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SYNTHESIS OF HYDROPHOBIC AND OLEOPHOBIC NYLON-COTTON FABRIC THROUGH MICROWAVE CATALYZED SILANE ATTACHMENT

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Synthesis of Hydrophobic and Oleophobic Nylon–Cotton Fabric through Microwave Catalyzed Silane Attachment

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Abstract

We report a microwave induced attachment of a perfluoroalkylsilane to produce highly hydrophobic and oleophobic (H–O) nylon–cotton material. A series of experiments explored the parameters of curing intervals, curing time, base catalysis, and concentration of silane. A single microwave interval of five seconds was able to produce H–O fabric when treated with a NH_4OH catalyzed solution of 1% perfluorosilane in isopropyl alcohol. Contact angles for samples treated in a multiple dip–cure sequence averaged 148° with water and 135° with *n*-hexadecane, with no droplet absorption either within 60 hours (*n*-hexadecane) or until complete evaporation (water).

1.0 Introduction

Low-surface-energy textiles and coatings possessing exceptional properties of hydrophobicity and oleophobicity are available for a multitude of applications from water scavenging to stain repellency. One of the most-prized features of these materials is their ability to self clean.¹ On fabrics that repel contact with most liquids, droplets—as they roll off—gather particles that have settled onto materials. Several methods for forming textiles with H–O properties have been developed.^{2,3,4,5,6,7,8} Some of the more successful approaches have attempted to mimic the hydrophobic processes found in Nature, such as the water strider or lotus leaf.⁹ Droplets are energetically favored to occupy the smallest possible area on the surface, that of a sphere, unless the energy of the contact surface offers an attractive binding force for the molecules. Without such an attraction, pockets of air are maintained and the droplets bead up. The lotus leaf provides an excellent example of this phenomenon.¹⁰

A combination of surface roughness and low surface energy is characteristic of superhydrophobic materials. Contact angles of 119° are the highest obtained on smooth surfaces with minimized surface energy.¹¹ Materials with static contact angles of 150° or greater have been considered superhydrophobic^{1,12,13}, but recent research has also required low sliding angles for droplets.^{14,15} Low sliding angles are key to the self-cleaning abilities of H–O materials. Formation of micro- and nanoscale surface corrugation creates a high surface area. Substrates treated with fluorocarbon chains possess extremely low surface energy, and for this reason are

the basis for non-stick cookware. By using fluoroalkanes in conjunction with corrugated surfaces one can create highly H-O surfaces. Hoefnagels et al.¹⁶ reported the use of condensed silanes to increase nano and micro structure corrugation and thus the H-O character of cotton textiles. Work in his lab applied to a nylon 6,6–cotton weave continued exploring this phenomenon and we were able to develop a method which produces the same effect with a reduction in the amount of time to covalently bind silanes to the fabrics. Previous publications have reported advantages of using microwave radiation to react silanes with primary alcohols and amines.¹⁷

We report a facile and quick treatment process of nylon–cotton fabric to endow hydrophobic and oleophobic properties. The treatment methods correlate easily to a wide variety of textiles that have primary alcohol or primary or secondary –NH– moieties, including plain cotton, nylon, and polyaramids. Fluoroalkyl chains can be attached to the –NH– or –OH site via a siloxane or silazane linkage as shown in Figure 1. Use of heat or microwave radiation in this process greatly speeds up the attachment, as does addition of a base.

