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Incorporation of the antibacterial agent, miconazole nitrate into a cellulosic fabric grafted with β-cyclodextrin

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Abstract

The aim of the study was to investigate the incorporation of the antibacterial agent, miconazole nitrate into cyclodextrin cavities covalently bonded onto cloth fibers. The cellulosic fabric was grafted with β-cyclodextrin molecules through reaction with monochlorotriaziny β-cyclodextrin (MCT-β-CD). The suitable bonded reaction conditions were found to be MCT-β-CD 60–100 g/L, catalyst Na_2CO_3 50–60 g/L, the reaction temperature 150–160 °C and the reaction time 5–8 min.

The modified and unmodified fabrics were characterized by UV spectrophotometry. The level of miconazole nitrate entrapped in the fabrics were determined by HPLC and was founded to be much higher (0.458% w/w) for the textile functionalized with MCT-β-CD compared to the unmodified fabric (0.056% w/w). The antibacterial abilities measured by shaker flask method showed that the antibacterial property was markedly enhanced by impregnation with miconazole nitrate of the MCT-β-CD grafted textile. The finished fabric kept the antibacterial abilities more than 70% even after washing 10 times, while the antibacterial activity of the unmodified textile was almost lost.

Keywords: Miconazole nitrate; Monochlorotriaziny β-cyclodextrin (MCT-β-CD); Grafting; Antibacterial textile

1. Introduction

Cyclodextrins are toroidal-shaped cyclic oligosaccharides with a hydrophilic outer surface and an internal hydrophobic hollow interior, which can entrap a vast number of lipophilic compounds into their hydrophobic cavity, depending on their size and molecular structure. The remarkable ability of cyclodextrins to include hydrophobic compounds has been exploited in several fields, spanning from pharmaceuticals to cosmetics, from food manufacturing to commodity (Jimenez Sanchez, 1997; Nakajuma & Hirobasbi, 1984; Vaios, Karathanos, & Ioammis Mourtzinos, 2007). In textile field, a novel functional surface treatment of cotton based on the permanent fixation of β-cyclodextrin on fabric is receiving increased attention (Buschmann, Denter, & Knittel, 1988; Wang & Chen, 2004, 2005). Some literatures have demonstrated that cyclodextrin fixed to cotton did not affect the hydrophilic properties of cellulose and the immobilized cavities of cyclodextrins did not lose their complexing power to form inclusion complexes with other molecules (Buschmann, Denter, & Knittel, 1995; Lo Nostro & Frantoni, 2002).

In our previous works, the inclusion complex between miconazole nitrate and β-cyclodextrin was found to be formed. The antibacterial textiles can be obtained by treating the prepared inclusion complexes onto the cotton fabric with bonder, but unfortunately, the treated fabric was stiff. The undesirable hand feeling might be overcome when not using the bonder, but instead of covalent binding (grafting) of the modified β-cyclodextrin to the cloth surface.

This study describes the chemical grafting of monochlorotriaziny β-cyclodextrin (MCT-β-CD) onto cellulosic fabric. MCT-β-CD was selected for its commercial availability and having no irritating or sensitizing effects (Reusher &

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Hinsenkorn, 1996). It contains an average of two to three monochlorotriazinyl groups that are able to from covalent bonds with nucleophilic groups, such as –OH in cellulose and this represents an efficient tool for surface modification of textiles (Denter & Schollmeyer, 1996; Lo Nostro, Frantoni, & Ridi, 2003). The antibacterial agent, miconazole nitrate was chosen for safety, high-efficiency and broad-spectrum antibacterial property, which performs the functions such as killing bacteria, diminishing inflammation and relieving tickle, etc. (National pharmacopeia committee, 2006). In addition, the present work also reports on the inclusion of miconazole nitrate into the β-CD cavities grafted onto the textile surface and the antibacterial property of the finished textile was then evaluated.

