1 - 3]. Efforts have been made to achieve nonformaldehyde alternatives, e.g. by means of ionic crosslinking, glutaraldehyde, polycarboxylic acids, to replace the traditional N-methylol reagents [4 -8].

One new concepts in textile surface modification is based on applying supramolecular compounds which chemically bind different desirable auxiliaries by means of complex formation. In this manner, cyclodextrins are the most prospective substances in the group of supramolecular compounds. Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides made of six, seven or eight glycosidic units linked by $\alpha(1\rightarrow4)$ bonds into a ring; the most common forms are called α-, β- and γ-CD, respectively. β-cyclodextrin is the most accessible, the lowest-priced and generally the most useful. CDs are created from the enzymatic degradation of starch, and belong to a group of saccharides which are also known as Schardinger's dextrins. Figure 1 shows the structure of a β-CD molecule [9, 10].

Because of the combination of the hydrophobic internal cavity and the hydrophilic exterior, CDs have certain original properties; the most notable feature of CDs is their ability to form solid inclusion complexes (host/guest complexes) with a very wide range of solid, liquid and gaseous compounds by the phenomenon of molecular complexation. CDs can make inclusions compounds with aliphatic and especially aromatic molecules. The ring size of CDs can be varied, since different CDs may have cavities of a different size, and only selected groups of molecules that fit in the cavities can be used in complex formation [10].

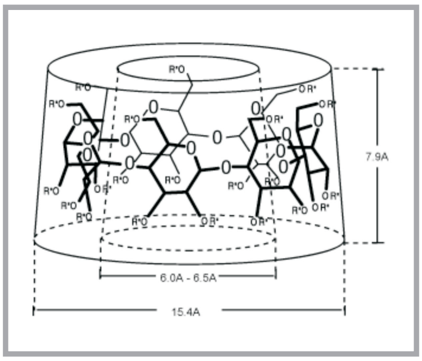

Figure 1. Schematically view of the 3D-structure of cyclodextrin.

Among the possible applications of CDs, the encapsulation of active substances, such as flavouring agents, fragrances, pesticides or drugs, for personal care and

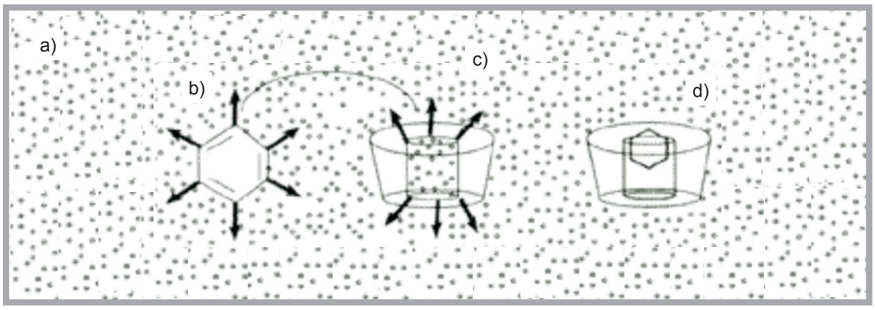

***Figure 2.** Molecule/cyclodextrin–inclusion complex; a) aqueous medium, b) molecule of an active substance in the aqueous medium, c) CD molecule with displaced aqueous medium, d) CD molecule with the included molecule of an active substance.*

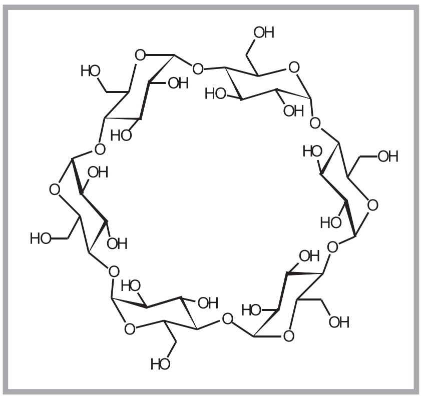

Figure 3. Chemical structure of CD that indicates the presence of OH groups to be crosslinked by DMDHEU.

pharmaceutical purposes, chemical synthesis, bioremediation, biocides, textile and food is generally known. CD-modified textiles can either absorb unpleasant odours by the complexation of sweat components, or they can release included guest substances such as fragrances or pharmaceuticals over a long period of time. This forms molecular complexation in an aqueous media; the schematic of such process is given in Figure 2. That process involves the flow of any solution towards the hydrophobic internal cavity of CDs, and the settlement of molecules released from the solution in the cavity of the CDs.

