

Surface Structure and Inert Surface Characteristics of Perfluorodecanoic Acid-Grafted Polyurethane

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SYNOPSIS

The surface compositions and characteristics of perfluorodecanoic acid (PFDA)-grafted polyurethane (PU) were investigated to understand its enhanced blood compatibility. The grafting of PFDA was identified by attenuated total reflectance-Fourier transform infrared (ATR-FTIR). The results from angular-dependent electron spectroscopy for chemical analysis (ADESCA) demonstrated the fluorocarbon enrichment at the outermost layer in PFDA-grafted PU. Static secondary ion mass spectroscopy (SIMS) experiments supported the results drawn from ATR-FTIR and ADESCA data about the surface compositions. Energy-dispersive X-ray analysis (EDXA) data by fluorine mapping also indicated a considerable coverage with fluoroalkyl groups on the PU-PFDA surface. The critical surface tension, γ_c , of the highly hydrophobic PU-PFDA surface revealed an extremely low value of 6.9 dyn/cm due to the optimal orientation of $-\text{CF}_3$ groups to the uppermost surface. Therefore, such an inert low-energy surface may contribute to improve blood compatibility of PFDA-grafted PU. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It is known that surface characteristics of biomaterials are no less important than their bulk properties because their surfaces interact first in contact with the body. Therefore, the investigation on surface properties of biomaterials plays a critical role in evaluating their biological responses and developing blood compatible polymers.¹⁻³ Of the surface characteristics with respect to biomaterials, surface composition, morphology, and wettability are mainly studied by many researchers.⁴

Fluorinated polymers having low-surface free energy were found to be relatively blood compatible.⁵ We have previously reported that perfluorodecanoic acid (PFDA)-grafted polyurethane (PU) showed an enhanced blood compatibility, probably due to the inertness, the low-energy surface, and/or the specific

textured surface.⁶ This PU-PFDA exhibited a highly hydrophobic surface with a large advancing angle of 115°, while the untreated PU gave a value of 86°.

Although contact-angle measurements give useful information to understand blood-material interactions, it does not allow us to obtain information about the surface structure and the chemical composition of the materials. Accordingly, attenuated total reflectance-infrared (ATR-IR) spectroscopy, microscopies, and, especially, ultra-vacuum surface spectroscopies have been used extensively.⁷

In this work, the surface structure and the chemical nature of highly hydrophobic PFDA-grafted PU prepared by surface modification are examined by using a series of surface analyses, specifically, attenuated total reflectance-Fourier transform infrared (ATR-FTIR), angular-dependent electron spectroscopy for chemical analysis (ADESCA), static secondary ion mass spectroscopy (SIMS), energy-dispersive X-ray analysis (EDXA), and critical surface tension to comprehend the effect of the hydrophobic surface on the enhanced blood compatibility.

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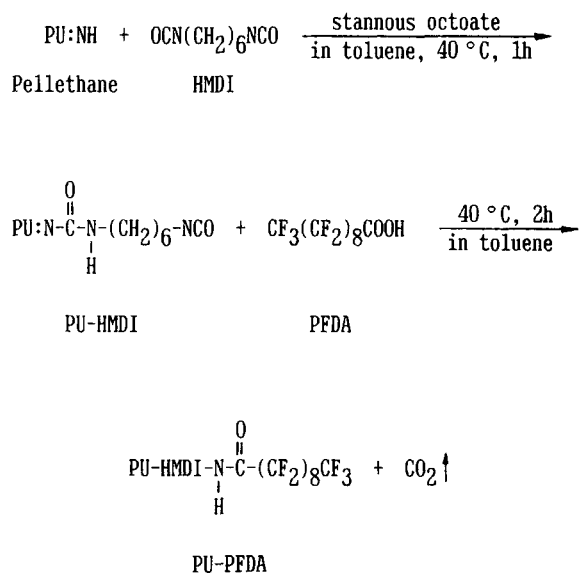


Figure 1 Surface modification scheme of PFDA-grafted PU (PU-PFDA).

