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PERFLUOROALKYLATION OF POLYURETHANE MEMBRANES AND THEIR SURFACE CHARACTERISTICS

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Key Words: 2-Aminomethyl-1,1,2,3,3,4,4-H-perfluorododecanol, Perfluorodecanoicacid, Pellethane, Perfluoroalkylation, Surface modification.

ABSTRACT

Two fluoroalkylating agents, 2-aminomethyl-1,1,2,3,3,4,4-H-perfluorodo- decanol and perfluorodecanoic acid, were used to modify the surfaces of polyurethane membranes and their fluoroalkylation efficiencies were compared. X-ray photoelectron spectroscopy showed that all the modified samples contained fluorine and that the amino alcohol-treated polyurethane had a slightly higher surface fluorine content than the perfluorodecanoic acid-treated one. Both the modifier concentration and the treatment time had no significant effect on the amount of fluorine incorporated. Evidence for fluorine incorporation was also provided by reflection infrared spectroscopy. Contact angle measurements indicated that the modified microporous membranes were both water- and oil-repellent and may, therefore, be used in protective clothing applications where good liquid barrier properties are desirable.

INTRODUCTION

The concern over the AIDS and Hepatitis B Virus infections has recently prompted the Occupational Safety and Health Administration (OSHA) to issue a directive requiring all employers to supply personnel protective equipment to employees who are at risk of exposure to blood or other potentially infectious body fluids [1]. For the health-care worker, a wide variety of surgical gowns is available commercially, but there are concerns over their barrier effectiveness and/or wearer comfort [2,3]. In creating comfortable barrier fabrics, a compromise has to be reached between permeability and penetrability. One approach to solving this problem involves the use of breathable membranes which are permeable to water vapor but impermeable to liquid water. Such breathable membranes may be either monolithic or microporous. Monolithic membranes provide effective barrier to liquid materials and permeation is by solution-diffusion mechanism. However, they tend to have low water vapor transmission rates and may require hydrophilic groups on the membrane material to improve the water vapor transmission properties and, hence, comfort. For microporous membranes to provide adequate barrier protection and at the same time be comfortable in clothing use, the pore sizes have to be small enough to minimize liquid penetration while allowing vapor permeation and the membrane has to be hydrophobic in order to repel liquid water (minimize liquid contact time). This can be achieved, in part, through surface modification. The most notable variations in surface properties of any organic polymer are known to occur when fluorine is incorporated into the system [4-8]. We are currently investigating the relative surface hydrophobicity and hydrophilicity of polyurethane materials intended for use in surgical gowns. This preliminary study deals with the relative efficiencies of two surface fluoroalkylation agents: a monofunctional perfluoro alkyl acid and a difunctional perfluoroalkyl amino alcohol. Work involving variation in the hydrophilicity of monolithic membranes and impact on water vapor transmission will be published subsequently.

Fluorine has been incorporated into polyurethanes, both during [9-12] and after manufacture [13-17]. Surface fluorination techniques range from physical deposition of coatings [13] to radiation induced grafting [16,17] and graft coupling [18-20]. For instance, Kaku *et al.* [13] employed a technique which involved physical deposition of 1% (w/v) aqueous solution of the amphiphilic fluorinated oxazoline block copolymer shown in Figure 1, on the blood contacting surface of a polyurethane tubing in order to improve its biocompatibility. Surface analysis of the modified sample by X-ray photoelectron spectroscopy (XPS) showed a fluorine content of 31.3% for the coated versus 0.3% for the uncoated samples.

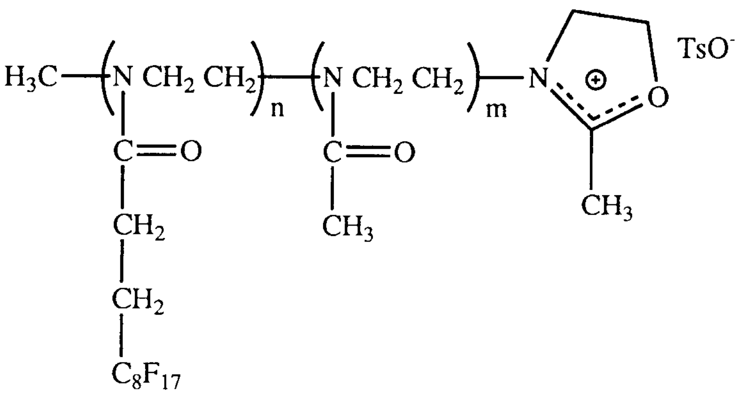
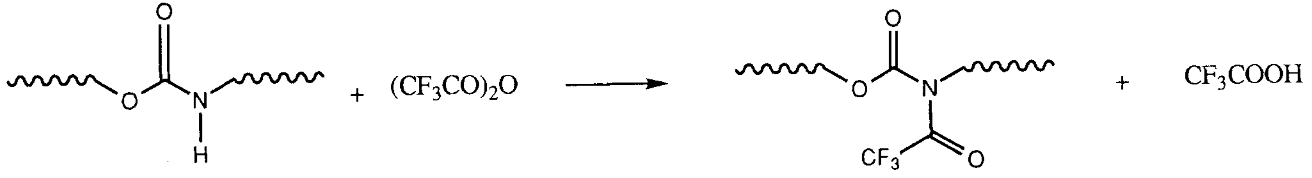


