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Textile Performance of Functionalized Cotton Fiber with 3-Glycidoxypropyltriethoxysilane

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Abstract

The surface modification of cotton fiber was successfully carried out by condensation polymerization with 3-glycidoxypropyltriethoxysilane (GPTES) in an ethanol-water medium. The purpose was to enhance the tensile strength and softness properties of the cotton, by introducing a more flexible Si-O bond between the silane coupling agents and the cotton fiber. The moisture absorption of modified cotton fiber is lower than the raw cotton fiber. The swelling behaviour of modified cotton fiber was decreased in the polar solvents, whereas swelling increased in nonpolar solvent. The FTIR spectra showed two additional peaks at 860 cm^{-1} (Si-OH symmetric stretch) and 1207 cm^{-1} (Si-O-C bending) respectively as a function of silane absorption by the fiber surface. Scanning electron microscopy (SEM) coupled with X-ray diffraction (XRD) was studied to identify the surface morphology and the structural characteristics of the raw and modified fibers respectively. The absorption of reactive brown 10 and reactive orange 14 by the modified fiber was comparatively higher than untreated cotton fiber. Color fastness of raw and modified fibers to spotting with soap washing, sunlight, acids and alkalis have been studied.

Keywords: Cotton fiber; 3-glycidoxypropyltriethoxysilane; Silane coupling agent; Modification; Siloxane

Introduction

Cotton a natural cellulose fiber is reasonably priced renewable, biodegradable and is the most abundant organic raw material in the world. It is the backbone of the world's textile trade and the textile industry provides the single source of economic growth in Bangladesh, a rapidly developing economy. Exports of textiles and garments are the principal source of foreign exchange earnings. Cotton contains approximately 95-98% cellulose, which contains three hydroxyl groups per each glucose unit [1,2].

Cotton fiber is one of the most important natural fibers which provide a wide range of application in textile materials because of its easy availability, low density, light weight, low cost, and above all environment friendly characteristics [3,4]. It can easily be transformed into diverse products, affecting every phase of our daily life because of its wide spread application. But the major problem of the cotton fiber is its lower flexibility and softness properties which limit an extended use of cotton as well as other fibers [5]. These properties affect the stability of cotton goods in their environments. Many physico- chemical modification steps were already done to overcome these properties: such as alkaline treatment, acetylation, benzoylation, acrylation, oxidation and isocynation of the natural fiber [6]. By these modifications, some new moieties are introduced on the fiber backbone that can improve its properties.

Recently, the modification of cotton fiber using a silane coupling agent has received considerable attention. The hydrophilic properties of this natural fiber are mainly responsible for the existence of hydroxyl groups on the fiber backbone. The modification of cotton fiber with silane coupling agent reduces the hydrophilic properties of the fiber. A silane coupling agent acts as a sort of intermediary between dye molecule and cellulose chain. During modification, the polar hydroxyl groups are blocked due to the covalent bond formation between the hydroxyl groups of the cotton and silane coupling agent. The interaction of silane coupling agents with cotton fibers mainly proceeds through four steps: (i) hydrolysis (ii) self- condensation (iii) adsorption (iv) grafting [7,8].

Although a lot of work has been done on chemical modification, little if any published research work has been found in which cotton fibers have been modified with silane coupling agent. The aim of such a strategy is the improvement of flexibility, softness and tensile strength, as well as comfort, of modified cotton fibers. The present study investigates the mechano-chemical properties of cotton fiber functionalized with 3-glycidoxypropyltriethoxysilane. The objective of this modification is to improve the properties of the textile while retaining comfort and mechanical strength.

In order to make the modification process more economic, attempt has been made to find out the optimum modification conditions, depending on the concentration of monomer, ethanol-water ratio, pH, modification time and temperature. Grafting was determined on the basis of weight increased. The grafted fiber was characterized with FTIR, SEM, XRD and TGA analyses. To observe the dye ability of silane-modified cotton, fibers dyed with reactive orange-14 and reactive brown-10 and color fastness to spotting with sunlight, soap washing, acid and alkali were studied.