EXPERIMENTAL

Preparation of PFDA-grafted PU

The preparation method of PFDA grafting onto polyurethane (PU) by surface modification is described in detail elsewhere⁶ and is shown in Figure 1. Methanol-extracted PU sheet (Pellethane 2363-80A, thickness 1 mm; Dow Chemical Co.) was kept in 80 mL of completely dried toluene followed by

the addition of 5 mL of hexamethylene diisocyanate (HMDI) and 0.25 mL of stannous octoate. After being left to react for 1 h at 40°C under nitrogen, the sheet was washed with toluene and then anhydrous ether to yield PU-HMDI. Consecutively, the PU-HMDI sheet was reacted with 0.2 g of perfluorodecanoic acid (PFDA) in 40 mL of toluene for 2 h at 40°C. The resultant sheet was rinsed with toluene and then acetone to produce PFDA-grafted PU (PU-PFDA).

Surface Analysis

ATR-FTIR data were obtained from the surface of the PFDA-grafted PU sheet using a Mattson Alpha Centauri FTIR spectrophotometer, coupled with an ATR accessory and 45° KRS-5 crystal.

All ADESCA data were obtained by using a V.G. Scientific ESCALAB MK II spectrometer with a monochromatic AlK α X-ray source. A low-energy electron flood gun was used to neutralize sample charging, and all the binding energies (BEs) were referenced by setting the CH_x peak maximum in the C_{1s} spectrum to 285.0 eV. ADESCA analysis was done at nominal photoelectron takeoff angles of 0°, 39°, 55°, 68°, and 80°. The takeoff angle was defined as the angle between the surface normal and the axis of the analyzer lens. Three types of spectra were recorded for PFDA-grafted PU. A survey scan (0–1000 eV BE, 100 eV pass energy) was recorded at 55°, whereas both detailed scans (20 eV BE regions, 100 eV pass energy) for the C_{1s}, O_{1s}, N_{1s}, and F_{1s}

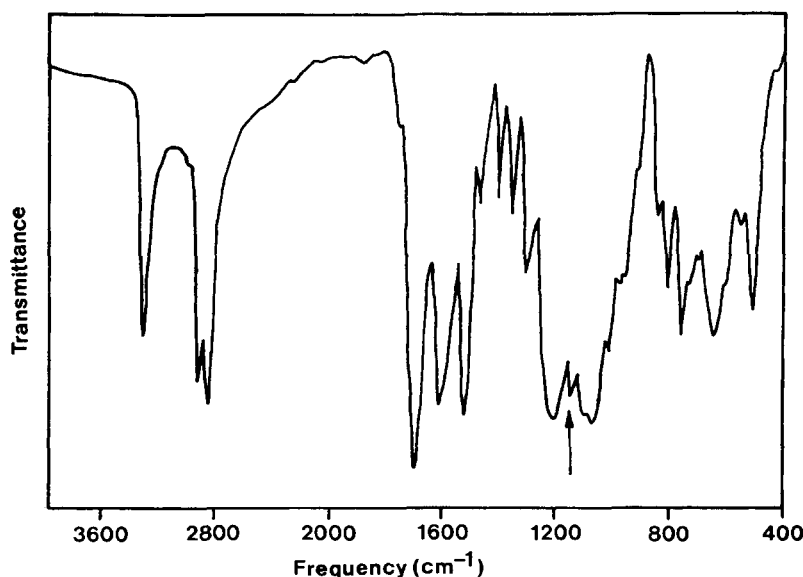


Figure 2 ATR-FTIR spectrum of PU-PFDA.

