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Surface modification of cellulose with plant triglycerides for hydrophobicity

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Abstract Hydrophobic cotton was achieved by surface modification of the cellulose with triglycerides from several plant oils including soybean, rapeseed, olive and coconut oils. These oils were delivered to the cellulose substrates in homogeneous solutions of ethanol or acetone as well as aqueous emulsions. Surface modification was facilitated by solvent evaporation followed by heating between 110 and 120 °C for 60 min. All oils, except for coconut, produced hydrophobic and less water-absorbing cotton, supporting the desirable role of higher unsaturation in the fatty acids to achieve crosslinked network. The most hydrophobic surfaces were obtained by the reaction with 1% soybean oil in acetone. On both bleached and scoured cotton, a water contact angle of 80° and water absorption value of 0.82 μL/mg were achieved. The acquired hydrophobicity was not only retained after water washing but also improved with subsequent exposures to elevated temperatures. The surface tension of scoured cotton cellulose was lowered from 63.81 mJ/m^2 to 25.74 mJ/m^2 when modified by soybean oil delivered in acetone, which is lower than that of poly(ethylene terephthalate). An aqueous emulsion of soybean oil also rendered the scoured cotton hydrophobic, which shows promise for a green chemistry and bio-based approach to achieve water repellency on cellulosic materials.

Keywords Cellulose · Cotton · Plant oils · Surface modification · Triglycerides · Hydrophobicity · Bio-based water repellency

Introduction

Hydrophobic cellulosic fabrics are in great demand in a wide variety of functional applications including water repellent outdoors gear, rainwear, stain resistant products, and bandages. Ideal water repellent cotton fabrics are hydrophobic on the fiber surfaces to resist water, yet porous to allow moisture transport for comfort. Efforts to reduce the hydrophilicity of cotton have involved surface modification using hydrophobic compounds, such as fluorocarbons (Jiang et al. 2005; McCord et al. 2003; Sato et al. 1994), silicones (Lee et al. 2005; Yuen et al. 2005) and hydrocarbons (Sawatari et al. 1998). These technologies have varying effectiveness and durability in achieving water repellent cotton fabrics although are limited by their sustainability and environmental concerns and cost. Finding more ecologically sustainable alternatives to current practice is urgently needed.

The esterification of cellulose is a well established technology that generates some of the most common commodity thermoplastics, e.g., cellulose acetate. Much of current interest in esterifying cellulose with

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fatty acid derivatives focuses on generating high degree of substitution for their thermoplastic properties (Heinze and Liebert 2001; Vaca-Garcia et al. 2003). The reactivity of cellulose hydroxyl groups with fatty acids is generally low and can be improved by converting the carboxylic acids to the more reactive moieties, such as tosyl chloride (Shimizu and Hayashi 1989) or mesyl chloride (Talaba et al. 1996). Without these moieties, the esterification of cellulose with fatty acids results in a low degree of substitution of the cellulose hydroxyl groups (DS < 0.3), such as hydrophobic cellulose powder (Peydecastaing et al. 2005) and hydrophobic cotton for improved oil absorbency (Deschamps et al. 2003).

The goal of this study is to generate water repellent cotton, by investigating the reactions of cellulose with vegetable oils for producing hydrophobic surfaces. Vegetable oils are abundant and renewable sources of triglycerides that have been mainly used in food applications, with only approximately 14% utilized by the oleochemical industry (Gunstone and Hamilton 2001). Extending their use in rendering cellulose fibers hydrophobic is a high value-added application and an excellent green alternative to current hydrocarbon based technologies.

Vegetable oil triglycerides contain three acyl chains of varying lengths and degrees of saturation attached to a glycerol backbone. Complete covering the surfaces of cellulose solids with the hydrophobic triglycerides should lead to hydrophobic cellulose, but without permanency. To achieve resilient hydrophobic surfaces, covalent bonded structures are most desirable. Transesterification reaction between triglycerides and cellulose hydroxyls forms the covalent bonded hydrophobic long acyl chains to the cotton cellulose. This reaction would lead to cellulosic fibers with hydrophobic surfaces with extended coverage of the acyl chains from the fatty acids (Fig. 1). The unsaturated fatty acyl chains offer further opportunities to form covalent bonded network by crosslinking reactions. The unsaturation levels in the fatty acyl chains may also affect surface coverage by altering the orientation of the acyl chains along the surface of the fiber in addition to crosslinking among the acyl chains.

In this study, soybean, rapeseed, olive, and coconut oils were chosen to represent the widest range of fatty acid compositions, from the most highly polyunsaturated soybean oil to the monounsaturated olive oil (Table 1). The spreading of the vegetable oils on cellulose surfaces critical to maximize a uniform coverage was compared among homogenous solutions of the oils in either acetone or ethanol. Optimization of the reaction between the triglycerides and cellulose was approached by studying the effects of delivery media, heating, oil concentrations and post-reaction rinses on the wetting and absorption properties of the modified cotton cellulose. Structural characterization was further aided by FTIR and DSC. Durability of the acquired hydrophobicity was evaluated by simulated washing experiments. The delivery of oils in aqueous emulsions with a surfactant was also explored because of its importance as a green chemistry method of achieving water repellent cotton.

