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Functionalization of Cotton Fabric with Vinyltrimethoxysilane

Abstract The surface of cotton fabric was successfully functionalized with vinyltrimethoxysilane in order to impart water repellency and wrinkle recovery and to introduce surface vinyl groups ($-\text{CH}=\text{CH}_2$) to the fabric, which could then be initiated for copolymerization reactions with various monomers. The introduction of active groups onto the fabric surface was evidenced from the universal attenuated total reflectance Fourier transform infrared (UATR-FTIR) spectrum of the treated fabric. The spectrum shows two peaks located at 1410 and 1600 cm^{-1} ($\text{C}=\text{C}$ stretch). An additional peak located at 756 cm^{-1} attributed to $\text{Si}-\text{O}-\text{Si}$ symmetric stretch was also observed. Excellent water contact angle and wrinkle recovery angle values were obtained.

Key words functionalization of polymers, wrinkles, surface modification, fabrics/fibers

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Textile surface modification provides a way to impart new and diverse properties to textiles while retaining comfort and mechanical strength. Chemical compounds containing silicon-oxygen bonds (such as polydimethylsiloxane) are used in the textile industry as finishing agents: antistatic, antisoil and anticrease [1]. The presence of siloxane bonds ($\text{Si}-\text{O}$) imparts interesting properties such as improved thermal stability, resistance to oxidation, retention of physical properties over a wide range of temperatures, water repellency and active surface properties, owing to the high flexibility of the $\text{Si}-\text{O}$ bond [1].

Surface engineering of materials can be achieved by chemically bonding functional polymer chains onto a substrate [2]. Free-radical surface graft polymerization has emerged as a simple method for establishing covalent bonds between the polymer and a substrate. In our previous work, we exposed a cotton fabric to microwave plasma to create radicals within the cellulose backbone, which were used to initiate copolymerization reactions with a vinyl laurate monomer ($\text{CH}_3-(\text{CH}_2)_{10}-\text{COO}-\text{CH}=\text{CH}_2$) [3]. This process imparted a hydrophobic character to lightweight cotton fabrics. The efficiency of grafting and the presence of grafted monomers on the fabric surface were confirmed using the universal attenuated total reflectance Fourier transform infrared (UATR-FTIR) spectrum. The grafting

process did not show any detrimental effect on the physical properties of the cotton fabrics. In addition, the grafted fabrics showed very good durability to repeated home launderings [4].

Another method for surface grafting consists of introducing active sites onto the surface by means of organosilane coupling agents [2, 5–7]. Previously, this concept was used to graft vinyl acetate onto silica [2], which consisted of surface activation with vinyltrimethoxysilane (VTMS), followed by free-radical graft polymerization of vinyl acetate in ethyl acetate with 2,2'-azobis(2,4-dimethylpentanenitrile) as the initiator.

In this paper, we report on the surface functionalization of cotton fabric with VTMS ($\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_3)_3$). The objective of this functionalization is to impart water repellency and wrinkle recovery properties and to introduce active vinyl groups ($-\text{HC}=\text{CH}_2$) onto the cellulose macromolecules that could potentially be initiated with microwave plasma for copolymerization reactions with different monomers for diverse applications.

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Experimental Details

Materials

Desized, scoured and bleached 100% cotton fabric was used in this study. Its construction was 65 ends, 79 picks, with a yarn count of 25.7×26.8 tex (23×22 English count) and its weight was 162.0 g m^{-2} (4.8 oz yd^{-2}). VTMS 97% ($\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_3)_3$) was purchased from Sigma-Aldrich Co. (Milwaukee, WI) and was used as received.

Fabric Functionalization with VTMS

Cotton fabric surface functionalization with VTMS was carried out in an aqueous environment. Varying amounts of the precursor $\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_3)_3$ (from 0.197 to 4.913 mol l^{-1}) was added drop-wise to distilled water containing four drops of concentrated hydrochloric acid. The pH of the solution was around 3.5. After complete addition of the VTMS, the solution was stirred for 10 min. The obtained solution was clear and homogenous.

