



UNIVERSITY OF LEEDS

This is a repository copy of *Fabrication of magnetized polyester fabric grafted with β -cyclodextrin for controlled release of menthol.*

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/102527/>

Version: Accepted Version

Article:

Zhang, H, Li, X, Mao, N orcid.org/0000-0003-1203-9773 et al. (2 more authors) (2018)
Fabrication of magnetized polyester fabric grafted with β -cyclodextrin for controlled release of menthol. *Journal of Industrial Textiles*, 47 (6). pp. 1060-1082. ISSN 1528-0837

<https://doi.org/10.1177/1528083716662586>

© 2016, SAGE Publications. This is an author produced version of a paper published in *Journal of Industrial Textiles*. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Fabrication of Magnetized Polyester Fabric Grafted with β -Cyclodextrin for Controlled Release of Menthol

Hui Zhang*¹, Xin Li¹, Ningtao Mao², Runjun Sun¹, and Jun Xu³

¹*School of Textile & Materials, Xi'an Polytechnic University, Xi'an 710048, China*

²*School of Design, University of Leeds, Leeds, LS2 9JT, United Kingdom*

³*School of Apparel & Art Design, Xi'an Polytechnic University, Xi'an 710048, China*

Abstract: The technology of producing a magnetized polyester fabric for controlled and accelerated release of menthol in potential biomedical applications is reported in this paper.

The magnetized polyester fabric is prepared in a facile hydrothermal process and subsequently modified with aminopropyltriethoxysilane, grafted with carboxylated β -Cyclodextrin (β -CD), and loaded with menthol under hydrothermal conditions. The microstructure, thermal and magnetic properties of both carboxylated β -CDs and magnetized polyester fabrics grafted with β -CDs are characterized by using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Diffraction (XRD), Vibrating Sample Magnetometry (VSM), Fourier Transform Infrared (FTIR) spectroscopy, Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Diffuse Reflectance Spectroscopy (DRS) techniques. It is evident that the carboxylated β -CD is synthesized and successfully grafted on the surface of the modified magnetic polyester fabric. Both hyperthermia effect and controlled release behavior of the magnetized polyester fabric loaded with menthol are measured under high-frequency alternating current magnetic fields. It is found that the menthol included in β -CD could be

released in a controlled and accelerated way under external alternating current magnetic fields.

Keywords: Polyester fabric; magnetic particle; β -Cyclodextrin; menthol

1 Introduction

Controlled release of medical active ingredients (e.g. menthol) onto skin is desirable for medication and has many medical and healthcare applications. In current practice, these medical active ingredients are usually volatile and need to be hosted in an adsorbent substance such as β -Cyclodextrin (β -CD) for gradual release of the ingredients when use. β -Cyclodextrin is one of the cyclic oligosaccharides composed of seven D-glucopyranose residues [1, 2] and has a hollow, toroidal and truncated cone structure [3, 4]. It can incorporate hydrophobic active ingredients into its internal hydrophobic cavity via van der Waals interactions [5, 6], and has thus been widely included into various polymeric products as a carrier to retain volatile ingredients such as amines, acids, ketones, and aliphatic alcohols [7]. Examples of such β -CD incorporated products include β -CD-linked-chitosan micro-particles fabricated by using tosylate intermediate and cross-linked by genipin [8], and β -CD-grafted-cellulose nanocrystals [9].

Functional polymeric nanofibers containing different cyclodextrin-inclusion complexes [10, 11] and textiles grafted with β -CDs loaded with various drugs or fragrant [12] have been developed for the gradual release of active ingredients for the application of either skin disease treatments or odor control. For instance, β -CD grafted viscose fabric loaded with aescin formulations has been obtained by means of a two-step ultrasound-assisted reaction

[13]. Cotton textiles containing β -CDs loaded with some natural active substances have been fabricated for control purposes [14-16]. However, the gradual release of ingredients from current β -CDs grafted textiles are not controllable. It is desirable for the release of active ingredients to be controllable in its amount when it is needed. There is currently little research on the active control of the release of volatile compounds from textile products.

Magnetite micro- and nano- particles having superparamagnetism properties have been used in biomedical applications for the controlled release drugs and targeted cancer medication. The release of drugs incorporated with β -CD grafted magnetite can be triggered through either the hyperthermic effect of the magnetic particles in High Frequency Magnetic Field (HFMF) or induction heat, and its amount is controllable by varying the intensity of HFMF or heat applied [17-19]. Aminopropyltriethoxysilane-coated magnetic Fe_3O_4 nanoparticles (APTES-MNPs) with β -cyclodextrin (β -CD) were reported to have saturation magnetization value as high as $69 \text{ emu}\cdot\text{g}^{-1}$ and the outermost CD moieties to function as inclusion sites for drugs and biomolecules in magnetic drug delivery and bioseparation applications [20]. The silane coating outside the magnetic Fe_3O_4 cores provided amino group ($-\text{NH}_2$) for linking the CD molecule, other silane coated magnetic nanoparticles with glycidylmethacrylate-grafted-maleated cyclodextrin composite hydrogel were used as a drug carrier for the controlled delivery of 5-fluorouracil [21]. However, the fibrous materials incorporated with magnetic particles grafted with β -CD loading with active ingredients for controlled release purposes have not been reported yet.

Menthol has been used as common cold medications like toothpastes, confectionery, cosmetics, insect repellent as well as components in traditional medicines for curing

infections, insomnia, and irritable bowel syndrome [22, 23]. It has been demonstrated that β -CD can form inclusion complexes with both enantiomers of menthol, resulting in the same stability constants for both complexes. The value of the stability constant is large enough to guarantee binding of highly volatile menthol inside β -CD cavity and small enough for a convenient release of the aroma from the host molecule [24, 25].

In this paper, menthol is used as a model flavor molecule loaded onto a polyester fabric incorporated with β -CD grafted magnetic particles. It is expected that the magnetic particles deposited on the polyester fabric can serve as the hyperthermia-inducing media using the exothermic properties to raise the temperature of polyester fabric in HFMF for the controlled release of menthol for the treatment of cutaneous diseases.

In this research, different analytical techniques including Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Diffraction (XRD), Vibrating Sample Magnetometry (VSM), Fourier Transform Infrared (FTIR) spectroscopy, Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Diffuse Reflectance Spectroscopy (DRS) are employed to determine the structural changes of the resultant β -CD grafted magnetized polyester fabric loaded with menthol. The release of menthol from β -CD grafted magnetized polyester fabric is characterized by using colorimetric method. Both the hyperthermia properties and controlled release properties of the resultant polyester fabric are measured under external high-frequency alternating current magnetic fields.

2 Experimental Section

The technical route for the fabrication of magnetized polyester fabrics grafted with

β -Cyclodextrin loaded with menthol is illustrated in Figure 1.

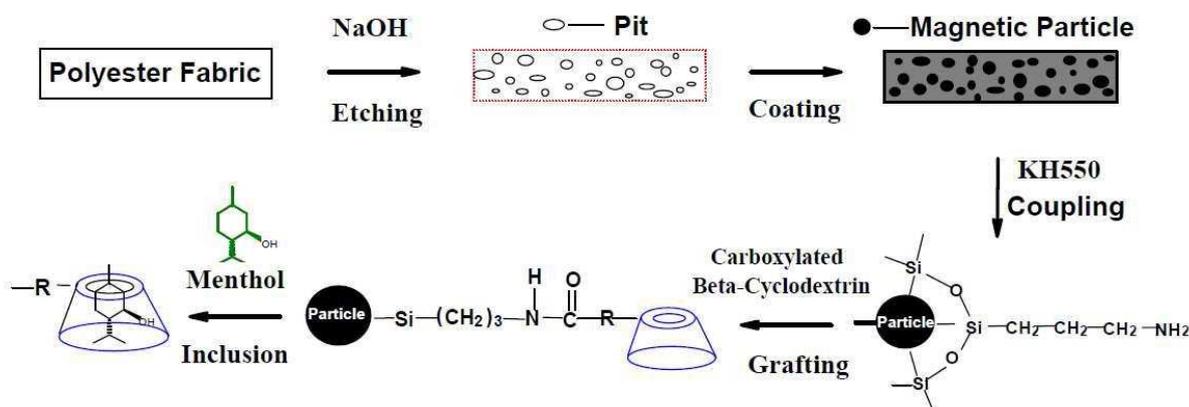


Figure 1. Schematic illustration of the technical route for the fabrication of magnetized polyester fabrics grafted with β -Cyclodextrin loaded with menthol

2.1 Materials and Reagents

A plain woven fabric made of 100% polyethylene terephthalate fibers was provided by a local textile mill. The yarn counts are 7.3tex identical in both warp and weft directions, and the numbers of threads in both warp and weft directions are 40 and 30 per centimeter respectively. Deionized water was used throughout the experiments and the chemicals used in this research are of analytical grade without further purification, including ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$, Tianjin Bodi Chemical Co., Ltd), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, Langfang Pengcai Fine Chemical Co., Ltd), urea ($\text{CO}(\text{NH}_2)_2$, Beijing Kangpu Huiwei Technology Co., Ltd), N,N-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, Nanjing Chemical Reagent Co., Ltd), maleic anhydride ($\text{C}_4\text{H}_2\text{O}_3$, Jining Baiyi Chemical Co., Ltd), trichloromethane (CHCl_3 , Jiangsu Pengyu Chemical Co., Ltd), menthol ($\text{C}_{10}\text{H}_{20}\text{O}$, CAS No. 89-78-1, Fortuneibo-tech Co., Ltd), 4-dimethylaminobenzaldehyde ($\text{C}_9\text{H}_{11}\text{NO}$, Guangzhou Boyang Chemical Industry Co., Ltd), 98% concentrated sulfuric acid (H_2SO_4 , Nanjing Senking Chemical Co., Ltd), acetone

(C₃H₆O, Nanchang Lanxiang Chemical Co., Ltd) and anhydrous ethanol (C₂H₆O, Nanchang Lanxiang Chemical Co., Ltd). β -Cyclodextrin (C₄₂H₇₀O₃₅, CAS No. 7585-39-9) of food grade was obtained from Zibo Qianhui Biological Technology Co., Ltd. The silane coupling agent KH550 (γ -aminopropyltriethoxysilane, NH₂(CH₂)₃Si(OC₂H₅)₃) was purchased from Dow Corning (Shanghai) Co., Ltd.

