

Surface Properties for Poly(perfluoroalkylethyl methacrylate)/Poly(*n*-alkyl methacrylate)s Mixtures

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SYNOPSIS

A poly(perfluoroalkylethyl methacrylate) and a series of poly(*n*-alkyl methacrylate)s such as poly(methyl methacrylate), poly(ethyl methacrylate), and poly(*n*-butyl methacrylate) were prepared and used to investigate the surface properties of polymer mixtures containing a fluorinated homopolymer and a nonfluorinated homopolymer and the effect of the side-chain length of poly(*n*-alkyl methacrylate) on the surface free energy for the polymer mixtures. Contact angles were measured for the surfaces of polymer mixtures by varying the concentration of poly(perfluoroalkylethyl methacrylate). From the contact angle data, it can be inferred that most of the poly(perfluoroalkylethyl methacrylate) added to poly(*n*-alkyl methacrylate)s is located in the outermost layer of polymer-mixture surface. Surface free energies for the outermost surfaces of polymer mixtures were calculated from the contact angle data using Owen and Wendt's equation. The decrease in the surface free energy for the polymer mixture with the poly(perfluoroalkylethyl methacrylate) addition is more pronounced as the side-chain length of poly(*n*-alkyl methacrylate) decreases. Due to the steric effect of the side chain of poly(*n*-alkyl methacrylate), the arrangement of the perfluoroalkylethyl group of poly(perfluoroalkylethyl methacrylate) to the air side is considerably hindered. The ESCA analysis of atomic compositions of the surface for the polymer mixture verified that poly(perfluoroalkylethyl methacrylate) is preferentially arranged and concentrates at the polymer mixture-air interface. The results of functional group compositions obtained by ESCA showed that the functional group composition of $-\text{CF}_3$ for the outermost layer has a more important effect on the surface free energy than that of $-\text{CF}_2-$ and confirmed the hindrance of the arrangement of perfluoroalkylethyl group to the air side by the side chain of poly(*n*-alkyl methacrylate). © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Fluorinated polymers exhibit extremely low surface free energy and are used as important raw materials for surface modification agents such as water-and-oil repellents, lubricants, soil release agents, and surfactants. Knowledge of wettability and surface free energy of the polymer surface is of importance in determining many physical properties. Numerous studies on the surface energy and wetting property of fluorinated polymers have been published.¹⁻³ However, research on polymer mixtures consisting

of a fluorinated homopolymer and a nonfluorinated homopolymer has rarely appeared.

To investigate the surface properties of polymer mixtures containing a fluorinated homopolymer and a nonfluorinated homopolymer, a poly(perfluoroalkylethyl methacrylate) (PFMA) and a series of poly(*n*-alkyl methacrylate)s (PAMA) were prepared, respectively, and used in this study. Measurements of contact angles for the surfaces of polymer mixtures, which can provide much useful information on the structure and surface free energy of a polymer surface, were carried out. Electron spectroscopy for chemical analysis (ESCA) techniques were quantitatively employed to obtain information on the molecular orientation of the surface layer.

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EXPERIMENTAL

Polymerization

The perfluoroalkylethyl methacrylate (1H, 1H, 2H, 2H-tridecafluoro octyl methacrylate) [$\text{CF}_3\text{-(CF}_2\text{)}_n\text{CH}_2\text{CH}_2\text{OCOC(CH}_3\text{)CH}_2$, $n = 5$] used was supplied by Hoechst Co., and n -alkyl methacrylate monomers [$\text{H(CH}_2\text{)}_n\text{OCOC(CH}_3\text{)CH}_2$, $n = 1, 2, 4$] of methyl methacrylate ($n = 1$), ethyl methacrylate ($n = 2$), and n -butyl methacrylate ($n = 4$) were obtained from Tokyo Kasei Co. Each monomer was purified by vacuum distillation.

Homopolymers were prepared by solvent polymerization at 70°C in α, α, α -trifluorotoluene (TFT) using 2,2'-azobisisobutyronitrile (AIBN) as the initiator. TFT and AIBN were obtained from Aldrich Co. AIBN used was recrystallized from methanol. Polymers were recovered as solids by dropwise precipitation in methanol and purified three times by dissolving in 1,1,2-trichlorotrifluoroethane (for PFMA) or in chloroform (for PAMA) and reprecipitation in methanol. Purified polymers were dried in a vacuum oven at 50°C and 200 mmHg for 3 days.

