FINISHING COTTON AND SILK FABRICS WITH GLYOXAL-β-CYCLODEXTRIN COMPLEXES

INTRODUCTION

In the textile industry, the quality of fabrics have always been developed and improved to meet the requirements of customers. Better quality can mean more added value to the fabric. Finishing, the last step in the production of textile fabrics, is the process where the final fabric properties are developed. This operation can improve the appearance or usefulness of fabrics. As an additional benefit for the consumer, a great variety of special properties can be achieved in this step. Finishing is typically divided into two categories, chemical and mechanical. In chemical finishing, chemicals are used to change the fabric's aesthetic or physical properties such as durable press finishes using wrinkle resistant chemicals, hand modification using softeners, and repellent finishes using water or oil repellents. Whereas in mechanical finishing, mechanical devices are used to physically manipulate the desired fabric changes. Examples of mechanical finishing are compacting (shrink proofing), calendaring, and raising.

Recently, odor finishing has become an interesting research topic. Much research has been carried out to enhance this property in fabrics. Pleasant smell fabrics could benefit textile fabric manufacturing in many applications, for example, bed sheet, towel, handkerchief, sport wear and cloth used in the spa business. Pleasant fragrances can improve our mood and sense of well-being. For instance, the essential oil derived from lavender, one of the most versatile therapeutic essences, is used in aromatherapy to treat anxiety, difficulty sleeping, nervousness, and restlessness. Jasmine is used to produce a feeling of optimism, confidence and euphoria. Basil is used to relieve headaches and migraines.

The microencapsulation process has been introduced to the textile industry as a means of applying durable fragrances to textile fabrics. With microencapsulation, fragrances are able to remain on a garment over a longer period of time. Encapsulating fragrances in gelatin or synthetic capsules e.g. melamine and polyurethane can protect the contents from evaporation, oxidation, and contamination. The encapsulated fragrance is released by slow and progressive diffusion through the shell. To be successful in binding microencapsules to fibers chemically, a suitable binder must be used. This binder plays an important role for the microencapsule to survive washing. At present, we still have to order the encapsulated fragrance which is quite expensive from aboard. Since Thailand has abundantly pleasant smell plants, it should be useful if we can produce the encapsulated fragrance in the country.

In this study β-cyclodextrin, which is a cyclic oligosaccharide with benign toxicological and ecological properties, will be used to form inclusion complexes with vanillin. Vanillin will be in the cavity of β-cyclodextrin which has a hydrophobic characteristic. Vanillin vapor pressure should be reduced and its release should be more gradual and controlled. Glyoxal will be studied as a binder between β-cyclodextrin and the fabrics, silk and cotton. The durability of vanillin on both fabric types will be analyzed after finishing.

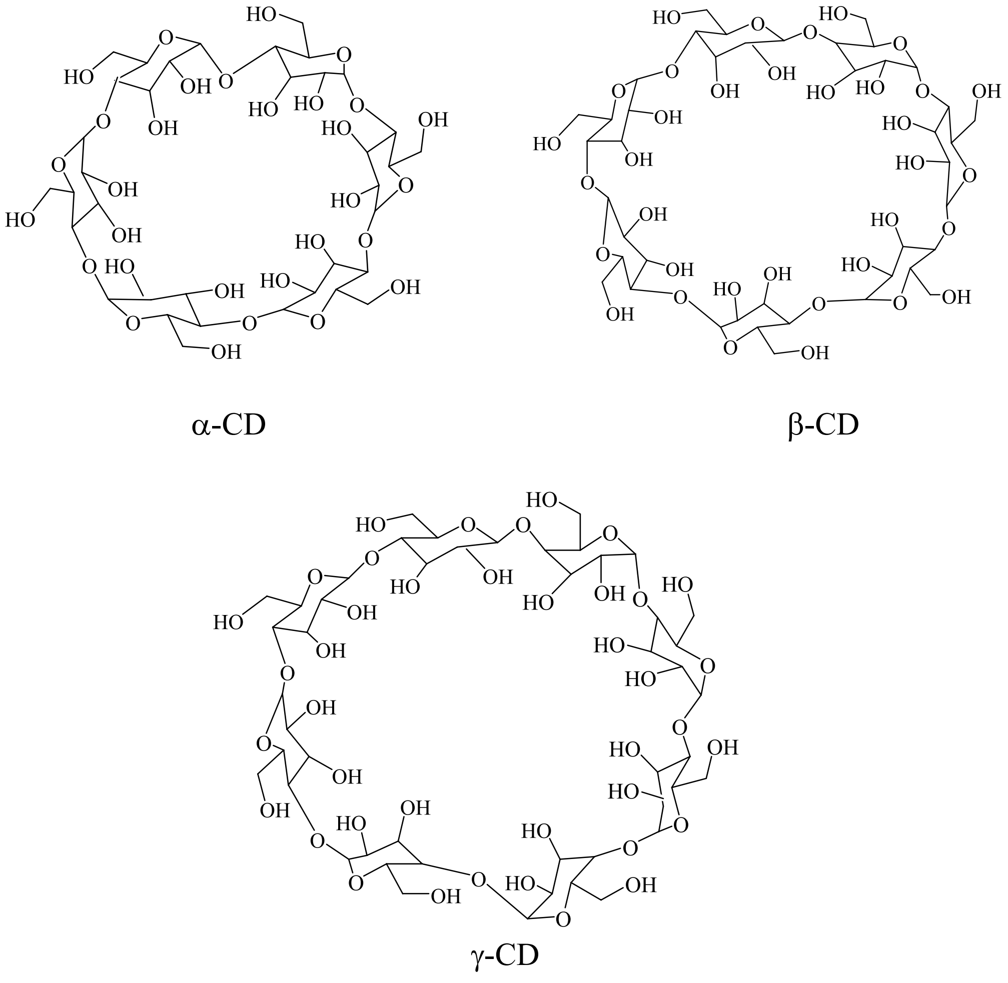
The objectives of this research are:

1. To study the preparation of glyoxal-β-cyclodextrin complexes.
2. To study the application of glyoxal-β-cyclodextrin complexes to cotton and silk fabrics by pad-dry-cure process.
3. To study and compare the results after finishing cotton and silk fabrics with glyoxal-β-cyclodextrin complexes which were vanillin durability and washfastness.

LITERATURE REVIEW

1. Structures and properties of β-cyclodextrin

Cyclodextrin (CD) was first discovered in 1891 by Villiers A. Compt Rendu. CDs were produced from starch by enzymatic degradation i.e. a cyclodextrin glucanotransferase enzyme (CGTase). In 1904, Schardinger characterized CDs as cyclic oligosaccharides that were composed of α-1,4-glycosidic linkages. Three types of CDs: α-CD, β-CD, and γ-CD were referred to as first generation or parent cyclodextrins. α-CD, β-CD, and γ-CD were composed of six, seven, and eight α-1,4-linked glucopyranose units, respectively, as shown in Figure 1 (Li and Purdy, 1992).



α-CD

β-CD

γ-CD

Figure 1 Chemical structures of α-, β- and γ-cyclodextrin.

CDs are viewed as torus or doughnut-shaped molecules. The primary hydroxyl groups (C_6) of glucopyranose units lie on the narrow rim and the secondary hydroxyl groups (C_2 and C_3) locate on the wider rim indicated in Figure 2 (Martin Del Valle, 2004). The cavity diameter and dimension of CDs depend on the number of glucose units as shown in Figure 3. The inclusion formation is principally affected by the geometric shape of the CD molecule rather than chemical interaction. This arrangement causes a CD molecule to have a hydrophilic outside surface and an apolar hydrophobic cavity (Hebeish and El-Hilw, 2001). The result of this cavity makes CD capable of forming inclusion complexes with a large variety of hydrophobic guest molecules. CD acts as a host for entrapping either totally or partially other chemical guest molecules. Compared among CDs, β-CD is the most accessible, simplest produced, and the lowest priced. Therefore, β-CD is generally the most useful one and counts for at least 95% of all produced and used CDs (Voncina and Marechal, 2005).

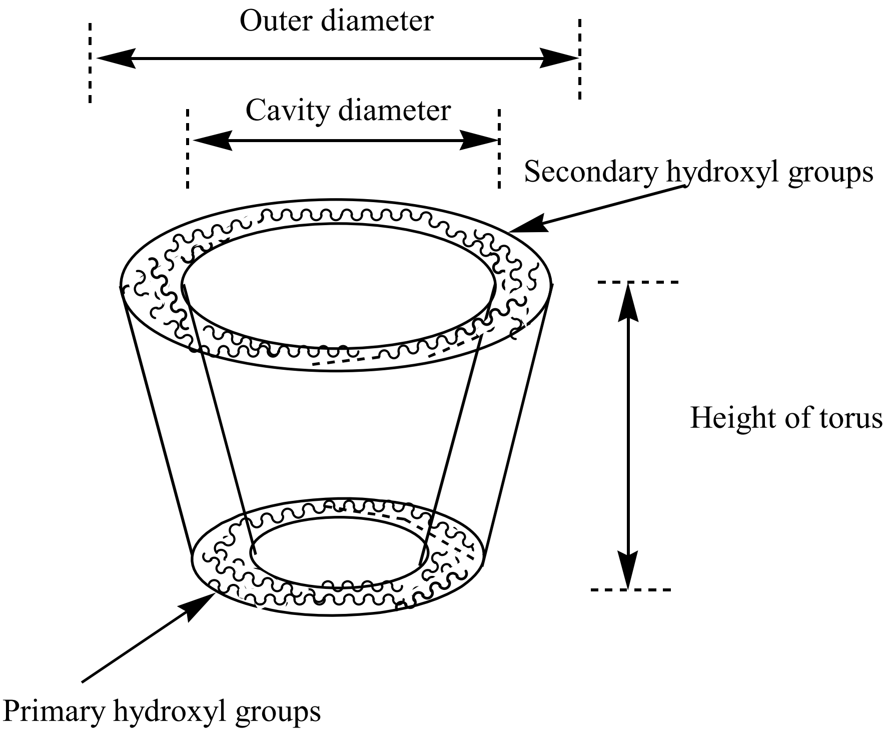


Figure 2 A structural scheme of a torus-shaped cyclodextrin molecule.

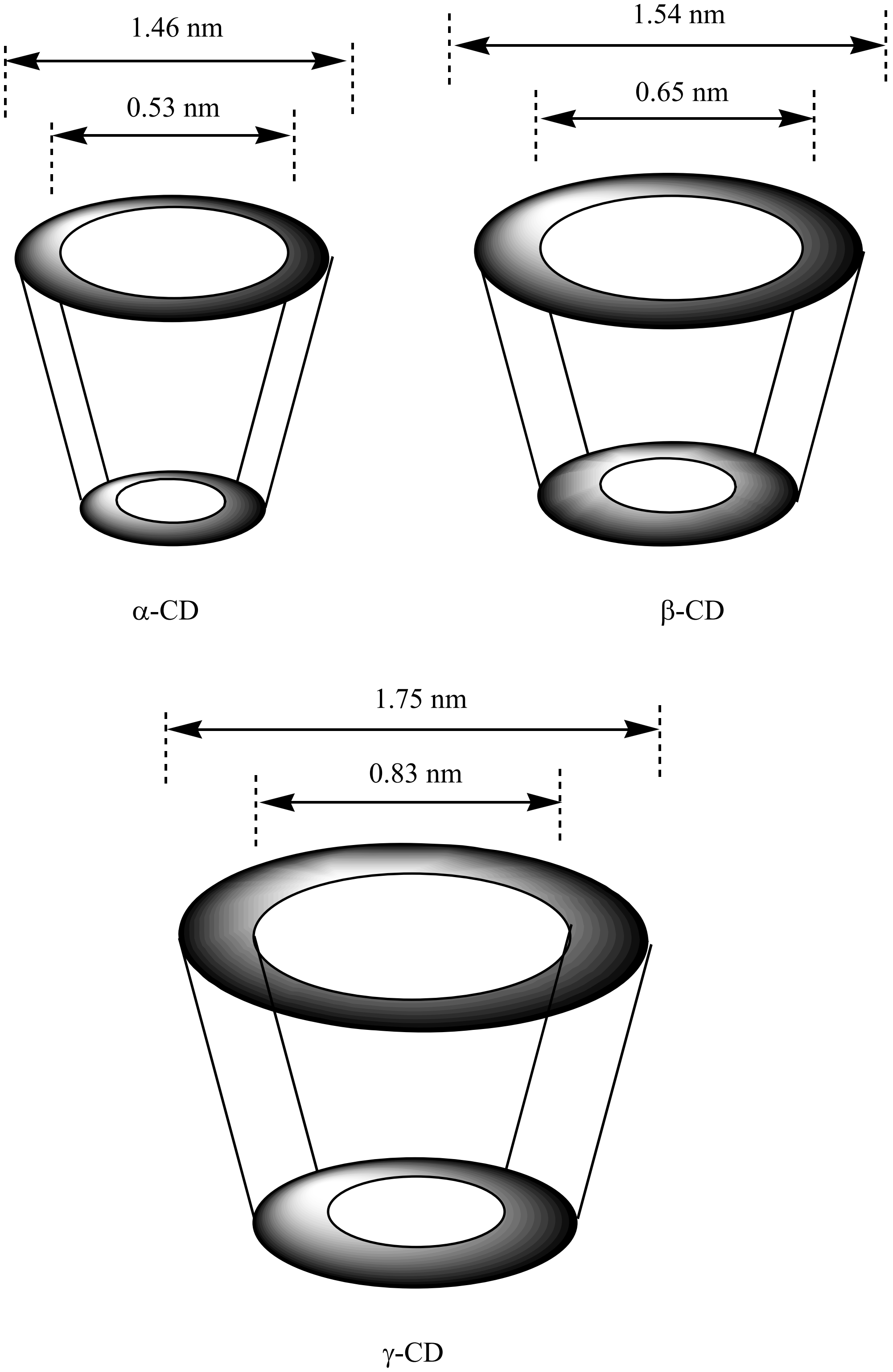


Figure 3 Molecular dimensions of α-, β- and γ-cyclodextrin.

The main physical properties of CDs are summarized in Table 1. Cyclodextrins are water soluble. They are stable in alkaline solutions but are susceptible to acid hydrolysis. The stability of CDs toward acid hydrolysis depends upon the temperature and acid concentration (Li and Purdy, 1992). However, the most important property is their inclusion complex forming capability. Because of their unique property, CDs are utilized in many applications such as food, cosmetics, pharmaceuticals, analytical chemistry, and other industrial areas (Singh *et al.*, 2002).

Table 1 The main physical properties of cyclodextrins.

Property	α-CD	β-CD	γ-CD
Number of glucopyranose	6	7	8
Molecular weight (g/mol)	972	1135	1297
Solubility in water at 25 ^{o}C (%, w/v)	14.5	1.85	23.2
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter (Å)	5.3	6.5	8.3
Height of torus (Å)	7.9	7.9	7.9

2. Microencapsulation of β-cyclodextrin molecules in textiles

Recently, needs for long-term durability of functional fibers and fabrics bring about the introduction of microcapsulation technique. Microcapsules have the ability to release of the guest molecules by an appropriate mechanism, stability and adequate mechanical strength, and non-toxicity of the material itself (Hong and Park, 1999). β-CDs are considered as the environmental friendly microcapsules because they are biodegradable and non-toxic (Wang and Chen, 2003). For example, the chemical oxygen demand is 1,060 mg/g and LD_{50} (oral, rat) is more than 5,000 mg/kg in case of β-CDs. In the host-guest complexes, a guest molecules is held within the cavity of the CD host molecule. The requirement for complex formation is a dimensional fit between host cavity and guest molecule, even if only partially. The hydrophobic cavity of cyclodextrin molecule gives a microenvironment into which the hydrophobic moieties of guest molecules can enter to form complex between host and guest molecules. It is not permanently fixed but is a dynamic equilibrium (Savarino *et al.*, 2004). Stability of inclusion complex depends on the geometric capability and polarity of guest molecules, solvent, and temperature. If the size of the guest molecule is too small, the interaction forces between the guest molecule and the host cavity will be little or no interaction at all. On the other hand, if the guest molecule is significantly larger than the cavity, only certain groups or side chains of the guest molecules penetrate into the CD-cavity. The stability of a complex is also proportional to the hydrophobic character of the guest molecule (Karathanos *et al.*, 2007). Highly hydrophilic guest molecules form complex very weakly or not at all. Inclusion complex can be accomplished in the presence of water, organic solvent, or co-solvent system. The stability strongly relies on the nature of the medium used for complexation. Normally, the guest molecules are only weakly complexed in organic solvent system. Moreover, the stability of an inclusion complex generally decreases with increasing temperature (Wang and Chen, 2004).

Cyclodextrin microencapsulation provides a profound effect on the physicochemical properties of guest molecules (Scalia *et al.*, 2006). The guest molecules are temporarily locked within the host cavity giving beneficial modification of guest molecules. The examples are solubility enhancement of highly insoluble guests, stabilization guest molecules against the degradative effects of oxidation, UV or visible light and heat, and of volatility and sublimation.

Savarino *et al.* (1999) studied the reactivity and effect of cyclodextrins in textile dyeing. Compared to dyeing without cyclodextrin, they found that dyeing nylon 6,6 and microfiber nylon 6 fabrics in the presence of cyclodextrin improved the color uniformity with only minor changes of color yield. The dye molecules formed complexes with cyclodextrins and were confirmed by ^{1}H-NMR data. They concluded that the positive effect on dyeing of cyclodextrin could be related to the relative stabilities of the dye-cyclodextrin complexes and to the relative rates of dye releasing from the complex and of diffusion through the fiber. They believed that cyclodextrin will have a very promising potential for the applications in dyeing technology.

Nostro *et al*. (2002) grafted β-CD onto the surface of tencel fabric. After the fabric modification, some chemicals as guest molecules were loaded to the grafted CD cavities by spraying their solutions on the modified fabric. The guest molecules used in this study were vanillin as a fragrance molecule, benzoic acid and iodine as antimicrobial agents, N,N-diethyl-m-toluamide and dimethylphthalate as insect repellents. The evidence from scanning electron microscopy, X-ray diffractometry, water absorbency, and breaking load loss showed that there was no significant change in the fabric's surface property. The UV-Visible profiles also showed that the guest molecule was presented in the grafted CD cavities even after prolonged washing. Fragrance activity tests indicated that vanillin was slowly released from the grafted fabric. Moreover, benzoic acid included in CD cavities could totally inhibit the bacteria growth underneath the fabric particularly against S. *aureus* and C. *albicans*.

Crini (2003) studied the use of polymers containing β-CD for the sorption of dyes. He found that β-CD polymers exhibited good adsorption properties towards dyes. The adsorption mechanism was both physical adsorption and hydrogen bonding because of the polymer and also the formation of an inclusion complex due to the β-CD molecules through host-guest interactions. The polymer strongly increased the sorption capacity. The study of the effect of the polymer particle size on dye removed showed that as the mean diameter of the polymer decreased, the adsorption capacity increased which probably due to the increase in surface area. Moreover, he studied the influence of the β-CD content on the adsorption capacity. He found that the adsorption capacity increased with increasing the amount of β-CD, corresponding to increasing interactions between β-CD and the dyes. Therefore, the inclusion phenomena between β-CD and dyes played the major role in the adsorption mechanism.

Wang and Chen (2003) anchored β-CD molecules to cotton by using the heterobifunctional reactive dyes. This host-guest functional textile was created for fragrance deposition. The purpose of using the combination of fragrances with textile fabrics was to allow the wearer to enjoy the aromatherapy or simply the present smell.

They formed complexes of β-CD with many fragrant oils, such as rosemary, lavender, jasmine, lemon, and sandalwood. The fragrance molecules were enclosed in the cavity of the β-CD by spraying. The lifetime of all fragrance oils on cotton was longer than 30 days. The laundering durability of β-CD on cotton was up to 6 cycles of washing at 60°C. The results showed that β-CD was an effective host for improving the lifetime of the fragrant oils on the fabric.

Savarino *et al.* (2004) used β-CD as a low environmental impact additive for the dyeing of nylon 6 and nylon 6,6 with a series of synthesized disperse dyes. Normally surfactants were employed as an additive but in this study β-CDs were used as an alternative. Low solubility of disperse dyes in water can be enhanced by the formation of complexes between β-CD and the dyes. Thermogravimetric analysis (TGA) and differential temperature analysis (DTA) studies were performed to evidence the formation of dye-β-CD complexes. Dyeing test in the presence of β-CD showed a positive effect on color uniformity and intensity. Therefore, β-CD can be used as a leveling agent in the dyeing of polyamide fibers with disperse dyes.

Scalia *et al.* (2006) studied the incorporation of the sunscreen agent, octyl methoxycinnamate (OMC), into cyclodextrin cavities which covalently bound to tencel fabric. The β-CD treated and untreated fabrics were soaked in the mixture of water-methanol (30:70, v/v) containing 2% (v/v) of the sunscreen agent. The amount of OMC entrapped in β-CD finished fabrics was evaluated by high performance liquid chromatography (HPLC). The results showed that β-CD modified fabric had much higher content of OMC (0.0203%, w/w) compared to unmodified fabric (0.0025%, w/w). Moreover, the β-CD finished fabric exhibited higher sunscreen agent retention to washing cycles and also photoprotective properties than the unmodified fabric.

3. Other applications of β-cyclodextrins

Besides the application in textile, β-CD is very useful in many industrial products and technologies. Because of the host-guest interaction, each guest molecule is surrounded by a β-CD which leads to beneficial changes in the physical and chemical properties of the guest molecules, examples of the changes are:

- Stabilization of light or oxygen-sensitive molecules
- Reduction of solubility of substances
- Fixation of volatile substances
- Improvement of substances' degradation by micro-organism
- Absorption of unpleasant smell and taste

These characteristics of β-CD make them appropriate in a lot of applications such as cosmetics, foods and flavors, pharmaceuticals, agricultural and chemical industries, adhesives, and coatings as shown in Table 2.

Table 2 Applications of β-CD in chemical industry.

Field	Applications
Cosmetics	- CD-complexed fragrances in skin products (Hedges, 1998) - Dry CD powder in diapers, paper towels (Woo *et al.*, 1999) - CDs in silica-based toothpastes (Loftsson *et al.*, 1999) - Tissues and underarm shields (Szetjli, 1998)
Food and flavors	- Removal of cholesterol from dairy products (Hedges, 1998) - Removal of bitterness from citrus fruit juices (Sojo, 1999) - Stabilisation and improvement of the taste of sweetening agents such as aspartame (Parrish, 1998)
Pharmaceuticals	- Enhancement of drug delivery (Kublik *et al.*, 1996) - Biological membranes (Rajewski and Stella, 1996) - Aqueous dermal formulations (Uekama *et al.*, 1992) - Aqueous mouthwash solution (Kristmundsdottir *et al.*, 1996) - Several eye drop solutions (Jarho *et al.*, 1996)

Table 2 (Continued)

Field	Applications
Agriculture	- Grain treated (Hedges, 1998) - Hydrolysis of racemic arylpropionic esters (Kamal *et al,* 1991) - Chymotrypsin mimic (Ekberg *et al*., 1989)
Agriculture	- Adsorption of contaminants (Wu and Fan, 1998) - Removal of organic pollutants and heavy metals from soil, water and atmosphere (Gao and Wang, 1998) - Determining bioavailability of pollutants (Reid *et al*., 1999)
Environment	- Scrub gaseous effluent from organic chemical industries (Szetjli, 1989) - Bioremediation process (Bardi *et al*., 2000) - Photodegradation of organophosphorous pesticides in humic water (Kamiya *et al*., 2001)

4. Binding between β-cyclodextrin and textile fibers

The potential benefits of utilization, the availability and economic factors of β-CD has resulted in increased interest on the applications of β-CD in textile finishing. However, it is evident that β-CD cannot form a direct covalent bond with textile fibers. Therefore, novel functional surface treatments based on the permanent fixation of β-CD on fabric have been studied. Many attempts have been made to chemically bond CD to fibers using different binders such as acrylamidomethylated β-cyclodextrin (CDNMA) (Nostro *et al*., 2003).

Reuscher and Hirsenkorn (1998) synthesized BETA W7 MCT which was the first reactive cyclodextrin derivative manufactured on an industrial scale. BETA W7 MCT had a monochlorotriazinyl (MCT) group, which was very well known from many reactive dyes, to act as a reactive anchor. BETA W7 MCT was synthesized in

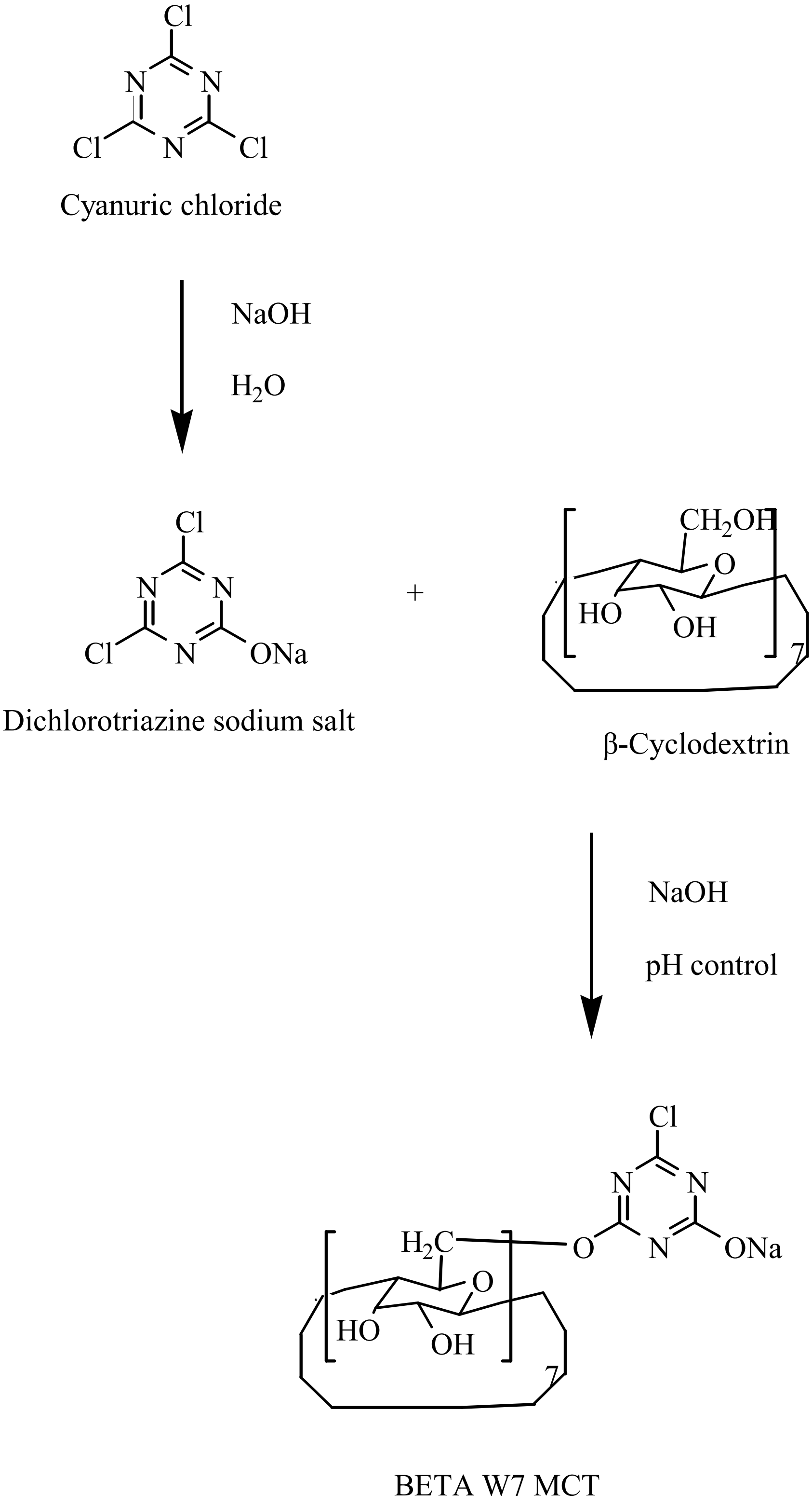


Figure 4 Synthesis of BETA W7 MCT.

two steps shown in Figure 4. The first step was the preparation of a clear aqueous solution of dichlorotriazine sodium salt at low temperature starting from a dispersion of cyanuric chloride in water. In the second reaction step, prepared dichlorotriazine compound reacted with β-CD in water at higher temperature under alkaline conditions and pH - control. The synthesized BETA W7 MCT was able to form a stable covalent bond to nucleophilic groups on textile materials by using the MCT group. For example, BETA W7 MCT could be applied on cotton by pad – roll process.
The properties of BETA W7 MCT were good water solubility, and very stable in a dry powder form for a minimum of a year. In alkaline solution BETA W7 MCT was more stable than in an acidic solution because of an autocatalytic effect at low pH value. Moreover, the amount of BETA W7 MCT on the textiles increased corresponded to increasing the amount of complexed guest molecules.

