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Wool Fabric Treated with Eco-Friendly Insect Repellent

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Abstract
In the research work presented, fabric made of wool was grafted with β-cyclodextrine (β-CD) using 1, 2, 3, 4 butanetetracarboxlic acid (BTCA) as a polyfunctional reagent. To reduce the grafting curing temperature, which could damage the wool fabric if too high, cyanamide (CA) in combination with ammonium dihydrogen phosphat (ADHP) were used as catalysts. The presence of cedar oil applied onto textile materials was determined by ATR FT-IR spectroscopy, as well as estimation of the add-on of cedar oil with the gravimetric approach, respectively. Finally the reduction in moths after being exposed to wool treated with a separate treatment formulation i.e. β-CD, cedar oil, and β-CD in combination with cedar oil was assessed visually after different time periods. Results showed that the wool after being treated with β-CD in combination with cedar oil shows significantly prolonged moth oppression activity compared to the wool treated with cedar oil only.

Key words: *wool, β-cyclodextrine, cedar oil, spectroscopy, gravimetry, moths.*

Introduction

Insect repellent is a substance usually applied to skin, clothing or other surfaces which discourages insects from landing or climbing onto those surfaces. Synthetic repellents, such as paradichlorobenzene (PDCB), tend to be more effective than 'natural' ones, but on the other hand they are usually toxic. However, some plant-based repellents are comparable to synthetic ones, and in some cases – depending on the type – are even better. Cedar oil is often used for its aromatic properties, especially in aromatherapy. It is also used as an insect repellent. In general, essential oil repellents tend to be short-lived in their effectiveness due to their volatile nature. There is interesting supramolecular chemistry which involves some intermolecular interactions where covalent bonds are not established between the interacting species i.e., molecules, ions, or radicals, respectively, as is the case in the example presented regarding wool treatment with CDs. Thus capsulation is considered a possible way to assure time-prolonged evaporation of essential oils from textile material, which was also the idea of the research work presented. The majority of these interactions are of the host-guest type. Among all potential hosts, cyclodextrins (CDs) seem to be the most important ones [1, 2]. CDs are seminatural products that are obtained from renewable natural materials, starch, or by a relatively simple enzymatic conversion. They are produced in thousands of tons per year by environmentally friendly technologies at an acceptable price. CDs can form inclusion complexes with various small molecules. This "molecular capsulation" is already widely utilized in many industrial products, technologies and analytical methods. In general, CDs are non-toxic, and any possible toxic effect is of secondary character and can be eliminated by selecting an appropriate CD type, derivative or mode of application, meaning that CDs can be consumed by humans as ingredients of medicines, foods, or cosmetics.

Cyclodextrins have a ring structure (***Figure 1***) which allows them to act as hosts and form inclusion complexes with various small molecules. Such complexes can be formed in a solution or solid state. In the case where CDs are applied onto a textile surface, they can act as permanent or temporary hosts to small molecules. According to the activity of capsulated small molecules, certain desirable functionality of textile, such as fragrance release or antimicrobial activity, can be performed [1-6]. CDs can be applied onto the surface of a potential textile substrate by using e.g. a conventional pad-dry procedure, but there is always a big concern that it must be fastened onto the surface as much as possible. For this purpose, polycarboxylic acids are very interesting for use as formaldehyde-free cross-linkers.

Polycarboxylic acids

Polycarboxylic acids such as 1, 2, 3, 4 butanetetracarboxlic acid (BTCA) are well known non-formaldehyde crosslinking reagents for the durable press finishing of cellulose materials. BTCA has four carboxylic acidic groups, which can react