Measurements

A specimen for contact angle and ESCA measurements was prepared by putting 1 mL of the polymer solution containing 1.5 wt % of the test polymer in 1,1,2-trichlorotrifluoroethane or in the mixture of 1,1,2-trichlorotrifluoroethane and chloroform (wt ratio = 1/2) onto a cleaned slide glass in a horizontal coating kit. The solvent then evaporated overnight at room temperature, leaving the polymer film. The residual solvent in the polymer film was removed by vacuum drying at room temperature for 6 h. SEM observations confirmed that the polymer surfaces obtained were smooth and had a uniform thickness of about 10 μm .

Contact angles were measured using the sessile drop method on a Rame-Hart goniometer. About 5 μL of wetting liquid was used for each measurement. Measurements were done at $20\text{--}22^\circ\text{C}$. To obtain contact angles at the equilibrium state, contact angle measurements were performed after 5 min of contact. Five drops of the liquid were placed on a horizontal slide glass coated with the test polymer. Ten readings of the contact angle (one on the "front" and other on the "back" of each drop) were taken. The average of the 10 readings was used as the contact angle. Wetting liquids used for contact angle measurements were methylene iodide and water, as suggested by Wu.⁴ The surface tensions and their dispersion and polar components for the wetting

Table I Surface Tensions and Their Dispersion and Polar Components of Wetting Liquids (20°C)

Wetting Liquid	Surface Tension (dynes/cm)		
	Total	Dispersion	Polar
Water	72.8	21.8	51.0
Methylene iodide	50.8	49.5	1.3

liquids are shown in Table I and are utilized for the calculations of surface free energies of polymer surfaces. The surface tensions of the wetting liquids in Table I could be confirmed by measuring with a dynamic contact angle analyzer (Cahn, DCA-322).

ESCA spectra for each coated polymer surface were obtained on a V.G. Scientific ESCALAB MK II spectrometer with an $\text{AlK}\alpha$ X-ray source and a hemispherical sector analyzer by changing the take-off angle from 5° to 60° . The take-off angle was defined as the small angle between the polymer surface and the analyzer axis. The Al anode voltage was 15 KeV and the filament current was 20 mA. The pressure in the spectrometer during analysis was typically in the 10^{-9} Torr range. Using a least-square curve fitting program (EDP package) installed in the spectrometer, the C_{1s} spectrum for a polymer surface was split into the several subpeaks of functional groups, and the concentrations of functional groups for the polymer surface were obtained. The five functional groups chosen for our analysis were —CF_3 , —CF_2 , —COO— , —CO— , and hydrocarbon. A typical splitting of the C_{1s} spectrum for the surface of a polymer mixture containing 1.0 wt % of PFMA with respect to poly(methyl methacrylate) (PMMA) is shown in Figure 1. The C_{1s} spectrum calculated from the results of C_{1s} splitting using EDP package coincided excellently with the original C_{1s} spectrum. The binding energies found in splitting the C_{1s} spectrum as shown in Figure 1 are given in Table II, which are comparable to the reported values.⁵ The functional group compositions can be calculated from the areas of functional groups obtained in the C_{1s} splitting.

Surface Free Energy

When a drop of liquid contacts, in equilibrium, a smooth and homogeneous solid surface in the absence of any gravitational efforts, the Young equation can be used to relate the surface forces:

$$\gamma_{\text{SV}} = \gamma_{\text{LV}} \cos \theta_c + \gamma_{\text{SL}} + \pi_e \quad (1)$$

where γ_{SV} , γ_{LV} , and γ_{SL} are the interfacial tensions at the solid, at the liquid, at the solid-liquid surfaces, respectively; θ_c , the contact angle that the liquid makes on the solid; and π_e , the equilibrium film pressure of adsorbed vapor on the solid surface. If the liquid has a high boiling point and the contact angle is large (conditions met in this study), the film pressure, π_e , is assumed to be zero.⁶ Fowkes⁷ suggested that the surface tension can be resolved into a dispersion component and a polar component:

$$\gamma = \gamma^d + \gamma^p \quad (2)$$

where γ is the surface tension, and γ^d and γ^p , the dispersion component and polar component, respectively. Owen and Wendt⁸ extended the Fowkes' concept and proposed the following well-known equation:

$$\gamma_{LV}(1 + \cos \theta_c) = 2(\gamma_{SV}^d \gamma_{LV}^d)^{1/2} + 2(\gamma_{SV}^p \gamma_{LV}^p)^{1/2} \quad (3)$$

If the contact angles formed on a solid surface with two liquids, for which the surface tensions and the dispersion and the polar components are known, are measured, one can calculate the surface free energy of the solid surface using eqs. (1)–(3). All the surface free energies mentioned below are calculated from these equations and the contact angle data.

