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Obtaining Composite Cotton Fabric by Cyclodextrin Grafting

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***Abstract*—**Finishing is an important part of fabric processing with which a wide range of features are imparted to greige or colored fabrics for various end-uses. Especially, by the addition or impartation of nano-scaled particles to the fabric structure composite fabrics, a kind of composite materials can be acquired. Composite materials, generally shortened as composites or in other words composition materials, are engineered or naturally occurring materials made from two or more component materials with significantly different physical, mechanical or chemical characteristics remaining separate and distinctive at the macroscopic or microscopic scale within the end product structure. Therefore, the technique finishing which is one of the fundamental methods to be applied on fabrics for obtainment of composite fabrics with many functionalities was used in the current study with the same purpose. However, regardless of the finishing materials applied, the efficient life of finished product on offering desired feature is low, since the durability of finishes on the material is limited. Any increase in durability of these finishes on textiles would enhance the life of use for textiles, which will result in happier users. Therefore, in this study, since higher durability was desired for the finishing materials fixed on the fabrics, nano-scaled hollow structured cyclodextrins were chemically imparted by grafting to the structure of conventional cotton fabrics by the help of finishing technique in order to be fixed permanently. By this way, a processed and functionalized base fabric having potential to be treated in the subsequent processes with many different finishing agents and nanomaterials could be obtained. Henceforth, this fabric can be used as a multi-functional fabric due to the encapturing ability of cyclodextrins to molecules/particles via physical/chemical means. In this study, scoured and rinsed woven bleached plain weave 100% cotton fabrics were utilized because textiles made of cotton are the most demanded textile products in the textile market by the textile consumers in daily life. Cotton fabric samples were immersed in treating baths containing β-cyclodextrin and 1,2,3,4-butanetetracarboxylic acid and to reduce the curing temperature the catalyst sodium hypophosphite monohydrate was used. All impregnated fabric samples were pre-dried. The reaction of grafting was performed in dry state. The treated and cured fabric samples were rinsed with warm distilled water and dried. The samples were dried for 4 h and weighed before and after finishing and rinsing. Stability and durability of β-cyclodextrins on fabric surface against external factors such as washing as well as strength of functionalized fabric in terms of tensile and tear strength were tested. Presence and homogeneity of distribution of β-cyclodextrins on fabric surface were characterized.

***Keywords*—**Cotton fabric, cyclodextrin, improved durability, multifunctional composite textile.

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I. Introduction

CYCLODEXTRINS (CDs) used in different applications and industries from cosmetics, pharmacology, filtration, textiles to even pesticides are contemporary and beneficial molecules. CDs are cyclic oligomers of a-D-glucopyranose that can be obtained with the conversion of starch by the help of certain bacteria [1], [2].

The production process of CDs consists of four fundamental steps such as culturing of the microorganism that produces the cyclodextrin glucosyl transferase enzyme; separation, concentration and purification of the enzyme from the fermentation medium; enzymatic conversion of prehydrolyzed starch in the mixture of cyclic and acyclic dextrins and as the last phase the separation of CDs from the mixture, their purification and crystallization. CDs consist of glucose units that are linked through 1,4-glycosidic bonds. There are three types of CD i.e. alpha-cyclodextrin, beta-cyclodextrin and gamma-cyclodextrin, that are known as first generation or parent CDs. Alpha, beta and gamma-CDs consist of six, seven and eight alpha-(1,4)-linked glycosyl units, respectively [1]-[3]. Gamma-CDs have advantages over the others in terms of the size of internal cavity, bioavailability and water solubility. However, beta-CD has the highest market potential and to lesser extent alpha-CD, whereas the market share of gamma-CD is considerably smaller because of low yield and high price [3]. Due to the dimensions of their cavities, alpha-CDs can make inclusion complexes only with low molecular weight molecules or compounds with aliphatic side chains [3]. The purification process of alpha and gama-CDs makes the cost of production considerably higher, therefore 97% of the CDs utilized in the market are β-CDs [1], [2].

The inclusion complexes are formed by the inclusion of one guest component which is included in the free space of the crystalline lattice of the second component, called as the host. The inclusion complexes of CD can exist both in solution and in solid state. In aqueous solution, due to polar nonpolar interactions, the weakly polar CD cavity is occupied by the water molecules that can be easily substituted by the guest molecules, less polar than the water. Exchange of water molecules with hydrophobic guest molecules causes the generation of inclusion complexes of CD. CDs are not bound with the guest molecules through strong chemical bonds instead van-der Waals forces, hydrophobic interactions and hydrogen bridges take place [1], [2].

CDs have many applications in textile industry such as: absorption of undesired odors; fragrance release after making complexes, skincare products. Textile products including CDs can be used in filtration for adsorption of small pollutants in

waste water. By making comprehensive studies regarding mutagenicity, toxicology, carcinogenity and teratogenity, the toxicological properties of the substances applied on the textiles should be investigated before utilizing them. CDs were proven to be not only non-toxic but also useful for making complexes with flavors, vitamins and natural colors. CDs have great importance for the textile industry because they can be utilized in the processes of dyeing, encapsulation, surface modification and washing of textiles, and preparation of polymers as well as in fiber formation [1], [2].

There are different studies in the scientific literature utilizing CDs. Wang and Cai studied incorporation of an antibacterial agent into CD cavities covalently bonded onto cotton fabric. The cotton fabric was grafted with β-CD molecules through reaction with monochlorotriazine β-CD (MCT-β-CD). Increasing the uptake of antibacterial agent and improving the resistance of the entrapped antibacterial agent to washing cycles, prolonging the antibacterial effect afforded by the fabric were obtained by finishing application of MCT-β-CD and analyzed by spectrophotometer and HPLC [4]. Abdel-Mohdy et al. investigated grafting of β-CD onto cotton fabric using monochlorotriazine to obtain insecticide treated fabrics which were durable against washing. MCT-β-CD finished cotton fabrics treated with insecticide showed fast repellent action, slower knockdown action and killing action and there are great losses in the amount of insecticides in blank samples by washing, while treated fabrics retain high amount of insecticides [5]. Abdel-Halim et al. investigated grafting of glycidyl methacrylate/β-CD onto cotton fabric to prepare cotton fabrics with durable antimicrobial activity to be capable of inhibiting the growth of microorganisms using chlorohexidin diacetate by linear electron beam radiation technique. It was found that as the amount of β-CD fixed on the fabric increases, the amount of incorporated antimicrobial agent and accordingly the antimicrobial activity of the fabric increases [6]. El Shafei et al. investigated the impact of grafting of MCT-β-CD with butyl acrylate onto cotton fabric along with epichlorohydrin and/or ZnO nanoparticles using conventional pad-dry-cure. The grafting imparted antibacterial activity that withstood 20 times washing and also improved air permeability that helped garments to display better breathability and comfortability. The characterization of the grafted fabrics using IR spectral analysis and scanning electron microscopy (SEM) was reported [7]. Ibrahim et al. investigated increasing disperse dye substantivity for cotton cellulose containing fabrics via modification with MCT-β-CD under different conditions. The obtained dyeing applications showed a remarkable improvement in their depth of shades along with a significant enhancement in their UV-protection properties [8]. Hebeish et al. investigated grafting of β-CD with poly butyl acrylic acid [βCD-g-PAA] onto cotton fabric. Silver nanoparticles colloidal solution was applied on this fabric along with epichlorohydrin in alkaline medium to obtain sufficient and durable antibacterial property. Characterization is done by color and UV–visible spectral analysis and transmission electron microscopy. The new finishing formulation resulted in good and durable bacterial properties for fabrics [9]. Abdel-Halim studied grafting of glycidyl methacrylate/ monochlorotriazinyl-β-CD mixture (GMA/MCT-β-CD) onto cotton fabric using linear electron beam radiation technique to obtain antimicrobial effect against different bacteria and fungi by loading chlorohexidin diacetate. It was demonstrated that GMA/MCT-β-CD grafted fabrics loaded with antimicrobial agent retained antimicrobial activity after five washings [10]. Nazi et al. studied grafting of β-CD modified with itaconic acid containing carboxyl and vinyl groups via the esterification reaction onto cotton fabric to create useful polyfunctional building blocks in different biomedical fields. The presence of bounded CD and its ability on the surface of the fibers were demonstrated by using SEM and infra-red spectroscopy (FTIR). This modification did not show any negative effects on the performance of cotton fabric [11]. Radu et al. studied grafting of MCT-β-CD onto cotton made pajamas as a support of an inclusion compound (IC) with natural anti-allergic active principles in order to improve the curative properties and the comfort. The textile material grafted with MCT-β-CD and with active principles absorbed in the CD cavity was investigated by EDX [12]. Hebeish et al. studied grafting of glycidyl methacrylate or grafting of its combination with β-CD onto cotton fabric by irradiation using fasting electron beam. Aim of this study was to produce high performance chemically modified cotton fabric against mosquitoes [13]. Abdel Halim et al. studied grafting of β-CD onto cotton fabric by use of butane tetracarboxylic acid as cross linking agent to give antimicrobial activity to cotton fabric. The antimicrobial cotton fabric was subjected to several washing cycles and the antimicrobial activity was measured after each washing cycle to examine the durability of this antimicrobial finishing against repeated washing. The measurements showed that the finished cotton fabrics retain reasonable amount of their antimicrobial activity even after 20 washing cycles [14]. Popescu et al. investigated grafting of β-CD with MCT and chitosan onto cotton fabric to obtain wrinkle-proofing and hydrophilizing effects by means of three pad-dry-cure treatment. FTIR, XPS, XRD, DSC and TGA analyses were used for characterization. CS increases the WRA and tensile strengths and MCT-β-CD makes the hydrophilicity higher than that of the witness sample, slightly improving the tensile strength [15]. Hebeish et al. studied treatment of cotton fabric with MCT-βCD and PAA to obtain antibacterial activity by means of inclusion of Ag nanoparticles. Characterization of cotton fabric before and after its chemical modification was carried out using FTIR, XRD and SEM. According to results, silver nanoparticle adsorption was much greater on cotton bearing CD moieties than unmodified cotton and antibacterial activity depends on the content of silver nanoparticles in the cotton sample [16]. Dehabadi et al. studied grafting of β-CD onto cotton fabric using polyaminocarboxylic acids (PACAs) as crosslinking agent for the fixation of β-CD onto cotton fabric. Fixation of β-CD was quantitatively estimated by measuring the weight increase of the treated samples. Using PACAs as crosslinking agents provides a useful way for fixation of CDs on cotton textiles [17]. Myung Hak Lee et al. studied grafting of β-CD

