

# Surface Properties of Miscible Poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate)/Phenoxy Blends

H. L. Huang,<sup>1</sup> S. H. Goh,<sup>1</sup> Doreen M. Y. Lai,<sup>2</sup> C. H. A. Huan,<sup>2,3</sup> A. T. S. Wee<sup>3</sup>

<sup>1</sup>Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543 Singapore

<sup>2</sup>Institute of Materials Research and Engineering, National University of Singapore, 3 Research Link, 117602 Singapore

<sup>3</sup>Department of Physics, National University of Singapore, 3 Science Drive 3, 117543 Singapore

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**ABSTRACT:** Poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) (PHF) is miscible with poly(hydroxyether of bisphenol-A) (phenoxy) as shown by the optical transparency and a single glass-transition temperature in each blend. FTIR spectroscopy shows that the interactions between PHF and phenoxy are not particularly strong. The surface properties of the blends were studied by contact angle measurements,

dynamic and static time-of-flight secondary ion mass spectroscopy, and X-ray photoelectron spectroscopy. The blend surfaces were enriched with PHF. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1798–1805, 2004

**Key words:** miscibility; blends; XPS; fluoropolymers; surface enrichment

## INTRODUCTION

The unique molecular properties associated with C—F bonding impart fluorinated polymers with specific, unique chemical and physical properties on air–polymer interfaces.<sup>1–4</sup> Although new fluorinated polymers have been synthesized, many of them are expensive and possess poor mechanical properties. As such, there is a need to develop new fluorinated materials that are less expensive and possess improved properties.<sup>5–11</sup> Blending of polymers offers a convenient and economical means of obtaining new materials that combine the advantages of the blend components.<sup>12,13</sup> For fluorinated/nonfluorinated polymer blends, the significantly lower surface energies of fluorinated polymers over their aliphatic analogs provide a substantial thermodynamic driving force for forming fluorinated surfaces. Therefore, the blends possess the surface properties of fluorinated polymers as well as the bulk properties of the nonfluorinated polymers.

When an amorphous fluorinated polymer is miscible with an amorphous nonfluorinated polymer arising from favorable specific interaction, the resulting miscible blend is optically clear. Such miscible blends may find applications as transparent coating materials with nonwetting surface characteristics. However, several recent studies have shown that specific interactions between component polymers in a miscible blend can affect the extent of surface enrichment of the

low surface energy component.<sup>14–16</sup> Strong interactions reduce or even eliminate the surface enrichment. Therefore to retain the nonwetting surface characteristics of miscible blends, the specific interactions are preferably not too strong and yet strong enough to ensure miscibility. This article reports the miscibility and surface properties of poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) (PHF)/poly(hydroxyether of bisphenol-A) (phenoxy) blends. Phenoxy is a commercially available thermoplastic with good mechanical properties and is miscible with some polymers through interactions involving its hydroxyl groups.<sup>17–20</sup> Among the poly(fluoroalkyl methacrylate)s we have studied, PHF is more readily miscible with other polymers presumably through the acidic hydrogens in its pendant hexafluoroisopropyl groups.<sup>21–23</sup>

## EXPERIMENTAL

### Materials

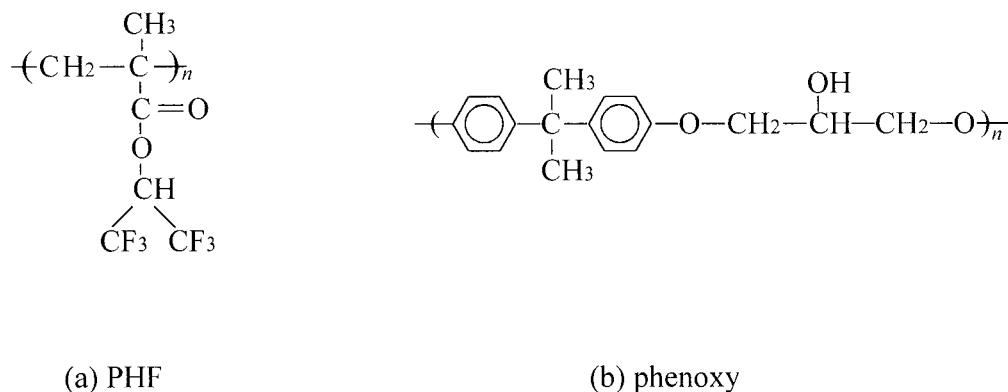
1,1,1,3,3,3-Hexafluoroisopropyl methacrylate (HF) was purchased from Aldrich Chemical Co. (Milwaukee, WI), and purified by distillation under reduced pressure. Poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) [PHF; weight-average molecular weight ( $M_w$ ) = 32 kg/mol] was synthesized by free-radical polymerization in tetrahydrofuran (THF) at 70°C using 0.2 wt % 2,2'-azobisisobutyronitrile (AIBN) as initiator. Phenoxy ( $M_w$  = 28 kg/mol) was purchased from Poly-science (Warrington, PA) and used as received.

