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Grafting of ethylcellulose microcapsules onto cotton fibers

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Abstract

In this paper a treatment of cotton with ethylcellulose (EC) microcapsules was investigated. EC microcapsules containing Rosemary oil were obtained by phase separation method. The surface and morphology of microcapsules were characterized by scanning electron microscopy (SEM). Microcapsules with a regular spherical shape in the 10–90 μm size range were prepared and grafted onto cotton using the crosslinking reagent 1,2,3,4-butanetetracarboxylic acid (BTCA) in the presence of catalysts. The influence of the two catalysts, cyanamide (CA) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) on curing efficiency (grafting) was investigated. SEM and Fourier transform infrared spectroscopy (FT-IR) were used to study the formation of ester bonds between BTCA and hydroxyl groups of cotton and/or hydroxyl groups of EC. When DCC was used as a catalyst, the esterification took place slowly at room temperature. In the case of CA, the cotton was cured at 110 °C for several minutes. After 2 min curing, the microcapsules, which kept their original shape, were bonded to the cotton fibers. Increasing the curing time altered the microcapsule shell. Grafting and crosslinking reactions of the thermofixed EC microcapsules onto cotton were proposed.

Keywords: Ethylcellulose; Grafting; BTCA; SEM; FT-IR; Microcapsule

1. Introduction

Ethylcellulose (EC) is frequently used as a hydrophobic polymeric coating material for extended drug release applications (Pearnchob & Bodmeier, 2003). Microcapsules were prepared from EC using various methods such as phase separation, coacervation, solvent evaporation, either by addition of a non-solvent, or of an incompatible polymer (Babtsov, Shapiro, & Kvitnitsky, 2005; Shen & Walter, 2005; Zandi, Pourjavadi, Hashemi, & Arabi, 1998; Zhang, Ping, & Xiao, 2000). Microencapsulation has become an active field in textiles as patent applications strongly outnumber the published scientific papers. In textiles, the major interest in microencapsulation is currently in the application of durable fragrances, phase-change materials, antimicrobial agents (Madene, Jacquot, Scher, & Desobry, 2006; Nelson, 2002; Wang & Chen, 2005). The capsules can be applied to fibers such as cotton as dispersion with a binder, using padding, spraying, impregnation, and exhaust or screen-printing techniques (Boh & Knez, 2006; Chow, Ho, Tong, & Ma, 1998; Nelson, 2002). Many companies offer new fabrics that emit natural aroma on movement of the wearer (Nelson, 2002). These can remain fragrant over several years, resist the dry cleaning, or keep the microcapsules over 25 washing cycles. Essential oils such as Rosemary, Lavender, Sage were microencapsulated for odor control applications; they have sedative, antibacterial and deodorant properties (Wang & Chen, 2005).

Binders play crucial role in microcapsule coating formulation for various textile materials, as they are required to fix microcapsules on textile supports permanently. To a large extend, binders determine the quality, durability and washability of textile materials with microencapsulated ingredients. Some of the most frequently used binders in textile are water-soluble polymers, such as starch and

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modified starches, carboxymethyl cellulose; synthetic latexes, such as styrene-butadiene, polyvinylacetate or acrylate latexes; and aminoaldehyde resins (Boh & Knez, 2006).

The binder is a film-forming substance made up of long-chain macromolecules which, when applied to the textile produce a three-dimensionally linked network. One of the main disadvantages of using film-forming binders in application of microcapsules onto textile materials is possible hindrance of the active substances release. To avoid this problem, microcapsules can be covalently linked onto textile substrate by using bi/polyfunctional crosslinking reagents. Polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid (BTCA) are well-known non-formaldehyde crosslinking reagents. The four carboxylic acid groups can react with hydroxyl groups of cellulose and form stable ester bonds (Yang & Bakshi, 1996; Yang, Yiping, & Lickfield, 2002). Esterification can occur with heat alone or can be accelerated by the presence of catalysts (Petrova, Manolova, Rashkov, Mincheva, & Kalcheva, 1998; Welch & Peters, 1997; Yang & Bakshi, 1996).