using N-methylol-acrylamide (NMA). The amount of chemically attached CD was determined by fluorescence measurements. The possibility of textile finishing of CD containing cotton fibers was investigated using benzoic acid as an antibacterial finishing agent or vanillin as an aroma finishing agent. According to results, the durability of the antimicrobial property to laundering was excellent and CD-NMA grafted cellulose fibers can be utilized in the aroma finishing of cotton [18]. Scalia et al. investigated grafting of β-CD with MCT onto cotton fabric to study the incorporation of the sunscreen agent, octyl methoxycinnamate into CD cavities covalently bound to cloth fibers. The unmodified and modified fabrics were characterized by UV spectrophotometry and thermogravimetric analysis (TGA). Hence, even after repeated washings, the β-CD finished fabric exhibits higher sunscreen agent retention and photoprotective properties than the unmodified textile material [19]. Nostro et al. studied grafting of β-CD onto surface of cellulosic fabrics according to different procedures. After the treatment, benzoic acid, vanillin, iodine, N,N-diethyl-mtoluamide, and dimethyl-phthalate were loaded, by either spraying their solutions on the CD-grafted fabric, or by grafting the previously prepared inclusion compound on CD. The untreated and treated fabrics were evaluated through SEM, differential scanning calorimetry (DSC), UV-vis spectra, X-ray diffractometry, water absorbency, breaking load loss, aroma and antimicrobial finishing tests [20]. Medronho et al. studied grafting of β-CD with BTCA onto cellulose to investigate physicochemical characterization of cellulose modified with CDs by means of FTIR, cross polarization magic angle spinning solid state nuclear magnetic resonance (CP-MAS NMR), polarized optical microscopy (POM) and TGA. NMR and FTIR showed that ester bonds are formed between cellulose and CDs however, it was not possible to fully dissolve the CD [21].

Recently, many different nanoparticles are utilized in textile industry in order to provide functionalities for textiles and improve their inherent properties in terms of physical and chemical properties, mechanical behavior and performance characteristics. In the current study, to achieve improved durability for the textile chemicals, CDs were chemically bonded to be fixed permanently by grafting to the structure of conventional cotton fabrics with the help of finishing technique, leading to a functionalized base fabric with potential to be treated in the subsequent processes with many different finishing agents and nanomaterials.

II. Experimental

A. Materials

1,2,3,4-Butanetetracarboxylic acid (BTCA) with a molecular weight of 234.16 g/l, sodium hypophosphite (SHP) (anhydrous 98-101%) with a molecular weight of 87.98 g/mol and beta cyclodextrin (β-CD) with a molecular weight of 1134.98 g/mol were purchased from Sigma Aldrich. Setazol Red GF that can be applied by impregnation, Setawash EWA a washing agent in dyeing process that is used for reactive dyed and printed fabrics and as well as Setalan GLN that is an auxiliary chemical that reacts with direct, reactive and vat dyes were all purchased from Setaş Chemical Company. ECE detergents including linear sodium alkyl benzene sulphonate (8%), ethoxylated tallow alcohol (2.9%), sodium soap (3.5%), sodium tripolyphosphate (43.7%), sodium silicate (7.5%), magnesium silicate (1.9%), carboxymethyl cellulose (1.2%), etylene diamine tetra acetic acid (0.2%), sodium sulphate (21.2%) and water (9.9%) were used for scouring of cotton fabrics. A desized and scoured 100% plain weave cotton fabric was obtained and used. It had basis weight of 138 g/m^2 and fabric density of 31 warp/cm and 34 weft/cm.

B. Machines, Equipment and Characterization

A laboratory scale padder with a width of 400 mm, diameter of 125 mm (LP) and 200 mm (LDP) was used. It had other specifications such as speed of 5 rpm (2 m/min) and adjustable pressure of 0.1-0.6 kg/cm² (1-6 bar) for different applications requiring different pickups of finishing agents. Initially in the trial steps, cotton fabric samples were treated by padder in order to arrange their wet pick-up to approximately 100%.

An oven that can be heated up to 300 °C with the capacity of 66 L and interior depth of 58.9 cm was used to test cotton fabric samples at 180 °C for 48 min by adding 20 g of detergent.

Wascator type of washing machine having maximum spin cycle of 1000 rpm, 15 washing programs and maximum capacity of 8 kg was used in the study. Cotton fabric used in the study was washed at 40 °C for 48 min by adding 20 g of detergent.

A tumble dryer having drum volume of 102 L, weight of 34 kg, height of 84.6 cm and depth of 53.0 cm was used in the study. Cotton fabric used in the study was dried for 25 min in the tumble dryer and then, further dried overnight using line drying technique.

James Heal Titan Strength Test Machine was used in order to evaluate tensile and tear strengths of each cotton fabric sample. Tensile and tear strengths of 16 fabric samples were found both for warp and weft directions according to EN ISO 13934-1 and EN ISO13937-2 standards.

Gyrowash is an instrument designed and developed for ultimate wash-fastness testing. A reactive solution that included 0.375 g Setazol Red (reactive dye), 10 g salt, 5 g sodium carbonate and 235 g water was prepared. Cotton fabric samples were put into Gyrowash simultaneously along with the reactive solution. Cotton fabric samples were processed in Gyrowash for 1 hour at 90 °C. In addition, washing fastness of cotton fabric samples were evaluated according to EN ISO 105-C06.

A spectrophotometer having 152 mm sphere diameter, 360-700 nm wavelength range, 4 position auto zoom, 10 nm reporting interval, 400-420 and 460 nm UV cutoff filters, 37.5 lbs. weight and as well as color display of 3.5 inch RGB LCD was used for color analysis. Sample placement can be ensured by the positioning camera and color LCD. The calibration status and instrument settings are displayed prominently by the LCD screen to validate proper set-up. By using

spectrophotometer, cotton fabric samples were tested four times to control coloring quality of the samples.

FTIR with Attenuated Total Reflectance (FTIR-ATR) was utilized to examine the bond structure and bonding energy of surfaces of the fabric samples and thereby to identify the types of chemical bonds (functional groups). Therefore, by FTIR-ATR technique, the presence and distribution of CD on the functionalized cotton fabric samples were investigated. The FTIR-ATR spectra were taken from 5 different areas of the surface of the cotton fabric samples in order to analyze if CD is distributed homogeneously on the entre fabric surface.

C. Methods

6 wt.% BTCA and 3 wt.% SHP were used with different amounts of β-CD such as 15, 20 and 25 wt.% in the study. Experimental design of the study can be seen in Fig. 1.

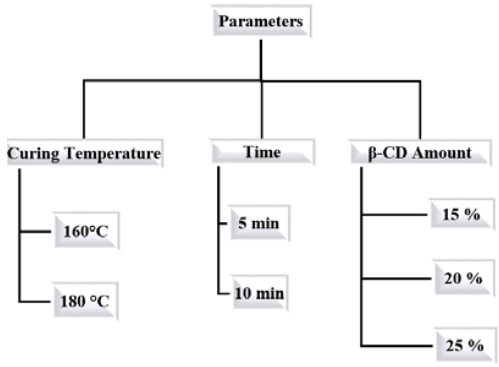

Fig. 1 Experimental design

Preparation of Treating Bath

For the preparation of treating bath, initially β-CD was put into water under mechanical effect. Then, BTCA was added during blending process.Blending was continued until the solution reaches the steady state. Subsequently, SHP as a catalyst was added into the solution and treating bath was obtained. In order to prepare treating baths for different amounts of β-CD as 15%, 20% and 25%, this process was executed three times and three different treating baths were obtained.

Impregnation of the Cotton Fabric Samples

Cotton fabric samples were immersed in the prepared treating baths for 60 minutes. In the meantime, the samples were squeezed in the beaker and again immersed into the same solution over and over.

Padding

The fabric samples were weighed at first and then they were immersed in the solution at the padder. Cotton fabric samples were padded to a wet pick-up of approximately 100%.

Pre-drying of the Cotton Fabric Samples

Cotton fabric samples were dried in an air oven at 110 °C for 20 minutes.

Grafting Reaction (Curing Step)

The reaction was carried out in dry-state at temperatures 160 °C and180 °C for 5 min. and 10 min, respectively.

As a result, 16 different fabric samples processed with different conditions in the curing step were obtained as shown in Table I.

Cleansing (Rinsing Step)

Treated and cured fabric samples were washed thoroughly with warm distilled water.