Table I ADESCA Results for PU-PFDA

Takeoff Angle	C _{1s}		O _{1s}		N _{1s}		F _{1s}	
	BE ^a	at % ^b	BE	at %	BE	at %	BE	at %
0°	285.0	24.6	533.0	14.4	400.0	1.9	687.0	29.1
	286.5	11.0						
	288.5	4.8						
	289.8	2.7						
	291.5	7.6						
	293.2	3.9						
39°	285.0	23.0	533.0	9.4	400.0	3.2	687.0	34.9
	286.6	8.2						
	288.4	5.0						
	289.9	2.8						
	291.7	9.5						
	293.3	4.0						
55°	285.0	20.5	533.0	5.3	400.0	4.7	687.0	42.0
	286.6	5.2						
	288.3	4.7						
	290.0	3.1						
	291.6	10.5						
	293.4	3.9						
68°	285.0	19.0	533.0	5.1	400.0	5.0	687.0	43.3
	286.5	4.6						
	288.3	4.8						
	289.9	3.3						
	291.6	10.9						
	293.4	4.0						
80°	285.0	17.4	533.0	5.0	400.0	5.4	687.0	44.1
	286.5	3.8						
	288.3	5.0						
	289.8	3.5						
	291.6	11.4						
	293.3	4.3						

^a Binding energies in eV.^b Atomic percentages.

and high-resolution scans of C_{1s} (20 eV BE regions, 20 eV pass energy) were recorded at all takeoff angles. The C_{1s} high-resolution spectra were resolved into individual Gaussian peaks using a least-squares curve-fitting program. From the C_{1s} curve-fitting and elemental composition, the amounts of each carbon species present at each takeoff angle were calculated and then used to determine a depth profile using the procedure described by Yih and Ratner.⁸

The static SIMS studies were performed by using a Perkin-Elmer 3500. A 3.5 KeV Ar⁺ primary beam of 1.5 nA cm⁻² current density was rastered over a 5 mm-square area of the sample. A quadrupole mass spectrometer with a range of 1–255 daltons was used

to detect the secondary ions. Surface charging of the sample was neutralized by flooding with 1.3 KeV electrons. A detailed review of the SIMS analysis has been reported elsewhere.⁹

EDXA (Kevex Delta IV) for the evaluation of the surface morphology by mapping of the PFDA-grafted PU has been carried out by using the scanning electron microscopy (SEM, Hitachi 2500C) combined with the quantum Si detector. The sample was mounted and sputter-coated with carbon using an ion coater and then observed at an accelerating voltage of 20 kV.

The surface wettability was assessed in the following ways: The static contact angles were mea-

sured by the sessile drop method using a Erma Contact Anglemeter G-I, and the dynamic advancing and receding contact angles were determined by the Wilhelmy plate method¹⁰ using a WET-TEK F100 apparatus. Also, the surface tension was determined by Owens technique¹¹ using water and methylene iodide, and the critical surface tension, γ_c was evaluated by the Zisman plot¹² using a series of hydrocarbons (C_8 , C_{10} , C_{12} , C_{14} , and C_{16}) where measured contact angles were extrapolated to $\cos \theta = 1$.

RESULTS AND DISCUSSION

ATR-FTIR

ATR-FTIR, which provides a great deal of information concerning the chemical nature of the polymer surface, can be used directly to examine PFDA grafting onto the PU surface.

Figure 2 presents the ATR-FTIR spectrum of the PFDA-grafted PU surface. The grafting of PFDA was confirmed by the existence of the characteristic peak of C—F at 1184 cm^{-1} .⁶ The location of this peak is similar to that of polytetrafluoroethylene (PTFE).¹³ The major peaks in PTFE at 1207 and 1152 cm^{-1} are assigned to $-\text{CF}_2$ asymmetric and symmetric modes, and peaks located at 980 and 1166

cm^{-1} are attributed to $-\text{CF}$ and $-\text{CF}_3$ stretching modes, respectively.

The reaction of PU-NCO with $\text{R}-\text{COOH}$ is strongly dependent on the kind of isocyanate and carboxylic acid and the reaction conditions. In general, when aliphatic isocyanate such as HMDI is used, it forms mixed anhydrides and, eventually, decomposes to amide and carbon dioxide.¹⁴

The degree of grafting of PU-PFDA was estimated from the relative ratios of C—F absorbance at 1184 cm^{-1} to C—O—C absorbance at 1210 cm^{-1} of the ATR-FTIR spectrum in order to find the maximum grafting. Toluene was found to be a good reaction medium because PFDA is dissolved completely in toluene over 40°C . Also, the reaction showed a better yield in the absence of catalyst than in the presence of bases such as triethylamine and triethylenediamine.