Experimental

Materials

Cotton fiber was gifted from Keya spinning mill, Dhaka, Bangladesh. The chemicals used for the functionalization were sodium hydroxide from Uni-chem (China), glacial acetic acid, methanol, ethanol and carbon tetrachloride from Merck, Germany, 3-glycidoxypropyl-triethoxysilane (GPTES) from Aldrich (USA). All chemicals used were of analytical reagent grade.

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Washing of cotton fiber

In order to obtain a well-defined reference fibre, alkaline washing was applied for the removal of non-cellulose compounds such as waxes, pectin, proteins from cotton with 0.2% Na_2CO_3 solution at 750°C for 30 min in a beaker in the ratio of 1:50. The fibers were then washed thoroughly with distilled water until neutralization and dried in the open air for 24 h. After that the fibers were dried in an oven at 60°C for 6 h.

Silane treatment

In order to treat cotton fibers with GPTES, first the required percentage of silane solution was prepared by mixing GPTES with an ethanol/water mixture, where the ratio of fiber to liquor was maintained at 1:50. This solution was allowed to stand for 1 h and silanol is formed (Figure 1). The solution pH was maintained at 3.5 by using 0.2 M acetic acid. Then cotton fibers were dipped in this solution and allowed to stand for 1.5 h by varying temperature. The cotton fiber was filtered from solution, and the fibers were dried in air and then in an oven at 600°C to a constant weight.

The grafting of GPTES on cotton fiber was measured by means of percent graft yield which was calculated according to the following formula:

$$\text{Graft yield } \% = \frac{A-B}{B} \times 100$$

Where, A is the weight of the fibers after modification, B is the weight of the fibers before modification.

Evaluation of Physical and Chemical Properties

Measurement of tensile strength

The tensile strength of raw and silane-modified cotton fibers were measured by using a "Portable Electronic Single Yarn Strength Tester YG021J" (Fanyuan Instrument (HF) Co., Ltd., China) for quick and reliable tensile strength measurement. The breaking load was gradually increased after starting the machine and at the point the specimen was broken down. The machine was stopped at the point of break. The breaking load was shown on the scale of the tensile tester in N/yarn.

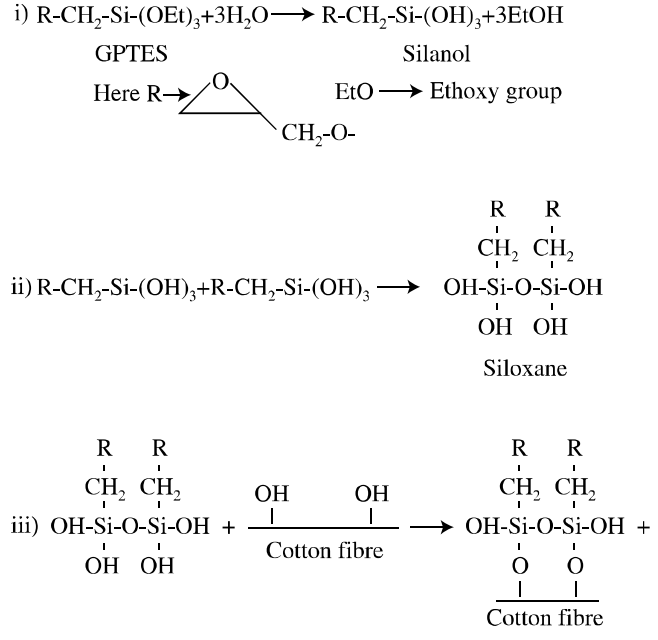

Figure 1: Formation of silanol to siloxane and reaction with cotton fibre.