Figure 1. Fluorinated oxazoline block copolymer.

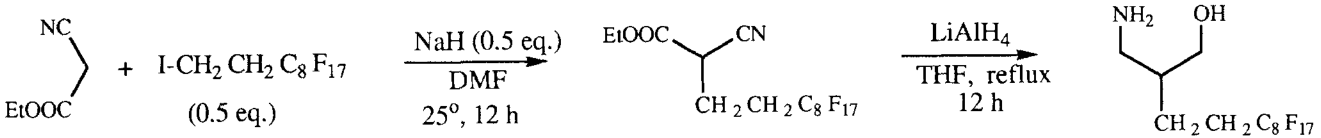
Petrovic and Korugic-Petrovic [15] employed trifluoroacetylation of polyurethane (Scheme 1) and noted that drastic conditions (long reaction times, 8 - 20 days and high TFA/NH ratios) were required. The process was accompanied by side reactions as well as degradation of the polyurethane, and the trifluoroacetylated samples were reported to be thermally unstable. Bruil *et al.* [17] employed radiation induced grafting techniques using a CF_4 plasma and obtained surface fluorine content of 50%. Plasma treatments, however, tend to yield grafted layers that are inhomogeneous as the glow discharge conditions can vary significantly over short distances within the reactor.

Graft coupling techniques, using aliphatic diisocyanates as coupler, have also been employed [18-20]. Han *et al.* [19,20] employed the technique to modify polyurethane using perfluorodecanoic acid (PFDA) and obtained surface fluorine composition of 29% to 44% at 0^{o} and 80^{o} take-off angles, respectively. Contact angles of 110^{o} (sessile drop) and 115^{o} (Wilhelmy plate, meniscus traverse rate = 3.3×10^{-4} m/sec) were reported for the modified membrane compared to 85^{o} and 86^{o}, respectively, for the unmodified one.

We report here in the synthesis and application of a novel amino alcohol, 2-aminomethyl-1,1,2,3,3,4,4-H-perfluorododecanol (APFD), and its application as a surface modifier for polyurethane. The efficiency of monofunctional perfluorodecanoic acid (PFDA) and APFD (**4**, Scheme 2), as fluorinating agents for polyurethanes, were compared. We had reasoned that since polyurethanes are step growth polymers with two terminal functional groups, a difunctional reagent might be superior to a monofunctional reagent for its modification. Additionally, both the



Scheme 1. Fluoroacetylation of polyurethane



Scheme 2. Synthesis of APFD

amine and the alcohol functional groups of APFD are expected to react more cleanly with isocyanates (no volatile is released) than the COOH group [21] of PFDA (releases CO_2).

MATERIALS AND METHODS

General

The polyurethane membranes used in this study were polytetramethylene glycol (PTMG) ether resins based on 4,4'-methylene bis(phenyl isocyanate) (MDI) designed by Dow Chemicals (Pellethane 2363-80A) specifically for health-care applications and extruded into films by Argotec Inc., Greenfield, MA. The membranes, 50 mm thick, were used after extraction with methanol for 24 hours at room temperature. Hexamethylene diisocyanate (HMDI, Aldrich Chemical Co.) was purified by distillation under reduced pressure. Toluene was dried over sodium metal and stannous octoate (28% Sn, Sigma Chemical Co.) was used as purchased. Perfluorodecanoic acid (PFDA) (Aldrich Chemical Co.) was recrystallized from toluene.

