

Surface Modification of Cotton Fibre with Functionalized Silane Coupling Agents

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Abstract

Vinyltriethoxysilane and 3-Glycidoxypropyl-triethoxysilane were used for surface functionalization to provide more attention of cotton fibre in textiles. The process was carried out in ethanol- water medium which accelerates the crosslinking reaction between cotton fibre and silane monomer and was optimized carefully as a function of fibre weight gain. 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 fibre. The modification of cotton fibre enhanced the tensile strength and water repellency properties due to higher flexibility of Si-O bond and fibre matrix interfacial strength properties. The optimized condition of modification for VTES and GPTES was 400% on the weight of fibre in ethanol/water mixture (60:40) containing surfactant by maintaining pH 3.5 at 35 °C for VTES and 30 °C for GPTES in the fibre-liquor⁰ ratio of 1:40. It was observed that swelling behavior and moisture absorption of modified cotton fibres were decreased in polar solvents whereas increased in nonpolar solvents. Fourier transform Infrared spectroscopy was used to identify the incorporation of silicon-containing molecules. Energy Disperse X-ray analysis determined the quantities of atomic silicon which directly reflects its valence bond with organic moieties. Scanning electron microscopy and thermogravimetric analysis were used to investigate the surface morphology and thermal behavior of the modified fibre, respectively.

Keywords - Cotton fibre; Surface modification; silane coupling agents.

INTRODUCTION

Cotton, a cellulose fibre is one of the most important natural fibre which provide a wide range of applications in textile materials because of its easy availability, low density, light weight, low cost, and above all environment friendly characteristics [1,2]. It can easily be transformed into multifarious products affecting every phases of our daily life

because of its wide spread applications. But the major problem of cotton products is hydrophilicity and moisture sensitivity in nature which limits an extended use of cotton as well as other fibres [3]. These properties affect the stability of cotton goods. Many physicochemical modifications have already been done to overcome these properties such as alkaline treatment, acetylation, benzylation, acrylation, oxidation and isocyanation of the natural fibre [4]. Therefore, chemical modification through condensation polymerization of silane-coupling agents onto cotton fibres has been receiving considerable interest in recent years. The modified cotton fibre by silane coupling agents exhibits versatile physico-chemical properties include improved tensile strength, elasticity, swelling properties, wrinkle recovery properties, colour fastness and thermal stability properties etc [5].

The present study investigates the chemical modification of cotton fibres treated with two organosilane coupling agents, such as vinyltriethoxysilane (VTES) and 3-Glycidoxy-propyl-triethoxysilane (GPTES), in an ethanol/ water system. The effect of various grafting parameters and chemical structure of organosilane on the grafting quantity and treated fibres were characterized using experimental techniques such as Scanning electron microscopy (SEM), Thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) and Energy disperse X-ray analysis (EDX). The moisture absorption & swelling behavior and tensile strength were also studied for physical characteristics of modified cotton fibre.

EXPERIMENTAL

Materials

Cotton fibres were collected from Keya spinning mills Ltd., Bangladesh. Ethanol, sodium carbonate and acetic acid were purchased from Merck Germany. The silane coupling agents vinyltrimethoxy silane (VTES) and 3-glycidoxy-propyltriethoxysilane (GPTES) was collected from Aldrich, USA. All other reagent and solvents were commercial products of high purity.

Methods

Washing of Cotton Fibre

The fibres were at first washed thoroughly with 0.2% Na₂CO₃ solution at 75 °C for 30 min in the ratio of 1: 50 [6].

Silane Treatment

The pretreated fibres (washed) were dipped in alcohol-water mixture (60:40 v/v) containing VTES and GPTES for 1h. The pH of the solution was maintained between 3.5 to 4 by using 0.2M acetic acid [7]. The treated fibres were washed with distilled water and subsequently dried in hot air at 60°C. The swelling behavior, moisture sorption, thermal properties and chemical resistance behavior of the silane treated fibres were studied.