2.2 Fabrication of Magnetized Polyester Fabrics

A certain amount of ferric sulfate (0.48 g) was completely dissolved in 40 mL of deionized water at 60⁰C with the aide of ultrasonic stirring (55 kHz, 100 W), followed by the addition of sodium thiosulfate. The molar ratio of sodium thiosulfate to ferric sulfate is 1:1. When the color of the suspension turned from dark purple to transparent, the pH value of the precursor suspension was adjusted between 1.8 and 2.5 ready to use by adding a certain amount of urea. Alkali-etched polyester fabrics were made according to the following procedures. A piece of polyester fabric was immersed in a sodium hydroxyl aqueous solution of 100 g/L at a liquor ratio of 1:50 in 100⁰C for 30 min, then successively washed with acetone, anhydrous ethanol and deionized water at 40⁰C for 10 min, respectively.

About 1.2 g of the alkali-etched polyester fabric was added to the ferric precursor suspension in a PTFE-lined stainless steel autoclave. The autoclave was sealed and then heated up in a furnace up to 130⁰C for 5 hours, rotating at 10 revolutions per minute (rpm). After cooling down to room temperature, the magnetized polyester fabric was rinsed in deionized water without stirring, and then dried ready for further surface modification.

2.3 Modification of β -CD and Inclusion of Menthol

About 5.68 g of β -CD was dissolved in 50 mL of 100% N,N-dimethylformamide solution at

80°C under continuous stirring for 30 minutes, followed by the addition of 4.9 g of maleic anhydride to reaction for 12 hours. Carboxylated β -CD was precipitated from the resultant suspensions by adding trichloromethane solution into it once the suspensions was cooled down. The resultant carboxylated β -CD was collected using a vacuum filtration set-up, then thoroughly washed with acetone solution, and dried in a vacuum oven at 80°C for 24 hours.

Menthol was used as a model guest molecule in this research work. β -CD-menthol inclusion complexes were obtained by using a hydrothermal process as described in literature [24]. A certain amount of carboxylated β -CD and menthol was added to 80 ml of deionized water at room temperature at the molar ratio of 1:1. The mixture solution was transferred to a 100 mL PTFE-lined stainless steel autoclave. The autoclave was sealed and placed in a furnace, and then heated to 120°C for 4 h at speed of 10 rpm. When the solution cooled down to room temperature, the white precipitant of β -CD-menthol inclusion complexes was obtained after being filtered, washed several times using anhydrous ethanol, and dried in a vacuum oven at 40°C.

2.4 Surface Modification and Grafting of Carboxylated β -CD to Magnetized Polyester Fabric

The surface of magnetized polyester fabric was modified with silane coupling agent KH550 prior to grafting with carboxylated β -CD. The silane coupling agent, KH550, (relative to the fabric weight 1%) was added to 200 mL of a 10% ethanol water solution with continuous stirring for 40 minutes. The resultant magnetized polyester fabric was immersed in the above KH550 solution for 30 min without stirring. Both sides of the saturated magnetized polyester fabric were then irradiated with an ultraviolet light of main wavelength 365 nm for 30 min,

respectively. Finally, the silane coupling agent modified magnetized polyester fabric was successively washed with acetone, anhydrous ethanol and deionized water respectively, and dried in a vacuum oven at 60°C for 3 hours.

The magnetized polyester fabrics modified with KH550 were immersed in 80 ml of deionized water solution containing 1.5 g of carboxylated β -CD in a PTFE-lined stainless steel autoclave, which was gradually heated up to 120° C at a speed of 30C per minute in a furnace. After 3 hours of reaction in 120° C, the autoclave cooled down naturally. The magnetized polyester fabric grafted with carboxylated β -CD was obtained after the fabric was successively washed with acetone, anhydrous ethanol and deionized water at 40oC for 15 min respectively, and dried at ambient temperature.

2.5 Inclusion of Menthol

The magnetized polyester fabric grafted with β -CD was dipped in 80 mL of deionized water containing 0.17 g of menthol at 30oC in a 100 mL PTFE-lined stainless steel autoclave. The autoclave was sealed and heated up to 120° C in a furnace while rotating at 10 rpm. After 2 hours of reaction at 120° C, the autoclave was cooled down naturally, and the magnetized polyester fabric loaded with menthol was successively rinsed with acetone, anhydrous ethanol and deionized water at 30° C for 10 min, respectively, and finally dried at room temperature.

β -CD-menthol inclusion complexes were also obtained by using a hydrothermal process as described in literature [26]. A certain amount of carboxylated β -CD and menthol was added to 80 ml of deionized water at room temperature at the molar ratio of 1:1. The mixture solution was transferred to a 100 mL PTFE-lined stainless steel autoclave, which was sealed

and heated up to 120° C in a furnace for 4 h while rotating at 10 rpm. When the solution cooled down to room temperature, the white precipitant of β -CD-menthol inclusion complexes was obtained after being filtered, washed several times using anhydrous ethanol, and dried in a vacuum oven at 40° C.

2.6 Characterization Techniques

All samples were purified with acetone, anhydrous ethanol and deionized water prior to characterization. The morphologies of the obtained fabrics and β -CDs prepared at different stages were examined using a ZEISS EVO18 field emission scanning electron microscope (FESEM). Energy Dispersive X-ray (EDX) analysis was conducted in an Oxford INCA Energy 350 EDX system attached to the FESEM.

The crystal structure of the magnetite particles in the resultant magnetized polyester fabric loaded with menthol was analyzed using a 7000S X-ray diffraction (XRD) spectroscopy diffractometer equipped with Cu $K\alpha_1$ radiation ($\lambda=0.154056$ nm, 40 kV and 40 mA) at a scan step of 0.02° and a scan rate of 5° per minute. The crystallite size of synthesized magnetic particles was calculated using Scherrer equation $D=K\lambda/\epsilon\cos\theta$ (where D is the diameter of a particle, λ is the X-ray wavelength, ϵ is the FWHM of the diffraction line, θ is the diffraction angle, and K is a constant of 0.89).

The chemical structures of the obtained fabrics and β -CDs prepared at different stages were determined via FTIR spectra analysis on a Perkin Elmer Frontier FTIR instrument in the range of 650–1800 cm^{-1} with a resolution of 4 cm^{-1} based on the attenuated total reflection (ATR) mode.

The thermal properties of the obtained fabrics and β -CDs prepared at different stages were

analyzed using thermogravimetry/derivative thermogravimetry (TG/DTG) analysis on a TGA Q500 instrument from 40°C to 550°C at a heating rate of 10 °C per minute and nitrogen flush rate of 20 mL per minute. The differential scanning calorimetry (DSC) analysis was also performed on a DSC Q2000 instrument from 40°C to 350°C under the same conditions.

The changes of the optical properties of the obtained fabrics and β -CDs prepared at different stages were investigated on a PE LAMBDA 950 UV-VIS-NIR spectrophotometer equipped with a 150 mm integrating sphere at a scan rate of 120 nm per minute over the wavelength 200–800 nm.

2.7 Measurement of Menthol Content

Two suspension solutions, solution A and solution B, were made firstly. 100 mL of the suspension solution A was made by adding 0.5 g of 4-dimethylaminobenzaldehyde into 100mL of sulfuric acid aqueous solution of 74% in concentration (prepared with the volumetric ratio of 98% sulfuric acid to deionized water at 1.6:1). A series of menthol aqueous solutions with various concentrations (1, 3, 4, 6, 8, and 10 g/L) were prepared by adding menthol of 0.1, 0.3, 0.4, 0.6, 0.8, and 1.0 g into 100 mL of a solution of the mixture of anhydrous ethanol and deionized water in the volume ratio of 1:1, respectively, which was denoted as solution B. 1mL of menthol solution B was completely mixed with 5 mL of solution A. The mixed solution was heated in water bath at 100° C for 2 min, then immediately cooled down. This mixed solution exhibited red grape color, and its absorbance at the maximum absorption wavelength of 550 nm was measured on a UV-1601 UV-VIS spectrophotometer (Beijing Beifen-Ruili Analytical Instrument (Group) Co., Ltd.). The reference solution is the solution of 1 mL of mixture of anhydrous ethanol and deionized

water mixed with 5 mL of solution A. A calibration curve for menthol solution could thus be obtained from the plot of absorbance against concentrations of menthol in resultant solutions. The magnetized polyester fabric loaded with menthol was kept in ventilated glass bottle and stored at constant air condition (temperature at $25 \pm 3^\circ \text{C}$ and relative humidity of $65 \pm 3\%$). The content of menthol loaded on the magnetized polyester fabric was obtained by firstly dissolving menthol loaded in the fabric of 5 g in 100 ml of deionized water at 100°C and then collecting the distilled menthol from this water solution. The distillate menthol was then dissolved in anhydrous ethanol solution and mixed with the solution A. The concentration of the mixture solution could be obtained by measuring its UV-VIS absorbance against calibration curve. Thus, the dynamic release rate of menthol from the magnetized polyester fabric at room temperature was obtained through the measurement of the changes of the contents of the menthol loaded on the magnetized polyester fabric at regular time intervals. The percentage of menthol released from the resultant fabric at time t , $M_t(\%)$, is defined as the relative change of the menthol contents in the fabric in relation to its initial menthol concentration, as shown in equation (1) below:

$$M = (1 - C_t/C_0) \times 100\% \quad (1)$$

where C_0 is the initial concentration of menthol included in the magnetized polyester fabric; C_t is the concentration of menthol remained in the magnetized polyester fabric at time t .