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with various hydroxyl groups of cellulose, thus forming stable ester bonds. Esterification of hydroxyl groups can occur with heat alone, or it can be accelerated by the presence of catalysts, which are usually salts of weak acids. In this way, the curing temperature can be reduced from 200 °C to 160 °C [7-10], which is an interesting fact considering that this method is also appropriate for wool, or wool mixed with polyethyleneterephthalate fibre (PET) treatment in order to consolidate a selected substance onto such surfaces where esterification is not possible. Due to the fact that PES is a synthetic fibre-forming polymer, it is considered that a temperature of 160 °C seems to be too high to treat this type of fibre [12]. This phenomenon is also stated within our previous research, therefore by inclusion of β-cyclodextrin in the system with BTCA and supported by appropriate catalysts, it was possible to achieve a satisfactory result of crosslinking by using a significantly lower temperature of curing (app 115 °C) [13, 14]. For this purpose the use of cyanamide (CA) with ammonium dihydrogen phosphat (ADHP) in combination with BTCA seems to be an excellent combination to achieve successful treatment efficiency/crosslinking [13-16].

This phenomenon is also confirmed by other literature sources [5 11, 16], where nanocapsules of (β-CD molecules) and microcapsules (ethyl cellulose microcapsules) were linked to hydroxyl groups of cotton cellulose using BTCA, confirming permanent linking of the compounds used to cellulose through the formation of stable ester bonds.

Starting from this, the current research comprises the method of beta-cyclodextrin (β-CD) grafting onto wool fabric using a polyfunctional reagent: 1, 2, 3, 4-buthanetertacarboxylic acid (BTCA), which is one of the very rare approaches when considering wool treatment with BTCA. With the aim to reduce the grafting curing temperature, cyanamide (CA) and ammonium dihydrogen phosphat (ADHP) were used as catalysts. Wool fabric treated with β-CD using BTCA as a cross-linker was further treated with cedar oil, which is known for being a natural insect repellent [17]. Cedar oil, which can be used as an environmentally-friendly moth repellent reagent, together with ß-CD that is attached onto a textile substrate, forms a complex from which it can be slowly released. Wool containing

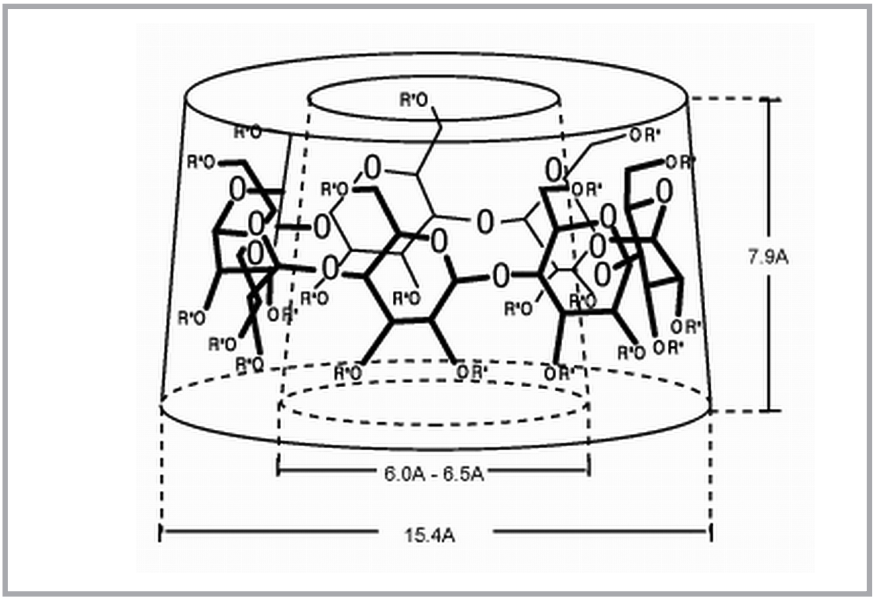

Figure 1. *Structure of β-cyclodextrin [13].*

β-CD after being subsequently treated with cedar oil showed prolonged insect resistance activity compared to those textile materials made of wool that were treated solely with cedar oil.

Experimental

Textile material

100% wool fabric, plain weave, fabric weight – 196.90 g/m^2, producer MERINKA d.o.o., Tovarna volnenih tkanin Maribor, Slovenia.

