

# Preparation and Application of Fluorocarbon Polymer/SiO<sub>2</sub> Hybrid Materials, Part 1: Preparation and Properties of Hybrid Materials

Jen-Taut Yeh,<sup>1,2</sup> Chin-Lai Chen,<sup>1</sup> Kuo-Shien Huang<sup>3</sup>

<sup>1</sup>Graduate School of Polymer Engineering, National Taiwan University of Technology, Taipei, Taiwan

<sup>2</sup>Department of Textile Engineering, Nanya Institute of Technology, Jiung Li, Taiwan

<sup>3</sup>Department of Polymer Materials, Kun Shan University of Technology, Yung Kang, Tainan, Taiwan 71016, Republic of China

Received 27 August 2004; accepted 17 August 2005

DOI 10.1002/app.25047

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** For this study, we first prepared a fluorocarbon polymer and its hybrid materials. We found that fluorocarbon copolymers can produce hydrogen bonds with SiO<sub>2</sub> to form hybrid materials. We also used thermogravimetric analyzer and tested the thermostabilities of the four products, which were ranked as follows: fluorocarbon copolymer/SiO<sub>2</sub> hybrid material > fluorocarbon polymer/SiO<sub>2</sub> hybrid material > fluorocarbon copolymer

> fluorocarbon polymer. In addition, we found that, due to the inorganic SiO<sub>2</sub> used, the number of pores and the specific surface areas of the hybrid materials both increased. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1140–1145, 2007

**Key words:** fluorocarbon polymer; hybrid material; thermostability

## INTRODUCTION

Inorganic/organic hybrids are high-performance materials, and comprise a new domain of recent material research and development. Because ceramic organic materials and macromolecular inorganic materials have complimentary properties, the former having high strength and heat resistance, while the latter has great durability and excellent processing properties, many researchers are looking for ways to combine these two materials and create new kinds of materials.

The sol-gel process is currently a very common way to produce inorganic/organic hybrid materials, although it was formerly a technique to make glassware and ceramics at very low temperatures. The process begins by combining organic and inorganic metallic solutions. First, the compounds in solution go through hydrolysis, condensation, polymerization, and transformation into a gel. Numerous researchers have attempted to create various types of hybrid materials using this technique and have thus improved their mechanical,<sup>1–4</sup> thermostability,<sup>5–7</sup> and optometric properties.<sup>8–10</sup>

Normally, because of the demands of processing and the properties of these agents, fabrics lessen in strength and etiolate after finishing, which damages the qualities of processed fabrics. The fluorocarbon

polymer that is used in oil and water repellent finishing is a prime example. Although hybrid materials that are produced by sol-gel processing can be spread over polymer materials,<sup>11–13</sup> their application to fabric processing is uncommon.

This research study first produces four types of fluorine-carbon polymers and their hybrid materials by the sol-gel method, then inquires into the feasibility of their application to oil and water repellent finishing in the processing of cotton textiles.

## EXPERIMENT

### Materials

Perfluoroacrylate ethylate monomer (M-FA) (ZONYL™, DuPont, Industrial Grade), tetraethyl orthosilicate (TEOS), vinyl trimethoxysilane (VTMS), 1-dodecanethiol (DT), tetrahydrofuran, and methyl ethyl ketone (MEK) all were obtained from U.S. ACROS. Chloroform, methanol, 2,2-azo bisbutyronitrile (AIBN), and hydrochloric acid are all from the Japan Reagent Industry (Japan), the nonionic interfacial agent (NP-50) was provided by the Taiwan Centro Chino, and trifluoroacetic acid (research grade) was purchased from Panreac Sythesis (Spain). The CF<sub>3</sub>COOD and CDCl<sub>3</sub> were of analytical grade and were purchased from Cambridge Isotope Laboratories (CIL). In addition, over-the-counter fluorine oil and water repellent finishing agent (ASAHI GUARD AG-7600) were provided by the Taiwan Global Shine Trading (Taiwan).

