

# Highly Wettable Polyethylene Films Generated by Spontaneous Surface Enrichment of Perfluoroalkylated Phosphorylcholines

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**ABSTRACT:** We report here a new feature for highly wettable polyethylene films prepared by spontaneous surface enrichment of perfluoroalkylated phosphorylcholine (PC) additives via a simple heat-press technique. Perfluoroalkylated PCs were newly synthesized from monohydroxyethyl ether compounds with hexafluoromethylene (C<sub>6</sub>F<sub>13</sub>PC), octafluoromethylene (C<sub>8</sub>F<sub>17</sub>PC), and decafluoromethylene (C<sub>10</sub>F<sub>21</sub>PC) chains. Hexadecyl phosphorylcholine (C<sub>16</sub>PC) was synthesized as a control. These PC additives were mixed well with low-density polyethylene (LDPE) microparticles ( $\phi = 6 \mu\text{m}$ ), placed between stainless plates, and pressed at 120°C. Perfluoroalkylated PCs effectively improved the surface wettability of the composite film compared with that of the alkylated PC. C<sub>8</sub>F<sub>17</sub>PC is extremely surface active in the

LDPE matrix and occupies  $\sim 95\%$  of the outermost  $\sim 10 \text{ \AA}$ . The water contact angle data for the LDPE film was decreased from  $94^\circ/81^\circ$  ( $\theta_A/\theta_R$ ) to  $28^\circ/8^\circ$  by the addition of an approximately low concentration of C<sub>8</sub>F<sub>17</sub>PC (3.3% w/w) because of spontaneous enrichment on the surface. When the elongation to break value of the films was slightly reduced with the PC additives, Young's modulus and the tensile strength of the composite films were similar to those of pure LDPE film. In conclusion, fluoroalkylated PCs have good potential as additives to improve the wettability of thermoplastic polymers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2868–2874, 2006

**Key words:** perfluoroalkylated phosphorylcholine; surface modification; wettability; low-density polyethylene (LDPE)

## INTRODUCTION

Recently, there has been a great deal of interest in the control of surface wettability in both research and technology because of the possibilities of many potential applications.<sup>1</sup> Improvements in the hydrophilicity of polymer surfaces can be accomplished by several methods<sup>2</sup> including chemical treatment, plasma-, corona-, photo-irradiation, etc. While these approaches have been quite successful, new processes for surface modification for use with specific equipment are always needed.

To this end, surface modification via surface enrichment of one component of a multicomponent system, the driving force of surface modification in such a system, is largely thermodynamic where the component with the lowest critical surface tension rises to the air/polymer interface, thereby lowering interfacial free energy. Consequently, fluorochemicals and fluoropolymers have often been studied as surface-modifying molecules for various applications.<sup>3–8</sup> To enhance additive efficiency, suitable conditions such as solvents,

annealing temperature, and chemical structures were optimized. The surfaces normally show a highly hydrophobic and lyophobic nature. In contrast, Yuan and Shoichet demonstrated that the application of trifluorovinyl ether polymers could enhance the surface wettability of poly(styrene) films.<sup>9</sup> They prepared blend film by the solvent casting method; the surface hydrophilicity on the film depended on the type of solvent.

We have been studying 2-methacryloyloxyethyl phosphorylcholine (MPC) polymers synthesized as biomimetics of biomembrane structures.<sup>10–13</sup> MPC is a highly hygroscopic monomer because of the zwitterionic phosphorylcholine group. MPC polymers have a surface that resists nonspecific protein adsorption and cell adhesion, i.e., “biofouling.”<sup>14,15</sup> Biofouling reduces a material's functionality and can induce an unexpected bioreaction. Further, it has been shown that cells in contact with MPC polymers do not exhibit activation or an inflammatory response.<sup>16,17</sup> Using MPC polymers, the surface modification of conventional polymers such as polyurethane,<sup>18</sup> polysulfone,<sup>19</sup> and polyolefine<sup>20</sup> by blending has been studied. Although these blend polymers showed excellent “nonbiofouling” properties, solvents and their evaporation conditions for casting polymers were found to be important for enriching the surfaces of MPC polymers.

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Recently, Nederberg et al. reported on the synthesis and characterization of phosphorylcholine-end capped poly( $\epsilon$ -caprolactone) (PCL-PC) as polymeric additives in a poly( $\epsilon$ -caprolactone) (PCL) membrane. Surface rearrangement and enrichment of the PCL-PC occurred on the PCL membrane by use of the hot-water treatment and resulted in improved surface wettability.<sup>21,22</sup> An environmentally responsive surface (smart surface) with a polymer blend was also demonstrated by Anastasiadis et al.<sup>23</sup> They synthesized polystyrene-*block*-polyisoprene diblocks with hydrophilic groups such as a sulfobetaine- and a dimethylamine group at the end of a low energy polyisoprene block and mixed with polystyrene homopolymer.<sup>23</sup> The wettability of the blend polymer changed with environmental humidity. The surface response demonstrated good harmonization of a hydrophilic functional group and the polyisoprene block. To make additives having PC groups and low energy chemicals or polymers, spontaneous PC-enriched surfaces would be obtained from polymer blending.

We report here on the preparation of highly wettable polyethylene films with small amounts of perfluoroalkylated phosphorylcholine (PC) additives by the heat-press technique. The effects of chemical structure and fluoroalkyl chain length on surface modification were studied.