Chemicals

All chemicals used in this work are as follows: β-cyclodextrin (β-CD), 1, 2, 3, 4-butanetertacarboxylic acid (BTCA), Cyanamid (CA), Ammonium dihydrogen phosphat (ADHP) and 1-metyl-etyl-tetradekanoat, of analytical grade, supplied by Aldrich. A commercial product of cedar oil (Producer: Egorov Vladimir, Tomsk, Russia) was used.

Fabric treatment

Wool fabric samples were treated with β-CD and BTCA, and to reduce the curing temperature CA was used, with ADHP being added as a proton donour. Concentrations in the treated baths varied (***Table 1***). From the preliminary studies (not shown in this paper) optimum results were obtained when textile materials were immersed in treating baths containing 8% of ß-CD, 6% of BTCA, 5% of CA & 1% of ADHP (pH of the bath was 2.3), where the wet pick-up was 100%, and all impregnated textile substrates were pre-dried at 100 °C for 10 minutes. Thermo-fixation was carried out at 115 °C for 3 min. The weight gain of the finished fabrics was measured to yield the efficiency of the treatment according to standard test method DIN 53814. The washing of textile materials was preceded at 40 °C by standard test method ISO 105-C10:2008. ***Table 1*** shows details of the concentrations of β-CD, BTCA and catalysts (CA, ADHP) within the finishing baths.

The bonding of β-CD onto textile materials using BTCA was proved by means of ATR FT-IR spectroscopy [5, 15].

β-CD treated wool fabric and untreated wool fabric were further treated with cedar oil. For this purpose, textile substrates

Table 1. *Concentrations of β-CD, BTCA and catalysts (CA and ADHP) within finishing baths.*

Conc. of β-CD, %	Conc. of BTCA, %	Conc. of CA, %	Conc. of ADHP, %
8	2	5	1
8	4	5	1
8	6	5	1
8	8	5	1
8	10	5	1