In our previous research, Voncina and Majcen-LeMarechal, 2005, we linked supramolecular compound (β-cyclodextrin) onto cotton cellulose via grafting or crosslinking with BTCA. In our current resexarch, we prepared EC microcapsules with Rosemary oil using phase separation method and grafted them onto cotton fabrics using BTCA. To reduce the temperature of linking two catalysts, cyanamide (CA), (Gillingham, Lewis, & Voncina, 1999) and *N*,*N*′-dicyclohexylcarbodiimide (DCC), (Petrova et al., 1998) were used. ATR FT-IR spectroscopy was used to study the formation of ester bonds between BTCA and hydroxyl groups of cotton and/or hydroxyl groups of EC.

2. Experimental

2.1. Materials

Ethylcellulose (EC) was purchased from Aldrich, Austria (viscosity 4 cP, 5% in toluene/ethanol 80:20, extent of labeling: 48% ethoxyl). Rosemary oil was provided from Etol, Celje, Slovenia. 1,2,3,4-Butane tetracarboxylic acid (BTCA) from Merck, cyanamide (CA) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) from Aldrich, sodium dodecylsulphate from Fluka 1 were used. All other chemicals were of analytical reagent grade.

Pure cotton with mass of 140 g/m^2 was used after it was first desized, scoured, bleached and mercerized on continuous production equipment. It was supplied by MTT, Maribor, Slovenia.

2.2. Preparation of ethylcellulose microcapsules

EC microcapsules were prepared as reported in the literature (Babtsov et al., 2005). Briefly, EC and Rosemary oil (1/2.5 w/w) dissolved in ethylacetate were dropped into a 1% sodium lauryl sulphate aqueous solution saturated with ethylacetate. Water was added to the formed emulsion, for extracting the organic solvent. The formed microcapsules were isolated by filtration, subsequently washed with water and dried. The microcapsule yield was determined as a weight percent (wt%) of the recovered microcapsules after drying, divided by the initial amount of ethylcellulose and oil employed (Zandi et al., 1998). In order to determine the oil content, a known amount of microcapsules containing Rosemary oil was poured into cyclohexane and ultrasonicated for 1 min. The suspension was then filtered through a 0.45 μm filter to separate EC which was dried until a constant weight was achieved. Each determination was carried out in duplicate.

2.3. Fabric treatment

2.3.1. Grafting of EC microcapsules on textile substrate using BTCA

The mercerized cotton was immersed in treating baths with different concentrations of EC microcapsules and BTCA (Kang, Yang, & Wei, 1999; Kitchens, Patton, & Nadar, 1991; Lewis & Voncina, 1997a, 1997b; Petrova et al., 1998; Yang & Bakshi, 1996), for the reduction of curing temperature the catalyst CA and DCC were used (Table 1). The pH of finishing bath was 2.2. The wet pick up was 100%; the impregnated cloth was predried at room temperature for 24 h and thermofixed at 150 °C for 20 min or at 110 °C for 22 min when CA as a catalyst was used. When DCC as a catalyst was used the thermofixation was omitted, the esterification occurred at room temperature. The treated textile material was rinsed in cold water. The weight gain of the finished fabrics was measured according to standard test method DIN 53814. The samples were dried for 4 h at 105 °C and weighed before and after finishing. All experiments were carried out in duplicate; the mean of the wt% values were calculated.

Table 1
Concentration of BTCA, EC microcapsules, CA or DCC in the finishing baths, curing temperatures and weight gain after treatments

Concentration (g/l)				Curing temperature (°C)	Weight gain (wt%)
BTCA	EC microcapsules	CA	DCC		
6	0.1	3	–	150/20 min	0.1
6	0.1	3	–	110/20 min	4.8
6	0.1	3	–	110/2 min	9.8
6	2.0	–	3	Room temperature	10

2.3.2. Qualitative determination of EC microcapsules on the textile substrate

Dried microcapsules and the textile substrate were analyzed by optical microscopy using a Sonny microscope equipped with a camera. The surface and morphology of microcapsules were examined by scanning electron microscopy (SEM). The samples were coated with gold for 3.5 min using an Emscope SC 500 and examined using a Philips XL30 ESEM operated in the secondary electron mode at 10 KV accelerating voltage. The microcapsules grafted onto cotton fabrics were not coated with gold. The Quanta is having a tungsten based electron optical column with a resolution of 3.5 nm and an ion resolution of 10 nm. The system was an ESEM using FEI Quanta 3 D 200. Measurements were taken in vacuum at different magnifications.

Fourier Transform Infrared spectroscopy (FT-IR) was carried out with a Perkin-Elmer spectrophotometer with a Golden Gate attenuated total reflection (ATR) attachment with a diamante crystal.