Correspondence to: K. S. Huang (hks45421@ms42.hinet.net).

**TABLE I**  
Molecular Weight and Elemental Analysis of  
FAP and FACP

Polymer	Molecular weight		Polydispersity $M_w/M_n$	Elemental content (%)	
	$M_w$	$M_n$		C	H
FAP	8570	4653	1.84	30.27	1.46
FACP	9621	5561	1.73	32.03	2.57

## Methods

### Preparation of fluorocarbon copolymer

A mixture of 12 g M-FA, 6 g VTMS, 0.4 g AIBN, 0.1 g DT, 1 g nonionic surfactant agent, and 30 mL MEK was placed into a 500-mL reaction tank, filled with condensation tubes. The tank was filled with nitrogen, and allowed to react for 6 h at 70°C. When the reaction was complete, the above emulsion was mixed with methanol and MEK, refined several times, and dried. As a result, solid, white, crystalline fluorocarbon copolymers (FACP) were formed. The FA polymer (FAP) was formed similarly without the addition of VTMS.

### Preparation of fluorocarbon copolymer/SiO<sub>2</sub> hybrid materials

Two grams each of FACP and FAP were added to trifluoroacetic acid and chloroform and stirred. Four grams of TEOS and 0.5 mL distilled water were added to the above solution and stirred at room temperature until a gel was formed. This gel was then placed into a hermetic oven to dry. This process formed the fluorocarbon hybrid material.

### Analysis and measurements

The molecular weight of the fluorocarbon polymer (FAP) and its copolymer (FACP) were measured with a GPC (Bio-Rad FTS-3000Mx). The standard polymer used for calibration was polystyrene with tetrahydrofuran as the solvent. The elemental analysis of the polymer and copolymer were measured by Elementar vario EL III. A Bio-Rad Digilab FTS-40 Fourier spectrometer was used to examine special functional groups. A Jeol 5610 electron microscope was used to observe the surface of the processed fabrics. A DuPont model 2200 thermogravimetric analyzer was used to examine the thermostability of the copolymers from 30°C up to 600°C, with a velocity that increased 20°C/min. Nuclear magnetic resonance (NMR) spectroscopy (Bruker Advance 40) was used to examine <sup>13</sup>C, <sup>29</sup>Si, and <sup>19</sup>F content of the copolymer and to record its spectrum. A Micromeritics ASAP 2010 B.E.T. analyzer was used to examine porosity.

## RESULTS AND DISCUSSION

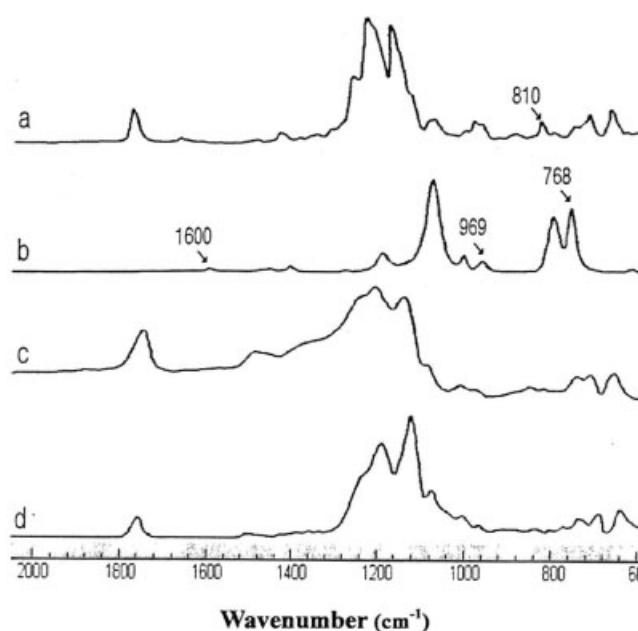
### Molecular weight and elemental analysis of FAP and FACP

From Table I, the molecular weight of the polymer is seen to increase due to copolymerization with VTMS, but the polydispersity is reduced, indicating that the molecular weight of FACP is distributed more narrowly. Secondly, an elemental analysis of both FAP and FACP reveals a greater carbon and hydrogen content of FACP.