The magnetic hyperthermia properties of the magnetized polyester fabric were measured using a GP-25A high frequency magnetic induction heating power supply (Shaanxi Let Big Power Technology Co., Ltd) with rated frequency of 70 kHz, and rated capacities of 1.5 kW and 0.6 kW respectively. A piece of magnetized fabric sample ($4.5 \text{ cm} \times 4.5 \text{ cm}$) in a glass

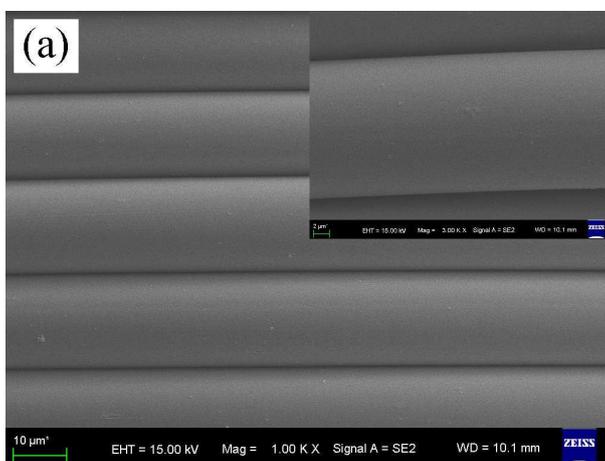
dish was placed on the surface of its magnetic heating induction coil. The temperature of the fabric sample was monitored with a GM531 infrared thermometer (Shenzhen Benetech Co., Ltd), and the dynamic temperature changes of magnetic fabrics were obtained from the average of dynamic temperature changes of three fabric specimens measured in this system. The schematic diagram is illustrated in the inset of Figure 8(b). The reusability of the magnetic polyester fabric loaded with menthol was also measured. The fabric sample was first heated in an oven at 100°C for 1 hour to release the menthol included within β -CDs, and re-loaded with menthol according to the method described in section 2.5. The morphology and chemical composition of the magnetized polyester fabric re-loaded with menthol were examined by employing FESEM and EDX techniques respectively.

3 Results and Discussions

3.1 The Morphology and Chemical Composition of Resultant Magnetized Polyester Fabrics Loaded with Menthol

The morphologies of polyester fabrics obtained at different stages are shown in the FESEM images shown in Figure 2. The surface of the original polyester fabric is clean and smooth without any other particulate substances observed [Fig. 2(a)]. After the polyester fabric is treated with alkali solution at 100°C for 30 minutes, many tiny indentations are formed on fiber surface (not given). This is due to the hydrolysis of ester linkage. These small cavities play a positive role in anchoring the deposition of magnetic particles. The tensile properties of the polyester fabrics before and after alkali treatment are measured using a YG(B)026D-500 tensile tester according to GB/T3923.1-1997. The gauge length is 200 mm and the fabric width is 50 mm. The testing rate is 100 mm/min and the pretension is 2 N. The

tensile strength of the fabrics in warp direction decreases from 633.2 N for untreated fabrics to 577.4 N for alkali treated fabrics, and in weft direction from 405.4 N to 367.0 N. The corresponding elongation decrease from 20.7% to 15.8% in warp direction and from 25.5% to 19.7% in weft direction, respectively. After the polyester fabrics are magnetized, a thin layer of granulates and agglomerated blocks of magnetic particles are deposited on the surface of the magnetized polyester fabrics. Many of granulates and agglomerates are in micrometer sizes, and are composed of submicrometer-sized particles less than 200 nm as shown in the upper right corner in the high-resolution FESEM image [Fig. 2(b)]. The magnetized fabrics modified with KH550 and grafted with β -CD are coated by a thick film of paste-like substances and scattered with some small particulates [Fig. 2(c)]. After the fabrics are loaded with menthol, no other distinct change is observed except the fabric surface becomes slightly smoother [Fig. 2(d)].



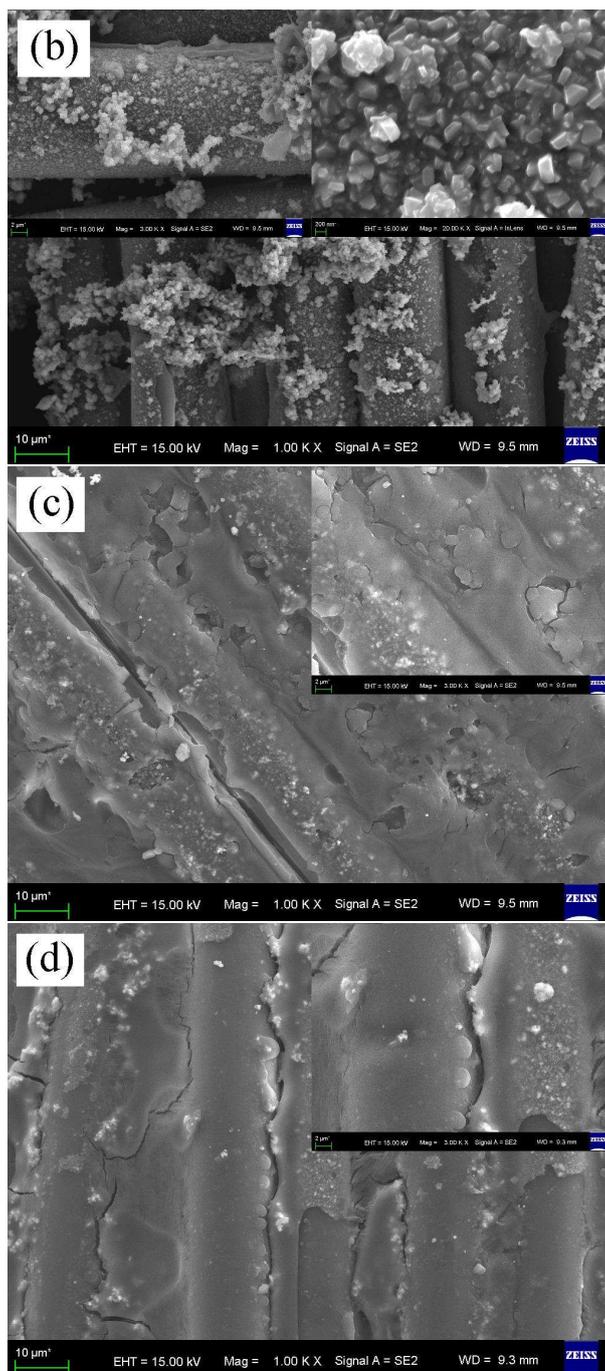


Figure 2. FESEM images of polyester fabrics obtained at different stages of treatments: (a) Original; (b) Magnetized fabric; (c) Modified with KH550 and then grafted with β -CD; (d)

Loaded with menthol

The composition analysis of these polyester fabrics obtained at different stages are shown in the EDX spectra in Figure 3, and the atom percentages of the elements of C, O, N, S and other metal elements are detected. It is noticed that the atom percentages of both C and O

elements in the original polyester fabric are 80.1% and 19.9% respectively [Fig. 3(a)], while additional elements of N (2.6%), Na (0.9%), S (5.4%), and Fe (41.3%) besides C (22.4%) and O (27.4%) are found in the surface of the magnetized polyester fabrics, indicating the existences of iron oxides. The element N, Na and S are likely from the residues of the contamination of the precipitant of urea and reducing agent of sodium thiosulfate [Fig. 3(b)].

After the magnetized polyester fabrics are modified with KH550 and grafted with β -CD [Fig.3(c)], apart from the elements of C (51.4%), N (6.4%), O (27.1%), Na (0.7%), S (0.4%) and Fe (5.2%), a small amount of element Si (8.8%) is detected and this indicates the incorporating of Si from the silane coupling agent, KH550, into the fabrics. It is also noticed that the contents of C and N significantly increase and the element of Fe decreases markedly in comparison with the magnetized polyester fabric. It is reasonable to conclude that magnetic particles are covered by grafted β -CD of which the additional C and N elements are detected from. The chemical compositions of the magnetized polyester fabric loaded with menthol in terms of atom percentages are C (68.8%), O (24.2%), Na (0.4%), Si (4.2%), and Fe (2.4%) respectively. This means that the magnetic particles, silane and grafted β -CD covered on the fabric surface are still detectable. However, the elements of N and S are not detected, this might be because the two elements from the contaminations are re-dissolved and washed away from the fabric during hydrothermal inclusion process and subsequently washing process [Fig. 3(d)].

