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Surface chemical analysis of tencel and cotton treated with a monochlorotriazinyl (MCT) β-cyclodextrin derivative

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The interaction and durability to laundering of a reactive β-cyclodextrin derivative, applied to Tencel fabric and bleached cotton fabric, was investigated using X-ray Photoelectron Spectroscopy (XPS). The N(1s) XPS spectra of the MCT β-cyclodextrin treated substrates revealed the presence of the applied finish on the fibre surface and that the surface concentration increased with increasing level of the applied finish. The bleached cotton had a relatively greater level of fixation of the chemical finish in comparison to the treated Tencel. The reactive β-cyclodextrin fixed onto Tencel and bleached cotton was durable to ISO CO6/C2S washes.

1. Introduction

Cyclodextrins are cyclic oligosaccharides, with the major cyclodextrin being the seven membered ring derivative β-cyclodextrin. Cyclodextrins are bulky ring molecules, capable of forming inclusion complexes with a great number of organic compounds and have found wide applications in many areas [1–7]. In textiles, cyclodextrins are a relatively new class of dyeing and finishing auxiliaries capable of influencing both the processing of the textile materials and their serviceability properties [1, 6–15]. Cyclodextrins maybe bound onto the fibre surface by two distinct interactions: (a) where no covalent bonds exists between the cyclodextrin molecules and the textile material, and physical bonding is the major force of interaction; (b) where the cyclodextrin molecule is permanently fixed to the textile material through covalent bonding.

Due to their structure and ability to form inclusion complexes cyclodextrins have been evaluated with a view to either slowly releasing perfume or absorbing unpleasant odours on textiles or other materials [11]. They are potentially useful in detergents and other textile care products, but due to their relatively weak adsorption would be lost during garment laundering and therefore their effects are not permanent. An alternative approach to improve durability has been to covalently fix a "reactive" cyclodextrin derivative to the textile fibre surface and the serviceability properties of the textile product may be renewed without reapplication of the finish. For cellulosics, the most promising approach has been the use of a monochlorotriazinyl (MCT) β-cyclodextrin derivative, which can be covalently fixed to nucleophilic substrates by a substitution reaction and contains two to three reactive triazinyl groups per cyclodextrin ring [1, 12–15]. The percentage fixation of the reactive cyclodextrin derivative to the substrate can be determined by fabric weight gain (gravimetric method) [7] or the Kjeldahl method [13] and although both methods are reported to be satisfactory neither is surface sensitive nor shows how the fibre surface may be adversely affected by textile processing.

In this study, the fibre surfaces are examined to monitor the deposition and interaction of the MCT β-cyclodextrin derivatives and its durability to laundering. The X-ray Photoelectron Spectroscopy (XPS) technique has been used to characterize the nature of the surface species (outer 10 nm) on both Tencel and cotton fibres treated with MCT

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β-cyclodextrin derivatives. The technique involves measuring the number of photoelectrons emitted from the textile surface, during exposure to an X-ray source, and determining their corresponding kinetic energies [16]. The surface species can thus be characterized from the binding energies (BE) of the photoelectrons and qualitative and quantitative information obtained. XPS provides the basis for identification of the surface species, their chemical state and the measurement of the spectral peak areas allows quantification of the surface composition of the fibres.

2. Experimental

2.1. Materials

Tencel fabric was kindly donated by Acordis Holdings, UK and bleached cotton by Socota Mills, Mauritius. All fabric samples were first washed in heptane, followed by acetone wash and rinse thoroughly with hot and cold tap water. A final rinse was given with deionised water. The samples were then air-dried.

The monochlorotriazinyl β-cyclodextrin derivative was kindly supplied by Wacker-Chemie, Germany, and identified as Cavasol W7 MCT.

ECE phosphate-based reference detergent and multifibre test fabric, used in the ISO 105 CO6/C2S test protocol, were purchased from the Society of Dyers and Colourists (SDC), Bradford, UK. All other textile auxiliaries were of laboratory grades and were used as received.