3. Results and discussion

3.1. Preparation of ethylcellulose microcapsules

EC microcapsules containing Rosemary oil were obtained by phase separation method. The yield of the process was about 75%. Microcapsules in the 10–90 μm size range were obtained (Fig. 1). The oil content of the dried microcapsules was 30%.

From the scanning electron micrograph shown in Fig. 2 it was observed that EC microcapsules had a regular spherical shape. Low viscosity EC was used as encapsulating material. Viscosity affects the range of particle size (Zandi et al., 1998). Particles produced from low viscosity polymers also have a regular and spherical shape and are less porous than those of higher viscosity.

Fig. 1. Optical microphotograph of EC microcapsules (120× magnification).

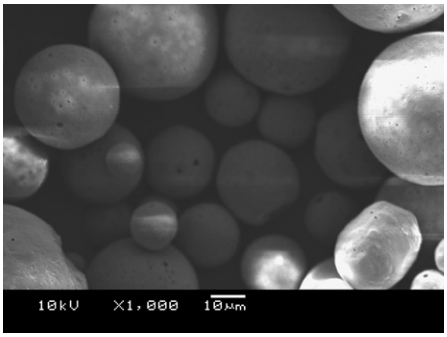

Fig. 2. Scanning electron micrograph of EC microcapsules (1000× magnification).

3.2. Grafting of EC microcapsules onto textile substrate

When cotton fabrics were treated with BTCA and EC microcapsules, esterification between BTCA and hydroxyl groups of EC and cellulose could occur. FT-IR is a consolidated technique for studying the crosslinking of hydroxyl groups of cellulose via BTCA (Choi, Mahmood, Li, & Schlup, 1995; Sricharussin, Ryo-Aree, Intasen, & Poungraksakirt, 2004; Yang & Bakshi, 1996; Yang et al., 2002). After the unreacted BTCA and catalyst are washed, the carbonyls retained in the fabrics exist in three forms – ester, carboxylic acid, and carboxylate anion (Yang & Bakshi, 1996; Yang et al., 2002). Fig. 3 shows the differential FT-IR spectra of a cotton fabrics which were treated with BTCA, EC microcapsules and CA at the elevated temperature (110 and 150 °C) and with BTCA, EC microcapsules and DCC at room temperature. When DCC is used as a catalyst, the esterification took place slowly at room temperature, as we could see on FT-IR spectra shoulder at 1730 cm^{-1} in spectrum c in Fig. 3. In the case of CA, the cotton should be cured at 110 °C for several minutes.

The bands due to an ester carbonyl appear around 1717–1730 cm^{-1}. However, a band at 1735–1715 cm^{-1} is ambiguous and can be interpreted either as an ester carbonyl band or a carboxyl carbonyl band (Voncina & Majcen-LeMarechal, 2005; Yang & Bakshi, 1996). The post-treatment of finished fabrics in an alkaline solution converts the acid to carboxylate anion, which absorbs at 1570 cm^{-1}, while the ester carbonyl is left unchanged. In FT-IR spectra of alkaline post-treated finished fabrics (0.1 g/l EC, 6 g/l BTCA, 3 g/l CA, 110 °C for 20 min), the band intensity near 1700 cm^{-1} decreased while the intensity of the carboxylate region centered at 1570 cm^{-1} increased (Fig. 4). The remaining band at around 1700 cm^{-1} can be contributed to the ester bonds.

The absorption band at 1737–1744 cm^{-1} could be ascribed to the carbonyl vibration of camphor or bornyl acetate from microencapsulated Rosemary oil. Fig. 5 shows the comparison of differential FT-IR spectra of the treated cotton with BTCA, EC microcapsules and CA, cured at 110 °C for 20 min and cotton where Rosemary oil was applied to cotton surface in drops.