Moldenhauer and Reuscher (1998) used monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) to fix on cotton covalently. The fixation process shown in Figure 5 was the nucleophilic substitution reaction of hydroxyl groups from cotton fiber at the chlorotriazine ring of MCT-β-CD. The process was induced by elevated temperature and can be run either under alkaline or acidic conditions of the MCT-β-CD solution. A good fixation yield of 80 – 85% was achieved when MCT-β-CD was applied by dry heat at 150 °C for 5 minutes under alkaline condition. However, the fixation yield did not depend on the concentration of the solution. The finished cotton was fast against washing.

Lee *et al.* (2000) attached β-CD molecules chemically to cotton fiber using N-methylol-acrylamine (NMA). They synthesized acrylamidomethyl cyclodextrin (CD - NMA) and then grafted it on cotton. CD - NMA was prepared from the reaction between purified CD and NMA with formic acid as an acid catalyst. Ceric ammonium nitrate (CAN) was used as an initiator in grafting CD - NMA onto cotton fabric. The maximum graft yield was at 40 ºC for 1 hour with 0.012 M CAN solution. The amount of chemically bond CD was determined by fluorescence measurement. They believed that the grafting was mostly at the surface of cotton.

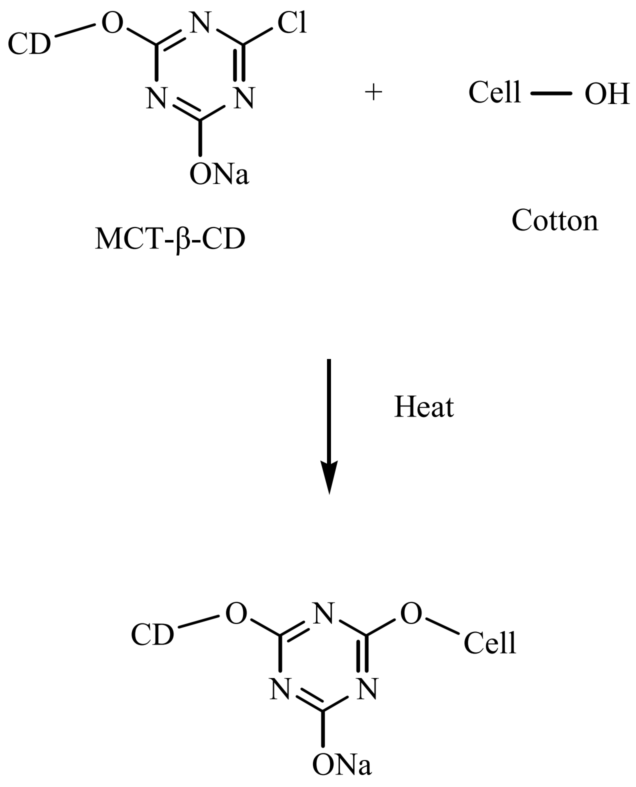


Figure 5 Reaction of MCT-β-CD and cotton.

Hebeish and El-Hilw (2001) finished cotton fabric by using monochlorotriaziny-β-CD (MCT-β-CD). They studied the reaction of MCT-β-CD and cotton in both the absence and presence of N-methylol compound (resin). The treatment was carried out by the pad-thermofixation method under different conditions e.g. concentrations of MCT-β-CD and resin, nature and concentration of catalysts (sodium hydroxide, sodium peroxide, sodium hydrogen carbonate or ethylamine) and also time and temperature of thermofixation. The results indicated that the extent of the reaction increased from increasing concentration of MCT-β-CD. Moreover, the reaction greatly increased as the alkaline catalyst increased. From the degree of substitution, they believed that one hydroxyl groups in at least every two anhydroglucose units of the cyclodextrin will be substituted by the monochlorotrizinyl moiety. With the alkaline catalyst, the MCT-β-CD was directly covalent-bonded to the cellulose. On the other hand, the attachment of the MCT-β-CD occurred through resin bridging with the acid catalyst.

Nostro *et al.* (2003) studied on grafting β-CD to tencel fabric. Tencel fabrics were processed in order to expand their potential performances. The ability of cyclodextrin to form complexes with hydrophobic molecules can be exploited to produce tencel with specific performances. In this study, β-CD can be anchored to tencel by means of a chemical linkage provided by N-methylol-acrylamide (NMA) and cyanuric chloride. They synthesized acrylamidomethylated β-cyclodextrin (CD-NMA) and then grafted onto tencel fabric using ceric ions to generate reactive sites on the tencel backbone. Monochlorotriazinyl-β-cyclodextrin (CD-MCT) was also grafted onto tencel fabric in basic condition using sodium carbonate. Both CD-NMA and CD-MCT grafted tencel were confirmed by UV-Vis spectroscopy. The results indicated that grafted tencel fabric has no significant change in its structural and surface properties. In addition the guest molecules such as fragrance, and an antimicrobial agent remained on the fabric surface.

Wang and Chen (2004) anchored β-CD molecules to cotton using heterobifunctional reactive dye to provide a chemical linkage. Heterobifunctional reactive dyes used were reactive dyes containing two different types of reactive groups. The chemical reaction of the reactive dye with β-CD and with fiber was a function to bond β-CD to cotton. The reactive dye acted as a crosslinker which the reactive groups on the dye was able to react with one of a hydroxyl group on β-CD and the other with a hydroxyl group on cellulose. They showed the proposed mechanism of the vinyl sulphone dye with cellulose and β-CD shown in Figure 6. The other possibility was that a β-CD molecule might be anchored by two reactive dyes, forming a longer bridge. The active chlorine atoms on the triazine reactive group can also react with a hydroxyl groups on both β-CD and cellulose. The β-CD concentration on the fabric increased with an increase in the initial concentration of β-CD in the dye bath. However, the β-CD concentration on cotton decreased gradually on washing. They suggested that the bond between β-CD and the dye was not as strong as that between the dye and cotton.

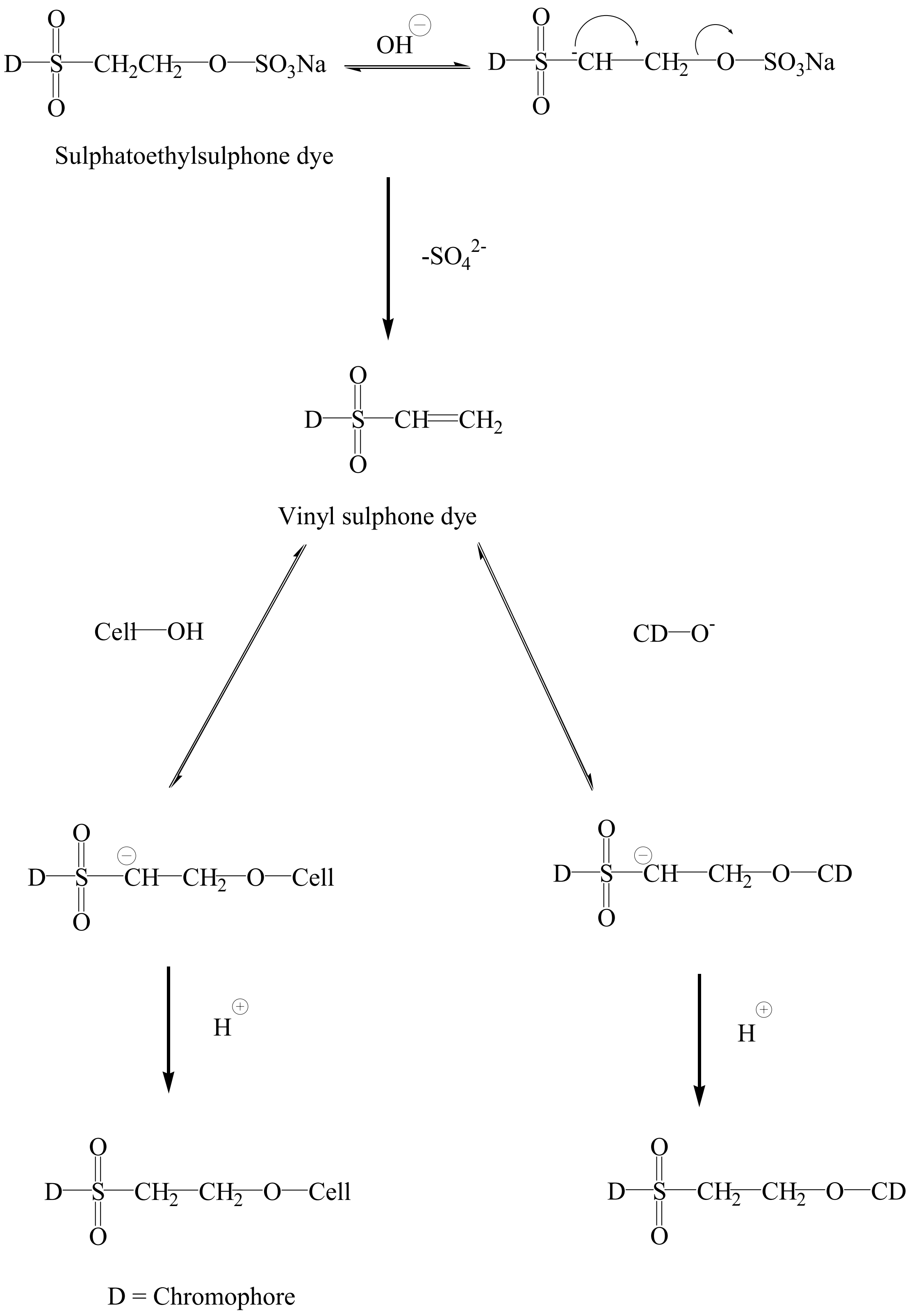


Figure 6 Reaction of the vinyl sulphone dye with cotton fabric and β-CD.

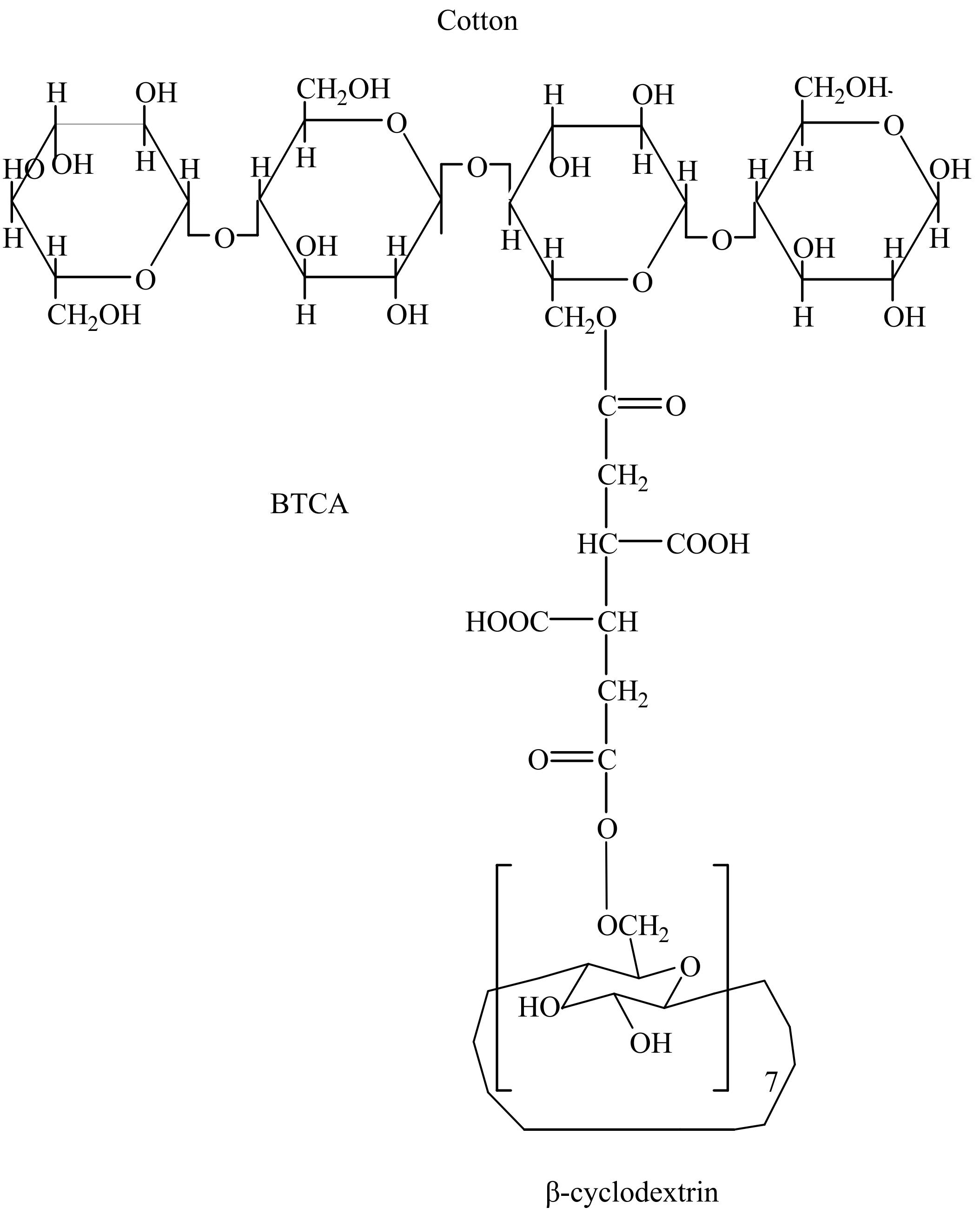


Figure 7 BTCA crosslinked β-CD and cotton.

Voncina and Marechal (2005) used 1,2,3,4-butane tetracarboxylic acid (BTCA) as a crosslinker between β-CD molecules and cotton fabric. Sodium hypophosphite (SHPI) was used as a catalyst. Carboxylic acid groups of BTCA can react with hydroxyl groups of cellulose and form stable ester bonds as shown in Figure 7. Cotton was immersed in treatment baths consisting different concentrations of β-CD and BTCA. SHPI was added to treatment baths for the reduction of the curing temperature. The fixation was carried out at 170 °C for 3 minutes when SHPI was used and at 200 °C for 3 minutes when fixation was carried out without the catalyst. The amount of β-CD molecules on the textile substrate was determined with the color change of phenolphthalein and phenol red. When β-CD was present on the fabric, phenol red changed color from red to yellow while phenolphthalein changed from red to colorless. They also used ATR-FTIR spectroscopy to verify the grafing of β-CD onto cellulosic fiber.

Wang and Chen (2005) studied a functional modification cotton fabric by using β-CD sol-gel coating method. The sol-gel method can create transparent and well adhesive film onto the fabric surface. The β-CD sol-gel solution was prepared by adding β-CD into a sol-gel solution which consisted of 3-glycidyloxypropyl-trimethoxysilane (GPTMS), tetraethoxysilane (TEOS), hydrochloric acid, ethanol and water. In order to ensure the stability of the sol-gel solution, the amount of β-CD used was less than 0.5 mol/l. The cotton was immersed in the solution of β-CD sol–gel at room temperature for 10 minutes, then the fabric was padded and heated at 80 °C for 5 minutes. This gelation process was able to anchor β-CD on cotton fabric. After forming complexes with various fragrance oils, the modified fabric was verified its functionally by greatly decreasing the rate of fragrance release. The durability of β-CD anchored on cotton can withstand laundering more than 15 times.

5. Glyoxal and its applications in textile

Glyoxal is the smallest dialdehyde with the chemical formula $C_2H_2O_2$. It is supplied typically as a 40% aqueous solution. For applications, glyoxal is usually used as a solubilizer and crosslink agent in polymer. It has been applied to textile fibers especially silk and cotton to enhance the mechanical properties such as resilience and dimensional stability. Since glyoxal is a formaldehyde-free reagent which is environmental friendly, it has been used to replace a formaldehyde-containing agent in durable press finishing. The formation of crosslinks in cotton or silk by glyoxal is through hemiacetal formation (Choi *et al*., 1999).

Kawahara *et al.* (1995) reported that silk fibers treated with a mixture of glyoxal and urethane resins help improve the durability of the fibers against ultraviolet light. The treated silk fibers also showed good durability against laundering even at 4 – 5 % add-on of the resins. In this study, they were interested in the resin system for preventing the reduction in strength of silk fibers during washing. Firstly, the fibers were immersed in a mixture of glyoxal and urethane resins and dried. After washing 6 times, the fibers were investigated by tensile test and scanning electron microscope. The results showed that the good durability was due to the occurrence of crosslinkings between fibrils from the treatment of the fibers with a mixture of glyoxal and urethane resins.

Choi *et al.* (1999) studied the feasibility of using glyoxal as a creasing – resistant finishing agent for silk fabric. They interested in glyoxal as a crosslinker because it was a non-formaldehyde reagent and was readily available. They treated the silk fabric with glyoxal in the presence of an acid such as sulfuric acid and formic acid, and aluminium sulfate. The results indicated that glyoxal greatly improved conditioned wrinkle recovery angle of the treated silk. The reaction between glyoxal and silk was dependent on the availability of hydroxyl and amine groups of fibroin. X-ray diffraction showed that this reaction mostly occurred in amorphous region of fibroin.

Schramm and Rinderer (2002) studied the quantification of glyoxal that has reacted with the cellulosic material. Magnesium dichloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and aluminum sulfate hexadecahydrate ($Al_2(SO_4)_3 \cdot 16H_2O$) were applied as catalysts and different hydroxycarboxylic acids as co-catalysts. They tested the influence of incorporating hydroxycarboxylic acids, such as citric, tartaric, and malic acids, on the amount of cotton-bound glyoxal with modification of a lower cure temperature. The amount of cotton-bound glyoxal was measured by isocratic HPLC method. The results from using magnesium chloride as the catalyst showed lower effectiveness of glyoxal bound to the fabric in comparison to aluminum sulfate. There was no influence on the amount of cotton-bound glyoxal from incorporating hydroxycarboxylic acids with the modification of a reduction of the cure temperature from 150 to 110 °C.

Xu *et al.* (2003) prepared β-CD crosslinked chitosan derivative using glyoxal as a crosslinker. The synthesis of β-CD crosslinked chitosan was by dissolving chitosan and β-CD (1 : 5 by weight) in hydrochloric acid at room temperature and then adding glyoxal at 80 ºC for 1-2 hours. The solution was adjusted to pH 7-8. After washing with water and acetone, the β-CD crosslinked chitosan was freeze-dried. The reaction of β-CD-crosslinked chitosans with glyoxal was shown in Figure 8. The structure of β-CD-crosslinked chitosans with glyoxal were characterized by IR spectroscopy. The IR spectrum showed that the N-H peak of chitosan at 1596 cm^{-1} disappeared but the O-H bending peak of β-CD at 1648 cm^{-1} appeared. Because carbonyl groups of glyoxal participated in the coupling reaction, the characteristic peak of carbonyl groups did not appear in the spectrum. This β-CD-chitosan was a novel adsorbent for small organic molecules e.g. nicotine.

Yang *et al.* (2005) employed glyoxal as a crosslinking agent to enhance the mechanical properties of chitosan fibers. The reaction between chitosan fiber and glyoxal solution was designed by taking tenacity as an evaluating target and four parameters i.e. time, temperature, pH, concentration were varied. They found that the best condition of glyoxal solution were at 4% (w/w) and pH 4. The best crosslink conditions were at 40 °C and 60 – 70 minutes. The results from IR spectra of chitosan fiber after crosslinking confirmed the possible mechanism for using glyoxal to enhance the mechanical properties of chitosan. The mechanism was found to be mainly due to the occurrence of acetolization and Schiff base reaction that probably take place between the glyoxal and the hydroxyls and amino groups of chitosan fiber.

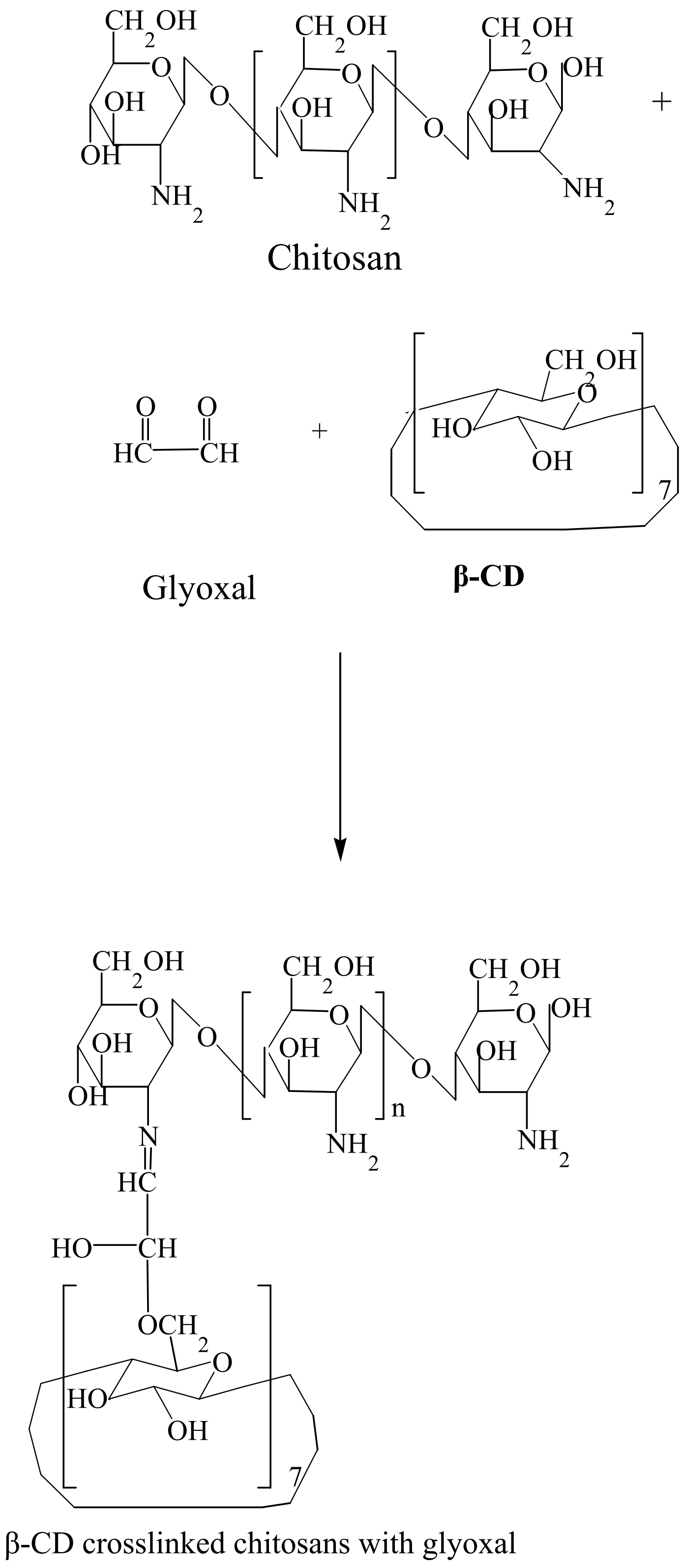


Figure 8 Synthesis of β-CD crosslinked chitosans with glyoxal.

MATERIALS AND METHODS

Materials

1. Fabrics

Commercially desized, scoured and bleached plain weave cotton and silk fabrics weighing 209 and 77 g/m^2, respectively, were purchased from local fabric companies, Thailand.

2. Reagents

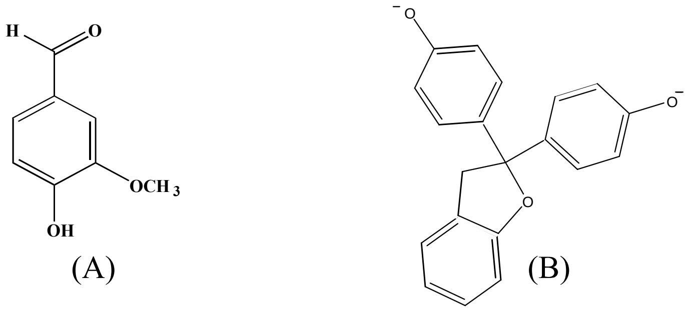
- β-Cyclodextrin powder was purchased from Wako Pure Chemical Industries.

- Aluminium sulphate ($Al_2(SO_4)_3$) was purchased from Ajax Finechem, Australia.

- Sodium carbonate (Na_2CO_3) was purchased from Riedel-dehaen, Germany.

- Sodium hydroxide (NaOH) was purchased from Labscan Asia, Thailand.

- Glyoxal (40% solution in water), vanillin and phenolphthalein were purchased from Merck Schuchardt OHG 85662 Hohenbrunn, Germany.



(A)

(B)

Figure 9 Structure of (A) vanillin; (B) phenolphthalein.

3. Apparatus

- Corning stirrer / hotplate model PC-420 was used in the preparation of glyoxal-β-CD compound.

- Padder from MingScape International Co, Ltd. was used for padding glyoxal-β-CD on fabrics.

- Mini dryer from MingScape International Co, Ltd. was used in the dry and cure steps of the fabric treatment.

- Shaker (Neslab EX-600) was used for the reaction between phenolphthalein and β-CD on fabrics.

-Whiteness CIE Index was measured using Gretag Macbeth i5 spectrophotometer with illuminat D_{65} and 10^o observer.

- UV – Vis spectrophotometer (Jasco V-530 uv/vis spectrophotometer) was used to measure the absorbance of phenolphthalein solutions (400 – 700 nm) and UV – Vis spectrophotometer from Perkin Elmer (Lambda 650 uv/vis spectrophotometer) was used to evaluate vanillin on the fabric (200 – 400 nm).

- Fourier Transform-Infrared Spectroscopy (FTIR) from Perkin Elmer 2000, England was used to characterize glyoxal-β-CD compound.

- Thermogravimetric Analysis (TGA) was from Mettler Toledo (TGA/SDTA 851^e). β-CD powder, 40% glyoxal and glyoxal-β-CD were analyzed from 30 to 600 ^oC with a heating rate of 20 ^oC/minute under a nitrogen atmosphere of 60 ml/minute and from 600 to 850 ^oC with a heating rate of 20 ^oC/minute under an oxygen atmosphere of 60 ml/minute. Silk fabric and cotton fabric were analyzed from

30 to 900 °C with a heating rate of 10 °C/minute under an oxygen atmosphere of 60 ml/minute.

- Differential Scanning Calorimetry (DSC) measurement was performed using DSC 822^e, Mettler Toledo. β-CD powder, 40% glyoxal and glyoxal-β-CD were scanned from 0 to 250 °C with a heating rate 20 °C/minute using a nitrogen atmosphere of 60 ml/minute.

- Scanning Electron Microscope (SEM) examined surface morphology of the different fabrics before and after surface coating with JSM 6301 from JEOL. Fabric samples were cut with a blade and covered with gold.