2.2. Application of MCT β-cyclodextrin derivative to tencel and cotton fabrics

Solutions containing varying concentrations of MCT β-cyclodextrin were prepared using deionised water. The solutions were adjusted to pH 11.0 using about 20g dm^{-3} of sodium carbonate. The fabric samples were then padded to 100% wet pick-up, dried at 70°C in an oven, cured on a mini-stenter at 150°C for 4 min. The fabric samples were then rinsed thoroughly using hot tap water, followed by cold tap rinse until the pH of the liquor in the fabric was around 6.9–7.1. The samples were given a final rinse with deionised water, hand-squeezed and air-dried.

2.3. ISO 105 CO6/C2S test

The fabric samples, about 10 cm $\times$ 4 cm, were sewn to a similar-sized multifibre test fabric. The detergent solution contained 4g of ECE phosphate-based reference detergent and 1g of sodium perborate tetrahydrate dissolved in 1000 ml of de-ionised water. The pH was adjusted to 10.5, if necessary, using sodium carbonate. 50 ml of the detergent solution was placed in a stainless steel pot along with 25 steel balls and the fabric sample. The pot was rotated in a Washtec-P machine (Roaches) with 40 revolutions per minute, at 60° for 30 mins. At the end of the wash cycle, the fabric sample was thoroughly rinsed with cold tap water, given a final rinse with deionised water and air-dried.

2.4. XPS analysis

XPS measurements were performed using a Kratos Axis Ultra spectrometer operating at a base pressure of 3.0–4.0 $\times$ 10^{-9} torr with an analytical depth of 3–5 nm. The samples were irradiated with monochromatic Al Ka X-rays (1486.6 eV) using a spot size of 400 μm $\times$ 1000 μm and a power of 150 W. Survey spectra were recorded with a pass energy of 160 eV, from which the surface chemical compositions were determined. In addition, high-resolution nitrogen (1s) spectra were recorded with a pass energy of 20 eV, from which the nitrogen chemical states were determined. All binding energy values were calculated relative to the carbon (1s) photoelectron at 285 eV. Charge compensation for these electrically insulating materials was achieved using a beam of low energy electrons

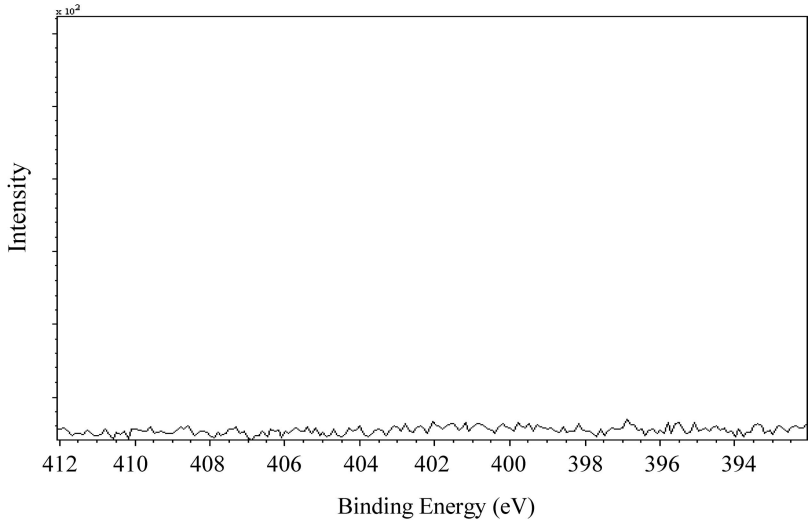

Figure 1 N (1s) XPS spectrum of untreated tencel fabric.