RESULTS AND DISCUSSION

Contact Angles and Surface Free Energies

The contact angles and surface free energies for four homopolymers of PFMA, PMMA, poly(ethyl methacrylate) (PEMA), and poly(*n*-butyl meth-

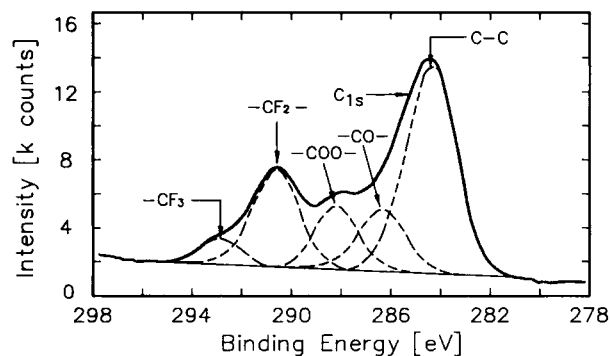


Figure 1 Splitting of C_{1s} spectrum into five associated subpeaks (take-off angle = 5° ; PFMA/PMMA = 1.0 wt %).

Table II Binding Energies for the Surface of PFMA (1.0 wt %)/PMMA Mixture According to Take-off Angles in Electron Volts

Atom	Functional Group	Take-off Angle (Deg)		
		5	10	20
F_{1s}		688.3	688.5	688.3
C_{1s}	hydrocarbon	285.0	285.0	285.0
	—CO—	286.9	286.6	286.7
	—COO—	288.8	288.7	288.6
	—CF ₂ —	291.2	291.2	291.1
	—CF ₃	293.5	293.3	293.3
O_{1s}		532.2	532.6	532.8

acrylate) (PBMA) are given in Table III. Three poly(*n*-alkyl methacrylate)s of PMMA, PEMA, and PBMA, whose side chains are —COOCH₃, —COOC₂H₅, and —COOC₄H₉, respectively, were used to investigate the effect of side-chain length on the contact angle and surface free energy. The surface free energy of the PFMA homopolymer, calculated from the contact angles for methylene iodide and water, is found to be 10.4 dynes/cm, which is comparable to the literature value of 10.6 dynes/cm for poly(1H,1H-pentafluoro octyl methacrylate).⁹ As can be also seen in Table III, the surface free energy of the PAMA homopolymer decreases with increasing length of the side chain. As the length of side chain increases, the distance between the wetting liquid and the substrate, to which the side chain is attached, increases. This may reduce the attraction force a small but finite amount, which can account for the decrease in surface free energy.

PFMA, which is one of the fluorinated polymers, exhibits exceptionally low surface energy as shown above. To examine the effect of adding a fluorinated polymer to a nonfluorinated polymer on the surface properties, PFMA and PAMA were used as a fluorinated polymer and nonfluorinated polymer, respectively.

Contact angles, for the wetting liquids of methylene iodide and water, were measured for the surfaces of polymer mixtures consisting of PFMA and PAMA by varying the concentration of PFMA with respect to PAMA. The results for contact angles are shown in Table IV. It is noticeable that the addition of even an extremely small amount (0.01 wt %) of PFMA to PAMA can increase significantly the contact angles of PAMA surfaces for both methylene iodide and water and that the increase in contact angle becomes smaller as the side-chain length of PAMA increases. It can be inferred that most of the

Table III Contact Angles for the Homopolymers Used in Our Experiments and Their Surface Free Energies

Homopolymer	Formula	Contact Angle (Deg)		Surface Energy (dynes/cm)		
		Methylene Iodide	Water	Dispersion	Polar	Total
PMMA	$-\text{[CH}_2\text{CCH}_3\text{COOCH}_3\text{]}_n-$	41.2	79.8	35.9	4.3	40.2
PEMA	$-\text{[CH}_2\text{CCH}_3\text{COOC}_2\text{H}_5\text{]}_n-$	45.6	83.6	34.1	3.4	37.5
PBMA	$-\text{[CH}_2\text{CCH}_3\text{COOC}_4\text{H}_9\text{]}_n-$	53.1	90.9	30.8	1.9	32.7

PFMA added to PAMA is located on the air side, because the contact angles reflect primarily the composition of the outermost atomic layer.

