Preparation and Application of Fluorocarbon Polymer/ SiO_2 Hybrid Materials, Part 2: Water and Oil Repellent Processing for Cotton Fabrics by Sol–Gel Method

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Received 23 August 2004; accepted 17 August 2005
DOI 10.1002/app.25048
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This research employed different procedures for out water and oil repellent finish on cotton fabrics with fluorocarbon copolymer or its hybrid materials. The experimental results indicated that fabrics processed with fluorocarbon copolymer have larger contact angle for water and oil repellent finish, and the fabric processed with simultaneous bathing of fluorocarbon copolymer/ TEOS is the strongest but has poorer softness. Furthermore, when processing with chemical compounds, the processes or orders had little effect on the fabric's angle of contact and bleaching, but had more significant influence on strength. Regarding to washing fastness, after ten-time water washing, the angle of contact of processed fabrics decreased by about 3%. Overall, the fabric pretreated with TEOS, followed by fluorocarbon polymer, had the best balance of physical properties. J Appl Polym Sci 103: 3019–3024, 2007

Key words: fluorocarbon polymer; hybrid materials; processed; strength

INTRODUCTION

Because of the requirement of processing conditions and the properties of medicament, process does not only dramatically decrease strength of fabric, but also cause yellowness, which seriously influences the quality of processed fabrics. A typical example is the water and oil repellent finish of fabrics. Lately, the use of nanotechnology has enabled the development of the so-called ''Super-Hydrophobics,''[1–3] which are referred to as ''self-cleaning.'' As discussed by Barthlott and Neinhuis,[4,5] removing stains on flat surface by water drop rolling requires high angles of contact, which is called as ''self-cleaning.'' This is similar to the lotus effect, which is formed by combining the decrease of surface tension and the increase of surface roughness.[6–15] Many experts have applied related techniques to solid surface such as steel with a thin membrane of zirconium oxide or aluminum oxide on its surface, followed by a covering of fluorocarbon polymer. Alternatively, organic zirconium compounds and precursors of fluorine-containing organic siloxane can be mixed and spread on solid objects such as glass. This can achieve the special structure described above previously, where water drops have an angle of contact up to 165°.[16,17] This gives solid objects such as glass the quality of ''Super Hydrophobics.'' However, previous reports have shown that high temperatures (over 400°C) are required to achieve ''Super Hydrophobics.'' Since this is not applicable to fabrics, another processing technique is necessary.

Currently, in terms of the stain repellent finish of fabrics, only certain medicaments (e.g., fluorocarbon compounds) are used to spread over the surface to achieve water and oil repelling function for fabrics. Therefore, the maximum contact angle between fabrics and water or oil drop is around 115°,[18] which cannot give excellent ''self-cleaning'' function. This is due to the lack of a structure resembling the small shattered pieces of lotus leaf or petals. Therefore, it is crucial to know how to produce this kind of small shattered pieces and the thin chemical membrane on fabrics, which produces the ''self-cleaning'' function. Another one important aspect is to reduce the damage to fabrics as much as possible while obtaining self-cleaning effects for fabrics.

Although hybrid materials produced by sol–gel processing can be spread over high molecular materials,[19–21] but as indicated in reports, its application to fabric processing is uncommon. Nevertheless, according to its basic principles, it is feasible and potentially useful to apply it on fabrics-based, since nanosolubilizing gel is easily converted physically and chemically; using different nanosolubilizing gels can significantly change fabrics' properties.[22] Different kinds of solubilizing gel can be spreaded on fabrics through weltering and immersing oppression, followed by drying and heat treatment under specific conditions. A thin and transparent membrane of metallic or nonmetallic oxide

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Journal of Applied Polymer Science, Vol. 103, 3019–3024 (2007)

will form on fabrics' surface. This can improve current processing deficiencies of using fluorocarbon compounds, and also increase the efficacy of treatment.

