Digitally Finished Cyclodextrin Based Controlled Release Functionality For Cotton Textiles

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Abstract

Digitally finished functional fabric with monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) for controlled release functionality has been produced with good wash fastness resistance. Optimization exercise has been conducted in terms of maximum loading of MCT-β-CD on cotton fiber surface, time and temperature for curing. The maximum amount of MCT-β-CD on the fabric sample achieved is 2.585 g/m^2 out of 3.2 g/m^2 delivered on the surface by drop-on-demand inkjet print head. Based on this a digital process for controlled release functionality has been proposed. Release kinetics of model drugs e.g. Aspirin and Ibuprofen were studied from β-Cyclodextrin textile by applying several external stimuli such as change in pH, electrolyte and phenolphthalein.

Key Words: *Functional textiles, inkjet technology, slow release textile, β-Cyclodextrin, chemical grafting,*

Introduction

Digital microdisposal has the ability of exact localization and patterning of functionalities in textile substrates ultimately leading to multifunctional materials with advanced functionalities. The main objective is to develop the technologies needed to create slow and controlled release systems suitable to be micro-disposed/patterned by inkjet technology on common textile substrates. Cotton based textile materials are versatile and widely used. Properties and functionalities of such materials are affected by physical-chemical treatments at micro, nano, meso and macroscopic levels. The open permeable structure and large surface area makes textile materials a useful basis to bring new functionalities [1]. An enormous progress over the years in supramolecular chemistry, nano-biotechnology, and polymer technology development of high performance functionalized textiles is evitable. This manuscript will essentially focus on aspects of functional slow-controlled release textiles bearing cyclodextrins.

Cyclodextrins have been selected as host system because of their ability to form inclusion complexes with a variety of long-chain aliphatic or aromatic molecules [2]. Cyclodextrins belongs to a family of cyclic oligosaccharides, composed of 5 or more α-D-glucopyranoside units linked 1->4, as in amylose. Most studies on the application of cyclodextrin based drug delivery systems focus on β-cyclodextrins. β-CD is licensed as food additive and available in large quantities. The cavity or the interior of the β-CD molecule is rather hydrophobic, whereas the outer surface is hydrophilic. The hydrophobic interior is mainly responsible for complex formation. Despite the hydrophilic character of the outer surface the solubility of β-CD is limited. Modification of the hydroxyl groups of the outer surface of the cyclodextrin can increase or decrease its solubility [3]. This manuscripts gives overall picture including attachment of host molecules e.g. β-CD to cotton fiber surface in a durable way, development of functional ink formulation for digital printing with drop-on-demand printhead and finally proof-of-principle by studying release kinetics of model drugs.

Materials and Methods

Textile Based Materials

The substrate used was industrially two sided singed, desized, scoured, bleached, 245 g/m^2 (±5%) plain woven 100% cotton fabric. The fabric sample was supplied by Ten Cate Technical Fabrics BV, the Netherlands. The uniformity of the fabric sample in terms of pore volume distribution (PVD) was ensured with an auto-porosimeter [4] to eliminate the effect of irregular or interconnected pores.

Chemical Grafting of MCT-β-CD on Cotton Fiber Surface

Permanent grafting of MCT-β-CD (monochlorotriazinyl-β-cyclodextrin) was carried out according to the procedure already reported in the literature [5]. Cavasol® - a MCT-β-CD was obtained from Wacker-Chemie, Germany and used as received.