Drying of the Cotton Fabric Samples

Rinsed cotton fabric samples were dried in oven and then left to dry overnight at room temperature.

Weight Gain of the Finished Cotton Fabric Samples

First of all, cotton fabric samples were weighed at initial conditions and after β-CD grafting was concluded fabric samples were again weighed in order to find out the amount of β-CD in the cotton fabric structure. The formula for the weight gain of the finished cotton fabric samples is:

$$\%GY = \left[(W_2 - W_1)/W_2\right] \times 100 \quad (1)$$

W_2= Dry weight of the grafted cotton fabric sample; W_1= Dry weight of the cotton fabric sample before grafting.

Dyeing

The solution used for the dyeing process was prepared with reactive dyes. The solution included 0.375 g Setazol red, 10 g salt, 5 g sodium carbonate and 235 g water. After that, it was put into Gyrowash at 90 °C for 1 h along with cotton fabric samples. Then, water was added slowly into Gyrowash to decrease the temperature to 60 °C. Both washing and rinsing processes were completed with hot water. Dyeing recipe can be seen in Fig. 2.

TABLE I
SAMPLES AND TREATMENT CONDITIONS

Sample #	Conditions
Sample 0	No use of chemicals, treatment with only water
Sample 1	15% CD,160 °C, 5 min
Sample 2	15% CD,160 °C, 10 min
Sample 3	15% CD,180 °C, 5 min
Sample 4	15% CD,180 °C, 10 min
Sample 5	20% CD,160 °C, 5 min
Sample 6	20% CD,160 °C, 10 min
Sample 7	20% CD,180 °C, 5 min
Sample 8	20% CD, 180 °C, 10min
Sample 9	25% CD,160 °C, 5 min
Sample 10	25% CD,160 °C, 10 min
Sample 11	25% CD,180 °C, 5 min
Sample 12	25% CD,180 °C, 10 min
Sample 13	BTCA and SHP, no CD, 180 °C, 10 min
Sample 14	20% CD and SHP, no BTCA, 180 °C, 10 min
Sample 15	No treatments

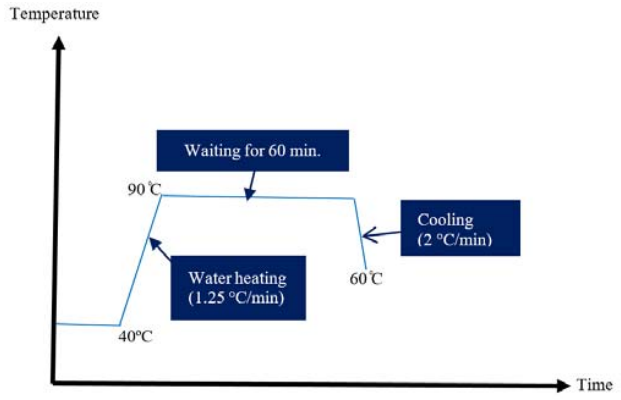

Fig. 2 Dyeing recipe

III. Results and Discussion

A. FTIR Spectroscopy Results

In Figs. 3-6, FTIR spectra of untreated cotton fabric, cotton fabric treated with only water, cotton fabrics treated with different amounts of CD under the same process conditions (160 °C, 10 min) and FTIR spectra of CD itself can be seen. The findings are summarized as:

1) There is no difference in between untreated fabric and fabric treated with only water meaning that there is no effect of water treatment and process conditions on chemical structure of cotton fabric.
2) There is a slight difference in between untreated fabric and cotton fabrics treated with different amounts of CD (15%, 20%, 25%) under the same process conditions (160 °C, 10 min) meaning that

a) Not many differences were identified due to the similarities in the content of the structures of CD and cotton fabric.
b) There is a difference at 1641 cm^{-1} wavelength caused by CD addition to the structure of the cotton fabric which can also be seen from FTIR spectra of CD (CD has a peak at 1641 cm^{-1} while cotton does not).
c) There is a difference at 2925 cm^{-1} wavelength caused by CD addition to the structure of the cotton fabric which can also be seen from FTIR spectra of CD (CD has a peak at 2925 cm^{-1} while pure cotton does not. Pure cotton has only at 2950 cm^{-1} and both of the peaks can be seen in the FTIR spectra of CD treated cotton fabrics.)
d) These show that CD is successfully imparted to the structure of the cotton fabric.

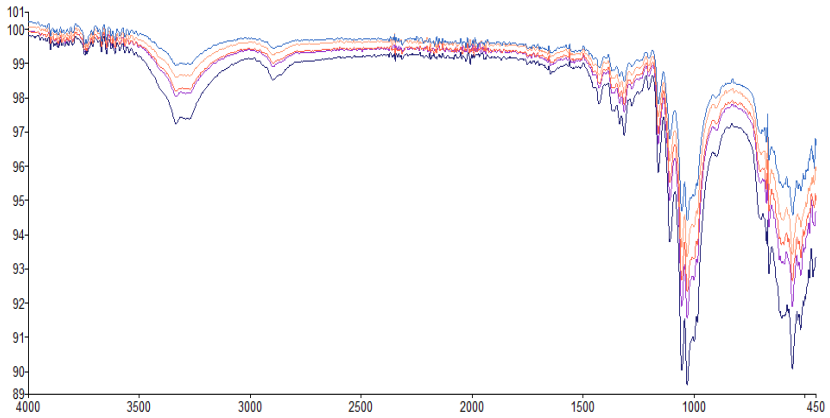

Fig. 3 FTIR spectra of sample 15 (untreated fabric)

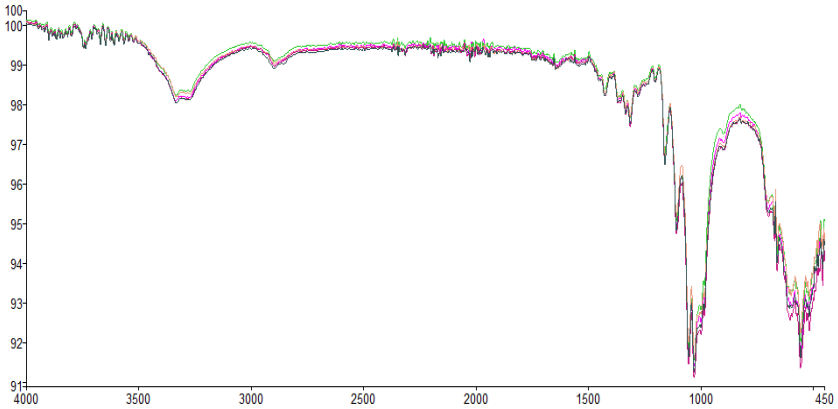

Fig. 4 FTIR spectra of sample 0 (no chemicals, treated with water)

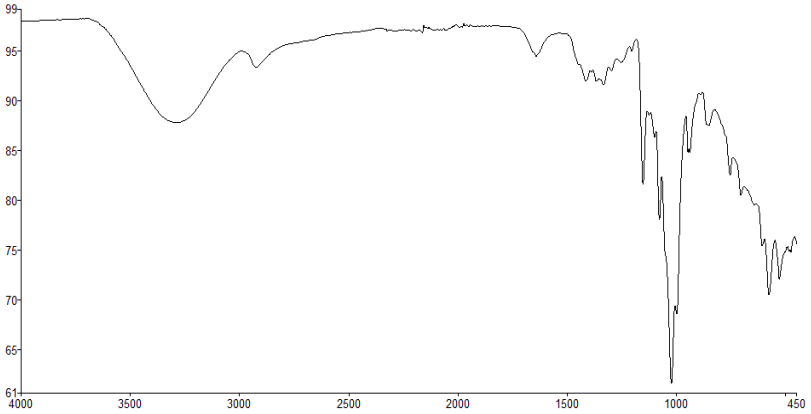

Fig. 5 FTIR spectra of CD

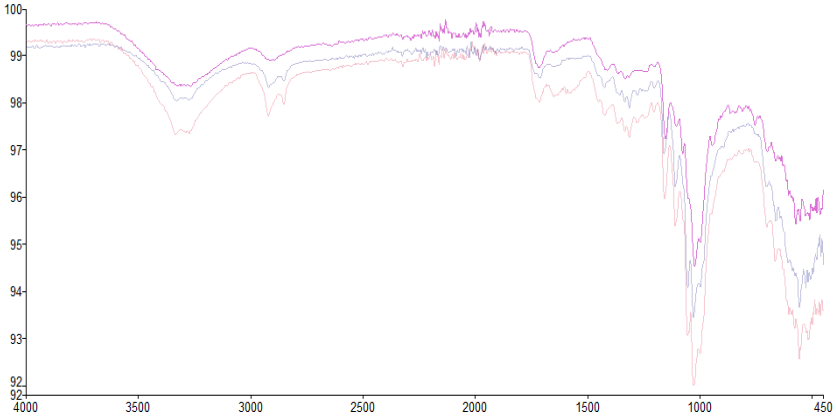

Fig. 6 FTIR spectra of sample 1, 5 and 9

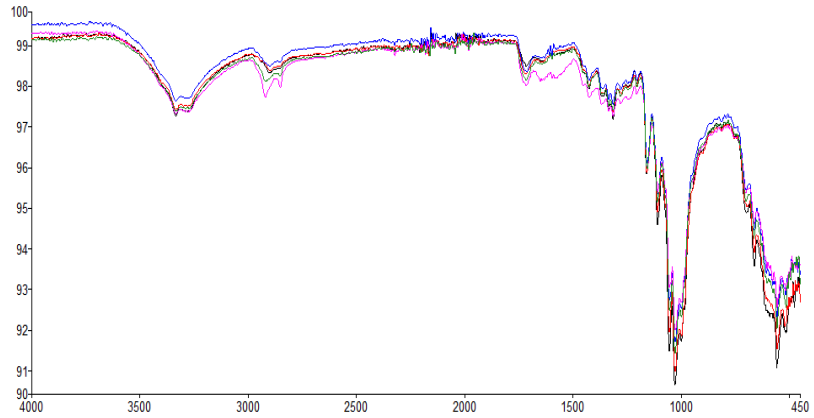

Fig. 7 FTIR spectra of sample 1 (15 % CD, 160°C, 5 min)