Ethyl 2-cyano-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorododecanoate (3)

A 2-L 3-neck flask equipped with a mechanical stirrer was purged with N_2 and charged with NaH (60% dispersion in mineral oil, 14 g, 0.36 mol) and DMF (250 mL). A solution of ethyl cyanoacetate (**1**, 83 mL, 0.78 mol) in DMF (80 mL)was added dropwise at 0°C and the mixture was stirred at room temperature for 1 hour. A solution of iodo-1H,1H,2H,2H-perfluorodecane (**2**, 200 g, 0.36 mol) in a mixture of DMF (100 mL) and dry THF (100 mL) was added dropwise and the mixture was stirred overnight at room temperature. The solvents were removed by rotatory evaporation under high vacuum. $CHCl_3$ (700 mL) was added to the residue and the cloudy solution was extracted with HCl (1M, 300 mL). The cloudy organic layer was heated until it turned clear. Upon cooling, white crystals formed which were isolated by filtration and shown to be the dialkylated product (54.5 g, 13% based on the iodide). The filtrate was evaporated and the residue was vacuum distilled to give the monoalkylated material (**3**) (94.3 g, 47%). Mp: 76-78°C. Bp: 110°C at 0.03 mmHg (98% pure by GC). ^{1}H NMR ($CDCl_3$): δ 1.3 (t, 3H, $J = 7.1$ Hz, CH_3), 2.3 (m, 4H, CH_2), 3.5 (dd, 1H, $J =$ 6.5, 6.5 Hz, CH), 4.3 (q, 2H, $J = 7.1$ Hz, CH_2). ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ 81.3, 114.7, 122.4 (6F), 123.2, 123.7, 126.6. ^{13}C NMR ($CDCl_3$, H-decoupled): δ13.9, 21.0 (t, $J_{CF} = 3.8$ Hz), 28.1 (t,

J_{CF} = 22.9 Hz), 36.4, 63.4, 115.3, 164.8. IR (KBr): 1750 (s) cm^{-1}. HRMS (EI): Calcd for $C_{15}H_{10}F_{17}NO_2$, m/z = 559.044 (M^+), found 559.044.

2-Aminomethyl-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorododecanol (4)

A dry 2-L 3-neck flask equipped with a mechanical stirrer and reflux condenser was purged with N_2 and charged with $LiAlH_4$ (22 g, 0.57 mol) and dry THF (500 mL). Compound **3** (94 g, 0.16 mol) in dry THF (50 mL) was carefully added dropwise to the suspension at 0°C. After the addition was complete, the mixture was refluxed overnight. The reaction mixture was cooled to 0°C and quenched very slowly with water (22 mL), making sure that each small drop of water had fully reacted and that most of the foam had disappeared before addition of the next drop of water. It was then treated successively with aqueous NaOH (22 mL, 15% w/w), and H_2O (66 mL). The fine granular inorganic precipitate was filtered and rinsed with ether. The filtrate, subjected to slow evaporation and then chasing (with benzene and absolute ethanol to remove any water), yielded a yellowish brown oil which upon distillation afforded 40 g (40%) of a sticky waxy solid. A small amount of the waxy solid was purified by column chromatography over silica using a 75:25:1 (v/v/v) mixture of CH_2Cl_2/MeOH/NH_3 for characterization. Mp: 45-54°C, clearing at 75°C. ^1H NMR ($CDCl_3$): δ 1-2 (m, 5H, CH_2-CH_2-CH), 2.7 (dd, 1H, J = 14. 9 Hz, CH_2-O), 3.0 (m, 1H, CH_2-O), 3.5 (dd, 1H, J = 12, 9 Hz, CH_2-N 3.9 (m, 1H, CH_2-O). ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ 81.4, 115.3, 122.4, 123.2, 123.9, 126.7. ^{13}C NMR ($CDCl_3$): δ 19.6, 29.0, 40.5, 47.9, 67.1 + impurities. 92% purity by GC. IR (KBr): 3360 (b), 1460 (s), 1203 (b) cm^{-1}. HRMS (EI): Calcd for $C_{13}H_{12}F_{17}NO$, m/z = 521.065 (M^+), found 521.065.