Determination of Cyclodextrin Contents Grafted To the Fabric

The concentration of β-CD and MCT- β-CD grafted to the cotton fabric was determined by the phenolphthalein assay method, in which the color fading of an alkaline phenolphthalein solution is proportional to the quantity of the cyclodextrin derivative present [6]. This method is a modified for better stability by incorporating phenolphthalein in Na_2CO_3 solution. This way a single reagent assay was developed that eliminate variation caused by concentrated phenolphthalein solution. With the volume of solution (V) and the mass of the treated sample, the molar cyclodextrin concentration $C_{M(CD)}$ can be determined by eq. 1 in which M_{CD} is the mass of cyclodextrin in [mg], w_{fabric} is the weight of fabric in [g] and $Mw_{(CD)}$ is molecular weight of cyclodextrin in [g/ml].

$$C_{M(CD)} = M_{CD} / w_{fabric} \times Mw_{(CD)} \quad (1)$$

Results and Discussion

Attachment of β-CD Molecules on Cotton Fiber Surface

Attachment of β-CD molecules on cotton textile provides

hosting cavities that can include a large variety of guest molecules for specific functionality. Five different new and existing techniques (chemical gratings and enzymatic coupling) were evaluated for permanently connecting β-CD and its derivatives to cotton surface [2]. A comparison has been made in terms of maximum attachment of β-CD on cotton surface. Novel chemical based cross-linking with homo-bi-functional reactive dye (C.I. reactive black 5) and grafting with reactive MCT-β-CD show maximum attachment to cotton fiber surface. As depicted in Figure 1, MCT-β-CD is covalently linked to nucleophilic substrates, a cotton fiber surface by a condensation reaction [7].

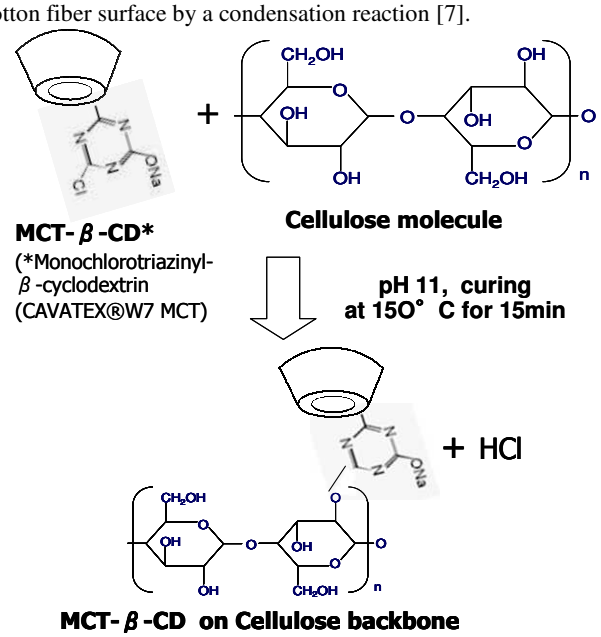

Figure 1: A schematic representation of chemical cross-linking reaction of MCT-β-CD on cotton fabric.

Tyrosinase mediated enzymatic coupling of especially synthesized 6-monodeoxy-6-mono(N-tyrosinyl)-β-cyclodextrin (Tyr-β-CD) on a textile surface is a very specific technique and can be done at low temperature [2]. Out of several grafting techniques attachment with MCT-β-CD was selected for ink formulation, because it is an easy and quick method with no requirements of spacers or other chemicals during the process.

MCT-β-CD Based Ink Formulation & Development of Digital Process

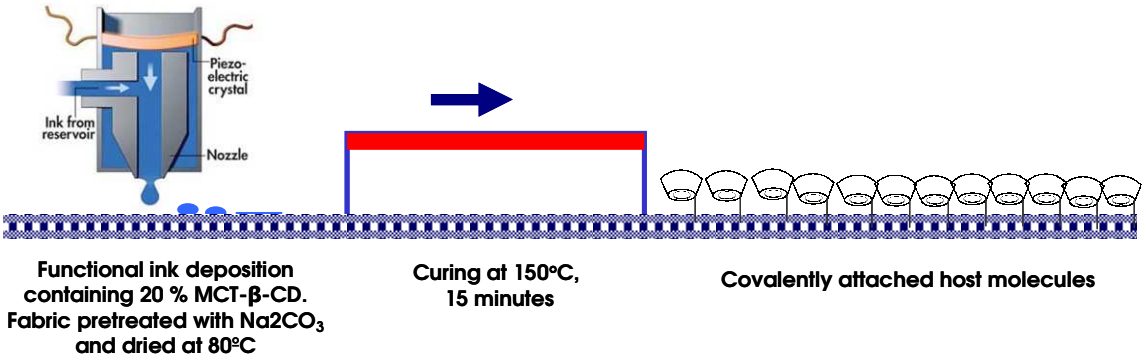

Figure 2: Optimization of digital finishing process for MCT-β-CD on cotton fabric.