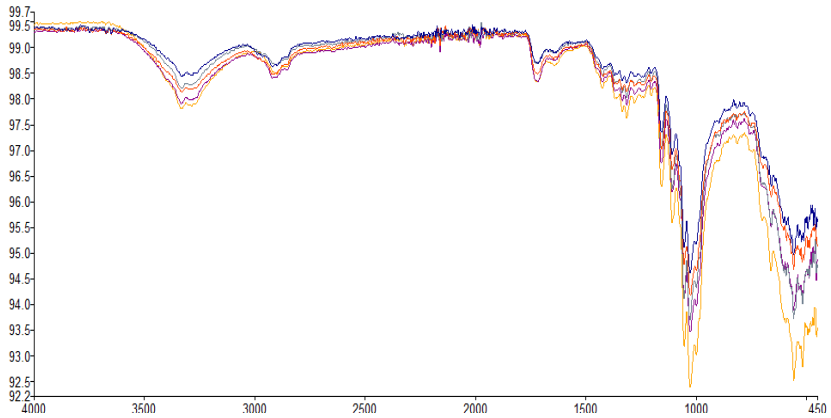

Fig. 8 FTIR spectra of sample 2 (15 % CD, 160°C, 10 min)

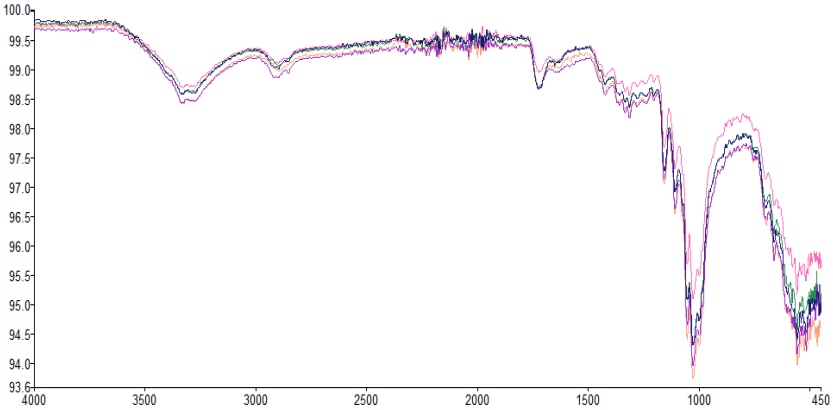

Fig. 9 FTIR spectra of sample 3 (15 % CD, 180°C, 5 min)

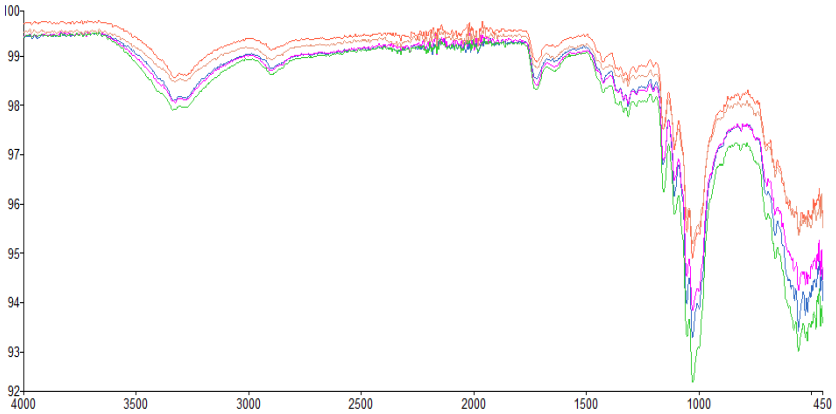

Fig. 10 FTIR spectra of sample 4 (15 % CD, 180°C, 10 min)

In Figs. 7-10, all of the peaks are at the same wavelengths for 5 different areas of the samples with 15% β-cyclodextrin with different process conditions. Therefore, it means that the process conducted properly. The findings are summarized as:

1) There are no contaminations and foreign materials.
2) There are no considerable variations on the fabrics surface with homogeneous distribution of CD.

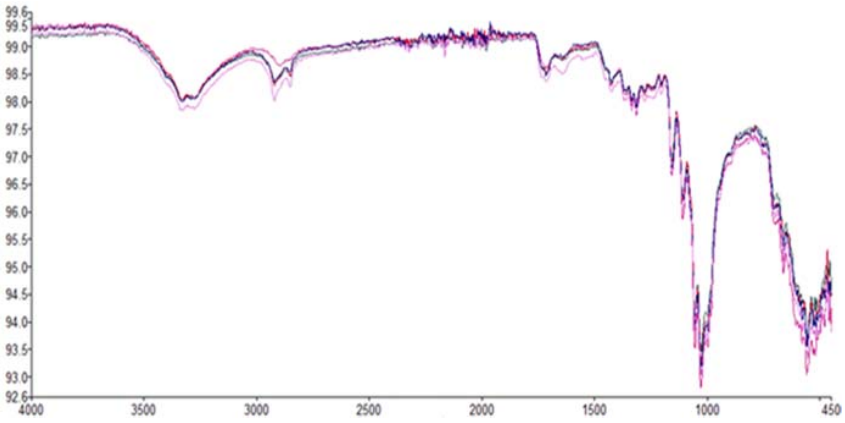

Fig. 11 FTIR spectra of sample 5 (20 % CD, 160°C, 5 min)

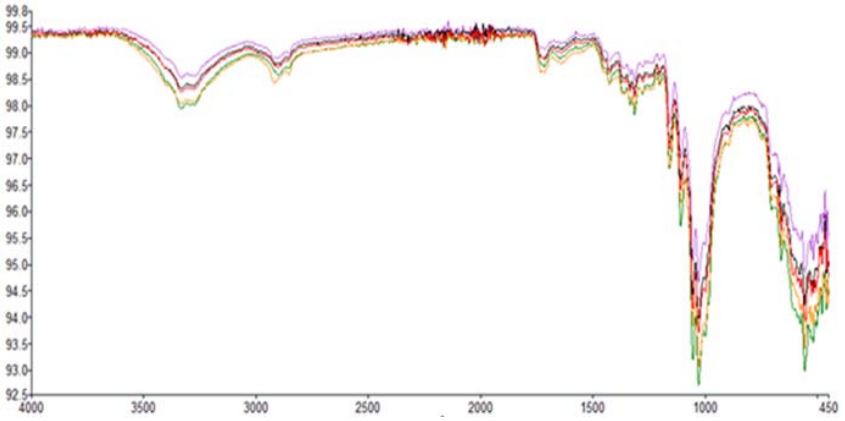

Fig. 12 FTIR spectra of sample 6 (20 % CD, 160°C, 10 min)

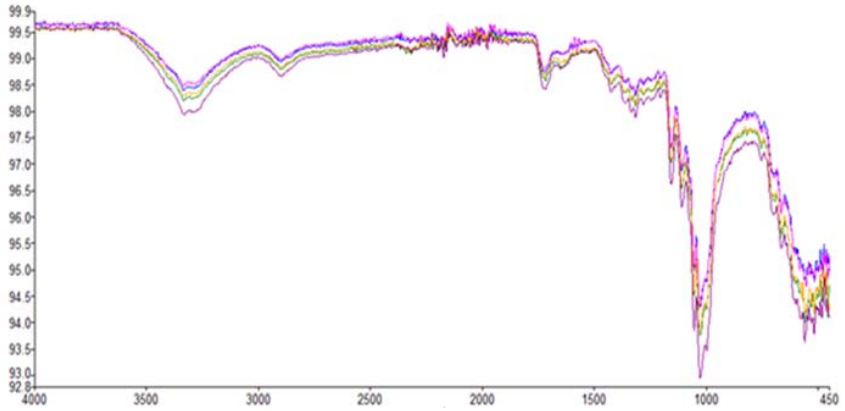

Fig. 13 FTIR spectra of sample 7 (20 % CD, 180°C, 5 min)

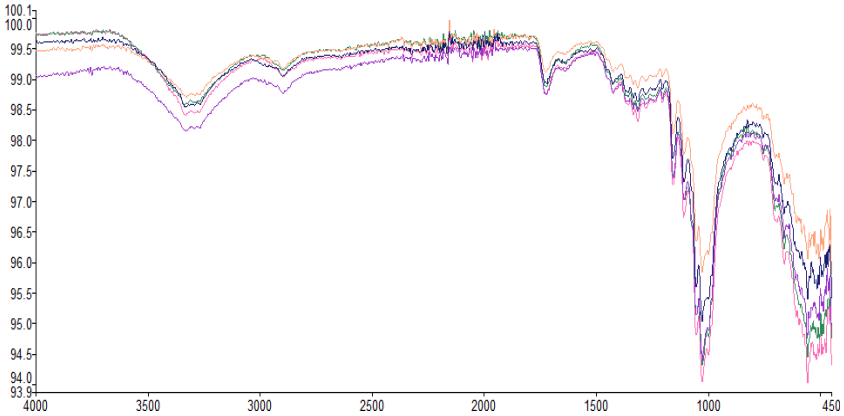

Fig. 14 FTIR spectra of sample 8 (20 % CD, 180°C, 10 min)