Moisture content

The moisture absorption study of the modified cotton fiber as well as unmodified fibers was performed at a constant humidity level. The samples were placed on a humidity chamber at 30°C for a 48 h where humidity was maintained at saturation level. After that the fibers were analysed at moisture analyser which gives the moisture content of the modified and unmodified fibers. Moisture content is determined using following formula:

$$\text{Moisture content } \% = \frac{W_f - W_i}{W_i} \times 100$$

Where, W_f is the weight of wet sample, W_i is the weight of dry sample.

Swelling behaviour

Swelling behaviour of the functionalized and unmodified cotton fibers was determined by dipping them in water, methanol, and carbon tetrachloride. The GPTES-treated and unmodified cotton fibers were immersed in 100 mL of solvents at 30°C for 72 h. The samples were filtered and the excess solvent was removed with the help of filter paper, then the final weight was determined. The percent swelling was calculated from the increase in initial weight in the following manner [9]:

$$\text{Swelling } \% = \frac{W_f - W_i}{W_i} \times 100$$

Where, W_i is the initial weight of fibre, W_f is the final weight of fibre.

Wrinkle recovery angle

A wrinkle recovery tester (Daiei Kagaku Seiki Ltd. Kyoto, Japan) was used to determine the wrinkle recovery angle. The samples were cut to a 4.4 cm × 1.5 cm size.

Then the cut samples were folded and kept under the weight of 500 g for 5 min. The folded samples were inserted inside a template and placed in the testing machine. The machine was switched on and the recovery angle was observed from the dial.

The machine was looked like a big round table clock and has marked angle 0 (zero) to 180°. Angle 0 degree means no recovery. Angle higher means that wrinkle recovery is higher.

Characterization of Unmodified and Surface Modified Cotton Fibers

Infrared spectroscopy

FTIR spectroscopy analysis was performed by using a Perkin Elmer Spectrum 100 infrared spectrometer. The silane-modified fibers and KBr (potassium bromide) were dried in an oven at 105°C to render them moisture free. The dried cotton fiber was made into a powder using mortar- pestle and about one percent of the powder was mixed with dried KBr to make pellet [10]. Then the samples were analysed in an attenuated total reflectance (ATR) detector over a range of 400-4000 cm^{-1} at a resolution of 4 cm^{-1}/min.

Scanning electron microscopy analysis

Scanning electron microscopy analysis of the washed and GPTES-functionalized cotton fibers was carried out in an electron microscope

(FEI Quanta Inspect, Model: S50, Kyoto, Japan) to observe the microstructure and the surface morphology. Since these materials are non-conducting, they were gold-plated. The analytical steps were performed with an acceleration voltage of 25 kV, working distance of 11 mm with 2000 times magnification.

Thermo-gravimetric analysis

Thermogravimetric analysis was used to determine the thermal decomposition rate and the thermal stability of the unmodified and GPTES functionalized cotton fibers. The samples, approximately 10 mg each were heated from 30 to 600°C under an inert atmosphere (argon), at a rate of 20°C min^{-1} in a SEIKO-EXTAR-TG/DTA-6300 (SEIKO-Japan).

XRD analysis

Samples were analysed by a X-ray diffractometer (Bruker D8 Advanced X-ray Diffractometer, Germany), operating at 40 kV and 30 mA with a Cu-Kα source. The diffraction intensity was measured in the range of 2θ angles between 5° and 40°C.

Results and Discussion

Optimization of modification

Figures 2a-d show the effect of parameter variables such as silane monomer concentration, ethanol/water ratio, pH and temperature on graft yield respectively. Figure 2a shows the effect of monomer concentration on modification of cotton fiber. The results show that the percent graft yield increased with an increase of silane concentration up to 400% for GPTES. The percent weight gain was increased due to higher crosslinking reaction between the cellulosic OH group of cotton and OH group of the siloxane at higher concentration. The rate of conversion of GPTES containing ethoxy group into reactive hydroxyl group by hydrolysis of GPTES is directly related to its initial concentration. But at concentration higher than the optimum value, the percent graft yield is decreased because of increasing rate of homopolymerization instead of copolymerization.