Jet-able functional fluid formulation was made by adding host molecules e.g. cyclodextrin together with additives, surfactants, drying enhancers and binders in a right proportion. Aqueous based functional ink was prepared with 20% MCT-β-CD. All the additives that were used in the formulations are water soluble and chemically stable to provide extended shelf life. Ultimately the ink formulation was deposited via Xaar Omnidot 760 drop-on-demand print head. A single pass delivers nearly 1.6 g/m^2 and a double pass delivers 3.2 g/m^2 of MCT-β-CD on the cotton textile surface.

Several samples were prepared to get the best possible attachment results. There were two main variations, first is an alkaline pretreatment of cotton fabric; another is the time and the temperature of the curing. The digitally printed fabric samples were evaluated by phenolphthalein method to calculate the amount of cyclodextrin attached to the cotton substrate. The best result shows 94.2% and 80.78% of attachment achieve by single and double pass inkjet printing respectively. For best samples pretreatment with Na_2CO_3 was carried out in order to get alkaline environment of fabric surface. The optimum fixation time and temperature found was 15 min. at 150ºC respectively. A double pass treatment shows overall maximum attachment of 2.58 g/m^2 MCT-β-CD out of 3.20 g/m^2 delivered on the textile surface. Wash fastness experiments were carried out by immersing digitally finished textile samples with MCT-β-CD in boiling water at 100ºC for 15 min. It can be concluded that around 75% of β-CD is still available even after 5 wash cycle for the best treatment.

The diffusion time for MCT-β-CD was calculated in order to develop continuous digital printing and curing process. The diffusion time of MCT-β-CD in cotton fabric has been calculated to 8 min. and proven experimentally. Considering porosity of cotton fabric 0.5 and the molecular weight of MCT-β-CD is 1563. A schematic illustration of a continuous digital process for MCT-β-CD grafting and curing is given in Figure 2.

β-CD Based Slow- Controlled Release System

Aspirin (acetyl salicylic acid) and Ibuprofen (iso-butyl-propanoic-phenolic acid) were selected as model guest molecule to study the stimuli based drug release. A phase analysis /solubility studies reveal that both Aspirin and Ibuprofen forms 1:1 complex with β-CD. To study the release kinetics of the selected drugs, a two step approach has been adopted. Step 1 is to load both the drugs on digitally printed textiles bearing cyclodextrin and step 2 is to study the release of these drugs with several stimuli. Loading of selected drugs on digitally prepared textile bearing β-CD have been conducted by immersing fabric sample in to a saturated solution of Aspirin and Ibuprofen in Q2 water. The complexation

of the drugs with β-CD was monitored in terms of change in pH and conductivity (mV) of the solution. Samples were rinsed with dematerialized water and dried overnight before studying stimuli based drug release.

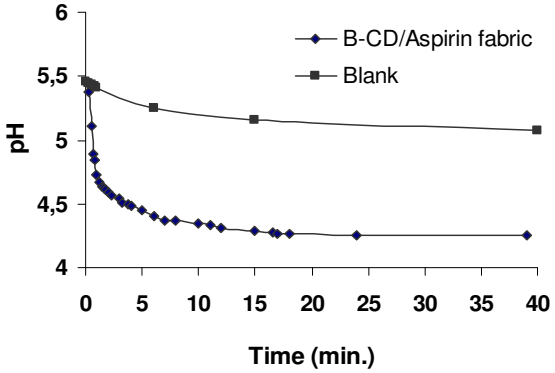

Figure 3: *Effect of strong guest molecule phenolphthalein on release of Aspirin loaded into β-CD cavities covalently attached to cotton fabric.*