## EXPERIMENTAL

### Materials

2-(Perfluorohexyl)ethanol ( $C_6F_{13}OH$ ), 2-(perfluorooctyl)ethanol ( $C_8F_{17}OH$ ), and 2-(perfluorodecyl)ethanol ( $C_{10}F_{21}OH$ ) were purchased from Daikin, Tokyo, Japan. 2-Chloro-2-oxo-1,3,2-dioxaphospholane (COP) was obtained from NOF, Tokyo, Japan. Tetrahydrofuran (THF), acetonitrile (MeCN), triethylamine (TEA), and trimethylamine (TMA) were purified by distillation. All other chemicals were used without further purification.

### Synthesis of perfluoroalkylated phosphorylcholines ( $C_nF_{2n+1}PCs$ )

Perfluoroalkylated phosphorylcholines ( $n = 6, 8, 10$ ) were synthesized by an improved process of MPC synthesis.<sup>24</sup> Briefly, a solution of 6.43 g (45.0 mmol) of 2-chloro-2-oxo-1,3,2-dioxaphospholane in 25 mL of dry THF was added dropwise to a mixture of 16.38 g (45.0 mmol) of  $C_6F_{13}OH$  and 4.55 g (45.0 mmol) of TEA in 120 mL dry THF at 0°C for 1 h and at room temperature for another 1 h under a nitrogen atmosphere. The triethylamine hydrochloride salt precipitate was filtered off. The filtrate was evaporated under reduced pressure up to half its volume. The concentrated solution of 1-(2-oxo-1,3,2-dioxaphospholan-2-yloxy)-2-

(perfluorohexyl)ethane and 150 mL of dry MeCN were placed in a glass pressure bottle. After the mixture was cooled to  $-20^\circ C$ , 15 mL of anhydrous TMA was added, and the reaction was allowed to continue at  $70^\circ C$  for 12 h. The reaction mixture was again cooled to  $-20^\circ C$  to precipitate 2-(perfluorohexyl)ethyl phosphorylcholine ( $C_6F_{13}PC$ ).

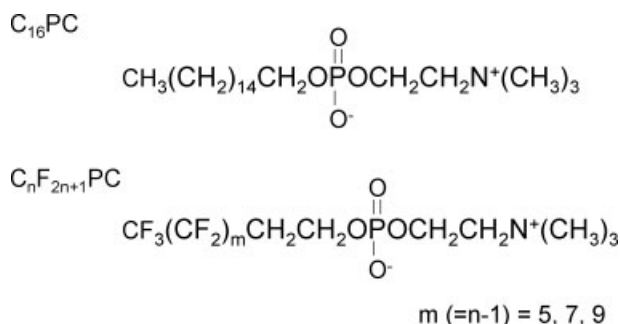
$^1H$  NMR ( $CD_3OD$ )  $\delta = 2.59$  (m,  $CF_2CH_2$ , 2H), 3.21 (s,  $-N^+(CH_3)_3$ , 9H), 3.63 (t,  $-CH_2N^+$ , 2H), 4.19 (m,  $-CH_2OP-$ , 2H), 4.27(br,  $-OPCH_2-$ , 2H);  $^{19}F$  NMR ( $CD_3OD$ )  $\delta = -81.40$  ( $CF_3$ , 3F),  $-113.39$  ( $CF_2CH_2$ , 2F),  $-121.75$  ( $(CF_2)_3CF_2CH_2$ , 6H),  $-122.58$  ( $CF_3CF_2CF_2CF_2CF_2$ , 2F),  $-123.49$  ( $CF_3CF_2CF_2$ , 2F),  $-126.11$  ( $CF_3CF_2$ , 2F); IR ( $cm^{-1}$ ): 2910 ( $-CH_2-$ ), 1300 (P=O), 1235 ( $-OPO-$ ), 1085 ( $-OPOCH_2-$ ), 970 ( $N^+(CH_3)_3$ ).

$C_8F_{17}PC$  and  $C_{10}F_{21}PC$  were also synthesized by a method similar to that described above. Hexadecyl phosphorylcholine ( $C_{16}PC$ ) was synthesized as previously reported.<sup>25</sup> Figure 1 shows the chemical structure of the PC additives synthesized in this study.

### Preparation of composite low-density polyethylene films with PC additives

The low-density polyethylene (LDPE) used as the base material in particle form was purchased from Sumitomo Seika Chemicals (Flow beads LE-1080, Osaka, Japan). The average diameter was 6  $\mu m$ .

The LDPE and composite films with PC additives were processed by a heat-press technique. Typically, the LDPE particles (0.5 g) and 2-(perfluorodecyl)ethyl phosphorylcholine ( $C_{10}F_{21}PC$ , 0.05 g,  $6.86 \times 10^{-5}$  mol) were mixed and thoroughly ground in a mortar. The mixed powder was then placed between two stainless steel plates and pressed at a pressure of about 5 MPa at  $120^\circ C$  for 3 min. To determine the appropriate  $C_{10}F_{21}PC$  composition, we prepared films with different blend ratios [ $C_{10}F_{21}PC/LDPE = 1/10$  (0.05 g,  $6.86 \times 10^{-5}$  mol/0.5 g);  $1/25$  (0.02 g,  $2.74 \times 10^{-5}$  mol/0.5 g);  $1/50$  (0.01 g,  $1.37 \times 10^{-5}$  mol/0.5 g); and  $1/100$  (0.005 g,  $6.86 \times 10^{-6}$  mol/0.5 g) by weight]. Other PC compounds were mixed with LDPE particles with molar compositions similar to that of  $C_{10}F_{21}PC$ .