Polyurethane Modification

The modifications were performed following literature procedure [19,20]. A typical procedure using PFDA as modifier involved the following: A 5 cm x 5 cm specimen of the original polyurethane membrane (PU) was extracted in methanol at room temperature for 24 hours and then air-dried overnight to yield PUMeOH. This was subsequently treated with HMDI (5 mL) and stannous octoate catalyst (0.25 mL) in toluene (80 mL) at 40°C under dry nitrogen for 1 hour. The resulting material was washed successively in toluene (3 x 20 mL) and anhy-drous ether (3 x 20 mL) to give PUHMDI. This was converted immediately to PUPFDA by treatment with PFDA (0.20 g, 3.9×10^{-4} mol) for 2 hours in toluene (40 mL) at 40°C under dry nitrogen. The resulting PUPFDA was washed successively with toluene (3 x 20 mL) and acetone (3 x 20 mL) and then dried overnight in a vacuum oven at ambient temperature. PUAPFD was similarly prepared using APFD in the place of PFDA.

Characterization

Fluorine incorporation was monitored by infrared spectroscopy (IR) and all samples were characterized by XPS and scanning electron microscopy (SEM). SEM micrographs were obtained on membranes sputter-coated with gold-palladium using a Model 4500 Hitachi field emission microscope at an accelerating voltage of 5 KV. Conventional XPS was performed on an SSL-100-03 photoelectron spectrometer using Al K_αx-rays at 1486.6 eV. It was difficult to obtain XPS spectra of the untreated polyurethane (PU) due to excessive outgassing. IR spectra were recorded on a Perkin Elmer 683 spectrophotometer equipped with a PE Model 3600 IR data station. Multiple internal reflection infrared (MIR) spectra were obtained using a 45° KRS-5 crystal. Static contact angles were obtained on an IMASS (Instruments for the Materials and Structural Sciences, Mass., US) Contact Angle Analyzer Model CAA2. Dynamic contact angles were obtained at 3×10^{-6} m/s via a modified Wilhelmy plate technique using a Textile Research Institute (Princeton, NJ) computer-controlled wettability/friction apparatus consisting of a Cahn model D200 electrobalance and a motion controller/motor for moving the probe liquid up or down.

RESULTS AND DISCUSSION

Synthesis

The synthesis of the amino alcohol started with alkylation of ethyl cyanoacetate to give a mixture of unreacted starting material, mono- (**3**) and dialkylated products (Scheme 2). It was necessary to use 1H,1H,2H,2H-perfluoroalkyl iodides. In absence of the ethyl spacer, no alkylated product was isolated. This could be due to either a slow alkylation reaction or more likely, to water solubility of the expected product since it has an acidic hydrogen.

The monoalkylated product was obtained in 80-95% (by GC) purity because complete removal of impurities by distillation proved difficult. The dialkylated product was removed from the reaction mixture by recrystallization which made distillation of the monoalkylated product easier. Reduction of monoalkylated product with $LiAlH_4$ yielded amino alcohol **4** in modest isolated yields.

PU

$\downarrow$ dry methanol, 24 hours

PUMeOH

$\downarrow$ 80ml toluene, 40°C, dry N_2
5 ml HMDI, 0.25ml $Sn(Oct)_2$, 1 h
wash in toluene (3x), ether (3x), air dry

PUHMDI

$\downarrow$ 40ml toluene, 40°C, dry N_2, 0.2 g PFDA, 2 h
wash in toluene (3x), acetone (3x), air dry