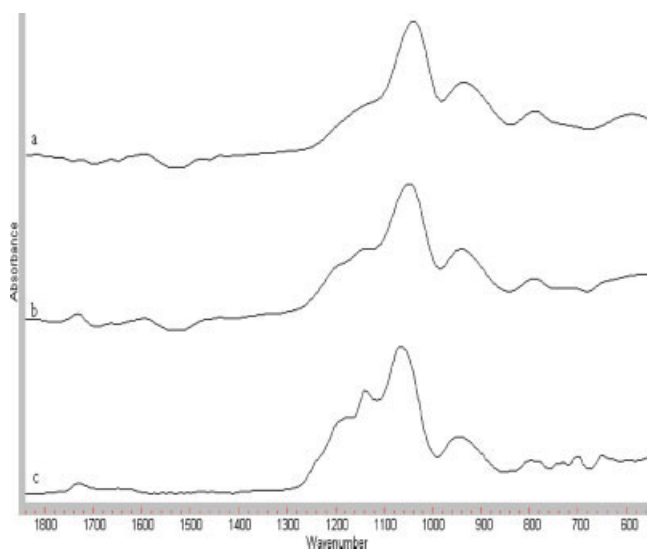
### FTIR analysis of the copolymer and its hybrid materials

Figure 1 shows the FTIR of M-FA, VTMS, FAP, and FACP. Panel (a) displays an apparent CF group with absorption peaks at 1174 and 1196 cm<sup>-1</sup>. There is also an absorption peak of C=O at 1735 cm<sup>-1</sup>. Vinyl group has absorption peaks at 1636, 982, 969, 810 and 768 cm<sup>-1</sup>. Panel (b) shows the FTIR of 1600, 969, and 810 cm<sup>-1</sup>, as well as the absorption peaks of the vinyl group and the Si—O—C at 768 cm<sup>-1</sup> and 1078 cm<sup>-1</sup>, respectively. The FTIR of FAP, seen in (c), shows that the absorption peak of the original vinyl group has already disappeared, but the absorption peaks of C=O and CF in the polymer still exist. The FTIR of FACP, seen in (d), has stronger absorption peak at 1082 and 1008 cm<sup>-1</sup>. The absorption peak of the Si—O—C proves that FAP and VTMS are copolymerized to form FACP.<sup>14</sup>

Figure 2 shows the FTIR of SiO<sub>2</sub> and its hybrid materials. Panel (a) shows SiO<sub>2</sub>, which through hy-



**Figure 1** FTIR of monomers and polymers: (a) M-FA, (b) VTMS, (c) FAP, and (d) FACP.



**Figure 2** FTIR of SiO<sub>2</sub> and hybrid materials: (a) SiO<sub>2</sub>, (b) FAP/SiO<sub>2</sub>, and (c) FACP/SiO<sub>2</sub>. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

drolysis and polycondensation with TEOS forms absorption peaks at 1040, 938, and 790 cm<sup>-1</sup>, representing Si—O—Si, Si—OH, and Si—O—C, respectively. Panel (b), together with (c), shows the FTIR of FAP/SiO<sub>2</sub> and FACP/SiO<sub>2</sub>, respectively, in addition to displaying the absorption peaks of the CF and the C=O functional groups. Comparison of Figures 1 and 2 shows that the FAP-CF absorption peak shifts from 1204 to 1193 cm<sup>-1</sup>, and the FACP peak shifts from 1196 to 1185 cm<sup>-1</sup>. We concluded that FAP and VTMS copolymerized to produce FACP. Previous reports have shown that in hybrid materials, inorganic SiO<sub>2</sub> can develop hydrogen bonds with CF or C=O groups.<sup>15,16</sup>