Angular-dependent ESCA

The surface atomic composition and chemical state of PFDA-grafted PU determined from ADESCA measurements are shown in Table I and Figures 3–5.

Figure 3 shows typical ESCA spectra of C_{1s} for PU-PFDA at takeoff angles of 0° and 80° . These

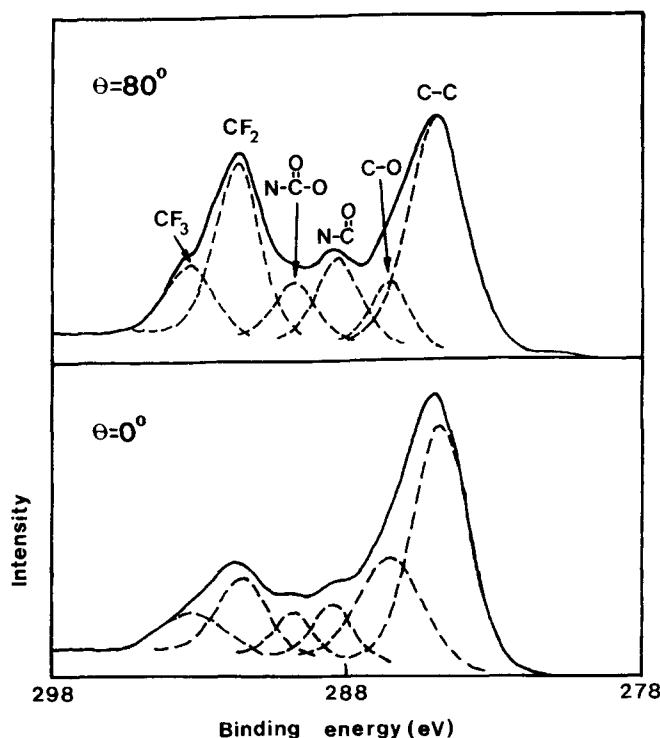


Figure 3 ESCA spectra of C_{1s} for PU-PFDA at takeoff angles of 0° and 80° .

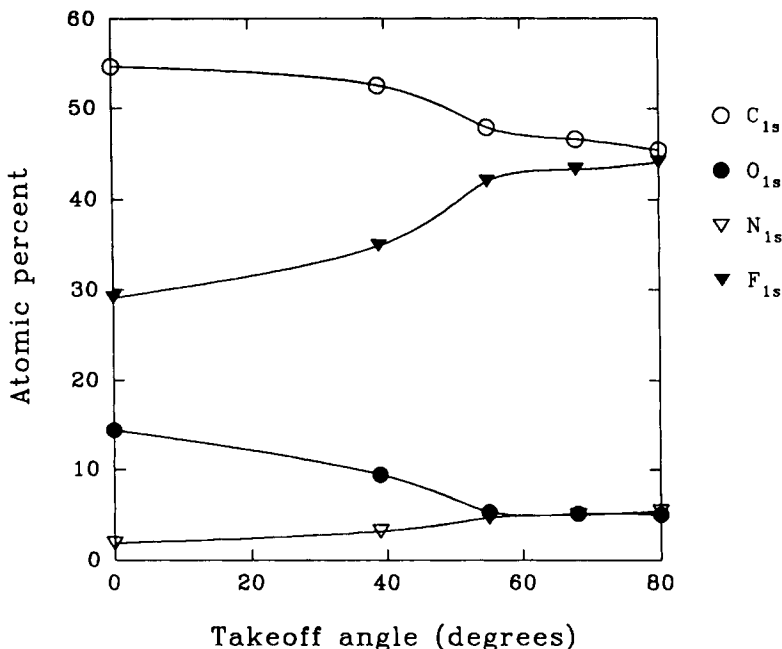


Figure 4 The compositional depth profiles on variable takeoff angles from detailed scan ESCA spectra for PU-PFDA.

spectra can be used to evaluate the relative concentrations of carbons in different bonding environments. These six subpeaks was assigned to the hydrocarbon (285.0 eV); ether (286.5 eV); amide (288.3 eV), which is produced from the reaction of