Cotton fabric samples were dipped into this solution, soaked for 5 min and passed through a two-roller laboratory padder (BTM-6-20-190) at a speed of 4 yd min^{-1} and an air pressure of $2.76 \times 10^5 \text{ Pa}$. The padded fabrics were then dried at 100°C for 4 min by passing them through a Ben Dry-Cure Thermosol Oven to evaporate water and then cured in the same oven at 150°C for 4 min. The samples were thoroughly rinsed under running water, dried and conditioned at $65 \pm 2\%$ relative humidity and $21 \pm 1^\circ\text{C}$ for at least 48 h before performing analyses. The amount of VTMS cross-linked to cellulose macromolecules was determined and expressed as the percent weight increase (weight increase % = $((m - m_0)/m_0) \times 100$, where m_0 is the initial weight of the conditioned fabric and m is the weight of the treated fabric after rinsing, drying and conditioning). Three replications were performed from each concentration of VTMS.

Surface Hydrophobicity

The efficiency of the treatment to impart a hydrophobic character to the fabric surface was evaluated by measuring the water contact angle using a sessile drop method with a Rame-Hart goniometer (model #100-00). The goniometer has an illuminating backlight source and an eyepiece to observe the droplet. The droplet of water is dispensed using a syringe assembly onto a three-axis stage. The three-phase contact angle was measured by placing a single drop of HPLC-grade water onto the cotton fabric and aligning a tangent at the point of contact of the air-liquid-solid interface. The average contact angle was obtained by measuring the angles on the left- and right-hand sides of each droplet and taking the average of three droplets on different regions of the fabric sample.

Wrinkle Recovery Angle Measurement

The wrinkle recovery angle was measured according to the AATCC Test Method 66 [8, p. 95]. The wrinkle recovery of a fabric is defined as the ability of the fabric to resist the formation of wrinkles when subjected to a folding deformation. In this test, a specimen is folded and compressed under controlled conditions of time and force to create a folded wrinkle. The test specimen is then suspended in a test instrument for a controlled recovery period, after which the recovery angle is recorded (the higher the angle, the better the recovery from the deformation). Four specimens per sample for both the warp and fill directions were tested and the wrinkle recovery angle results were reported in degrees as the sum of both warp and fill directions.

Evidence of Fabric Functionalization and Grafting

We used a Spectrum-One spectrometer (Perkin-Elmer, Norwalk, CT) equipped with a UATR-FTIR accessory to acquire the Fourier transform infrared (FT-IR) spectra of the control and the fabrics functionalized with VTMS [3, 4, 9]. The fabrics were placed on top of the ZnSe-Diamond crystal and pressure was applied to ensure good contact with the incident infrared (IR) beam and prevent loss of the IR radiation. The pressure applied was kept constant for all samples. A background scan of clean ZnSe-Diamond crystal was acquired before acquiring the spectra of the sample. The FT-IR spectra were collected using 32 scans with 4 cm^{-1} spectral resolution between 650 and 4000 cm^{-1} . Six FT-IR spectra were acquired from each specimen. Perkin-Elmer software was used to perform automatic baseline correction, normalization and peak integration.

Statistical Analysis

The statistical analysis was performed using the STATISTICA software package (StatSoft Inc., Tulsa, OK).

Results and Discussion

Figure 1 shows the UATR-FTIR spectra of the control fabric and the fabric functionalized with VTMS. The UATR-FTIR spectrum of pure VTMS liquid is shown in Figure 2. The presence of additional peaks located at 1600 and 1410 cm^{-1} are evidence of the cross-linking of VTMS with the cellulose OH groups. The peaks located at 1600 and 1410 cm^{-1} are characteristics of the C=C bonds from the vinyl group of the VTMS [2]. An additional peak is also observed at 762 cm^{-1} and is attributed to Si-O-Si symmetric stretch [10].

Figure 1 UATR-FTIR spectra of the control fabric and the fabric functionalized with VTMS.

Figure 2 UATR-FTIR spectrum of VTMS.