**Figure 1** Chemical structure of alkylated and perfluoroalkylated PC.

To determine the elution amount of the PC additives from the composite films, the films were immersed in water or ethanol with gentle shaking. The solvents were changed three times at 2-h intervals, and the concentration of the PC additives was determined by phosphorus analysis.

### Surface analysis

X-ray photoelectron spectroscopy (XPS) was performed on a Scienta ESCA-200 spectrometer with Al K $\alpha$ . Survey scan spectra of C<sub>1s</sub>, O<sub>1s</sub>, N<sub>1s</sub>, P<sub>2p</sub>, and F<sub>1s</sub> were obtained. All XPS data were collected at takeoff angles of 15° and 75° (between the specimen surface and the detector).

The dynamic contact angles for the samples were recorded as the probe fluid, water (deionized to 18.2 M $\Omega$ ), using a First Ten Angstroms FT-125 goniometer and Gilmont syringes. The advancing ( $\theta_A$ ) and receding ( $\theta_R$ ) contact angles were measured at addition to and withdrawal from the drop, respectively.

### Evaluation of mechanical properties

Tensile strength measurements were performed using an STA-1150 (ORIENTEC, Tokyo, Japan). The samples

were cut into dog-bone shape (size, 12.5 mm  $\times$  2.5 mm). The crosshead speed was 2 mm/min. Four specimens were tested. Within the region of elongation from 0 to 5%, the strain–stress curves were linear. Young's modulus was then obtained from this initial elastic region.

## RESULTS AND DISCUSSION

### Surface activity of perfluoroalkylated PCs

The perfluoroalkylated PCs with different perfluoroalkyl chain lengths were obtained as a white powder. C<sub>6</sub>F<sub>13</sub>PC was readily soluble in water and ethanol. C<sub>8</sub>F<sub>17</sub>PC and C<sub>16</sub>PC were soluble in water, but the solutions at this concentration were very viscous, resembling hydrogel, indicating that the intramolecular interaction of these molecules is high in an aqueous solution. In addition, the C<sub>16</sub>PC aqueous solution was turbid. These additives were easily soluble in ethanol. In contrast, C<sub>10</sub>F<sub>21</sub>PC was not soluble in water or ethanol.

Several groups have shown that perfluoroalkyl groups that are incorporated into polymers are surface active<sup>7,26–33</sup> and adsorb at free polymer interfaces due to minimization of surface free energy. We tested the incorporation of the perfluoroalkyl groups with the PC groups to enhance the efficiency of the