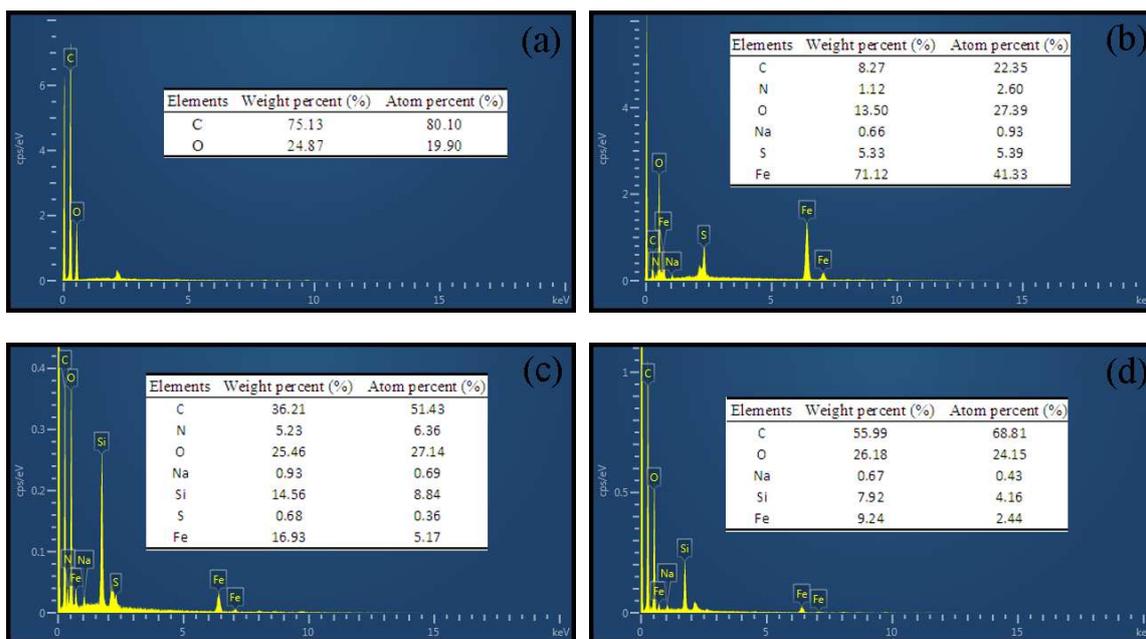
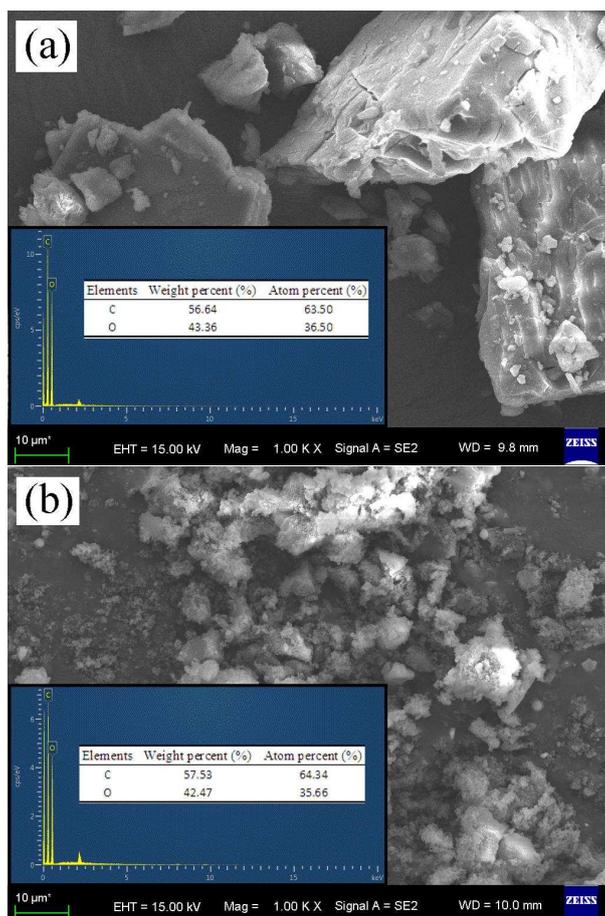


Figure 3. EDX spectra of polyester fabrics obtained at different stages: (a) Original; (b) Coated with particles; (c) Modified with KH550 and then grafted with β -CD; (d) Loaded with menthol

3.2 The Morphology and Chemical Composition of β -Cyclodextrin Loaded with Menthol

The morphologies of β -CDs modified at different processing stages are shown in their FESEM images as shown in Figure 4, and their EDX spectra are also inserted in their corresponding FESEM images. The untreated β -CD agglomerates together to form larger clusters with irregular shape [Fig. 4(a)]. β -CD modified with maleic anhydride appears to be in the form of smaller powder particles [Fig. 4(b)]. After inclusion of menthol, the smaller β -CD particle with lamellar structure is formed [Fig. 4(c)]. It is also observed that only two elements, C and O, are detected for all of these samples. However, the atomic ratios of C to O in them are quite different. After treatment with maleic anhydride, the atomic content of C in the β -CD has a slightly change from 63.5% to 64.3%, but increases significantly to 68.4%

after subsequently inclusion with menthol. Meanwhile, the atomic content of O also slightly changes from 36.5% to 35.7% after being treated with maleic anhydride, then markedly decreases to 31.6% after following by inclusion with menthol. Thus, it is confirmed in the EDX elemental composition analysis that the changes of organic substances in β -CD after each chemical modifications. This is because β -CD has a cavity of approximately 7.0 Å in diameter and 7.5 Å in depth [4]. The cavity has a hollow hydrophobic interior and hydrophilic exterior and thus can act as a host to catch other small guest molecule chemicals inside it. The driving force for this host-guest complex formation is attributed to the hydrophobic and hydrophilic interactions [27].



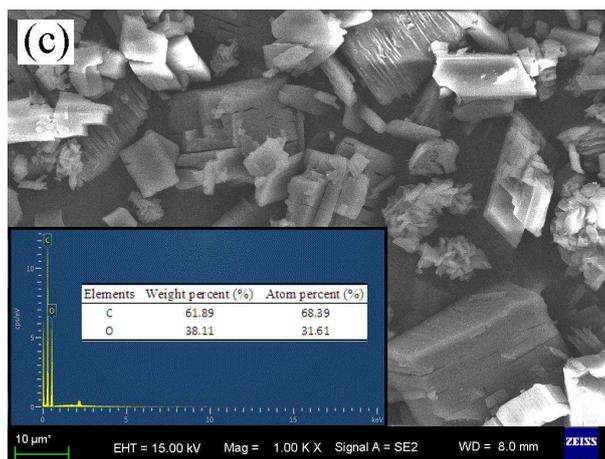


Figure 4. FESEM images and EDX spectra of β -CDs obtained at different stages: (a) Untreated; (b) Carboxylated; (c) Included with menthol

3.3 Changes of Characteristic Groups in Polyester Fabrics and β -CDs Analyzed Using FTIR Techniques

3.3.1 Polyester Fabrics

The characteristic bonds of polyester fabrics obtained at different stages are shown in the FTIR spectra in Figure 5. The characteristic bands of the original polyester fabric appear in the FTIR spectrum at 1505 cm^{-1} (C-C stretching vibration of benzene ring skeleton, $\nu_{\text{C-C}}$), 1408 cm^{-1} ($-\text{CH}_2\text{COCH}_2-$ absorption band), 1339 cm^{-1} (CH_2 wagging vibration, ω_{CH_2}), 1240 , 1176 , 1094 , and 970 cm^{-1} (C-O stretching vibration, $\nu_{\text{C-O}}$), 1017 and 872 cm^{-1} (C-H out-of-plane bending vibration of benzene ring, $\gamma_{\text{C-H}}$), 847 cm^{-1} (CH_2 rocking vibration, ρ_{CH_2}), 792 and 723 cm^{-1} (CH out-of-plane bending vibration of benzene ring, γ_{CH}) cm^{-1} . In addition, the carboxyl band at 1714 cm^{-1} (C=O stretching vibration, $\nu_{\text{C=O}}$) forms as a result of the hydrolysis reaction of the ester bond of polyester etched by alkali [28] It is also noted that, after the fabric is deposited with magnetic particles, the frequency of this band (C=O stretching vibration, $\nu_{\text{C=O}}$) slightly decreases to 1711 cm^{-1} , and the $\nu_{\text{C-O}}$ bands at 1240 , 1094 and 970 cm^{-1} are also shifted to 1235 , 1087 and 971 cm^{-1} , respectively. After being

treated with KH550, four additional bands form in the fabric at 1195, 1080, 1008 and 693 cm^{-1} due to Si-O-Si groups in the silane coupling agent [29]. After being grafted with a thick layer of carboxylated β -CD in the fabric, two broad $\nu_{(\text{C-O})}$ bands at 1103 and 1003 cm^{-1} and two small bands at 752 and 691 cm^{-1} are noticed. In the magnetized polyester fabric loaded with menthol, the $\nu_{(\text{C-O})}$ bands are shifted to 1238, 1084, and 1017 cm^{-1} due to the existence of menthol [30].

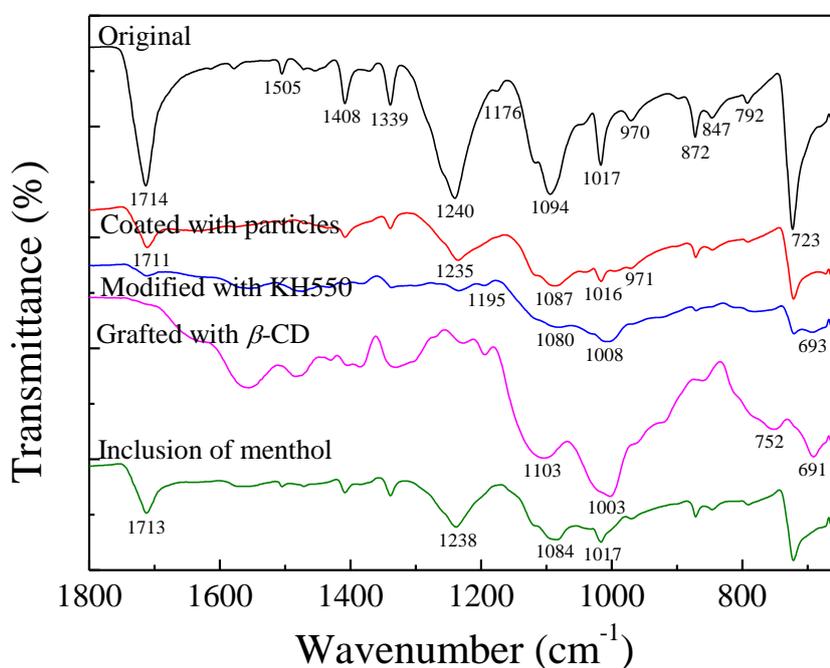


Figure 5. FTIR spectra of polyester fabrics obtained at different stages

3.3.2 β -Cyclodextrins and Menthol

The interactions involved in the formation and stabilization of supramolecular assemblies with β -CD can be investigated by using FTIR [31]. The FTIR spectra of β -CDs prepared at different stages as well as menthol are shown in Figure 6. It is apparent that the characteristic band at 1648 cm^{-1} in the FTIR spectrum of untreated β -CD is ascribed to the O-H in-plane bending vibration ($\beta_{(\text{O-H})}$), the band at 1153 cm^{-1} is attributed to the anti-symmetric glycosidic

C-O-C stretching vibration ($\nu_{a(C-O-C)}$) and the band at 1079 cm^{-1} corresponds to the C-O bending vibration ($\delta_{(C-O)}$). The bands at 1023 and 1000 cm^{-1} are assigned to the coupled C-C and C-O stretching vibrations ($\nu_{(C-C/C-O)}$). The band at 946 cm^{-1} corresponds to the α -1,4-bond skeleton vibrations of β -CD [18]. The band at 851 cm^{-1} is due to the glycosidic linkage of pyran rings. The bands at 755 and 705 cm^{-1} are caused by the vibrations of β -CD ring [19]. After treatment with maleic anhydride, the $\nu_{(C=O)}$ band at 1723 cm^{-1} appears. The $\beta_{(O-H)}$ and $\delta_{(C-O)}$ bands are shifted to 1634 and 1078 cm^{-1} , while the $\nu_{(C-C/C-O)}$ bands at 1023 and 1000 cm^{-1} are shifted to 1026 and 1003 cm^{-1} , respectively. Meanwhile, the band at 851 cm^{-1} is shifted to 863 cm^{-1} . After inclusion of menthol, being influenced by the absorption bands at 1105 and 1078 cm^{-1} (C-C stretching vibration, $\nu_{(C-C)}$), 1045 and 1026 cm^{-1} (C-O stretching vibration, $\nu_{(C-O)}$) of menthol, the $\nu_{(C-C/C-O)}$ bands at 1026 and 1003 cm^{-1} are shifted to 1024 and 1002 cm^{-1} , respectively. However, the $\beta_{(O-H)}$ band is shifted to 1643 cm^{-1} and a new band at 1101 cm^{-1} appears. So the FTIR results confirm the formation of the inclusion complex of menthol and carboxylated β -CD.