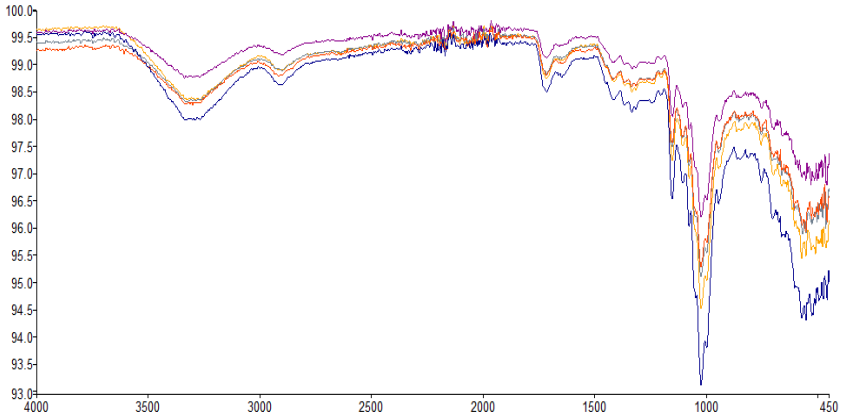

Fig. 15 FTIR spectra of sample 9 (25 % CD, 160°C, 5 min)

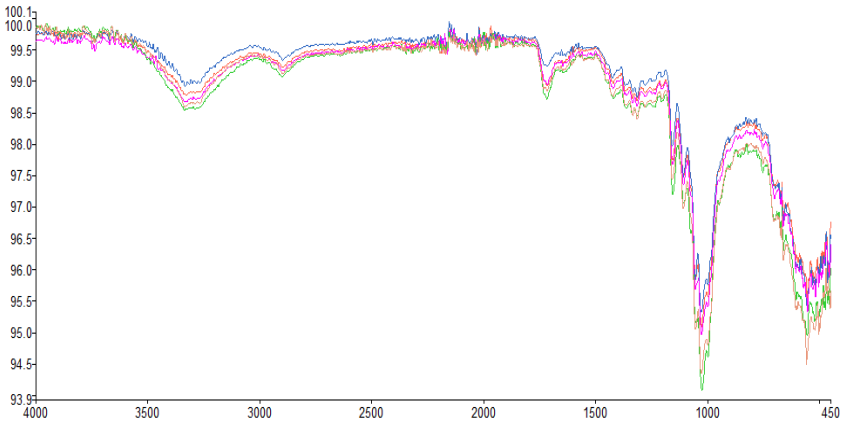

Fig. 16 FTIR spectra of sample 10 (25 % CD, 160°C, 10 min)

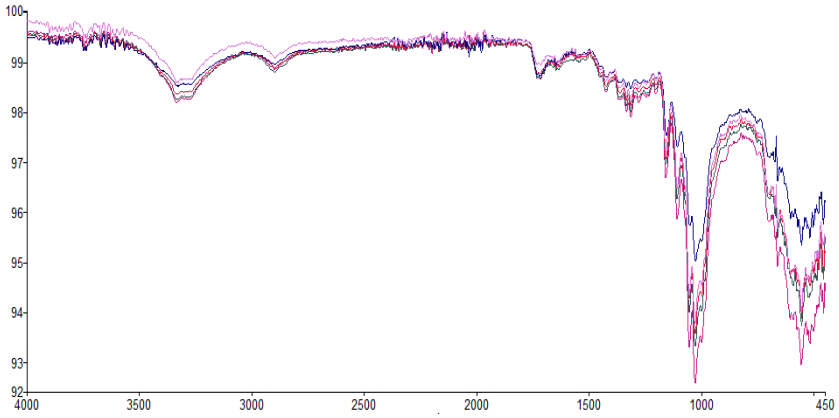

Fig. 17 FTIR spectra of sample 11 (25 % CD, 180°C, 5 min)

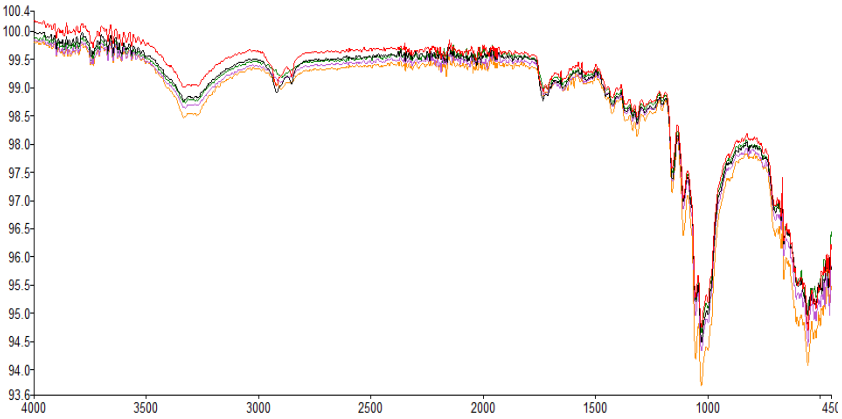

Fig. 18 FTIR spectra of sample 12 (25 % CD, 180°C, 10 min)

In Figs. 11-14, all of the peaks are at the same wavelengths for 5 different areas of the samples with 20% β-cyclodextrin with different process conditions. Therefore, it means that the process conducted properly. The findings are summarized as:

1) There are no contaminations and foreign materials.
2) There are no considerable variations on the fabrics surface with homogeneous distribution of CD.

In Figs. 15-18, all of the peaks are at the same wavelengths for 5 different areas of the samples with 25% β-cyclodextrin with different process conditions. Therefore, it means that the process conducted properly. The findings are summarized as:

1) There are no contaminations and foreign materials.
2) There are no considerable variations on the fabrics surface with homogeneous distribution of CD.

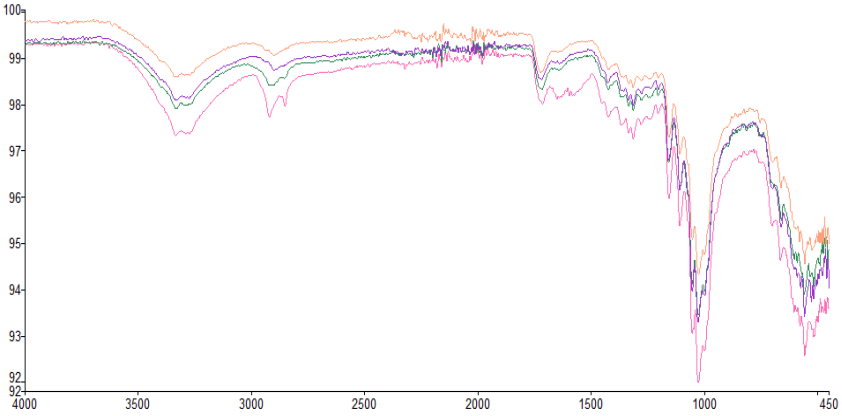

Fig. 19 FTIR spectra of samples including 15 % CD

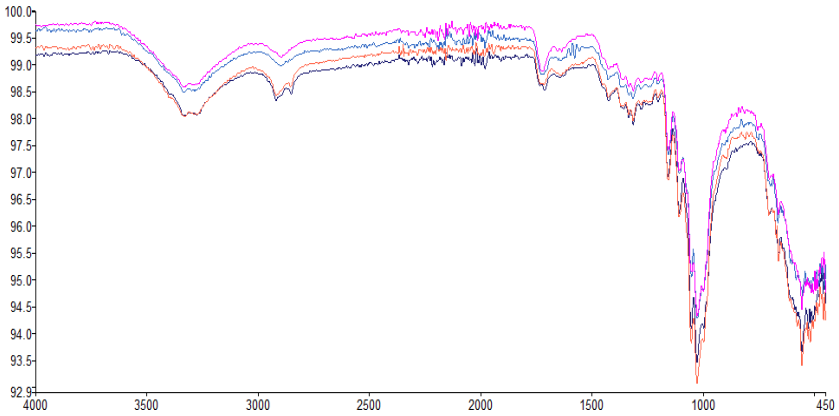

Fig. 20 FTIR spectra of samples including 20 % CD

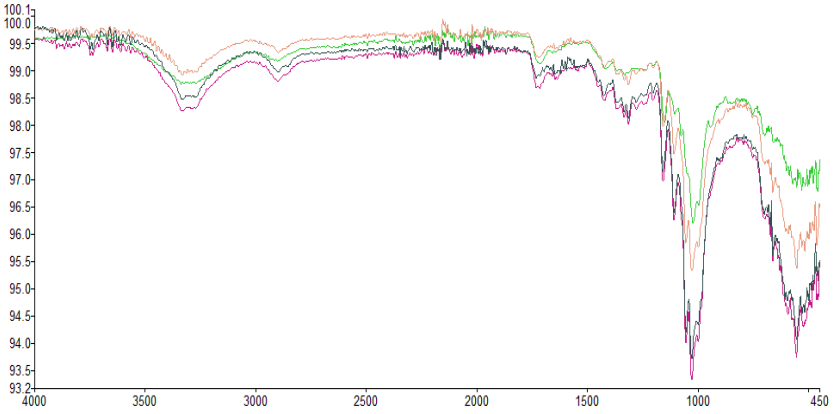

Fig. 21 FTIR spectra of samples including 25 % CD

In Figs. 19-21, fabric samples (S1, S2, S3, S4) having 15% β-CD, fabric samples (S5, S6, S7, S8) having 20% CD and fabric samples (S9, S10, S11, S12) having 25% β-CD can be seen, respectively. The findings are summarized as:

1) Characteristic peaks are at the same wavelength except the one for 2925 cm^{-1}.
2) As the temperature and duration increases, CD impartation efficiency increases as can be seen from Figs. 19-21, since the peak at 2925 cm^{-1} becomes more apparent. (Two peaks at 2950 cm^{-1} and 2925 cm^{-1} can be most clearly seen for the one treated at 180°C and 10 min.) There are no considerable variations on the fabrics surface with homogeneous distribution of CD.
3) This shows that temperature and duration has positive effect on CD impartation meaning that the process conditions are really important for the reaction.