### NMR analysis of FACP or FAP and its hybrid materials

#### <sup>13</sup>C NMR analysis

The results from <sup>13</sup>C NMR analysis can be used to examine the chemical shift of <sup>13</sup>C in the fine structure of macromolecular compounds (e.g., cubic regularity, comonomeric sequences, and structural defects).<sup>17</sup> Recently, macromolecules were shown to develop strength of a different conformation in their fine structure from displacement of local molecular chains.<sup>18</sup> Figure 3 shows the <sup>13</sup>C NMR spectrum of a copolymer and its hybrid materials. It also shows that in FAP, there is a C=O group at 178.11 ppm. Panel (b) shows the spectrum of the FAP/SiO<sub>2</sub> hybrid material with a C=O group at 178.59, proving that there was no chemical shift of the C=O group. Panel (c) shows the FACP spectrum with a C=O group at

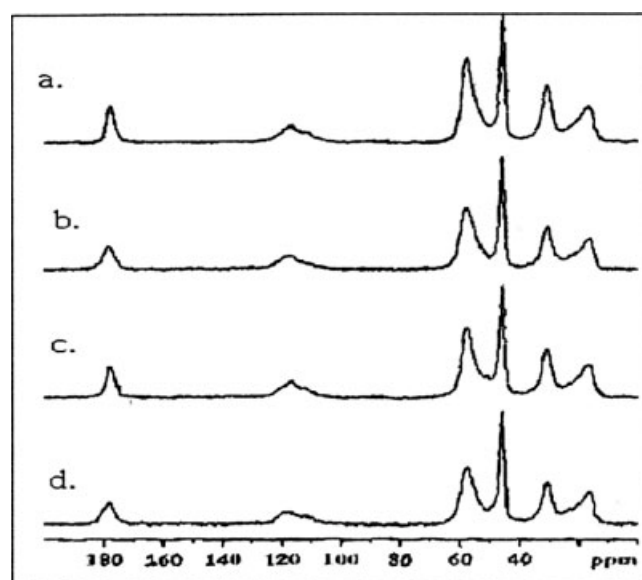
177.86. Panel (d) shows the spectrum of the FACP/SiO<sub>2</sub> hybrid material with a C=O group absorption peak at 178.18 ppm, proving that there is no apparent shift for this group. From many past reports, we can see that in a hybrid material, if hydrogen bonds form between two kinds of materials, there will be chemical shifts for certain groups in the <sup>13</sup>C NMR spectrum, and these shifts will be toward the high frequency area.<sup>19,20</sup> In summary, we see that no hydrogen bonds developed between the C=O group and SiO<sub>2</sub>. Moreover, this observation was due to the fact that the fluorine atoms carry more negative charge than oxygen, so that there can be no hydrogen bonds formed between the C=O group and SiO<sub>2</sub>. Therefore, we know from the FTIR and C NMR analyses of the FTIR and the C NMR hybrid materials that, the SiO<sub>2</sub> formed a hydrogen bond with the CF group.

#### <sup>19</sup>F NMR analysis

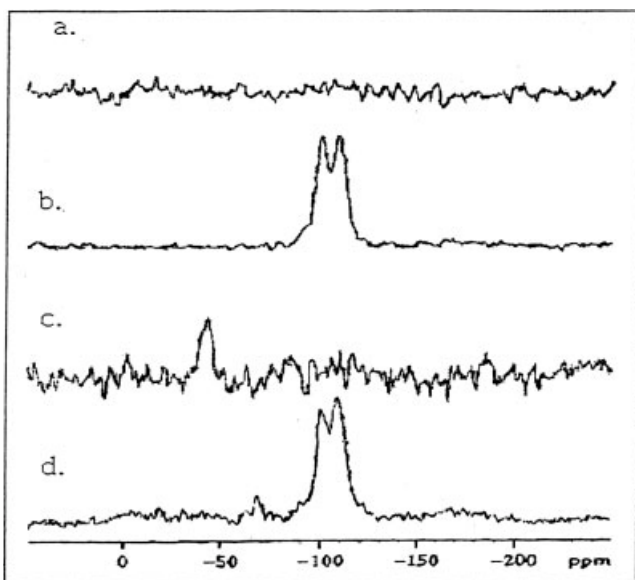
The <sup>19</sup>F NMR analysis of FAP has a 3F (CF<sub>3</sub>) absorption peak that ranges from -85.0 to -90.0 ppm, and from -30.1 to -135.1 ppm for 2F (CF<sub>2</sub>). Moreover, the <sup>19</sup>F NMR of FACP has a 3F (CF<sub>3</sub>) absorption peak that ranges from -84.4 to -90.0 ppm and a 2F (CF<sub>2</sub>) absorption peak that ranges from -129.9 to -134.7 ppm.