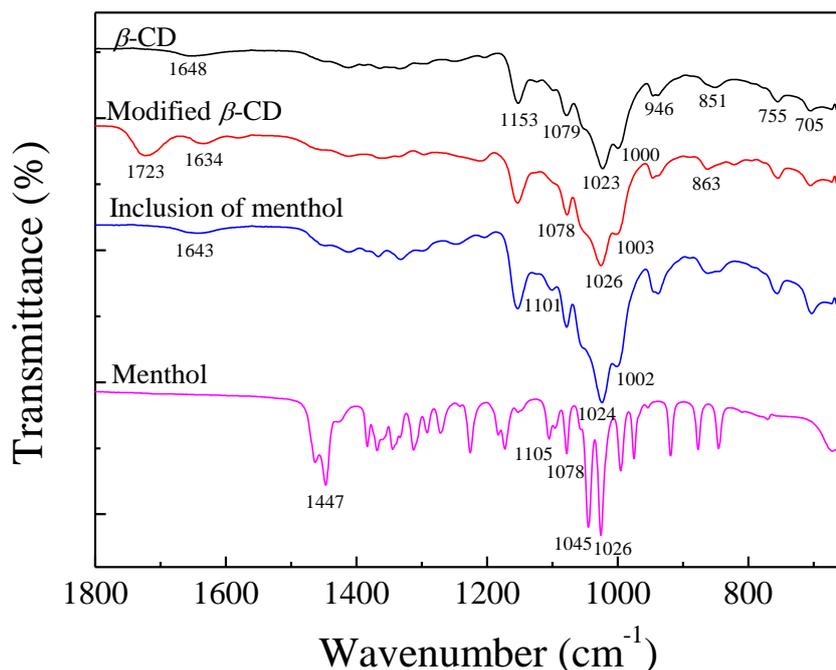


Figure 6. FTIR spectra of β -CDs obtained at different stages and menthol

3.4 X-Ray Diffraction

The XRD pattern of the finally obtained polyester fabric loaded with menthol is shown in Figure 7. The diffraction peaks at around 18° , 23° , and 26° are attributed to $\{010\}$, $\{-110\}$ and $\{110\}$ planes of typical polyester polymer phase. At the same time, a series of characteristic peaks at $2\theta = 30.4^\circ$, 35.7° , 37.3° , 43.3° , 53.7° , 57.2° and 62.7° are noticed, which are ascribed to the planes of $\{220\}$, $\{311\}$, $\{222\}$, $\{400\}$, $\{422\}$, $\{511\}$ and $\{440\}$ in the magnetite (Fe_3O_4) with a cubic spinel type structure (JCPDS Card No.19-0629) [32]. In addition, several small diffraction peaks at about 33.2° , 40.9° , 44.5° and 64.8° are also detected, which are assigned to the planes of $\{104\}$, $\{113\}$, $\{202\}$ and $\{300\}$ in the rhombohedral hematite (Fe_2O_3) (JCPDS card no. 33-0664) [33]. Thus, the magnetic particles, which are mainly constituted with magnetite Fe_3O_4 together with a small amount of hematite Fe_2O_3 , are successfully coated on the surface of polyester fabric. The average crystallite size

of the synthesized magnetic particle is 23.0 nm calculated by using Scherrer's equation based on the width of the peaks at 30.4°, 35.7° and 62.7°, which is far smaller than that measured from the FESEM image. However, the crystal structure of β -CD inclusion complex is not detected because of the small amount of β -CD and menthol with respect to other components.

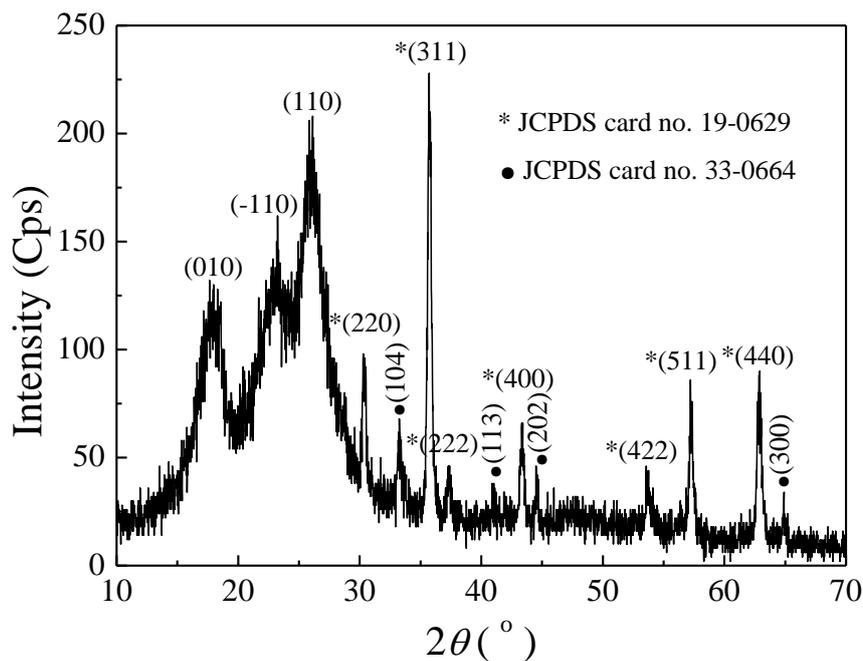
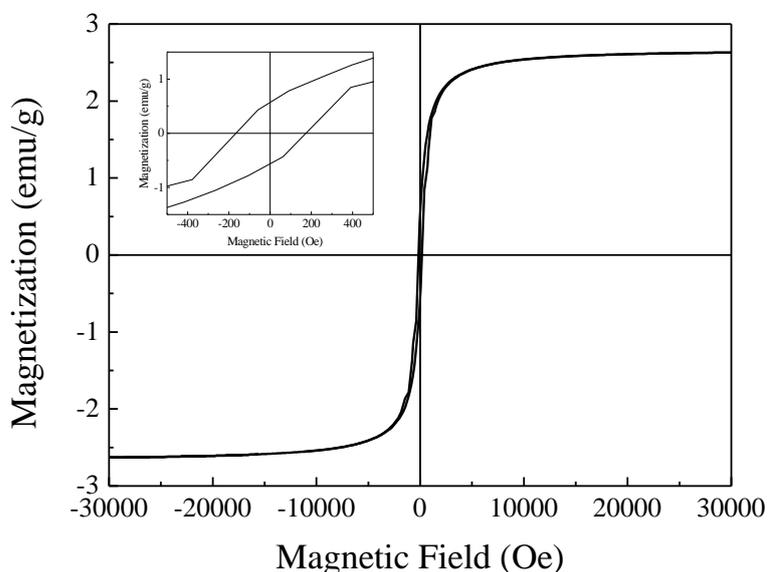


Figure 7. XRD pattern of the finally obtained polyester fabric

3.5 Magnetic Properties and Hyperthermia Effect of Magnetized Polyester Fabrics

The hysteresis loop of the resultant magnetized polyester fabric loaded with menthol at room temperature is shown in Figure 8(a). It is evident that the magnetization sharply increases with the increases of the applied magnetic field intensity when it is smaller than 5000 Oe, and the magnetization hardly changes after the magnetic field intensity is greater than 10000 Oe. The magnetized polyester fabric loaded with menthol has a saturation magnetization of 2.62 emu/g, and the coercivity force is determined as 0.56 emu/g and the remnant magnetization is calculated as 170 Oe judged from the inset in Figure 8(a).

The magnetocaloric heating curves of the magnetized polyester fabrics loaded with menthol under external high frequency alternating current magnetic field at 1.5 kW and 0.6 kW rated capacities are shown in Figure 8(b). It is clear that the temperature of the magnetized polyester fabric increases rapidly in the early stage of heating process (less than 30 seconds) under a specific alternating current magnetic field. After 90 seconds, the temperature of the magnetized polyester fabric increases slowly with the elapse of heating time. Under the magnetic field of 70 kHz in frequency, it takes 120 seconds for the magnetized polyester fabric to reach at 49.5oC when the magnetic field at the rated capacity of 1.5 kW, and it takes 230 seconds to rise to 48oC when the magnetic field at the rated capacity of 0.6 kW. The heat generated by magnetic particles is attributed to hysteresis loss, Neel and Brownian relaxation mechanisms [34].