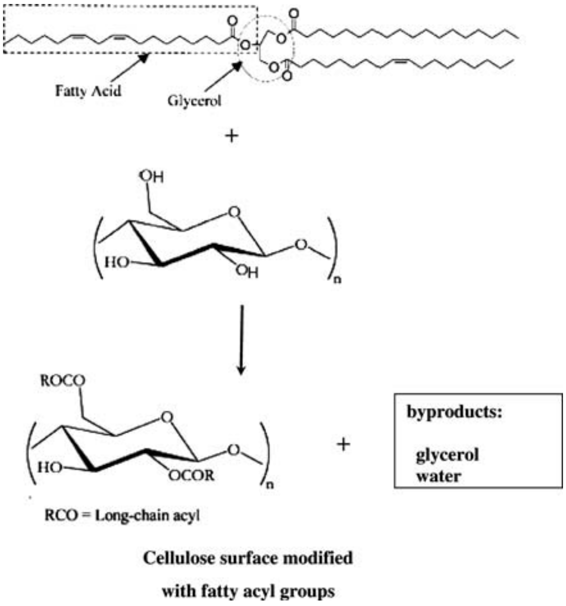

Fig. 1 Transesterification reaction between cellulose and triglycerides

Materials and methods

Cellulose materials

Four types of cellulosic materials: commercially bleached cotton, laboratory scoured cotton, microcrystalline cellulose powder, and cellulosic filter paper were used. Plain weave bleached cotton

Table 1 Vegetable oil fatty acid compositions & production percentages[a]

Vegetable oil	Global production[b] (%)	Unsat'd/Sat'd ratio	Total unsat'd (%)	Saturated				Monounsaturated			Polyunsaturated	
				Lauric 12:0	Myristic 14:0	Palmitic 16:0	Stearic 18:0	Oleic 18:1	Gondoic 20:1	Erucic 22:1	Linoleic 18:2n6	α-Linoleic 18:3n3
Rapeseed[c]	12.6	15.7	94	–	–	4	2	62	–	–	22	10
Rapeseed[d]	12.6	24	96	–	–	3	1	16	6	50	14	10
Flaxseed	0.7	9	90	–	–	3	7	21	–	–	16	53
Sunflower	9.1	7.3	88	–	–	7	5	19	<0.5	–	68	1
Corn	1.9	6.7	87	–	–	11	2	28	–	–	58	1
Soybean	23.1	5.7	85	–	–	11	4	24	<0.4	–	54	7
Olive	2.5	4.6	82	–	–	13	3	71	–	–	10	1
Palm Kernal	18.7	0.2	17	48	16	8	3	15	–	–	2	–
Coconut	3	0.1	8	47	18	9	3	6	–	–	2	–

Source: [a]http://www.iseo.org

[b] Gunstone and Hamilton (2001)

[c] Low erucic

[d] High erucic

(#400) and raw cotton fabrics (#400R) were supplied by Test Fabric, Inc. Microcrystalline cellulose powder (20 micron) was supplied by Sigma-Aldrich. Cellulosic filter paper was supplied by Whatman, Inc. (Q3). Raw cotton fabric was scoured in a 4% NaOH solution at a 150:1 liquid (mL) to cotton (g) ratio at a boil for 60 min, under a nitrogen blanket. The fabrics were then rinsed with fresh hot water baths for 30 min followed by several room temperature water baths for 30 min until neutrality was reached.

Vegetable oils and chemicals

Four vegetable oils, i.e. coconut oil (MP Biomedicals, Inc.), olive oil (Acros Organics), rapeseed oil (MP Biomedicials, Inc.), soybean oil (Fisher Scientific), and fatty acids, i.e. stearic acid (Acros), were used without further purification. Acetone, ethanol, dioxane, Triton X-100, pyridine, and *N*,*N*-dimethylformamide were obtained from EMD chemicals. Decane, hexadecane, ethylene glycol, and formamide were supplied by Fisher Scientific. Diiodomethane (Acros Organics) and dimethyl sulfoxide (Sigma-Aldrich) were also used. AATCC Standard Reference detergent (without brightening agents) from 1993 was provided by AATCC. For all treatments, and measurements millipore water (Mill-Q System) was used.

Oil application

Oils were delivered either in homogeneous solutions or emulsion to the cellulose materials a drop wise manner. To saturate the cellulose materials, excess oil solutions were applied with twice the mass of oil solution to the cellulose mass. Homogeneous oil solutions were prepared using either ethanol or acetone as the solvents at varying concentrations. Aqueous emulsions were prepared with addition of a non-ionic surfactant Triton X-100 at selected concentrations. Following oil applications, all samples were air dried, then heated at 110 °C for 60 min, except for those used to study the heating effects. Removal of excess and unreacted oil and byproducts were attempted by immersion in copious amount of acetone or ethanol, and in some cases also water, for 5 min three times, each time in a fresh batch of solvent. Samples were dried under the ambient environment and conditioned at 65% R.H. and 20 °C for 48 h prior to characterization. Unless otherwise noted, the numbers of measurements per sample were three.

Liquid wetting and absorption

Liquid wetting and retention properties of fibrous samples were measured using a previously reported method using a Kruss tensiometer K100 (Hsieh 1995).

Samples were cut to 25.4 mm by 9.8 mm with a die and weighed. The samples were held vertically with the lower edge in contact to the surface of Millipore water (Mill-Q Water System) to allow wetting and wicking. Following water wetting, samples were allowed to dry (21 °C and 65% RH) for 48 h, and then measured in a total wetting liquid, hexadecane (hexa).

In general for any solvent, the difference in steady state force (ΔB_{st}) and the wetting force (W_f) of the wetting liquid, the fabric wetting force can be determined:

$$F_W = (\Delta B_{st} - W_f)g \tag{1}$$

where g is the gravitational acceleration constant. The fabric wetting force in hexadecane is used to calculate the fabric-liquid perimeter (p):

$$p = \frac{F_{W(\text{hexa})}}{\gamma_{\text{hexa}} \times \cos(\theta)} \tag{2}$$

where γ_{hexa} is the surface tension of hexadecane, and $\cos\theta$ is assumed to be 1 (due to total wetting for hexadecane). Equation 2 is modified to find the water wetting contact angle (θ) as:

$$\theta = \cos^{-1}\left(\frac{F_{W(\text{water})}}{p\gamma_{\text{water}}}\right) \tag{3}$$

where γ_{water} is the surface tension of water. The vertical liquid retention capacity (also called pore volume) (H,μL/mg) measured in hexadecane and the water retention (W, μL/mg) were expressed as:

$$H = \frac{W_{f(\text{hexa})}}{\rho \times m_{\text{fabric}}} \tag{4}$$

$$W = \frac{W_{f(\text{water})}}{\rho \times m_{\text{fabric}}} \tag{5}$$

where ρ is the solvent density and m is the fabric mass. Last, the ratio of water retention relative to the total liquid retention capacity of the fabric, or W/H ratio was reported.