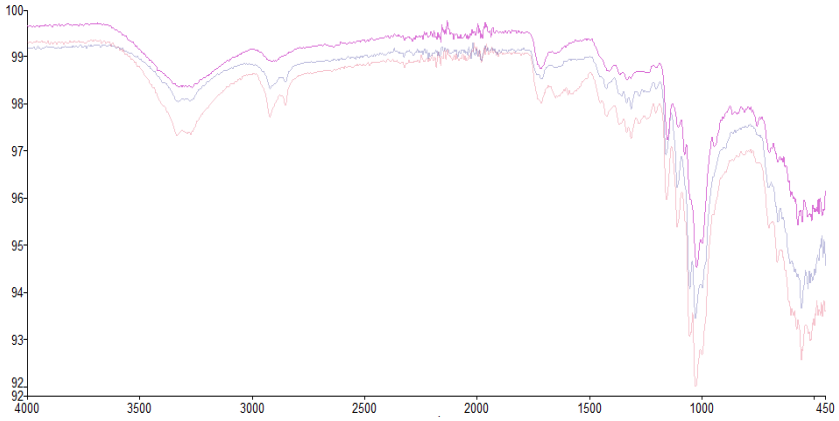

Fig. 22 FTIR spectra of samples 1, 5 and 9 with 15, 20 and 25% CD

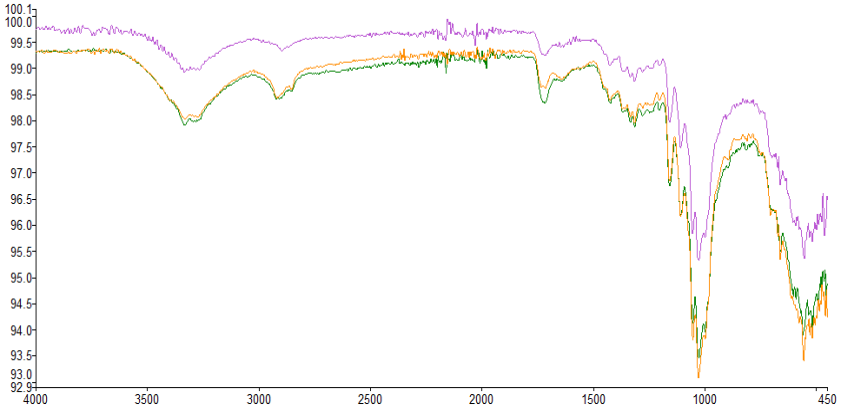

Fig. 23 FTIR spectra of samples 2, 6 and 10 with 15, 20 and 25% CD

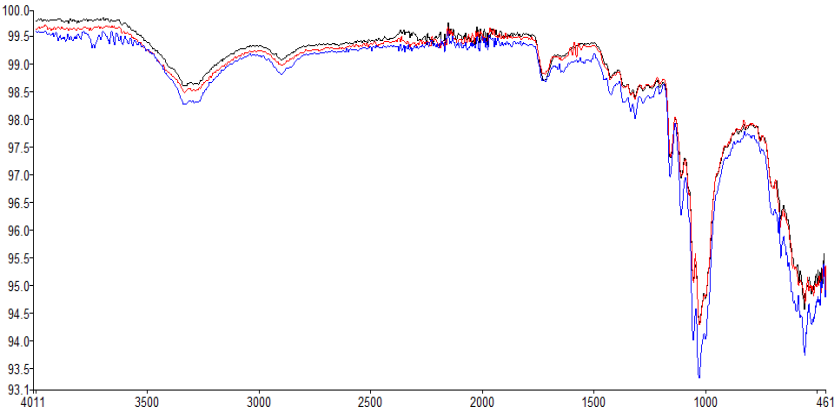

Fig. 24 FTIR spectra of samples 3, 7and 11 with 15, 20 and 25% CD

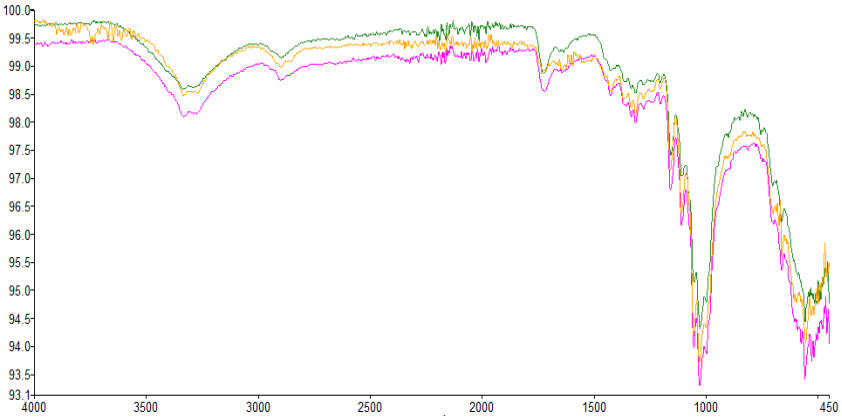

Fig. 25 FTIR spectra of samples 4, 8 and 12 with 15, 20 and 25% CD

In Figs. 22-25, fabric samples (S1-15%CD, S5-20% CD, S9-25% CD) treated at 160 °C for 5 min, fabric samples (S2-15% CD, S6-20% CD, S10-25% CD) treated at 160 °C for 10 min, fabric samples (S3-15% CD, S7-20% CD, S11-25% CD) treated at 180 °C for 5 min and fabric samples (S4-15% CD, S8-20% CD, S12-25% CD) treated at 180 °C for 10 min can be seen, respectively. The findings are summarized as:

1) Characteristic peaks are at the same wavelength except the one for 2925 cm^{-1}.
2) As the amount of CD increases, CD impartation efficiency correspondingly CD amount on the fabric surface increases as can be seen from Figs. 22-25, since the peak at 2925 cm^{-1} becomes more apparent. (At the same process conditions, two peaks at 2950 cm^{-1} and 2925 cm^{-1} can be most clearly seen for the one treated with 25% CD amount.)

3) This shows that CD amount has positive effect on the CD impartation efficiency meaning that to some extent as the amount of CD increases, the amount of CD imparted to the structure of cotton fabric increases.

B. Weight Gain Analysis Results

According to the weight gain analysis, when the weights of the fabric samples before and after treatment with CD are compared, it is apparent that certain amount of weight gain is obtained for all of the fabric samples, which demonstrates the successful CD incorporation to the fabric structure (Table II).

C. Tear Strength Results

Tear strength of the warp yarns decreases when the curing temperature and curing time are increased according to the findings shown in Fig. 26. It was also found that tear strength values of the warp yarns of the fabrics treated with different amounts of CD are lower than tear strength value of the warp yarns of the untreated fabric which is approximately 7.64 N. The decrease in the strength of warp yarns of cotton fabric is expected, because the treatment in acidic medium causes some degree of depolymerization for cotton materials. The best result is obtained for the CD treated fabric sample with 20% β-CD.

TABLE II
SAMPLES AND THEIR WEIGHTS BEFORE AND AFTER TREATMENT

Sample #	Weight before treatments (g)	Weight after treatments (g)
Sample 1	33,09	37,93
Sample 2	32,52	37,49
Sample 3	30,07	35,15
Sample 4	32,09	38,01
Sample 5	30,70	34,10
Sample 6	29,31	33,96
Sample 7	29,71	34,68
Sample 8	30,86	36,07
Sample 9	30,03	36,94
Sample 10	29,69	37,20
Sample 11	28,13	33,65
Sample 12	28,99	34,86
Sample 13	27,74	28,47
Sample 14	30,61	32,21