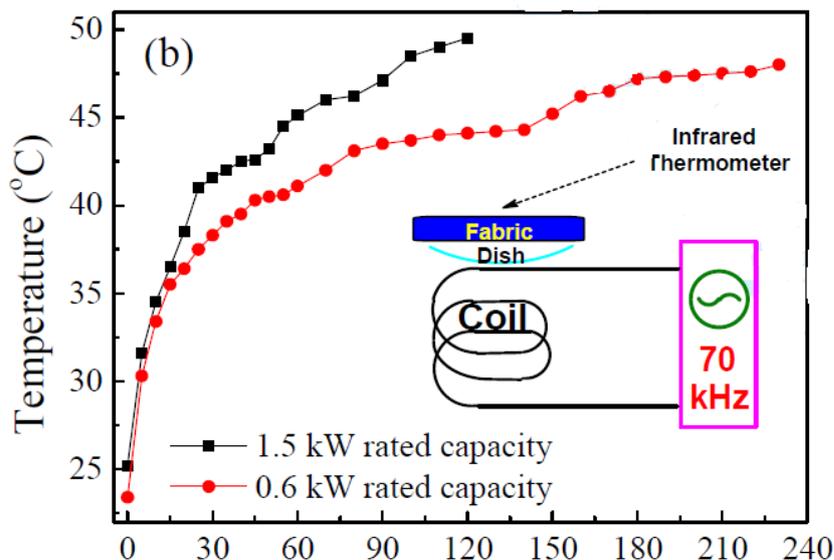


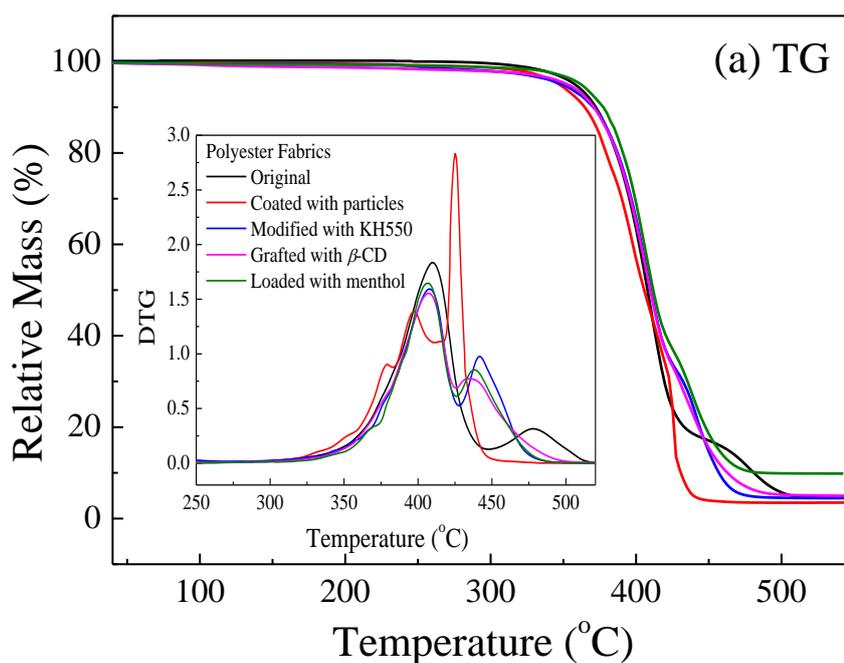
Figure 8. Figure 8. (a) Magnetic hysteresis loop of the finally obtained polyester fabric loaded with menthol, and (b) magnetocaloric heating curves of the magnetized polyester loaded with menthol under alternating current magnetic field at 70 kHz

3.6 Thermal Stabilities

3.6.1 Resultant Polyester Fabrics

The TG/DTG and DSC curves of polyester fabrics obtained at different stages are shown in Figure 9. It is noted from TG/DTG curves that when the original polyester fabric is coated with magnetic particles, the heat decomposition temperature decreases from 380.8°C to 358.8°C. After being modified with KH550, the heat decomposition temperature is shifted to 372.7°C. After being grafted with carboxylated β -CD, the heat decomposition temperature has no change. When loaded with menthol, the heat decomposition temperature increases slightly to 374.8°C. The weight losses are 95.4%, 96.3%, 95.5%, 94.9%, and 90.2% for the original, coated, modified, grafted, and loaded fabrics at the temperature of 550°C, respectively. The thermal decomposition process can be divided into two periods for all samples except for the coated polyester fabric (see inset of Fig. 9a). It is noticed from DSC

curves that the endothermic peaks change a little, which are in the temperature range from 250.0°C to 255.2°C. The reaction enthalpies are determined as 60.5, 64.8, 51.5, 58.7, and 47.8 J/g for the original, coated, modified, grafted, and loaded fabrics, respectively. Moreover, a small endothermic peak at 20°C is observed in the finally obtained polyester fabric, and the corresponding reaction enthalpy is 5.97 J/g (see inset of Fig. 9b), suggesting that the menthol molecules are included inside the β -CD cavity. As a result, it is inferred that the menthol is loaded on the magnetic polyester fabric, and the successive process has a little effect on the thermal stability of polyester fabric.



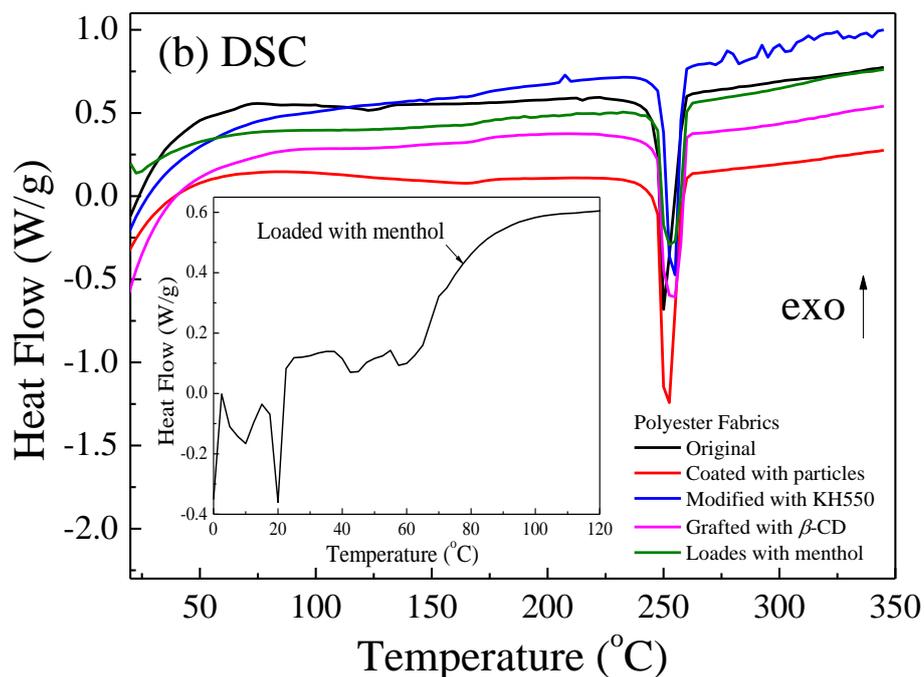


Figure 9. TG/DTG (a) and DSC (b) curves of polyester fabrics obtained at different processing procedures

3.6.2 β -Cyclodextrins

The TG/DTG and DSC curves of β -CDs obtained at different stages are shown in Figure 10. It is clear from TG/DTG curves that a small decomposition temperature occurs at 89.5°C in the TG/DTG curve of the untreated β -CD. After treatment with maleic anhydride, the heat decomposition temperature decreases from 318.6°C to 262.7°C. After inclusion of menthol, the heat decomposition temperature increases to 307.5°C. The weight losses are 79.0%, 76.1%, and 87.5% for the untreated, modified, and included β -CDs at the temperature of 550°C, respectively. It is obvious from DSC curves that there are two endothermic peaks at 90.0°C and 327.5°C for the untreated β -CD, and the corresponding reaction enthalpies are 49.9 and 44.1 J/g. For the modified β -CD, the initial endothermic peak is shifted 77.4°C,

while the main endothermic peak is disappeared. After inclusion of menthol, the endothermic temperatures occur at 96.8°C and 310.3°C, and the corresponding reaction enthalpies are 20.5 and 80.2 J/g. In brief, it is concluded that the carboxylated β -CD included with menthol is obtained.