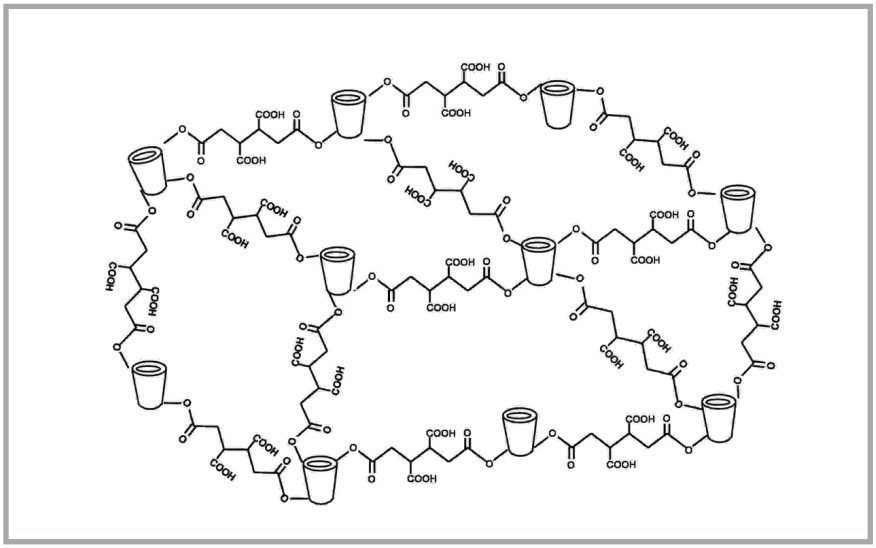

Figure 2. *Supramolecular assembly between β-CD and BTCA [13].*

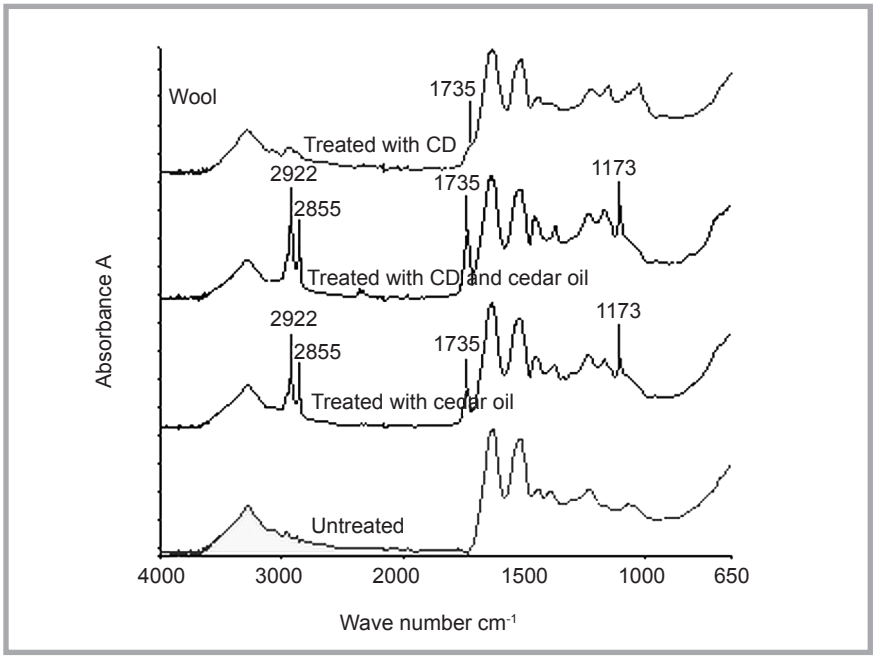

Figure 3. *ATR FTIR spectra of β-CD treated wool fabric, wool treated with β-CD and post-treated with cedar oil, wool fabric treated with cedar oil only, and the spectrum of untreated wool fabric.*

were immersed in a mixture of cedar oil and 1-methyl-ethyl-tetradecanoat in a weight ratio of 1:1 and stirred at room temperature. After 8 hours of stirring, the textile materials were dried at room temperature. The presence of cedar oil on the textile materials was determined using ATR IR spectroscopy. Spectroscopy was carried out using a Perkin-Elmer Fourier Transform infrared (FTIR) spectrophotometer with a Golden Gate attenuated total reflection (ATR) attachment with a diamond crystal. Resolutions of all spectra was 4 cm^{-1} and 100 scans were collected for each measurement.

The resistance of wool to the larvae of moths [18] was determined as well following in-vivo observation. Wool samples treated with β-CD and afterwards treated with cedar oil were exposed to 4 larvae of moths. The control specimens were wool samples treated with cedar oil, and untreated wool samples. The natural environment was simulated, where each of three specimens (2.5 g of β-CD/ cedar oil treated wool, cedar oil treated wool and untreated wool) were inserted into glass jars and kept in a dark place at ambient temperature and humidity for 56 days. Visual assessment regarding damage and larval condition was performed.

Results and discussion

Gravimetrical method

The mass gain of 9% was obtained when wool textile material was treated with the β-CD/BTCA system using the thermos-fixation method (treating bath: 8% ß-CD, 6% BTCA, 5% CA, 1% ADHP). When lower concentrations of BTCA as a binder were used, the mass gain after the treatments was less than 9%. A different trend is seen with concentrations higher than 6% of BTCA within the treatment bath, where the mass gain did not change significantly. Hence it is anticipated that the optimal concentration of BTCA that should be used within the finishing bath is 6%. As reported in [14], a supramolecular assembly was formed between β-CD and BTCA, and such an assembly was physically anchored onto the textile substrate's surface simultaneously. ***Figure 2*** schematically presents the assembly of nanocapsules linked via ester bonds of BTCA.

Further treatment of wool with cedar oil

Wool fabrics treated with nanocapsules were further treated with cedar oil. The presence of cedar oil on the wool textile substrate treated with cedar oil and on that containing the supramolecular assembly of β-CD/ BTCA and cedar oil was determined by ATR IR spectroscopy. ***Figure 3*** presents ATR IR spectra of wool fabric treaded with β-CD, wool fabric treated with β-CD and post-treated with cedar oil, wool fabric treated with cedar oil, and untreated wool fabric.