CDs have been successfully immobilised upon textiles by physical or chemical attachment. The physical attachment can be classified as 'entrapment' when cyclodextrin is spun into the fibre, or as penetrations of CD derivates (the so-called 'anchor groups') into textile fibres in their amorphous state. The chemical fixation of CDs can be achieved by reacting textile fibre functional groups with the functional groups in the cyclodextrin; alternatively, a third molecule can be used as a kind of intermediate between the fibre and cyclodextrin, for example a polymer. By this kind of polymerisation, some network formation takes place which leads to a combined fixation of CDs. CDs are incorporated into the fabrics mostly to entrap and mask odours from sweat and cigarette smoke. These favourable CD properties, such as masking odours and the slow release of guest compounds, can be transferred to different substrates by a finishing process well-known from dyeing technology. Cellulosic materials are especially suitable for modification with CDs. The investigation of application methods revealed that CDs could be successfully fixed to cotton textiles by either a Foulard process with dry heat or contact heat, or by a printing process. Some papers also report CDs usage for dying PA and PES fabrics to increase the fabric's dye uptake and reduce the amount of dye lost in the wastewater [10,11].

When CDs are applied with cross-linking agent, such as DMDHEU, it is reported that the agent cross-links the fibre's functional groups, i.e. the hydroxyl group of cellulose, with that of CDs [9, 12]. Figure 3 shows the structure of CD which is to be cross-linked with DMDHEU.

Besides the papers investigating the application of CDs along with polycarboxylic acids [9, 12], in this paper we evaluated the possibility of using CDs along with DMDHEU to achieve molecular complexation with formaldehyde in order to prevent formaldehyde emission; to the best of our knowledge, this has not been studied before. We considered that the cross-linking agent would react with textile fibre and CDs, and that such a reaction might increase the crease recovery property. Also, the unique non-toxicity property of CDs may be a certain solution to the problem of formaldehyde formation during crease recovery treatments with DMDHEU.

Experimental

We used woven plain fabric (246 g/m^2, 65% viscose / 35% flax), 24 × 17 ends 49.17 tex (Ne 12/1) and picks 49.17 tex (Ne 12/1). After weaving, the raw fabric was scoured, and bleached. To investigate the possibility of using CDs in crease-resistant finish for the above-mentioned purposes, we treated fabrics with classical crease-resistant finish with and without the presence of β-type CD. The treatments were performed at various chemical concentrations as given in Table 1; the cross-linking chemical was DMDHEU, and the catalyst here was magnesium chloride. Treatments were performed by a laboratory-type padder, the fabrics were squeezed up to 70% pick up, dried at 130 °C for 3 minutes and then cured at 170 °C for 1 minute.

To evaluate the effect of CD usage within crease-resistant finish, the content of formaldehyde in the treated fabrics was determined in accordance with the test method DIN EN ISO 14184-T1 (water extraction method at 40 °C for 12 hours), and the dry-wrinkle recovery angles of the treated fabrics were measured by means of a James Heal wrinkle recovery tester, which measures the angle formed when a 10 N load is applied on the folded specimen with directions of 15 × 40 mm for 5 minutes, in accordance with the test method AATCC 66.