Methods

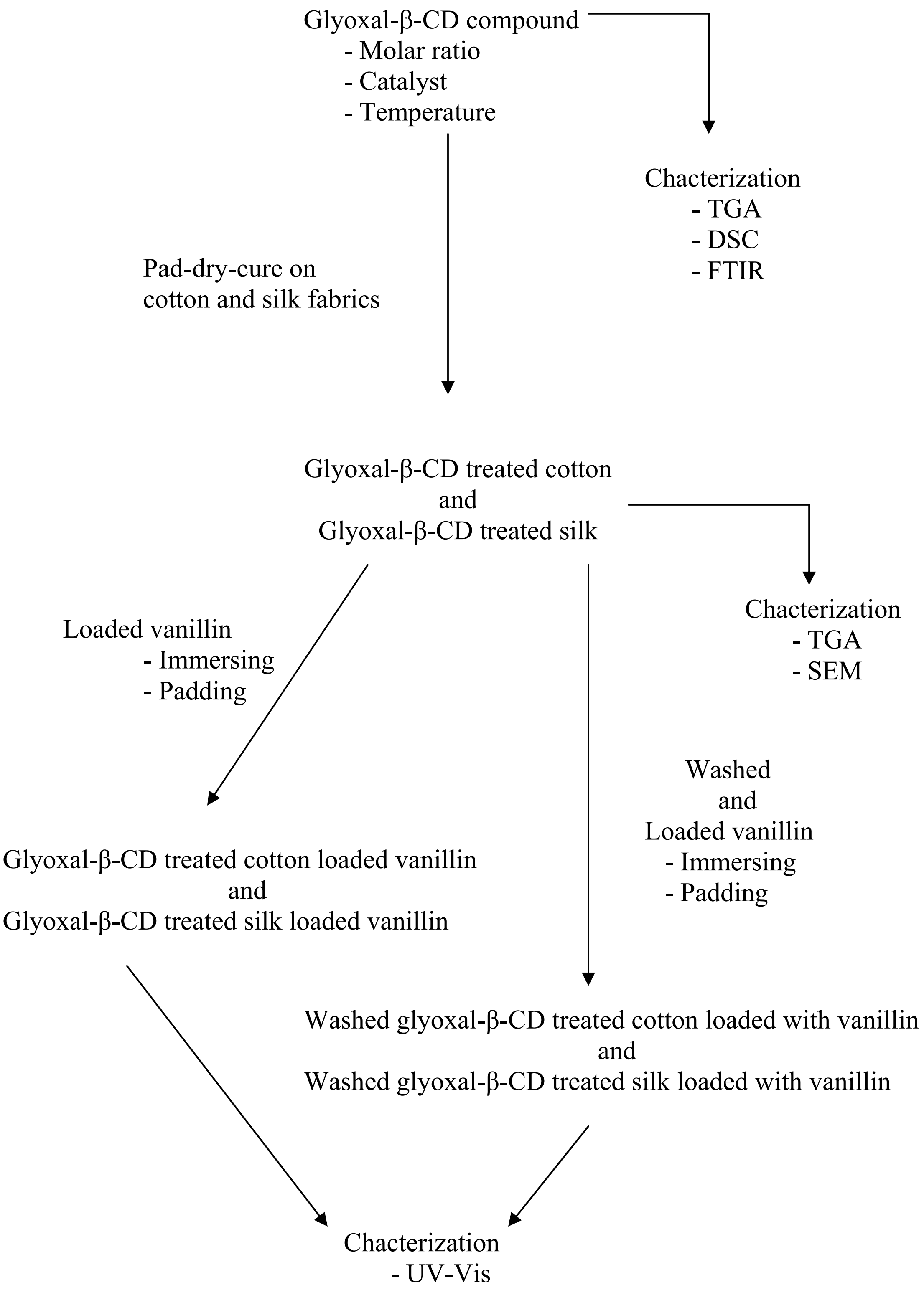


Figure 10 Flow chart of the experiment procedure.

1. Preparation of glyoxal-β-cyclodextrin

β-CD powder was dissolved in distilled water with stirring for 10 minutes. The required amount of glyoxal and a catalyst (either $Al_2(SO_4)_3$ or Na_2CO_3) were added into β-CD solution and the reaction was continued for 20 minutes. The glyoxal-β-CD solution was characterized by FTIR, TGA and DSC.

2. Effect of molar ratios of β-CD to glyoxal, catalysts, and temperatures

The effects of β-CD and glyoxal ratios, catalysts, and reaction temperatures on the preparation of glyoxal-β-CD were studied. The molar ratios of β-CD to glyoxal were studied at 1 : 7, 1 : 14 and 1 : 21. The actual weight of β-CD and glyoxal in a liter of water was shown in Table 3. The amount of β-CD was fixed at 18 grams. Two catalysts, $Al_2(SO_4)_3$ and Na_2CO_3, were fixed at 1 % w/v. The reaction was carried out at room temperature (RT), 50 ^{o}C, and 80 ^{o}C. Glyoxal-β-CD was treated on cotton (samples 1C-12C) and silk (samples 1S-12S) as shown in Tables 4 and 5.

Table 3 Ratios of β-CD to glyoxal and their actual weight.

β-CD : glyoxal	β-CD (g)	40 % Glyoxal (g)
1 : 7	18	16.10
1 : 14	18	32.20
1 : 21	18	48.30

Table 4 The catalysts and temperatures used in the preparation of glyoxal-β-CD.

Cotton No.	Silk No.	Catalyst	Temperature (°C)
1C	1S	$Al_2(SO_4)_3$	RT
2C	2S	Na_2CO_3	
3C	3S	$Al_2(SO_4)_3$	50
4C	4S	Na_2CO_3	
5C	5S	$Al_2(SO_4)_3$	80
6C	6S	Na_2CO_3	

Molar ratio of β-CD : glyoxal is 1 : 7.

Table 5 The molar ratios of glyoxal to β-CD and temperatures used in the preparation of glyoxal-β-CD.

Cotton No.	Silk No.	Temperature (°C)	β-CD : Glyoxal
1C	1S	RT	1 : 7
3C	3S	50	
5C	5S	80	
7C	7S	RT	1 : 14
8C	8S	50	
9C	9S	80	
10C	10S	RT	1 : 21
11C	11S	50	
12C	12S	80	

$Al_2(SO_4)_3$ was used as a catalyst.

3. Effect of temperatures on dry and cure processes

The fabric sample was cut into 10 inches x 12 inches. The synthesized glyoxal-β-CD solution was applied on cotton and silk fabrics by pad-dry-cure process. First, the fabric was impregnated for 5 minutes in 250 ml solution of glyoxal-β-CD. Then the fabrics were roll-squeezed through a padder to get a wet pick up of 80 ± 1.5 %. The speed of the padder was at 5 rpm for both fabrics. The pressures used were 0.25 Kg / cm^2 and 0.5 Kg / cm^2 for cotton and silk, respectively. After the application of glyoxal-β-CD on fabrics by padding, the fabrics were dried and cured in the Mini dryer as the conditions indicated in Tables 6 and 7.

Table 6 The conditions used in dry and cure processes for cotton fabric.

Cotton No.	Drying conditions		Curing conditions	
	Temperature (^{o}C)	Time	Temperature (^{o}C)	Time (minutes)
13C	RT	24 hours	-	-
14C	50	5 minutes	-	-
15C	80	5 minutes	-	-
16C	100	5 minutes	-	-
17C	100	3 minutes	-	-
18C	100	5 minutes	110	3
19C	100	5 minutes	130	3
20C	100	5 minutes	150	3
21C	100	5 minutes	170	3

Table 7 The conditions used in dry and cure processes for silk fabric.

Silk No.	Drying conditions		Curing conditions	
	Temperature (^oC)	Time	Temperature (^oC)	Time (minutes)
13S	RT	24 hours	-	-
14S	50	5 minutes	-	-
15S	80	5 minutes	-	-
16S	100	5 minutes	-	-
17S	100	3 minutes	-	-
18S	50	5 minutes	80	3
19S	50	5 minutes	80	5

4. Concentration of β-CD on glyoxal-β-CD treated fabrics

The concentration of β-CD on the fabric was measured using a phenolphthalein indicator. The color intensity of the phenolphthalein was proportional to the β-CD concentration on the fabric at low concentration (Wang and Chen, 2004). To prepare 5 x 10^{-5} M phenolphthalein solution, phenolphthalein powder was dissolved in distilled water and the pH was adjusted to 10.5 using 0.5 M NaOH under magnetic stirring for 30 minutes. The glyoxal-β-CD treated fabric was cut to 2.5 inches x 2.5 inches and weighed. The fabric sample was immersed in 50 ml phenolphthalein solution and shaken at room temperature for 1 hour on a shaker. After removed the fabric, the phenolphthalein solution was measured the absorbance at the maximum absorption i.e. 551 nm. The amount of β-CD on the fabric was calculated using the calibration curve (see Appendix A). The glyoxal-β-CD treated fabrics were evaluated by TGA and SEM.

5. Application of vanillin on fabrics

Fabric treated with glyoxal-β-CD was loaded with vanillin solution by padding and immersing methods. 0.5% w/v of vanillin solution was prepared by dissolving 2.5 g vanillin powder in 500 ml of 10% ethanol. The solution was stirred for 5 minutes at room temperature. For the padding method, the samples of untreated and treated fabrics were cut to 2.5 inches x 2.5 inches and immersed in 50 ml of the prepared vanillin solution for 5 minutes. Then cotton fabrics were padded at 5 rpm and 0.25 Kg / cm^2, while silk fabrics were padded at 5 rpm and 0.5 Kg / cm^2. The fabrics were then dried at room temperature. For the immersing method, the untreated and treated fabric samples with the same size were immersed in 50 ml vanillin solution for 24 hours at room temperature in the shaker.

6. Amount of vanillin on fabrics

After vanillin loaded fabrics were air-dried, they were measured the concentration of vanillin by UV-Vis spectrophotometer (Perkin Elmer, 2000). The data of vanillin concentration on fabric were collected after drying for 3, 5, 10, 13, 18, 20, and 25 days. The measurement was collected from 200 – 400 nm.

7. Durability of glyoxal-β-cyclodextrin on the fabrics

Untreated and glyoxal-β-CD treated fabrics with the size of 4 cm x 10 cm were washed according to ISO 105-C01:1989 with 5 grams soap per liter of water and a liquor ratio of 50 : 1. The fabrics were laundered at 40 ^{o}C ± 2 ^{o}C for 30 minutes. The washed fabrics were rinsed with running tap water for 10 minutes and dried at room temperature (ISO 105-C01, 1989). Then, the washed fabric were loaded with vanillin solution using both padding and immersing as previous described. The amount of vanillin on washed fabrics were also evaluated using UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

1. Preparation of glyoxal-β-cyclodextrin

The reaction between glyoxal and β-CD is believed to be a hemiacetal and an acetal formation as shown in Figures 11 and 12. Hemiacetal formation is a nucleophilic addition from hydroxyl groups of β-CD to the carbonyl group of glyoxal. A hemiacetal can be formed under either acidic or basic conditions. Acetal can also formed from glyoxal and β-CD. However, acetal formation is only acid-catalyzed. Both formations are reversible. Therefore, acetals undergo hydrolysis under acidic conditions, but are stable in basic condition (Choi *et al.*, 1999). In this study, $Al_2(SO_4)_3$ and Na_2CO_3 were used as acid and basic catalysts, respectively.

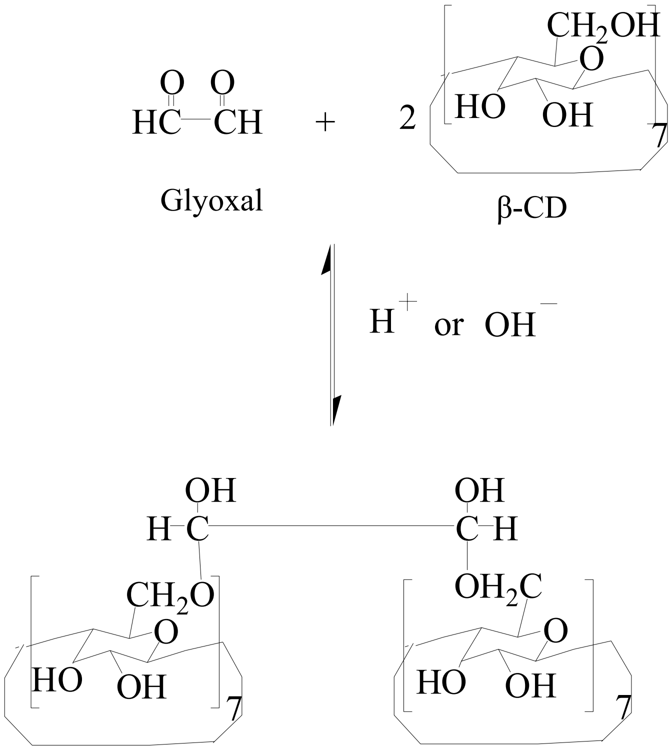


Figure 11 Hemiacetal formations.

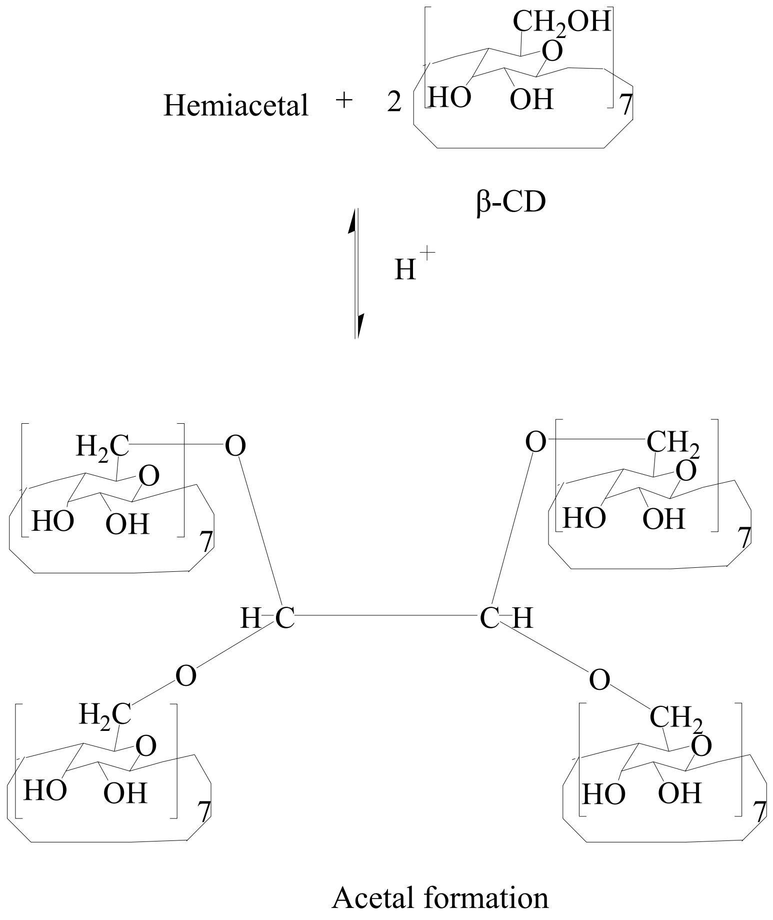
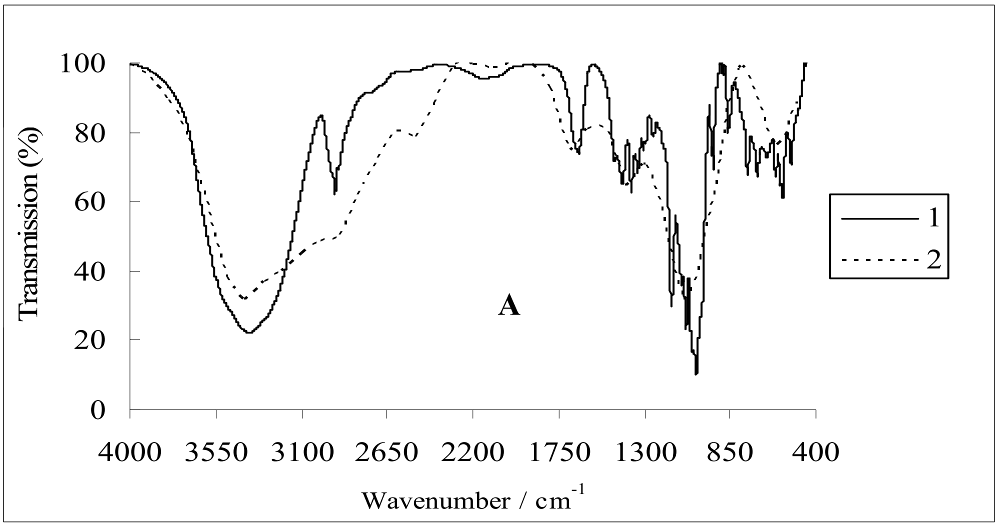


Figure 12 Acetal formations.

After the preparation of glyoxal-β-CD solution, FTIR analysis was performed to confirm the reaction. Figure 13A showed the FTIR spectra of β-CD powder and synthesized glyoxal-β-CD, while Figure 13B showed the FTIR spectrum of 40% glyoxal. Absorption bands of hydroxyl groups of β-CD powder and glyoxal-β-CD solution were shown at 3370 cm^{-1}, and 3387 cm^{-1}, respectively. Hydroxyl groups of 40% glyoxal showed the absorption band at 3400 cm^{-1}. Compared the percent transmission (%T) of hydroxyl groups between both reactants, β-CD powder and glyoxal, and the glyoxal-β-CD product, the spectra showed that the product had the highest percent transmission which referred to the lowest number of hydroxyl groups. This indicated that hydroxyl groups of β-CD and glyoxal were used in the formations of hemiacetal and acetal products. The absorption band of carbonyl groups at

1750 cm^{-1} in Figure 13B was disappeared after the reaction with β-CD as shown in Figure 13A. The disappearance of the carbonyl groups indicated that there were formations of hemiacetal and acetal products. The absorption bands at 1070-1150 cm^{-1} was from the C-O-C bond in β-CD rings, other absorption bands were C-H stretching (2920-2935 cm^{-1}) and C-H bending (1340-1470 cm^{-1}) (Trotta *et al.*, 2000).



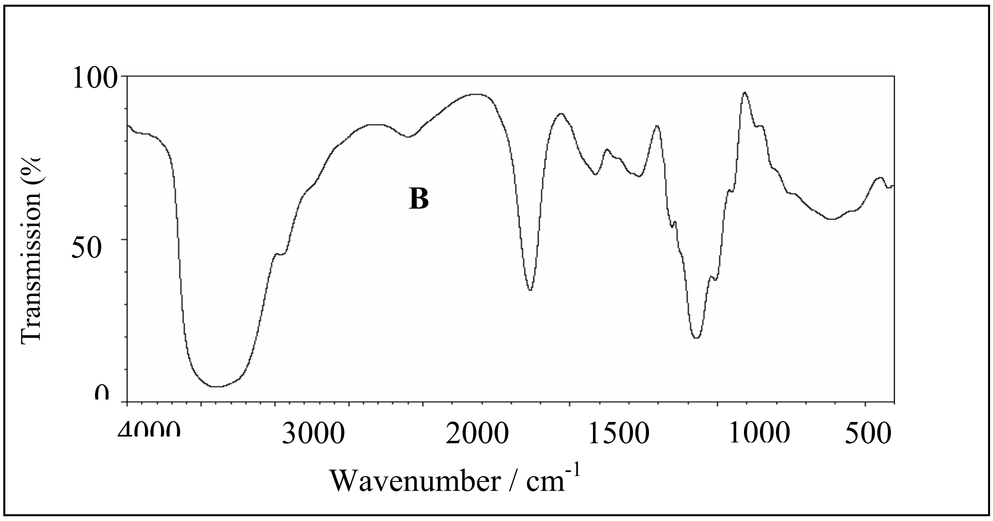


Figure 13 FTIR spectra: A (1) β-CD powder; (2) glyoxal-β-CD and B 40% glyoxal.

It was clearly observed that FTIR spectrum for glyoxal-β-CD was almost identical to that of β-CD alone. The similarity between the spectra of β-CD powder and synthesized glyoxal-β-CD indicated that the basic structural units of β-CD were preserved. However, the decreases in the intensity of hydroxyl peaks at 3370-3400 cm^{-1} and the intensity of carbonyl peaks at 1750 cm^{-1} confirmed that the reaction between β-CD and glyoxal occurred.

Thermogravimetric curves of β-CD powder, 40% glyoxal, and glyoxal-β-CD were shown in Figure 14. After initial loss of moisture (15% weight loss) at about 100-120 °C, a major decomposition proceeded from 340 to 350 °C for β-CD powder. There were about 15% residue of β-CD after decomposition. In case of glyoxal, there were at least three decomposition steps from 130 to 150 °C. Meanwhile, TGA curve of glyoxal-β-CD solution showed a major weight loss from 4% to 90% at the temperature from 90 to 110 °C. There was no evidence of free glyoxal and β-CD in the glyoxal-β-CD solution. Thermal stability depended mainly on the crystallinity of β-CD. Therefore, the shift of decomposition temperatures of glyoxal-β-CD can be attributed to the increase in the amorphous or disordered region which was decomposed by thermal treatment. Therefore, the glyoxal-β-CD had lower decomposition temperature than those of β-CD power and glyoxal.

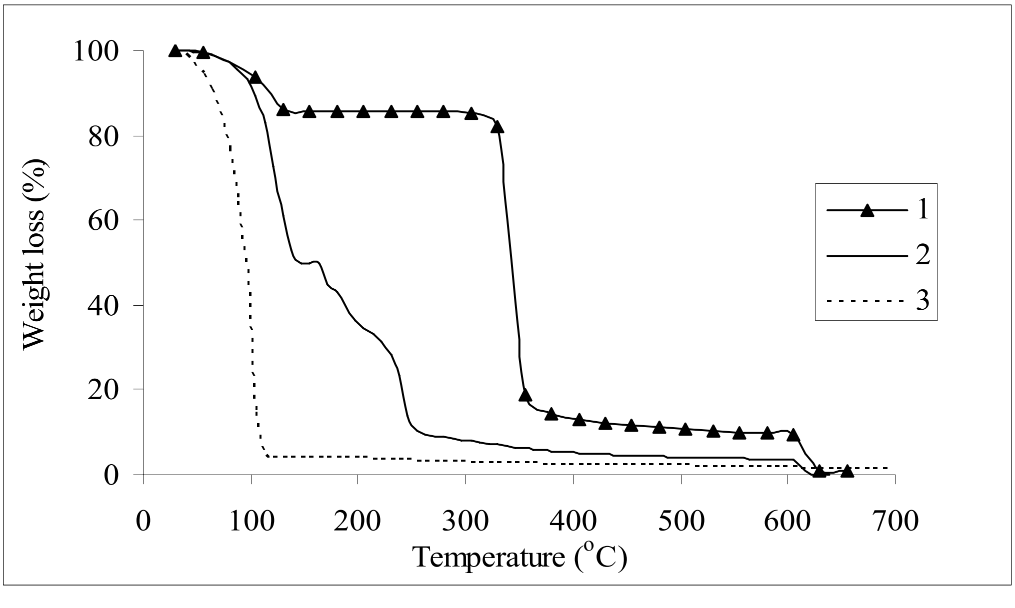


Figure 14 TGA curves: (1) β-CD powder; (2) 40 % glyoxal; (3) glyoxal-β-CD.

Figure 15 represented the differential scanning calorimetry (DSC) results of β-CD powder, 40% glyoxal, and glyoxal-β-CD. The curve of β-CD powder showed a single endothermic peak at 133 °C which assigned to its melting. There were three main endothermic peaks of glyoxal from 120 to 140 °C which corresponded to the results of TGA. The curve of glyoxal-β-CD complex showed only single absorption peak at 117 °C with no evidence of free β-CD and glyoxal at all.

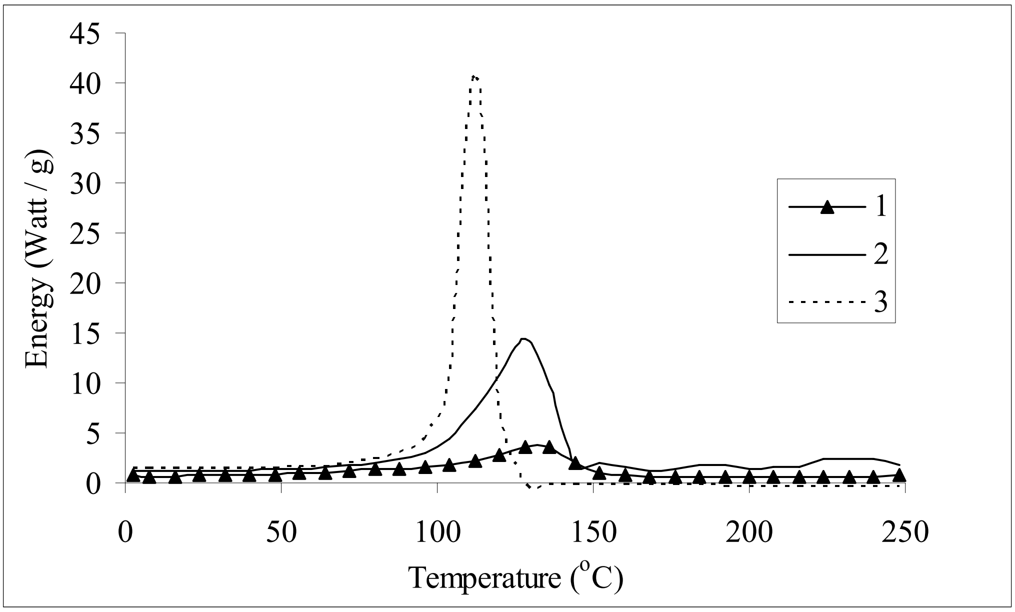


Figure 15 DSC curves: (1) β-CD powder; (2) 40 % glyoxal; (3) glyoxal-β-CD.

2. Effect of molar ratios of β-CD to glyoxal, catalysts, and temperatures

To study the effect of catalysts on the reaction between β-CD and glyoxal, $Al_2(SO_4)_3$ (an acid catalyst) and Na_2CO_3 (a basic catalyst) were used in the reaction composed of 1 : 7 of β-CD to glyoxal. The amount of β-CD on fabrics indicated that the reaction should be carried out with the acidic catalyst. As results shown in Tables 8 and 9 for all three temperatures, the reaction that had $Al_2(SO_4)_3$ as a catalyst gave higher amount of β-CD on the fabric than the one that had Na_2CO_3 as a catalyst. Therefore, $Al_2(SO_4)_3$ was used as a catalyst in the glyoxal-β-CD preparation.

Table 8 The amount of β-CD on the cotton fabric from defined catalysts and temperatures.

Cotton No.	Catalyst	Temperature(°C)	β-CD (mg) / g of fabric
1C	$Al_2(SO_4)_3$	RT	1.163
2C	Na_2CO_3	RT	0.348
3C	$Al_2(SO_4)_3$	50	1.084
4C	Na_2CO_3	50	0.070
5C	$Al_2(SO_4)_3$	80	1.157
6C	Na_2CO_3	80	0.462

Molar ratio of β-CD : glyoxal is 1 : 7.

Table 9 The amount of β-CD on the silk fabric from defined catalysts and temperatures.

Silk No.	Catalyst	Temperature(°C)	β-CD (mg) / g of fabric
1S	$Al_2(SO_4)_3$	RT	2.452
2S	Na_2CO_3	RT	0.350
3S	$Al_2(SO_4)_3$	50	2.761
4S	Na_2CO_3	50	0.355
5S	$Al_2(SO_4)_3$	80	2.485
6S	Na_2CO_3	80	0.633

Molar ratio of β-CD : glyoxal is 1 : 7.

The next study was the effect of the molar ratio of glyoxal to β-CD used in the reaction. Since β-CD had two secondary hydroxyl groups and one primary hydroxyl group in each glucose unit, the ratios of 1 : 7, 1 : 14 and 1 : 21 of β-CD to glyoxal were investigated. As shown in Tables 10 and 11, the highest amount of β-CD on the fabrics was at the ratio of 1 : 21 (β-CD : glyoxal) at room temperature. Based on this results, it was believed that almost every hydroxyl group of β-CD reacted with glyoxal. Therefore, glyoxal-β-CD was prepared with β-CD : glyoxal of 1 : 21 at room temperature using 1% (w/v) $Al_2(SO_4)_3$ as a catalyst.

Table 10 The amount of β-CD on the cotton fabric from defined ratios of glyoxal and β-CD and temperatures.

Cotton No.	β-CD : Glyoxal	Temperature(^oC)	β-CD (mg) / g of fabric
1C	1 : 7	RT	1.163
3C	1 : 7	50	1.084
5C	1 : 7	80	1.157
7C	1 : 14	RT	2.341
8C	1 : 14	50	2.051
9C	1 : 14	80	1.580
10C	1 : 21	RT	2.827
11C	1 : 21	50	1.989
12C	1 : 21	80	2.180

$Al_2(SO_4)_3$ was used as a catalyst.

Table 11 The amount of β-CD on the silk fabric from defined ratios of glyoxal and β-CD and temperatures.

Silk No.	β-CD : Glyoxal	Temperature(^{O}C)	β-CD (mg) / g of fabric
1S	1 : 7	RT	2.452
3S	1 : 7	50	2.761
5S	1 : 7	80	2.485
7S	1 : 14	RT	4.665
8S	1 : 14	50	5.992
9S	1 : 14	80	6.045
10S	1 : 21	RT	7.966
11S	1 : 21	50	7.456
12S	1 : 21	80	7.514

$Al_2(SO_4)_3$ was used as a catalyst.

3. Effect of temperatures on dry and cure processes

After padding the fabric with glyoxal-β-CD solution, the padded fabric was underwent the defined dry process as shown in Tables 12 and 13. For both cotton and silk fabrics, drying at 100 ^{o}C for 5 minutes gave the highest amount of β-CD on the fabric. At this dry method, there was insignificant effect on the whiteness of cotton as shown in Table 12. However, silk fabric showed the off-white color at 80 ^{o}C and yellow at 100 ^{o}C as we can see from the whiteness index in Table 13. Therefore, the condition used to dry silk was at 50 ^{o}C for 5 minutes while the condition used to dry cotton was at 100 ^{o}C for 5 minutes.

Table 12 The amount of glyoxal-β-CD on the cotton fabric after dry and process.