### Preparation of blends

Appropriate amounts of PHF and phenoxy were dissolved in THF to form 2% (w/v) solutions and me-

Correspondence to: S. Goh (chmgohsh@nus.edu.sg).

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Scheme 1

chanically stirred for 24 h. Blends with PHF content lower than 1 wt % were prepared by diluting the PHF/phenoxy (1/99) blend with additional pure phenoxy. For films used in contact angle measurements, the polymer solutions were directly spin-coated onto 1 × 1 in. glass slides using a Laurell spin coater (WS-200-4T2/25P/HSP) (North Wales, PA) at a speed of 1400 rpm. For time-of-flight secondary ion mass spectroscopy (ToF-SIMS) measurements, the polymer solutions were spin-coated onto conductive aluminum foils. For attenuated total reflectance Fourier transform infrared (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) measurements, films (about 30 μm) were cast onto a clean Teflon wafer, and the films were allowed to air-dry, followed by further drying in a vacuum oven at 60°C. For DSC measurements, the solutions were poured into petri dishes where the solvent was allowed to evaporate slowly at room temperature, and further dried in a vacuum oven at 90°C for 2 weeks.

#### DSC measurements

The glass-transition temperature ( $T_g$ ) values of various blends were measured with a TA Instruments 2920 differential scanning calorimeter (DSC; TA Instruments, New Castle, DE) using a heating rate of 20°C/min. Each sample was subjected to three heating/cooling cycles to obtain reproducible  $T_g$  values. The initial onset point of the change of slope in the DSC curve was taken to be the  $T_g$ .

#### FTIR measurements

Both transmission Fourier transform infrared (TX-FTIR) and ATR-FTIR measurements were performed on a Bio-Rad 165 FTIR spectrophotometer (Bio-Rad, Hercules, CA). The TX-FTIR samples were prepared by adding polymer blend solutions onto KBr powder. The dried polymer blend-KBr mixtures were ground and pressed to form disks. For the collection of both

TX-FTIR and ATR-FTIR spectra, 256 scans were signal-averaged at a resolution of 2 cm<sup>-1</sup>. A Ge prism with 45° face cut was used as the internal reflectance element for all ATR-FTIR collections. The depth of penetration ( $d_p$ ) in the polymer films for the ATR-FTIR was estimated to be 0.8–1.0 μm, corresponding to a sampling depth ( $d_s$ , which is defined as  $d_s = 3d_p$ ) of 2.4–3.0 μm.<sup>24</sup>

#### Contact angle measurements

The static contact angles of water and diiodomethane on various samples were measured with an NRL-100-00-230 optical goniometer (Ramé-Hart, Mountain Lakes, NJ) using the sessile drop method in air atmosphere. The reported contact angles are an average of at least five measurements at different locations on the film surface. The measured angles were generally within ±2°. The surface energy ( $\gamma_s$ ) was calculated by means of the harmonic mean approximation<sup>25</sup>

$$(1 + \cos \theta_i) \gamma_i = 4 \left( \frac{\gamma_i^d \gamma_s^d}{\gamma_i^d + \gamma_s^d} + \frac{\gamma_i^p \gamma_s^p}{\gamma_i^p + \gamma_s^p} \right)$$

where superscripts  $d$  and  $p$  correspond to the dispersive and polar components of the surface energy, respectively; subscripts  $i$  and  $s$  denote the probe liquid and polymer film, respectively.