Evaluation of Physical and Chemical properties

Chemical Resistant

The chemical resistant of the silane-treated fibre was studied as a function of percent weight loss of fibre when treated with different chemicals. A known amount of untreated and silane treated fibre was dipped in 1N 100 ml solution of hydrochloric acid and 1N 100 ml solution of sodium hydroxide of for a time interval (12-48 h) and percent chemical resistance was calculated using the following formula [6].

$$\text{Chemical resistant, \%} = \frac{W_i - W_f}{W_i} \times 100$$

Where W_i and W_f indicates the initial and final weight of the fibres respectively.

Moisture Absorption

The moisture absorption of the VTES and GPTES treated fibres as well as untreated fibres were performed at a constant humidity level. The treated and untreated samples of cotton fibres were dried at 60°C in a oven until a constant weight was obtained. The percent moisture absorption was studied as a function of weight gain and was calculated using the following formula [6].

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

Where W_i and W_f are the weight of the dried samples and the final weight of the sample taken out from the humidity chamber.

Swelling Behavior

Swelling behavior of the modified (treated) and unmodified (untreated) cotton fibres were determined by treating with water, methanol, and carbon tetrachloride. The VTES and GPTES treated and untreated samples were immersed in 100 mL of solvent 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 W_f was measured. The percent swelling was calculated [6] as:

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

Where W_i and W_f are indicate the initial and final weight of the fibres respectively.

Characterization of Untreated and Silane Treated Cotton Fibre

Infrared Spectroscopy

FTIR spectra of the silane treated and untreated fibres were recorded with KBr pellets on shimadzu IR-8900 spectrophotometer (Shimadzu Kyoto Japan) between 4000 and 400 cm⁻¹.

Thermal Analysis

The experiments were performed using a Seiko-Extar-TG/DTA-6300 (Seiko, Japan). The tests were conducted between 25-600°C under an inert atmosphere (argon). The heating rate and the air flow rate were 10°C/min and 200 mL/min.

Scanning Electron Microscopy and Energy Disperse X-ray Analysis

Scanning electron microscopy (SEM) and Energy disperse X-ray (EDX) analysis were performed using a scanning electron microscope (FEI Quanta Inspect, Model: S50, Kyoto Japan) to observe the micro structure, the surface morphology and elemental analysis of the treated and untreated fibres. The fibres surface was coated with thin film of carbon to render them conductive [8].

RESULTS AND DISCUSSION

The percent graft yield was increased with an increase of silane concentration upto 400% for VTES and GPTES on the basis of fibre and then it decreased. This gradual increase in weight gain was due to the cross-linking reaction between the –OH groups of cellulose and the –OH groups of the silane coupling agents at higher concentrations. The increase in weight gain was also related to the increasing rate of diffusion of monomer into the fibre structure, which produced a higher graft yield as well. The decrease in graft yield can be explained by the increase of homopolymer formation at higher monomer concentrations [5]. The rate of conversion of VTES

and GPTES containing ethoxy groups into reactive hydroxyl group by hydrolysis of silane is directly related to the ethanol/water ratio, pH value and reaction temperature. At 60:40 ratio of ethanol/water, the maximum amount of silane coupling agents was hydrolyzed because of insolubility of silane coupling agents in water. The formation of silanol was enhanced by the protonation of ethoxy ($-\text{OCH}_2\text{CH}_3$) groups in acidic pH value and that was 3.5 for both VTES and GPTES respectively. At pH value lower than 3.5, the formation of silanol group was insufficient [9]. As increase of temperature decreased the activation energy of the reactant and increase the molecular collision between the reactant molecules. The graft yield increased with the increase of reaction temperature upto 35°C and 30°C for VTES and GPTES respectively [10].

FTIR Analysis

FTIR spectra of untreated, VTES and GPTES modified cotton fibres are shown in **Fig. 1(a-c)** respectively. The spectra of the modified cotton fibre are more or less similar to the untreated cotton fibre, except the peaks at 761 cm^{-1} and 1280 cm^{-1} for Si-O-Si and Si-O-C bond for VTES modified cotton fibres and at 860 cm^{-1} and 1207 cm^{-1} for Si-OH and Si-O- CH_3 [11] for GPTES modified fibres. The peaks are indicated by arrow in the spectra, which confirmed the presence of silicon containing species on the modified cellulosic fibre.