—NCO with —COOH; carbamate (289.8 eV); —CF₂ (291.6 eV); and —CF₃ (293.3 eV).⁶ The relative intensity of fluorocarbon in the total C_{1s} for a takeoff angle of 80° was larger than that for a takeoff angle of 0°, indicating that there is an en-

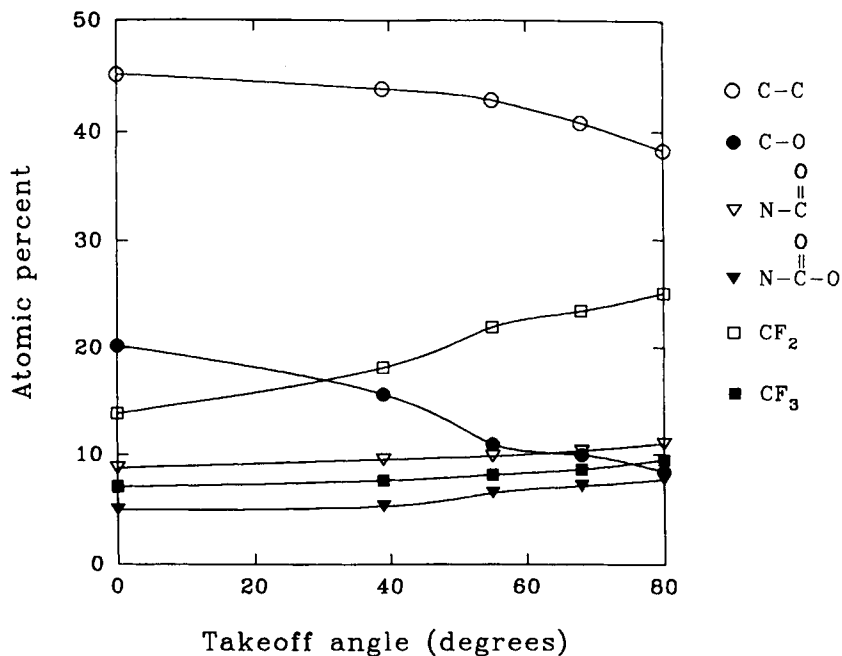


Figure 5 The compositional depth profiles on variable takeoff angles from high-resolution ESCA spectra of C_{1s} for PU-PFDA.

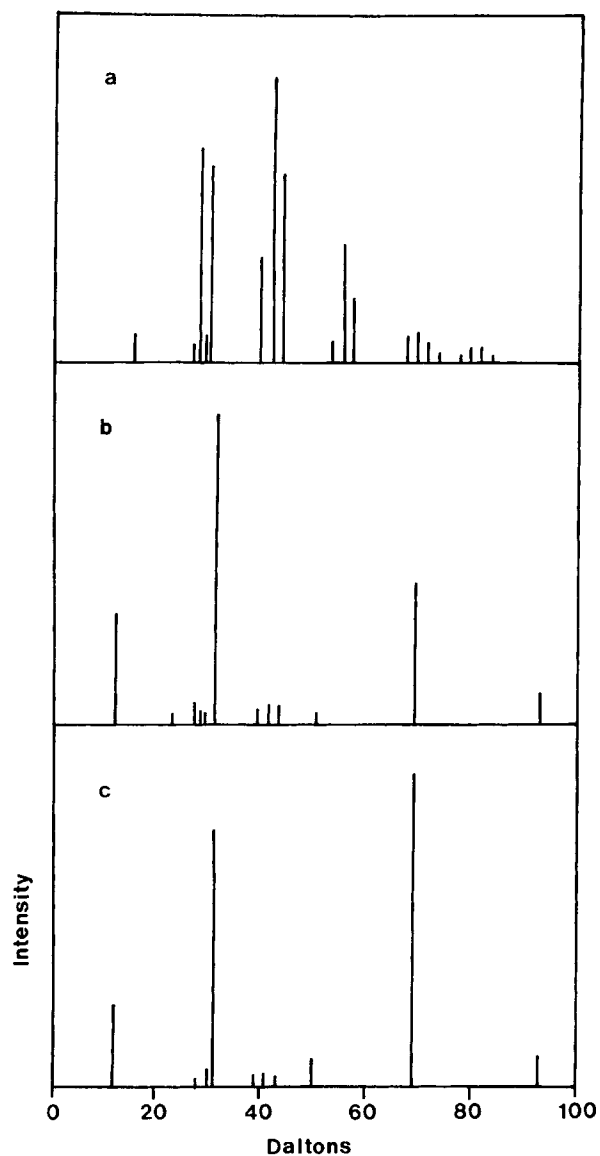


Figure 6 Positive ion static SIMS spectra: (a) untreated PU; (b) PTFE; (c) PU-PFDA.