#### ToF-SIMS measurements

High-resolution mass spectra were obtained with a ToF-SIMS spectrometer, ION-ToF SIMS IV (ION-TOF, GmbH, Muenster, Germany). A pulsed primary ion source (Ar<sup>+</sup>, 10 keV, ~ 3 pA) was rastered over the sample area of 500 × 500 μm<sup>2</sup>. Mass spectra were acquired for 100 s with a fluence of <10<sup>12</sup> ions/cm<sup>2</sup> to ensure static conditions. No charge compensation was needed and mass resolution ( $m/\Delta m$ ) was typically >3000 at  $m/z > 15$ . To obtain information on the

variation of composition with depth below the surface of these samples, depth profiles were conducted with a dual beam, a low-energy sputter ion beam ( $\text{Ar}^+$ , 3 keV, 10 nA, sputter area:  $500 \times 500 \mu\text{m}^2$ ), and a high-energy analysis ion beam ( $\text{Ga}^+$ , 25 keV, 2 pA, analysis area:  $200 \times 200 \mu\text{m}^2$ ). Charge compensation with a low energy electron flood gun was used during depth profiling.

### XPS measurements

XPS measurements were carried out on a VG Scientific ESCALAB spectrometer (East Grinstead, UK) using a  $\text{Mg-K}\alpha$  X-ray source (1253.6 eV photons). Test films were mounted on a standard sample stud by use of double-sided adhesive tape. The X-ray source was run at 12 kV and 10 mA. To compensate for surface charge effects, all core-level spectra were referenced to the  $\text{C1s}$  neutral carbon peak at a binding energy of 285.0 eV. The pressure in the analysis chamber was maintained at  $\leq 10^{-8}$  mbar during measurements. All spectra were obtained at a take-off angle of  $75^\circ$  and curve-fitted with VGX-900I software.

To quantify the surface compositions of PHF/phenoxy blends, the fluorine atom was selected to label PHF in the blends, and the integrated peak area of  $\text{F1s}$  was used to monitor the relative surface concentration of PHF. Although there is no unique element suitable for labeling phenoxy unambiguously, the surface concentration of phenoxy in the blend can be indirectly calculated by subtracting the  $\text{C1s}$  peak component attributed to PHF from the total  $\text{C1s}$  peak attributed to both PHF and phenoxy. Because there are six F atoms and seven C atoms in one PHF repeat unit (relative molecular mass = 236) and 18 C atoms in each phenoxy repeat unit (relative molecular mass = 284), the surface composition of a blend can be calculated from the experimental F/C atomic ratio as follows. If  $X$  represents the mole fraction of PHF and  $(1 - X)$  the mole fraction of phenoxy in the blend, the F/C atomic ratio is then

$$\frac{F}{C} = \frac{6X}{7X + 18(1 - X)}$$

Furthermore, if  $W$  represents the weight fraction of PHF, the above equation can be transformed to

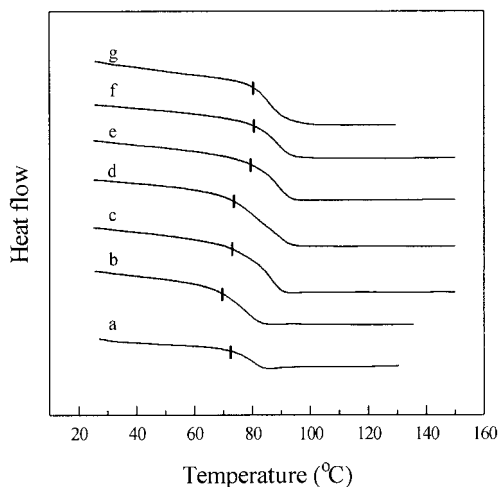
$$\frac{F}{C} = \frac{6W/236}{7W/236 + 18(1 - W)/284}$$

## RESULTS AND DISCUSSION

### Miscibility behavior

#### DSC characterization

All the blend films were transparent, indicating that the two polymers mix well to form a homogeneous