Surface tension

Eleven solvents were used to determine the surface tension properties of cotton fabric. Based on surface tension, vapor pressure, density, and viscosity, dispersive solvents including decane, hexadecane, dioxane, pyridine, and diiodomethane and polar solvents including ethanol, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethylene glycol, formamide, and water were selected.

The wetting force for fabric samples was determined in each of the solvents mentioned above to the same procedure described earlier (Eq. 1). From the wetting force, the (cos θ) was determined by modifying Eq. 2:

$$\cos(\theta) = \left(\frac{Fw}{p * \gamma_{\text{lv}}}\right) \tag{6}$$

where γ_{lv} is the surface tension of the liquid (in mJ/m^2) and p is the fabric-liquid perimeter (in cm). The perimeter values were average values obtained through hexadecane measurements in the water wetting analyses from Eq. 2.

From the contact angles, the work of adhesion (W) can be calculated by the following equation:

$$W = \gamma_{\text{lv}}(1 + \cos\theta) \tag{7}$$

The work of adhesion value is used as an index of wetting ability of a liquid for a solid.

Geometric mean method divides surface energy into two components: polar and dispersive (Fowkes et al. 1990; Kwok et al. 1994; Owens and Wendt 1969). Therefore the surface energy can be expressed by the following equation:

$$\gamma_{\text{s}} = \gamma^{\text{d}} + \gamma^{\text{p}} \tag{8}$$

where γ^{d} is the dispersive component and γ^{p} is the polar component of the surface tension. The geometric mean is used to combine their contributions, in the following equation:

$$W = 2\left[(\gamma_l^{\text{p}}\gamma_{\text{s}}^{\text{p}})^{1/2} + (\gamma_l^{\text{d}}\gamma_{\text{s}}^{\text{d}})^{1/2}\right] \tag{9}$$

Using the work of adhesion results (calculated from contact angle in Eq. 7) of polar and dispersive liquid pairs, the specific values for the dispersive and polar components of the surface tension of the solid can be determined. However, different liquid pairs will give different results, and it should be noted which probe liquids' work of adhesion values are being used in the analysis. Water and diiodomethane were used for the geometric means method.

Characterization

FTIR spectra were obtained at 4-cm^{-1} resolution and 64 scans per sample on a Nicolet 6700 FTIR spectrometer using the KBr method. The percent transmittance of the IR band was defined as the peak height from the baseline of the band. Thermal properties were evaluated by a differential scanning calorimeter (DSC-60, Shimadzu, Japan) at a 10 °C/min heating rate from 30 °C to 400 °C.

To test for washing durability of the surface modification, either heating and detergent was applied by stirring the 17 g samples in 200 mL of water for 45 min. Both ambient and elevated temperatures as well as the 1993 AATCC standard reference detergent (without fluorescent whitening agent) were included.

Results and discussion

Surface modification of bleached cotton with stearic acid

Surface modification of cotton cellulose was studied first using a fatty acid, i.e., stearic acid. The commercially bleached cotton samples were saturated with stearic acid solutions in either acetone or ethanol (at concentrations ranging from 0.98–2.86 w/w%), air dried, heated at 105 °C for 45 min, then rinsed with respective solvent. The bleached cotton as received showed a water contact angle (WCA) of 40.6° and absorbed 1.97 μL/mg water. The controls which were rinsed in either ethanol or acetone and heated at 120 °C for 60 min became slightly more hydrophilic with WCAs of 27.1° and 26.2° WCA, respectively (Table 2). The slightly improved hydrophilicity is consistent with the expectation that these solvents remove residual waxes and hydrophobic compounds that commercial bleaching process did not. A 4% mass loss was observed with ethanol rinse, higher than the negligible 0.4% from the acetone rinse, which is indicative of ethanol being more effective in dissolving residual compounds. The pore volume both controls decreased slightly, from 1.90 uL/mg to 1.76 uL/mg, indicative of the compaction of fibers and yarns most likely from heating.

Stearic acid delivered in either solvent caused mass gains on cotton, significantly higher from ethanol (up to 16%) than from the acetone (less than 6%) (Table 2). The greater and concentration-dependent mass gains indicate more effective and significant deposition of stearic acid from the ethanol solutions. While the WCAs for those treated with stearic acid in acetone increased from 28° to 40°, those treated with ethanol solutions was slightly less hydrophobic, i.e., WCA increased from 24° to 34°. Water absorption also slightly decreased, but not consistently. The slightly increased surface hydrophobicity confirms the low level of esterification between the carboxylic acid and cellulose hydroxyls under these conditions. Therefore, vegetable oil triglycerides were used for their potential to form bonded structures on cellulose surfaces via transeferification as well as crosslinking reactions.

Surface modification with soybean oil on bleached cotton: heating conditions

The first triglyceride investigated was soybean oil which was delivered to bleached cotton in either ethanol at 4.76% or acetone at 1%. The temperature and length of heating were varied to determine the most favorable conditions to achieve hydrophobic surfaces. All heating conditions studied resulted in increased hydrophobicity on the bleached cotton, but to different extents, with WCA ranging from 43° to 75° (Fig. 2a). The most hydrophobic ones were achieved at temperatures between 110 and 120 °C for 60 min, in either solvent (Fig. 2a). Likewise, the water absorption was reduced from 1.90 to 0.41 μL/mg, with the lowest observed under the same condition that produced the most hydrophobic cotton (Fig. 2b). With prolonged heating over 60 min, WCA decreased and water absorbency increased slightly for both solvents, possibly due to the oxidization of unsaturated groups in the soybean oil. The pore volume was not affected by soybean oil delivered in acetone solutions, but was reduced by up to 10% from those in ethanol (Fig. 2c). These data are consistent with the different extents of mass gains between these two solution series. In the case of