2. Experiment

2.1. Materials

Plain cotton fabric was obtained from Shanghai No. 1 dyeing and finishing factory. Miconazole nitrate (Fig. 1) was kindly provided by Zhejiang Shengda Pharmaceutical Co. Ltd. MCT-β-CD (Fig. 2) was purchased from Shanghai Chemical Reagent Co. Ltd. Sodium carbonate and all other reagents were of analytical grade. The water used was double-distilled and deionized.

2.2. Apparatus

High Performance Liquid Chromatography (HPLC-Waters 2695) (Waters Corporation, USA); Shimadzu-3000 ultraviolet spectrophotometer (UV-3000) (Shimadzu Corporation, Japan); Aspetic operating board 4HC-24 (Sun-great Technology Co., Ltd., Shanghai, China); vacuum oven and ultrasonicator (Precision apparatus factory, Shanghai, China).

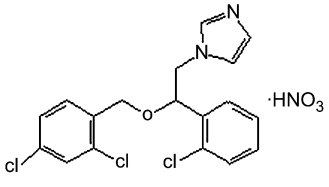

Fig. 1. The structure of miconazole nitrate.

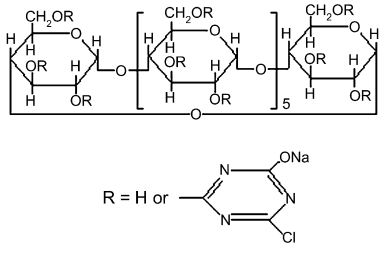

Fig. 2. The structure of MCT-β-CD (sodium salt).

2.3. Grafting of cellulose fabric with MCT-β-CD

MCT-β-CD is a reactive cyclodextrin capable of forming covalent bonds with nucleophilic groups. The following approach to bond MCT-β-CD onto the cellulose fabric was developed based on the method by Rehmann, Yoshii, and Furuta (2003).

The procedure (Fig. 3) consisted in soaking the fabric samples (typically 4 cm × 4 cm) for 5 min at room temperature in an aqueous solution of MCT-β-CD (80 g/L) and catalyst Na_2CO_3 (50 g/L) under magnetic stirring (the liquor ratio 1:20). The samples were then squeezed to remove the excess solution to wet pickup 70–80%, and dried under vacuum at 50 °C in a vacuum oven. To minimize the reaction of MCT-β-CD with air moisture, the impregnated samples were cured in an oven at 150 °C for 3 min at atmospheric pressure (dry heat) for a thermal fixing reaction. The resulted fabric was then washed under running water for 10 min to remove any unreacted MCT-β-CD and dried in vacuum for 8 h at 60 °C. The quantity of MCT-β-CD bonded to the cellulose fabric was estimated by the weight difference of the sample of fabric before and after the fixing process described. Conveniently, MCT-β-CD bonded cellulose fabric will be designated hereafter as MCT-β-CD-fabric.

2.4. Impregnation of grafted cotton fabric with miconazole nitrate

Modified and unmodified fabric samples were treated with antibacterial agent by dipping the textiles at room temperature for 2 h under stirring in ethanol solution containing 5% (w/v) of the miconazole nitrate with a liquor ratio 1:10. The samples were then roll-squeezed and washed three times with 30% (v/v) ethanol–water solution to remove the absorbed antibacterial agent from the fabric surface and then rinsed with running tap water for 10 min. The modified and unmodified fabrics, as well as the samples impregnated miconazole nitrate were characterized by spectrophotometric analysis.

2.5. Extraction of miconazole nitrate from fabric

The extraction solutions were obtained by cutting sections (2.5 cm × 2.5 cm) of cloth from the modified and unmodified fabric samples impregnated miconazole nitrate. The cloth strips were accurately weighted, cut into small pieces and extracted with ethanol (10 mL) under stirring at 70 °C for 10 min. The extraction was repeated with fresh solvent and the combined ethanol fractions were adjusted to volume (20 mL). A portion of the resulting suspension was filtered through 0.45 μm membrane filters and analysed for miconazole nitrate by HPLC described as below.