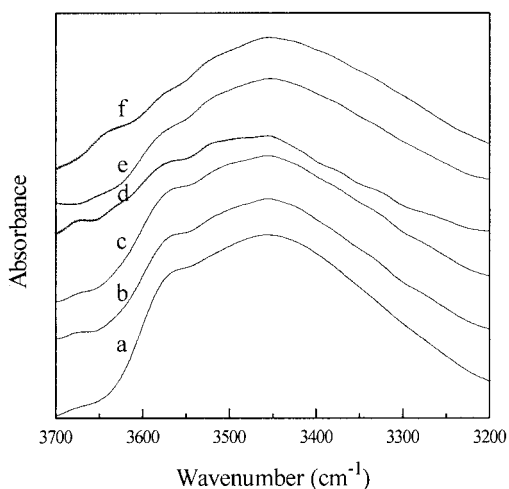
**Figure 1.** DSC curves of PHF/phenoxy blends containing PHF (in wt %): (a) 100; (b) 80; (c) 65; (d) 50; (e) 35; (f) 20; (g) 0.

phase. Figure 1 shows the DSC curves of various PHF/phenoxy blends. Each blend shows a single glass transition, indicating that PHF is miscible with phenoxy over the entire composition range. Because the  $T_g$  difference between the two components is not very large, physical mixtures of the two polymers were also prepared for comparison. All physical mixtures exhibited two distinct glass transitions. Therefore, the single  $T_g$  observed in each blend truly reflects the single-phase nature of the blend.

#### TX-FTIR characterization

As shown in Figure 2(a), the hydroxyl band of phenoxy consists of two components: a relatively narrow band at  $3567 \text{ cm}^{-1}$  for free hydroxyl groups and a broad band centered at  $3455 \text{ cm}^{-1}$  for a wide distribution of hydrogen-bonded hydroxyl groups. Upon the addition of PHF, the intensity of the free hydroxyl band decreases, showing that more hydroxyl groups are involved in interactions. The hydrogen-bonded hydroxyl band appears to be further broadened. However, there is no significant change on the frequency of the center of the broad band. Thus, the phenoxy-PHF interaction is of the same magnitude as the self-association of phenoxy. In contrast, the hydrogen-bonded hydroxyl band of phenoxy shows a low-frequency shift of  $110 \text{ cm}^{-1}$  upon blending with poly(ethylene oxide) (PEO), indicating a very strong phenoxy-PEO interaction.<sup>19</sup>

On the other hand, the carbonyl band of PHF does not show significant changes upon the addition of phenoxy, showing that the involvement of carbonyl groups in interactions with phenoxy is not significant. In comparison, the carbonyl band of poly( $\epsilon$ -caprolactone) (PCL) shows the development of a shoulder band at a lower frequency upon blending with phe-



**Figure 2.** FTIR spectra, recorded at 110°C, of the hydroxyl stretching band of PHF/phenoxy blends containing PHF (in wt %): (a) 0; (b) 20; (c) 35; (d) 50; (e) 65; (f) 80.

noxy.<sup>26</sup> As mentioned earlier, the acidic hydrogen atom of the pendant hexafluoroisopropyl group may be involved in interactions. However, as in the case of miscible PCL/poly(vinyl chloride) blends, the change in the methine C—H vibration cannot be studied because the C—H band is weak and submerged beneath the strong methylene bands.<sup>26</sup> Nevertheless, the FTIR results based on the hydroxyl band of phenoxy show that the interactions between PHF and phenoxy are not particularly strong.

## Surface properties

### Contact angle characterization

Table I shows the surface energies of various PHF/phenoxy blends determined by contact angle measurements. The surface energy decreases sharply with increasing PHF content over the range of 0.01–1 wt % and changes slightly for blends containing more than 1 wt % of PHF. The slight fluctuation of surface energies for blends with more than 35 wt % of PHF may be attributed to surface roughness. PHF is not a good film-forming polymer, whereas phenoxy has an excellent film-forming property. The blend film surfaces become more irregular with increasing PHF content in the blend. In any case, the contact angle results show that the presence of 1 wt % of PHF in the blend is sufficient to create a fluorine-covered surface with low surface energy.

### XPS characterization

As shown in Figure 3(a), for blends with more than 35 wt % of PHF, the XPS spectra are very similar to that of pure PHF. For blends with 35 wt % or less of PHF,

the C1s peak (283.3 eV) attributed to the phenylene carbons of phenoxy appears. As shown in Figure 3(b), for blends with more than 35 wt % of PHF, the surface regions contain more than 90 wt % of PHF, indicating that the blend surface is mainly occupied by PHF at a depth of 10 nm. The XPS results are in agreement with the contact angle results that all the blends show a surface enrichment of PHF component well above its bulk level.