Table 2 Water wetting contact angle (θ), water absorption (W) and pore volume (H) of bleached cotton saturated with stearic acid in ethanol or acetone solution, heated at 105 °C for 45 min then rinsed with respective solvent[a]

Stearic acid (w/w%)	Mass (%)	H (μL/mg)	θ (deg)	W (μL/mg)
None	0	1.90 (0.19)	40.6 (2.9)	1.97 (0.28)
Acetone				
0%[b]	−0.4 (1.8)	1.76 (0.03)	26.2 (11.2)	1.81 (0.04)
0.98%	1.3 (0.7)	2.00 (0.05)	37.2 (2.9)	2.00 (0.12)
1.96%	−7.0 (1.9)	1.94 (0.10)	40.3 (3.7)	1.59 (0.04)
Ethanol				
0%[b]	−4.1 (1.6)	1.76 (0.01)	27.1 (9.5)	1.79 (0.05)
1.43%	8.4 (5.5)	n/a	24.9 (0.2)	1.84 (0.01)
2.86%	9.3 (7.7)	n/a	33.3 (5.0)	1.80 (0.03)
2.86% (applied twice)	16.2 (5.1)	n/a	29.7 (10.6)	1.75 (0.05)

[a] Standard deviation in parentheses

[b] Solvent rinsed and heated at 120 °C for 60 min

ethanol solutions, decreasing interstice spaces with concentrations confirm higher surface deposition. Overall, for both solvent delivery systems, the optimal heating condition was 110–120 °C for 60 min.

Surface modification with vegetable oils in ethanol: post-ethanol rinse

Three unsaturated vegetable oils: soybean, olive, and rapeseed, were delivered to bleached cotton cellulose in ethanol solutions. The oils were dissolved in ethanol at 70 °C and applied to fabric at room temperature. At a 20%, all three unsaturated vegetable oils significantly improved the surface hydrophobicity of the bleached cotton fabrics (Table 3). The bleach cotton treated with rapeseed oil was the most hydrophobic, with a WCA of 60° (up from 17.1°) and water absorption of 0.33 μL/mg (down from 1.79 μL/mg). The pore volume of all oil treated fabrics was also lowered by 34% to 40%, which is consistent with excessive vegetable oil deposition on the fabrics, or 28% to 56% mass gain. In that regard, the coconut oil treated cotton had the least reduction in pore volume consistent with the lowest mass gain.

To remove excess unreacted oils, glycerol, and other reaction by-products, the oil treated samples were rinsed in ethanol following heating. The ethanol rinse lowered the mass gains by about 16–17% for the soybean and rapeseed oil treated fabrics, but did not affect those treated with olive and coconut oils, the two with the highest monounsaturated and saturated fatty acids, respectively. In any case, a significant mass gain of greater than 30% was still observed for all oil treated fabrics. The eventual substantial mass gains following ethanol rinses suggest inter-mingled triglycerides or fatty acid chains, some aided by crosslinking, forming thick coating layers on the fabric surfaces as well as physical impregnation of vegetable oils into fiber pores.

Following the ethanol rinse, the WCAs increased for cotton treated with all except for coconut oil, with both olive and rapeseed oils showing the highest values around 72°. The water absorption values also decreased for those treated with olive and rapeseed oils to 0.42 μL/mg and 0.28 μL/mg, respectively, while staying fairly constant for the other two oils (Table 3). For all except olive oil, the ethanol rinse also resulted in increased liquid retention capacity, nearly 50% increase with soybean oil and about 15% with rapeseed and coconut oils. This is consistent with the mass loss and removal of the residual oils and byproducts that filled the inter-fiber and inter-yarn pores in the fabrics.

These results show that all oils except coconut have promise for producing hydrophobic and less water-absorbent cotton, confirming that higher unsaturation in the fatty acids are more desirable. Therefore, coconut oil was excluded from further study. The substantially reduced pore volumes also suggest the need to reduce the oil deposition by using substantially lowered oil concentrations. Although the higher

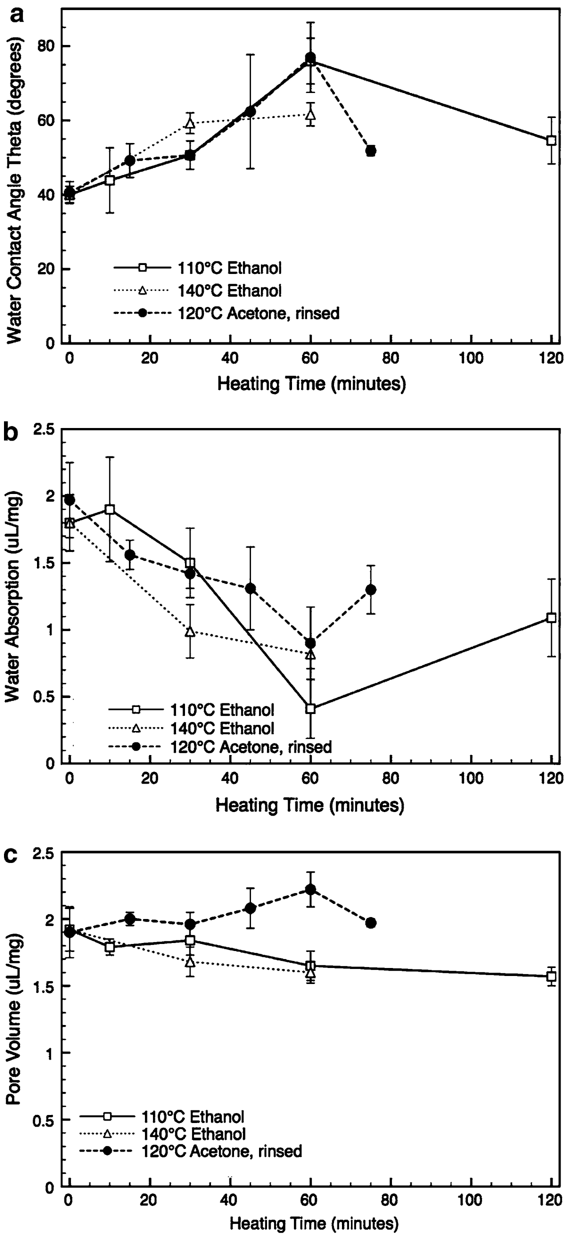

Fig. 2 Effects of heating conditions on (**a**) water wettability, (**b**) water absorption and (**c**) pore volume of soybean oil (4.76% in ethanol and 1% in acetone) treated bleached cotton fabrics

oil deposition via ethanol solutions suggests ethanol to be a better wetting liquid for cotton, dissolution of these oils in ethanol required heating at 70 °C. All subsequent applications were conducted in acetone in which these oils had far better solubility (exceed 50%) at ambient temperature.