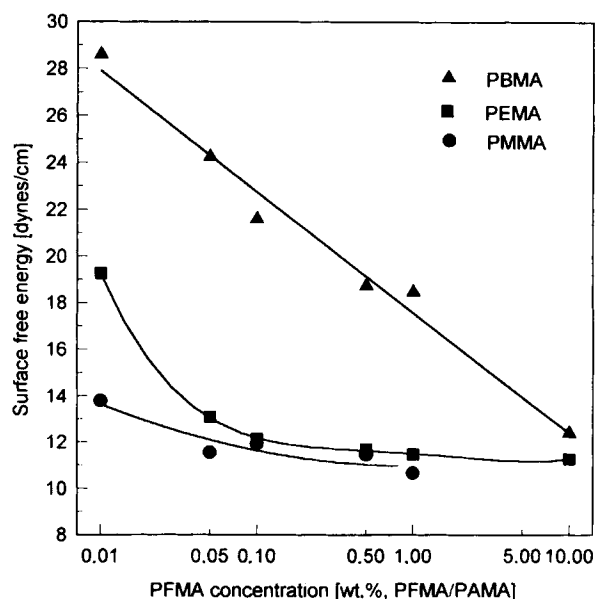
The surface free energies for the outermost surfaces of PFMA/PAMA mixtures were calculated from the contact angle data using eqs. (1)–(3) and are illustrated in Figure 2. For PFMA/PMMA and PFMA/PEMA mixtures, the surface free energies decrease drastically compared with those for PMMA and PEMA homopolymers (Table III), respectively, as the PFMA concentration increases up to 0.1 wt %. Addition of PFMA above 0.1 wt % cannot affect significantly the surface free energies. The surface

free energies for PFMA/PMMA and PFMA/PEMA mixtures approach to a value of about 11 dynes/cm with increasing PFMA concentration, which is nearly the same as that for PFMA homopolymer. In these cases, the addition of a small amount of PFMA, even if it is as low as 0.1 wt %, has a great effect on reducing the surface free energy for the polymer mixture to the level of PFMA. However, for a PFMA/PBMA mixture, the surface free energy, which shows much higher values than those for PFMA/PMMA and PFMA/PEMA mixtures, decreases continuously, but does not approach a limiting value with increasing PFMA concentration within the range up to 10 wt %.

The addition of PFMA to PBMA also lowers significantly the surface free energy of PBMA. These results indicate that most of the PFMA introduced into PAMA must be located in the outermost layer

Table IV Contact Angles for the Surfaces of PFMA/PAMA Mixtures

Polymer Mixture	PFMA Concentration ^a (wt. %)	Contact Angle (Deg)	
		Methylene Iodide	Water
PFMA/PMMA	0.01	93.5	101.3
	0.05	95.4	104.9
	0.1	95.6	105.9
	0.5	95.2	108.6
	1.0	96.0	112.1
PFMA/PEMA	0.01	78.0	100.0
	0.05	94.3	102.8
	0.1	96.2	104.6
	0.5	96.0	106.5
	1.0	96.5	106.8
	10.0	96.6	107.6
PFMA/PBMA	0.01	60.7	93.2
	0.05	67.6	104.3
	0.1	72.4	103.3
	0.5	77.8	105.2
	1.0	78.2	106.5
	10.0	93.1	106.9

^a PFMA wt/PAMA wt × 100.**Figure 2** Surface free energies for PFMA/PAMA mixtures according to PFMA concentration.

of the polymer mixture surface. The difference in the decreasing trend of surface free energy, with the addition of PFMA, for PMMA, PEMA, and PBMA, may be due to the effect of side-chain length. It can be found from Figure 2 that the effect of the addition of PFMA on reducing the surface free energy diminishes as the side-chain length of PAMA increases, i.e., the decrease in the surface free energy for the PFMA/PAMA mixture with the PFMA addition is more pronounced in the order of PMMA, PEMA, and PBMA, which have the side chains of $-\text{COOCH}_3$, $-\text{COOC}_2\text{H}_5$, and $-\text{COOC}_4\text{H}_9$, respectively. There appears to be considerable hindrance to the arrangement of the perfluoroalkylethyl group ($-\text{COOC}_2\text{H}_4\text{C}_6\text{F}_{13}$) of PFMA to the air side due to the steric effect of the side chain of PAMA. The side chains of PMMA and PEMA may not substantially interfere with the arrangement of perfluoroalkylethyl group of PFMA to the air side. On the other hand, it seems that the arrangement of the perfluoroalkylethyl group to the air side for the PFMA/PBMA mixture is significantly interfered with by the side chain of PBMA, which is much longer than those of both PMMA and PEMA.