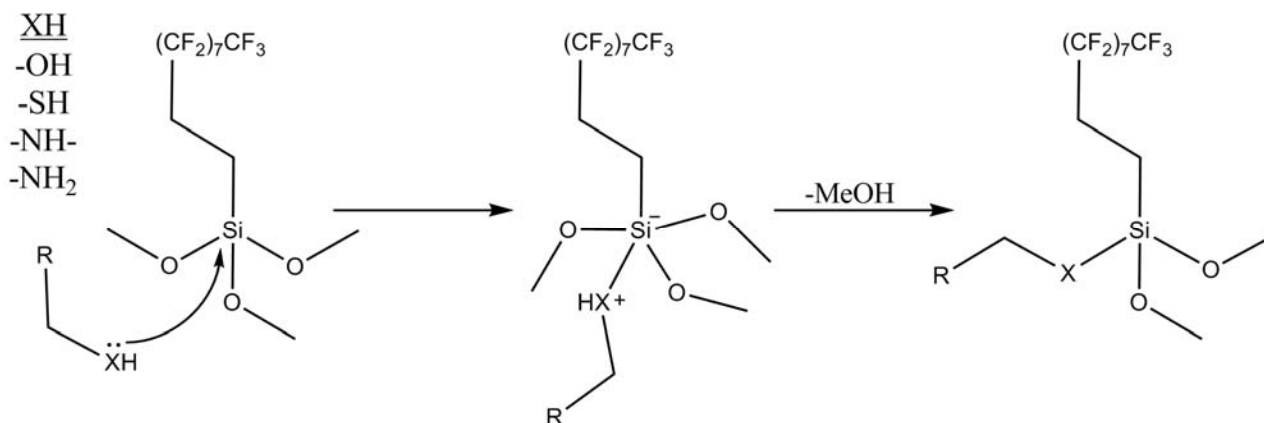


Figure 1. Reaction of an alcohol, amine, or thiol with a perfluoroalkyltriethoxysilane.

2.0 Experimental Section

2.1 Materials and Instrumentation

Swatches of 50:50 nylon 6,6–cotton (NyCo) were received from Bradford Dyeing Associates and washed in isopropyl alcohol or toluene before modification. Isopropyl alcohol (Fisher), toluene (Burdick and Jackson), and ammonium hydroxide (Mallinckrodt) were used as received. Tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS) and 3-aminopropyltriethoxysilane (APTS) were purchased from Sigma–Aldrich and used without further purification. (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (FS) was purchased from Gelest, Inc., and used as received.

Samples were cured in a Panasonic NN-SD967S microwave oven. The power output for this system is 1250 watts. Scanning electron microscope (SEM) pictures were taken on a Hitachi

S-2600N instrument. Contact angle measurements were made on a Kruss DSA 100 goniometer with tilting table.

2.2 Synthesis of FS NyCo

Experimentation began using a three pot synthesis to replicate the preparation by Hoefnagels et al.¹⁶, except that the reported technique was modified to use microwave radiation. A “pot” here represents a synthetic step that is carried out using a single reaction solution. This approach to preparation of FS NyCo is based on the Stöber method.¹⁸ Single-, two-, and three-pot syntheses were attempted with varying amounts of TEOS, APTS, and FS.

A typical treatment cycle consisted of a three-dip-three-cure process. A swatch of fabric was saturated in a solution containing 0–15% silane, lightly wrung to remove excess liquid, and microwave cured for 30 seconds at full power. This dip/cure process was performed twice more, for a total of three 30-second microwave irradiation intervals. Samples were synthesized singularly with each of the silanes, and in combination in one-, two-, and three-pot methods.

Three-pot methods started with three dip/cure steps in TEOS followed by a three dip/cure sequence in APTS and final three dip/cure cycles in FS. Two-pot methods used either TEOS, APTS, or a combination of the two in a single solution for the first dip-and-cure set of curing and FS for the final dip/cure set. The one-pot synthesis combined all reactants into a single reaction vessel. Fabrics were dipped into the reaction solution and cured by irradiation with microwaves for three-30 second intervals. All samples were washed with isopropyl alcohol and water after curing.

To investigate the effect of a base catalyst (NH_4OH), a series of NyCo, swatches were prepared as described above in the presence and absence of ammonium hydroxide. Subsequent experiments substituted toluene for isopropyl alcohol as the solvent, due to its weaker microwave absorption characteristics.

A series of samples were cured and tested to determine the effects of the length of cure time and the number of dipping and curing cycles on the hydro- and oleophobicity of samples.

2.3 Characterization

Contact angle and time-to-absorption measurements of treated fabrics were collected using 10- μL droplets of water, diiodomethane, and *n*-hexadecane. Contact angles were measured according to the Cassie–Baxter method.¹⁹ For the contact angle measurements five droplets were measured for each fabric and the range is reported. Outliers were discarded by the *Q* test based on 95% confidence.