Figure 2b shows that the percent graft yield increased with the increase of ethanol/water ratio up to 40:60. Beyond this value, the graft yield started to decrease. At 40:60 ratio of ethanol/water, the maximum amount of silane-coupling agents are hydrolysed, which is the key to dominating the chemical reaction by which silanol is generated into the modification process. At higher alcohol percentage from the optimum value the interaction between the water and alkoxy ($-OCH_2CH_3$) groups during hydrolysis was limited. At lower alcohol concentration from the optimum value, the hydrolysis rate is lower because of insolubility of silane coupling agent [11] (Figures 2a-2d).

It can be observed from Figure 2c that the percent graft yield increased with the increase of pH value up to 3.5 for GPTES and then decreased. This is because of the fact that the hydrolysis reaction of GPTES gradually reached higher values with the increase of pH of the liquor up to 3.5. At this pH value, the reaction between the silanol and hydroxyl group of the fiber occurs easily. Above this pH value, the hydrolysis of GPTES decreases gradually, due to the decreasing rate of protonation of alkoxy group. At pH values lower than 3.5, the formation of silanol group was insufficient [12].

The graft yield increased with the increase of reaction temperature upto 30°C for GPTES and then decreased with further increase of temperature which is shown in Figure 2d. The increase in percent graft

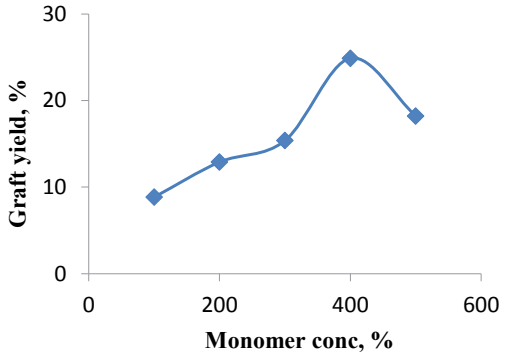

Figure 2a: Effect of silane concentration on graft yield.

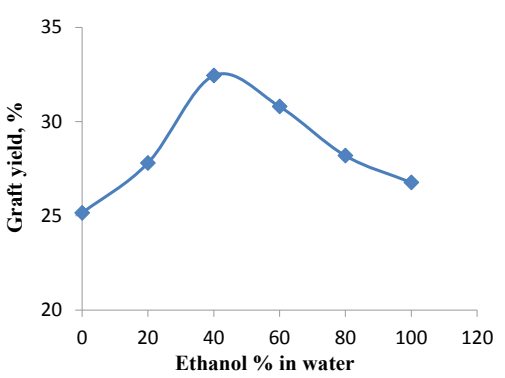

Figure 2b: Effect of aqueous ethanol concentration on graft yield.

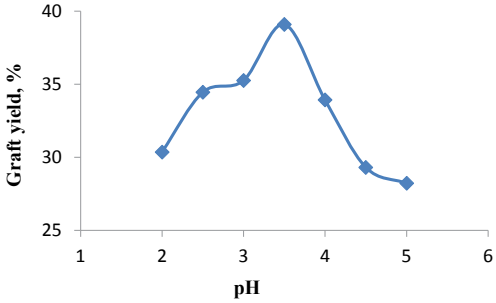

Figure 2c: Effect of pH on graft yield.

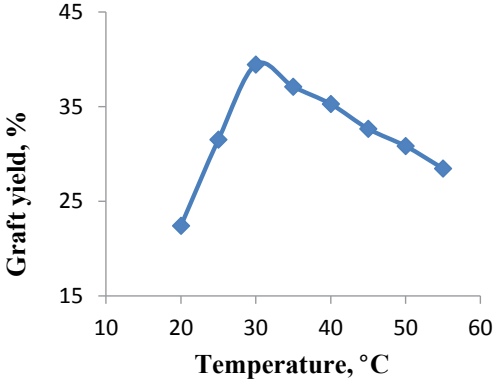

Figure 2d: Effect of temperature on graft yield.

yield up to 30°C may be ascribed to the increase of molecular collision between the reactant molecule which increases the rate of reaction and the maximum modification occurs. The decrease in percent graft yield above optimum temperature may be attributed to the increase in activation energy and evaporation of silane from the reaction media. As a result, the weight gain decreased [8].