Surface modification with vegetable oils in acetone: varied concentrations

Soybean, olive, and rapeseed oils were applied to the bleached cotton fabrics in acetone solutions at concentrations up to 10%. The most hydrophobic cotton was achieved with soybean oil at 1%, yielding a very high water contact angle of 81.0° and low water absorption of 0.82 μL/mg (Fig. 3). The slightly reduced liquid retention capacity of 1.62 μL/mg indicated little change in fabric pore structure with these oil treatments. Soybean oil imposed similar effects on the scoured and bleached cotton in terms of wettability and pore volume, but resulted in slightly lower water absorption on the scoured cotton. Therefore, the subsequent analyses were mostly conducted using soybean oil treatments on either bleached or scoured cotton fabric.

The most hydrophobic cotton resulted from soybean oil application is likely due to its high polyunsaturated fatty acid content, comparing to either rapeseed or olive oil. Although rapeseed and olive oils are highly unsaturated oils, most of their fatty acids are monounsaturated and have more flexible chains than the polyunsaturated ones. Not only the polyunsaturated fatty acids have higher capacity to crosslink into hydrophobic networks, their more compact structure can also lower water access through the surface, such as in the case with soybean oil treated cotton.

The soybean oil treated cotton fabrics gained only 2.4% mass, lower than those treated with other oils. The ability to attain hydrophobicity at low mass gains of vegetable oils is highly desirable, but not completely unexpected. Native cotton fibers, which are hydrophobic, contain only up to 0.6–1.2% by weight of wax (Freytag et al. 1983). Also, low degrees of substitution of 0.41–1.06 on cellulose with saturated fatty acids with 8–18 carbon chain lengths resulted in water contact angles between 79° and 89° (Vaca-Garcia et al. 1998). Therefore, a highly hydrophobic surface could be achieved with a low degree of surface modification.

The FT-IR spectra of 1% soybean oil treated cotton showed a very small peak at 1,746 cm^{-1}, corresponding to the ester carbonyl (Fig. 4a). The weak intensity of this peak is expected from the surface nature and the overall low extent of this reaction. In other surface esterified cellulose,

Table 3 Water wetting contact angle (θ), water absorption (W) and pore volume (H) of bleached cotton treated with vegetable oils (in ethanol solutions, heated at 110 °C for 60 min. and rinsed with ethanol)[a]

Concentration v/v %	Mass gain (%)	θ	W µL/mg	H µL/mg
None, Ethanol rinsed	−4.1 (1.6)	27.1 (9.5)	1.79 (0.05)	1.76 (0.01)
Soybean oil				
20	48.1 (9.2)	50.2 (3.2)	0.72 (0.07)	1.04 (0.06)
20[b]	32.0 (5.3)	59.3 (3.1)	0.84 (0.08)	1.53 (0.09)
Olive oil				
20	56.4 (12.0)	51.5 (3.1)	0.79 (0.07)	1.11 (0.12)
20[b]	59.4 (6.7)	72.6 (17.0)	0.42 (0.20)	1.08 (0.12)
Rapeseed oil				
20	47.8 (10.1)	60.1 (1.9)	0.33 (0.08)	1.15 (0.08)
20[b]	30.8 (9.1)	72.1 (5.6)	0.28 (0.19)	1.31 (0.16)
Coconut oil				
20	28.7 (6.0)	47.4 (2.8)	1.06 (0.11)	1.50 (0.05)
20[b]	28.7 (8.3)	49.6 (2.6)	1.39 (0.04)	1.66 (0.10)

[a] Standard deviation in parentheses

[b] Rinsed in ethanol after heating

similarly low carbonyl peak intensities were reported (Baiardo et al. 2002). The scoured cotton showed a decomposition endotherm at 364 °C which was preceded by a small endotherm at 324 °C. The 1% soybean oil treated cotton showed a slightly raised decomposition temperature (369 °C) (Fig. 4b).

Soybean, rapeseed and olive oils were also applied to microcrystalline cellulose (MC) that had a higher specific surface. All three oil treated MC cellulose showed similar ester carbonyl at 1,746 cm^{-1}, with only that from olive oil slightly higher in intensity that the soybean oil modified cotton (Fig. 5a). Although the oils were applied at a much higher 10% concentration on the higher specific surface MC cellulose, the weak carbonyl peaks still emerged, indicating the removal of most residual oils. However, it cannot rule out the possibility that some triglycerides may be imbedded or trapped among the fully or partially transesterified layer on either cotton or MC cellulose.

Microcrystalline cellulose showed a decomposition endotherm at 344 °C, preceded by an exotherm at 320 °C (Fig. 5b). The lower decomposition peak than cotton cellulose is likely due to their particulated crystalline structures versus the fibrilliar ones in cotton cellulose. The thermograms of both olive and soybean oils showed base line shifts at the corresponding smoke point temperatures. The cellulose decomposition peak was raised by 9 °C when reacted with soybean oil and an even higher 14 °C with olive oil. The exotherm in microcrystalline cellulose disappears with both oil treatments. The olive oil treated cellulose has a sloped region preceding the endotherm at 358 °C, which parallels that in olive oil. This parallel slope may indicate incomplete reactions, where a diglceride or triglyceride is grafted on to the cellulose surface, or physical adsorption of vegetable oil to the cellulosic surface. Cellulose grafted with methacrylates and acrylates have also shown higher cellulose decomposition temperatures that increased with greater grafting percentages (Shukla et al. 1992; Princi et al. 2005).