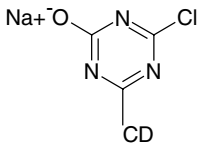

Figure 2 Chemical structure of the monochlorotriazinyl functional group of MCT-cyclodextrin molecule.

from a flood gun. To ensure reproducibility, the samples were analysed in duplicate or triplicate. Where appropriate curve fitted spectra are presented to clearly define the peak for qualitative analysis.

3. Results and discussion

3.1. XPS analysis of untreated and MCT β-cyclodextrin treated tencel

Tencel is a regenerated cellulosic fibre, which is free of natural impurities such as nitrogen-based proteins, pectins and waxes typically associated with raw unscoured cotton. The N1(s) XPS spectrum for untreated "clean" Tencel substrate revealed that nitrogen species were absent from the fibre surfaces, Fig. 1 Since the MCT β-cyclodextrin contains nitrogen-based triazinyl functionalities, its nitrogen "label" could be utilised as an elemental tag to establish the presence of the applied finish at the fibre surfaces, Fig. 2

In a typical N1(s) XPS spectrum, nitrogen bound to carbon in primary, secondary or tertiary amines or amides, occurs at a BE value of 399.0–400.2 eV [16, 17]. The N1(s) spectra of unwashed and washed (× 5) treated Tencel clearly indicate the obvious presence of surface nitrogen species at approximately a BE value of 399.5 eV which may be assigned to the presence of a triazinyl system of MCT β-cyclodextrin, Figs 3 and 4. Nitrogen species located in C_3N^3 aromatic ring systems would typically occur at BE values around 399.2 and 399.4 eV [18]. The presence of nitrogen on the fabric surface indicates strong covalent bonding between the MCT β-cyclodextrin and the cellulosic fibre surface, even after five washes.

3.2. XPS analysis of tencel treated with varying levels of MCT β-cyclodextrin

Tencel fabrics were treated with increasing levels of the MCT β-cyclodextrin derivative to demonstrate the build-up properties of the finish onto the surface of the fibre. The treated fabrics were then subjected to multiple ISO 105 C06/C2S wash cycles in order to assess the durability of the surface finish. The % atomic nitrogen content, as determined by XPS, was used as a measure of the surface concentration of the finish. It is evident that the percentage atomic nitrogen content concomitantly increases with concentration of MCT β-cyclodextrin applied and the increase is a reflection of the greater availability of the cyclodextrin molecules available for reaction with the cellulose hydroxyl groups, Table I [13]. There is little increase in % atomic nitrogen content at the fibre surface as the MCT-CD concentration increases from 8 to 10% omf and suggests that the optimum application concentration is approximately 8% omf. Although it is unlikely the bulky MCT-β-cyclodextrin derivative will penetrate easily into the fibre sub-surface for further reaction under these application conditions, further work is currently underway to confirm this proposal. Also the carbon to nitrogen, C/N, atomic ratio of pure MCT-β-cyclodextrin molecule is about 6:1 (with an average of 2.8 MCT groups per β-cyclodextrin molecule [4]) and it is observed that as the concentration of the applied finish increases, the C/N atomic ratio similarly decreases from 62 at 2% omf concentration to 40 at 10% omf concentration where it appears to plateau.

TABLE I Surface XPS percentage atomic composition of tencel fabric treated with varying levels of MCT β-cyclodextrin

Sample treatment (% o.m.f.)	% Atomic composition			
	C	O	N	C/N ratio
Untreated	67.6	32.4	0.0	–
2%	61.7	37.2	1.0	62
5%	63.3	35.7	1.1	58
8%	63.9	34.6	1.5	43
10%	63.7	34.7	1.6	40

3.3. XPS analysis of untreated and MCT β-cyclodextrin treated tencel subjected to repeat wash tests, ISO 105 CO6/C2S

Table II shows the % atomic compositions of Tencel treated with 10% o.m.f. MCT β-cyclodextrin and subjected to repeated ISO 105 CO6/C2S wash tests. It was again observed that after three washes the % atomic composition of nitrogen is still significant although it is lower than that of the unwashed treated sample. This suggests the formation of stable covalent bonds between the MCT β-cyclodextrin and the cellulosic fibre surface and that these bonds offer some resistance to laundering conditions even after five washes.