EXPERIMENT

Materials

The specifications of cotton fabrics before processing were $32^S \times 32^S$ ends (100) and picks (56) (supplied by Yi Hwa Textile Company). Perfluoroaylacrylkyl ethylate monomer (M-FA) (ZONYL, DuPont, Industrial Grade, USA), tetraethyl orthosilieate (TEOS), vinyltrimethoxysilane (VTMS), 1-dodecanethiol (DT), tetrahydrofuran, and methyl ethyl ketone (MEK) are all tested chemicals, purchased from USA ACROS. Chloroform, methanol, 2,2-azo bisbutyronitrile (AIBN), and hydrochloric acid were all tested chemicals, purchased from the Japanese Research Chemicals Industrial. Nonionic surfactants (NP-50) were provided by the Taiwan Centro Chino. Trifluoroacetic acid (research grade) was purchased from Panreac Synthesis Co., Ltd. (Spain). The two chemicals, CF_3COOD and $CDCL_3$, were of analytical grade, purchased from Cambridge Isotope Laboratories (CIL, USA). In addition, a fluoride water and oil repellent (FA, ASAHI GUARD AG-7600) sold on the market was obtained from Taiwan Global Shine Trading.

Methods

Preparation of fluorocarbon copolymer

Fluorocarbon monomer (M-FA) 12 g, VTMS 6 g, AIBN 0.4 g, DT 0.1 g, nonionic surfactant 1 g, and MEK 30 g were added to a 500-mL reactive bath, which had a condenser and was filled with nitrogen. The reaction was allowed to proceed at 70°C for 6 h, and upon completion, there was extraction with MEK and methanol for several times, after which, the solution was dried. The white crystal solid particles obtained were fluorocarbon compound (abbreviated as FACP). Another FA compound was also prepared without addition of VTMS (abbreviated as FAP).

Processing cotton fabrics with water and oil repellent by sol–gel method (mixed type)

Processing cotton fabrics with FACP and FAP. FACP or FAP 2 g was dissolved by stirring with appropriate amount of trifluoride acetic acid and chloroform. Cotton fabrics were soaked in this for 1 min and dried at room temperature before testing their physical properties.

Processing cotton fabrics with FACP or FAP/SiO_2 compounds. FACP or FAP 6 g was dissolved by stirring with trifluoride acetic acid and chloroform. Following the addition of 12 g TEOS and 0.5 mL distilled water, it was then stirred for 30 min. Cotton fabrics were soaked in it for 1 min, dried at room temperature, and tested for their physical properties.

Processing cotton fabrics with water and oil repellent by sol–gel method (two-steps)

Solution A: TEOS 10 g was dissolved in 50 mL of THF, followed by adding 2 mL of 0.05*N* HCL (TEOS solution), and stirring for 30 min.

Solution B: Self-synthesized fluorocarbon polymer (FAP) or fluorocarbon copolymer (FACP) solution.

1. Cotton fabrics were soaked in solution A for 1 min, and then placed in solution B for 1 min. Cotton fabrics were treated by the two dips and two nips. Finally, cotton fabrics were predried at 100°C for 2 min, followed by 3 min of curing at 150°C before testing for physical properties.
2. Two pieces of cotton fabrics were soaked in solution B for 1 min, the two dips and two nips step, and predried at 100°C for 2 min. Following curing at 150°C for 3 min, one piece of these treated cotton fabrics was immersed in solution A for 1 min, and allowed to dry naturally before testing its physical properties.

Thin membrane production by various methods of materials

FAP and FACP solutions were separately placed in beakers. A glass slide was vertically immersed in each solution for 1 min and dried at room temperature for 24 h. Other processing procedures for producing thin membranes were followed, as described above.

Analysis and measurement

A Bio-rad Digilab FTS-40 Fourier optical spectrum analyzer was used to test for special functional groups, and the processed cloth surface was observed using a Jeol 5610 electronic microscope. The angle of contact for processed fabrics was measured using a FACE CA-5 150 angle of contact measuring machine. Processed fabrics' yarn was tested for its strength using Alphaten 400 power machine. INTECO, which meets JIS standard 45° angle, was used to test fabrics' softness. Whiteness of processed fabrics was tested by HunterLab D25 H/L-2 color difference using ASTM method E313-73. Various kinds of thin membrane materials were measured for roughness using AFM of Seiko SPA 300HV (SII Nano Technology, Japan). Fabrics represented by each symbol are shown in Table I.