Surface modification with vegetable oils in aqueous oil emulsions

The aqueous emulsions of soybean oil from 0.1% to 8% concentrations were prepared with the aid of 0.4% Triton X-100. The application of soybean emulsions was made on laboratory-scoured cotton which was more uniformly hydrophilic due to more thorough removal of the non-cellulosic materials. The scoured cotton had a 39° WCA, 2.01 µL/mg water absorption and a pore volume of 2.30 µL/mg. The cotton became hydrophobic with the 1% soybean emulsions, with a WCA of 58° and slightly lowered water absorption of 1.59 µL/mg, and no change in pore volume (Fig. 6a). These wetting and absorbent behaviors were independent of oil concentrations at up to 8%.

The soybean oil delivered by the aqueous emulsions produced less hydrophobic surfaces than those by acetone. The possibility that adsorption of the

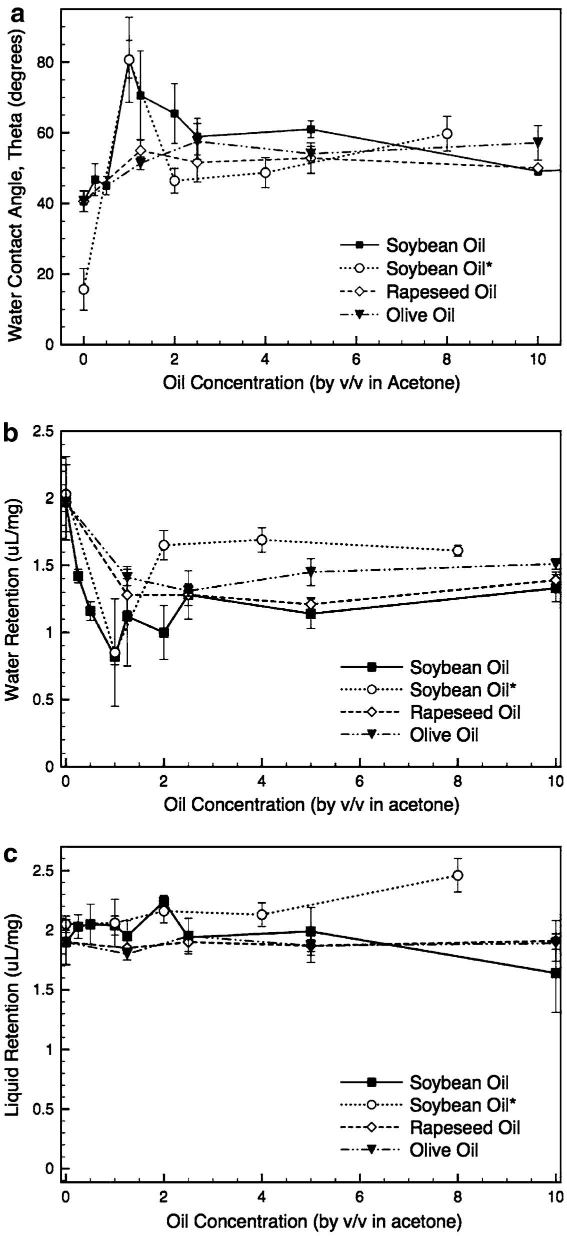

Fig. 3 Effects of soybean, rapeseed and olive oils and their concentrations delivered in acetone on (**a**) water wettability, (**b**) water absorption and (**c**) pore volume of bleached (*scoured) cotton fabrics (heated at 110 °C for 60 min then acetone rinsed three times, 5 min each)

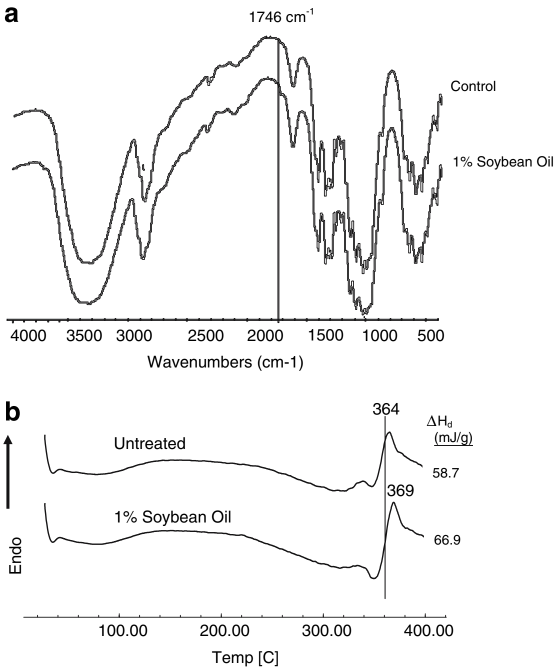

Fig. 4 (**a**) FTIR and (**b**) DSC thermograms of scoured cotton: untreated and treated with 1% soybean oil in acetone solution (heated at 110 °C for 60 min then acetone rinsed three times, 5 min each)

surfactant in the emulsions may have caused this was unlikely as an additional water rinsing did not alter the outcome (Fig. 6a). Nevertheless, the surfactant concentration was lowered. On the scoured cotton, same surface hydrophobicity was achieved at a much lower 0.05 surfactant-to-oil ratio or 0.05% concentration (Fig. 6b). On the bleached cotton, a slightly higher 0.15% Triton X concentration was required.

Aqueous emulsions of soybean oil was also applied to the MC cellulose. The FT-IR spectra (Fig. 7) showed much more pronounced carbonyl peak than that delivered in acetone (Fig. 5a) and when heated at a higher 170 °C. The aqueous deliver system raised the decomposition temperature (T_d) of MC cellulose by 21 °C (Fig. 8), significantly higher than from acetone solutions (Fig. 5b). The higher heating temperature, however, led to a lesser increase in T_d and a straight baseline similar to the soybean oil. These results indicate the products of incomplete reactions, thus reaffirm the previous conclusion on heating (Fig. 2).