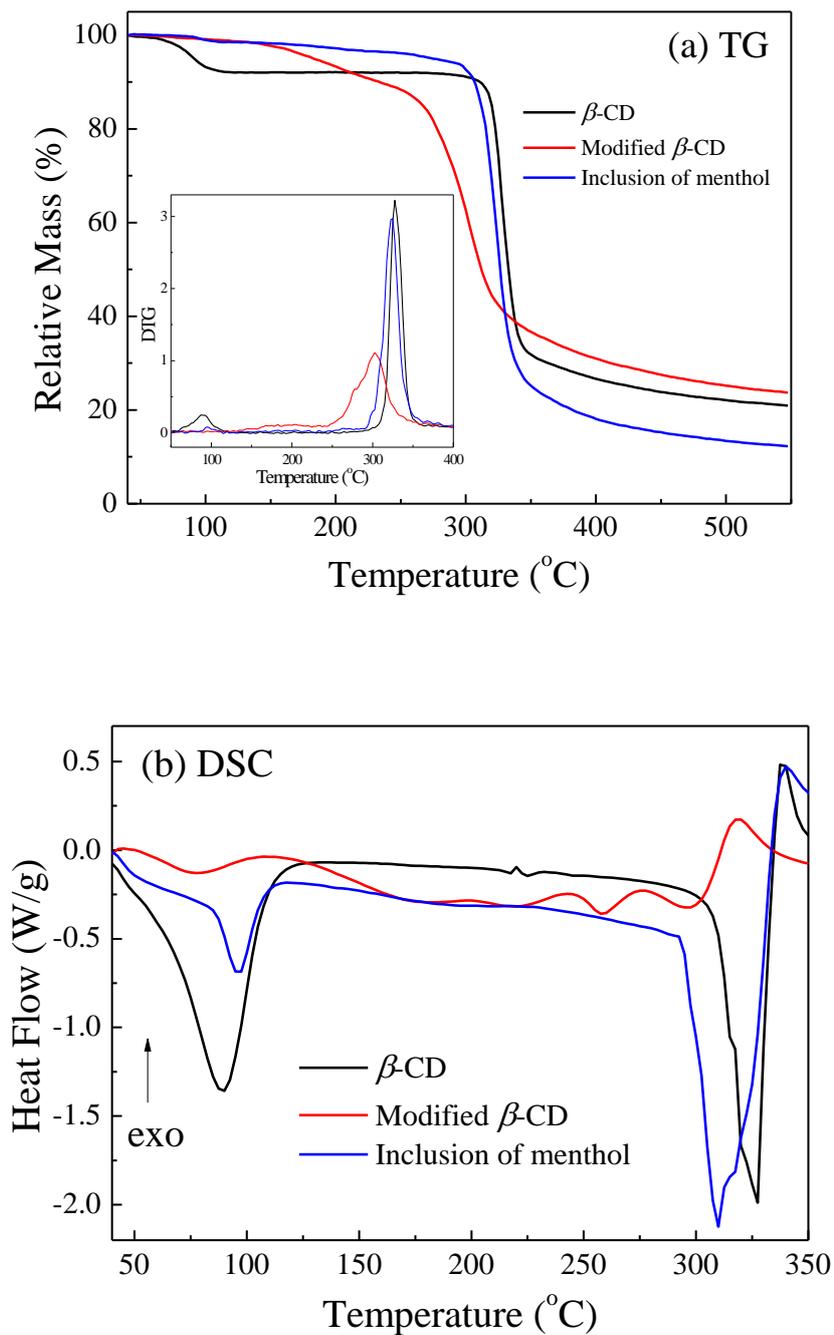


Figure 10. TG/DTG (a) and DSC (b) curves of β -CDs obtained at different stages

3.7 Optical Properties

3.7.1 Polyester Fabrics

The diffuse reflectance spectra of polyester fabrics obtained at different stages are shown in Figure 11. It is clear that the typical reflectance spectrum is noticed in the original polyester fabric, and the characteristic absorption peaks are observed at about 228 nm and 300 nm and there is a significant increase of reflectance in the range of wave length between 300 nm and 400 nm. For the magnetic particle coated polyester fabrics, the reflectance is very small (less than 5%) in the whole range of wave length between 200 nm and 800 nm owing to the deposition of black magnetic particles. After the fabric is treated with KH550, the reflectance gradually increases from around 5% to around 10% with the increases of wave length across the whole wave length (200 – 800 nm). After being grafted with carboxylated β -CD, the overall reflectance decreases slightly [35]. However, after being loaded with menthol, the reflectance increases to the similar level of the modified polyester fabrics.

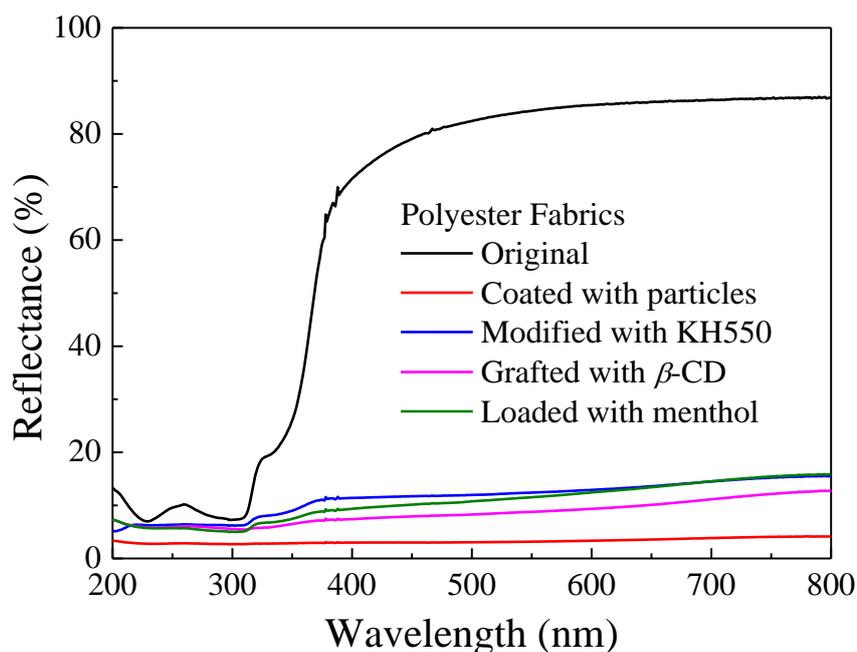


Figure 11. Diffuse reflectance spectra of polyester fabrics obtained at different stages

3.7.2 β -Cyclodextrins

It has been demonstrated that the UV and/or visible absorption spectrum of the guest may be altered to some extent once the β -CD inclusion complex is formed [4]. The diffuse reflectance spectra of menthol and β -CDs obtained at different stages are shown in Figure 12. It is evident that when β -CD is modified with maleic anhydride, a red shift is significantly noticed. After inclusion of menthol, a broad reflectance spectrum (230-380 nm) is observed, which is mainly influenced by the characteristic spectrum of menthol. This is ascribed to the partial shielding of the excitable electrons in the β -CD cavity [36].

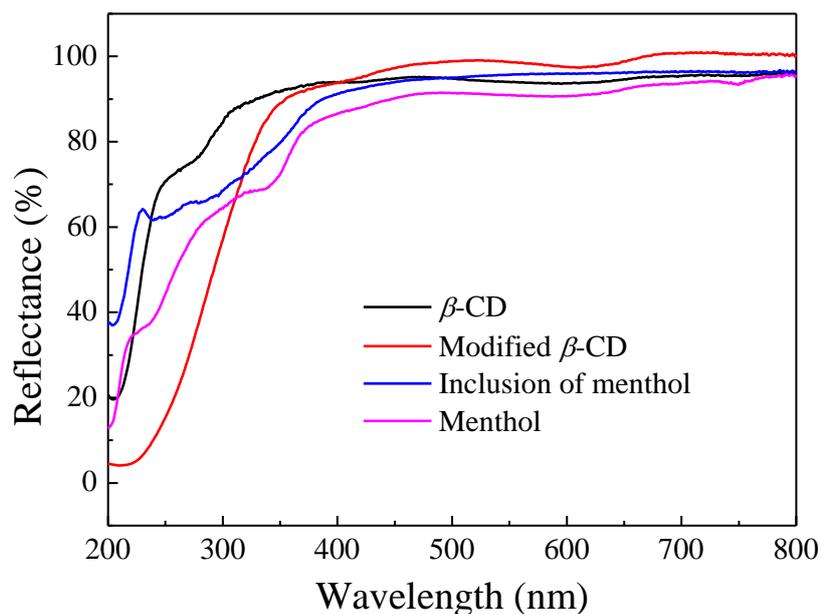


Figure 12. Diffuse reflectance spectra of β -CDs obtained at different stages

3.8 Measurement of Menthol Contents

Menthol is gradually released from the magnetized fabrics in ambient conditions (20° C, 65% relative humidity). The dynamic change of the percentage of menthol released from the

magnetized polyester fabric in ambient conditions is shown in Figure 13(a). The relationship between the UV-VIS absorbance of menthol and its concentration of menthol is given in the insert of Fig.13(a). The average of menthol content remained in the magnetized polyester fabric is about 8% after 90 days of menthol release.

It was found that the menthol residue in the magnetized polyester fabric was 7.9% after it was gradually released in ambient temperature for 90 days. For comparison purposes, a controlled accelerated release of menthol from the magnetized polyester fabrics under electromagnetic induced hyperthermia (see section 3.5) were also performed. When the magnetized polyester fabrics were heated up under electromagnetic induced hyperthermia at 1.5 kW rated capacity for 120 seconds, the menthol contents remained in the fabrics are 7.2%; when the fabrics were heated up at 0.6 kW rated capacity for 230 second, the residue menthol contents are 7.6%. it is evident that there is a controlled and accelerated release of menthol onto targeted surface when electromagnetic induced hyperthermia heating is introduced in the magnetized polyester fabrics.

After 5 cycles of repeated inclusion of menthol, the FESEM image of the magnetized polyester fabric loaded with menthol is shown in Figure 13(b). It is found that part of substances coated on the fabric surface fall off due to repeatedly hydrothermal treatments. It is indicated in the EDX results that the composition elements of the magnetized polyester fabrics loaded with menthol repeatedly are composed of elements C (64.1%), O (35.3%), Na (0.1%), Si (0.4%) and Fe (0.1%).