Table 1. *Recipes of experimental study; [a] DMDHEU, [b] silicone microemulsion, [c] magnesium chloride.*

Crease resistant finish without CD		Crease resistant finish with CD	
Recipe Code	**Content**	**Recipe Code**	**Content**
R1	25 g/L[a], 15 g/L[b], 8 g/L[c]	R1C	R1 + 20 g/L CD
R2	45 g/L[a], 30 g/L[b], 15 g/L[c]	R2C	R2 + 20 g/L CD
R3	60 g/L[a], 40 g/L[b], 20 g/L[c]	R3C	R3 + 20 g/L CD
R4	80 g/L[a], 50 g/L[b], 25 g/L[c]	R4C	R4 + 20 g/L CD
R5	100 g/L[a], 60 g/L[b], 30 g/L[c]	R5C	R5 + 20 g/L CD

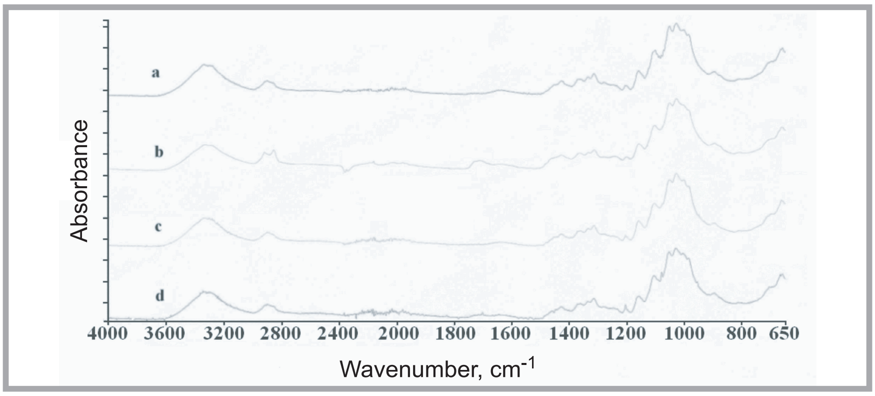

Figure 4. *Infrared spectrum of fabric samples (a) untreated (b) treated with DMDHEU (recipe R3) (c) treated with 20 g/L CDs (d) treated with DMDHEU + CDs (recipe R3C).*

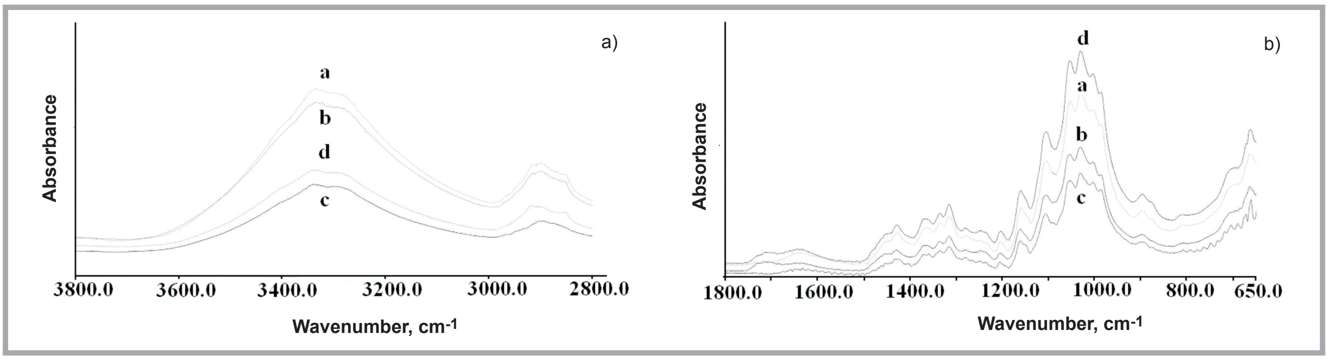

__Figure 5.__ Partial infrared spectrum of fabric samples (a) untreated (b) treated with DMDHEU (recipe R3) (c) treated with 20 g/L CDs (d) treated with DMDHEU + CDs (recipe R3C).

A FTIR with ATR study was also carried out by the transmission method (KBr pellets) with a Perkin Elmer Spectrum 2000 GX spectrometer to investigate the surface of the treated fabric samples. Resolution for the infrared spectra was 4 cm^{-1}, and there were four scans for each spectrum.