Surface Composition Analysis by ESCA

ESCA analysis can give information about the atomic and group compositions of a surface region to only 0–50 Å. ESCA measurements, therefore,

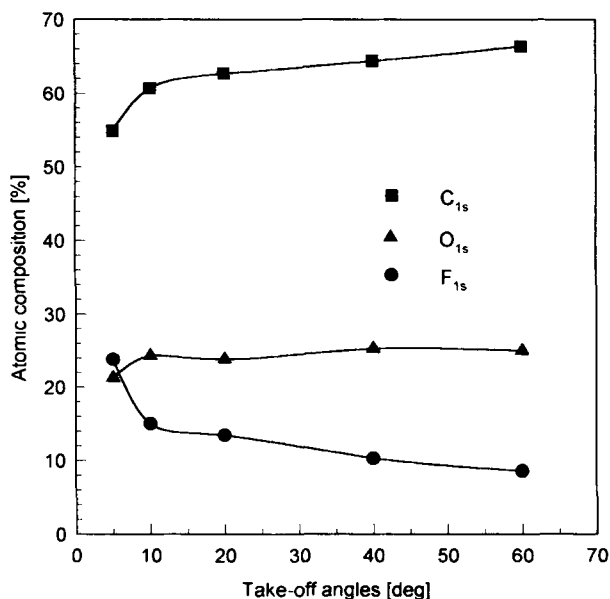


Figure 3 Atomic compositions of the surface for PFMA (0.01 wt %)/PMMA mixture according to take-off angle of ESCA.

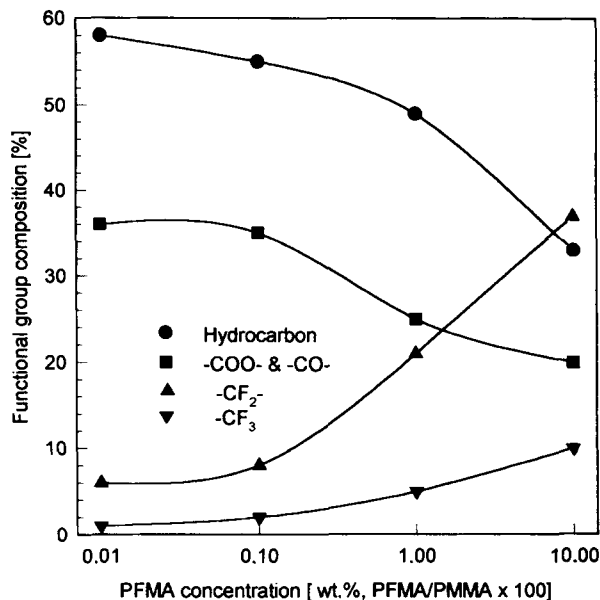


Figure 4 Functional group compositions of the surfaces for PFMA/PMMA mixtures according to PFMA concentration (take-off angle = 5°).

complement contact angle measurements, which reflect the compositions of the outermost layer.

The atomic compositions of the surface for a PFMA/PAMA mixture containing 0.01 wt % of PFMA measured by ESCA as a function of the take-off angle are shown in Figure 3. The take-off angle corresponds to the depth of a surface from the polymer mixture–air interface. Fluorine content (F_{1s}) decreases rapidly with increasing the take-off angle from 5° to 10°, but decreases slowly with the further increase in the take-off angle. On the contrary, both carbon (C_{1s}) and oxygen (O_{1s}) contents increase rapidly with increasing the take-off angle up to 10°, but increase slowly above 10°. It can be also found that, although the PFMA/PMMA mixture contains only 0.01 wt % of PFMA on average, the fluorine content for the take-off angle of 5° shows a very high value of about 24%. These results indicate that PFMA is preferentially arranged and concentrates at the polymer mixture–air interface and that the outermost layer region of the surface for the polymer mixture, which corresponds to the take-off angle of less than 5°, contains more than 24% of fluorine. This accounts well for the reason why the large contact angle appears even for a PFMA/PMMA mixture containing an extremely small amount of PFMA.