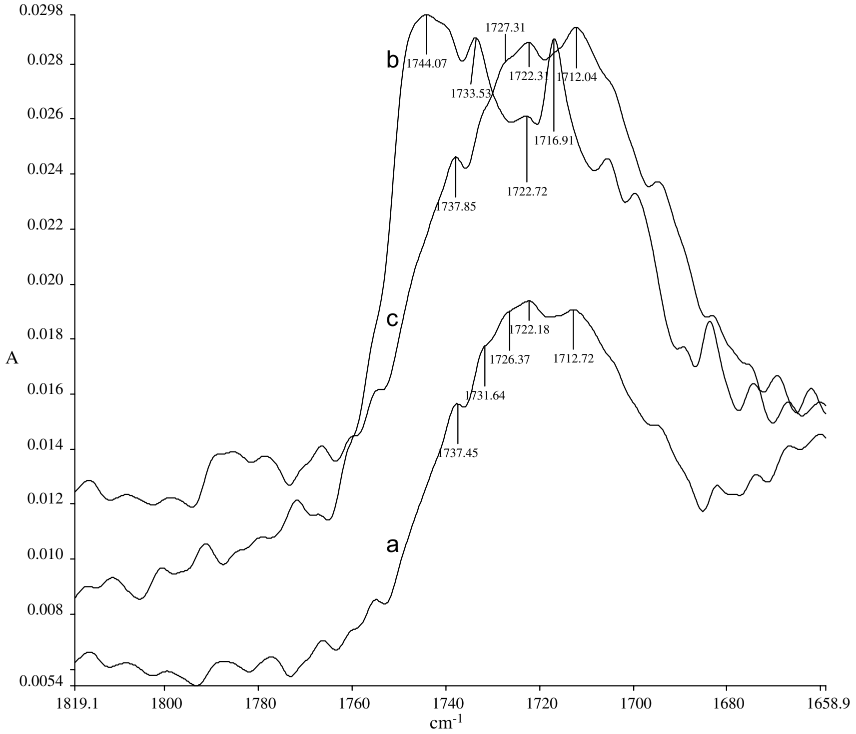

Fig. 3. Differential FT-IR spectra of cotton treated with (a) BTCA, EC microcapsules, CA 110 °C 20 min (cotton spectrum was substracted); (b) BTCA, EC microcapsules, CA 150 °C 20 min (cotton spectrum was substracted) and (c) BTCA, EC microcapsules, DCC, room temperature (cotton spectrum was substracted).

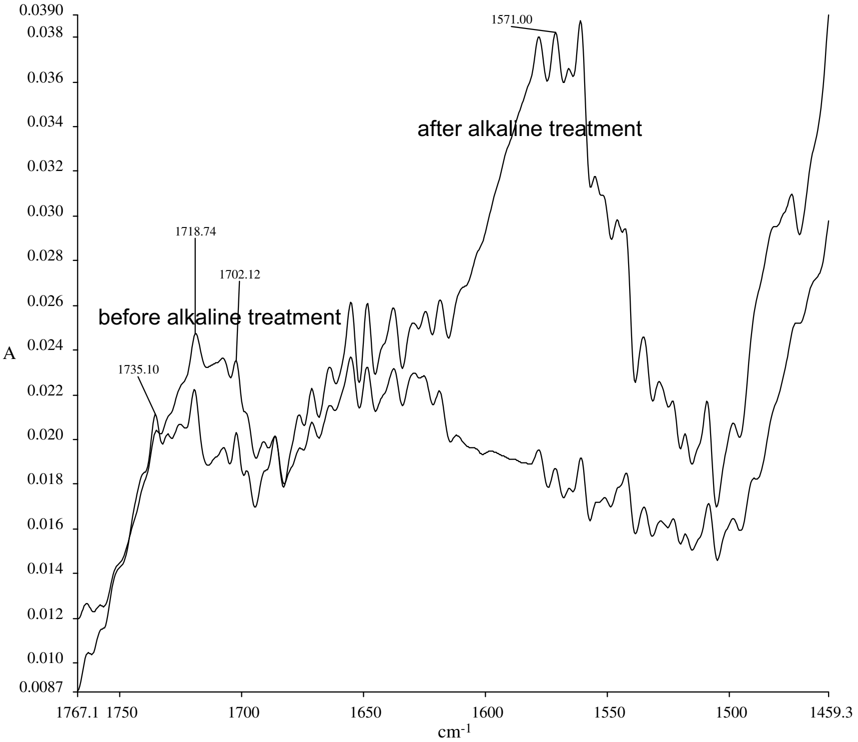

Fig. 4. FT-IR spectra of the finished cotton fabrics (CA was used as catalyst) before and after alkaline treatment.