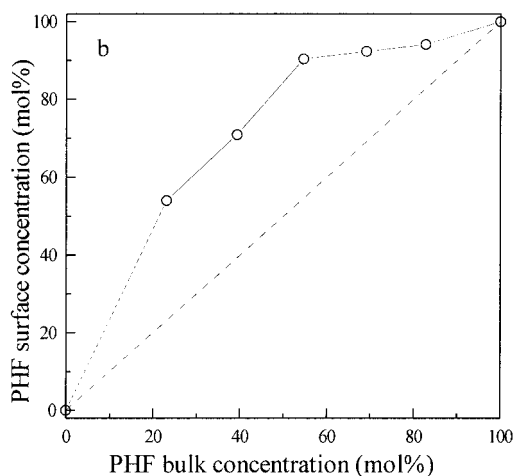
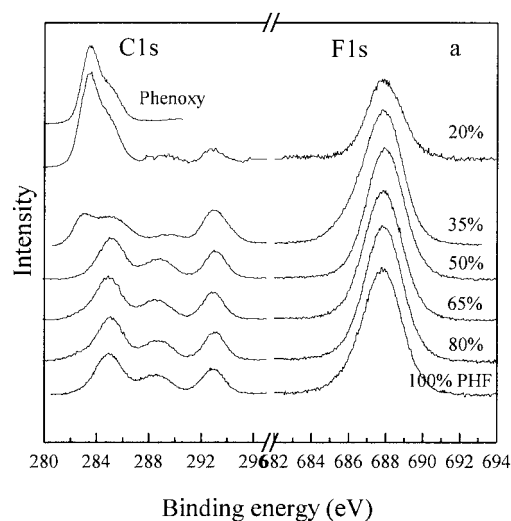
### ToF-SIMS characterization

In the static mode, cursory investigation of the negative spectra of the blends revealed that the spectra were dominated by the F<sup>-</sup> secondary ion. Therefore, we focused on the positive spectra because they offer more fragment information. Figure 4(a) shows the positive static ToF-SIMS spectrum of PHF homopolymer. Three ions were chosen as the characteristic ions of PHF,  $m/z = 19$  (F<sup>+</sup>),  $m/z = 31$  (CF<sup>+</sup>), and  $m/z = 69$  (CF<sub>3</sub><sup>+</sup>), given that these three positive secondary ion peaks are only single component and do not overlap with other fragments having the same  $m/z$  values but different structures. Even for the blend containing only 1.0 wt % of PHF [Fig. 4(b)], the three characteristic ions are still the dominant ions in the spectrum, and there is no significant reduction of intensity, indicating that the outmost layer of the blend is mainly covered by PHF.

The surface enrichment phenomenon revealed by static ToF-SIMS positive spectra implies that a gradient of PHF exists from the surface into the bulk. To obtain deeper insight into the surface rearrangement or the accumulation phenomenon, dynamic ToF-SIMS depth profiles were performed. Figure 5 shows the dynamic ToF-SIMS depth profiling data for PHF, PHF/phenoxy (10/90), PHF/phenoxy (1/99), PHF/phenoxy (0.1/99.9), and PHF/phenoxy (0.01/99.99).