Figure 3 shows the schematic of a possible mechanism of the reaction between VTMS and cellulose macromolecules. In acidic aqueous solution, the methoxy groups ($\text{Si}-\text{O}-\text{CH}_3$) could undergo hydrolysis reactions as shown in A and B in Figure 3 [11, 12]. Silanol groups could react with the hydroxyl groups ($-\text{OH}$) of the cellulose macromolecules ($\beta(1-4)\text{D}$ -anhydroglucopyranose), leading to the formation of a silylated cotton fabric surface (see C in Figure 3) [11, 12]. This process allows the functionalization

of the cotton fabric surface by introducing several vinyl groups ($-\text{CH}=\text{CH}_2$). These vinyl groups could then be used as anchoring sites for monomers that could be grafted onto the surface via microwave plasma-radical graft copolymerization. In addition to the hydrolysis process, polycondensation reactions could occur between $\text{Si}-\text{OH}$ groups (see D in Figure 3) leading to the formation of a polysilane network. Owing to its size, this polysilane network would probably not travel between the cellulosic chains and estab-

Figure 3 The functionalization mechanism of the surface of the cotton fabric with $(\text{CH}_3)_3\text{Si}-\text{CH}=\text{CH}_2$

Table 1 Variance analysis: the effect of VTMS concentration on the percent weight increase.

Parameter	df ^a	F ^b	Probability	Weight increase (%) ^c
Intercept	1	55002.95	0.000001	
$[(\text{CH}_3\text{-O})_3\text{Si-CH=CH}_2]$ (mol l ⁻¹)	8	2124.86	0.000001	
0.197				0.25 i
0.655				2.35 h
1.114				5.33 g
1.638				7.40 f
2.293				8.56 e
2.948				9.79 d
3.603				10.60 c
4.258				12.86 b
4.913				14.77 a
Error	18			

^a Degrees of freedom.^b Variance ratio.^c Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to the Newman-Keuls test).

lish cross-links. It would react preferably with the surface OH groups of the cellulose (see E in Figure 3) [12]. This occurs when the concentration of the VTMS increases, as explained later.

The statistical analysis of the results showed the significant effect of the VTMS concentration on the percent weight increase (Table 1). Figure 4 shows the relationship between the amount of VTMS cross-linked to the cotton fabric (percent weight increase) and the VTMS concentration in the solution: $\text{weight increase \%} = 0.013 + 4.371 \times [(\text{CH}_3\text{-O})_3\text{Si-CH=CH}_2] - 0.308 \times [(\text{CH}_3\text{-O})_3\text{Si-CH=CH}_2]^2$, adjusted $R^2 = 0.967$, $F(2,6) = 118.222$, $p < 0.001$, standard error of estimate = 0.8596. The non-linear relationship is attributed to the unavailability of cellulosic OH groups for cross-linking with the OH groups of the VTMS at higher concentrations (the saturation phenomenon). Figures 5(a) and (b) show the relationships between the integrated intensities of the peaks located at 1600, 1410 and 762 cm⁻¹ and the VTMS concentration in the solution. The statistical analysis showed the significant effect of the VTMS concentration on the peak intensities (for 1600 cm⁻¹, degrees of freedom (df) = 8, F -value = 50.065, p -value = 0.000001; for 1410 cm⁻¹, df = 8, F -value = 52.025, p -value = 0.000001; for 762 cm⁻¹, df = 8, F -value = 58.300, p -value = 0.000001). The FT-IR results indicate that the integrated intensities I_{1600} , I_{1410} and I_{762} reached a plateau around 1.6 mol l⁻¹ and no further increase was observed. However, the percent weight increase showed that the saturation phenomenon occurs at higher concentrations of VTMS

Figure 4 Percent weight increase versus VTMS concentration (dashed curves represent confidence limits).

(above 5 mol l⁻¹). This discrepancy could be attributed to the fact that the number of VTMS molecules establishing covalent cross-links between cellulose macromolecules may not be evaluated correctly because UATR-FTIR only measures the surface. At lower concentrations, VTMS molecules react with the surface OH groups first. When

(a)

(b)

Figure 5 (a) Integrated intensities of the peaks located at 1600 and 1410 cm⁻¹ versus VTMS concentration. (b) Integrated intensity of the peak located at 762 cm⁻¹ versus VTMS concentration.

the concentration increases, VTMS molecules gain access to the internal surface and establish cross-links between cellulose macromolecules as depicted in C of Figure 3. This cross-linkage replaces the hydrogen bonds between cellulose macromolecules with covalent bonds. Therefore, the cellulosic chain slippage that normally occurs in untreated cotton fabric, when subjected to a deformation, is prevented. Consequently, functionalized cotton fabric could have wrinkle-resistant properties. Figure 6 shows the evolution of the wrinkle recovery angle with increasing VTMS concentration. The statistical analysis showed the

Figure 6 Wrinkle recovery angle versus VTMS concentration.