TABLE II Surface XPS percentage atomic composition of tencel fabric treated 10% o.m.f. MCT β-cyclodextrin and repeat washed, ISO 105 CO6/C2S wash test

Sample treatment	% Atomic compositions			
	C	O	N	C/N ratio
Untreated	67.6	32.4	0.0	–
0 × wash	63.7	34.7	1.6	40
1 × wash	63.9	35.0	1.1	58
3 × washes	64.5	34.3	1.2	54
5 × washes	63.8	35.4	0.8	80

The atomic ratio of carbon to nitrogen increases with washing cycles and this would suggest the loss of the MCT β-cyclodextrin finish from the fibre surface. In addition, the treated Tencel showed an increase in the ratio of oxygen to carbon atomic content during washing, which may be due to surface oxidation of cellulose during the detergent/sodium perborate washing.

3.4. XPS analysis of untreated and MCT β-cyclodextrin treated cotton fabric

Raw cotton fibre contains natural impurities such as nitrogen-based proteins, pectins and waxes, most of which lie on the surface of the fibre [19]. The N1(s) XPS spectrum of the scoured, bleached, cleaned cotton fabric indicated there were no nitrogen species at the fibre surface. Therefore the nitrogen containing triazinyl functionality could again be used as an elemental tag to establish the presence of the applied finish at the fibre surface. For the unwashed and washed ($\times 5$) treated cotton, similar N1(s) XPS spectra were obtained to that of treated Tencel, Figs 5 and 6. Nitrogen species were detected at BE values around 399.0–399.6 eV, which may be assigned to the presence of a triazinyl system of MCT β-cyclodextrin.

TABLE III Surface XPS percentage atomic composition of cotton fabric treated with varying levels of MCT β-cyclodextrin

Sample treatment (% o.m.f.)	% Atomic composition			
	C	O	N	C/N ratio
Untreated	63.2	36.8	0.0	–
2%	66.0	32.8	1.2	55
5%	65.1	33.0	1.8	36
8%	66.3	31.6	2.1	32
10%	64.3	33.4	2.3	28

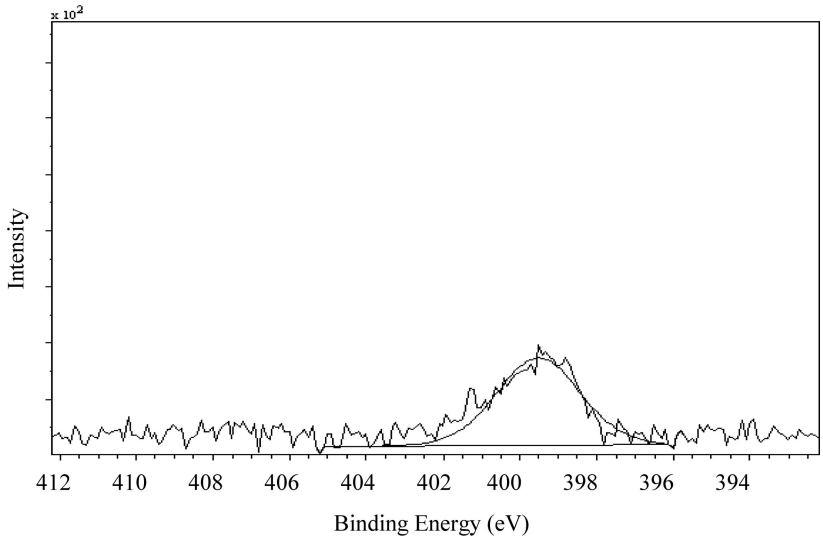

Figure 3 N (1s) XPS spectrum of 10% o.m.f. MCT-CD treated tencel fabric.