Dyeing behaviour

The exhaustion of direct dyes by raw and modified cotton fibers is listed in Table 1. The dye exhaustion of the GPTES-modified cotton fiber was higher than that of unmodified washed cotton fiber and the dye exhaustion increased with an increase in the percent graft yield. The modification of cotton fiber has enhanced the dye site in cellulose macromolecule of cotton fibers. As a result, the modified fiber absorbed more dyes than the unmodified sample and this absorption has increased the exhaustion percentage of dye in the modified cotton fibers (Table 1).

FTIR spectroscopy

The FTIR spectra of unmodified cotton fiber and GPTM-modified cotton fibers were recorded with a spectrophotometer (Spectrum-100, FTIR Spectrum, Perkin Elmer, Japan) and are shown in Figure 3. Figure 3a shows the spectra of unmodified cotton fiber washed with Na_2CO_3 and Figure 3b for 400% GPTES-modified cotton fibers for the evidence of modification onto cotton fibers. The FTIR spectra of unmodified and silane-modified cotton fibers were mostly similar, as the absorption peaks were obtained in the spectra for entire sample, except the new additional peak in the modified cotton fiber. The FTIR spectra of 3-glycidoxypropyl-triethoxysilane-treated cotton fiber displays an additional peak at 860 cm^{-1} and 1207 cm^{-1} for Si-OH symmetric stretch and Si-O-C bond, respectively as a function of silane absorption by the fiber surface [13-15]. Thus, the FTIR analytical data indicate the functional attachment of GPTES monomer on the cotton fiber surface (Figure 3).

Thermal behaviour

Thermal behaviour of unmodified and GPTES-modified cotton fibers were examined by a study of TGA thermogram. Each of the figures represents two thermo gram curves namely TGA and DTG. From the Figure 4a and 4b, it can be seen that the loss in weight is around 60% at 370°C for washed unmodified cotton and 49.4% at 350°C for GPTES-modified cotton. From the DTG curve, the rate of decomposition of unmodified cotton fiber is higher than that of GPTES-modified cotton fiber. Thus, the thermal stability of GPTES-modified fibers are higher than that of unmodified fibers, which may be happen due to the incorporation of silane coupling agents with the cellulosic fibers (Figures 4a and 4b).

Type of cotton sample	Dye exhaustion, %	
	Reactive orange 14	Reactive brown 10
Unmodified fibre	69	65
3-Glycidoxypropyltriethoxysilane modified fibre	77	71

Table 1: Effect of dye absorption on dyeing of unmodified and GPTES modified cotton fibers.

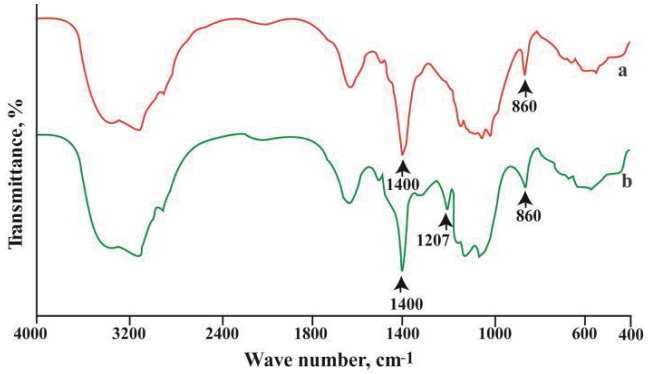

Figure 3: FTIR spectra of raw and GPTES modified cotton fibre.