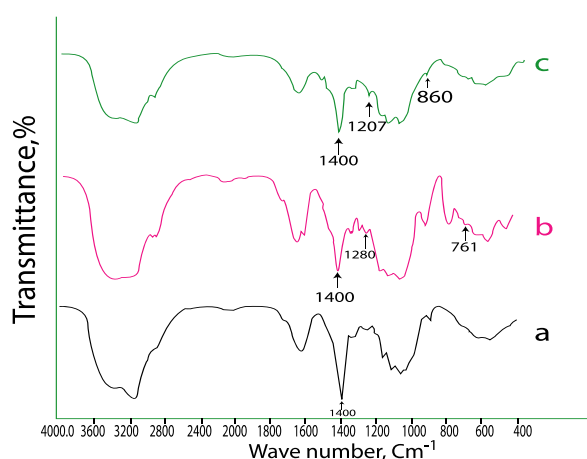


Fig. 1. FTIR spectra of (a) untreated cotton, (b) VTES treated and (c) GPTES treated cotton fibres.

Surface Morphology

Fig. 2(a-c), shows the SEM micrograph of untreated, VTES and GPTES modified cotton fibres respectively. The untreated cotton fibre shows the presence of the large amount of micro pores on its surface. After VTES and GPTES treatment, the cotton fibre surfaces are coated with an outer layer of silane monomer [12] which represents in the **Fig. 2(b)** and **Fig. 2(c)** by black colored circle. The

rupture surface of the modified fibre indicates the excess deposition of the silane layer on the fibre hair present in the cotton fibre.

Elementary Analysis

Fig. 3, 4 and 5 represent the EDX analyses of untreated cotton, VTES and GPTES treated cotton fibres. From EDX analysis, it can be observed that the untreated cotton fibre has no silicon atom, but after modification with VTES and GPTES, the presence of Si atom has been observed. The presence of tetravalent silicon on the functionalized cotton fibres ensure the presence of inorganic moiety with silicon atoms.

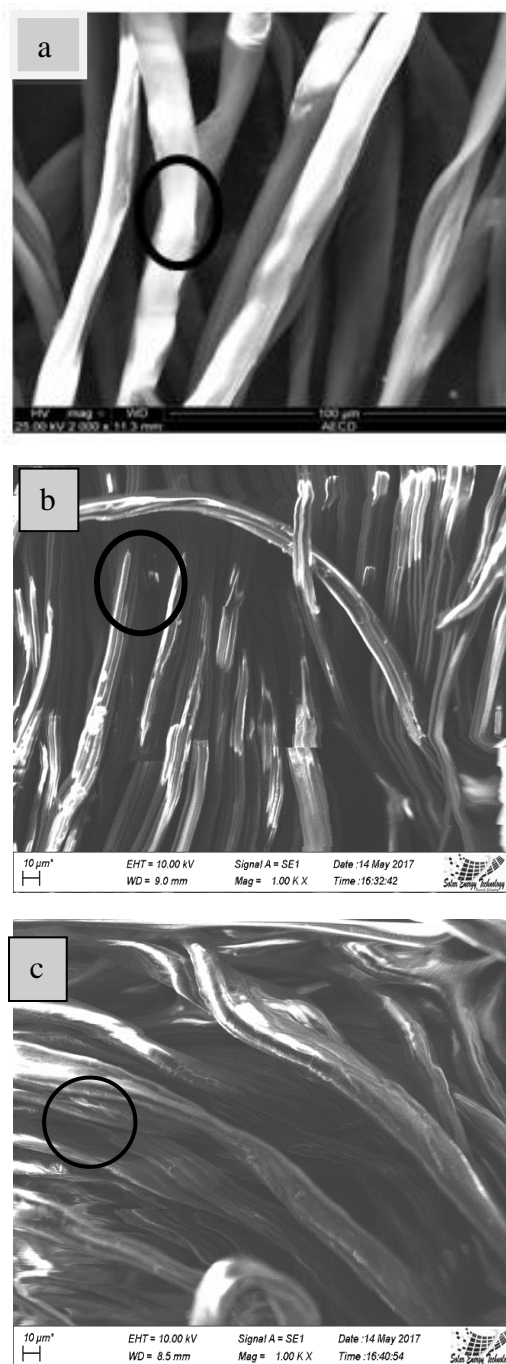


Fig. 2. SEM of (a) untreated cotton, (b) VTES treated and (c) GPTES treated cotton fibres.