RESULTS AND DISCUSSIONS

FTIR analysis of processed fabrics

Figure 1 displays the FTIR spectra of each processed fabric by copolymer and its hybrid materials. In

TABLE I
Meaning of Symbols

Symbol of processing methods	Meaning
FAP processing	Processed with M-FA-polymerized fluorocarbon polymer
FACP processing	Processed with (M-FA + VTMS)-copolymerized fluorocarbon polymer
TEOS processing	Sample fabric was hydrolyzed and polymerized only with TEOS
FAP→TEOS separate processing	Pretreated with FAP, followed by hydrolysis and polymerization with TEOS
FACP→TEOS separate processing	Pretreated with FACP, followed by hydrolysis and polymerization with TEOS
TEOS→FAP separate processing	Hydrolyzed and polymerized with TEOS, followed by FAP treatment
TEOS→FACP separate processing	Hydrolyzed and polymerized with TEOS, followed by FACP treatment

Figure 1, line (a) depicts original fabrics, and (b) is the spectrum of FAP-processed fabrics. It can be seen that it is >C=0 functional group at 1729 cm^{-1}. Line (c) is the spectrum of FAP/TEOS bathing processed fabrics, which is also >C=0 functional group at 1726 cm^{-1}. Besides, fabrics processed by simultaneous bathing of FACP and FACP/TEOS show absorbance peak of >C=0 functional group at 1723 and 1727 cm^{-1}, as depicted in lines (d) and (e). In summary, fabric clearly has combination to copolymer and its hybrid.

SEM analysis of processed fabrics

Figure 2 illustrates SEM results of water and oil repelling process on cotton fabrics using polymer and its compounds. Figures 2(a) and 2(e) show processed fabrics treated with TEOS that have smooth yarn surface. Figures 2(b) and 2(f) show fabrics pretreated with TEOS, followed by FAP processing, where chemicals are clearly attached to the yarn, giving a ''flow pattern.'' This is because the TEOS produces solid granules of SiO_2 by hydrolysis and polymerization, and these granules possibly form hydrogen bonds to —OH functional group in fabrics. However, when fabrics reacting to FAP again, copolymers would form thin membranes with a flow pattern after heat treatment. Figures 2(c) and 2(g) show processed fabrics by FAP/TEOS simultaneous bathing, and while Figures 2(d) and 2(h) are those processed by FACP/TEOS. Their results are as seen in Figures 2(a) and 2(e), where both yarn and fiber have substances attached. However, their surface pattern is different from that seen in Figures 2(a) and 2(e), because the later two are from a simultaneous bathing process, which is after TEOS hydrolysis and polymerization, so it reacts with fibers and FAP simultaneously. Thereby, the surface it forms is similar to chunk structure, and appears rougher. This situation is especially obvious on fabrics processed with FACP/TEOS, because this processing forms more SiO_2, which causes yarn to stick together, giving less space between yarn.

Analysis of processed fabrics' physical properties

In Table II, strength, softness, and angles of contact for each type of processed fabric are shown. The fabric processed with TEOS is the only one with higher strength than the original because TEOS reaction produces a reticular structure of SiO_2, and only FAP- or FACP-processed fabrics showed less strength. This indicates that high temperature treatment and chemicals themselves can cause significant damage to processed fabrics. The FACP/TEOS simultaneous bathing process produces high amount of SiO_2 in fabrics, giving a higher chance of forming reticular structure with fibers, and thus has the optimal strength. It can also be seen from the table that in two-stage processing, fabrics treated with TEOS, followed by FAP or FACP, have higher strength than those processed with FAP or FACP and TEOS, because TEOS treatment can protect fibers from damage by high temper-

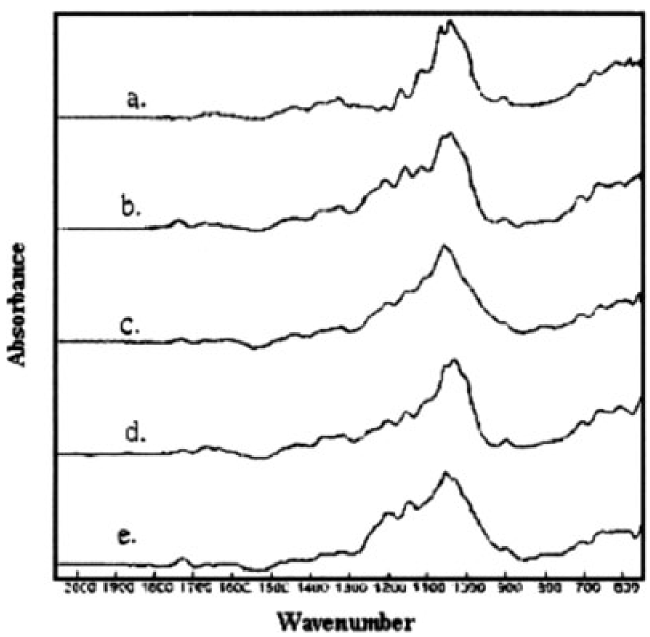

Figure 1 FTIR spectra of fabrics processed by fluorocarbon copolymer and its hybrids; (a) original fabrics; (b) FAP treatment; (c) FAP/SiO_2 hybrid processing; (d) FACP treatment; (e) FACP/SiO_2 hybrid processing.