Washing durability

To simulate washing, 1% soybean oil treated bleached cotton samples were stirred for 45 min in one of three scenarios: a hot water bath (120 °F), an ambient water bath (80 °F), and an ambient bath with

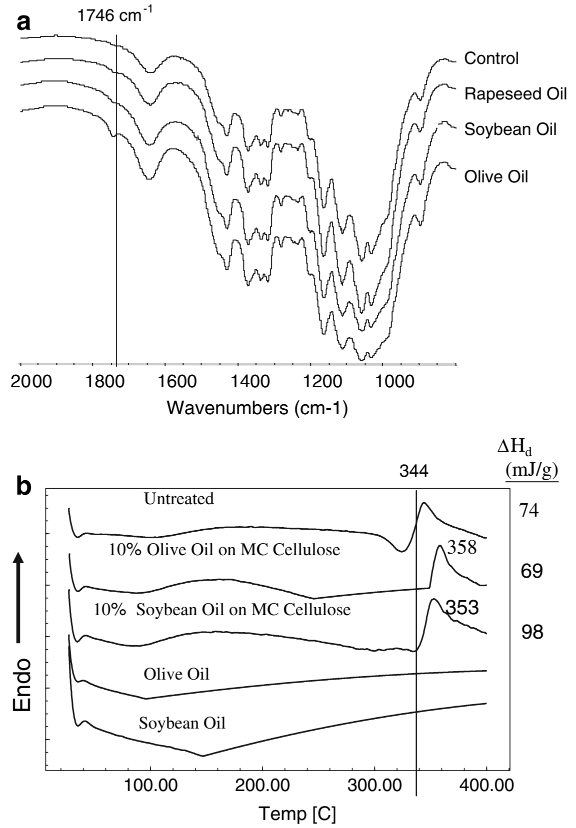

Fig. 5 (**a**) FTIR-KBr spectra and (**b**) DSC thermograms of microcrystalline cellulose: untreated and treated with 10% (in acetone) rapeseed, soybean, and olive oils (heated at 110 °C for 60 min then acetone rinsed three times, 5 min each).

0.37% AATCC detergent. Washing in water resulted in increased hydrophobicity, i.e., higher contact angles of 80° and 88° for ambient and hot water washing, respectively. However, wash with the detergent decreased contact angle to 63° (Fig. 9a). The water absorbency decreased for both the water washed samples to 0.76 μL/mg and 0.28 μL/mg for ambient water and hot water, respectively (Fig. 9b). Washing appeared to cause fiber/yarn shifting and increased the pore volume of the fabrics as indicated by the increased liquid retention values. The improved hydrophobicity for the samples in the water bath durability tests could be due to the softening of the fatty acyl groups on the cotton surface, improving the spreading of the fatty acyl groups on the fiber surfaces. The increased water absorption may be due to fibrillation of the fibers caused by the mechanical action, i.e., allow water molecules to gain surface access.

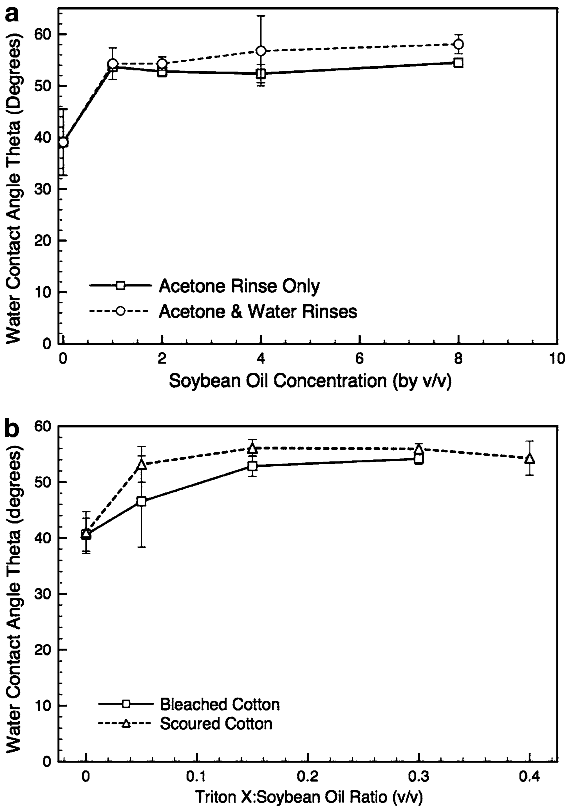

Fig. 6 Effects of aqueous emulsions of soybean oil on water wettability of scoured cotton fabrics: (**a**) at varying soybean oil concentrations (with 0.4% Triton X); (**b**) at varying Triton X concentrations (with 1% soybean oil). All samples were heated at 120 °C for 60 min then rinsed in acetone and DI water

Surface tension of fabrics

The geometric mean method was employed to derive the surface tensions of three cellulose solids and the soybean oil treated scoured cotton. The work of adhesion values from diiodomethane and water were used to derive the dispersive and polar components, respectively. The total surface energy of the solids was the summation of the polar and dispersive components (Table 4). The surface tension of the scoured cotton was slightly higher than that of the bleached cotton, consistent with the wetting behavior observed earlier. The soybean oil treated scoured cotton showed a greatly reduced overall surface energy of 25.74 mJ/m^2, compared to the 63.81 mJ/m^2 for the scoured cotton control. In comparison to other studies, the surface tension of the soybean oil