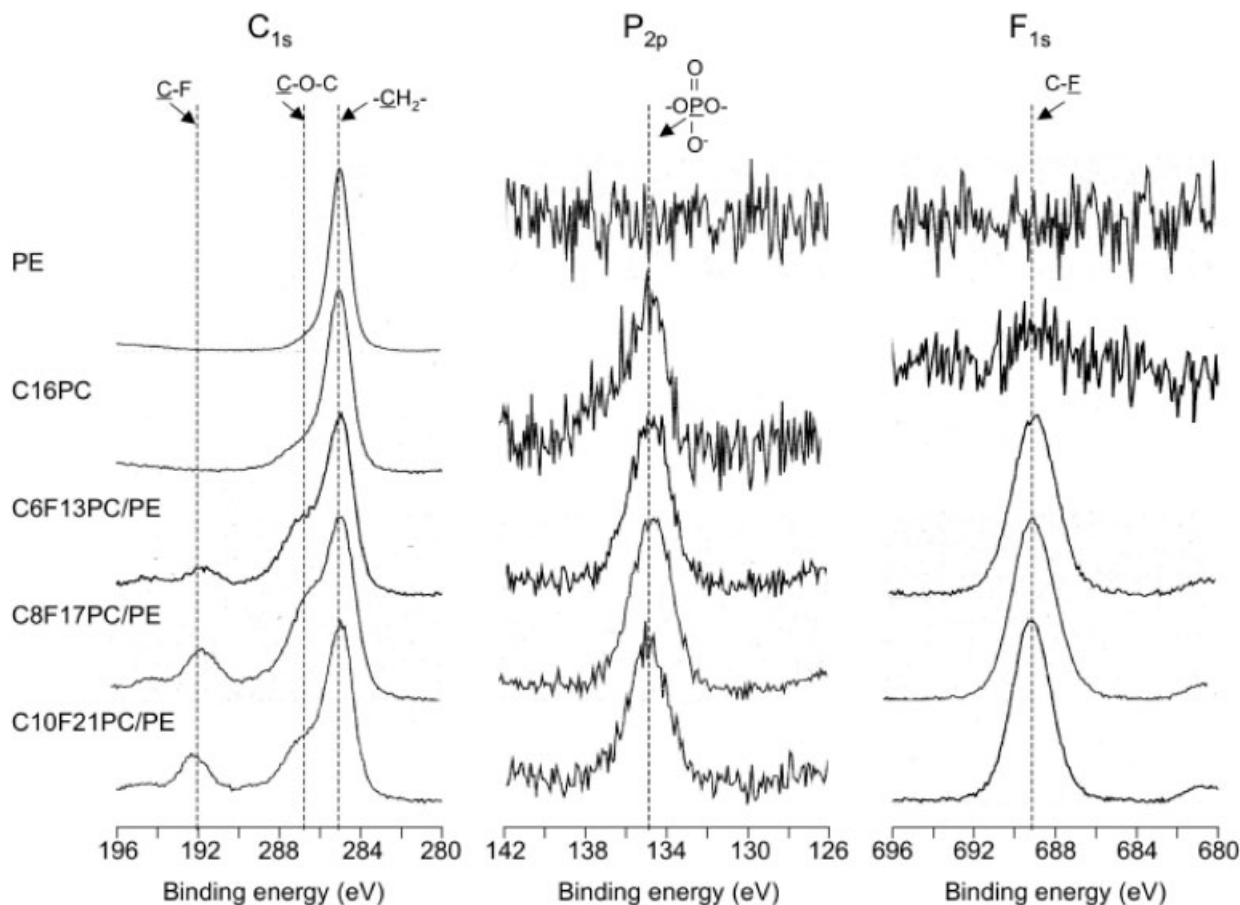


Figure 2 XPS spectra of PE and composite polymer films.

TABLE I  
XPS Data for Polymer Films

Films	Composition of PC additives		Takeoff angle (°)	XPS elemental data (%)				
	(mol)	(% w/w)		C	O	N	P	F
C <sub>16</sub> PC/PE	6.86 × 10 <sup>-6</sup>	0.6	15	90.07	8.96	0.34	0.63	
			75	98.71	1.07	0.19	0.03	
	1.37 × 10 <sup>-5</sup>	1.1	15	94.21	4.43	0.45	0.91	
			75	96.54	2.65	0.45	0.36	
			75	91.40	6.71	0.82	1.07	
2.74 × 10 <sup>-5</sup>	2.2	15	88.74	8.84	1.18	1.24		
6.86 × 10 <sup>-5</sup>	5.3	15	93.75	3.20	1.50	1.55		
C <sub>10</sub> F <sub>21</sub> /PC/PE	6.86 × 10 <sup>-6</sup>	1.0	15	84.45	7.06	0.64	0.58	7.27
			75	80.73	4.97	0.33	0.54	13.43
	1.37 × 10 <sup>-5</sup>	2.0	15	76.17	7.03	0.42	0.93	15.45
			75	82.93	4.07	0.33	0.43	12.24
			75	56.30	9.17	0.67	1.48	32.38
2.74 × 10 <sup>-5</sup>	3.8	15	42.49	10.33	1.19	1.95	44.04	
6.86 × 10 <sup>-5</sup>	9.1	15	65.10	7.20	2.40	2.30	23.00	
C <sub>8</sub> F <sub>17</sub> /PC/PE	6.86 × 10 <sup>-6</sup>	0.9	15	84.51	7.30	0.37	1.18	6.64
			75	89.04	2.87	0.23	0.36	7.50
	1.37 × 10 <sup>-5</sup>	1.7	15	36.37	6.71	1.07	2.62	53.23
			75	47.67	10.04	1.20	1.73	39.36
			75	38.26	8.02	1.76	2.64	49.32
2.74 × 10 <sup>-5</sup>	3.3	15	48.32	10.62	1.07	1.94	38.05	
6.86 × 10 <sup>-5</sup>	7.9	15	37.50	8.00	2.00	2.80	49.70	
C <sub>6</sub> F <sub>15</sub> /PC/PE	6.86 × 10 <sup>-6</sup>	0.7	15	80.77	8.89	0.47	1.08	8.79
			75	75.34	7.38	0.68	0.81	15.79
	1.37 × 10 <sup>-5</sup>	1.4	15	79.32	3.88	0.49	1.36	14.95
			75	85.63	3.14	0.46	0.57	10.20
			75	58.17	13.27	1.25	1.80	25.51
2.74 × 10 <sup>-5</sup>	2.8	15	60.98	11.03	1.14	1.80	25.05	
6.86 × 10 <sup>-5</sup>	6.8	15	52.90	10.90	2.50	2.10	31.60	

additives in the LDPE films that resulted in highly hydrophilic surfaces.

Figure 2 shows the XPS spectra of LDPE and composite films, which are corrected at a takeoff angle of 15°. For the original LDPE film, a strong intensity at 285 eV was observed and attributed to carbon atoms in the methylene chains of the polyethylene backbone. Mixing the PC additives with the PE particles dramatically changed the XPS spectra of the fabricated films. In every C<sub>1s</sub> spectrum of the composite films, a shoulder was observed at 286.5 eV. This shoulder could be attributed to the ether bonds (C—O) of the PC additives. In addition, for films mixed with fluoroalkylated PCs a peak was observed at 290 eV. This peak corresponded to the carbon atom bonded to fluorine (C—F). A peak ascribed to phosphorus was observed at 134.1 eV. This could be attributed to the phosphorylcholine group in the PC additives. The spectra of the phosphorus of the films containing fluoroalkylated PCs were clearer than that of those containing C<sub>16</sub>PC. This means that enrichment of fluoroalkylated PC is preferred. At 680 eV, a fluorine signal was also observed on the fluoroalkylated PC composite film.