Cotton No.	Drying conditions		β-CD (mg) / g of fabric	Whiteness index
	Temperature	Time		
13C	RT	24 hours	1.431	58.20
14C	50 °C	5 minutes	0.655	57.59
15C	80 °C	5 minutes	0.918	57.99
16C	100 °C	5 minutes	1.592	58.25
17C	100 °C	3 minutes	1.240	58.66

Molar ratio of β-CD : glyoxal is 1 : 21.

$Al_2(SO_4)_3$ was used as a catalyst.

The whiteness CIE Index of untreated cotton was 62.24.

Table 13 The amount of glyoxal-β-CD on the silk fabric after the dry process.

Silk No.	Drying conditions		β-CD (mg) / g of fabric	Whiteness index
	Temperature	Time		
13S	RT	24 hours	4.539	46.01
14S	50 °C	5 minutes	4.946	47.88
15S	80 °C	5 minutes	4.874	36.07
16S	100 °C	5 minutes	5.801	14.50
17S	100 °C	3 minutes	5.667	14.22

Molar ratio of β-CD : glyoxal is 1 : 21.

$Al_2(SO_4)_3$ was used as a catalyst.

The whiteness CIE Index of untreated silk was 59.18.

Curing conditions for cotton and silk were shown in Tables 14 and 15. From the amount of glyoxal-β-CD on the fabrics, the best condition used to cure cotton and silk fabrics were at 130 °C for 3 minutes and 80 °C for 5 minutes, respectively.

Table 14 The amount of glyoxal-β-CD on the cotton fabric after dry and cure processes.

Cotton No.	Curing conditions		β-CD (mg) / g of fabric
	Temperature (^{o}C)	Time (minutes)	
18C	110	5	2.495
19C	130	5	2.799
20C	150	5	1.694
21C	170	5	1.813

molar ratio of β-CD : glyoxal is 1 : 21.
$Al_2(SO_4)_3$ was used as a catalyst.

Table 15 The amount of glyoxal-β-CD on the silk fabric after dry and cure processes.

Silk No.	Curing conditions		β-CD (mg) / g of fabric
	Temperature (^{o}C)	Time (minutes)	
18S	80	3	5.542
19S	80	5	5.613

molar ratio of β-CD : glyoxal is 1 : 21.
$Al_2(SO_4)_3$ was used as a catalyst.

Cotton and silk fabrics treated with glyoxal-β-CD were evaluated by TGA compared with the untreated ones. Thermogravimetric curves of untreated and treated cotton were shown in Figure 16. For untreated cotton, the initial loss of moisture was at about 60 ^{o}C and the main decomposition was from 300 to 360 ^{o}C. For treated cotton, there was also the loss of moisture at about 50 ^{o}C and the major decomposition process from 280 to 320 ^{o}C. The decomposition temperature of treated cotton was little lower than that of the untreated one because of the increase in the amorphous region of the treated cotton. The results were similar for untreated and treated silk fabrics as shown in Figure 17. The major decomposition proceeded from 280 °C for both fabrics. However, the treated silk decomposed at a little lower temperature than the untreated one.

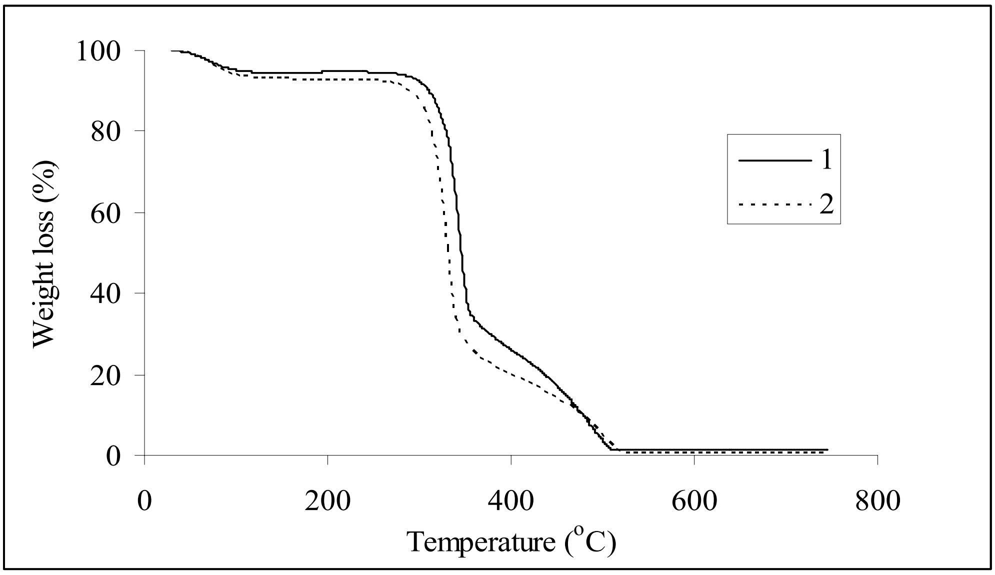


Figure 16 TGA curves: (1) untreated cotton; (2) glyoxal-β-CD treated cotton.

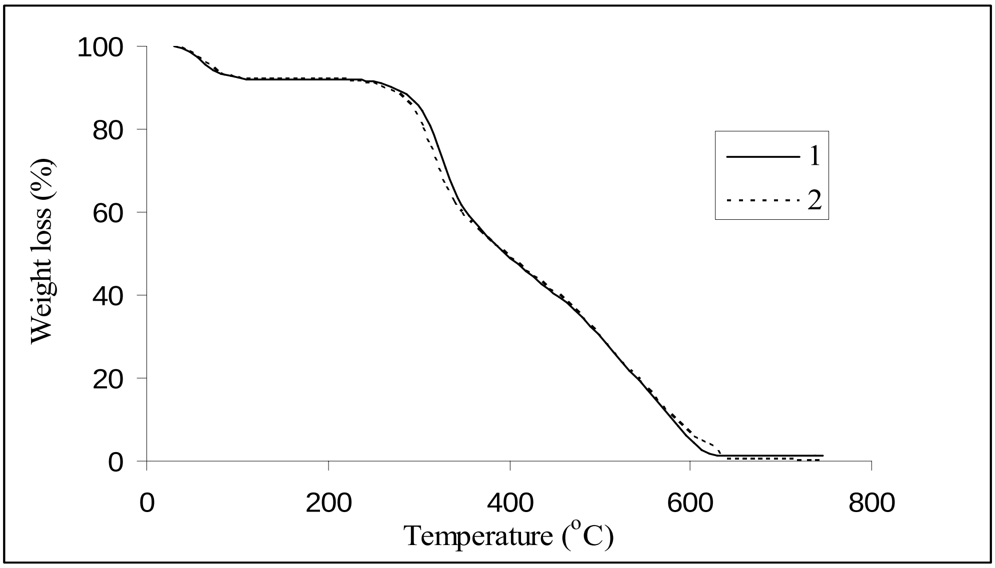
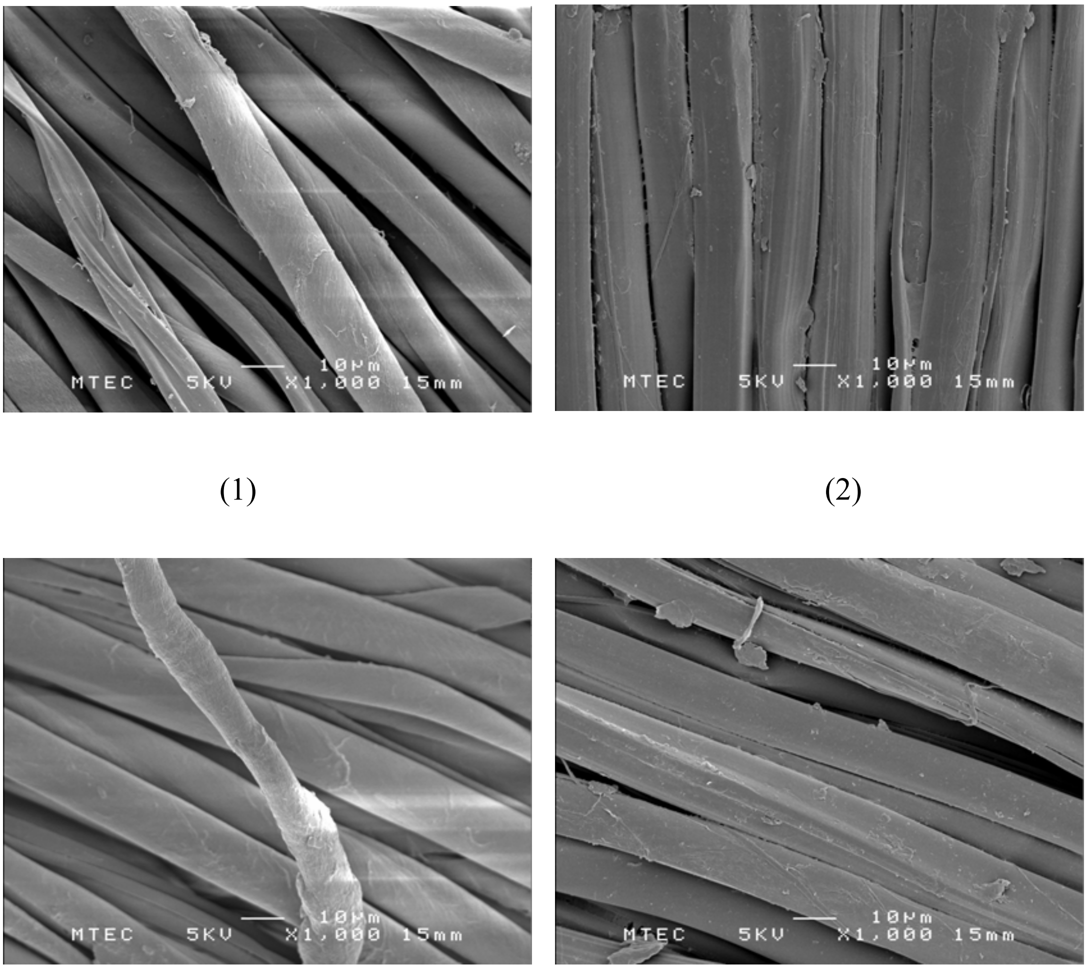


Figure 17 TGA curves: (1) untreated silk; (2) glyoxal-β-CD treated silk.

Scanning electron microscope photographs of untreated cotton, untreated silk, glyoxal-β-CD treated cotton and silk were shown in Figures 18. Glyoxal-β-CD compounds were coated on the surface of both cotton and silk fibers. The glyoxal-β-CD treated cotton and silk photographs showed that there was white material coated on their surfaces compared with the untreated ones.



(1) (2)

(3) (4)

Figure 18 SEM photographs: (1) untreated cotton; (2) untreated silk; (3) glyoxal-β-CD treated cotton; (4) glyoxal-β-CD treated silk.

4. Concentration of vanillin on fabrics

4.1 The comparison of untreated and glyoxal-β-CD treated fabrics

Vanillin was loaded on untreated and glyoxal-β-CD treated fabrics by either immersing or padding. After air-dried for 3 and 25 days, the results from UV spectra were shown in Figures 19 – 22. Figures 19 and 20 showed the absorbance of vanillin on cotton applied by immersing and padding, respectively. In both cases, the absorbance spectra of vanillin on glyoxal-β-CD treated cottons were higher than those on the corresponding untreated samples. Therefore, the amount of vanillin on glyoxal -β-CD treated cotton was more than that on the untreated cotton. This was due to the ability of vanillin to fit into the cavities of β-CD on treated cotton, so that the evaporation of the vanillin on treated fabrics was slower even after 25 days. Figures 21 and 22 showed the absorbance of vanillin on silk fabrics applied by immersing and padding processes, respectively. The results were similar to cotton fabrics that the untreated silk fabrics contained less amount of vanillin than the glyoxal-β-CD treated silk.

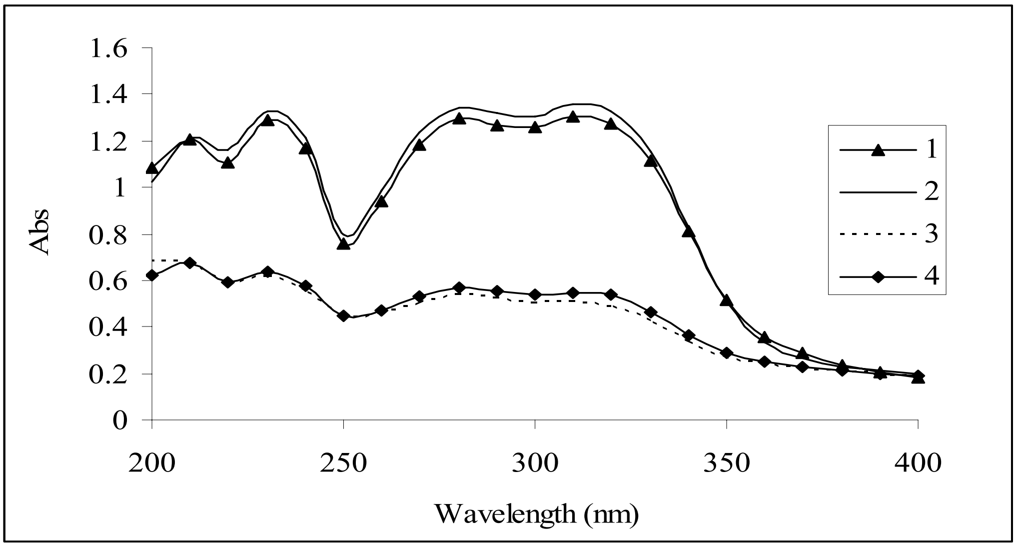


Figure 19 UV spectra of cotton fabrics loaded with vanillin by immersing: measured after 3 days (1) untreated cotton; (2) glyoxal-β-CD treated cotton; measured after 25 days (3) untreated cotton; (4) glyoxal-β-CD treated cotton.

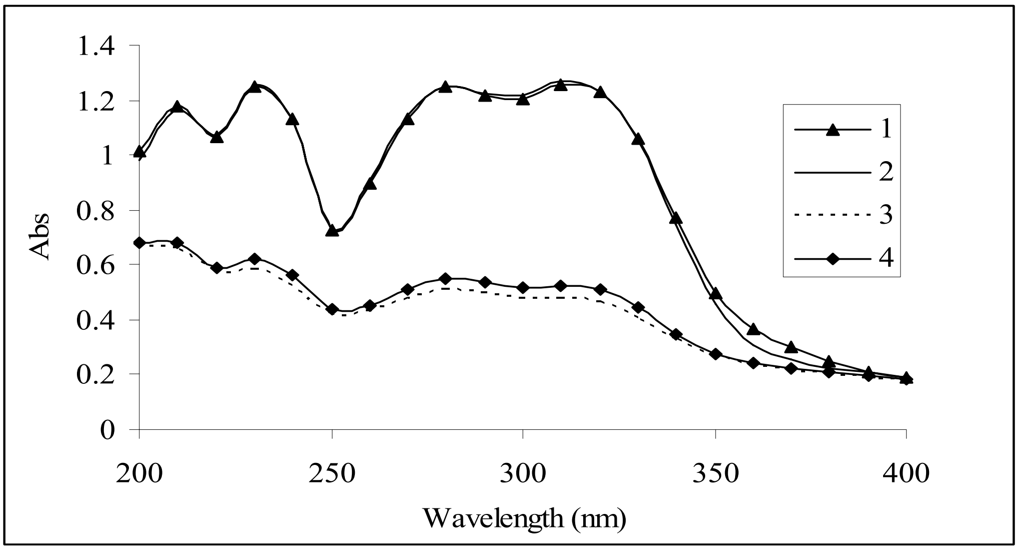


Figure 20 UV spectra of cotton fabrics loaded with vanillin by padding: measured after 3 days (1) untreated cotton; (2) glyoxal-β-CD treated cotton; measured after 25 days (3) untreated cotton; (4) glyoxal-β-CD treated cotton.

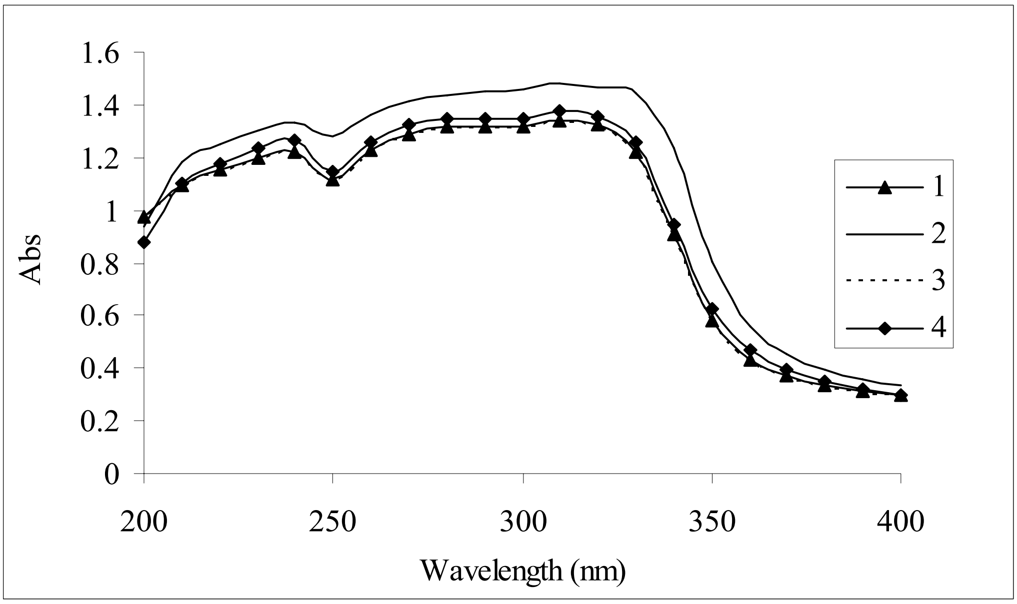


Figure 21 UV spectra of silk fabrics loaded with vanillin by immersing: measured after 3 days (1) untreated silk; (2) glyoxal-β-CD treated silk; measured after 25 days (3)untreated silk; (4) glyoxal-β-CD treated silk.

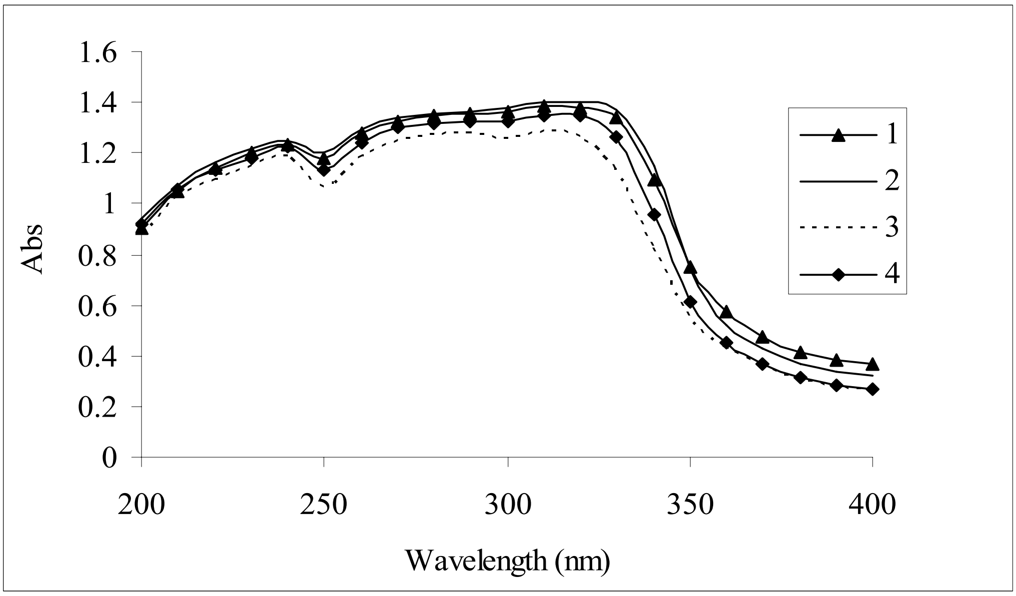


Figure 22 UV spectra of silk fabrics loaded with vanillin by padding: measured after 3 days (1) untreated silk; (2) glyoxal-β-CD treated silk; measured after 25 days (3) untreated silk; (4) glyoxal-β-CD treated silk.

The amount of vanillin on fabrics were evaluated after immersing and padding for 3, 5, 10, 13, 18, 20, and 25 days. Figures 23 and 24 showed the results from the immersing methods of untreated and glyoxal-β-CD treated cotton, respectively. The results of corresponding padding method were shown in Figures 25 and 26, respectively. It was clear that the treated cotton retained vanillin more than the untreated cotton throughout the twenty-five-day experiment. Vanillin was encapsulated by β-CDs on the surface of the fabric. β-CDs were able to decrease and controll the rate of vanillin release. Therefore, vanillin can release from the untreated cotton faster than the glyoxal-β-CD treated cotton. The results of silk fabrics were shown in Figures 27 - 30. They showed the same results as of cotton. The glyoxal-β-CD treated silks contained more vanillin than the untreated silk throughout the 25 day period.

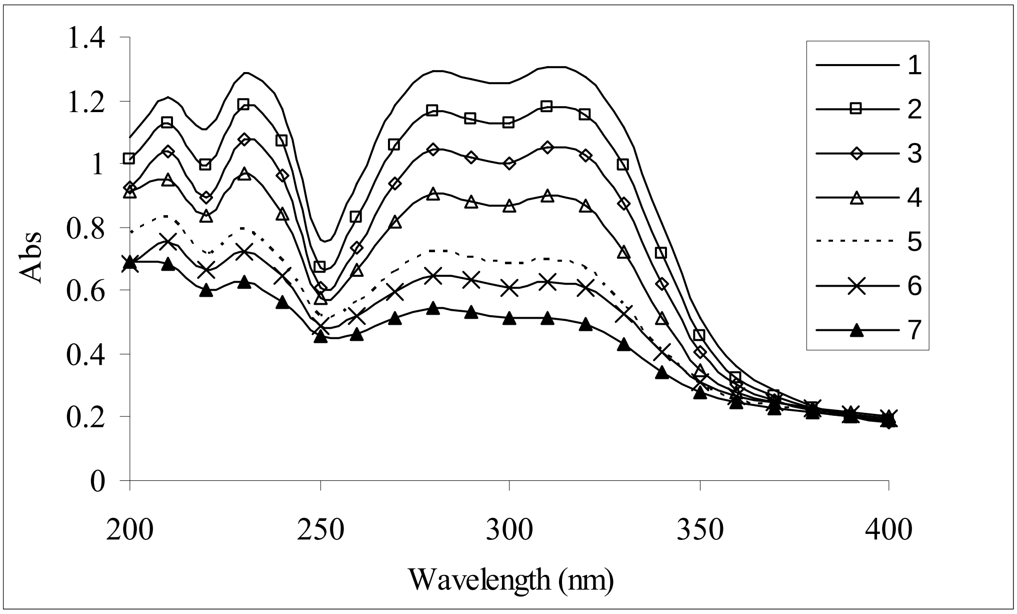


Figure 23 UV spectra of untreated cotton fabrics loaded with vanillin by immersing measured after: (1) 3 days; (2) 5 days; (3) 10 days; (4) 13 days; (5) 18 days; (6) 20 days; (7) 25 days.

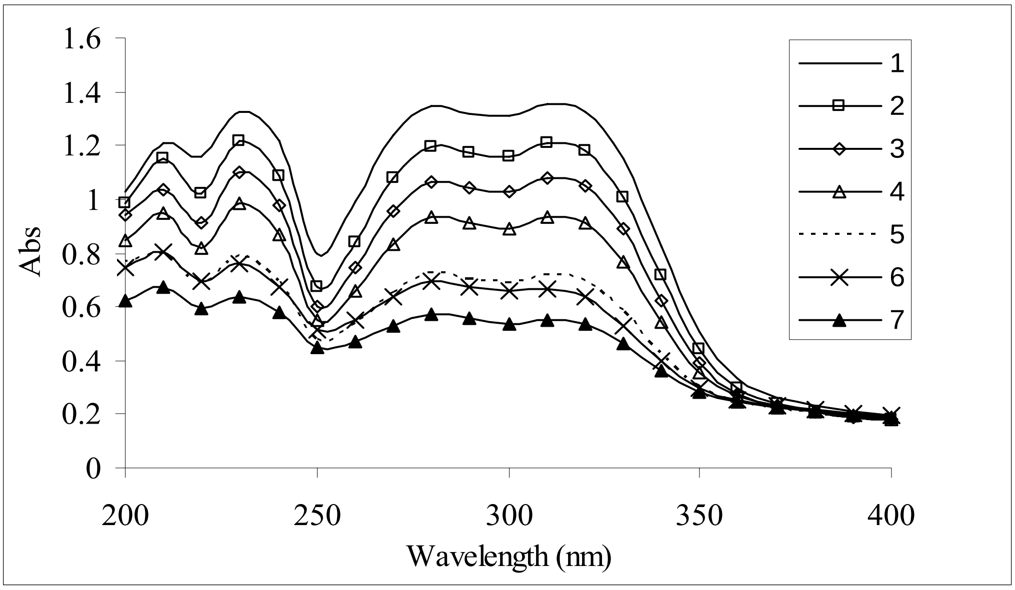


Figure 24 UV spectra of glyoxal-β-CD treated cotton fabrics loaded with vanillin by immersing after: (1) 3 days; (2) 5 days; (3) 10 days; (4) 13 days; (5) 18 days;) 20 days; (7) 25 days.

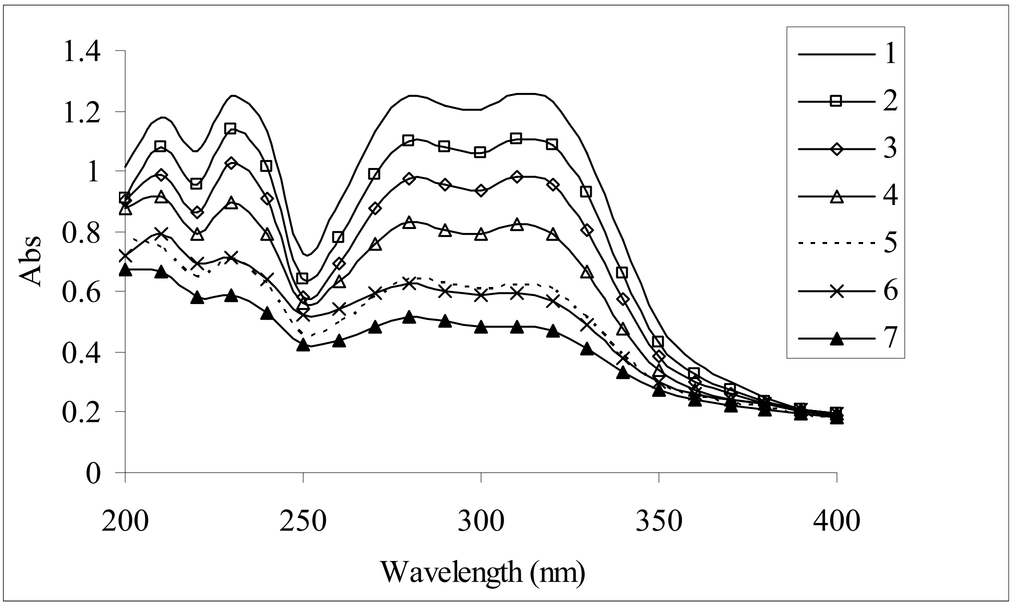


Figure 25 UV spectra of untreated cotton fabrics loaded with vanillin by padding measured after: (1) 3 days; (2) 5 days; (3) 10 days; (4) 13 days; (5) 18 days; (6) 20 days; (7) 25 days.