#### <sup>29</sup>Si NMR analysis

Figure 4 shows the <sup>29</sup>Si NMR analysis of the copolymer and its hybrid materials. Line (a) shows FAP; it



**Figure 3** The <sup>13</sup>C NMR of the fluorocarbon copolymer and its hybrid material: (a) FAP, (b) FAP/SiO<sub>2</sub> hybrid material; (c) FACP, (d) FACP/SiO<sub>2</sub> hybrid material.



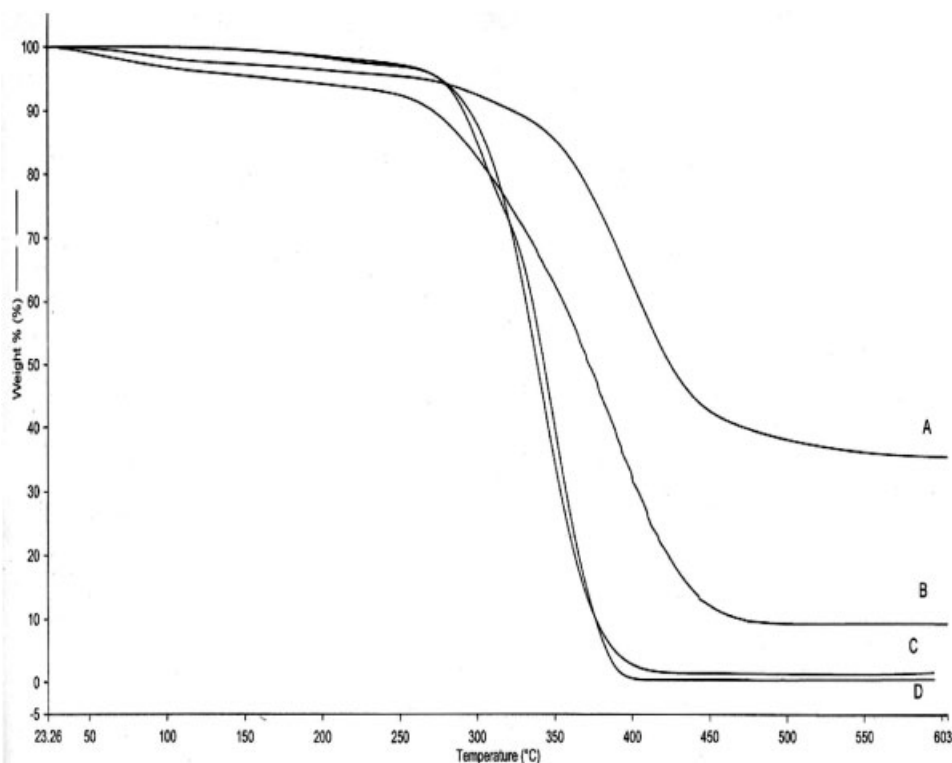
**Figure 4** <sup>29</sup>Si NMR of the fluorocarbon copolymer and its hybrid material: (a) FAP, (b) FAP/SiO<sub>2</sub> hybrid material, (c) FACP, (d) FACP/SiO<sub>2</sub> hybrid material.