2.6. Analysis of included miconazole nitrate by HPLC

The HPLC apparatus consisted in a Model LabFlow 3000 pump, a Model 7125 injection valve with a 10 μL

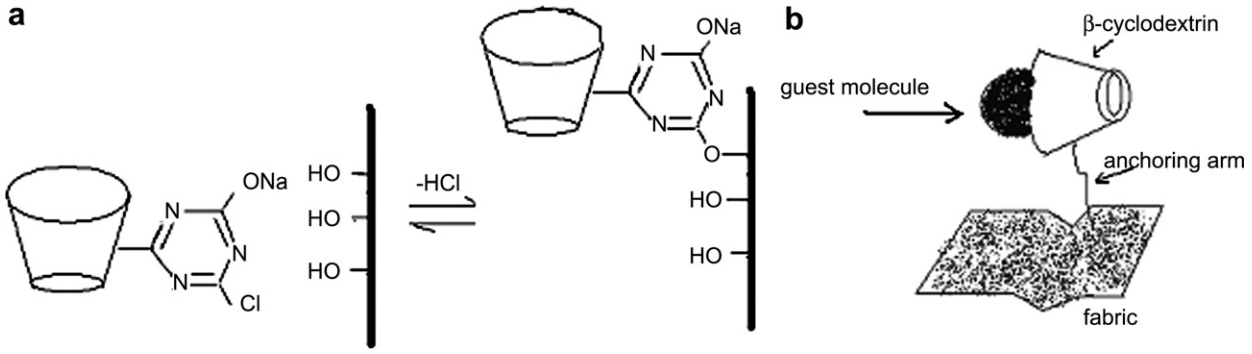

Fig. 3. Chemical grafting of MCT-β-CD onto a cellulosic fibre (a). Scheme of host-guest inclusion complex grafted on the textile surface (b).

sample loop and a Model 975-UV variable wavelength UV–vis detector set at 318 nm. Date acquisition and processing were accomplished with a personal computer using Borwin software. Sample injections were performed with a Model 701 syringe (10 μL). Separations were performed on a 5-μm Zorbax SB-CN column (150 mm × 3.0 mm) eluting isocratically, at a flow rate of 0.4 mL/min, with methanol–acetonitrile–water (40:25:35, v/v/v). Chromatography was performed at room temperature. The identity of the miconazole nitrate peak was assigned by co-chromatography with the authentic standard. Quantification was carried out by integration of the peak areas using the external standardization method.

2.7. Antibacterial property of the fabrics loaded miconazole nitrate

The determination of antibacterial property of the different fabric samples were carried out according to the Downing's shaker flask method. Three kinds of fungus – *Candida albicans*, *Aurococcus* and colon bacillus were selected to investigate the antibacterial property of miconazole nitrate impregnated into the fabric. In addition, in order to investigate the durability of antibacterial performance, the washing fastness of antibacterial fabrics was also tested after washing 0, 5 and 10 times with 2 g/L soap solution at 60 °C for 10 min.

3. Results and discussion

3.1. Characterization of MCT-β-CD modified fabric

Plain cotton fabric or the fabric functionalized with MCT-β-CD (Fig. 3) was charged with miconazole nitrate, carefully rinsed (see Section 2) and subjected to spectrophotometric analysis (Fig. 4).

The UV spectra have been ordered in the vertical direction in order to avoid overlapping of the profiles and improve the clarity of the plot. The ethanol solution containing 5.0% miconazole nitrate (open circles) showed the typical peaks at 272, 280 and 318 nm. The untreated fabric