During the grafting of EC microcapsules via BTCA onto hydroxyl groups of cellulose, an increase in the weight occurred (see Table 1). This indicates that linking of EC microcapsules on cotton cellulose occurs. The presence of 1717–1722 cm^{-1} absorption indicates that there are ester links between BTCA and hydroxyl groups of cellulose

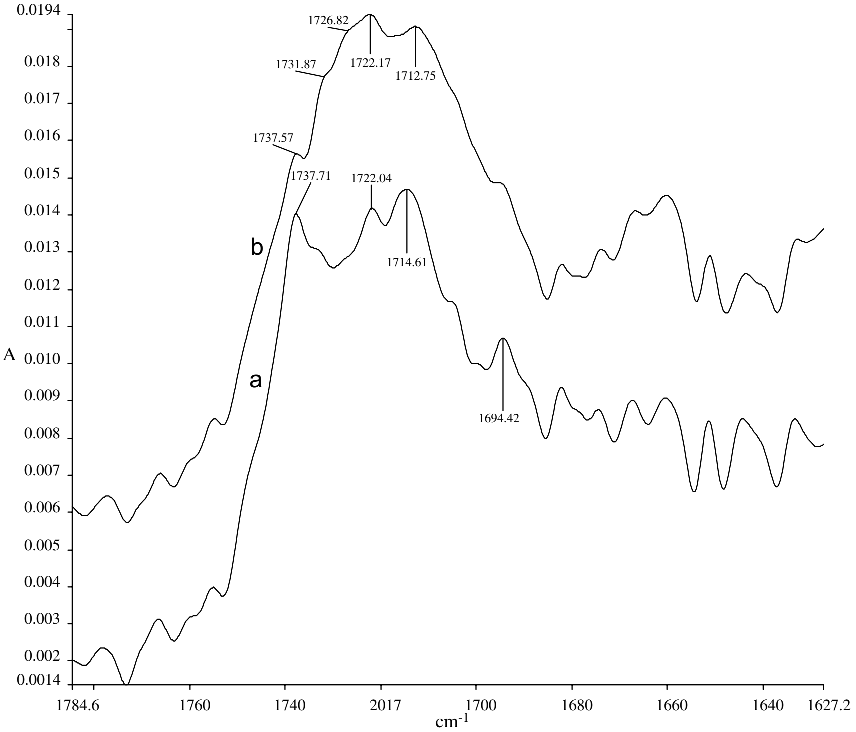

Fig. 5. Differential FT-IR spectra of: (a) cotton impregnated with Rosemary oil and (b) EC/ BTCA/CA finished cotton fabrics (cotton spectrum was subtracted).

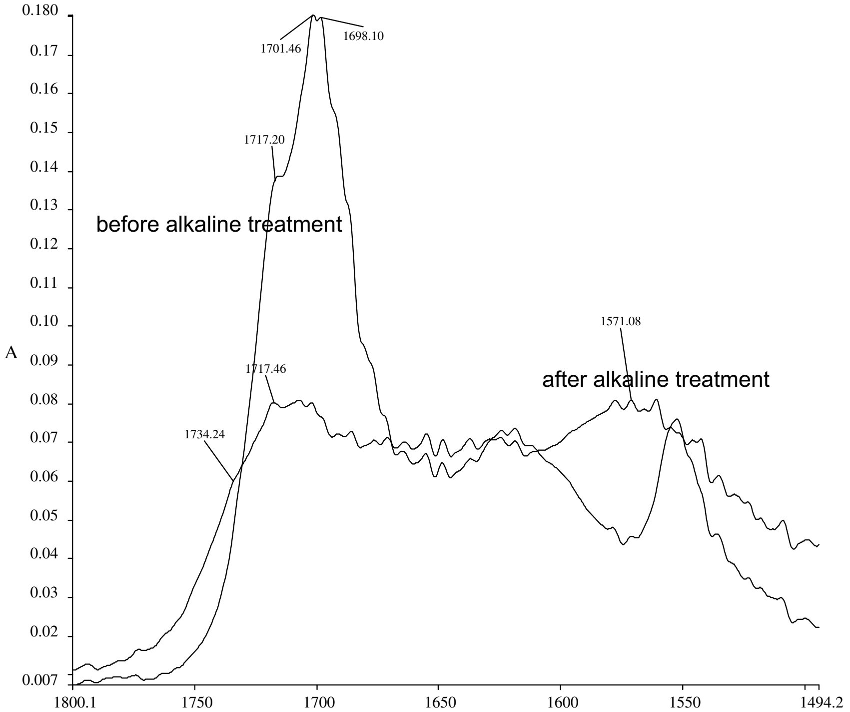

Fig. 6. FT-IR spectra of the EC microcapsules treated with BTCA and CA at 110 °C for 20 min before and after alkaline treatment on inert polypropylene support.