can be seen that there are no  $-\text{Si}(\text{OCH}_3)_3$  groups present, so there is no atomic Si absorption peak. Line (b) shows the FAP/SiO<sub>2</sub> hybrid material spectrum; from  $-100.39$  and  $-109.61$  ppm is the SiO<sub>2</sub> absorption peak, created by the reaction of the copolymer and TEOS. Line (c) shows FACP; the  $-\text{Si}(\text{OCH}_3)_3$

group in the copolymer contributes to an absorption peak at  $-43.96$  ppm. Line (d) shows the FACP/SiO<sub>2</sub> hybrid material with absorption peaks of SiO<sub>2</sub>, created from the reaction of the copolymer and TEOS. Moreover, the  $-\text{Si}(\text{OCH}_3)_3$  absorption peak at  $-43.96$  ppm of FACP has disappeared due to hydrolysis, resulting in a weak absorption peak at  $-71.86$  ppm. In summary, we show that after polymerization, VTMS monomers polymerized with FA monomers, forming a FACP copolymer. In addition, either FAP or FACP can, through the sol-gel process, form a very solid bond with SiO<sub>2</sub> and TEOS after hydrolysis and polymerization.

### Thermogravimetric analysis

Figure 5 and Table II show the TGA and thermal properties, respectively, of the copolymer and its hybrid materials. Results indicate that FAP has the lowest initiation decompose temperature (IDT) and that FACP is higher. From this observation, we see that FACP has a better thermal resistance due to the presence of  $-\text{Si}(\text{OCH}_3)_3$  groups. In addition, after comparison of FAP with hybrid materials in temperatures exceeding  $100^\circ\text{C}$ , the speed of decomposition of hybrid materials significantly drops, which is due to the fact that hybrid materials contain little water. Another reason for this decrease is that the hybrid material still contains Si(OH)<sub>4</sub>, which has not undergone polymerization. Additionally, the thermal



**Figure 5** TGA of fluorocarbon copolymer and its hybrid material: (A) FACP/SiO<sub>2</sub>; (B) FAP/SiO<sub>2</sub>; (C) FACP; (D) FAP.

**TABLE II**  
**Thermal Properties of FAP, FACP, and Its Hybrid Materials**

Materials	Properties		
	Initiation decomposit temperature (°C)	Decomposition speed (g/°C)	Remnant (%) <sup>a</sup>
FAP	304.3	-0.863	0.387
FACP	307.9	-0.840	1.235
FAP/SiO <sub>2</sub>	310.2	-0.492	12.391
FACP/SiO <sub>2</sub>	347.8	-0.468	38.536

<sup>a</sup> The remnant is what remains after the temperature reaches 500°C.

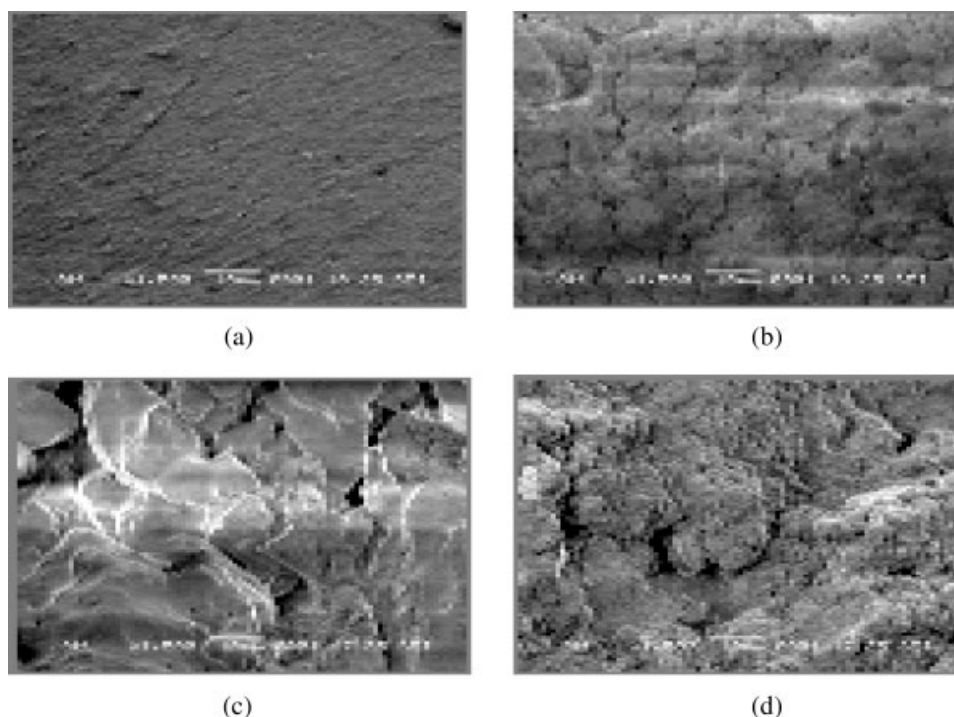
resistance of hybrid materials compares quite well to the polymer, primarily because of the SiO<sub>2</sub> within the net structure. Since the FACP/SiO<sub>2</sub> hybrid material has the Si(OCH<sub>3</sub>)<sub>3</sub>s net structure its thermal stability is the best.