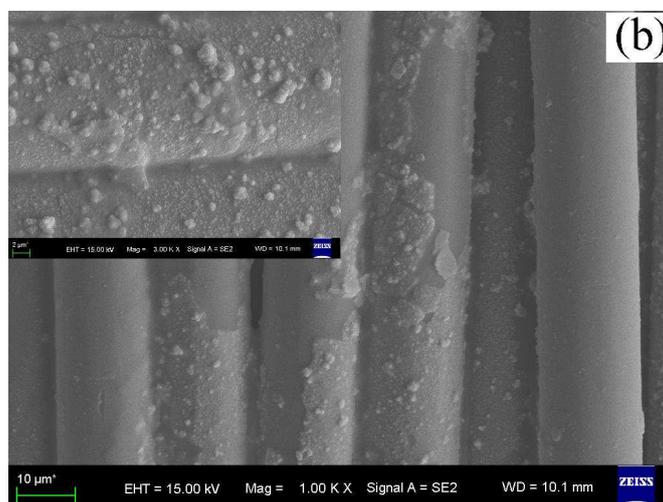
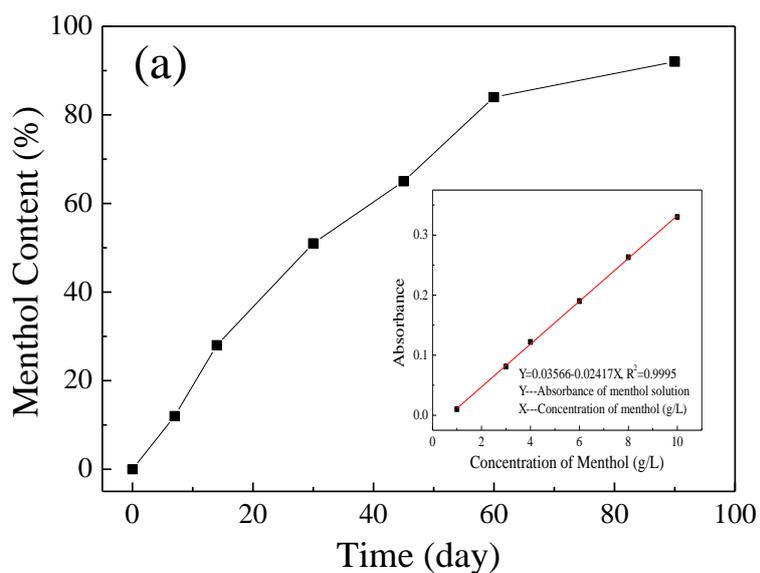


Figure 13. (a) dynamic rate of menthol release from the resultant magnetized polyester fabric, and (b) FESEM image of the magnetized polyester fabric loaded with menthol after 5 repeated inclusions

Conclusions

In this study, a technical route to fabricate magnetized polyester fabrics grafted with β -Cyclodextrin loaded with menthol mainly based on hydrothermal method are reported. The characteristics of the structure and properties of magnetized polyester fabrics prepared at

various treatment stages are analyzed and discussed. The magnetic particles deposited on the fabric surface are primarily constituted with magnetite Fe_3O_4 and a small proportion of hematite Fe_2O_3 . A thick layer of β -CD submicrometer-sized particles and membrane are coated on the surface of the magnetized polyester fabric. The magnetized polyester fabric exhibits a saturation magnetization of 2.62 emu/g, coercivity force of 0.56 emu/g, and remnant magnetization of 170 Oe. The magnetized polyester fabric loaded with menthol in carboxylated β -CD has demonstrated both apparent hyperthermia effect and the capability of controlled accelerated release of menthol on targeted surface; this fabrics are able to be reloaded with menthol repeatedly.

References

- [1] Ciobanu A, Landy D, Fourmentin S. Complexation efficiency of cyclodextrins for volatile flavor compounds. *Food Res Int* 2013; 53: 110–114.
- [2] Correia A, Shahbazi MA, Makila E, et al. Cyclodextrin-modified porous silicon nanoparticles for efficient sustained drug delivery and proliferation inhibition of breast cancer cells. *ACS Appl Mater Inter* 2015; 7: 23197–23204.
- [3] Tan S, Ladewig K, Fu Q, et al. Cyclodextrin-based supramolecular assemblies and hydrogels: recent advances and future perspectives. *Macromol Rapid Comm* 2014; 35: 1166–1184.
- [4] Marques HMC. A review on cyclodextrin encapsulation of essential oils and volatiles. *Flavour Frag J* 2010; 25: 313–326.
- [5] Voskuhl J, Schaepe K, Ravoo BJ. Enhanced chiral recognition by cyclodextrin dimers. *Int J Mol Sci* 2011; 12: 4637–4646.

- [6] Sambasevam KP, Mohamad S, Sarih NM, et al. Synthesis and characterization of the inclusion complex of β -cyclodextrin and azomethine. *Int J Mol Sci* 2013; 14: 3671–3682.
- [7] Singh S. Nanomedicine–nanoscale drugs and delivery systems. *J Nanosci Nanotechno* 2010; 10: 7906–7918.
- [8] Luzardo-Alvarez A, Antelo-Queijo A, Soto VH, et al. Preparation and characterization of β -cyclodextrin-linked chitosan microparticles. *J Appl Polym Sci* 2012; 123: 3595–3604.
- [9] Lin N, Dufresne A. Supramolecular hydrogels from In situ host–guest inclusion between chemically modified cellulose nanocrystals and cyclodextrin. *Biomacromolecules* 2013; 14: 871–880.
- [10] Celebioglu A, Uyar T. Electrospinning of polymer-free nanofibers from cyclodextrin inclusion complexes. *Langmuir* 2011; 27: 6218–6226.
- [11] Uyar T, Hacaloglu J, Besenbacher F. Electrospun polyethylene oxide (PEO) nanofibers containing cyclodextrin inclusion complex. *J Nanosci Nanotechno* 2011, 11: 3949–3958.
- [12] Radu CD, Salariu M, Avadanei M, et al. Cotton-made cellulose support for anti-allergic pajamas. *Carbohydr Polym* 2013; 95: 479–486.
- [13] Cravotto G, Beltramo L, Sapino S, et al. A new cyclodextrin-grafted viscose loaded with aescin formulations for a cosmeo-textile approach to chronic venous insufficiency. *J Mater Sci–Mater M* 2011; 22: 2387–2395.
- [14] Hritcu M, Radu CD, Ferri A, et al. Anti-allergic cellulose support at the epidermis–environment interface. *Cell Chem Technol* 2013; 47: 257–266.
- [15] Specos MMM, Garcia JJ, Tornesello J, et al. Microencapsulated citronella oil for mosquito repellent finishing of cotton textiles. *T Roy Soc Trop Med H* 2010; 104:

653–658.

- [16] Hu J, Xiao ZB, Zhou RJ, et al. Comparison of compounded fragrance and chitosan nanoparticles loaded with fragrance applied in cotton fabrics. *Text Res J* 2011; 81: 2056–2064.
- [17] Hayashi K, Ono K, Suzuki H, et al. High-frequency, magnetic-field-responsive drug release from magnetic nanoparticle/organic hybrid based on hyperthermic effect. *ACS Appl Mater Inter* 2010; 2: 1903–1911.
- [18] Zhu J, He J, Du XY, et al. A facile and flexible process of β -cyclodextrin grafted on Fe_3O_4 magnetic nanoparticles and host–guest inclusion studies. *Appl Surf Sci* 2011; 257: 9056–9062.
- [19] Ghosh S, Badruddoza AZM, Hidajat K, et al. Adsorptive removal of emerging contaminants from water using superparamagnetic Fe_3O_4 nanoparticles bearing aminated β -cyclodextrin. *J Environ Chem Eng* 2013; 1: 122–130.
- [20] Cao HN, He J, Deng L, et al. Fabrication of cyclodextrin-functionalized superparamagnetic Fe_3O_4 /amino-silane core–shell nanoparticles via layer-by-layer method. *Appl Surf Sci* 2009; 255: 7974–7980.
- [21] Anirudhan TS, Divya PL, Nima J. Synthesis and characterization of silane coated magnetic nanoparticles/glycidylmethacrylate-grafted-maleated cyclodextrin composite hydrogel as a drug carrier for the controlled delivery of 5-fluorouracil. *Mater Sci Eng C* 2015; 55: 471–481.
- [22] Eccles R. Menthol and related cooling compounds. *J Pharm Pharmacol* 1994; 46: 618–630.

- [23] Joseph AF, Oliver G. Menthol - pharmacology of an important naturally medicinal “cool”. *Mini Rev Med Chem*, 2013; 13: 124–131.
- [24] Ceborska M, Asztemborska M, Lipkowski J. Rare ‘head-to-tail’ arrangement of guest molecules in the inclusion complexes of (+)- and (-)-menthol with β -cyclodextrin. *Chem Phys Lett* 2012; 553: 64–67.
- [25] Ma M, Tan LL, Dai Y, et al. An investigation of flavor encapsulation comprising of regenerated cellulose as core and carboxymethyl cellulose as wall. *Iran Polym J* 2013; 22: 689–695.
- [26] Nakai Y, Yamamoto K, Terada k, et al. New methods for preparing cyclodextrin inclusion compounds I. Heating in a sealed container. *Chem Pharm Bull* 1987; 35: 4609–4615.
- [27] Astray G, Mejuto JC, Morales J, et al. Factors controlling flavors binding constants to cyclodextrins and their applications in foods. *Food Res Int* 2010; 43: 1212–1218.
- [28] Kormunda M, Pavlik J. Characterization of oxygen and argon ion flux interaction with PET surfaces by in-situ XPS and ex-situ FTIR. *Polym Degrad Stabil* 2010; 95: 1783–1788.
- [29] Tong XM, Zhang M, Wang MS, et al. Effects of surface modification of self-healing poly(melamine-urea-formaldehyde) microcapsules on the properties of unsaturated polyester composites. *J Appl Polym Sci* 2013; 127: 3954–3961.
- [30] Hu JS, Li D, Zhang WC, et al. Synthesis, structure, and properties of chiral liquid crystal monomers and polymers based on menthol. *J Polym Sci Pol Chem* 2012; 50: 5049–5059.
- [31] Crupi V, Majolino D, Venuti V, et al. Temperature effect on the vibrational dynamics of

- cyclodextrin inclusion complexes: investigation by FTIR-ATR spectroscopy and numerical simulation. *J Phys Chem A* 2010; 114: 6811–6817.
- [32] Ahmed MA, Okasha N, El-Dek SI. Influence of Co content on the characterization and magnetic properties of magnetite. *Ceram Int* 2010; 36: 1529–1533.
- [33] Singh J, Srivastava M, Dutta J, et al. Preparation and properties of hybrid monodispersed magnetic α -Fe₂O₃ based chitosan nanocomposite film for industrial and biomedical applications. *Int J Biol Macromol* 2011; 48: 170–176.
- [34] Gkanas EI. In vitro magnetic hyperthermia response of iron oxide MNP's incorporated in DA3, MCF-7 and HeLa cancer cell lines. *Cent Eur J Chem* 2013; 11: 1042–1054.
- [35] Chattah AK, Mroue KH, Pfund LY, et al. Insights into novel supramolecular complexes of two solid forms of norfloxacin and β -cyclodextrin. *J Pharm Sci-US* 2013; 102: 3717–3724.
- [36] Szejtli J. Cyclodextrins and their inclusion complexes. *Akademiai Kiado* 1982; 62: 1–18.