In the spectra of fibres treated with β-CD and post-treated with cedar oil, it is possible to see a peak at 1736 cm^{-1}, which could be due to the C = O bond of α- and γ-atlantone. These atlantones are two major components of cedar oil. The same peak appears in the spectra of pure cedar oil introduced onto the textile substrate. Similarly peaks around 2924 cm^{-1} appear in the spectrum of fibres treated with β-CD and subsequently treated with cedar oil and in that of the textile substrate treated with pure cedar oil only; this peak could be due to the CH groups of components that are a part of cedar oil. By comparing the spectrum of cedar oil introduced onto the textile substrate where characteristic peaks at 1736 cm^{-1} and

around 2924 cm^{-1} appear in the spectrum of wool fibres treated with nanocapsules and post-treated with cedar oil, it can be concluded that cedar oil is actually present in the case of the textile material treated.

With ATR FT-IR spectroscopy it is not possible to determine if cedar oil is deposited onto textile materials, or if there is also a complex formation among β-CD bonded to wool fibres and the cedar oil molecule. Therefore, subsequently, an experiment where wool substrates were exposed to moth larvae was performed.

Determination of resistance to insects (moths)

The size of the wool sample was of dimensions of 20 x 20 cm, and three moth larvae were added to it. Each test specimen was examined, any visible damage to the textile materials, detected, and the larval conditions reviewed.

No visible damage was observable to the naked eye when β-CD/cedar oil treated wool was exposed to a moth colony for 2 months. In the control (wool samples treated with cedar oil only) no damage was observed for the first few days; the larvae even died after a few days, similar to the experiment where larvae were exposed to β-CD/cedar oil treated wool. After new larvae were added to the wool textile, the β-CD/cedar oil treated wool was still active, but in the control samples the cedar oil had evaporated and the wool cloth was not protected anymore. In contrast, when cedar oil was encapsulated into the β-CD cavity, evaporation was hindered and resistance to insect activities by cedar oil remained. Regarding longer resistance activities to moths (2 months if compared to the control; the resistance lasted 3 days only) it could be presumed that molecules of cedar oil form complexes with β-CD cavities. The mechanism of prolonged insect resistance activity is the evaporation hindrance of cedar oil.

Conslusions

The research work presented deals with wool treated with nanocapsules. The molecules of BTCA crosslinked hydroxyl groups of β-cyclodextrins form a network which is simultaneously and physically anchored onto the surface of the textile substrate. Wool fibres treated in such a way were post-treated with cedar oil. The presence of cedar oil on textile materials was determined using ATR IR spectroscopy. When β-cyclodextrin treated textile materials were treated with cedar oil, the prolonged insect repellent activity of cedar oil was observed, and thus we could conclude that cedar oil was encapsulated into the β-cyclodextrin cavity, which hinders the evaporation of the oil.

The main driving force for complex formation is the release of enthalpy-rich water molecules from the cavity. Water molecules are displaced by a more hydrophobic guest, cedar oil molecules. It is established that such treatment could increase the price of the modified impregnation in the range of about 3-5% when using chemicals with a very high grade of purity.

Table 2. *Estimation of damage to wool and larval conditions according to the time of the exposure.*

Time	β-CD/cedar oil treated wool	Cedar oil treated wool	Untreated wool
After 48 hour	No detectable damage	No detectable damage	Very slight visible damage
	Larval conditions:live	Larval conditions:live	Larval conditions:live
After 72 hour	No detectable damage	No detectable damage	Moderate visible damage
	Larval conditions: dead	Larval conditions: dead	Larval conditions: live
After 7 days	Addition of new larvae	Addition of new larvae	–
After 14 days	No detectable damage	Very slight visible damage	Very heavy damage
	Larval conditions: dead	Larval conditions: live	Larval conditions: live
After 56 days	No detectable damage	Moderate visible damage	Very heavy damage
	Larval conditions: dead	Larval conditions: live	Larval conditions: live, pupating

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