Five time-to-absorption measurements were taken for each liquid on each fabric over a 20 minute interval. The time until the droplet was fully absorbed into the fabric was recorded and the average of the five data points is reported.

3.0 Results and Discussion

The use of alkaline materials to condense silica particles from tetraethyl orthosilicate is well characterized^{18,20}. For ease of synthesis, ammonium hydroxide was used as a substitute, although any soluble base should be an efficient catalyst. The purpose of ammonium hydroxide in this synthesis was twofold: one, to speed up the displacement of the methoxy and ethoxy substituents, and two, to facilitate the formation of the corrugated microscale structure. Base-catalyzed covalent attachment of colloidal particles that formed in solution has been shown to create a surface morphology with two distinct size surface structures. Hoefnagels et al.¹⁶ reported that the presence of this dual-sized structural morphology increased contact angles and decreases sliding angles.

Table 1 is a compilation of 30 FS-NyCo preparations under the conditions described above. Samples 5 and 6 are unfluorinated controls, pointing out the profound effect of the FS substituent on oleophobicity. Figure 2 shows graphically that increasing the content of FS used above 1% provides no increase in oleophobicity.

Results from a set of experiments to test the effect of NH_4OH catalysis and the time and mode of application of microwave power on the one-pot reaction of NyCo with FS are presented in Table 2. With NH_4OH present the contact angle for hexadecane increases slightly from 5- to 10-second cure time and remains constant thereafter. Absent NH_4OH , erratic incidence of oleophobicity occurs only after microwave irradiation for at least three 30-second intervals demonstrating the necessity for base catalysis.

Particulate condensates were observed to form on all samples prepared from irradiated TEOS or TMOS (Figure 3) regardless of the presence or absence of base; however, the attachment of condensates in solutions of FS occurred only in the presence of ammonium hydroxide. This suggests that the microwave curing regimen alone is sufficient to initiate the precipitation process within the TMOS and TEOS samples, but not the FS samples. It is surmised that the alkyl group on FS serves to stabilize the silane from methoxy/ethoxy displacement through a combination of steric hindrance and lower Lewis acidity of the silicone center. These two effects make the silicon in an alkylsiloxane much less prone to nucleophilic attack than its tetraalkoxysilane counterpart.

Additionally, samples treated with NH_4OH were significantly more H-O. Initial contact angles for base-catalyzed and uncatalyzed swatches were similar; however, uncatalyzed swatches tended to absorb the liquids over time, while swatches treated with ammonium

hydroxide repelled water droplets until the droplets fully evaporated, and repelled hexadecane for extended periods of time. This may indicate that the dual-size morphology is necessary to sustain strong repulsion of liquids over time. A two-pot synthesis with TMOS and FS in base-free conditions should add the silane particles (confirmed in Figure 3, D) and also functionalize the surface with FS. However, while this sample averaged a contact angle of 143° with water for well over 20 minutes, it only locally repelled *n*-hexadecane droplets, indicating an uneven coating. Thus, NH₄OH is necessary not only for formation of a microscale structure with FS, but also for adequate attachment of FS to the base material.

The presence of additional silanes, residues of TEOS and ATS, on perfluorosilane treated materials provided no benefit to the hydrophobicity or oleophobicity of NyCo. Hayek et al.²¹ noted that the use of silanes in conjunction with fluorochemicals can reduce the effectiveness of the treatment at repelling oils. Since the low-energy attachment described here is a silane, using TMOS or TEOS as a pretreatment to condense particles without the use of a base, and subsequently coating the fabric with FS does synthesize H–O samples; however, doing so provides no advantage over a single, base-catalyzed treatment with FS other than the ease of condensing silane particles from TEOS or TMOS using microwaves.

A three-dip treatment of NyCo in 1% perfluorosilane in isopropyl alcohol–NH₄OH cured for 30-second intervals consistently synthesized fabric swatches with an average contact angle of 147° with water and 135° with *n*-hexadecane. These swatches prevented absorption of water droplets until complete evaporation and repelled *n*-hexadecane for over 60 hours with minimal (less than 5°) loss in contact angles (not shown). Untreated fabrics were fully wetted within 10 seconds by all liquids tested. Uncured fabrics, samples 31 and 32 in Table 2, gave high initial contact angles but fully absorbed most droplets within 10 minutes and all droplets within 20 minutes.