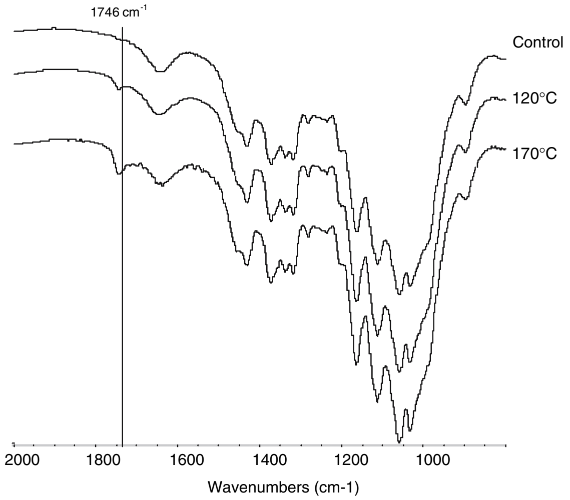

Fig. 7 FTIR-KBr spectra of microcrystalline cellulose: untreated and treated with a 10% aqueous emulsion of soybean oil in (by v/v) with 0.5% Triton X (heated for 60 min at 120 and 170 °C, and rinsed in acetone three times, 5 min each)

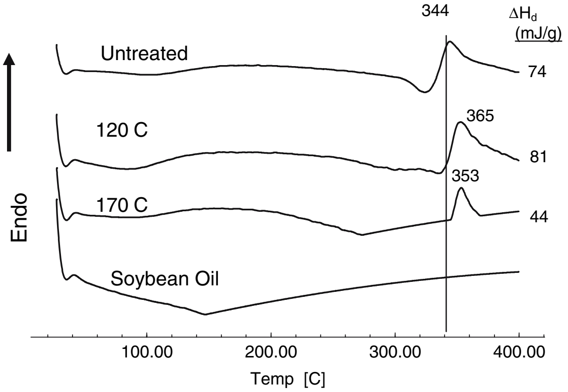

Fig. 8 DSC thermograms of microcrystalline cellulose, soybean oil and MC cellulose treated with a 10% soybean oil in aqueous emulsion with 0.5% Triton X, heated for 60 min at 120 °C and 170 °C, and rinsed in acetone three times, 5 min each

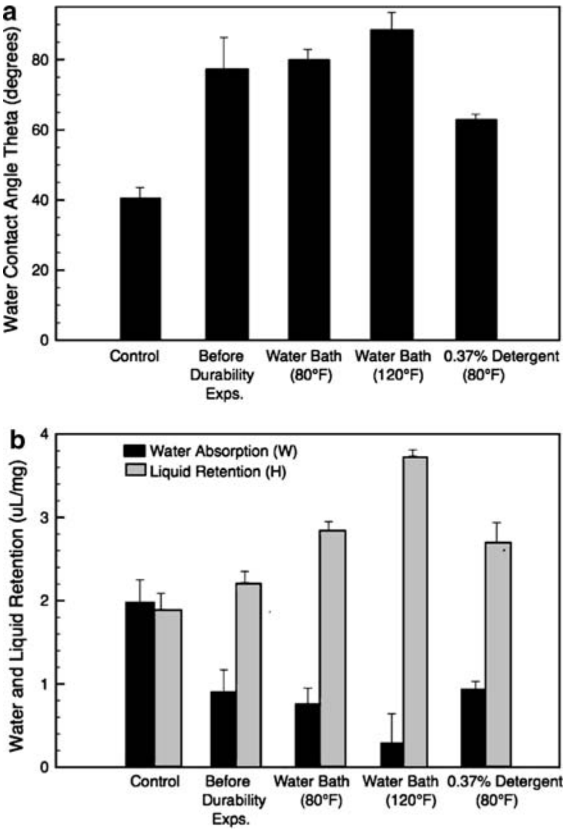

Fig. 9 Exposure to simulated washing conditions on: (**a**) water wettability and (**b**) water absorption of 1% soybean oil (in acetone) treated bleached cotton fabrics

Table 4 Geometric means method results for the surface tension of solids

Surface tension (mJ/m^2)	Bleached cotton	Scoured cotton	Soybean oil treated scoured cotton
Dispersive	36.73	42.1	22.3
Polar	24.66	21.71	3.44
Total	61.39	63.81	25.74

treated cotton is higher than fluorocarbons (~12.0 mJ/m^2) and teflon (~17.5 mJ/m^2), but lower than polyethylene terephthalate (~35.5 mJ/m^2) (Kwok et al. 1994).

Conclusion

Surface modification of cellulose with triglycerides from coconut, olive, rapeseed and soybean oils has been investigated with respect to their ability to render cotton hydrophobic. The oils were delivered by homogeneous solutions in either acetone or ethanol as well as aqueous emulsions. Heating at temperatures between 110 and 120 °C for 60 min was optimal in producing the most hydrophobic cotton cellulose. Soybean oil–acetone solutions were the most effective delivery system, out of the five oils and fatty acids and the three solutions studied.

Soybean oil delivered in 1% acetone solution, followed by heating and acetone immersions produced the most hydrophobic cotton fabric. These effects were observed on both scoured and bleached cotton through the highest water wettability (80° WCA) and lowest water absorbency (0.82 μL/mg). Soybean oil delivered by the aqueous emulsion also improved the hydrophobicity of cotton to a WCA of 58° and slightly lowered water absorption of 1.59 μL/mg, but not nearly as effective as those by homogeneous solutions. Surface modification with oils also raised the decomposition temperature and endotherm of the cellulose. A baseline similar to that of the vegetable oil emerged in some treated samples, indicative of grafting of di- and/or tri-glycerides to the surface of cellulose.

Homogeneous solutions proved to be more effective in delivering the oil triglycerides to cotton cellulose surfaces. That more hydrophobic surfaces were achieved with triglycerides having higher unsaturated fatty acyl chains supports the role of crosslinking among the long acyl chains in enhancing coverage with covalent bonded network.

Extended (45 min) washing in water at ambient (80 °F) and hot temperatures (120 °F) significantly improved the acquired hydrophobicity, i.e., WCA increased to 88.2°, and water absorption decreased to 0.28 μL/mg. The presence of detergent in the washing liquid, however, reduced the hydrophobicity, although the resulted surfaces were still more hydrophobic than the untreated control sample. Work is underway to improve the delivery of oils via aqueous emulsions and to study durability.

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