richment of fluorocarbon to the outermost layer compared with the inner region.

The binding energies and atomic percentages resulting from detailed and high-resolution C_{1s} spectra at each takeoff angle are summarized in Table I. Figure 4 shows the compositional depth profiles on variable takeoff angles from detailed scan ESCA spectra for PU-PFDA. There is a clear difference in surface composition with takeoff angles for the F_{1s} component. As the takeoff angle is increased from 0° to 80° , the F_{1s} component varies from ca. 29 to 44%. This demonstrates that the concentration of fluorocarbon to surface direction is much higher than to the bulk one. In contrast, the amount of C_{1s}

and O_{1s} decreased and that of N_{1s} increased with increasing takeoff angles.

Generally, it was known that the sample depth from ADESCA analysis should decrease from ca. 90 to 15 Å as the takeoff angle is increased from 0° to 80° .¹⁵ Therefore, in the case of PU-PFDA, the concentration of the fluorine atom in the uppermost ca. 15 Å layer showed an almost equivalent value to that of carbon atom, meaning that the surface is considerably covered with fluoroalkyl groups.

Figure 5 shows the compositional depth profiles on variable takeoff angles from high-resolution ESCA spectra of C_{1s} for PU-PFDA. As expected, as the takeoff angle was increased, the amount of CF_2 component showed a marked increase, while the amount of C—C and C—O components exhibited substantial decreases. Moreover, the concentration of CF_3 groups somewhat increased with increasing takeoff angle as well.

Static SIMS

Static SIMS is much more surface-sensitive than ESCA, for it can observe a surface region of ca. 10

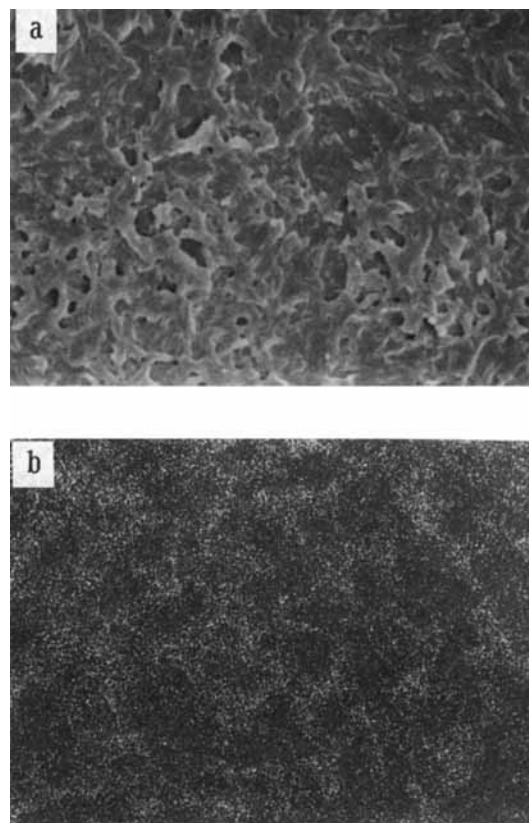


Figure 7 EDXA photographs of PU-PFDA ($\times 3000$): (a) by SEM; (b) by mapping of fluorine.