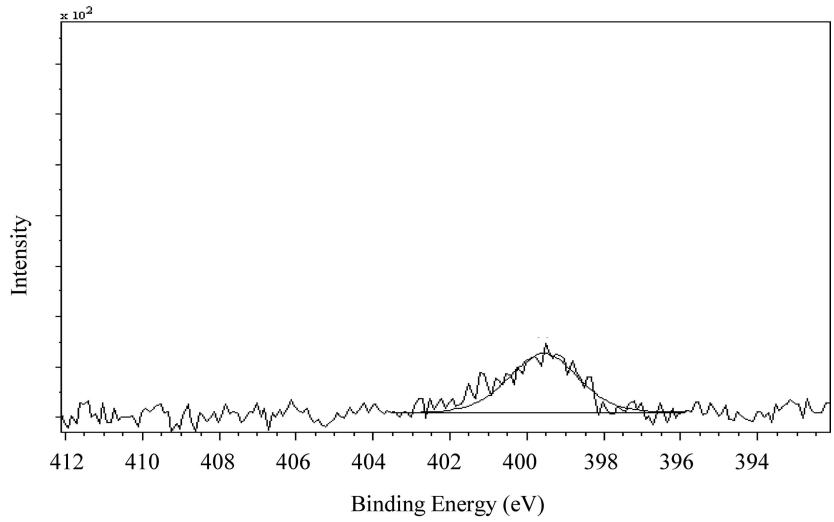

Figure 4 N (1s) XPS spectrum of 10% o.m.f. MCT-CD treated tencel fabric, washed $\times$ 5.

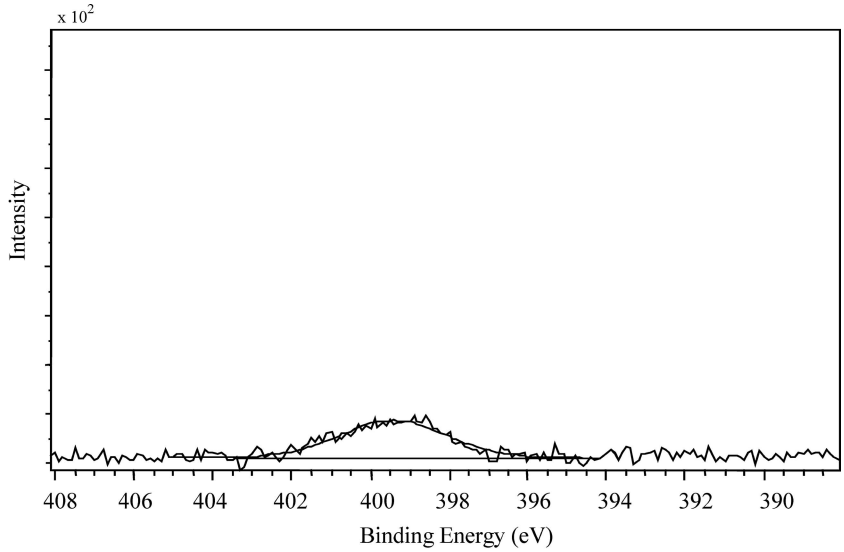

Figure 5 N (1s) XPS spectrum of 10% o.m.f. MCT-CD treated cotton fabric.