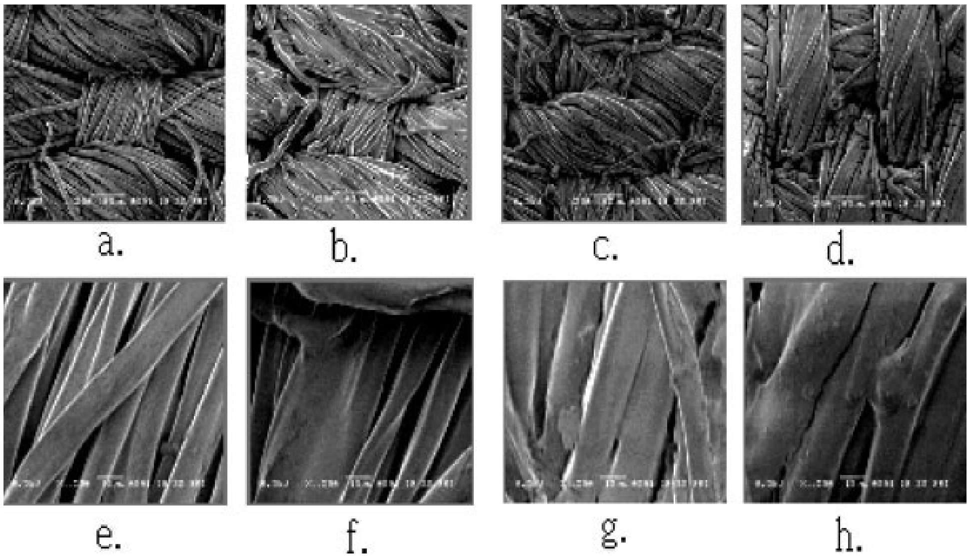

Figure 2 SEM pictures of cotton fabrics processed by water and oil repellent copolymers; (a, e) TEOS Pretreatment; (b, f) TEOS pretreatment prior to FAP processing; (c, g) FAP/TEOS simultaneous bathing processing; (d,h) FACP/TEOS simultaneous bathing processing.

ature and chemicals in the processing of FAP or FACP, thus giving higher strength.

In terms of whiteness, as it involves to commercial ethics, those chemically processed fabrics' whiteness is now shown in this report. As listed in the table, except for fabrics processed with FAP or FACP, which have poorer whiteness, others have good whiteness with little difference. The main reason for this is that SiO_2 protects fabrics from yellowness, caused by high temperature. For softness, the Table indicates only fabrics treated with TEOS have higher softness than those processed with simultaneous bathing or two-stage processing. In simultaneous bathing or two-stage processing, fabrics finished with TEOS have significantly poorer softness. This may be due to the formation of SiO_2 from TEOS attaching to fabric surface.

The table also shows that, except for TEOS-treated fabrics, which do not have high contact angles to water and have less oil repelling property (methylene Iodide), others have excellent contact angles to water and oil repellency. The TEOS-treated fabrics have residues of —OH functional groups during hydrolysis and polymerization.[23] These, although SiO_2 has a reticular structure, still can absorb water molecules. When four kinds of fabrics, including FAP, FACP, FACP/TEOS simultaneous bathing, pretreated with TEOS prior to FACP processing etc, are compared for

TABLE II
Physical Properties of Processed Fabrics

Processing methods	Strength (kg)	Whiteness	Softness (cm)	Angles of contact: No washing, Water	No washing, Methylene iodide	10-times washing, Water	10-times washing, Methylene iodide
Original fabrics	0.338	73.84	3.2	0	0	0	0
Processed with commercial chemicals	0.302	–[a]	5.7	124	119	118	112
FAP processing	0.290	67.32	6.1	137	128	136	120
FACP processing	0.305	68.92	6.0	147	132	138	128
TEOS processing	0.382	73.46	5.0	0	72	0	0
FAP/TEOS simultaneous bathing	0.320	72.26	6.6	142	134	138	129
FACP/TEOS simultaneous bathing	0.372	72.38	7.2	136	128	132	120
FAP→TEOS separate processing	0.272	71.58	6.8	142	130	139	120
FACP→TEOS separate processing	0.283	71.74	7.0	143	132	137	122
TEOS→FAP separate processing	0.346	71.19	6.1	140	128	133	127
TEOS→FACP separate processing	0.347	71.39	6.2	141	125	134	125

[a] Not shown here because it has commercial security.