Release kinetics for loaded guest molecules from textile bearing β-CD were conducted in four different conditions. 1) Release was monitored in Q2 water and considered as blank, 2) effect of pH, 3) electrolyte (100mM NaCl), and 4) 10mM phenolphthalein were studied for both Aspirin and Ibuprofen. The release progress has been monitored by studying change in pH and conductivity. To study the release kinetics in Q2 water, drug loaded samples of Aspirin and Ibuprofen were immersed in 70 ml of Q2 water and pH was monitored at regular interval of 15 sec. In contrast to Ibuprofen, there is almost no effect of Q2 water on release of Aspirin. It seems that Ibuprofen slowly start releasing even without any external stimuli. Effect of pH was monitored by adding 0.5 ml of 0.1M NaOH to 70 ml of Q2 water. This increases the pH of bulk to 11.2 for Aspirin and pH10.2 in case of Ibuprofen. The steady release of both the drugs into the bulk was observed as evident in terms of decrease in pH. The change in pH for aspirin larger than Ibuprofen, this may be attributed to partly hydrolysis of Aspirin into salicylic acid which is more acidic than Aspirin itself.

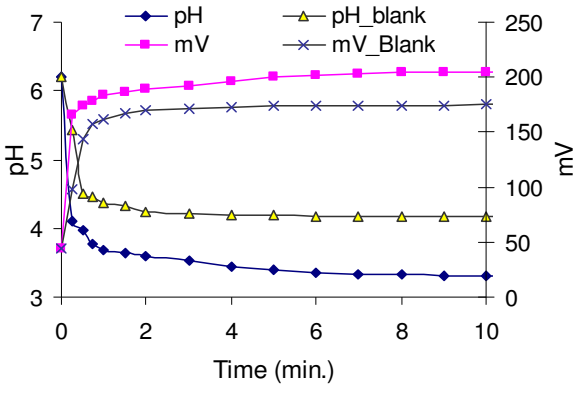

Figure 4: *Effect of electrolyte on release of Aspirin loaded into β-CD cavities covalently attached to cotton fabric.*

Phenolphthalein is a strong guest molecule for the β-CD and forms 1:1 complex. It was hypothesized that addition of phenolphthalein in bulk medium will quickly replace loaded Aspirin and Ibuprofen from β-CD fabric. To study this, 0.5 ml of 10 mM phenolphthalein was added to 70 ml of Q2 water containing loaded guest molecules samples. It takes less than 1 min. to release nearly 75% Aspirin, which is at least 3 times faster than release of Ibuprofen (Figure 4).

Effect of electrolyte was also studied by adding 100 mM NaCl to 70 ml of Q2 water. The results were monitored in terms of change in pH and conductivity (mV). It is clear that both Aspirin and Ibuprofen follows the same release pattern. However the release of Aspirin is faster compared to Ibuprofen, which as also observed earlier. For all blank samples there are hardly any difference in terms of release is observed.

Conclusions

Functional ink suitable for drop-on-demand print head has been formulated using 20% MCT-β-CD solution and jet-ability tested on cotton textiles. Digitally finished functional fabric with MCT-β-CD for controlled release functionality has been produced with good wash fastness resistance. Based on the finding, a digital process for controlled release functionality has been proposed. Stimuli based release kinetics of Aspirin and Ibuprofen were successfully studied from MCT-β-CD digitally attached to cotton textiles.

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Author Biography

Pramod graduated as a pharmacist, followed by a master's degree in Bioprocess Technology from University of Mumbai, India, and a PhD in 2005, from University of Twente, the Netherlands, in the field of Textile Biotechnology. Currently, he is leading a project on functionalization of textiles with inkjet technologies at the same university. He is the principal inventor of two international patents, and has many journal publications, journal referee, besides delivering several lectures at international conferences.