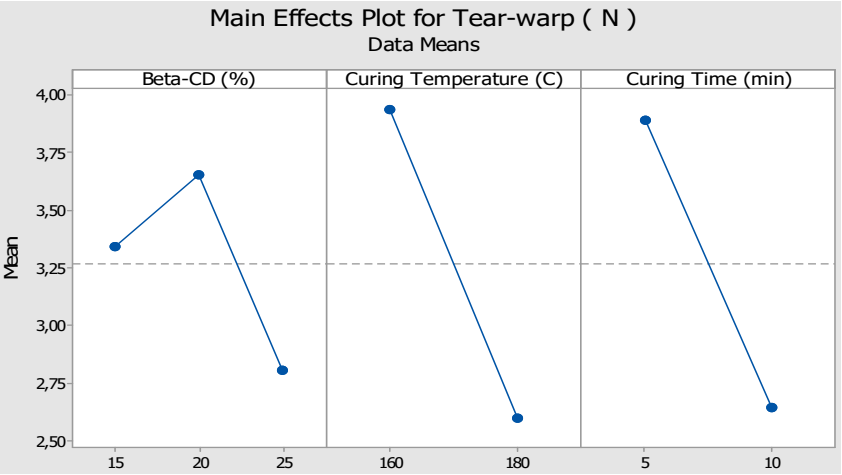

Fig. 26 Main effects plot for tear strength of the warp yarns

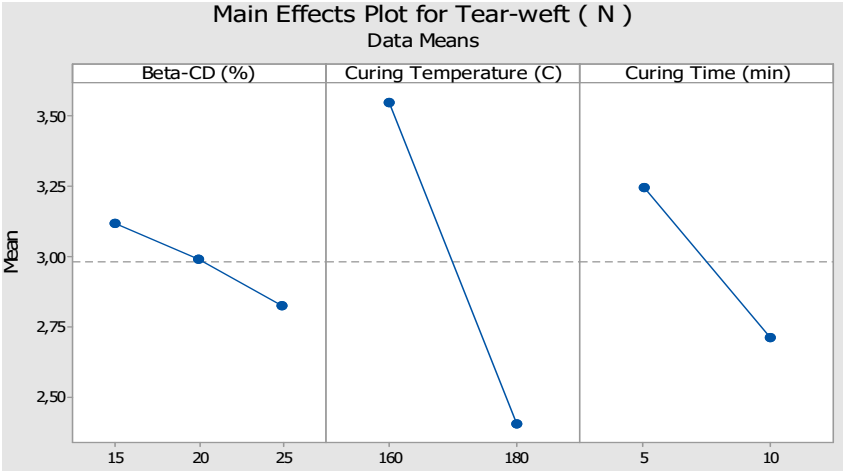

Fig. 27 Main effects plot for tear strength of the weft yarns

Tear strength of the weft yarns decreases, when the curing temperature and curing time are increased as shown in Fig. 27 as is the case with the warp yarns. Additionally, tear strength values of the weft yarns of the fabrics treated with different amounts of CD are lower than tear strength value of the weft yarns of the untreated fabric which is around 7.21 N. The decrease in the strength of weft yarns of cotton fabric is expected, since the treatment in acidic medium causes some degree of depolymerization for cotton materials. Unlike the case for the warp yarns, almost the same values are obtained for the fabric samples in the presence of different amounts of β-CD.

As can be observed in Fig. 28, tear strength values of the warp yarns of each fabric sample treated with β-CD decrease with the increasing curing time, since the structure of cotton degrades by the increase in the curing time. The maximal change in tear strength obtained is the one for the fabric sample with 15% β-CD. However, the values obtained for each fabric samples with different amounts of β-CD are found to be close to each other for the both separate cases.

As seen in Fig. 29, tear strength values of the weft yarns of each fabric sample treated with β-CD get lower with the increasing curing time, because the structure of cotton degrades by the increase in the curing time, which is similar with the case for the warp yarns. The highest change in tear strength obtained is the one for the fabric sample with 15% β-CD. However, the values obtained for each fabric samples with different amounts of β-CD are close to each other for the both individual cases.

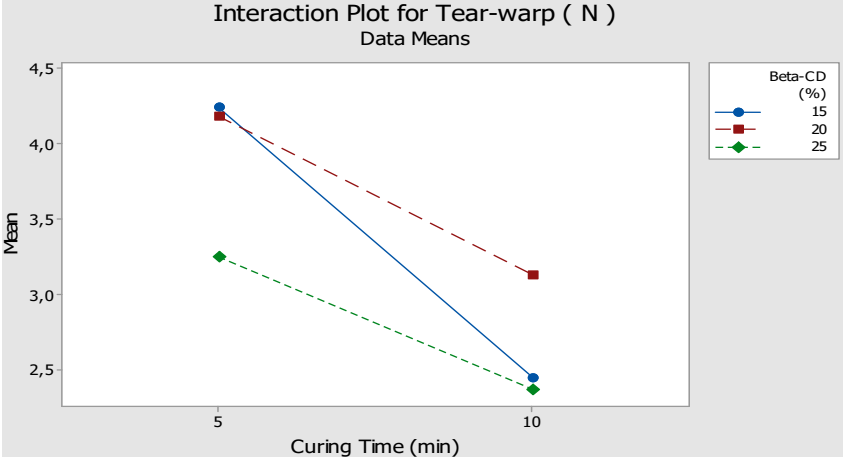

Fig. 28 Interaction plot for the change in tear strength of the warp yarns according to curing time

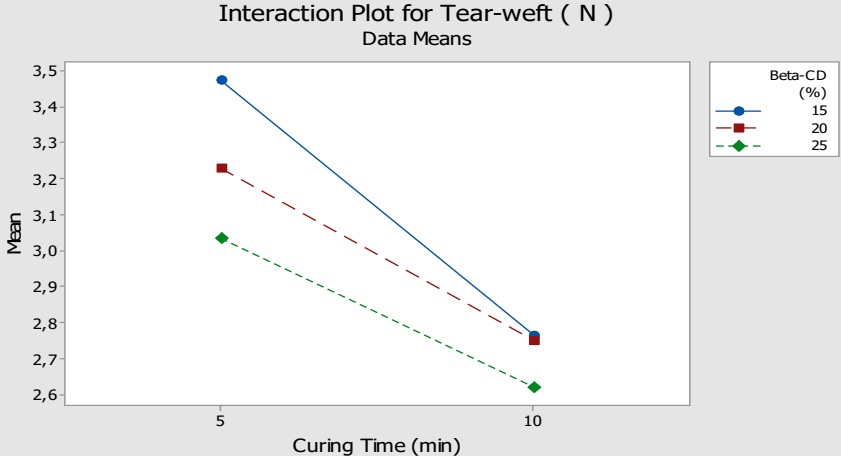

Fig. 29 Interaction plot for the change in tear strength of the weft yarns according to curing time

D. Tensile Strength Results

Tensile strength of the warp yarns decreases, when the curing temperature and curing time increase as displayed in Fig. 30. It was also obtained that tensile strength values of the warp yarns of the fabrics having different amounts of β-CD in their structure are lower than tensile strength value of the warp yarns of the untreated fabric which is approximately 451 N. The decrease in the strength of warp yarns of cotton fabric is expected due to some degree of depolymerization of cotton materials caused by the treatment in acidic medium. The best

result is obtained for the CD treated fabric sample possessing 20% β-CD in its structure.

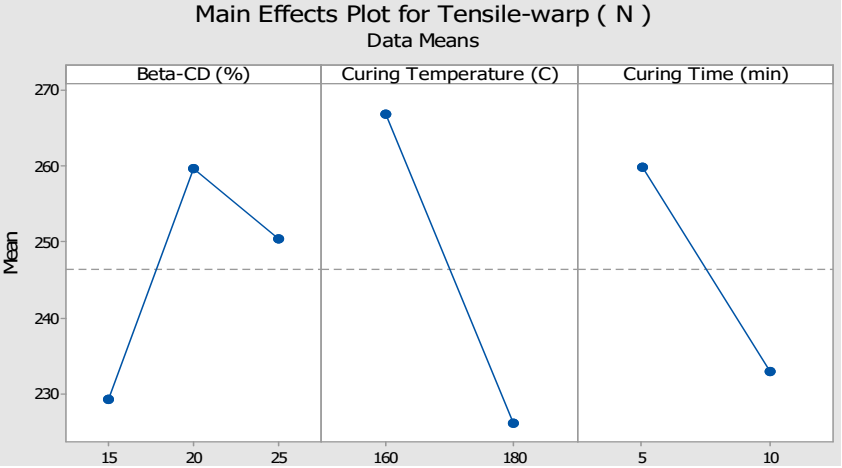

Fig. 30 Main effects plot for tensile strength of the warp yarns

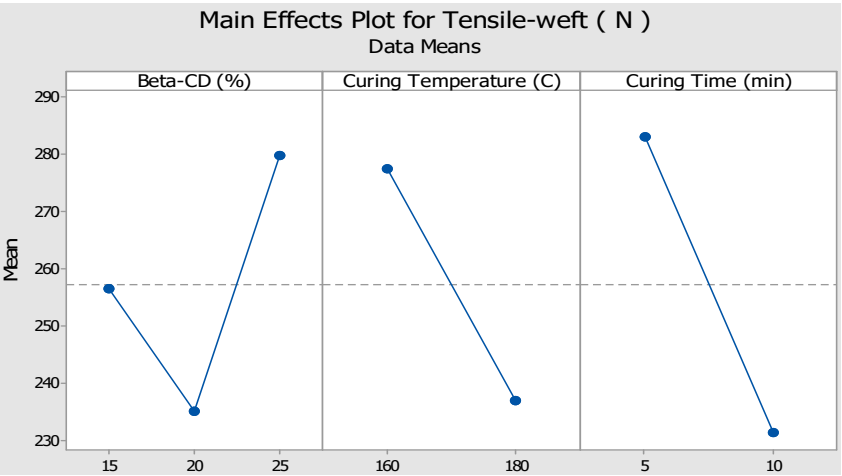

Fig. 31 Main effects plot for tensile strength of the weft yarns

Tensile strength of the weft yarns decreases, when the curing temperature and curing time are increased as shown in Fig. 31 as is the case with the warp yarns. Additionally, tensile strength values of the weft yarns of the fabrics treated with different amounts of CD are lower than tensile strength value of the weft yarns of the untreated fabric which is around 295 N. The decrease in the strength of weft yarns of cotton fabric is expected, since the treatment in acidic medium causes some degree of depolymerization for cotton materials. The best result is obtained for the β-CD treated fabric sample with 25% β-CD.