Results and discussions

Infrared spectra (FTIR-ATR)

The IR spectra of the untreated and treated samples are given in Figure 4. Because of the similarity of the structure of cellulose (untreated sample) and CDs, they can barely be distinguished on the spectrum, even though the CDs are applied with DMDHEU. The fabric treated with DMDHEU shows an additional peak at around 2900-3000 cm^{-1}, confirming the introduction of the NH groups, but it disappears when CDs are applied.

The differences at absorbance vales are observed when spectrums are detailed between 3800-2800 cm^{-1} (Figure 5.a) and 1800-650 cm^{-1} (Figure 5b). Figure 5.a shows that CDs block more ‒OH groups in the fabric than the DMDHEU reagent does, due to the lowered typical O-H absorption band at around 3300 cm^{-1}. When CDs and DMDHEU are applied together, the spectrum is similar to that of the CDs' applied sample. The appearance of the increased absorption band at the 1000-1100 cm^{-1} region in Figure 5.b (spectrum d) confirms that grafting CD onto the fabric has been better achieved when applied with DMDHEU, which also highlights the cross-links between CDs and DMDHEU.

Amounts of formaldehyde

Table 2 shows the measured formaldehyde content of treated fabrics in ppm units. The results reveal that the formaldehyde content decreases as the DMDHEU concentration increases, due to the increased resin formation; however the presence of CDs is found to cause additional increases at each concentration. It is clear that the encapsulation of formaldehyde molecules did not occur; moreover, the CD causes more formaldehyde to be emitted. The greater the DMDHEU concentration, the more the amount of formaldehyde emitted in the presence of CD than without, as seen in Table 2.

Wrinkle recovery

The wrinkle-recovery angles (WRA) of the treated fabrics were measured in warp and weft directions respectively, and the measurements were repeated three times. The results given in Table 3 are the sum of the mean values of the wrinkle-recovery angle values in warp and weft directions. The larger the WRA value, the greater crease resistance the fabric exhibits. It is clearly seen that the presence of CD reduces the crease-resistance property of the fabrics, since the WRA values are decreased when CD is added in crease-resistant finish.

__Table 2.__ Formaldehyde contents of treated fabrics.

Finish without CD		Finish with CD		Increase (%)
Recipe Code	ppm	Recipe Code	ppm	
R1	232	R1C	231	--
R2	169	R2C	182	7,7
R3	140	R3C	159	13,5
R4	110	R4C	138	25
R5	111	R5C	138	25

__Table 3.__ WRA values of treated fabrics; c Warp + Weft.

Finish without CD			Finish with CD		
Recipe Code	WRA (Wa+Wf)c	C.V., %	Recipe Code	WRA (Wa+Wf)c	C.V., %
R1	224	3,3	R1C	210	5,5
R2	238	2,8	R2C	224	4,6
R3	266	3,7	R3C	252	3,9
R4	272	1,9	R4C	254	7,9
R5	269	4,4	R5C	255	5,7

Summary

In this paper, we investigated the possibility of using β-type CD in classical resistance finish to prevent formaldehyde emission. For this purpose, we treated fabrics with a classical crease-resistant finish that uses DMDHEU as a cross-linking agent, with and without the presence of CDs and to evaluate the effect of CDs; we carried out FTIR with ATR study of treated and untreated fabrics, and also determined the formaldehyde content and dry wrinkle-recovery angles of the treated fabrics by standard test methods.

Our expectation was that it would be possible to take advantage of the CDs' property of entrapping and masking guest molecules, and that the formaldehyde molecules would settle in the cavity of the CDs. However, we found that the CDs behaved poorly in terms of formaldehyde content and wrinkle-recovery angle; the presence of CDs in the crease-resistant finish allows more formaldehyde to be emitted, and decreased the WRA values of the treated fabrics. The IR spectra showed that CD settlement onto the fibre surface covered a larger area than that of DMDHEU, and that the cross-linking which occurred between CDs and DMDHEU disturbed and reduced the resin formation between the agent and fibres, which is observed as a decrease in crease-resistant property; this also caused the pores to remain open, through which the formaldehyde was sent out. It can also be assumed that formaldehyde molecules did not fit into the cavities of CDs, and complexation did not occur.

Acknowledgments

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