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Photochemical Modification of a Fluoropolymer Surface

Introduction. Fluoropolymers are thermally stable and chemically inert with low dielectric constants and surface energy.[1] These characteristics make poly(tetrafluoroethylene) (PTFE) useful in many applications but also difficult to adhere to other materials, and for such purposes the surface has to be modified. Known methods for surface treatment of PTFE include chemical etching, electrochemical reduction, treatment with corona discharge, plasma, ion or electron beams, laser ablation, and metal-induced crystallization.[2] Only very strong chemical reducing agents, such as sodium/naphthalene complex, alkali metals in liquid ammonia, or benzoin dianion,[3] react with PTFE, generating a colored surface rich in unsaturated carbons and retaining only minor amounts of fluorine. The reduced surface is hydrophilic with much improved adhesion but is also sensitive toward moisture and light.

Recently, it was found that perfluorodecalin reacts thermally with thiophenoxide salts under mild conditions, forming octakis(phenylthio)naphthalene in good yield.[4] The reaction was reported to require the presence of tertiary fluorines in the substrate, and experiments with fluoropolymers like PTFE and FEP were unsuccessful. However, this unexpected reaction suggests the possibility for new methods to functionalize perfluorocarbon surfaces. We now find that UV irradiation of certain organic electron donor solutions in contact with a PTFE film will form a modified surface on the fluoropolymer and that images can be generated on the surface by irradiation through a mask. This is the first demonstration of one-step image formation on PTFE using UV light. In addition, model experiments show that photoexcited organic donors can indeed react with "inert" perfluorocarbons in organic solutions.

Results. In a typical experiment, a 2 × 3 cm Teflon PTFE film, which had been washed overnight with THF and dried under vacuum, was placed on a thin aluminum foil frame in a quartz beaker and covered with a glass plate. A deoxygenated solution containing the organic donor(s) in a solvent, such as DMF, was added so that the underside of the film was contacted by the solution. The beaker was flushed with nitrogen and irradiated for 1 h through the bottom with a 100-W medium-pressure mercury lamp with main emittance at 366 nm. After UV exposure, the film was rinsed with acetone, immersed in boiling water for 1 h, and extracted in boiling acetone for 18 h. Advancing contact angles were measured by applying a 10-μL water droplet on the PTFE surface and measuring the diameter of the surface.[5] Results are summarized in Table I.

When exposed to UV light in the presence of a reducing agent, the PTFE surface became more hydrophilic and, in some cases, turned yellow or gray with a metallic shine. With reducing agents like tetramethylphenylenediamine and the sodium salt of 2,4-pentadione, the reduced surface was only faintly yellow, while the thiol and phenol salts gave highly colored surfaces. Parts of the film that were shielded from UV exposure remained white and hydrophobic. ESCA measurements show extensive loss of fluorine from the surface, with a corresponding increase in carbon and oxygen. Many of the reducing agents are also good nucleophiles and may react with the unsaturation or radicals on the reduced surface, as evidenced by the ESCA detection of sulfur or nitrogen.

The surface modification process is actually quite rapid under these conditions; as shown in Figure 1, significant effects on the contact angle are observed within a few minutes. Additional improvements can be observed by adding a neutral sensitizer, such as benzophenone or naphthalene. Figure 2 shows the change in the aqueous contact angle that occurs on irradiation of the disodium salt of 3-mercapto-2-butanol in the presence or absence of the sensitizers.

Imagewise modification of a PTFE surface has been demonstrated (Figure 3). A film in contact with a solution of 0.1 M monosodium 2-mercaptoethanol and 0.025 M thioxanthone in DMF was irradiated for 0.5 h through a mask. The irradiated areas were dark and hydrophilic with a metallic shine, while the shielded areas remained white and hydrophobic. Resolution to 0.1 mm was demonstrated.

Preliminary tests show improved adhesion of metals to the photomodified surfaces. In one example, a PTFE film was irradiated in the presence of monosodium 2-mercaptoethanol and benzophenone in DMF, activated by treatment with 0.1% aqueous $PdCl_2$ and sodium borohydride, and subjected to electroless nickel plating. Peel tests showed an adhesive strength of 4 lb/linear in., while no metal adhesion was observed on an unmodified surface. However, if the modified surface was boiled in water for 1 h before plating, the adhesive strength decreased to 0.15 lb/in.

Confirmation that photoexcited organic donors can react with perfluorocarbons was obtained in model experiments. Thus, the fluorine NMR spectrum of perfluorodecalin in

Table I
Effect of Photoexcited Reducing Agents on PTFE Surface Properties[a]

entry	donor[b]	contact angle,[c] deg	surface composn,[d] %					
			F	C	O	S	N	Na
1	none	78	68.4	31.3	0.2		0.1	
2	*N*,*N*-dimethylaniline	63	66.5	32.1	0.8			
3	2-naphthol, sodium salt	46	28.7	59.3	11.4		0.5	
4	benzenethiol, sodium salt	35	11.4	66.5	15.5	3.9	2.1	0.4
5	tetramethyl-*p*-phenylenediamine	33	47.8	45.1	5.0		1.7	
6	benzhydrol, sodium salt	29	34.4	53.0	10.1		1.5	0.3
7	2,4-pentanedione, sodium salt	29	46.8	45.3	7.0		0.6	
8	1,2-ethanedithiol disodium salt	27	25.9	56.7	10.8	6.3	0.4	0.4
9	4-aminobenzenethiol sodium salt	27	20.9	63.9	6.4	4.4	4.4	0.1
10	4-hydroxyaniline, sodium salt	23	15.2	62.0	20.1		2.7	0.2
11	4-hydroxythiophenol, disodium salt	11	6.5	67.5	18.9	5.3	0.5	0.1
12	3-mercapto-2-butanol disodium salt	10	5.3	67.2	19.4	6.1	1.1	

[a] 1-h irradiation using medium-pressure mercury lamp. [b] DMF solution, 0.05 M donor. [c] Advancing angle, 1/3 $EtOH/H_2O$. [d] From ESCA, using Mg Kα radiation. Photoelectron emission angle was 15° off normal. Estimated sampling depth is about 100 Å. No depth profiling has been done.