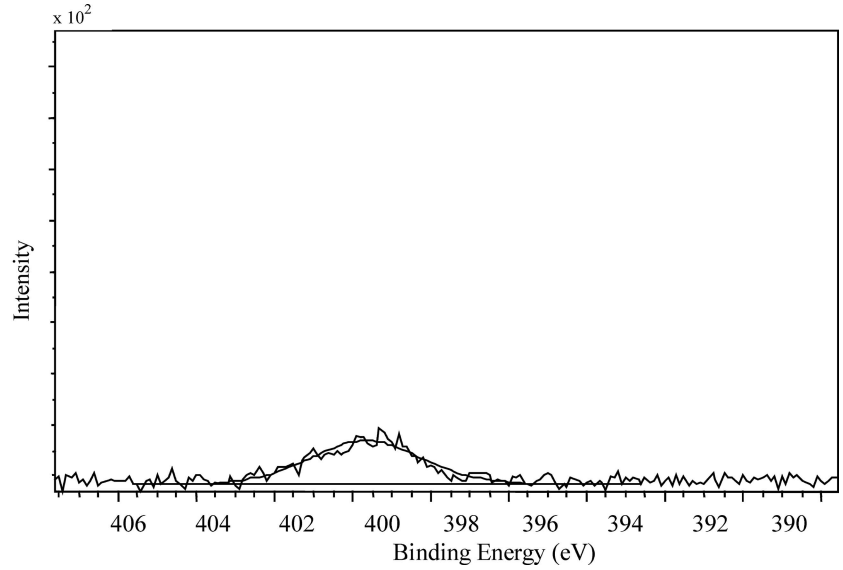

Figure 6 N (1s) XPS spectrum of 10% o.m.f. MCT-CD treated cotton fabric, washed × 5.

3.5. XPS analysis of cotton treated withx varying levels of MCT β-cyclodextrin

Increasing concentrations of MCT β-cyclodextrin were applied to the bleached cotton in order to determine the build-up profile of the finish on the fibre surface, Table III. It is apparent that the surface XPS percentage atomic nitrogen content increases with the concentration of applied MCT β-cyclodextrin, as similarly observed with the treated Tencel. Comparison of Tables 1 and 3 indicates there is a relatively greater fixation of the chemical finish to the bleached cotton relative to the Tencel substrate. The C/N ratios obtained for the bleached cotton are generally lower than those for the Tencel, suggesting there is more nitrogen species are present on the treated bleached cotton. This difference in chemical fixation may be due to a greater availability of nucleophilic hydroxyl sites at the bleached cotton fibre/chemical interface for reaction to occur.

3.6. XPS Analysis of untreated and MCT β-cyclodextrin treated cotton subjected to repeat wash tests, ISO 105 CO6/C2S

Table IV shows the % surface atomic composition of bleached cotton treated with 10% o.m.f. MCT β-cyclodextrin subjected to repeated washing, ISO 105 CO6/C2S wash test. Even after five washes the loss of the surface finish is relatively small, again indicating the stability of the covalent bond between the MCT β-cyclodextrin and the cellulosic cotton fibre surface. The ratio of oxygen to carbon atomic content increases slightly during washing and this again may be due to the

TABLE IV Surface XPS percentage atomic composition of cotton fabric treated 10% o.m.f. MCT β-cyclodextrin and repeat washed, ISO 105 CO6/C2S wash test

Sample treatment	% Atomic compositions			
	C	O	N	C/N ratio
Untreated	63.2	36.8	0.0	–
0 × wash	64.3	33.4	2.3	28
1 × wash	65.0	33.0	2.0	33
3 × washes	63.5	34.7	1.8	35
5 × washes	62.7	35.6	1.7	37

surface oxidation of cellulose during the sodium perborate/detergent washing.

4. Conclusions

The surface reaction of a MCT β-cyclodextrin derivative with cellulosic materials, Tencel and bleached cotton fabrics, has been successfully investigated by X-ray Photoelectron Spectroscopy. The nitrogen content at the surface of both Tencel and bleached cotton increased with increasing levels of MCT β-cyclodextrin application. In addition, the bleached cotton exhibited a relatively greater fixation of the chemical finish in comparison to the Tencel fibre surface. This difference in chemical interaction may be due to a greater availability of nucleophilic hydroxyl functionalities at the bleached cotton fibre surface interface.

The wash durability of the MCT β-cyclodextrin treatment on Tencel and bleached cotton substrates was clearly demonstrated, even after five ISO CO6/C2S washes.

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