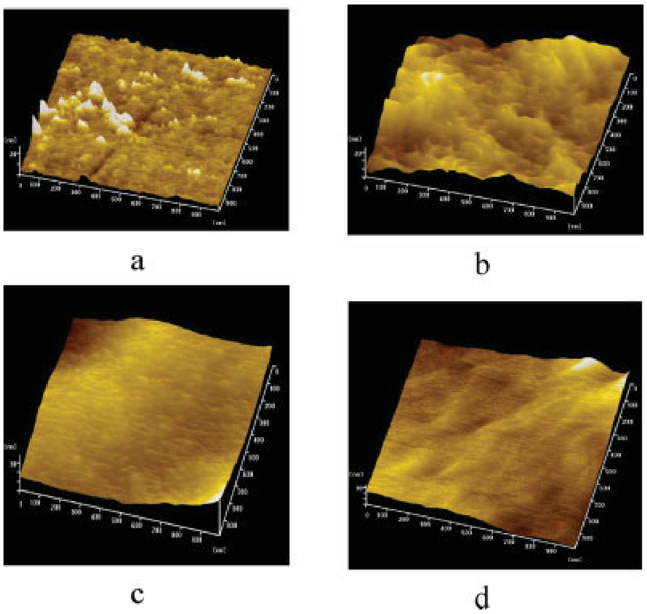

Figure 3 AFM image of the film surface with various materials: (a) SiO_2; (b) FACP; (c) FACP/TEOS (simultaneous bathing); (d) TEOS → FACP (separate treatment). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

their contact angles, the fabrics pretreated with TEOS prior to FACP processing have the best angles of contact. The main reasons are (1) in FACP/TEOS processing, incomplete hydrolysis and polymerization will cause more SiO_2 —OH residue, which can easily absorb water molecules; (2) holes in the reticular structure may be too large, allowing more water molecules to permeate through; (3) while pretreating with TEOS, fabrics have a certain degree of surface roughness after FACP processing, so it tends to form the ''lotus effect''; (4) fabrics treated only with FACP have higher surface roughness due to the reticular structure of SiO_2 in FACP. Corresponding AFM and roughness of previously described fabrics are depicted in Figure 3 and Table III. In terms of water washing fastness, after ten-times water washing, fabrics only treated with TEOS and without heat treatment show the poorest fastness. Other processed fabrics only show 3% decrease of contact angle, and thus

TABLE III
Membrane Surface Roughness of Various Materials

Roughness	Materials				
	SiO_2	FAP	FACP	FACP/TEOS (simultaneous bathing)	TEOS → FACP (separate treatment)
R_a (nm)	1.031	3.634	4.968	3.518	4.337
RMS (nm)	1.598	4.524	7.129	4.376	6.410

have excellent fastness. However, in terms of the balance of fabrics' entire physical properties, fabrics pretreated with TEOS, followed by treatment of fluorocarbon polymers or copolymers, have the most balanced physical properties.

CONCLUSIONS

This research used different processing methods to conduct water and oil repelling processing using fluorocarbon copolymer and its hybrids, to study their feasibility. The experimental results are as follows:

1. While processing water and oil repellents using solubilizing gel, the analysis of FTIR and SEM proved that processed fabrics absorb chemicals, giving them water and oil repellency.
2. FACP-processed fabrics have better contact angles of water and oil repellency, while fabrics processed by FACP/TEOS simultaneous bathing are the strongest strength, but have poorer softness.
3. Processing order and methods have insignificant influence on angles of contact and whiteness, but have significant effects on strength, especially those fabrics processed with FAP or FACP prior to TEOS treatment, having the poorest strength.
4. Except for TEOS-treated fabrics, other processed fabrics have only 3% decrease of contact angles after ten-times water washing.
5. Over all, TEOS-pretreated fabrics prior to the processing of fluorocarbon polymer and copolymer will have the most balanced physical properties.

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