and of EC microcapsules, or both. To see if EC microcapsules are crosslinked between each other or linked with hydroxyl groups of cellulose only, the EC microcapsules were crosslinked with BTCA using CA as catalyst on inert polypropylene support. The FT-IR spectra are presented in Fig. 6. Ester presence could be indicated by 1717 and

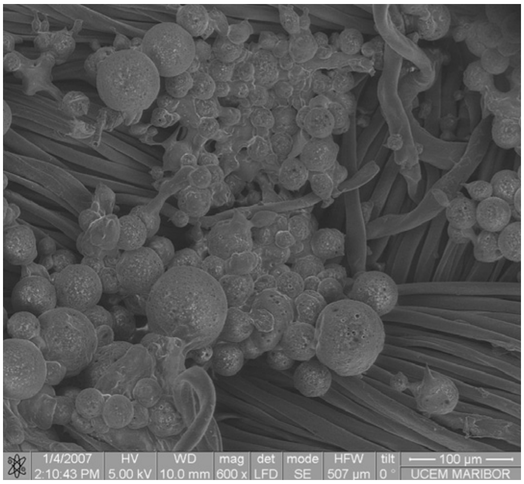

Fig. 7. SEM microphotograph of EC microcapsules linked on cotton via BTCA using CA as catalyst at 110 °C 2 min (600× magnification).

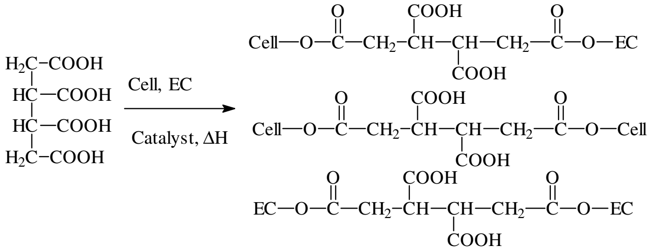

Fig. 8. Proposed grafting and crosslinking reactions when EC microcapsules are thermofixed on cellulose via BTCA.

1734 cm^{-1} shoulder. The large absorption centered at 1700 cm^{-1} is due to the carboxylic acid of unreacted BTCA. This band decreases its intensity drastically when crosslinking of hydroxyl groups of EC with BTCA occurs. The overlapped bands at 1700 and 1690 cm^{-1} are due to the hydrogen bonded and free carboxylic groups of BTCA (Yang et al., 2002). From FT-IR spectra we have got the evidence that some crosslinking between hydroxyl groups of EC microcapsules via ester bonds occurs when BTCA as a polyfunctional reagent is used.

The morphology of the surfaces of the linked microcapsules via BTCA was examined prior to and after curing. Fig. 7 shows SEM image of EC microcapsules linked on cotton at 110 °C using CA as catalyst. After curing for 2 min, the microcapsules kept their original shape and were bound to the cotton fibers. It was proved by microphotography that EC microcapsules are stable after cold water washing as well. The increasing of curing time alters the microcapsule shell. After 20 min curing at 150 °C, the microcapsules could not survive and the oil content is released as shown by FT-IR spectroscopy (the band intensity of carbonyl groups from oil was increased).

According to previous research on the crosslinking of hydroxyl groups of cellulose with BTCA and our current research, we can propose a grafting reaction of EC microcapsules onto hydroxyl groups of cellulose via BTCA (see Fig. 8), where three types of reactions can occur simultaneously: the grafting of EC microcapsules via BTCA onto hydroxyl groups of cellulose, and the crosslinking between the hydroxyl groups of cotton and between the hydroxyl groups of EC microcapsules.

4. Conclusion

This work described the cotton treatment with EC microcapsules prepared by phase separation method. EC microcapsules were grafted onto cotton fabrics via esterification using BTCA. Optical microphotography, SEM and FT-IR analysis indicated the EC microcapsules were grafted onto the cotton-processed fabrics. Esterification between BTCA, EC microcapsules and hydroxyl groups of cellulose can occur simultaneously.

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