significant effect of the increase in VTMS concentration on the wrinkle recovery angle (Table 2). The treatment of the cotton fabric with a solution containing 3.603 mol l⁻¹ of VTMS increased the wrinkle recovery angle by 80%. This means that the tendency of the functionalized cotton fabric to recover from a deformation is higher than for the untreated fabric, thus producing a wrinkle-free fabric. There is a slight decrease in the wrinkle recovery angle when the VTMS concentration is higher than 3.603 mol l⁻¹. A possible explanation of this behavior is that at higher VTMS concentrations, the formation of polysilane networks (polycondensation of more than two VTMS molecules) results in larger molecules that cannot travel between cellulosic chains and establish covalent cross-links. Therefore, cellulose chain slippage could still occur because of the presence of hydrogen bonding (see E in Figure 3).

To assess the hydrophobicity of the VTMS-functionalized cotton fabric surface, we measured the water contact angles. The coefficient of variation (CV%) for contact angle measurements was between 2.6% and 4.5%. The statistical analysis showed the significant effect of the VTMS concentration on the water contact angle (Table 3). The untreated bleached cotton fabric surface was hydrophilic (contact angle of 0°). At low VTMS concentrations (below 1.114 mol l⁻¹), the treated fabric remained hydrophilic. An increase in the VTMS concentration above this value leads to a significant increase in the contact angle and the cotton fabric surface becomes hydrophobic (Figure 7). This result suggests that when the VTMS concentration is above 1.114 mol l⁻¹, the VTMS-functionalized cotton surface becomes densely populated with ≡Si-CH=CH₂ chains that isolate the native cellulose surface from contacting

Table 2 Variance analysis: the effect of VTMS concentration on the wrinkle recovery angle.

Parameter	df ^a	F ^b	Probability	Wrinkle recovery angle (degrees) ^c
Intercept	1	12006.81	0.000001	
$[(\text{CH}_3\text{-O})_3\text{Si-CH=CH}_2]$ (mol l ⁻¹)	9	56.07	0.000001	
0				145.1 e
0.197				150.5 e
0.655				161.0 e
1.114				186.3 d
1.638				204.1 c
2.293				246.0 a
2.948				252.6 a
3.603				260.7 a
4.258				247.8 a
4.913				222.2 b
Error	29			

^a Degrees of freedom.^b Variance ratio.^c Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to the Newman-Keuls test).**Table 3** Variance analysis: the effect of VTMS concentration on the water contact angle.

Parameter	df ^a	F ^b	Probability	Water contact angle (degrees) ^c
Intercept	1	96845.97	0.000001	
$[(\text{CH}_3\text{-O})_3\text{Si-CH=CH}_2]$ (mol l ⁻¹)	7	4695.74	0.000001	
0.197				0 e
0.655				0 e
1.114				103 d
1.638				104 d
2.293				112 c
3.603				113 c
4.258				118 b
4.913				125 a
Error	136			

^a Degrees of freedom.^b Variance ratio.^c Values not followed by the same letter are significantly different with $\alpha = 5\%$ (according to the Newman-Keuls test).

water or other fluids. There is a slight linear increase in the water contact angle between 1.114 and 4.913 mol l⁻¹.

The functionalization of the cotton fabric surface with VTMS is of particular interest because it allows several vinyl

groups ($-\text{CH=CH}_2$) to be introduced into the cellulose macromolecules, which could then be easily initiated for copolymerization reactions with various monomers using, for example, microwave plasma. Depending on the mono-

Figure 7 Water contact angle versus VTMS concentration.

mer grafted onto the VTMS-functionalized surface, new properties could be imparted to the cotton fabric. To assess the feasibility of this concept, functionalized cotton fabric with VTMS ($[(\text{CH}_3\text{-O})_3\text{Si-CH=CH}_2] = 2.948 \text{ mol l}^{-1}$) was exposed to a microwave Ar-plasma for 240 s. This leads to the conversion of vinyl groups into radicals. These radicals are then used to initiate copolymerization reactions with various monomers. The results of this study will be reported in a future publication.

Conclusions

In this study we investigated the functionalization of the cotton fabric surface with VTMS. The presence of VTMS

on the surface of the cotton fabric was evident from the presence of additional peaks attributed to the vinyl groups and Si-O-Si belonging to VTMS molecules. Excellent surface hydrophobicity and wrinkle-recovery properties were obtained.

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