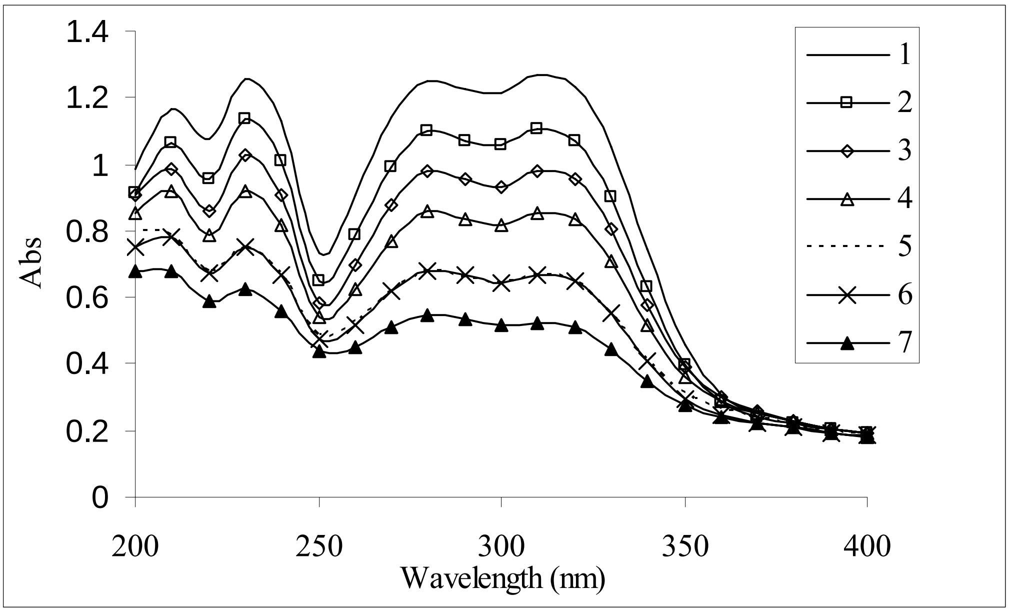


Figure 26 UV spectra of glyoxal-β-CD treated cotton fabrics loaded with vanillin by padding measured after: (1) 3 days; (2) 5 days; (3) 10 days; (4) 13 days; (5) 18 days; (6) 20 days; (7) 25 days.

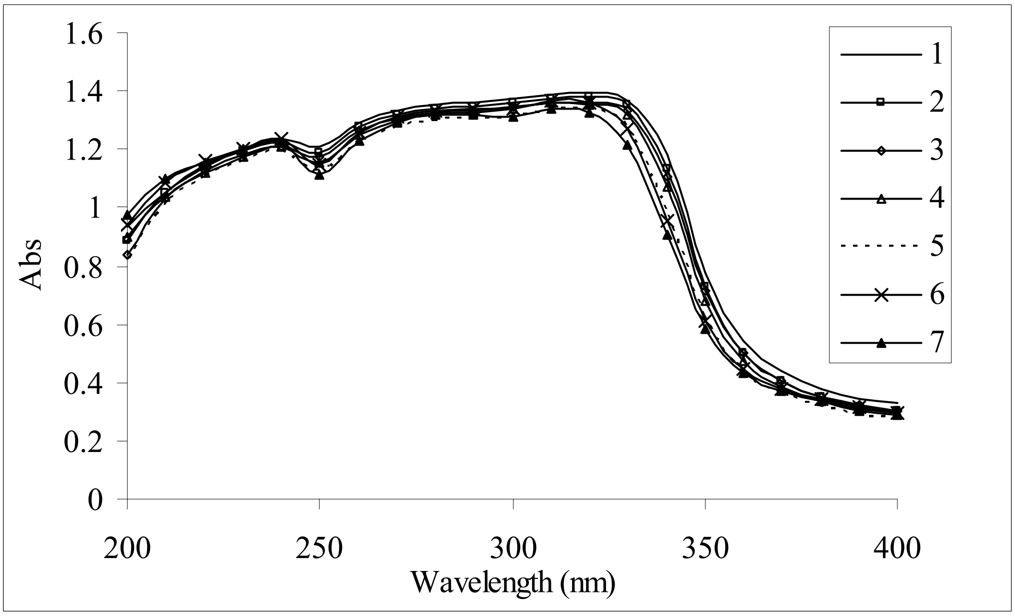


Figure 27 UV spectra of untreated silk fabrics loaded with vanillin by immersing measured after: (1) 3 days; (2) 5 days; (3) 10 days; (4) 13 days; (5) 18 days; (6) 20 days; (7) 25 days.

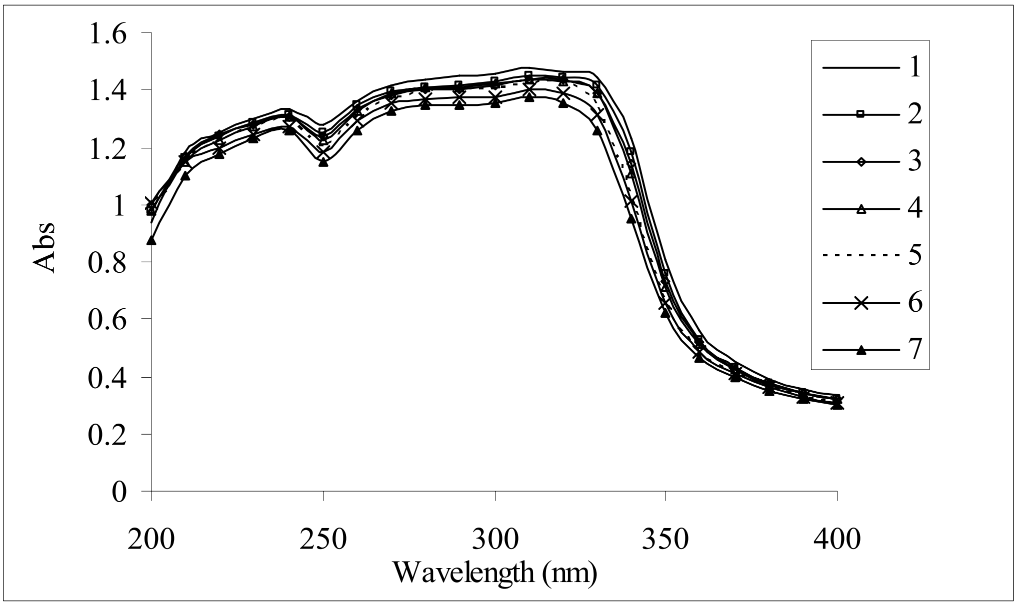


Figure 28 UV spectra of glyoxal-β-CD treated silk fabric loaded with vanillin by immersing measured after: (1) 3 days; (2) 5 days; (3) 10 days; (4) 13 days; (5) 18 days; (6) 20 days; (7) 25 days.

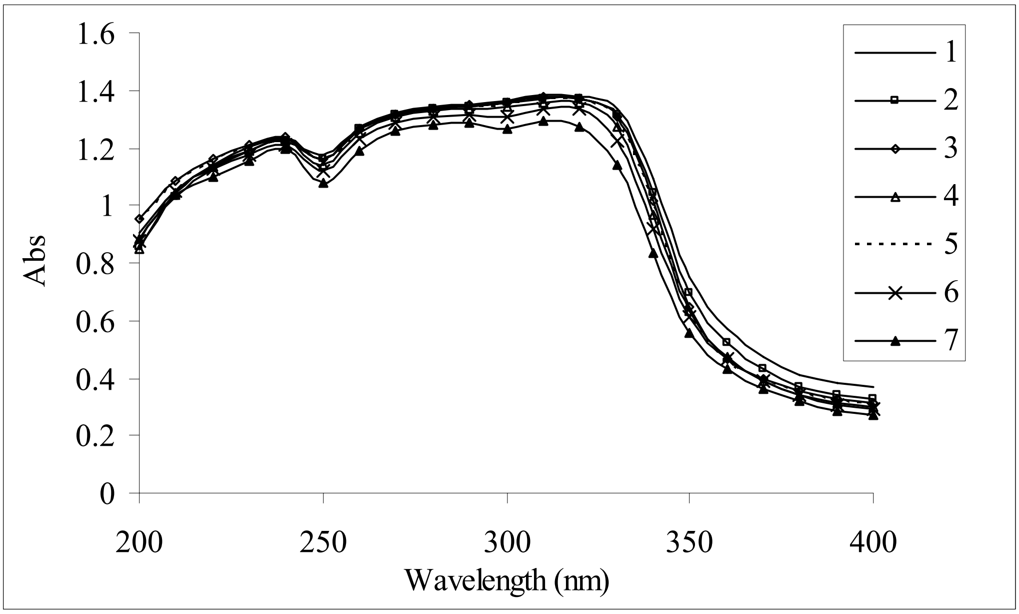


Figure 29 UV spectra of untreated silk fabrics loaded with vanillin by padding measured after: (1) 3 days; (2) 5 days; (3) 10 days; (4) 13 days; (5) 18 days; (6) 20 days; (7) 25 days.

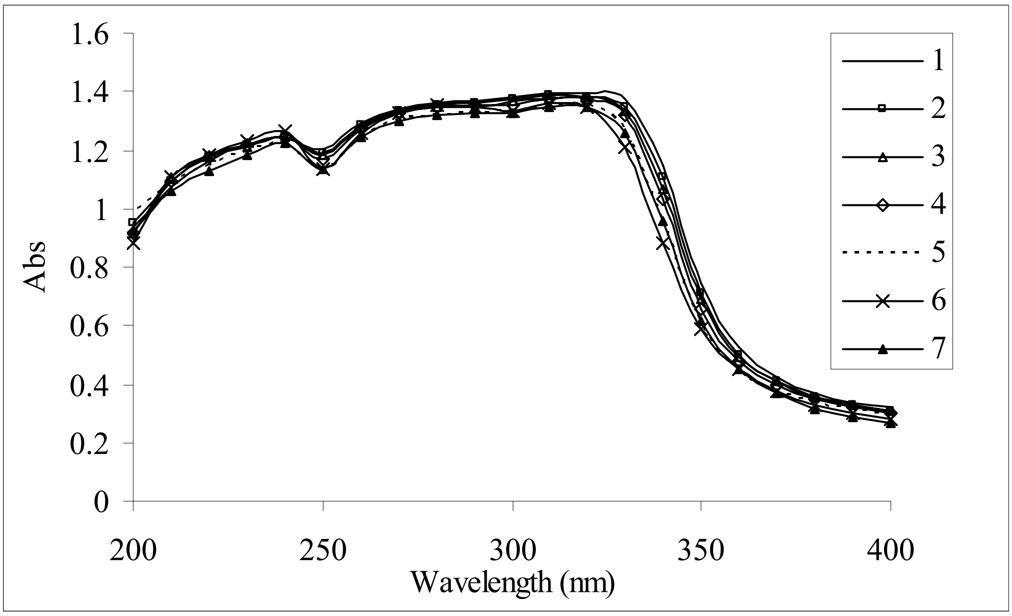


Figure 30 UV spectra of glyoxal-β-CD treated silk fabric loaded with vanillin by padding measured after: (1) 3 days; (2) 5 days; (3) 10 days; (4) 13 days; (5) 18 days; (6) 20 days; (7) 25 days.

4.2 The comparison of immersing and padding processes

The UV spectra in Figures 31 and 32 showed the results from immersing and padding in the application of vanillin on cotton and silk fabrics, respectively. The results indicated that immersing gave higher amount of vanillin on fabrics. We believed that because in padding method, the fabrics were in vanillin solution only for 10 minutes and then using the pressure from the padder to fix vanillin on the fabric. On the other hand, the fabrics were in the vanillin solution for 24 hours in immersing which gave longer contact time for the fabric.

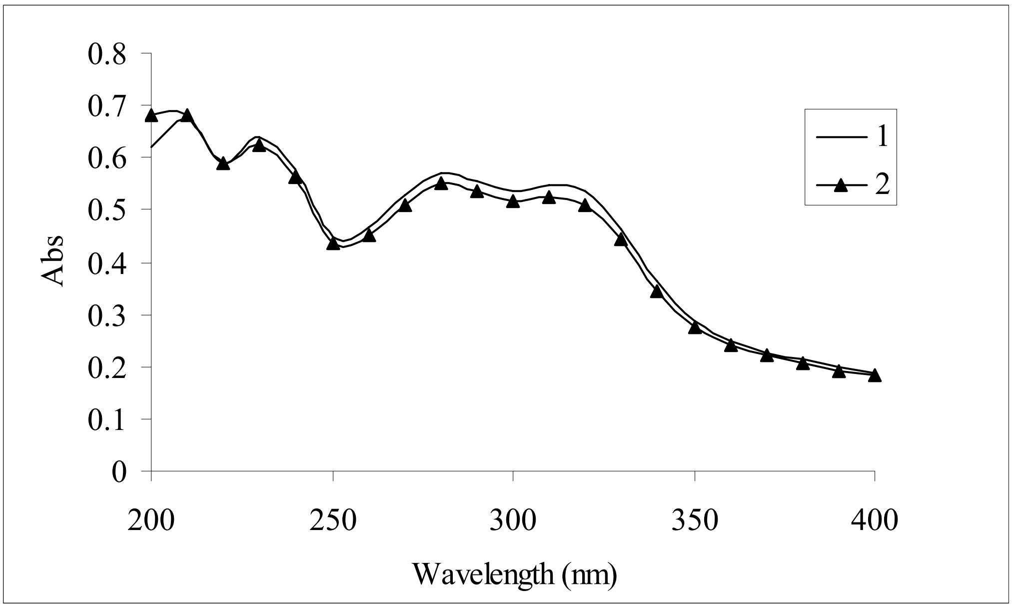


Figure 31 UV spectra of glyoxal-β-CD treated cotton fabrics loaded with vanillin by: (1) immersing; (2) padding (measured after 25 days).

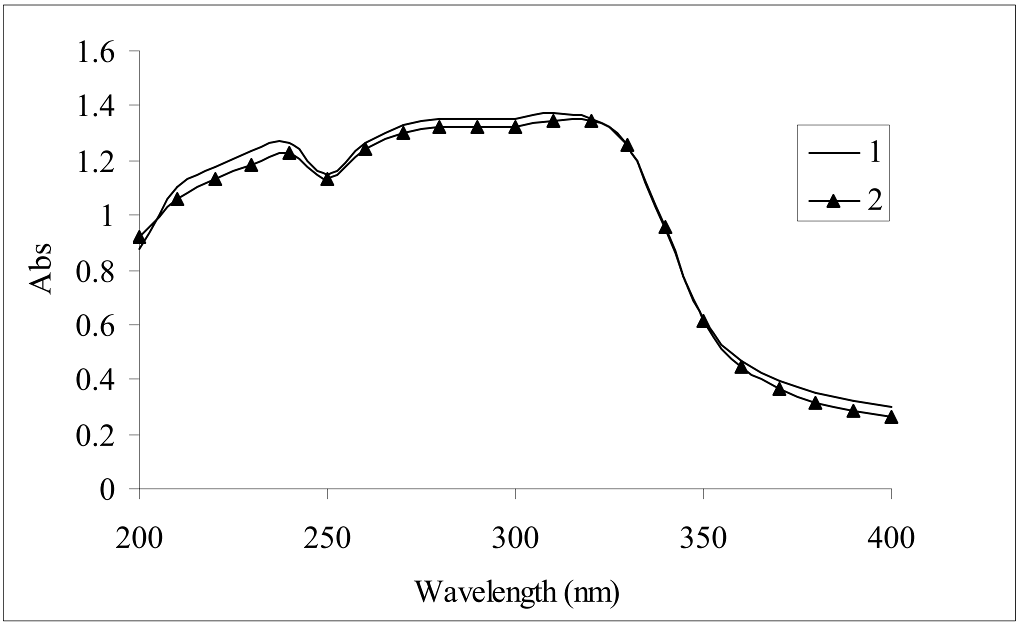


Figure 32 UV spectra of glyoxal-β-CD treated silk fabrics loaded with vanillin by: (1) immersing; (2) padding (measured after 25 days).

4.3 Durability of glyoxal-β-CD on fabrics

Figures 33 and 34 showed the amount of vanillin on treated cotton compared with after washed cotton using immersing and padding processes, respectively. The results were similar to the treated silk and after washed silk fabrics in Figures 35 and 36. Even the fabrics were washed after treated with glyoxal-β-CD, β-CDs were still anchored on the fabrics by glyoxal. The results from Figures 33 – 36 showed that the amount of vanillin on both washed and unwashed fabric was almost the same. Therefore, glyoxal anchored β-CD on fabric can withstand at least one wash of laundering.

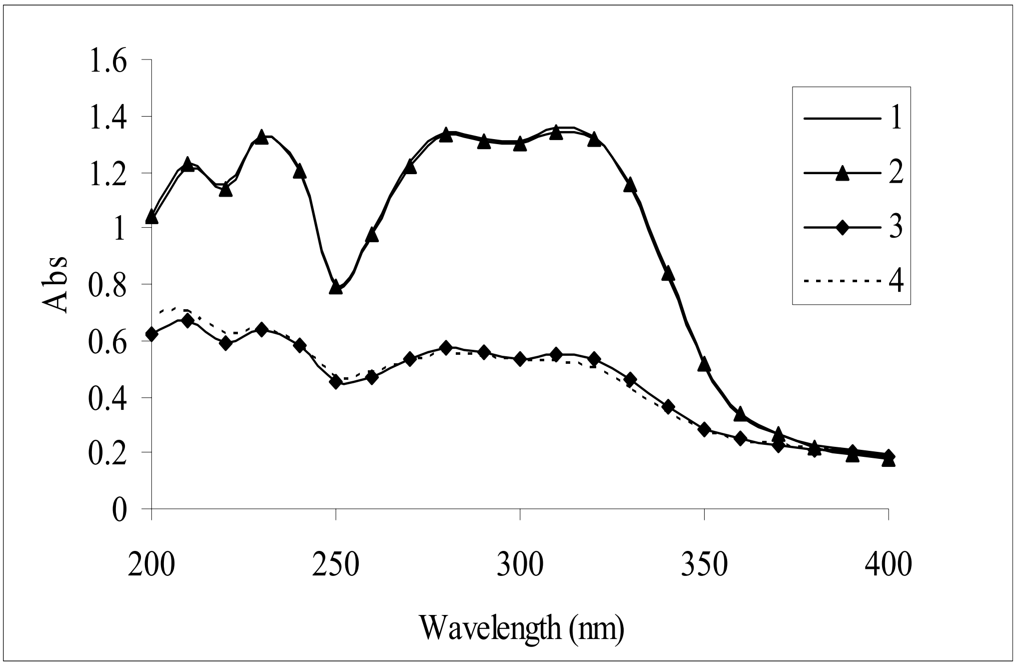


Figure 33 UV spectra of glyoxal-β-CD treated cotton loaded with vanillin by immersing: measured after 3 days (1) unwashed; (2) washed; measured after 25 days (3) unwashed; (4) washed.

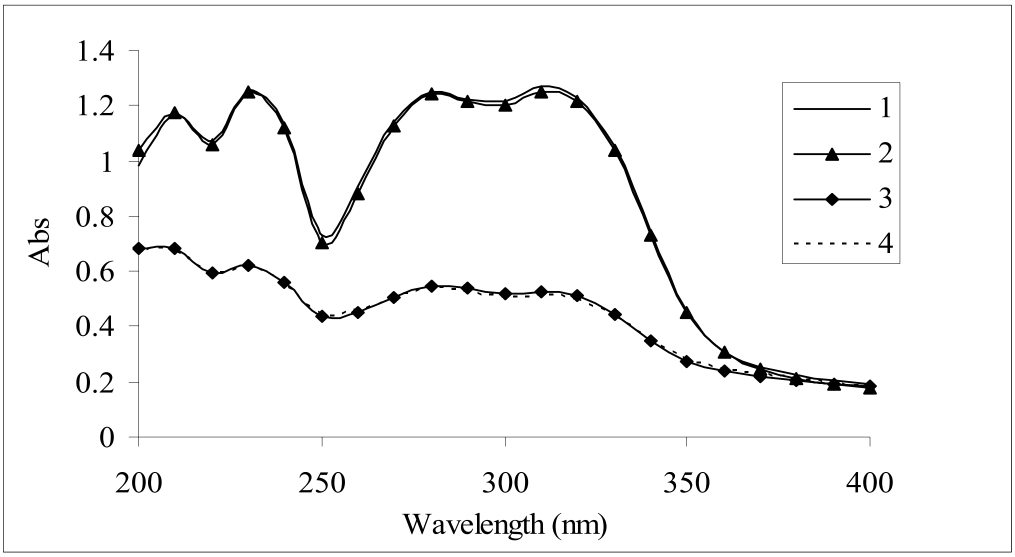


Figure 34 UV spectra of glyoxal-β-CD treated cotton loaded with vanillin by padding: measured after 3 days (1) unwashed; (2) washed; measured after 25 days (3) unwashed; (4) washed.

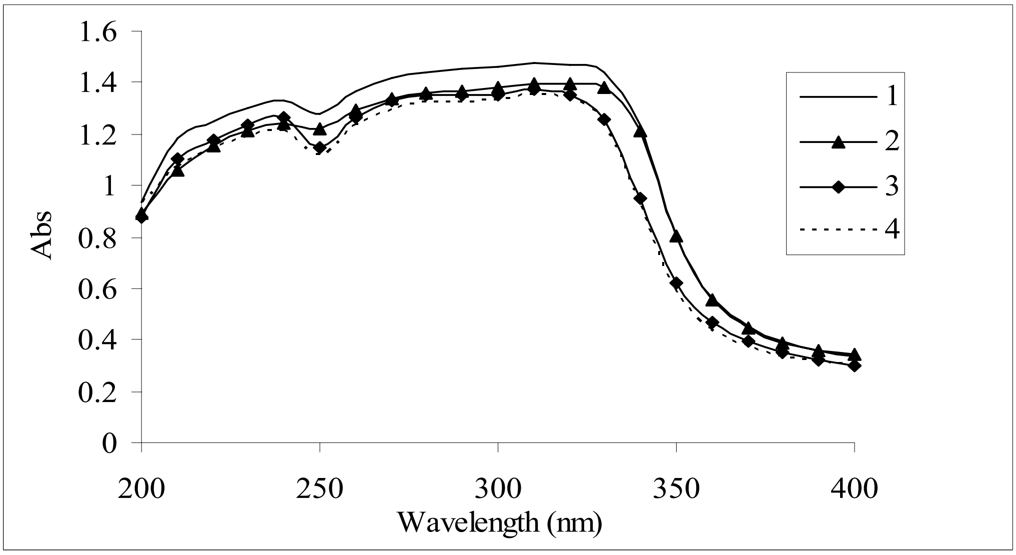


Figure 35 UV spectra of glyoxal-β-CD treated silk loaded with vanillin by immersing: measured after 3 days (1) unwashed; (2) washed; measured after 25 days (3) unwashed; (4) washed.

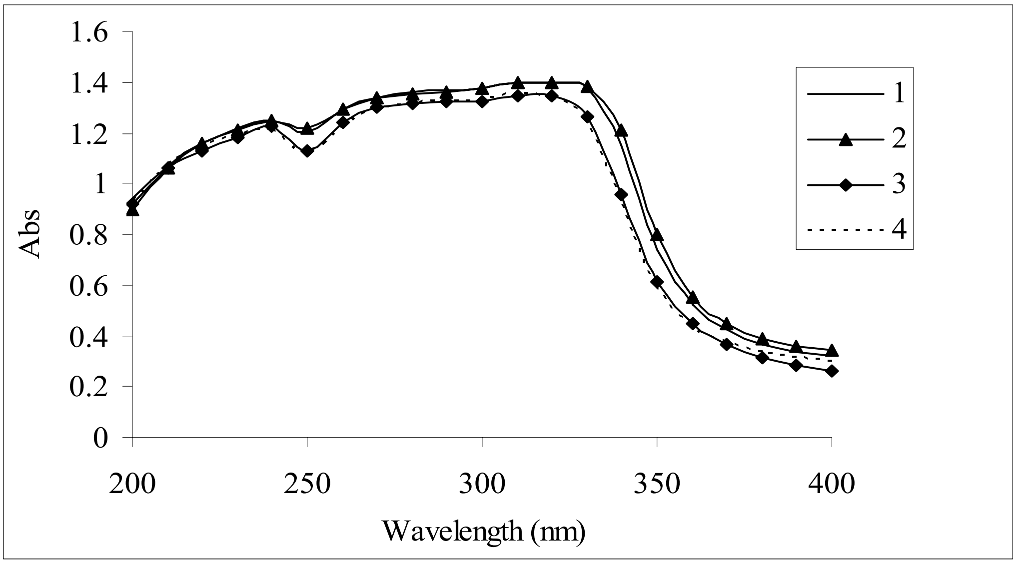


Figure 36 UV spectra of glyoxal-β-CD treated silk loaded with vanillin by padding: measured after 3 days (1) unwashed; (2) washed; measured after 25 days (3) unwashed; (4) washed.

CONCLUSION

In this present study, the synthesis of glyoxal and β-cyclodextrin was investigated in terms of three different molar ratios of β-cyclodextrin to glyoxal (1 : 7, 1 : 14 and 1 : 21), two types of catalysts ($Al_2(SO_4)_3$ and Na_2CO_3) and three reaction temperatures (room temperature (RT), 50 °C, and 80 °C). FTIR, TGA, DSC techniques were used to confirm the formation of glyoxal-β-cyclodextrin complexes.

The resultant glyoxal-β-cyclodextrin complexes were applied on cotton and silk fabrics using pad-dry-cure process. Based on the amounts of β-CD on treated fabrics, which were determined by the use of phenolphthalein indicator, the 1:21 molar ratios of β-cyclodextrin to glyoxal with catalysts $Al_2(SO_4)_3$ and room reaction temperature yielded the highest amount of β-CD.

Besides, temperature and time during drying and curing steps affected the whiteness of glyoxal-β-cyclodextrin treated fabrics, especially on silk. The whiteness index of treated silk decreased considerably with higher temperature and longer time. Thus, in order to maintain the whiteness and obtain the high amount of β-CD on treated fabric, cotton was dried at 100 °C for 5 minutes and cured at 130 °C for 3 minutes, while silk was dried at 50 °C for 5 minutes and cured at 80 °C for 5 minutes. SEM photographs and TGA analysis confirmed the existence of glyoxal-β-cyclodextrin complexes on treated fabrics. Furthermore, glyoxal-β-cyclodextrin complexes on the fabrics could at least withstand a cycle of washing.

In view of the ability of β-CD on treated fabric to encapsulate fragrance molecules, vanillin was deposited on fabrics either by immersing or padding methods. Of these two methods, immersing seemed to be more effective for loading vanillin. This is because the fabric had longer contact time in vanillin solution, so that more vanillin molecules could encapsulate in the cavity of β-CD. After vanillin loading for 25 days, it was also evident that the amount of vanillin on glyoxal-β-cyclodextrin treated fabrics was higher than the counterpart untreated for both cotton and silk.

Based on the results of this study, it would be possible to employ glyoxal-β-cyclodextrin complexes to control or prolong the release of fragrance in textile products but require further studies. As future work, spraying might be utilized as an alternative method of loading vanillin on fabrics. Sensory tests could be also performed as another assessment of the intensity of vanillin over time.

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APPENDICES

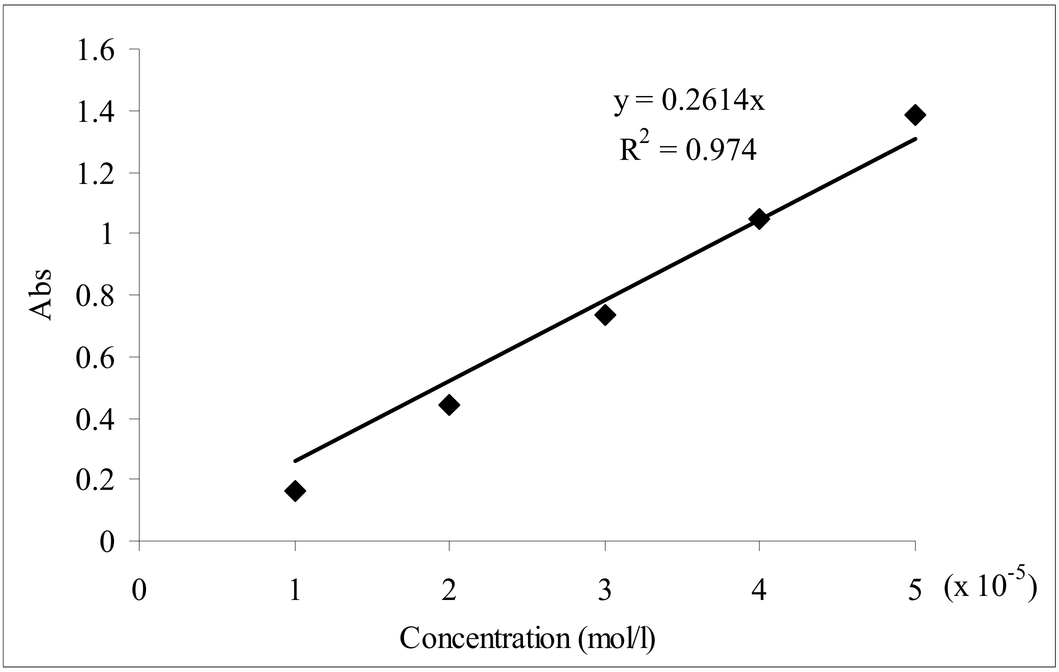
Appendix A

Calculation examples

Amount of glyoxal-β-CD on the fabrics

The graph was ploted between absorbances (Abs) and concentrations of phenolphthalein (Conc.) in mol/l. The slope of the linear line was calculated. The equation is :

y = mx + b
Abs = (Slope x Conc.) + 0
= 0.2614 x Conc.