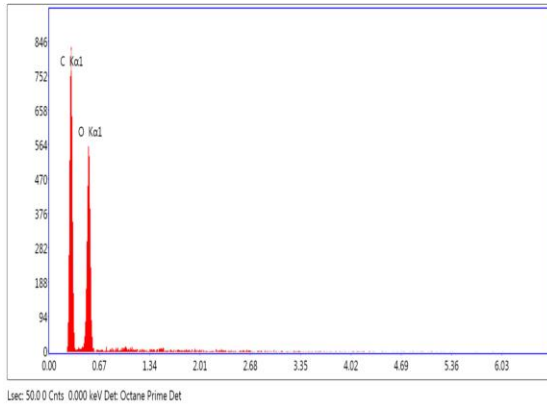


Fig. 3. EDAX of washed cotton fibre.

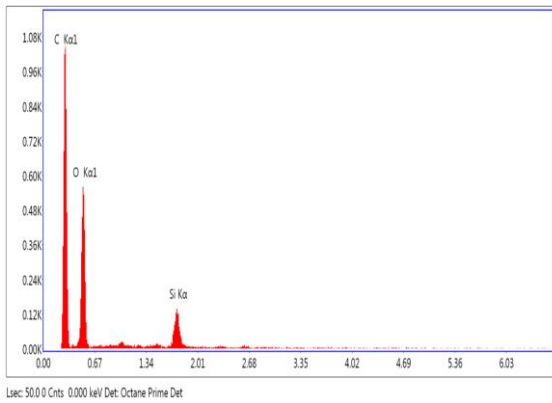


Fig. 4. EDAX of VTES modified cotton fibre.

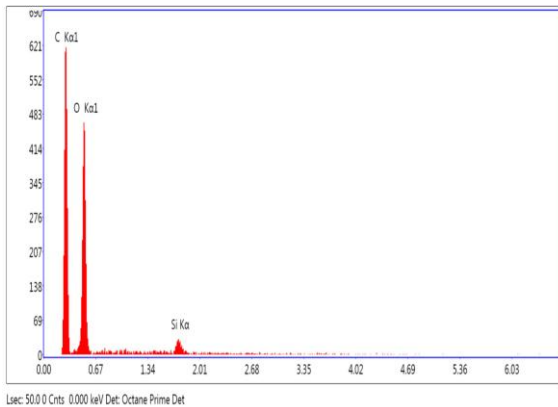


Fig. 5. EDAX of GPTES modified cotton fibre.

Thermal Analysis

Thermal behavior of untreated, VTES and GPTES modified cotton fibres were examined by a study of TGA thermogram which is shown in **Fig. 6(a-c)**. Each of the figures represent two thermogram curves namely TGA and DTG. The actual pyrolysis region of unmodified cotton fibre is 321 °C to 369.7 °C and that for the VTES and GPTES modified cotton fibres are 333.9°C to 372.4°C and 304°C to 350°C respectively and the corresponding weight loss

is about 60.0%, 52.0% and 49.4% respectively. From the DTG curve, the rate of decomposition of untreated cotton fibre is higher than that of VTES and GPTES modified cotton fibres. So it can be seen that the thermal stability of silane modified fibres increased, compared to unmodified fibre. This may have happened due to the incorporation of silane monomers with the fibre [5].