Å in depth.¹⁶ Figure 6 compares the positive ion static SIMS spectra obtained from untreated PU (a), PTFE (b), and PU-PFDA (c). Although untreated PU (a) showed only representative hydrocarbon peaks, the PU-PFDA (c) displayed ion fragments at 31 and 69 daltons resulting from respective CF^+ and CF_3^+ of grafted perfluoroalkyl chains. Especially, the location of prominent peaks of the PU-PFDA spectrum (c) was identical to that of PTFE (b); however, changes in peak intensity were noted. It is expected from this result that the uppermost surface of PFDA-grafted PU has a similar but not exact structure to that of PTFE. Therefore, static SIMS experiments supported the conclusions drawn from ATR-FTIR and ADESCA data about the surface structure of PFDA-grafted PU.

EDXA

The morphology and chemical nature of PFDA-grafted PU surface were characterized by using SEM and EDXA fluorine mapping, as shown in Figure 7. PFDA-grafted PU exhibited a relatively rough but uniquely textured surface due to the grafting of the perfluoroalkyl groups.⁶

In fact, the homogeneity and distribution of surface grafting of polymers have been demonstrated with the technique of EDXA mapping. In the case of the PU-PFDA surface, EDXA fluorine mapping indicated a considerable coverage with fluorocarbon on the surface. Figure 8 presents the EDXA spec-

trum for PU-PFDA, and the existence of the fluorine atom in the surface was again confirmed from peak of 0.68 KeV. This spectrum could be obtained by using only quantum Si detector, which is possible to detect down to atomic number of 4.

Wettability

The wettability of polymer surface is a powerful way to characterize the outermost surface of the polymer. Contact angle and surface tension of some polymer surfaces containing PU-PFDA are listed in Table II. The untreated PU surface was relatively hydrophobic, whereas the PFDA-grafted PU surface was as highly hydrophobic as was PTFE, a typical hydrophobic polymer. However, only the receding contact angle (θ_{rec}) of PU-PFDA showed a value less than that of PTFE. According to the results of Johnson and Dettre on surface roughness, the receding contact angle decreases with increasing roughness.¹⁷ Therefore, it is highly likely that the lower receding contact angle of PU-PFDA may be due to its characteristic roughness, as seen in Figure 7(a) from SEM observation.

Meanwhile, the surface tension of PFDA-grafted PU was far lower than those of PU and even PTFE. Nevertheless, it showed low dispersive surface tension (γ_s^d) and high polar surface tension (γ_s^p). It means that the former result in the surface of PU-PFDA is due to relatively loose packing of PFDA, unlike PTFE, whereas the latter is closely related

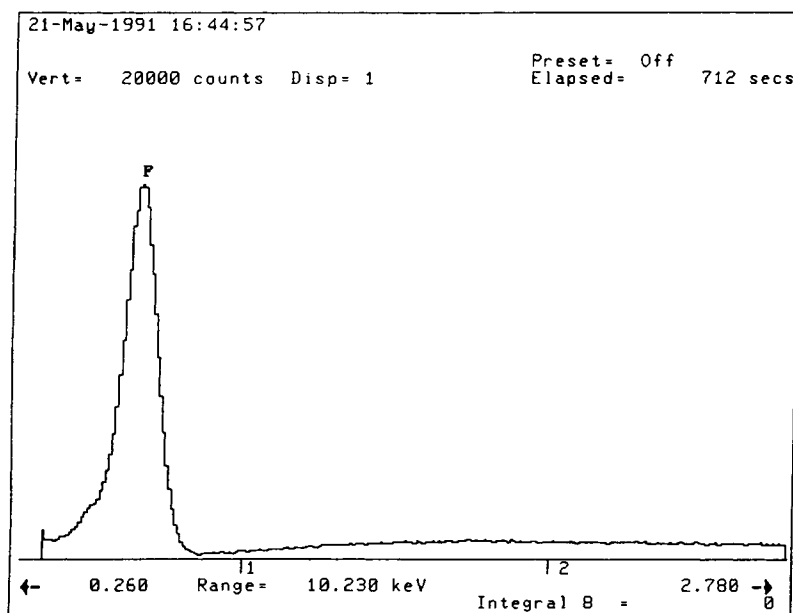


Figure 8 EDXA spectrum of PU-PFDA.