Appendix Figure 1 The calibration curve of phenolphthalein.

1. The calculation amount of β-CD on one gram fabric

Untreated fabric : Conc. $= \dfrac{Abs}{0.2614} = A \times 10^{-5}$ mol/l

Treated fabric : Conc. $= \dfrac{Abs}{0.2614} = B \times 10^{-5}$ mol/l

The concentration of phenolphthalein on fabric $= (A - B) \times 10^{-5}$ mol/l

$= C$ mol/l

(Molecular weight of phenolphthalein is 318 g/mol) $= C\ \dfrac{mol}{l} \times 318\ \dfrac{g}{mol}$

$= E\ \dfrac{g}{l} \times 1{,}000\ \dfrac{mg}{g}$

$= F$ mg/l

In the experiment, 50 ml phenolphthalein was used.

$\therefore$ Amount of phenolphthalein on fabric $= \dfrac{Fmg}{1000ml} \times 50\text{ ml} = G\text{ mg}$

If the fabric weighed H g

$\therefore$ Amount of phenolphthalein on one gram fabric $= \dfrac{Gmg}{Hg} \times 1\text{ g} = J\text{ mg}$

Assumed that mole ratio of phenolphthalein : β-CD = 1 : 1

Molecular weight of β-CD is 1135 g

$\therefore$ Amount of β-CD on one gram fabric $= J\text{ mg} \times \dfrac{1135g/mol}{318g/mol} = K\text{ mg}$

2. The example of calculation

2.1 Calculation of glyoxal-β-cyclodextrin on cotton (the sample 1C)

Untreated cotton : Conc. $= \dfrac{Abs}{0.2614}$

Conc. $= \dfrac{1.53720}{0.2614} = 5.881 \times 10^{-5}$ mol/l

The sample 1 C : Conc. $= \dfrac{1.07117}{0.2614} = 4.098 \times 10^{-5}$ mol/l

The concentration of phenolphthalein on the sample 1C $= (5.881 - 4.098) \times 10^{-5}$

$= 1.783 \times 10^{-5}$ mol/l

$$= 1.783 \times 10^{-5} \frac{mol}{l} \times 318 \frac{g}{mol}$$

$$= 5.670 \times 10^{-3} \frac{g}{l} \times 1{,}000 \frac{mg}{g}$$

$= 5.670$ mg/l

In the experiment, 50 ml phenolphthalein was used.

$\therefore$ Amount of phenolphthalein on the sample 1C $= \dfrac{5.670mg}{1000ml} \times 50\text{ml} = 0.284$ mg

The sample 1C weighed 0.87 g

$\therefore$ Amount of phenolphthalein on one gram of the sample 1C $= \dfrac{0.284mg}{0.87g} \times 1\text{g}$

$= 0.326$ mg

Assumed that mole ratio of phenolphthalein : β-CD = 1 : 1

Molecular weight of β-CD is 1135 g

$\therefore$ Amount of β-CD on one gram of the sample 1C $= 0.326 \text{ mg} \times \dfrac{1135g/mol}{318g/mol}$

$= 1.163$ mg

2.2 Calculation of glyoxal-β-cyclodextrin on silk (the sample 1S)

Untreated silk : Conc. = $\frac{Abs}{0.2614}$

Conc. = $\frac{1.50918}{0.2614}$ = 5.773×10^{-5} mol/l

The sample 1S : Conc. = $\frac{1.16946}{0.2614}$ = 4.474×10^{-5} mol/l

The concentration of phenolphthalein on the sample 1S = $(5.773 - 4.474) \times 10^{-5}$

$= 1.299 \times 10^{-5}$ mol/l

$= 1.299 \times 10^{-5} \frac{mol}{l} \times 318 \frac{g}{mol}$

$= 4.131 \times 10^{-3} \frac{g}{l} \times 1{,}000 \frac{mg}{g}$

= 4.131 mg/l

In the experiment, 50 ml phenolphthalein was used.

$\therefore$ Amount of phenolphthalein on the sample 1S = $\frac{4.131mg}{1000ml} \times 50$ ml = 0.206 mg

The sample 1S weight 0.30 g

$\therefore$ Amount of phenolphthalein on one gram of the sample 1C = $\frac{0.206mg}{0.30g} \times 1$ g

= 0.687 mg

Assumed that mole ratio of phenolphthalein : β-CD = 1 : 1

Molecular weight of β-CD is 1135 g

$\therefore$ Amount of β-CD on one gram of the sample 1S = 0.687 mg x $\frac{1135g/mol}{318g/mol}$

= 2.452 mg

Appendix Table 1 The amount of glyoxal-β-CD on the cotton fabric.

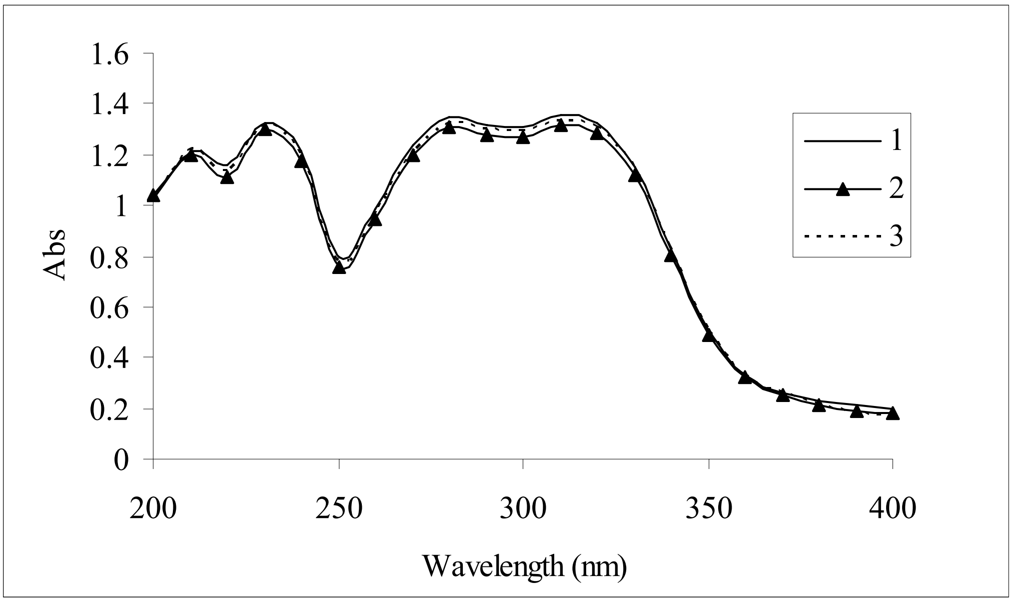
Cotton No.	Abs	β-CD (mg) / g of fabric
Untreated cotton	1.5372	
1C	1.07117	1.163
2C	1.39788	0.348
3C	1.10294	1.084
4C	1.50911	0.070
5C	1.07894	1.157
6C	1.34993	0.462
7C	0.5989	2.341
10C	0.41728	2.827
Untreated cotton	1.3751	
8C	0.55346	2.051
9C	0.74962	1.580
11C	0.58731	1.989
12C	0.49182	2.180
Untreated cotton	1.47409	
13C	0.90054	1.431
14C	1.21177	0.655
15C	1.10218	0.918
16C	0.82872	1.592
17C	0.97716	1.240
Cotton untreated	1.03426	
18C	0.3593	2.495
19C	0.22164	2.799
20C	0.68734	1.694
21C	0.66376	1.813

Appendix Table 2 The amount of glyoxal-β-CD on the silk fabric.

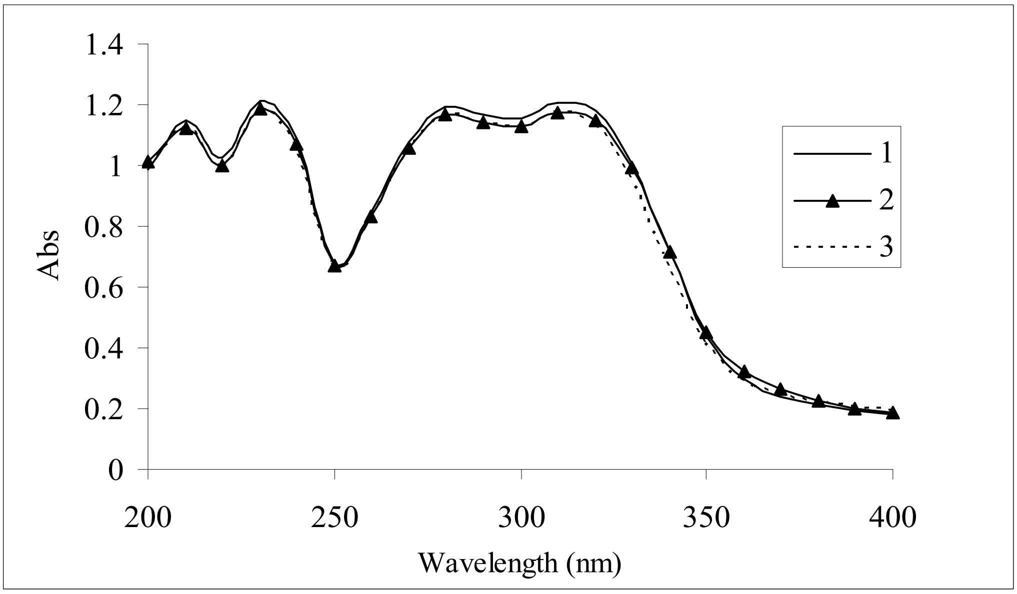
Silk No.	**Abs**	**β-CD (mg) / g of fabric**
Untreated silk	1.50918	
1S	1.16946	2.452
2S	1.45918	0.350
3S	1.11499	2.761
4S	1.45976	0.355
5S	1.16581	2.485
6S	1.4217	0.633
Untreated silk	1.33981	
7S	0.69513	4.665
8S	0.48424	6.992
9S	0.50454	6.045
10S	0.60837	7.966
11S	0.49372	7.456
12S	0.42444	7.514
Untreated silk	1.36464	
13S	0.73735	4.539
14S	0.63568	4.946
15S	0.69114	4.874
16S	0.53627	5.801
17S	0.58151	5.667
18S	0.54783	5.542
19S	0.53725	5.613

Appendix B

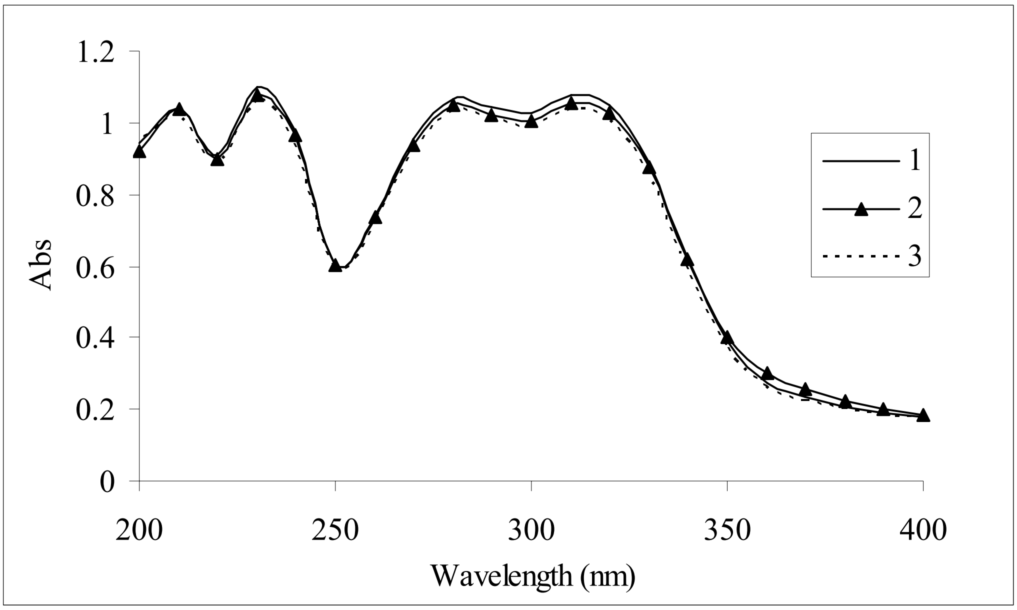
UV spectra of cotton fabrics loaded with vanillin



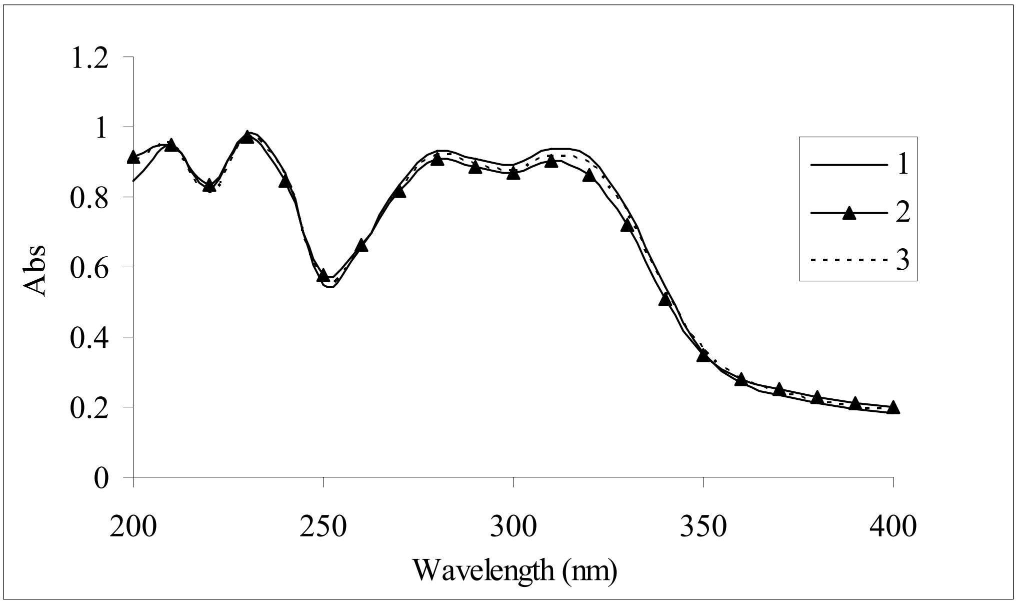
Appendix Figure 2 UV spectra of cotton fabrics loaded with vanillin by immersing (measure after 3 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



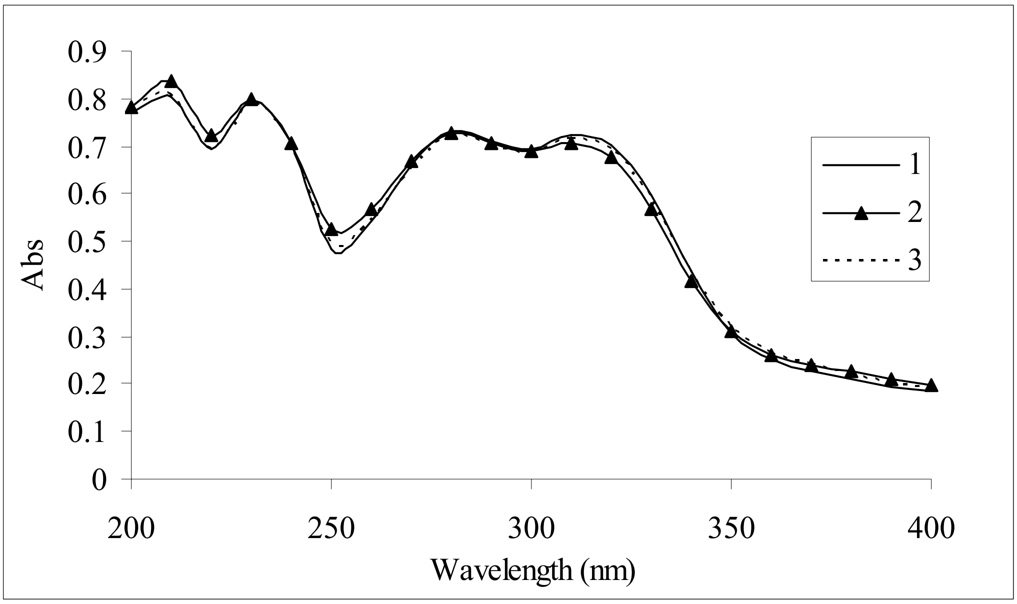
Appendix Figure 3 UV spectra of cotton fabrics loaded with vanillin by immersing (measure after 5 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



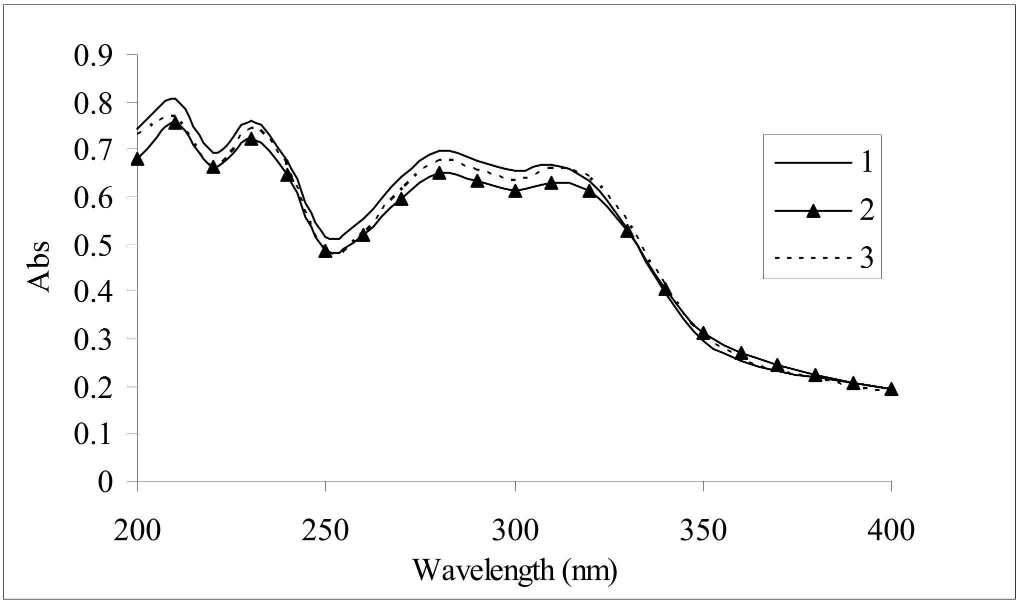
Appendix Figure 4 UV spectra of cotton fabrics loaded with vanillin by immersing (measure after 10 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



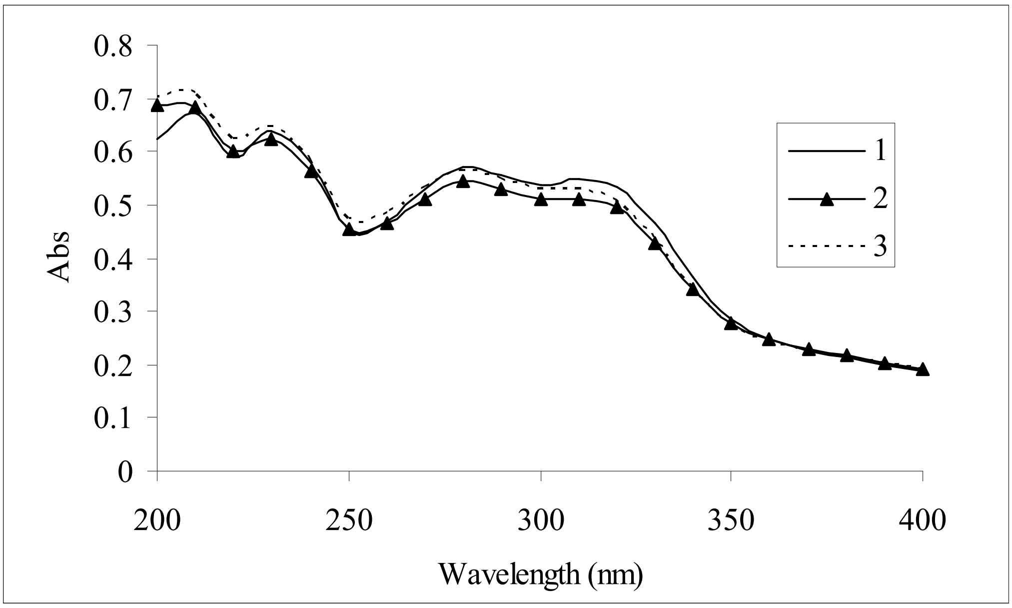
Appendix Figure 5 UV spectra of cotton fabrics loaded with vanillin by immersing (measure after 13 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



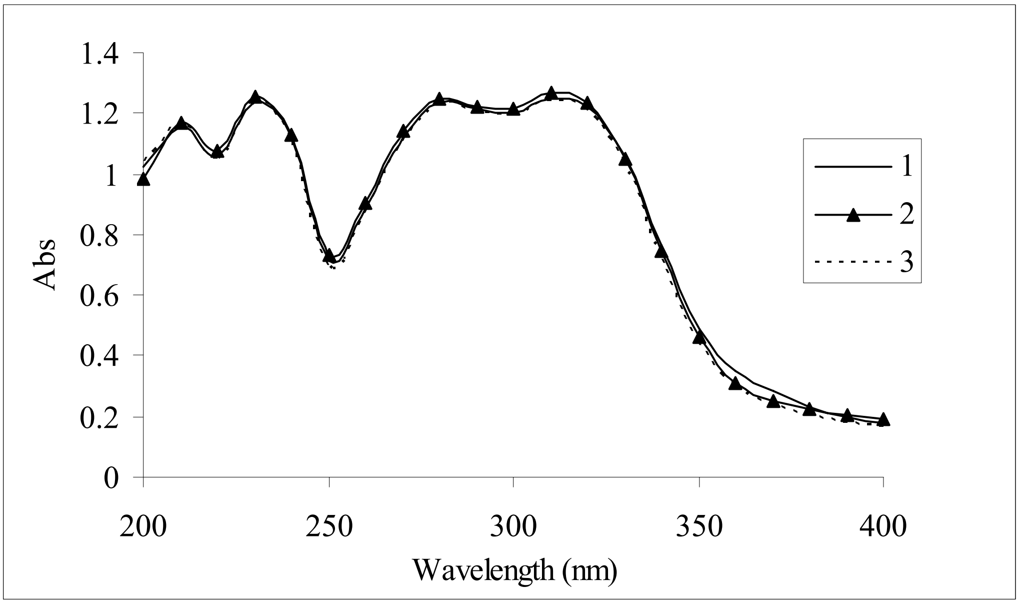
Appendix Figure 6 UV spectra of cotton fabrics loaded with vanillin by immersing (measure after 18 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



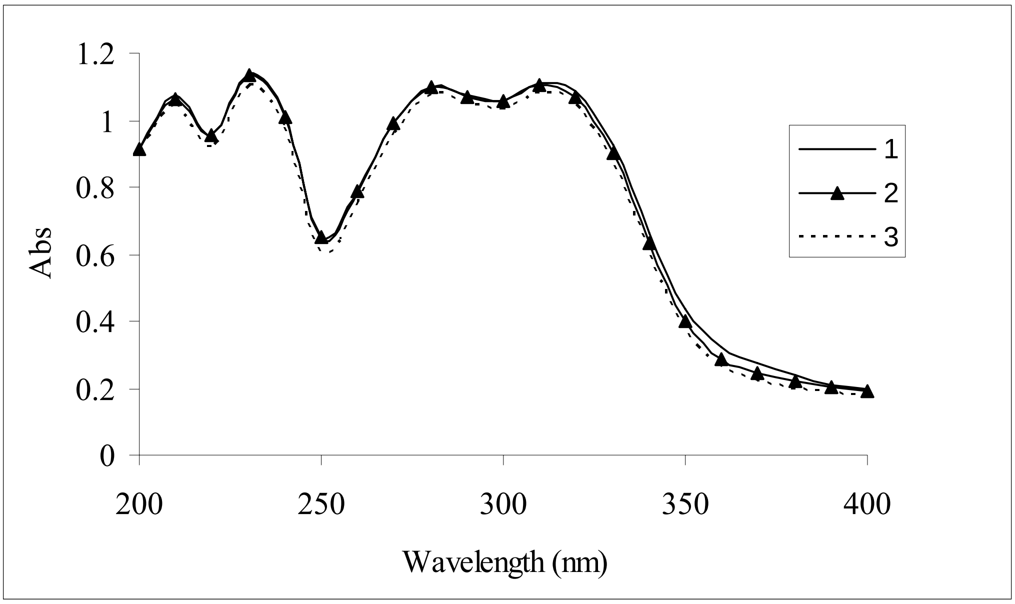
Appendix Figure 7 UV spectra of cotton fabrics loaded with vanillin by immersing (measure after 20 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



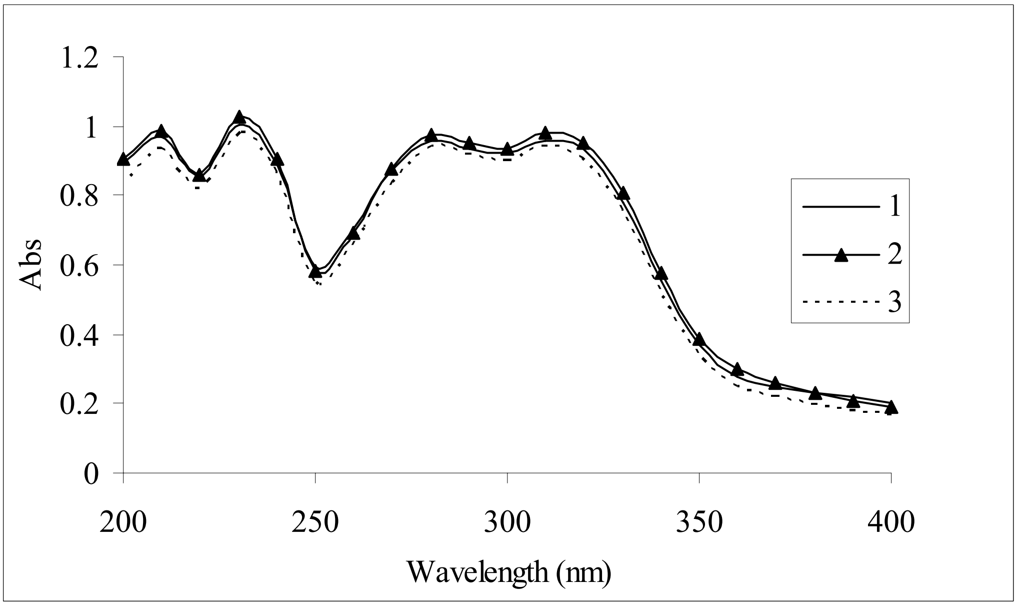
Appendix Figure 8 UV spectra of cotton fabrics loaded with vanillin by immersing (measure after 25 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



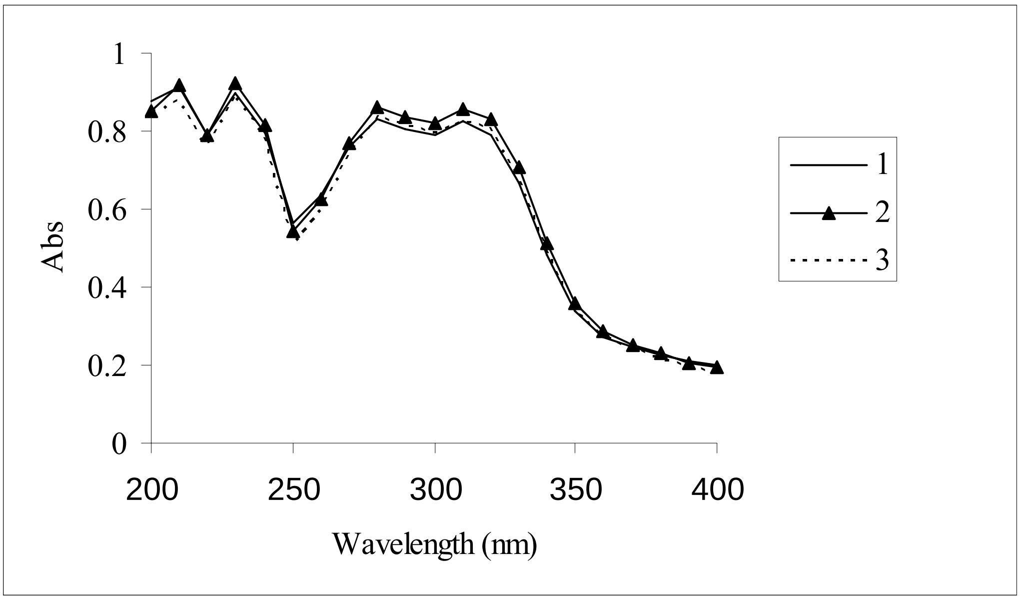
Appendix Figure 9 UV spectra of cotton fabrics loaded with vanillin by padding (measure after 3 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