The XPS elemental concentrations for the polymer films are summarized in Table I. The nitrogen and

phosphorus concentrations increased with an increase in the composition of the PC additives in the feed. In particular, the surface concentrations for these elements were remarkably high when C<sub>8</sub>F<sub>17</sub>PC was used as the additive. Figure 3 shows the effect of the PC additives on surface enrichment of the composite films. While the P/C ratio did not change remarkably with the bulk composition of C<sub>16</sub>PC, the ratio did increase with an increase in the composition of perfluoroalkylated phos-

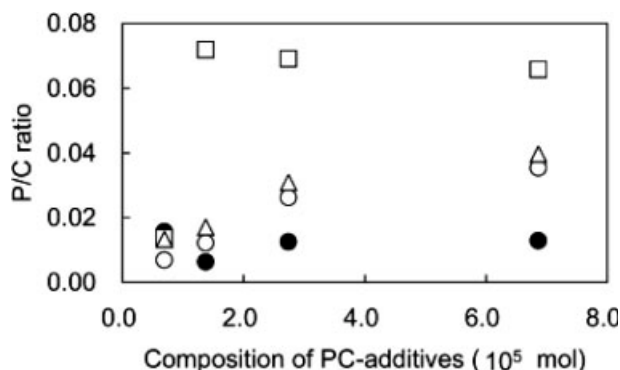


Figure 3 Surface P/C ratio versus bulk composition films. Filled circle: C<sub>16</sub>PC/PE, Open circle: C<sub>6</sub>F<sub>13</sub>PC/PE, Open square: C<sub>8</sub>F<sub>17</sub>PC/PE, Open triangle: C<sub>10</sub>F<sub>21</sub>PC/PE.



phorylcholine. In particular, the phosphorus concentration of the C<sub>8</sub>F<sub>17</sub>PC/LDPE film was significantly higher than that of other composite films with low molar C<sub>8</sub>F<sub>17</sub>PC ( $1.37 \times 10^{-5}$  mol, 1.7% w/w).

The 15° takeoff angle data indicate the composition of the outermost ~ 10 Å of the samples; the 75° takeoff angle spectra assess the outer ~ 40 Å.<sup>34</sup> Comparison of the atomic concentration obtained from XPS to the chemical composition of C<sub>8</sub>F<sub>17</sub>PC (C, 29.63%; O, 10.17%, N, 2.23; P, 4.92%; F, 51.33%) indicates that there is ~ 95% C<sub>8</sub>F<sub>17</sub>PC in the outer 10 Å and ~ 75% C<sub>8</sub>F<sub>17</sub>PC in the outer 40 Å when the compositions are calculated from the concentration of fluorine. From the concentration of phosphorus, there is ~ 55% C<sub>8</sub>F<sub>17</sub>PC in the outer 10 Å and ~ 40% C<sub>8</sub>F<sub>17</sub>PC in the outer 40 Å. The molecular size of C<sub>8</sub>F<sub>17</sub>PC is ~ 18 Å, and the fluoroalkyl chains of C<sub>8</sub>F<sub>17</sub>PC were partially oriented to the outer surface. When C<sub>6</sub>F<sub>13</sub>PC and C<sub>10</sub>F<sub>21</sub>PC were added to LDPE with a similar concentration ( $2.74 \times 10^{-5}$  mol), the surface coverage calculated from the concentration of fluorine was ~ 55% and ~ 60% in the outer 10 Å, respectively. For C<sub>6</sub>F<sub>13</sub>PC, the surface coverage calculated from the concentration of phosphorus was 30%; the XPS elemental concentrations at 15° and 75° were quite similar. This result indicated that the distribution of C<sub>6</sub>F<sub>13</sub>PC in the outer 40 Å was uniform. Moreover, the concentration of fluorine in the outer 40 Å was higher than that in the outer 10 Å when C<sub>10</sub>F<sub>21</sub>PC ( $2.74 \times 10^{-5}$  mol) was added. The surface activity and dispersity of C<sub>8</sub>F<sub>17</sub>PC in the LDPE matrix may be optimum for the enrichment of LDPE film surfaces.

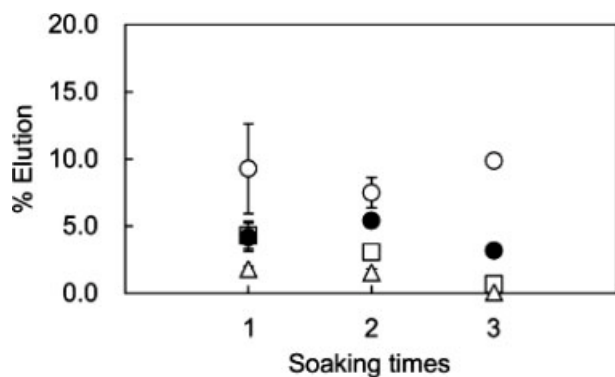
Surface contact angle data for polymer films were measured with water, as shown in Table II. The water contact angle data for the LDPE film was  $\theta_A/\theta_R = 97^\circ/81^\circ$ . The contact angles decreased with an increase in the composition of the PC additives. On the C<sub>16</sub>PC/LDPE surface, the contact angles reached  $\theta_A/\theta_R = 43^\circ/15^\circ$  when the composition of C<sub>16</sub>PC was  $6.86 \times 10^{-5}$  mol (5.3% w/w). At this concentration, the surface coverage of C<sub>16</sub>PC was ~ 15% calculated from XPS data and was lower than that of fluoroalkylated PCs. The water contact angles of the C<sub>16</sub>PC/LDPE film were then relatively high.