Interestingly, the initial aqueous contact angles of all FS treated samples were very similar. FS concentration, time of curing, or number of curing intervals provided little effect on the hydrophobicity of the samples in the form of contact angle. Instead it was observed that samples with lower FS concentration, curing time, or number of curing intervals absorbed water droplets faster than some fabrics treated with increases in the above parameters. This indicates that contact angle cannot be significantly improved by any of the parameters discussed above. It also suggests that contact angle might not be the only value of choice for examining a surface for hydro- or oleophobicity.

4.0 Conclusions

A base-catalyzed method for the synthesis of H–O NyCo has been established that requires as little as 1% of a perfluorosilane and can be cured via microwaves in 5 seconds. NH₄OH as a catalyst was determined to be critical for synthesizing fabric that would repel *n*-hexadecane. Fabrics that were dipped in solutions, but not microwave cured slowly absorbed

water and readily absorbed hexadecane. Fabrics synthesized using a multiple dip-cure technique demonstrated absorption of no *n*-hexadecane, even after 60 hours. Such fabrics had an average sliding angle of 21.6° for 50-μL water droplets. A light coating of perfluoroalkylsilane appears to surround each fiber. It is this composition, as well as the inherent microstructure of the nylon-cotton weave, that allows for both superhydrophobicity and high oleophobicity. Additional silane in the form of condensed TMOS or TEOS particles had no effect on the hydrophobicity or oleophobicity of samples.

5.0 Acknowledgements

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Figures and Tables

Table 1. Static contact angles of one-, two-, and three-pot preparations of silylated 50:50 Nylon–Cotton.^a

Sample Name	Treatment Parameters				Static Contact Angle (°)	
	Number of Pots	% TEOS	% APTS	% FS	Water	Diiodomethane
1	1	-	-	1	141–158	122–136
2	1	-	-	5	143–161	126–140
3	1	-	-	10	145–154	132–137
4	1	-	-	15	146–149	129–139
5	3	10	-	-	142–149	0–0
6	3	-	10	-	140–150	0–0
7	1	1	1	1	148–153	128–137
8	1	1	1	15	144–157	126–132
9	1	1	10	1	141–148	131–134
10	1	1	10	15	145–151	129–141
11	1	20	1	1	143–156	121–131
12	1	20	1	15	140–151	131–135

13	1	20	10	1	141–152	128–134
14	1	20	10	15	143–151	124–138
15	2	1	1	1	145–150	136–140
16	2	1	1	15	144–150	130–144
17	2	1	10	1	146–157	132–140
18	2	1	10	15	144–154	124–141
19	2	20	1	1	146–155	128–139
20	2	20	1	15	149–155	127–139
21	2	20	10	1	147–162	108–136
22	2	20	10	15	143–145	131–134
23	3	1	1	1	149–152	131–138
24	3	1	1	15	150–155	128–138
25	3	1	10	1	149–153	126–131
26	3	1	10	15	145–153	126–141
27	3	20	1	1	145–151	128–135
28	3	20	1	15	144–150	123–140
29	3	20	10	1	142–154	123–134
30	3	20	10	15	143–148	124–131

^a Samples 1–30 were treated in an effort to replicate the work performed by Hoefnagels et al.¹⁶ using microwave radiation to speed up the attachment process. All samples used 5% NH_4OH solution to catalyze the reaction.