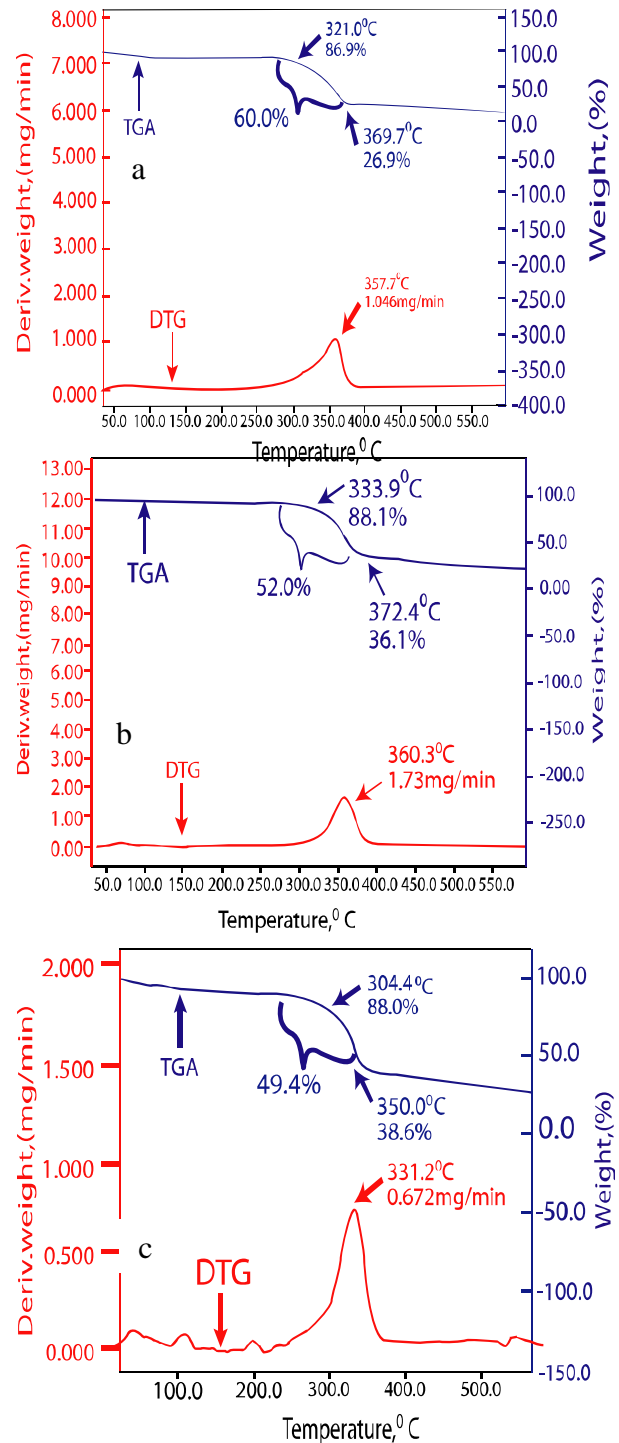


Fig. 6. TGA and DTG of (a) Untreated, (b) VTES and (c) GPTES modified cotton fibres.

Physical Properties of Untreated and Silane Modified Cotton Fibres

Table 1 shows the swelling behavior, tensile strength and moisture absorption of untreated, VTES and GPTES modified cotton fibres. Swelling ability reflects the relationship between void structures in polymer backbone and nature of solvents [13,14]. The untreated cotton fibres exhibit maximum swelling with polar solvents like water and methanol and 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 where as increase in the nonpolar solvent because of decreasing the hydrophilic character of untreated cotton fibre. The tensile strength of modified cotton fibre was higher than that of untreated cotton fibre and these are due to the modification of cotton fibre with VTES and GPTES (ISO 5081-1977 (E)) [15]. The wrinkle recovery angle of modified cotton fabric was higher than that of unmodified cotton fabric for warp and weft direction respectively. Because, the presence of Si-O bond in the functionalized fabric shows high flexibility that recover the wrinkle which exerted on the fabric surface by loading [16]. The moisture absorption sites are blocked after incorporation of silane chain through surface modification by showing the less affinity for moisture than the original fibre.

Table 1. Swelling behavior, tensile strength and moisture absorption properties of untreated and modified cotton fibres

Fibre type	Swelling behaviour %			Tensile strength		Moisture absorption %
	H_2O	CH_3OH	CCl_4	Breaking load, Kg/yarn	Elongation %	
Untreated cotton	273	142	11	2.40	2.00	6.66
VTES modified cotton	140	92	35	3.10	2.80	3.15
GPTES modified cotton	130	84	25	3.85	3.21	5.12

CONCLUSION

Chemical modification of cotton fibres with silane coupling agents was investigated. Maximum weight gain percent 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 group of cotton fibres were evaluated by FTIR and EDX analysis. The modified fibres showed improved physico-chemical properties such as tensile

properties, moisture absorption, elongation at break and thermal stability properties than that of the unmodified cotton fibres. 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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