The surface contact angles ( $\theta_A/\theta_R$ ) of C<sub>8</sub>F<sub>17</sub>PC/LDPE were dramatically decreased at 28°/8° with  $2.74 \times 10^{-5}$  mol C<sub>8</sub>F<sub>17</sub>PC (3.3% w/w) and 17°/< 5° with  $6.86 \times 10^{-5}$  mol C<sub>8</sub>F<sub>17</sub>PC (7.9% w/w). The effects of C<sub>6</sub>F<sub>13</sub>PC and C<sub>10</sub>F<sub>21</sub>PC on improving surface wettability were less than that of C<sub>8</sub>F<sub>17</sub>PC because of their low surface coverage.

Figure 4 shows % elution of PC additives from composite films after soaking films containing  $6.86 \times 10^{-5}$  mol of PC additives in ethanol for 2 h. The elution amount of fluoroalkyl PCs was significantly lower than that of alkyl PCs. In particular, the elution amount of C<sub>8</sub>F<sub>17</sub>PC and C<sub>10</sub>F<sub>21</sub>PC was reduced with an increase in the soaking frequency and elution did not occur after three soakings. The elution amount of PC additives from LDPE films in water was also determined to be much lower than that in ethanol and C<sub>8</sub>F<sub>17</sub>PC after 24 h of soaking under gentle shaking. The amount was 0.4% or less for  $6.86 \times 10^{-5}$  mol (7.9% w/w) and 0.1% or less for  $1.37 \times 10^{-5}$  mol

TABLE II  
Water Contact Angle Data for Polymer Films

Films	Composition of PC additives		$\theta_A/\theta_R$ (°)	
	(mol)	(% w/w)	Post-preparation	After soaking in EtOH
PE			98/81	105/92
C <sub>16</sub> PC/PE	$6.86 \times 10^{-6}$	0.6	87/61	
	$1.37 \times 10^{-5}$	1.1	87/68	
	$2.74 \times 10^{-5}$	2.2	64/30	75/17
	$6.86 \times 10^{-5}$	5.3	43/15	41/17
C <sub>10</sub> F <sub>21</sub> /PC/PE	$6.86 \times 10^{-6}$	1.0	86/65	
	$1.37 \times 10^{-5}$	2.0	93/55	
	$2.74 \times 10^{-5}$	3.8	90/59	81/26
	$6.86 \times 10^{-5}$	9.1	38/10	91/21
C <sub>8</sub> F <sub>17</sub> /PC/PE	$6.86 \times 10^{-6}$	0.9	82/67	
	$1.37 \times 10^{-5}$	1.7	81/8	
	$2.74 \times 10^{-5}$	3.3	28/8	16/10
	$6.86 \times 10^{-5}$	7.9	17/<5	18/10
C <sub>6</sub> F <sub>15</sub> /PC/PE	$6.86 \times 10^{-6}$	0.7	84/62	
	$1.37 \times 10^{-5}$	1.4	79/29	
	$2.74 \times 10^{-5}$	2.8	68/32	94/55
	$6.86 \times 10^{-5}$	6.8	26/11	26/10



**Figure 4** Percentage elution of PC additives from composite films soaked in ethanol. Filled circle: C<sub>16</sub>PC/PE, Open circle: C<sub>6</sub>F<sub>13</sub>PC/PE, Open square: C<sub>8</sub>F<sub>17</sub>PC/PE, Open triangle: C<sub>10</sub>F<sub>21</sub>PC/PE.

(1.7% w/w). This solvent dependence of the elution might be due to the solubility of the PC additives.

Molecular design such as macromolecular approaches to improve stability and further surface treatments to reduce elution of PC additives from composite films are now under study.

Figure 5 shows photographs of typical water drops on LDPE and C<sub>8</sub>F<sub>17</sub>PC/LDPE after the elution test in ethanol. When a water drop on LDPE film is round in shape, the shape spreads out completely on the C<sub>8</sub>F<sub>17</sub>PC/PE film with  $2.74 \times 10^{-5}$  mol of C<sub>8</sub>F<sub>17</sub>PC (3.3% w/w). The surface wettability of the composite film was present even after ethanol soaking, as shown in Table II.