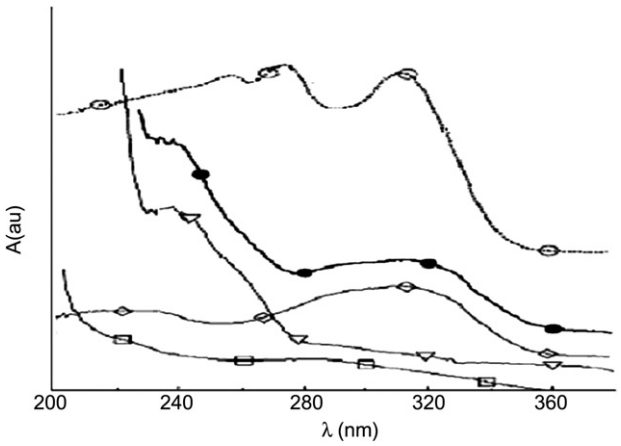

Fig. 4. UV spectra of: (⬭) miconazole nitrate (5%) in ethanol; (□) untreated cotton fabric; (○) fabric loaded with miconazole nitrate; (▽) fabric grafted with MCT-β-CD; and (●) fabric grafted with MCT-β-CD and loaded with miconazole nitrate.

sample (squares) gave almost no absorption between 220 and 360 nm. The fabric that was simply coated with miconazole nitrate (diamonds) revealed the presence of miconazole nitrate through the main peak at 318 nm. After grafting with MCT-β-CD, the textile (open downward triangles) exhibited a significant absorption below 280 nm, with a maximum around 230 nm, due to the triazinyl chromophore (Lo Nostro et al., 2003). The MCT-β-CD grafted sample treated with miconazole nitrate (bole line, full circles) showed the typical peaks of the MCT-β-CD-grafted textile at lower wavelengths and a small bathochromic shift to 322 nm for the main peak of miconazole nitrate (see Fig. 4). The red shift can be ascribed to the more hydrophobic environment experienced by miconazole nitrate and suggested the formation of the host-guest inclusion complex between miconazole nitrate and MCT-β-CD at the fabric's surface.

3.2. Factors influencing the amount of MCT-β-CD bonded to fabric

The quantity of MCT-β-CD on the fabric was determined by gravimetric measurements. The amount of

MCT-β-CD bonded on the fabric was mostly dependent on the MCT-β-CD concentration, the catalyst concentration, the curing temperature and the curing time.

The concentration of MCT-β-CD in aqueous solution influenced the bonded amount on the fabric, as shown in Fig. 5. An almost linear increase against the concentration was founded.

Fig. 6 shows the effect of catalyst concentration on the bonded MCT-β-CD to the fabric. The rate of weight gain of the fabric grows with Na_2CO_3 concentration increasing. But it decreases when Na_2CO_3 concentration is over 60 g/L. The reasons may be the hydrolysis of MCT-β-CD at a higher pH.

The effect of temperature is shown in Fig. 7. The bonded amount of MCT-β-CD was nearly proportional to the heating temperature between 100 and 180 °C. However, the high temperature may be harmful for the fabric and the degree of whiteness of fabric decreases. So, 150–160 °C is a suitable temperature span.

The time of heat treatment was also investigated. The longer the treated time, the more the amount of bonded miconazole nitrate onto the fabric. Fig. 8 demonstrates the trend of the rate of weight gain with extending the time.

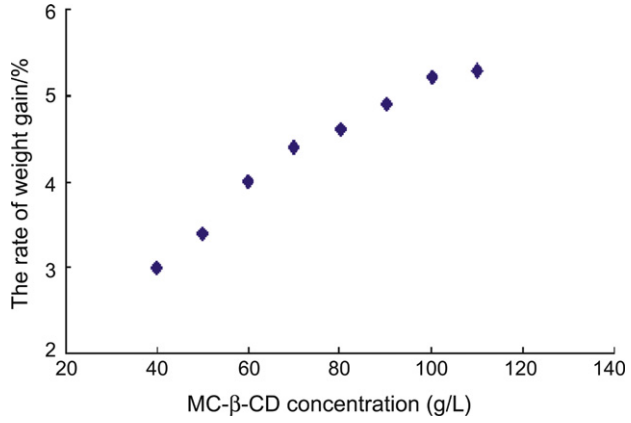

Fig. 5. Influence of MCT-β-CD concentration on the rate of weight gain. Other conditions are Na_2CO_3 50 g/L curing temperature 150 °C and curing time 3 min.