#### Surface properties and porosity analysis

Figure 6 shows the SEM of the copolymer and its hybrid materials. From the SEM of FAP (a), we see that the surface is smooth, immaculate, and evenly distributed. In photo (b), which shows the surface of the FAP/SiO<sub>2</sub> hybrid material, we see that the particle size becomes significantly larger. This change is

mainly due to the combination of FAP and SiO<sub>2</sub>, which shortens the distance between particles and forms larger crystals. In (c), granular crystals are shown, which are significantly different from those of FAP because of a lack of VTMS participation in the polymerization process. In addition, when comparing with (d), which shows the surface of the FACP/SiO<sub>2</sub> hybrid material with FACP, the particles appear more densely packed and smaller. This observation is due to the fact that the VTMS itself was hydrolyzed and polymerized, and formed a structure similar to that of SiO<sub>2</sub>. Moreover, the added TEOS produces SiO<sub>2</sub> after hydrolysis and polymerization, which will bond to FAP. Therefore, from these results, we see that if the copolymer contains a Si(OCH<sub>3</sub>)<sub>3</sub> group or develops hydrogen bonds with SiO<sub>2</sub>, the distance between particles will be reduced and crystals will be formed.

From Table III, the diameter of the FAP pores is reported as 26.85 nm, which is smaller than those of the hybrid material, and the FACP pores are too small to be measured. The diameter of the FACP/SiO<sub>2</sub> pores is 83.07 nm. Since FAP and FACP are macromolecular polymers with no inorganic compounds mixed with them, the pore diameter is actually the distance between molecules in the macromolecular compound. The FACP pores are smaller than those of FAP, since FACP is a copolymer; VTMS molecules in the copolymer may shorten the distances between molecules, since they diffuse



**Figure 6** SEM of the fluorocarbon copolymer and its hybrid material: (a) FAP; (b) FAP/SiO<sub>2</sub> hybrid material; (c) FACP; (d) FACP/SiO<sub>2</sub> hybrid material.

**TABLE III**  
**Porosity of the Fluorocarbon Copolymer and Its Hybrid Materials**

Materials	Properties		
	BET specific surface area (m <sup>2</sup> /g)	Specific volume (10 <sup>-3</sup> ) (cm <sup>3</sup> /g)	Size (nm)
FAP	2.175	1.460	26.85
FAP/SiO <sub>2</sub>	23.877	100.359	168.13
FACP	0.213	0.134	- <sup>a</sup>
FACP/SiO <sub>2</sub>	9.862	20.481	83.07

<sup>a</sup> Too small to be measured.

through the FAP molecules. Perhaps it may be due to the effect of hydrogen bonds, which reduce the distance between copolymer particles, forming small crystals and small pores.