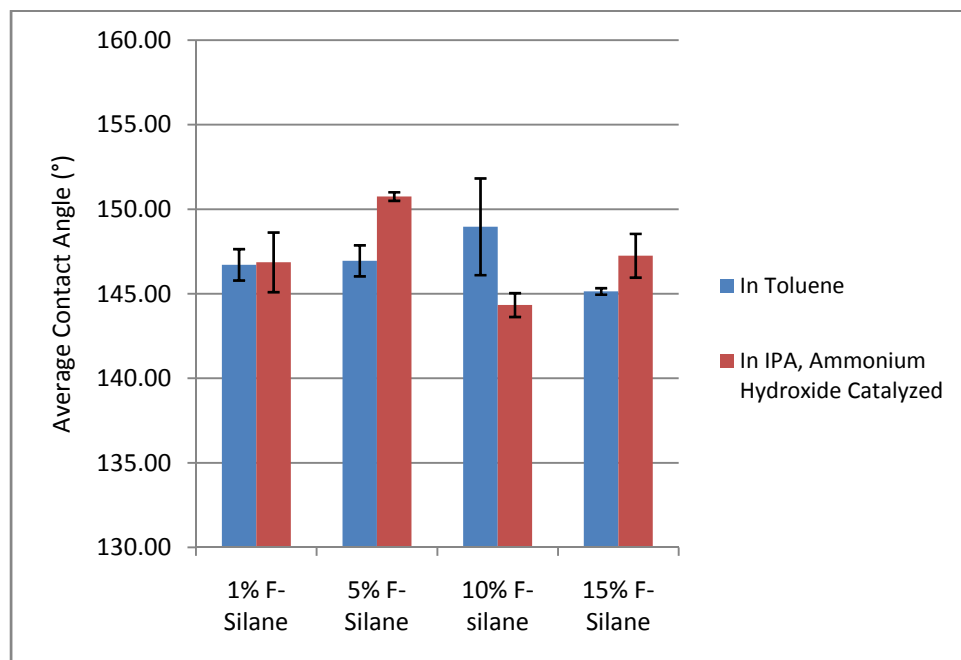


Figure 2. Dependence of aqueous contact angle on perfluorosilane concentration. Fabrics shown in Figure 2 were treated in isopropyl alcohol with 5% ammonium hydroxide solution or in toluene with no chemical catalyst. Fabrics were cured three times for 30-second intervals.

Table 2. Effect of 1% NH_4OH catalysis and curing time and treatment cycles on hydro- and oleophobicity of nylon–cotton fabric treated with a fluorosiloxane.^a

Sample	Treatment Parameters			Contact Angle (°)		Time to Absorption (sec)	
	Catalyst	Time of Cure	Number of Cures	Water	$n\text{-C}_{16}\text{H}_{34}$	Water	$n\text{-C}_{16}\text{H}_{34}$
31	NH_4OH	0	0	142–152	0–0	734	<1
32	H_2O	0	0	145–151	0–0	519	<1
33	NH_4OH	5	1	143–161	123–136	>1200	>1200
34	H_2O	5	1	140–156	0–0	125	<1
35	NH_4OH	10	1	145–149	129–141	>1200	>1200
36	H_2O	10	1	150–151	0–0	310	2
37	NH_4OH	15	1	145–151	135–137	>1200	>1200
38	H_2O	15	1	147–157	0–0	1044	3
39	NH_4OH	30	1	143–155	130–139	>1200	>1200
40	H_2O	30	1	136–160	0–0	193	<1
41	NH_4OH	45	1	142–153	126–136	>1200	>1200
42	H_2O	45	1	144–162	0–0	407	<1
43	NH_4OH	60	1	143–157	131–133	>1200	>1200
44	H_2O	60	1	145–154	0–0	865	<1
45	NH_4OH	30	1	142–161	126–141	>1200	>1200
46	H_2O	30	1	139–156	0–0	<1	<1
47	NH_4OH	30	2	143–154	133–152	>1200	>1200
48	H_2O	30	2	142–158	0–0	<1	<1
49	NH_4OH	30	3	142–158	130–156	>1200	>1200
50	H_2O	30	3	144–159	0–129 ^b	>1200	305
51	NH_4OH	30	4	146–155	131–141	>1200	>1200
52	H_2O	30	4	142–160	0–126 ^b	>1200	864
53	NH_4OH	30	5	146–152	130–140	>1200	>1200
54	H_2O	30	5	155–157	0–130 ^b	>1200	590

^a Samples were treated by dipping in a 1% v/v solution of FS in isopropyl alcohol with 1% NH_4OH , or 1% H_2O as indicated. Number of cures indicates the number of times treated (dipped and cured). Ammonium hydroxide was observed to be critical for synthesizing oleophobic swatches and increased the time to absorption of droplets.