Table II Contact Angle and Surface Tension of Some Polymer Surfaces^a

Material	Contact Angle (degree) ^b			Surface Tension (dyn/cm) ^c			
	θ	θ_{adv}	θ_{rec}	γ_s^d	γ_s^p	γ_s	γ_c
PU	85	86	41	39.10	1.99	41.09	21.2
PTFE	111	115	86	17.61	0.29	17.91	18.6
PU-PFDA	110	115	50	7.70	2.38	10.08	6.9

^a All values are measured triplicate at least.

^b θ : by sessile drop method; θ_{adv} and θ_{rec} : by Wilhelmy plate method.

^c $\gamma_s = \gamma_s^d + \gamma_s^p$: by Owens technique; γ_c : by Zisman plot.

to their inherently asymmetric polarity of fluoro-carbon groups grafted onto the PU surface.

The critical surface tension, γ_c , an approximation to the surface free energy of the polymer surfaces, was obtained by using the Zisman plot, as shown in Figure 9 and Table II. The values of γ_c were 21.2 dyn/cm for PU, 18.6 dyn/cm for PTFE, and 6.9 dyn/cm for PFDA-grafted PU, respectively. In particular, the PU-PFDA surface revealed the lowest γ_c , which was less wettable than PTFE, suggesting the presence of the extremely inert $-\text{CF}_3$ groups on the surface. Similar results have also been reported for fluorinated polymer surfaces prepared by different methods.^{12,18,19}

Fluoropolymers having γ_c of 5–10 dyn/cm are known to exhibit a water/oil repellency because of very inert property and low surface-free energy.²⁰ Accordingly, it is thought that the PFDA-grafted PU surface that is directed away from the external surface by optimal orientation of perfluoroalkyl chains may contribute to improve blood compatibility when placed in blood whose main component

is water. Hence, the enhanced antithrombogenicity of PU-PFDA as described in detail earlier⁶ might be ascribed to the inertness by an extremely low energy surface, although we can not neglect an effect from the unique textured surface.

CONCLUSIONS

The surface composition and characteristics of PFDA-grafted PU were investigated to understand the effect of the fluorinated surface on the enhanced blood compatibility.

On the PFDA-grafted PU surface, the grafting of C—F groups was confirmed at 1184 cm^{-1} by ATR-FTIR, and ADESCA results showed the increase in the relative fluorocarbon concentration by increasing the takeoff angle from 0° to 80° , suggesting the fluorocarbon enrichment at the outermost layer in PU-PFDA. Static SIMS data also supported the results drawn from ATR-FTIR and ADESCA about the surface compositions. From the EDXA results,

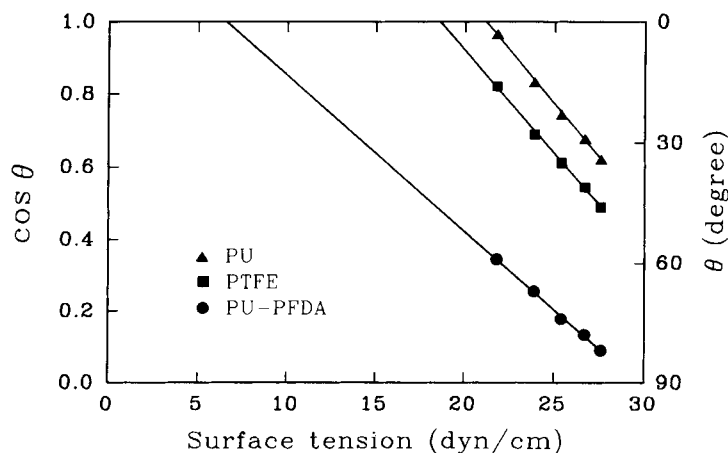


Figure 9 Determination of critical surface tension (γ_c) by Zisman plot.

fluorine mapping on the PU-PFDA surface indicated a considerable coverage with fluoroalkyl groups.

The surface of PFDA-grafted PU was highly hydrophobic, and its critical surface tension, γ_c , showed an extremely low value of 6.9 dyn/cm, which was much smaller than that of PTFE, demonstrating the inert low-energy surface by $-\text{CF}_3$ groups on the uppermost surface. Therefore, the improved blood compatibility of PU-PFDA may have resulted from such an inert low-energy surface.

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