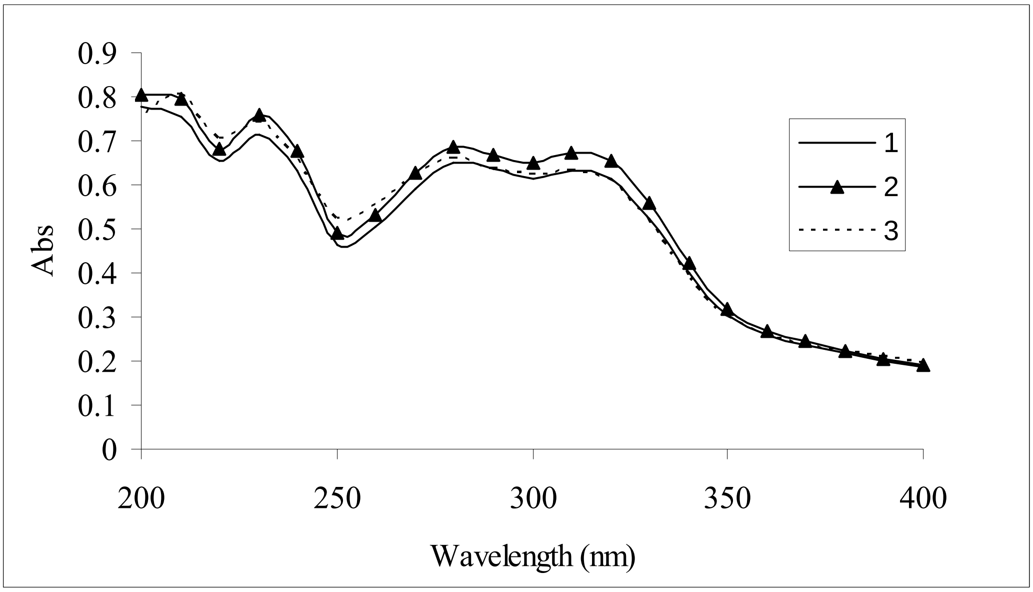
Appendix Figure 10 UV spectra of cotton fabrics loaded with vanillin by padding (measure after 5 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



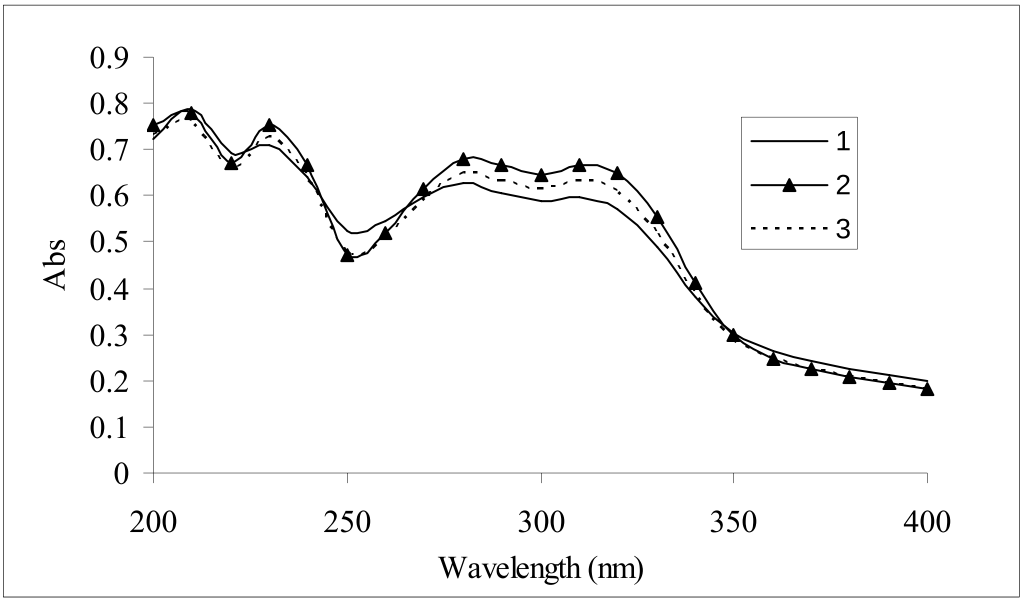
Appendix Figure 11 UV spectra of cotton fabrics loaded with vanillin by padding (measure after 10 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



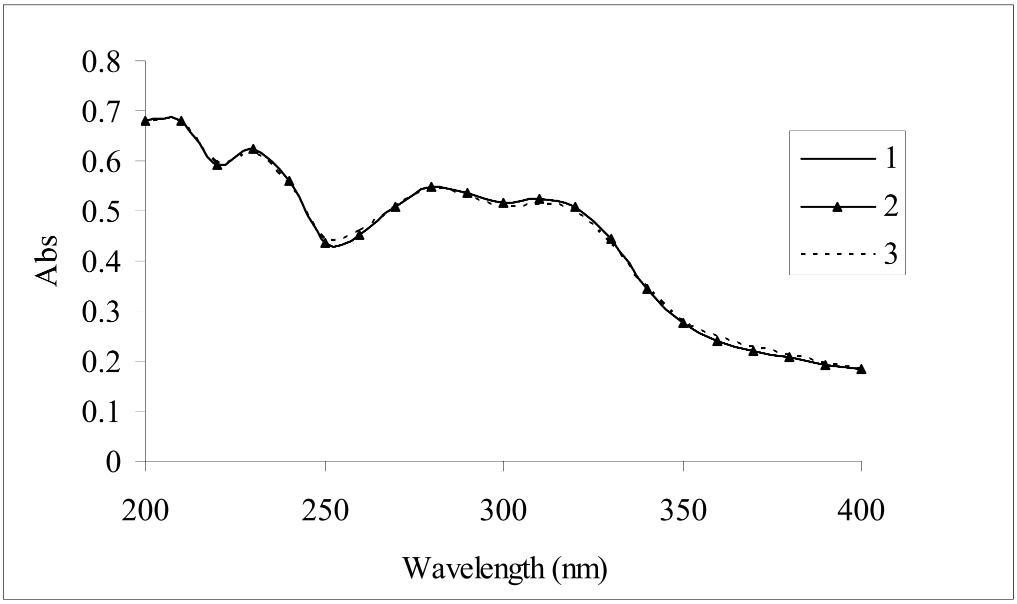
Appendix Figure 12 UV spectra of cotton fabrics loaded with vanillin by padding (measure after 13 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



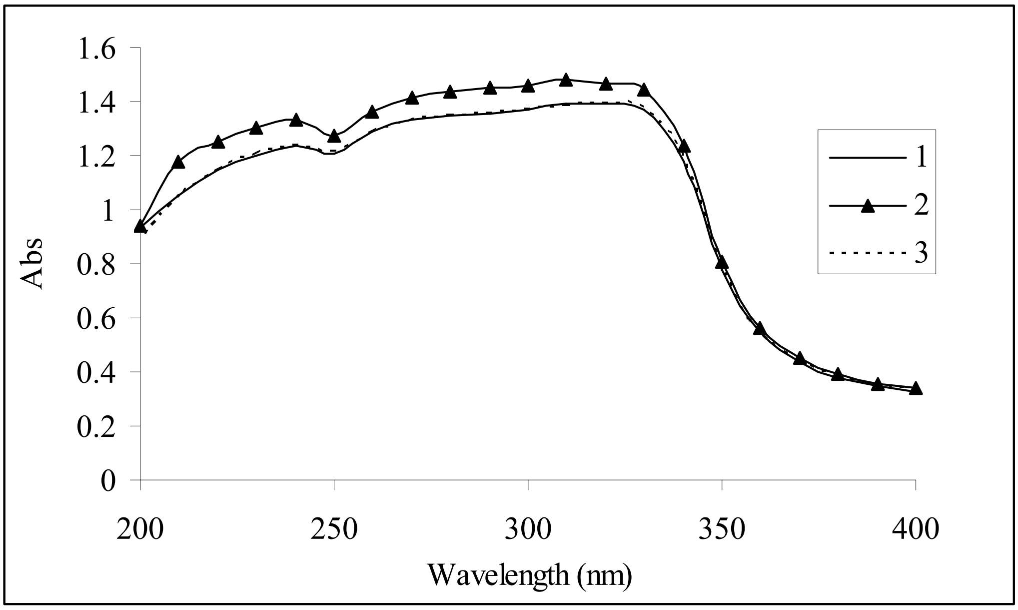
Appendix Figure 13 UV spectra of cotton fabrics loaded with vanillin by padding (measure after 18 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



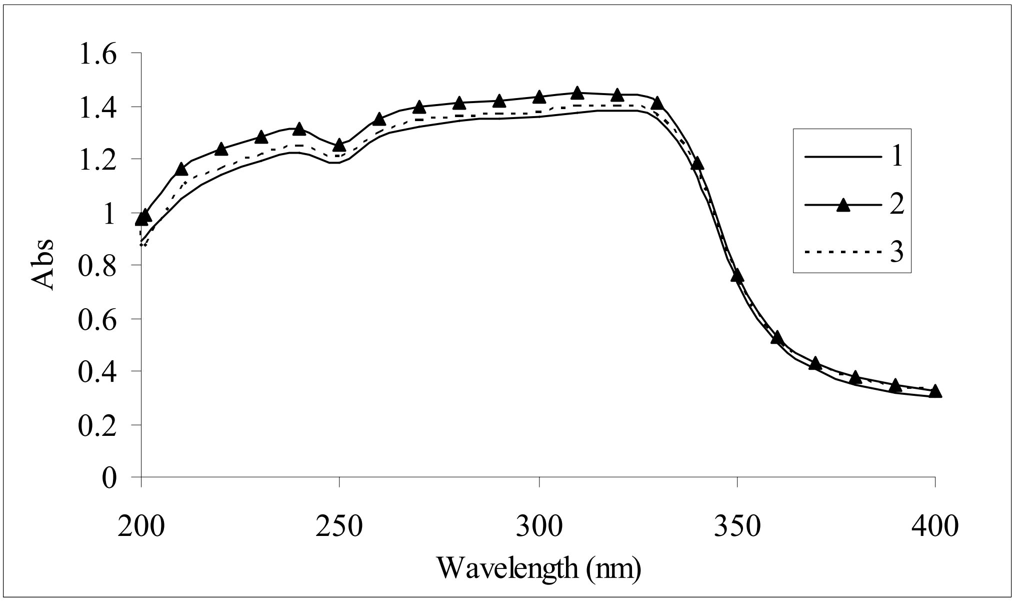
Appendix Figure 14 UV spectra of cotton fabrics loaded with vanillin by padding (measure after 20 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



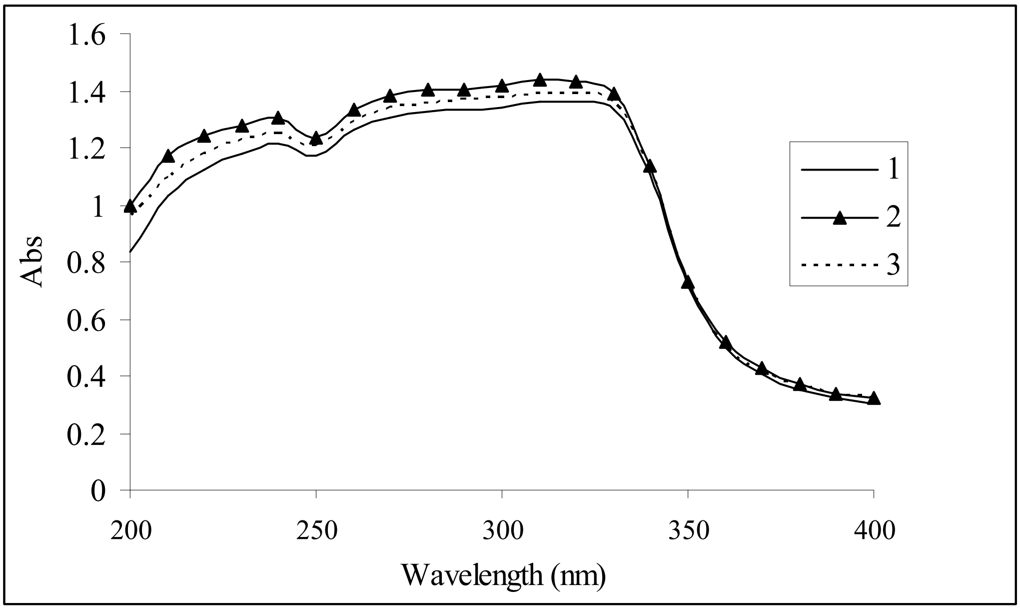
Appendix Figure 15 UV spectra of cotton fabrics loaded with vanillin by padding (measure after 25 days): (1) untreated cotton; (2) glyoxal-β-CD treated cotton; (3) glyoxal-β-CD treated cotton after washing.



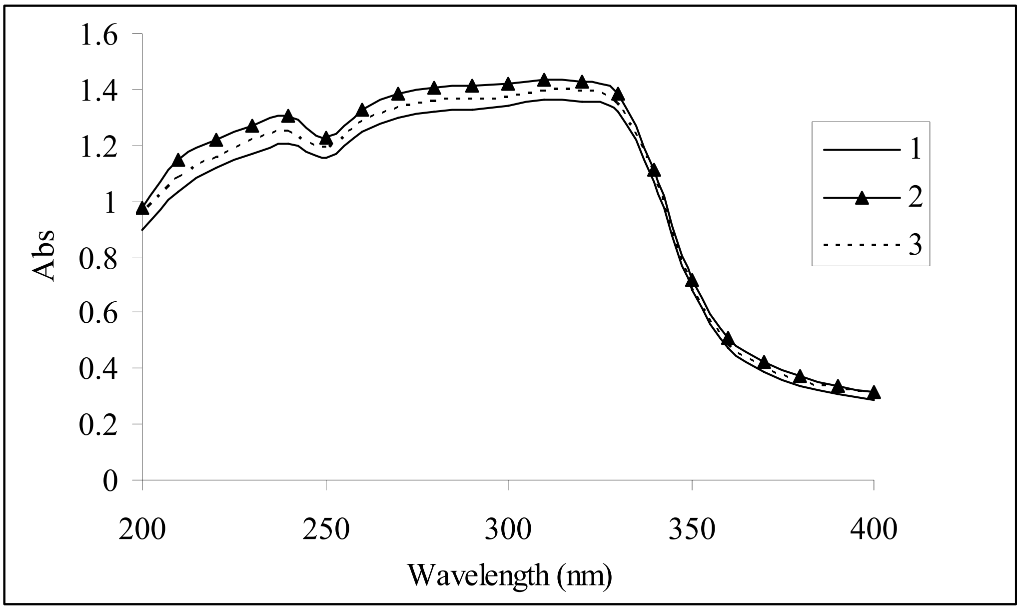
Appendix Figure 16 UV spectra of silk fabrics loaded with vanillin by immersing (measure after 3 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



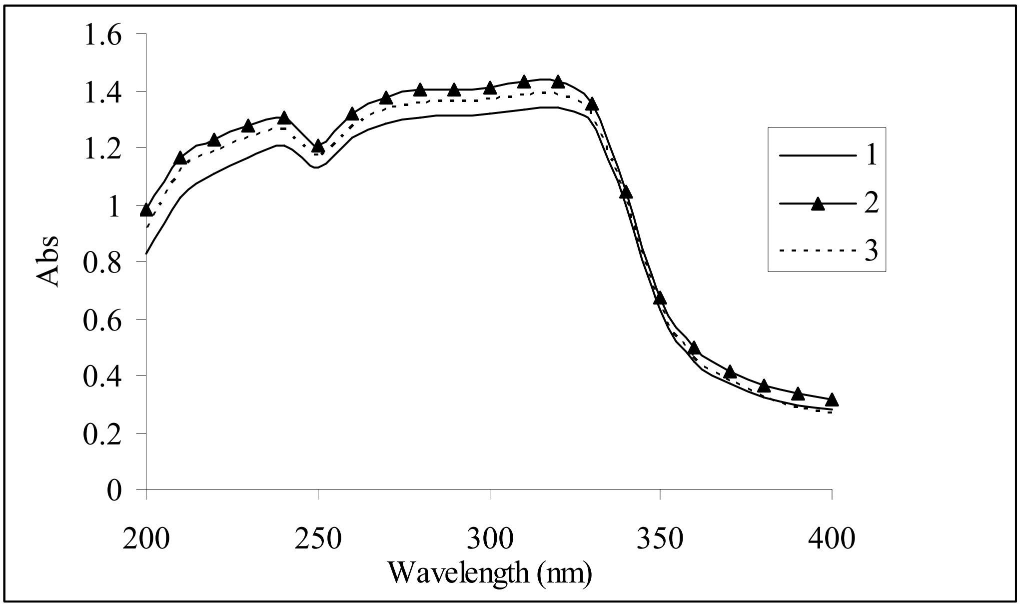
Appendix Figure 17 UV spectra of silk fabrics loaded with vanillin by immersing (measure after 5 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



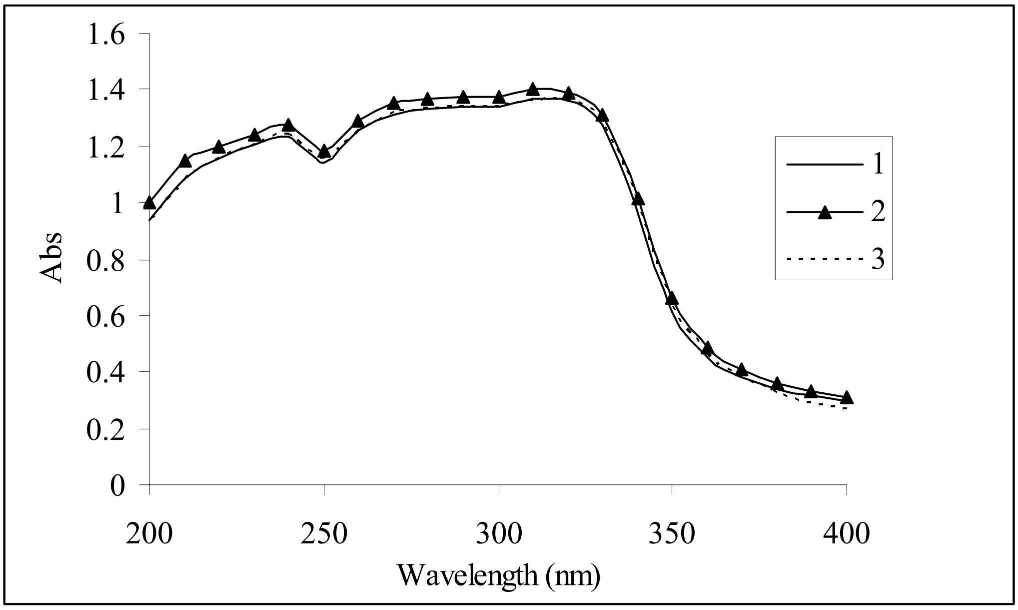
Appendix Figure 18 UV spectra of silk fabrics loaded with vanillin by immersing (measure after 10 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



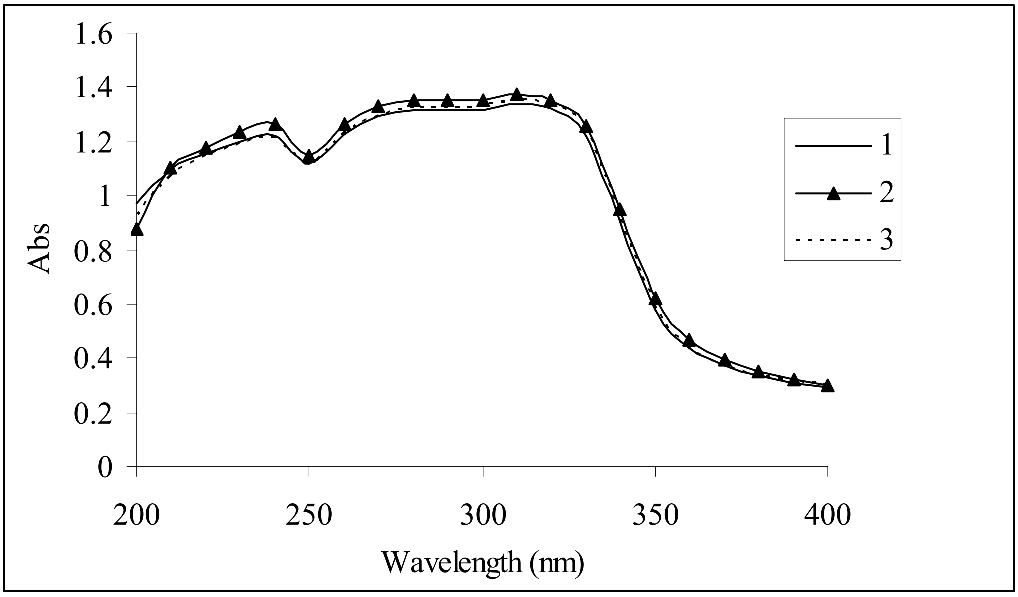
Appendix Figure 19 UV spectra of silk fabrics loaded with vanillin by immersing (measure after 13 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



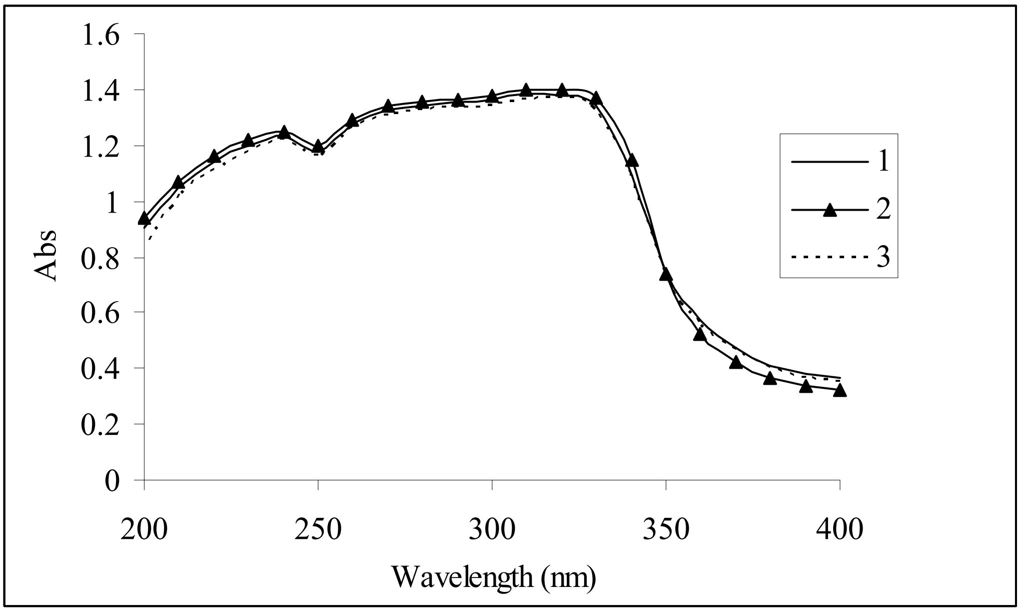
Appendix Figure 20 UV spectra of silk fabrics loaded with vanillin by immersing (measure after 18 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



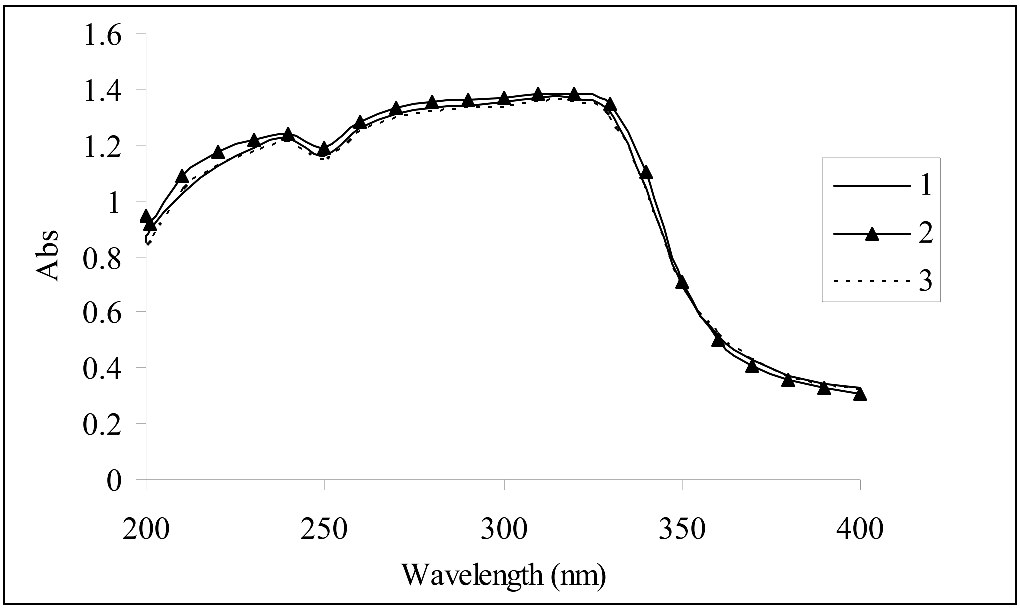
Appendix Figure 21 UV spectra of silk fabrics loaded with vanillin by immersing (measure after 20 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



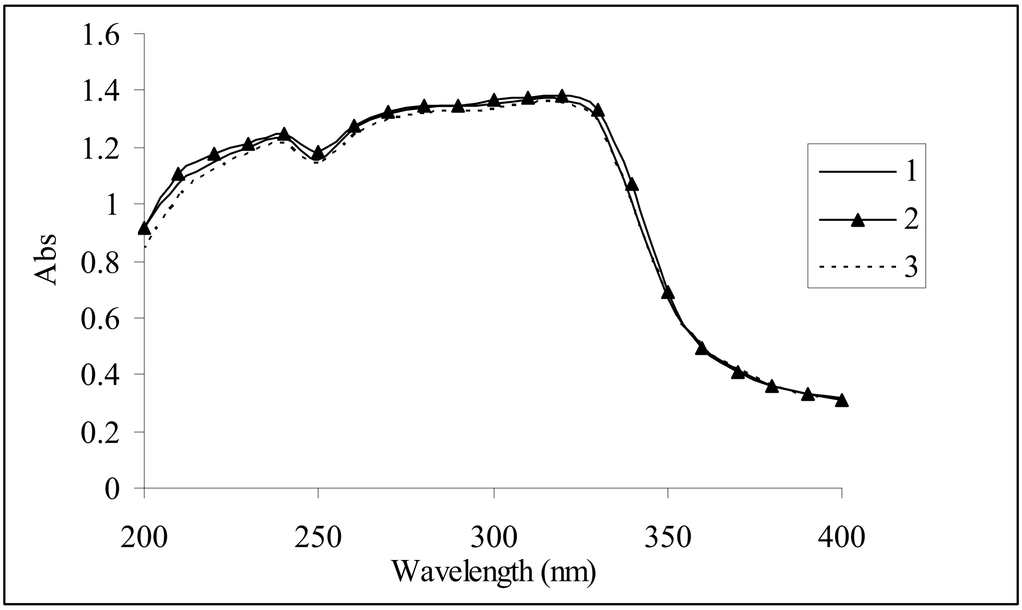
Appendix Figure 22 UV spectra of silk fabrics loaded with vanillin by immersing (measure after 25 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