Figure 4 shows the functional group compositions of the surfaces for PFMA/PMMA mixtures measured as a function of PFMA concentration for the

take-off angle of 5° . The functional group composition of $-\text{CF}_3$ increases very slowly with the PFMA concentration. On the other hand, the functional group composition of $-\text{CF}_2-$ increases much more rapidly with the PFMA concentration as compared with that of $-\text{CF}_3$. It is likely that the trend of the increase in the functional group composition of $-\text{CF}_3$ with the PFMA concentration (Fig. 4) is similar to the trend of the decrease in the surface free energy with the PFMA concentration for PFMA/PMMA mixtures (Fig. 2). Therefore, it may be deduced from the results that, although the fluorine composition of the outermost layer of a surface affects the surface free energy as mentioned above, the functional group composition of $-\text{CF}_3$ for the outermost layer has a more important effect on the surface free energy than that of $-\text{CF}_2-$.

The variation of functional group composition of the surfaces for PFMA/PAMA mixtures containing 0.01 wt % of PFMA according to PAMA is illustrated in Figure 5. It seems that the functional group composition may be significantly affected by the side-chain length of PAMA. The functional group composition of $-\text{CF}_3$ for the outermost layer, which plays an important role in lowering the surface free energy of the surface for the PFMA/PAMA mixture, decreases as the carbon number of methylene group (n) in the side chain of PAMA increases from PMMA to PBMA. On the other hand, the functional group composition of hydrocarbon attributed mainly to PAMA increases with the carbon number of methylene group (n) of PAMA. The decrease in the functional group composition of $-\text{CF}_3$ for the PFMA/PBMA mixture is especially much more significant than that for PFMA/PEMA. This may account for the differences in the surface free energy for PFMA/PAMA mixtures containing 0.01 wt % of PFMA, which are shown in Figure 2. It is likely that, as discussed above, the side chain of PAMA interferes with the arrangement of perfluoroalkylethyl group to the outermost layer of the surface for the PFMA/PAMA mixture.

CONCLUSIONS

Contact angle and ESCA measurements were carried out to analyze the surface properties for PFMA/PAMA mixtures. The addition of an extremely small amount of PFMA to PAMA was found to be very effective in reducing significantly the surface free energy of PAMA. PFMA may preferentially concentrate at the outermost layer in PFMA/PAMA mixtures. The length of the side chain of PAMA

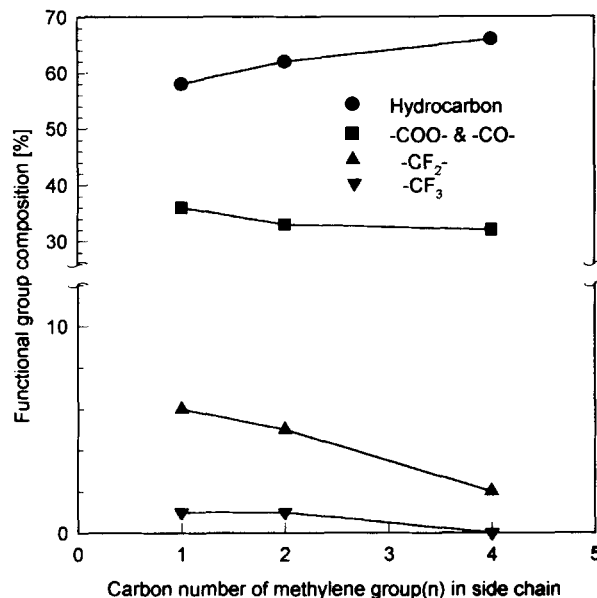


Figure 5 Functional group compositions of the surfaces for PFMA/PAMA mixtures according to carbon number of methylene group (n) in the side chain of PAMA (take-off angle = 5° ; PFMA concentration = 0.01 wt %).

affects the surface free energy for the PFMA/PAMA mixture by hindering the arrangement of perfluoroalkylethyl group of PFMA to the air side. As the length of the side chain of PAMA increases, it is likely that the arrangement of perfluoroalkylethyl group to the outermost layer is more significantly interfered with due to the steric effect.

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