^bSamples 50, 52, and 54 sporadically repelled *n*-hexadecane droplets. Sample 50 immediately absorbed two of five droplets; samples 52 and 54 each absorbed one of five droplets instantly. Contact angles for the other points ranged from 72°–129° (sample 50), 53°–126° (sample 52), and 80°–130° (sample 54).

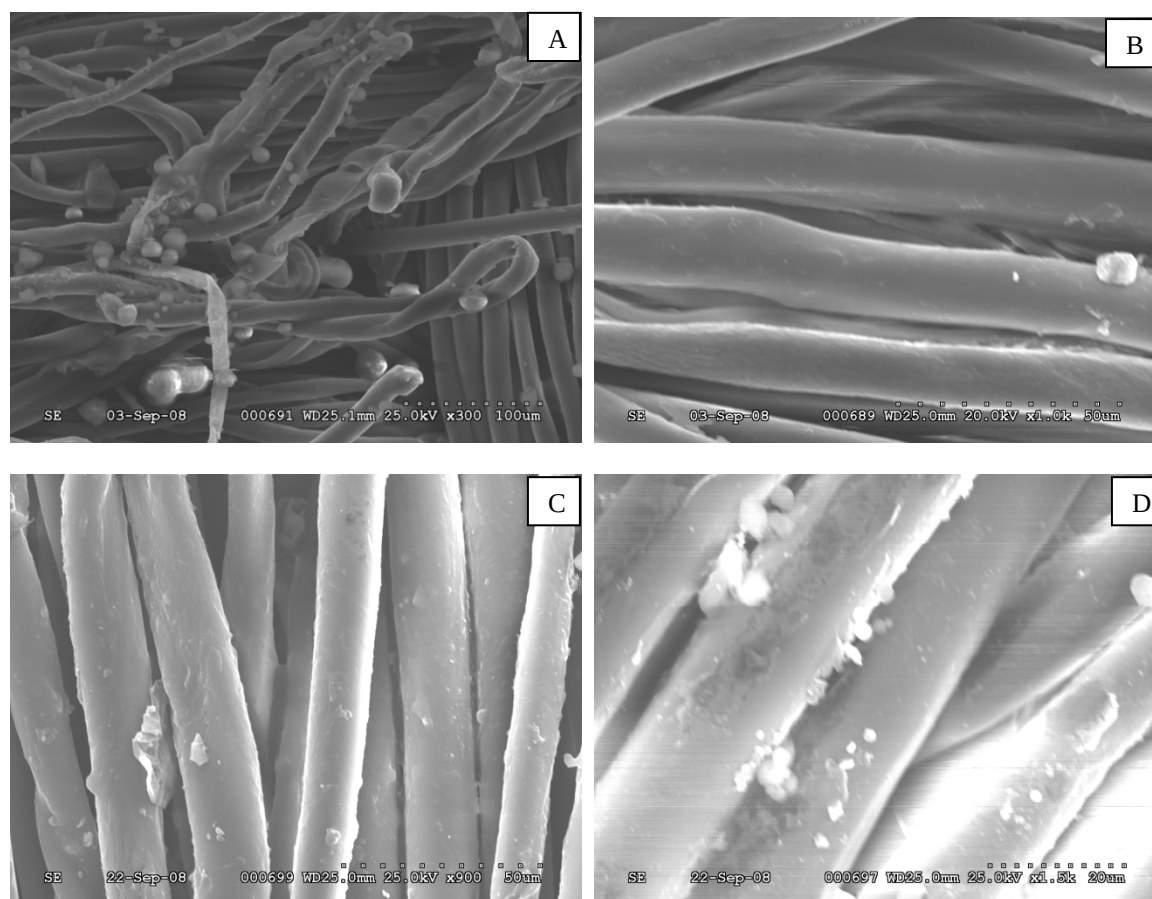


Figure 3. A. Swatch of NyCo treated in a 10% solution of TMOS with no base. B. Swatch treated in a 10% solution of FS with no base. C. Swatch treated in 1% FS with NH_4OH . D. Swatch treated in 5% TMOS followed by 1% FS, both without NH_4OH . Note that Sample B, FS treated without a base catalyst has little particulate condensed to fibers, as compared to the other TMOS treated samples, or FS samples treated with NH_4OH .