**TABLE I**  
Surface Energies of PHF/Phenoxy Blends Calculated from Contact Angle Results

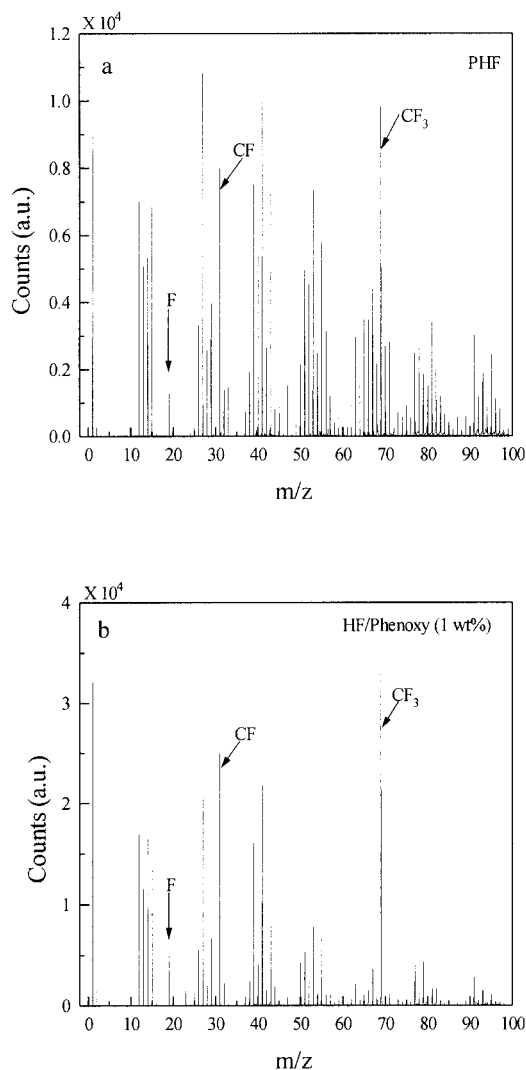
PHF fraction	Bulk (wt %)	$\gamma_d$ (mN/m)	$\gamma_p$ (mN/m)	$\gamma$ (mN/m)	Polarity ( $\gamma_p/\gamma$ )
Phenoxy		16.8	25.1	41.9	0.60
0.01		17.8	17.9	35.7	0.50
0.1		17.4	14.3	31.7	0.45
0.5		16.6	12.4	29.0	0.43
1.0		14.1	8.4	22.5	0.37
5.0		12.8	5.5	18.3	0.30
10		12.8	3.3	16.1	0.20
20		14.8	4.8	19.6	0.24
35		15.8	5.3	21.1	0.25
50		15.3	5.5	20.8	0.26
65		14.5	5.5	20.0	0.28
80		16.9	5.3	22.2	0.24
PHF		16.1	5.0	21.1	0.24



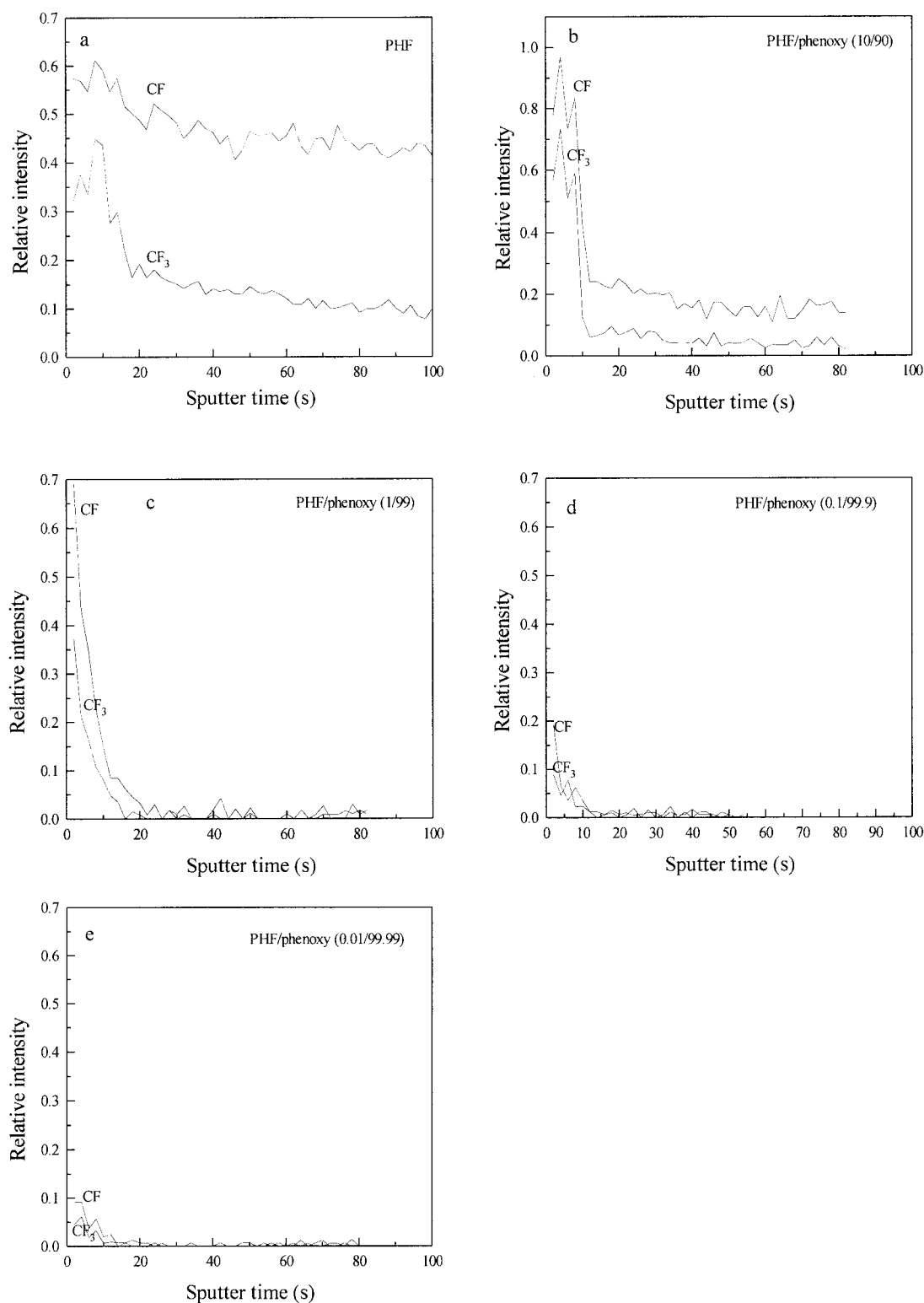
**Figure 3.** (a) XPS spectra of polymers and blends; (b) surface compositions of blends.