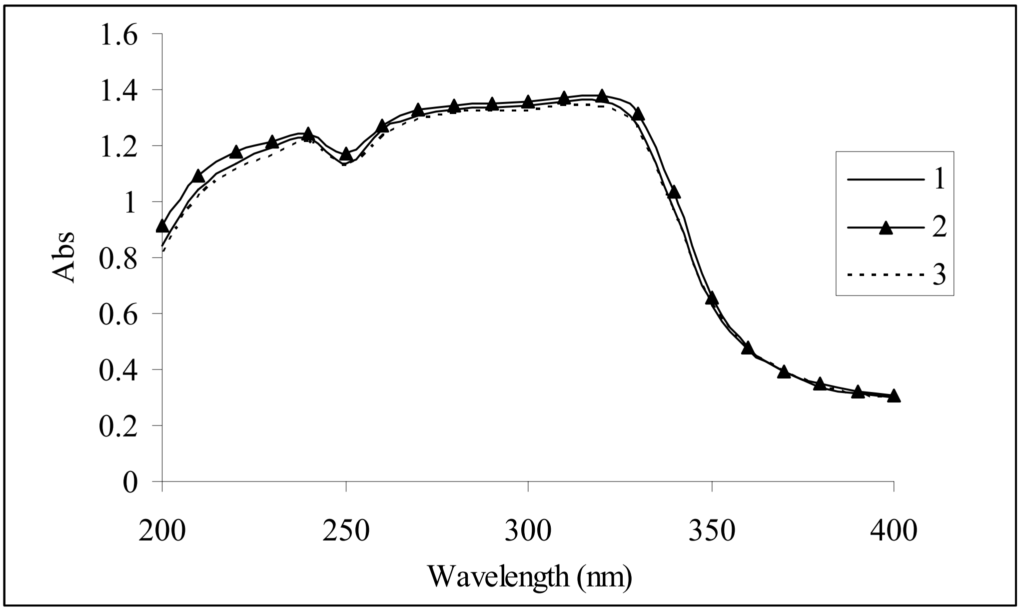
Appendix Figure 23 UV spectra of silk fabrics loaded with vanillin by padding (measure after 3 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



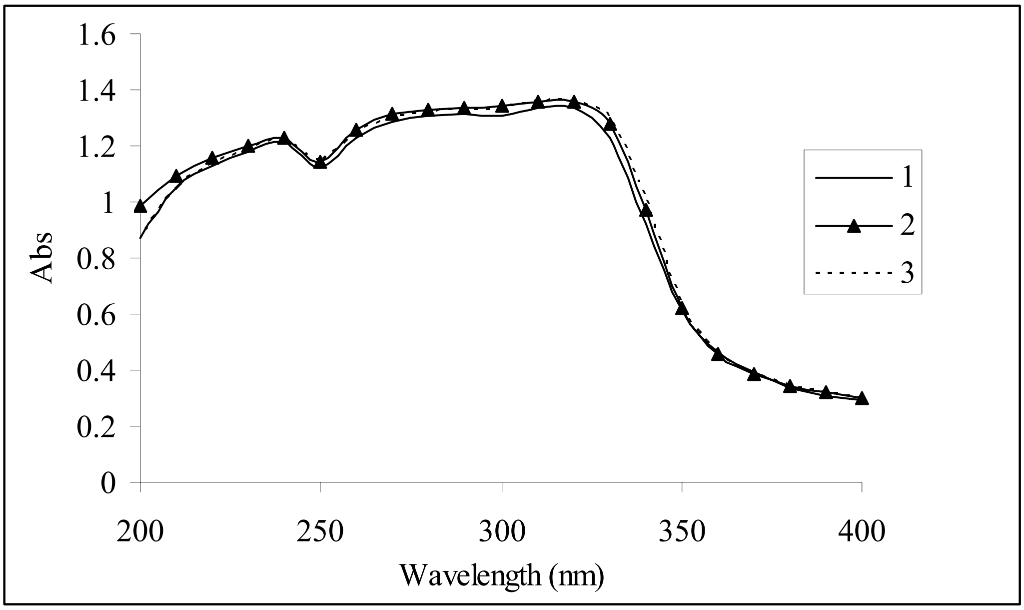
Appendix Figure 24 UV spectra of silk fabrics loaded with vanillin by padding (measure after 5 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



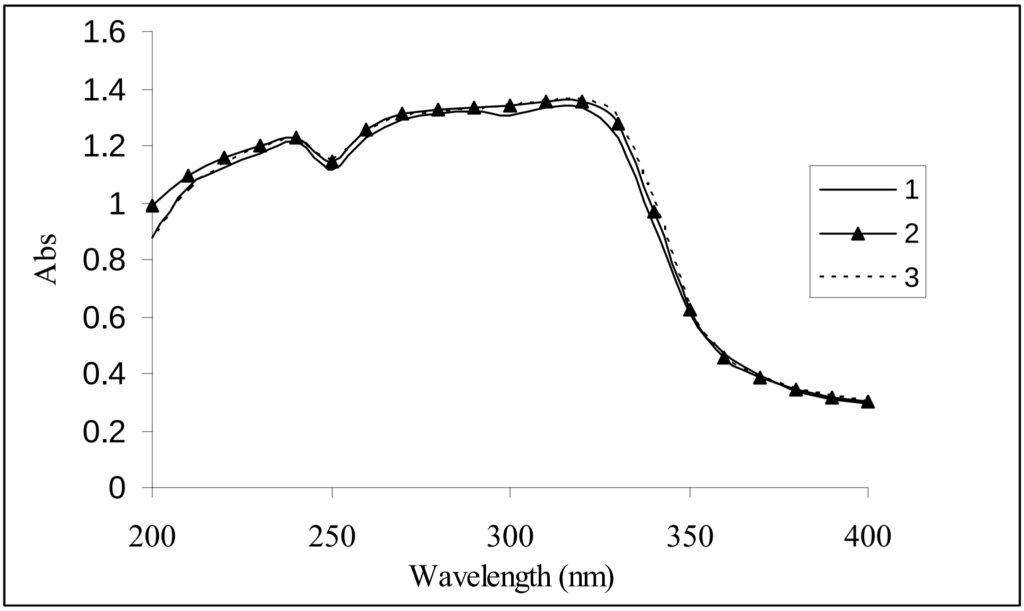
Appendix Figure 25 UV spectra of silk fabrics loaded with vanillin by padding (measure after 10 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing..



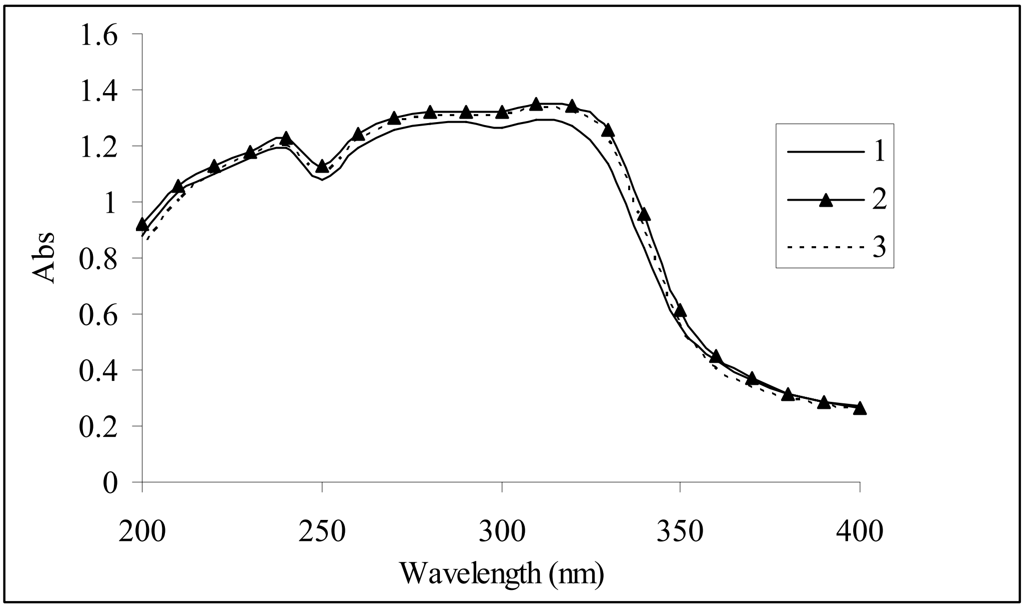
Appendix Figure 26 UV spectra of silk fabrics loaded with vanillin by padding (measure after 13 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



Appendix Figure 27 UV spectra of silk fabrics loaded with vanillin by padding (measure after 18 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



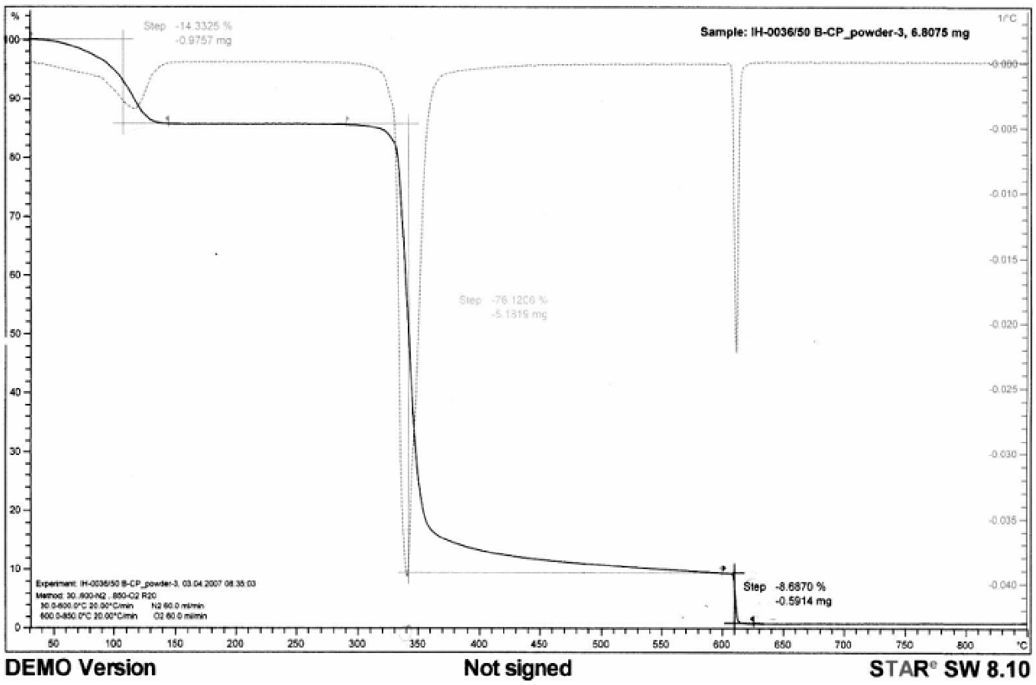
Appendix Figure 28 UV spectra of silk fabrics loaded with vanillin by padding (measure after 20 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.



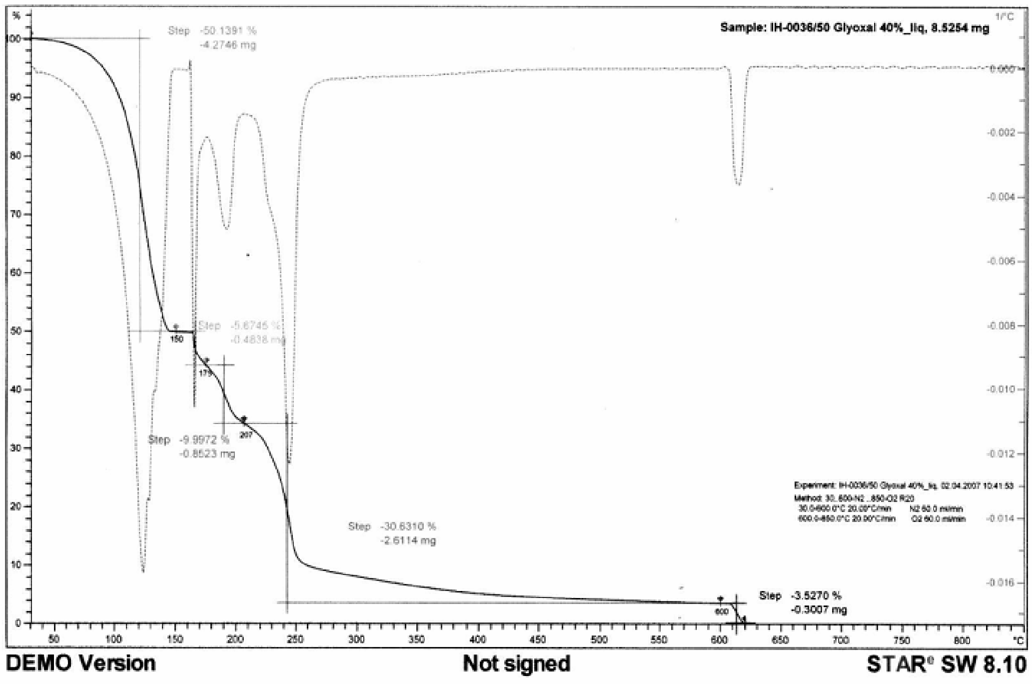
Appendix Figure 29 UV spectra of silk fabrics loaded with vanillin by padding (measure after 25 days): (1) untreated silk; (2) glyoxal-β-CD treated silk; (3) glyoxal-β-CD treated silk after washing.

Appendix C

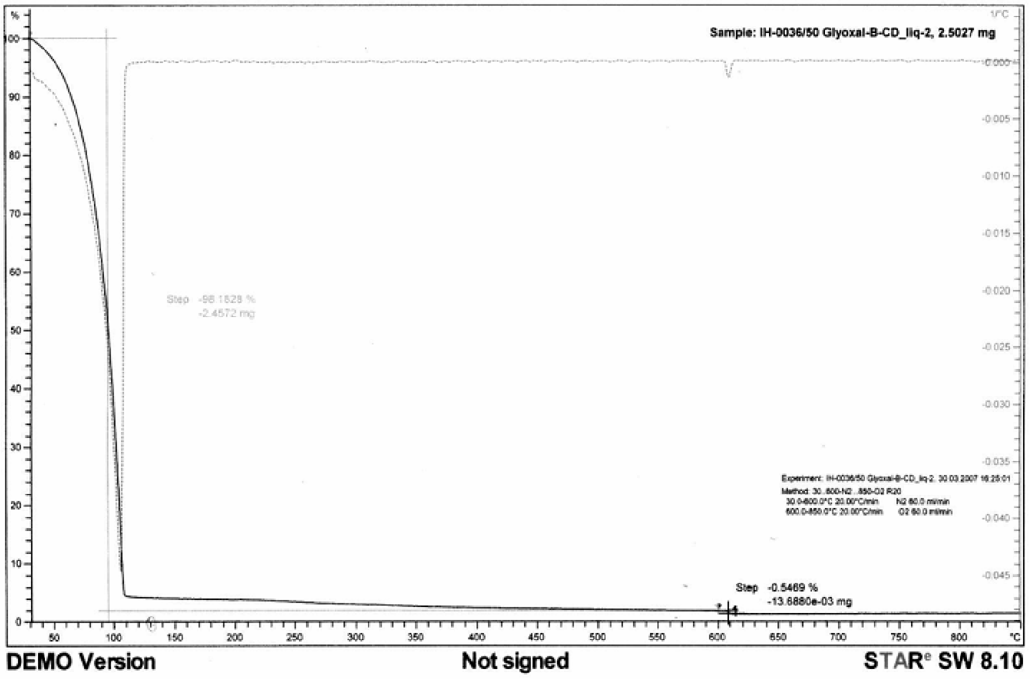
TGA curves



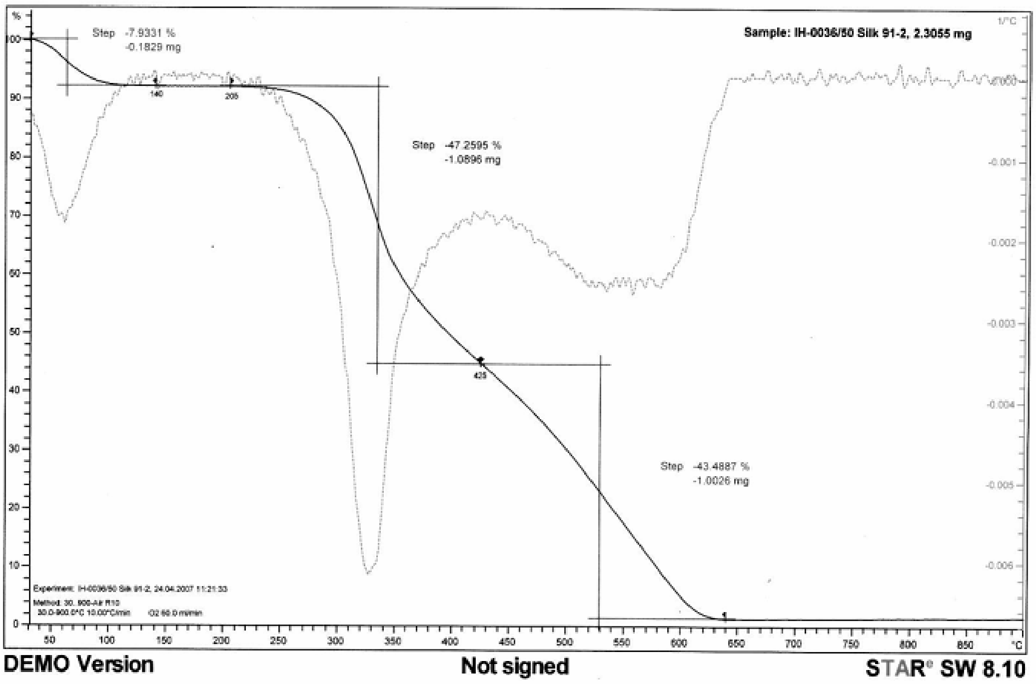
Appendix Figure 30 TGA curve of β-CD powder.



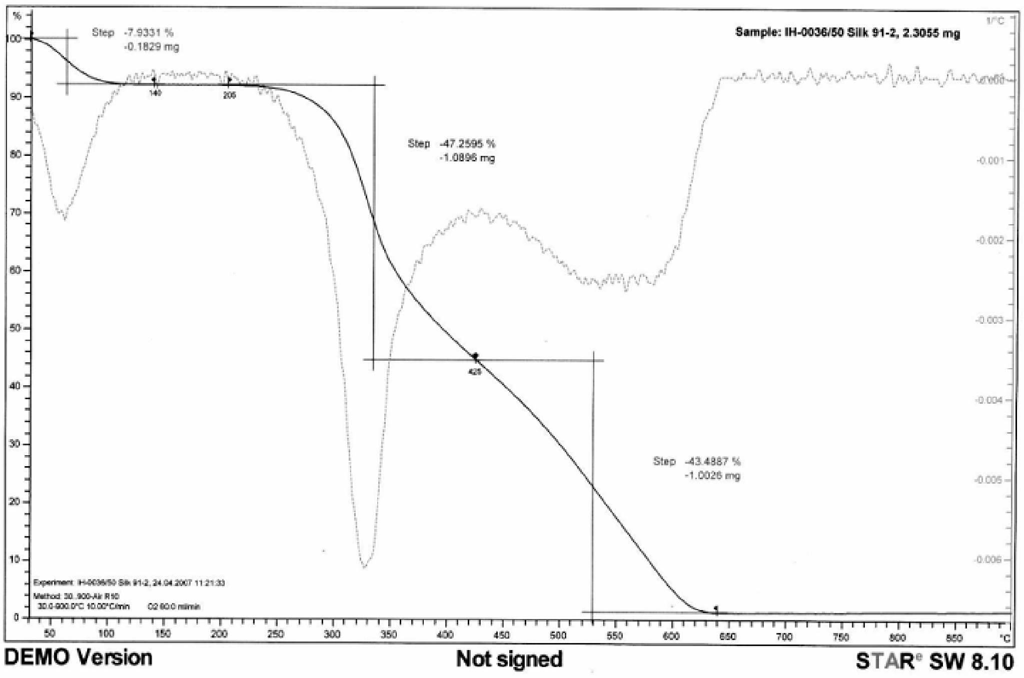
Appendix Figure 31 TGA curve of 40 % glyoxal.



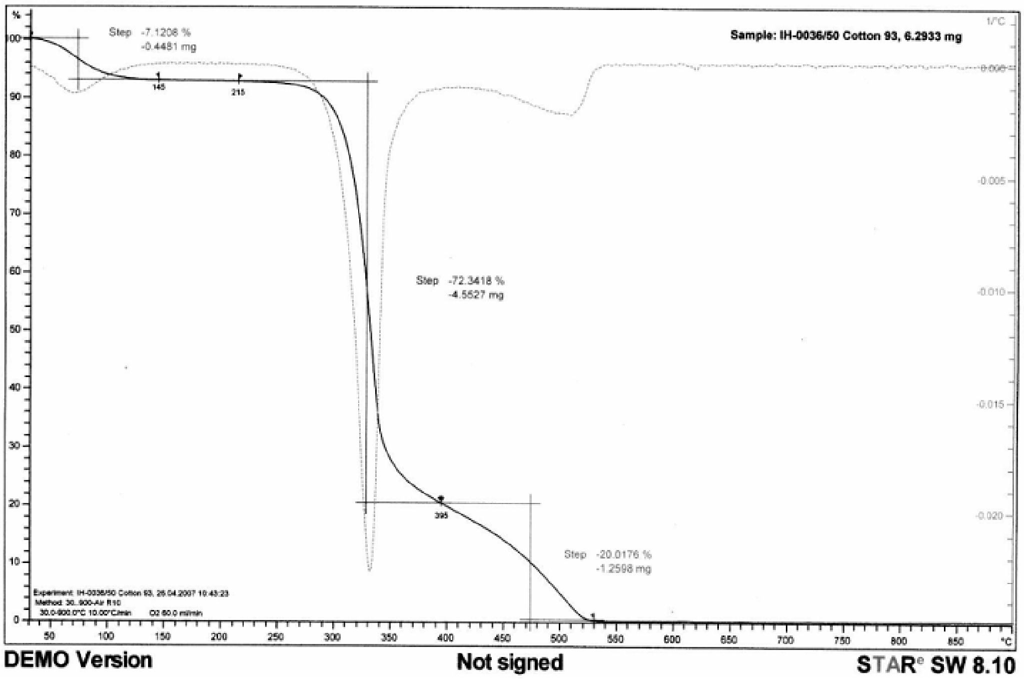
Appendix Figure 32 TGA curve of glyoxal-β-CD.



Appendix Figure 33 TGA curve of untreated silk fabric.



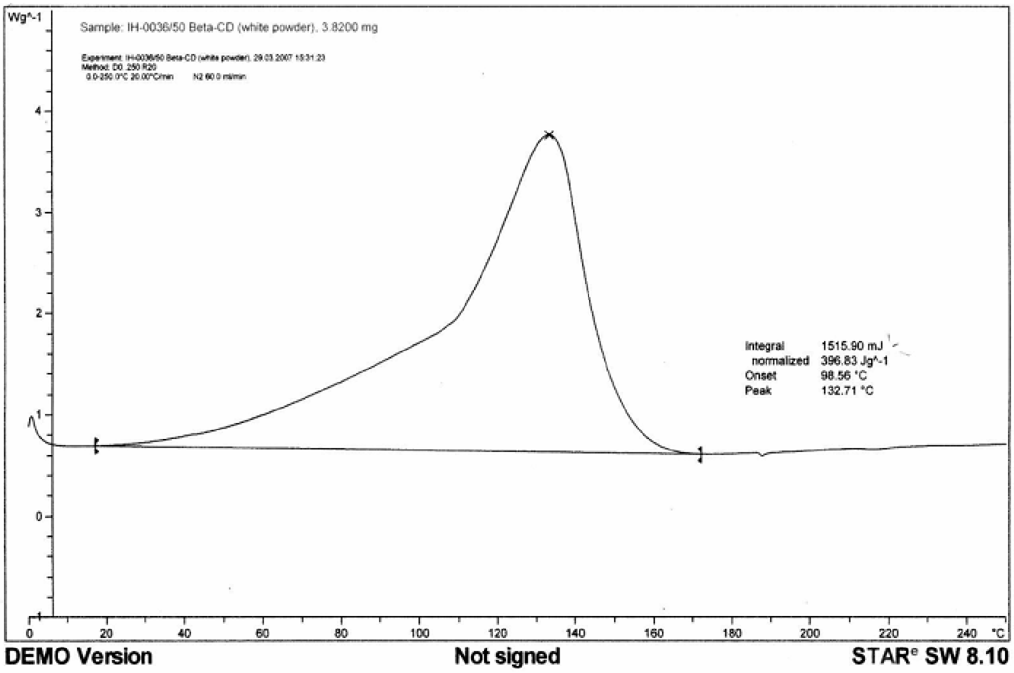
Appendix Figure 34 TGA curve of glyoxal-β-CD treated silk.



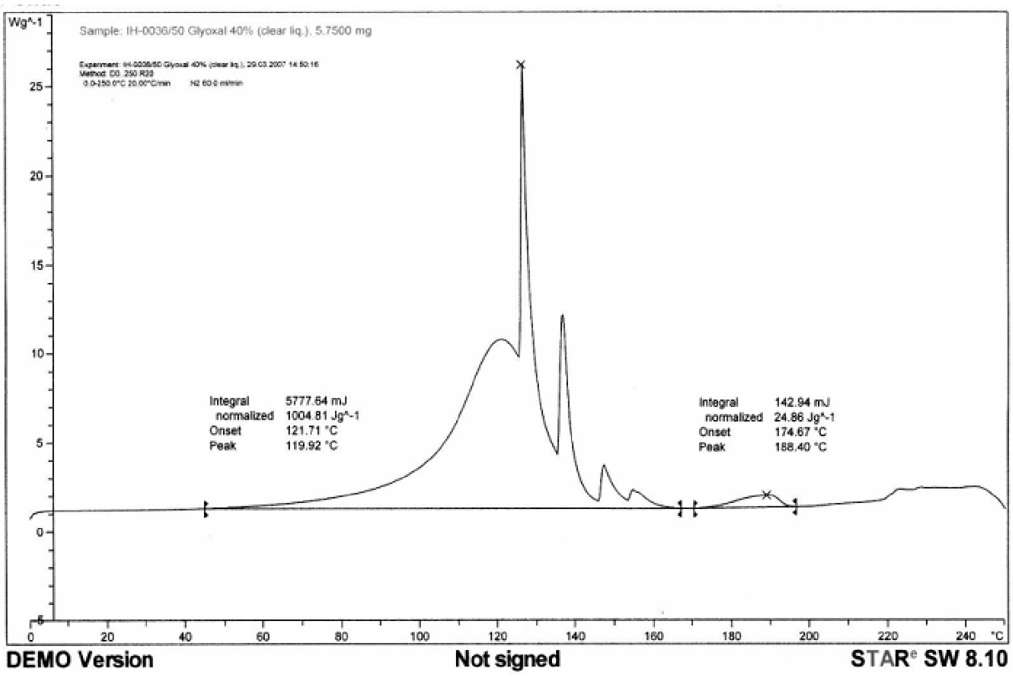
Appendix Figure 35 TGA curve of glyoxal-β-CD treated cotton.

Appendix D

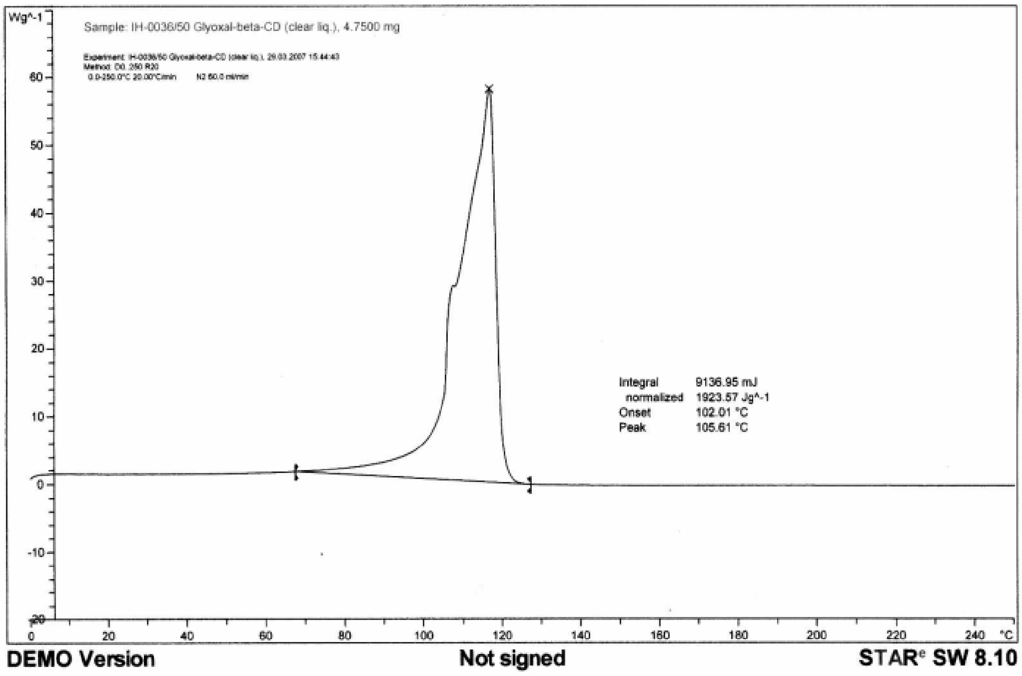
DSC curves



Appendix Figure 36 DSC curve of β-CD powder.



Appendix Figure 37 DSC curve of 40 % glyoxal.



Appendix Figure 38 The DSC curve of glyoxal-β-CD .