#### Mechanical properties of LDPE films containing PC additives

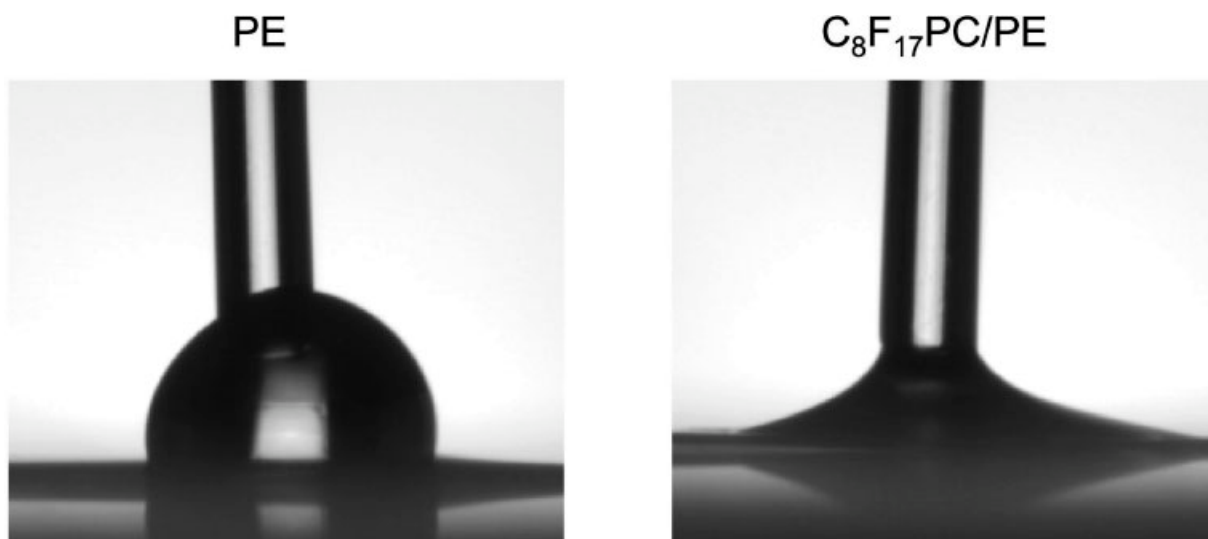
Table III shows the mechanical properties of the composite films. By mixing PC additives, Young's modu-

lus of films was relatively higher than that of the LDPE film. Every PC additive was a powdery solid at the measuring temperature and the composite films were then rigid. When the fracture strength was not changed by the addition of PC additives, the elongation of the composite films was reduced. This phenomenon might be due to an incompatibility of the PC additives and LDPE matrix. Although C<sub>16</sub>PC has a long alkyl chain, which would be more compatible with PE compared with that of the perfluoroalkylated chain, the elongation of the composite film with C<sub>16</sub>PC was much less. Fluoroalkylated PCs effectively enriched the LDPE surface and had less influence on the bulk property of the LDPE films.

#### CONCLUSIONS

Perfluoroalkylated PCs are potential additives for improving the wettability of LDPE film. Perfluoroalkylated PC was spontaneously enriched on the film surface using a heat-press technique. High wettability can be obtained without chemical or physical treatment. In addition, no solvent was needed. In particular, C<sub>8</sub>F<sub>17</sub>PC, which has an octafluoromethylene chain, is most effective for achieving this. The thermal stability of phosphorylcholine groups has been assured at 150°C.<sup>35</sup> Therefore, perfluoroalkylated PCs can be applied for surface modification of other thermoplastic polymers.

There has been a considerable amount of physicochemical- and biotechnological-related interest in PC-enriched surfaces, which show unique properties such as hydrophilicity,<sup>36</sup> zero  $\zeta$ -potential (neutral),<sup>37</sup> high lubrication,<sup>38</sup> and biocompatibility.<sup>39</sup> Therefore, surface modification with spontaneous PC enrichment is important for producing high performance polymeric materials.



**Figure 5** Photographs of water drops on PE and C<sub>8</sub>F<sub>17</sub>PC/PE films (C<sub>8</sub>F<sub>17</sub>PC =  $1.37 \times 10^{-5}$  mol) after elution test.

TABLE III  
Mechanical Properties of Polymer Films

	Composition of PC additives		Young's modulus (MPa)	Fracture strength (MPa)	Averaged fracture strain (%)
	(mol)	(% w/w)			
PE			61.9 ± 1.5	5.83 ± 0.32	80.1
C <sub>16</sub> PC/PE	2.74	2.2	71.6 ± 4.4	5.49 ± 0.44	45.9
	6.86	5.3	60.8 ± 2.7	5.45 ± 0.32	46.3
C <sub>10</sub> F <sub>21</sub> /PC/PE	2.74	3.8	75.7 ± 5.3	5.72 ± 0.36	52.1
	6.86	9.1	68.3 ± 3.1	5.49 ± 0.25	58.3
C <sub>8</sub> F <sub>17</sub> /PC/PE	2.74	3.3	79.3 ± 6.9	6.00 ± 0.23	57.4
	6.86	7.9	68.9 ± 3.6	5.53 ± 0.19	56.5
C <sub>6</sub> F <sub>15</sub> /PC/PE	2.74	2.8	75.2 ± 1.1	5.68 ± 0.43	60.3
	6.86	6.8	68.5 ± 4.4	5.56 ± 0.28	54.1