Surface morphology

Surface morphology of the unmodified cotton and GPTES-modified cotton samples was subjected to SEM analysis. The scanning electron micrographs could easily verify the difference between unmodified cotton fibers and surface modified fibers, as shown in Figures 5a and 5b. It can be seen from Figures 5a, and 5b that the surface roughness of the GPTES-modified cotton fiber is higher than that of unmodified cotton fibers. The roughness of GPTES-modified fiber is due to the high deposition of GPTES on the surface of fibers after the modification. The GPTES-molecules were able to crosslink with the hydroxyl groups of the cellulosic molecules effectively, especially in the acidic medium. As a result, the surface was altered significantly as shown in Figure 5.

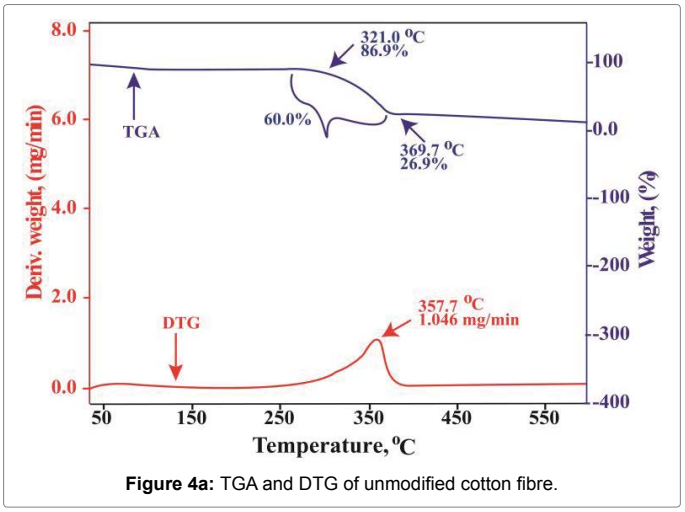

Figure 4a: TGA and DTG of unmodified cotton fibre.

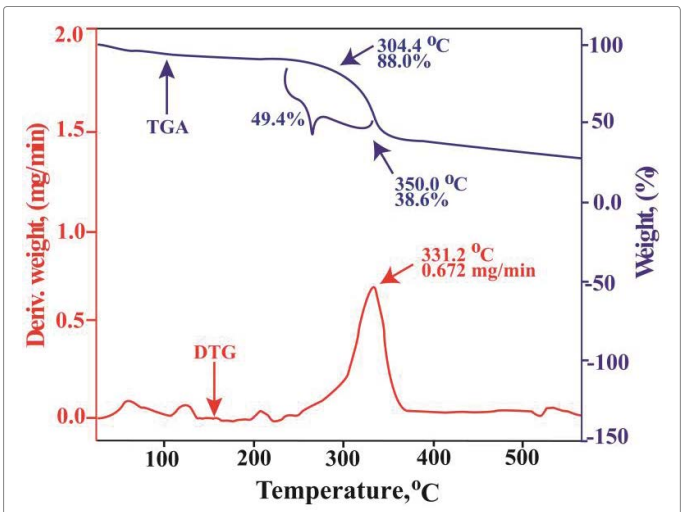

Figure 4b: TGA and DTG of GPTES treated cotton fibre.

Fibre type	Swelling behavior, %			Tensile strength (N)	Wrinkle recovery angle, degree		Moisture absorption, %
	H_2O	CH_3OH	CCl_4		Warp	Weft	
Unmodified cotton	321	305	205	207	28	50	12.49
GPTES modified cotton	73	151	235	285	60	52	8.89

Table 2: Swelling behavior, tensile strength, wrinkle recovery angle and moisture absorption properties of unmodified and modified cotton fibers.

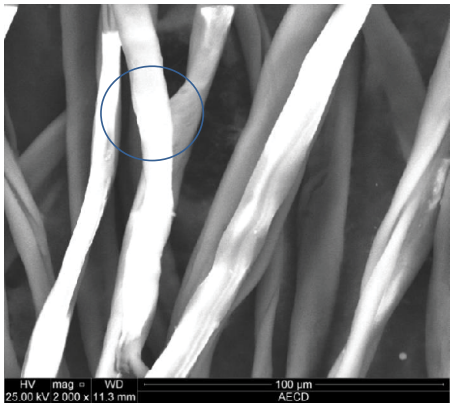

Figure 5a: SEM of raw cotton fibre.