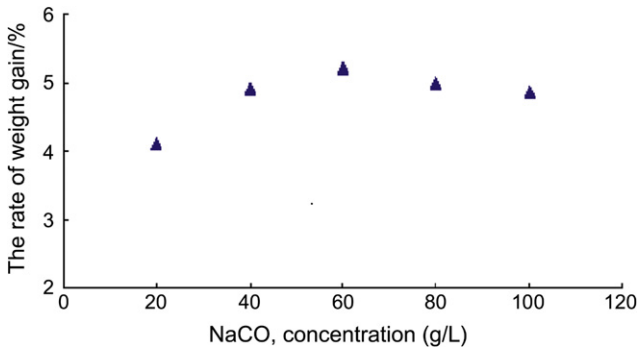

Fig. 6. Influence of Na_2CO_3 concentration on the rate of weight gain. Other conditions are MCT-β-CD 80 g/L curing temperature 150 °C and curing time 3 min.

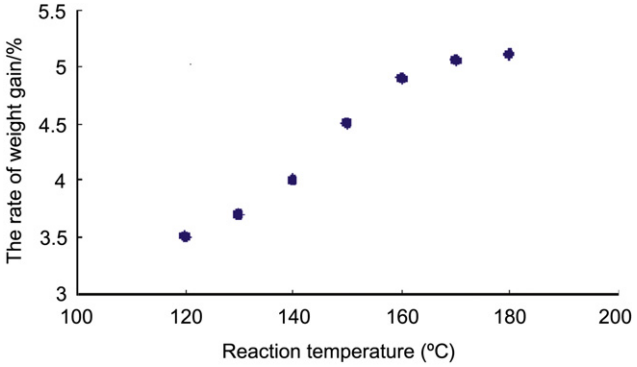

Fig. 7. Influence of reaction temperature on the rate of weight gain. Other conditions are MCT-β-CD 80 g/L, Na_2CO_3 50 g/L and reaction time 3 min.

From it, we can see 6–8 min is enough to obtain the desirable result.

Considering these influences mentioned above, we obtain the suitable bonded reaction conditions, that is, MCT-β-CD 60–100 g/L, Na_2CO_3 50–60 g/L, the reaction temperature 150–160 °C and the reaction time 5–8 min.

3.3. The content analysis of miconazole nitrate impregnated into fabric by HPLC

In order to quantify the actual amount of miconazole nitrate entrapped into the different fabric (unmodified cotton fabric and MCT-β-CD-fabric), the antibacterial agent miconazole nitrate was extracted from the fabric specimen and assayed by HPLC. Several parameters affecting the release of miconazole nitrate from the textile material were examined, including different liquid solvents (i.e., methanol, ethanol, acetonitrile), the use of mixing or ultrasonication, extraction temperature and time. The highest miconazole nitrate levels were produced by two sequential 10 min extractions of the fabric in ethanol at 70 °C, under magnetic stirring. The recovery of miconazole nitrate from the fabric was evaluated by subjecting the sample, processed according to the method outlined

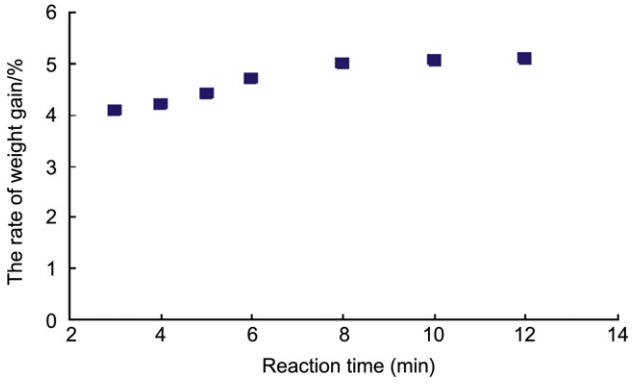

Fig. 8. Influence of reaction time on the rate of weight gain. Other conditions are MCT-β-CD 80 g/L, Na_2CO_3 50 g/L and curing temperature 150 °C.