All ion intensities shown in Figure 5 are normalized with  $C^+$  ( $m/z = 12$ ) because the  $C^+$  ion shows a flat trace during the whole experimental period, illustrating the stability of the sputtering beam. The depth profile of PHF homopolymer also shows an enrichment of fluorine. The sharp decreases of the intensities of fluorinated ions are mainly attributed to two factors. First, the film surface is rough initially, and thus the actual surface area is larger than the set sputter area. After sputtering for some time, the surface becomes flatter and the actual surface area decreases. Second, the surface composition of homopolymer is still not the same as the bulk, given that the low-surface energy  $-\text{CH}(\text{CF}_3)_2$  pendant chain of PHF tends to rearrange at the air-polymer interface to form a fluorinated surface. The  $\text{CF}_3^+$  and  $\text{CF}^+$  ions are still detectable after 30 s. For the PHF/phenoxy (10/90) blend, Figure 5(b) demonstrates the surface enrichment of fluorinated component on the blend surface.

Initially, the  $\text{CF}_3^+$  and  $\text{CF}^+$  ion intensities are comparable to those of PHF homopolymer, but decrease sharply with increasing depth. After 20 s, the relative intensity is below 0.1. For the blend containing 1 wt % of PHF, the blend surface is still enriched with PHF. However, the  $\text{CF}^+$  and  $\text{CF}_3^+$  intensities decrease to almost zero after 20 s, indicating that practically all the PHF component resides on the surface. For blends containing less than 1 wt % of PHF, even though all the PHF component migrates to the air-polymer interface, there is not enough PHF to completely cover the outmost layer, and thus the initial intensities of  $\text{CF}^+$  and  $\text{CF}_3^+$  are lower compared with that of PHF homopolymer. The initial intensities of depth profiles are consistent with the contact angle results. The two different methods reveal that for blends with more than 1 wt % of PHF, the surface composition changes slightly with increasing PHF content because the surface has already been occupied by the fluorinated