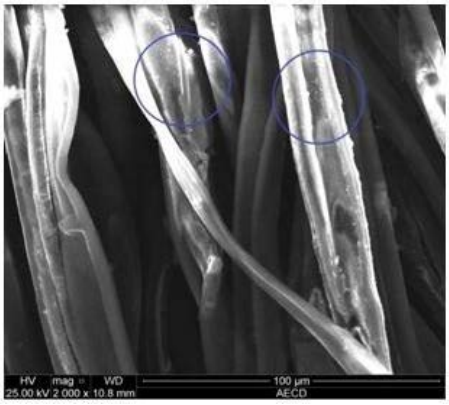

Figure 5b: SEM of GPTES-modified cotton fibre.

XRD analysis

XRD analysis is a technique for estimating the degree of crystallinity in polymer. The XRD could easily verify the difference between unmodified cotton fibers and 3-Glycidoxypropyl-triethoxysilane-modified cotton fibers which are shown in Figure 6a and 6b, respectively. From figure it is seen that unmodified cotton fibers exhibit sharp peaks, while broad peaks are found for silane-modified cotton fibers. The silane treated cotton became more amorphous as a consequence of further hydrolysis of the crystalline regions of cotton [15]. Therefore, the surface roughness of the 3-Glycidoxypropyltriethoxysilane-treated cotton fiber was higher than that of untreated cotton fibers.

Physical properties

Table 2 show the swelling behaviour of unmodified cotton, as well as GPTES- modified cotton fibers, both for polar and non-polar solvents. Swelling ability reflects the relationship between void structures in backbone polymer and size of solvent's molecule [16,17]. The unmodified cotton fibers exhibited maximum swelling with polar

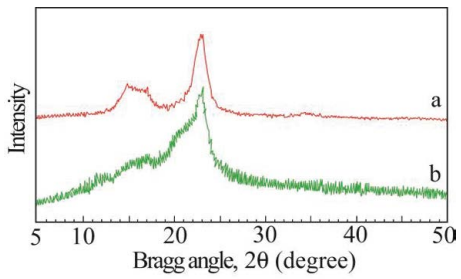

Figure 6: XRD of (a) unmodified cotton fibre and (b) GPTES modified cotton fibre.

solvents like water and methanol and the least swelling with nonpolar solvents like CCl_4. After treating with silane coupling agents, there is a decrease of the swelling in the polar solvents and an increase in the nonpolar solvent. This is because of the less- hydrophilic character of the unmodified cotton fiber. The tensile strength of modified cotton fiber was higher than that of unmodified cotton fiber and this is due to the modification of cotton fiber with silane coupling agents [18]. The wrinkle recovery angle of modified cotton fabric was higher than that of unmodified cotton fabric for both warp and weft directions, respectively. The presence of Si-O bond in the functionalized fabric shows high flexibility that recovers the winkle, exerted on the fabric surface by loading [19]. The moisture absorption sites are blocked after incorporation of silane chains through surface modification so the adapted fiber has less affinity for moisture than the original fiber (Table 2).

Conclusion

In this work, we have presented the results of chemical modification of cotton fibers with silane coupling agents. Maximum weight gain, by percentage is obtained at optimum value of the reaction parameters, such as silane concentration, pH, ethanol- water ratio and temperature. The chemical attachment between silanol and hydroxyl groups of cotton fibers were evaluated by FTIR analysis. The modified fibers shows improved physicochemical properties such as tensile properties, moisture absorption, elongation, wrinkle recovery and thermal stability properties than that of the unmodified cotton fibers. This new type of cotton was obtained through modification with silane coupling agents which enhance the application of garment products, textiles etc.

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