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## References

- Andrade, J. D. *Surface and Interfacial Aspects of Biomedical Polymers*, Vol. 1: Surface Chemistry and Physics; Plenum: New York, 1985.
- Ruardy, T. G.; Schakenraad, J. M.; vanderMei, H. C.; Busscher, H. J. *Surf Sci Rep* 1997, 29, 3.
- Kano, Y.; Akiyama, S. *Polymer* 1996, 37, 4497.
- Thomas, R. T.; Anton, D. R.; Graham, W. F.; Darmon, M. J.; Sauer, B. B.; Stika, K. M.; Swartzfager, D. G. *Macromolecules* 1997, 30, 2883.
- Chen, W.; McCarthy, T. J. *Macromolecules* 1999, 32, 2342.
- Ebbens, S. J.; Badyal, J. P. S. *Langmuir* 2001, 17, 4050.
- Walters, K. B.; Schwark, D. W.; Hirt, D. E. *Langmuir* 2003, 19, 5851.
- McCloskey, C. B.; Yip, C. M.; Santerre, J. P. *Macromolecules* 2002, 35, 924.
- Yuan, Y.; Shoichet, M. S. *Macromolecules* 2000, 33, 4926.
- Iwasaki, Y.; Mikami, A.; Kurita, K.; Yui, N.; Ishihara, K.; Nakabayashi, N. *J Biomed Mater Res* 1997, 36, 508.
- Iwasaki, Y.; Sawada, S.; Nakabayashi, N.; Khang, G.; Lee, H. B.; Ishihara, K. *Biomaterials* 1999, 20, 2185.
- Ishihara, K.; Ishikawa, E.; Iwasaki, Y.; Nakabayashi, N. *J Biomater Sci Polym Ed* 1999, 10, 1047.
- Iwasaki, Y.; Nakabayashi, N.; Ishihara, K. *J Biomed Mater Res* 2001, 57, 72.
- Ishihara, K.; Oshida, H.; Endo, Y.; Ueda, T.; Watanabe, A.; Nakabayashi, N. *J Biomed Mater Res* 1992, 26, 1543.
- Ishihara, K.; Nomura, H.; Mihara, T.; Kurita, K.; Iwasaki, Y.; Nakabayashi, N. *J Biomed Mater Res* 1998, 39, 323.
- Iwasaki, Y.; Sawada, S.; Ishihara, K.; Khang, G.; Lee, H. B. *Biomaterials* 2002, 23, 3897.
- Sawada, S.; Sakaki, S.; Iwasaki, Y.; Nakabayashi, N.; Ishihara, K. *J Biomed Mater Res A* 2003, 64, 411.
- Ishihara, K.; Shibata, N.; Tanaka, S.; Iwasaki, Y.; Kurosaki, T.; Nakabayashi, N. *J Biomed Mater Res* 1996, 32, 401.
- Hasegawa, T.; Iwasaki, Y.; Ishihara, K. *Biomaterials* 2001, 22, 243.
- Ishihara, K.; Nishiuchi, D.; Watanabe, J.; Iwasaki, Y. *Biomaterials* 2004, 25, 1115.
- Nederberg, F.; Bowden, T.; Nilsson, B.; Hong, J.; Hilborn, J. *J Am Chem Soc* 2004, 126, 15350.
- Nederberg, F.; Bowden, T.; Hilborn, J. *Macromolecules* 2004, 37, 954.
- Anastasiadis, S. H.; Retsos, H.; Pispas, S.; Hadjichristidis, N.; Neophytides, S. *Macromolecules* 1994, 2003, 36.
- Ishihara, K.; Ueda, T.; Nakabayashi, N. *Polym J* 1990, 22, 355.
- Kang, E. C.; Kataoka, S.; Kato, K. *Bull Chem Soc Jpn* 2005, 78, 1558.
- Iyengar, D. R.; Perutz, S. M.; Dai, C.-A.; Ober, C. K.; Kramer, E. J. *Macromolecules* 1996, 29, 1229.
- Schaub, T. F.; Kellogg, G. J.; Mayes, A. M.; Kulasekera, R.; Ankner, J. F.; Kaiser, H. *Macromolecules* 1996, 29, 3982.
- Affrossman, S.; Bertrand, P.; Hartshorne, M.; Kiff, T.; Leonard, D.; Pethrick, R. A.; Richards, R. W. *Macromolecules* 1996, 29, 5432.
- Affrossman, S.; Hartshorne, M.; Kiff, T.; Pethrick, R. A.; Richards, R. W. *Macromolecules* 1994, 27, 1588.
- Elman, J. F.; Johs, B. D.; Long, T. E.; Koberstein, J. T. *Macromolecules* 1994, 27, 5341.
- Hunt, M. O., Jr.; Belu, A. M.; Linton, R. W.; DeSimone, J. M. *Macromolecules* 1993, 26, 4854.
- Su, Z.; Wu, D.; Hsu, S. L.; McCarthy, T. J. *Macromolecules* 1997, 30, 840.
- Chen, W.; Franchina, N. L.; Viviano, K.; McCarthy, T. J. *Polym Mater Sci Eng* 1996, 75, 44.
- Clark, D. T.; Thomas, H. R. *J Polym Sci Polym Chem Ed* 1977, 15, 2843.
- Ogawa, R.; Iwasaki, Y.; Ishihara, K. *J Biomed Mater Res* 2003, 62, 214.
- Iwata, R.; Suk-In, P.; Hoven, V. P.; Takahara, A.; Akiyoshi, K.; Iwasaki, Y. *Biomacromolecules* 2004, 5, 2308.
- Ishihara, K.; Inoue, H.; Kurita, K.; Nakabayashi, N. *J Biomed Mater Res* 1994, 28, 1347.
- Moro, T.; Takatori, Y.; Ishihara, K.; Konno, T.; Takigawa, Y.; Matsushita, T.; Chung, U. I.; Nakamura, K.; Kawaguchi, H. *Nat Mater* 2004, 3, 829.
- Iwasaki, Y.; Ishihara, K.; 2005, *Anal Bioanal Chem* 2005, 381, 534.