The pure SiO<sub>2</sub> particles, which are heat-treated at 140°C, have larger pores, with a size of about 30 nm.<sup>21</sup> Therefore, when they form a hybrid material with organic compounds, the distance between particles is reduced and larger crystals are formed, enlarging the pore diameter. The pore sizes of both FAP/SiO<sub>2</sub> and FACP/SiO<sub>2</sub> hybrid materials are not smaller than the TEOS polymer. The same tendency is displayed regarding the pore's surface area and volume. As shown from these results, the hybrid material created from this experiment has a nano-scale pore size.

### CONCLUSIONS

In this research, we first prepared a fluorocarbon copolymer with SiO<sub>2</sub> nano-hybrid materials and discussed its properties. We further used different methods to process cotton fabrics with water and oil repellent finishes to determine its feasibility. The following are the experiment results:

1. After FTIR, NMR, and SEM analyses, we confirmed that the fluorocarbon copolymer devel-

ops hydrogen bonds with SiO<sub>2</sub>. We produced fluorocarbon copolymer/SiO<sub>2</sub> hybrid materials.

2. The thermostability of the four products were ranked as follows: fluorocarbon copolymer/SiO<sub>2</sub> hybrid material > fluorocarbon polymer/SiO hybrid material > fluorocarbon copolymer > fluorocarbon polymer.
3. With the addition of inorganic SiO<sub>2</sub>, the pores and specific surface areas of hybrid materials are increased.

### References

1. Weng, W. H.; Hui, C.; Tsai, S. P.; Wu, J. C. *J Appl Polym Sci* 2003, 91, 532.
2. Kojima, Y.; Matsuoka, T.; Takahashi, H.; Kurauchi, T. *J Appl Polym Sci* 1994, 51, 683.
3. Sheu, T. S.; Ou, C. J.; Hon, L. Y.; Chen, D. Y. *Proc Natl Acad Sci USA* 2000, 24, 301.
4. Liu, Y. L.; Hsu, C. Y.; Wei, W. L.; Jeng, R. J. *Polymer* 2003, 44, 5159.
5. Liu, Y. L.; Chiu, Y. C.; Wu, C. S. *J Appl Polym Sci* 2003, 87, 404.
6. Yano, S. *Polymer* 1994, 35, 5565.
7. Zhu, Y.; Sun, D. X. *J Appl Polym Sci* 2004, 92, 2013.
8. Novak, B. M. *Adv Mater* 1993, 5, 422.
9. Goto, K. *J Appl Phys* 1998, 37, 2274.
10. Kador, L.; Fischer, R.; Haarer, D.; Kasemann, R.; Brück, S.; Schmidt, H.; Dürr, H. *Adv Mater* 1993, 5, 270.
11. Wang, B.; Wilkes, G. L. *J Macromol Sci Pure Appl Chem* 1994, 31, 249.
12. Mizutani, R.; Oono, Y.; Matsuoka, J.; Nsu, H.; Kamiya, K. *J Mater Sci* 1994, 29, 5773.
13. Chalapathi, V. V.; Ramiah, K. V. *Curr Sci* 1968, 16, 453.
14. Changhai, Y. L.; Xuming, X. *Binding*, Beijing 2002, 23, 1.
15. Zhang, X.; Takegoshi, K.; Hickichi, K. *Polymer* 1992, 33, 712.
16. Bovey, F. A. *High-Resolution NMR of Macromolecules*; Academic Press: New York, 1972.
17. Qin, C.; Priesm, A. T. N.; Belifore, L. A. *Polym Commun* 1990, 31, 177.
18. Miyoshi, T.; Takegoshi, K.; Hikichi, K. *Polymer* 1997, 38, 2315.
19. Mayhias, L. J. *Solid State NMR of Polymers*; Plenum: New York, 1988.
20. Lee, G. L. *Organic Silicon Macromolecule Chemistry*; Beijing Science Publisher: Beijing, China, 1998; p 150.
21. Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979; p 541.