As can be observed in Fig. 32, tensile strength values of the warp yarns of fabric samples treated with 20% and 25% β-CD decrease with the increasing curing time, since the structure of cotton degrades by the increase in the curing time. However, no significant change is observed for the one with 15% β-CD. The maximal change in tensile strength obtained is the one for the fabric sample with 20% β-CD. However, the values obtained for each fabric samples with different amounts of β-CD are found to be very close to each other for the case of 10 minutes.

As it is shown in Fig. 33, tensile strength values of the weft yarns of each fabric sample treated with β-CD get lower with the increasing curing time, because the structure of cotton degrades by the increase in the curing time, which is similar with the case for the warp yarns. The highest change in tensile strength obtained is the one for the fabric sample with 25% β-CD. However, the values obtained for each fabric samples with different amounts of β-CD are close to each other for case of 10 minutes.

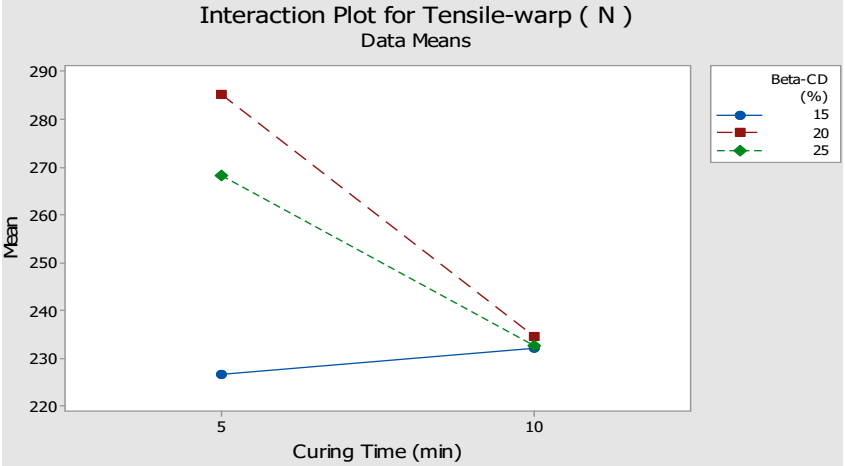

Fig. 32 Interaction plot for the change in tensile strength of the warp yarns according to curing time

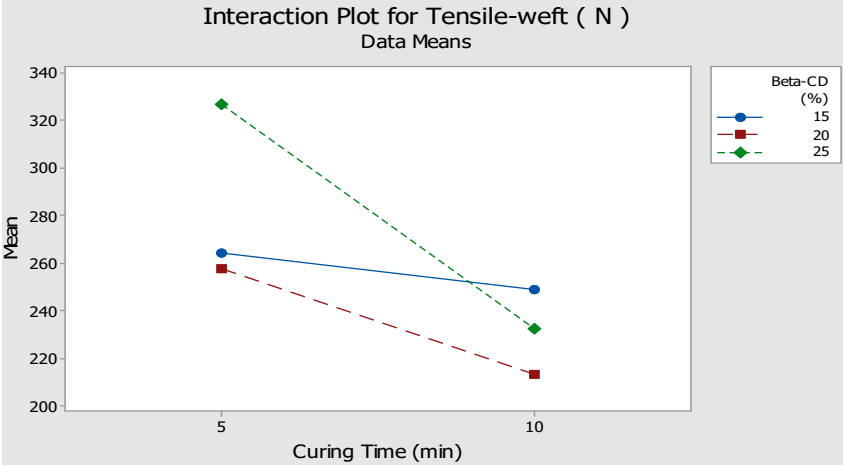

Fig. 33 Interaction plot for the change in tensile strength of the weft yarns according to curing time

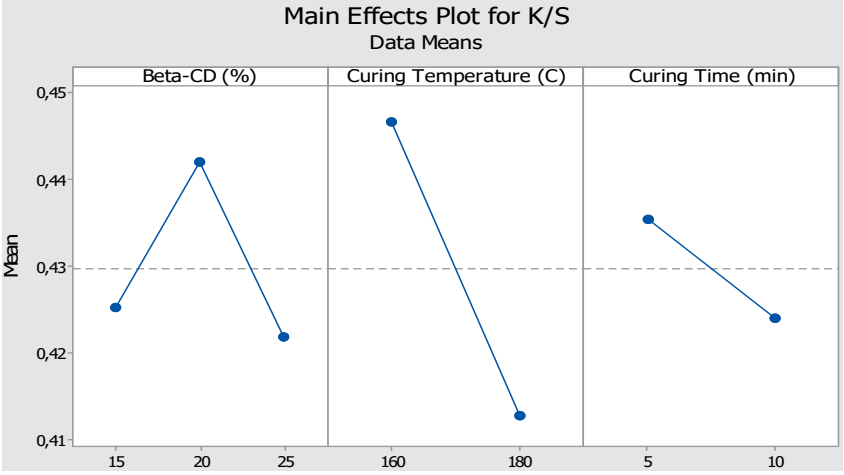

Fig. 34 Main effects plot for K/S

E. Color Analysis

Because of the grafting of β-CD onto cotton fabric, the number of [-OH] bonds that reactive dye can attach is increased and correspondingly fabric surface takes much more dyestuff on itself, which is demonstrated by the increase in K/S value. In Fig. 34 the decrease in K/S value can be observed with the increase in the curing temperature and curing time. Additionally, the highest K/S value is obtained with 20% CD.

As seen in Fig. 35, washing fastness of cotton fabric with 20% β-CD is found to be the highest when compared to the other fabric samples treated with β-CD. In addition to this, the level of staining of cotton fabric samples treated with 15% and 20% β-CD are higher than the untreated one whose value is 4.

As mentioned before, when fabric surface takes much more dyestuff, K/S value of that fabric increases due to a darker color shade, which means lightness of dyed fabric is decreased. In Fig. 36, it is seen that the lowest lightness is obtained for the fabric sample with 20% β-CD.

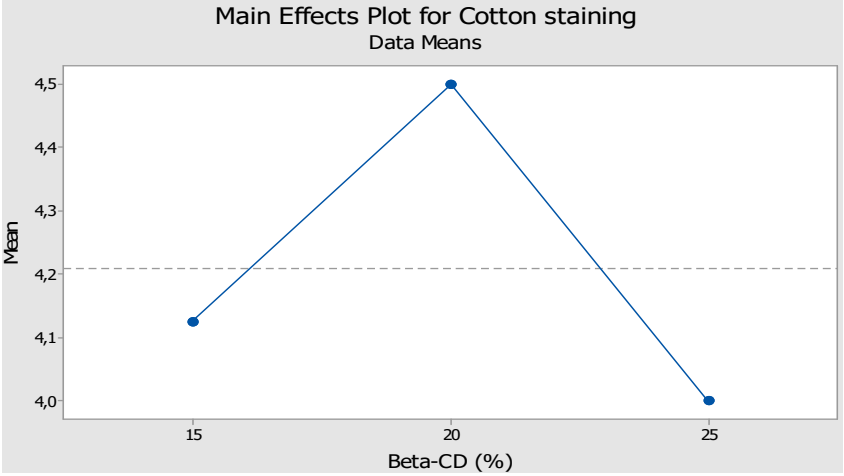

Fig. 35 Main effects plot for cotton staining with respect to the amount of β-CD

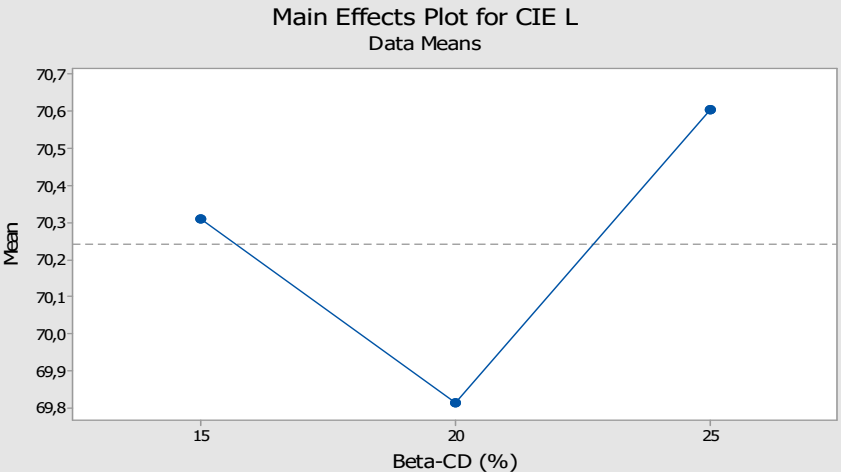

Fig. 36 Main effects plot for lightness with respect to the amount of β-CD

IV. Conclusion

In this study a conventional cotton fabric was functionalized with β-CDs by grafting method in conventional textile finishing process for improved durability against external factors caused by many activities during use such as laundering without any sacrifice from the inherent performance characteristics of cotton fabric to obtain a multi-functional fabric having the ability of encapturing molecules/ particles via physical/chemical means resulting in some potential for the fabrics to be easily dyed with various dyestuff, good level of printability, being easily treated with various finishing agents. The results of the study are promising; however, they need to be improved with further studies by tuning the process conditions.

Acknowledgment

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