above, to Soxhlet extraction with ethanol for 6 h. Less than 9.3% of the total miconazole nitrate content remained in the textile material (as determined by Soxhlet extraction and HPLC analysis), thus indicating a satisfactory extraction efficiency. In the unmodified tissue impregnated with miconazole nitrate, the concentration of antibacterial was $(0.056 \pm 0.013)\%$ (w/w), while the concentration measured in the MCT-β-CD-fabric was $(0.458 \pm 0.072)\%$ (w/w). The high dispersion of miconazole nitrate assay results can be probably traced to the non-homogeneous structure of the fabric surface. In addition, according to the producer's specification, one or more (two or three) triazinyl groups can be bound to a single cyclodextrin macrocycle (Fig. 2). Since it is the triazinyl chlorine atom, which reacts with the nucleophilic residues (e.g., hydroxyls, amines) present in the textile fibres (Fig. 3), also the number of anchoring arms between the hosting species and the fabric can be variable. However, the MCT-β-CD-fabric markedly enhances its antibacterial agent retention capacity (8.2-fold increase) compared to the unmodified fabric.

3.4. Antibacterial property of the treated fabrics

The antibacterial fabrics can be obtained by means of the method 2.4. The antibacterial abilities were tested using shaker flask method, and the results are shown in Fig. 9.

From Fig. 9, we can see the antibacterial activity of MCT-β-CD-fabric is much higher than that of the unmodified fabric. This phenomenon was resulted from the different existing forms of antibacterial agents on the fabrics. For the MCT-β-CD-fabric, the antibacterial agents were included in the cavities of β-CD. While absorbed physically for the unmodified fabrics, which made the antibacterial agents easy to wash from the fabric. Based on this, the durability of antibacterial property of the former is much better than the later. The antibacterial abilities of MCT-β-CD-fabric still kept more than 70% even after washing 10 times, while the antibacterial activity was almost lost for the unmodified fabric. In addition, the activity of anti-*Candida albicans* is a litter better than that of anti-*Aurococcus* and anti-colon bacillus.

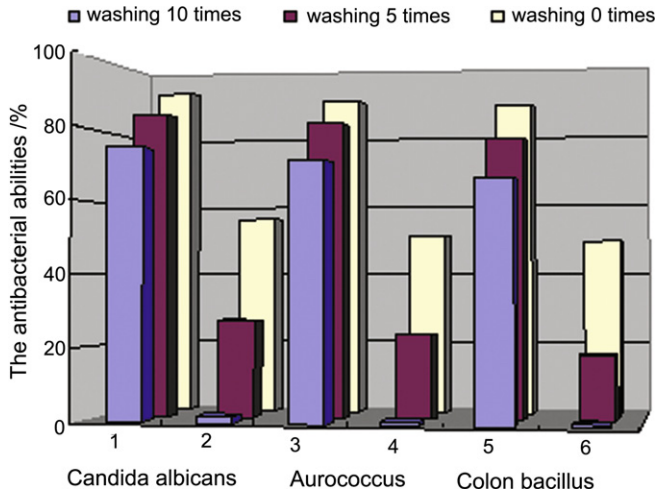

Fig. 9. Influence of washing times on the antibacterial abilities 1,3,5 – MCT-β-CD fabric loaded antibacterial agent 2,4,6 – unmodified fabric loaded antibacterial agent.

4. Conclusions

The results reported in this study demonstrate that textile finishing with MCT-β-CD increases the uptake of antibacterial agent, miconazole nitrate by the tissue material, thereby enhancing the antibacterial properties of the clothing fabrics. In addition, the covalent binding of β-CD to the textile fibres improves the resistance of the entrapped antibacterial agent to washing cycles, prolonging the antibacterial effect afforded by the fabric. The chemical grafting of cyclodextrins onto cotton fibres represents a useful strategy for the production of antibacterial clothing.

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