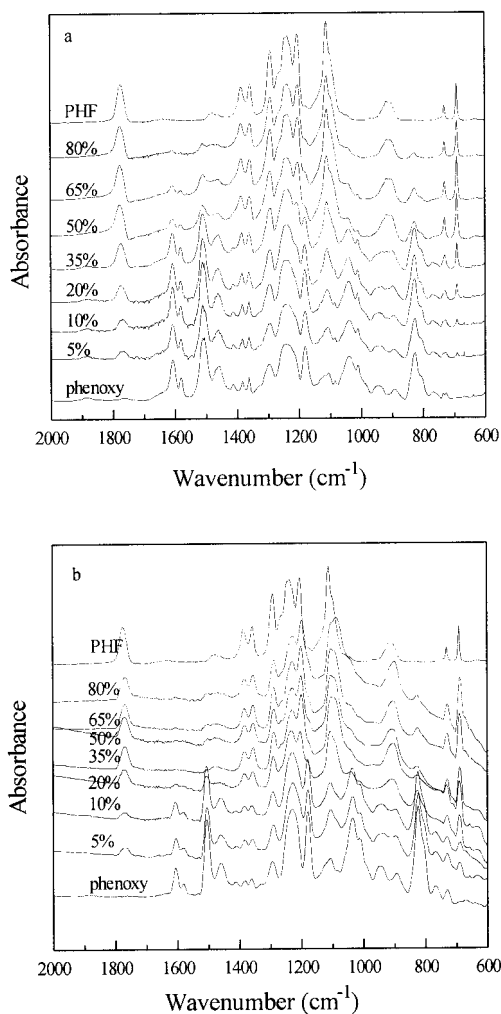
**Figure 4.** (a) Positive static ToF-SIMS spectrum of PHF; (b) PHF/phenoxy (1 wt % PHF).



**Figure 5.** Dynamic ToF-SIMS depth profiles of (a) PHF; (b) PHF/phenoxy (10 wt % PHF); (c) PHF/phenoxy (1 wt % PHF); (d) PHF/phenoxy (0.1 wt % PHF); (e) PHF/phenoxy (0.01 wt % PHF).

group. However, when the bulk concentration of PHF is less than 1 wt %, the surface composition begins to change. Part of the outermost layer is occupied by the phenoxy component and the surface becomes more

hydrophilic, as detected by contact angle measurements. Nevertheless, even when the PHF content is only 0.01 wt % in the blend, the  $\text{CF}^+$  and  $\text{CF}_3^+$  ions are still detectable initially. From the SIMS results, we



**Figure 6.** Comparison of (a) TX-FTIR spectra and (b) ATR-FTIR spectra of PHF/phenoxy blends.

conclude that the PHF component migrates to the blend's surface, leading to the surface enrichment phenomenon.

#### ATR-FTIR characterization

FTIR can be used to obtain compositional profiles at a greater sampling depth than XPS by comparing the TX-FTIR [Fig. 6(a)] and ATR-FTIR spectra [Fig. 6(b)]. In the TX-FTIR spectra, the phenoxy characteristic bands, 1630–1570, 1530–1440 (phenyl ring vibration modes), and 850–780  $\text{cm}^{-1}$  ( $=\text{C}-\text{H}$  out-of-plane blending vibration)<sup>27</sup> decrease step by step with increasing PHF content in the blends, and they are still very obvious even for the PHF/phenoxy (50/50) blend. In the ATR-FTIR spectra, the intensities of the phenoxy characteristic bands decrease sharply and are almost undetectable, whereas the PHF characteristic band intensities (1830–1740  $\text{cm}^{-1}$ ,  $\text{C}=\text{O}$  stretching and 710–660  $\text{cm}^{-1}$   $\text{C}-\text{F}$  deformation vibration) in-

crease sharply for blends containing more than 20 wt % of PHF. Even though the FTIR spectra cannot be used to make a precise quantitative comparison because the penetration depth is a function of the refractive indices, the angle of incidence, and the frequency,<sup>28,29</sup> the ATR-FTIR spectra clearly show the enrichment of PHF at a depth of about 3  $\mu\text{m}$ .

#### CONCLUSIONS

Normally, fluorinated polymers are immiscible with hydrocarbon polymers. However, for PHF/phenoxy blends, the interaction between PHF and phenoxy enables the formation of miscible blends over the entire composition range. Surface investigations by contact angle measurements, XPS, ToF-SIMS, and ATR-FTIR reveal that the blend surfaces are enriched with PHF component because of its extremely low surface energy. For blends with more than 1 wt % of PHF, the surfaces are almost covered with PHF to form air-fluorinated polymer interface. Although interactions between PHF and phenoxy give rise to miscibility, the interactions are not strong enough to prevent the surface enrichment of PHF in various miscible blends.

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