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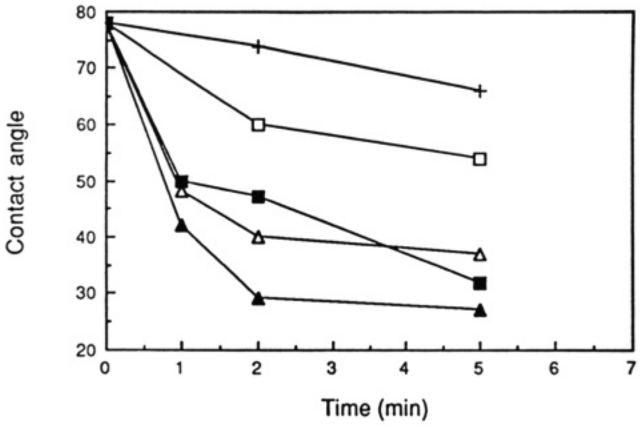

Figure 1. Reduction of PTFE film as measured by the change in contact angle (3/1 EtOH/H_2O) as a function of exposure time. Donors are 0.05 M in DMF: disodium ethanedithiolate (+), *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (□), sodium 4-aminothiophenoxide (△), disodium salt of 3-mercapto-2-butanol (■), and disodium salt of 4-hydroxythiophenol (▲).

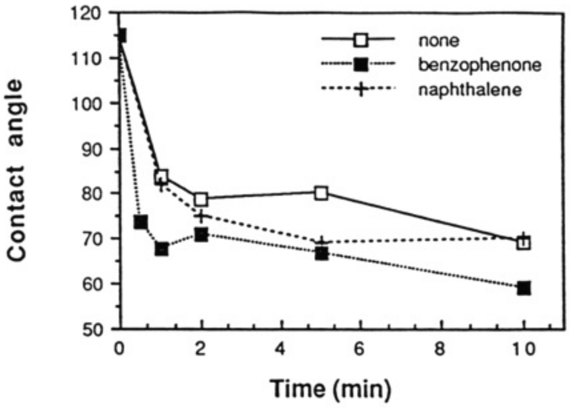

Figure 2. Effect of added accelerators on reduction of PTFE film as measured by changes in contact angle (H_2O) as a function of exposure time. The reducing agent is 0.025 M $NaSCH(CH_3)CH(CH_3)ONa$ in DMF.

2/1 DMF/THF solution containing sodium thiophenoxide was recorded, showing the expected peaks. The NMR tube was then irradiated with a 100-W 366-nm lamp for 1-3 h. The ^{19}F NMR spectrum clearly showed the appearance of new peaks, while an identical sample in the dark showed no change. Similarly, an irradiated solution of perfluorodecalin or perfluorocyclohexane and tetramethyl-*p*-phenylenediamine turned dark blue and showed the appearance of NMR signals[6] for perfluorobicyclo[4.4.0]dec-9(10)-ene (δ (CCl_3F) −111 (8 F), −135 (8 F)) or perfluorocyclohexene (δ (CCl_3F) −119 (2 F), −134 (2 F), −151 (2 F)), respectively, and other materials.

Discussion. The mechanism of this novel photochemical modification of the PTFE surface is not known. Since the reducing power of many organic donors is known to be increased by photoexcitation,[7] it is tempting to speculate that it involves electron transfer from the excited donor to the PTFE surface. Sequential electron transfer and fluoride ion loss, similar to that proposed for chemical reductions of fluoropolymers,[3,8] will generate an unsaturated, defluorinated surface, which is hydrophilic and can react with nucleophiles or other polar materials in solution.

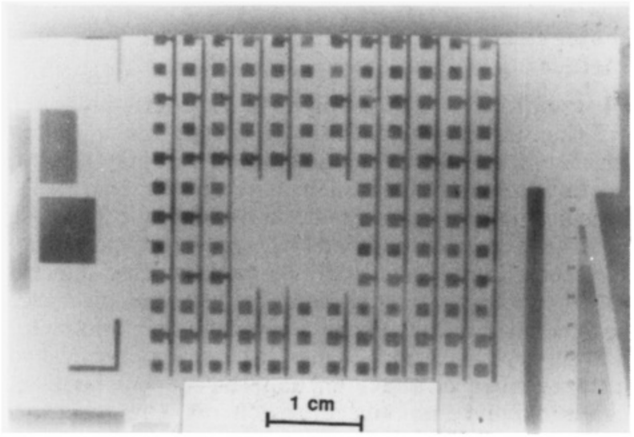

Figure 3. Photograph of PTFE film surface after irradiated through a mask in the presence of 0.1 M monosodium 2-mercaptoethanol and 0.025 M thioxanthone in DMF. Irradiation time was 0.5 h.

Regardless of the mechanism, this novel, one-step method for the imagewise introduction of surface functionality on perfluoropolymers may have a number of potential applications, including the preparation of circuit boards and lithographic plates. In contrast to the known methods, it requires neither dangerous reagents nor complex equipment. Investigations on the scope and applications of the process, and on the mechanism of the small molecule reactions, are in progress.

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