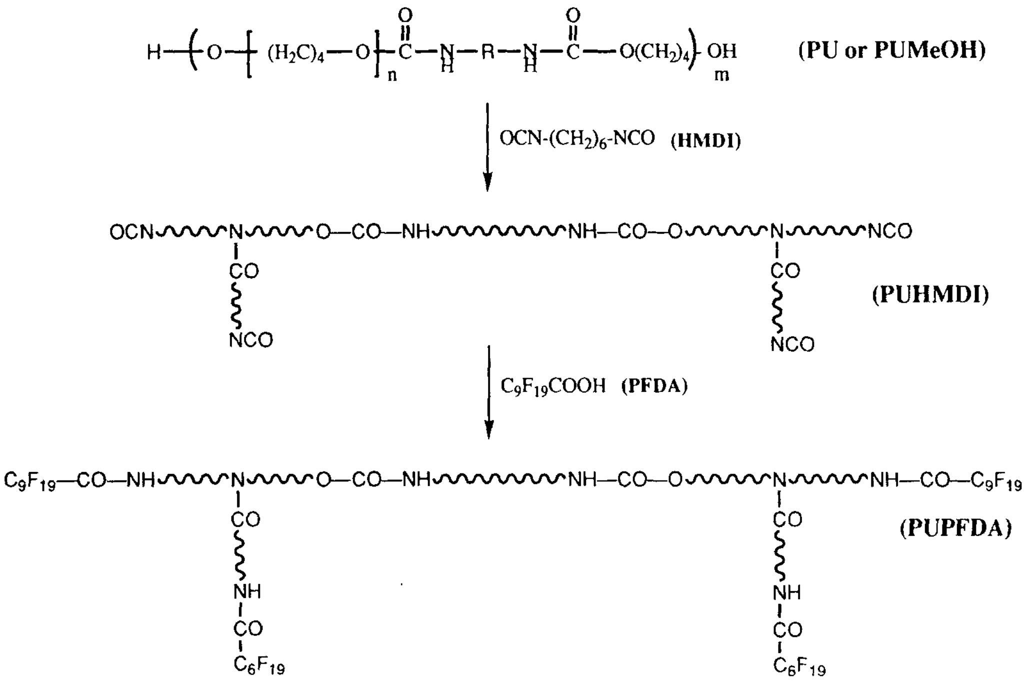
PUPFDA + CO_2

Scheme 3. Typical modification process for the polyurethane membrane

This is probably due to side reactions caused by the presence of the acidic α-hydrogen in the starting material. The yield of the reaction improved when the lithium and aluminum salts were neutralized carefully to form a fine granular precipitate that could be filtered easily. Strong complexation of the amino alcohol salts to lithium and aluminum salts made the work-up more complex and sensitive to the amount of water added. ^{1}H NMR analysis showed that the methylene protons next to nitrogen and oxygen had a clear AB splitting pattern. Since the monoalkylated product possesses a chiral center, all methylene protons are diastereotopic and couple with each other. The structures of the products were confirmed by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy. The ^{19}F NMR spectrum remained unchanged during the entire synthesis indicating that the fluoroalkyl group was unaffected.

Polyurethane Modification

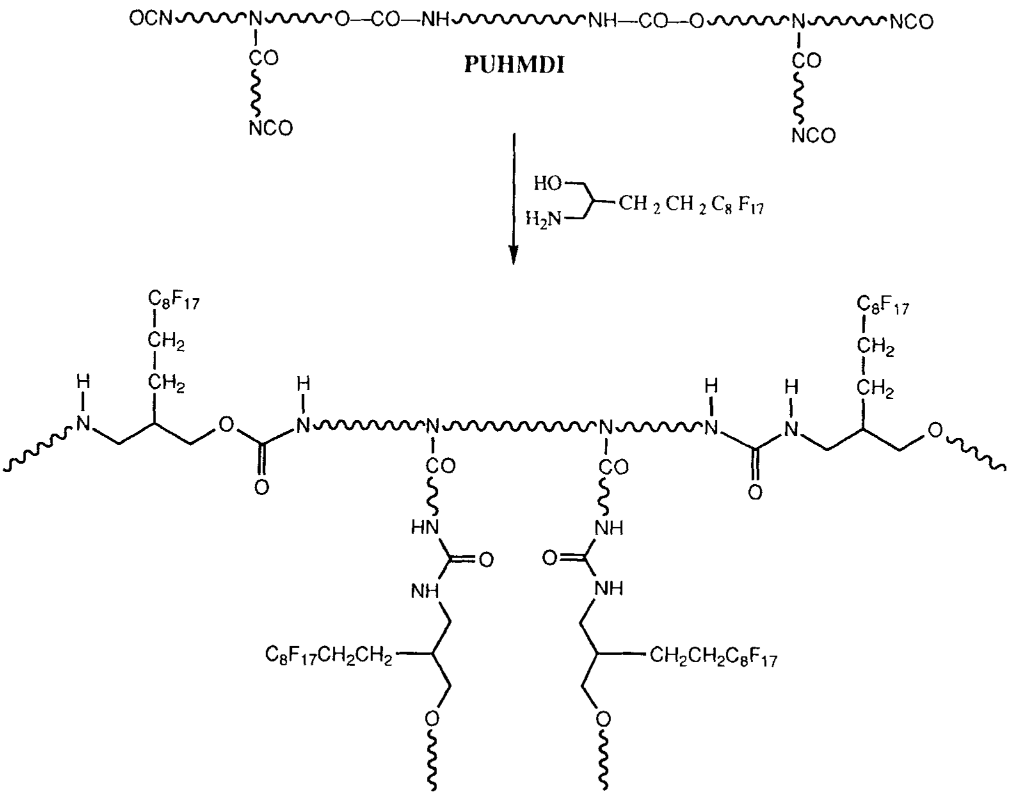
A typical polyurethane modification using PFDA as modifier is outlined in Scheme 3. All of the characterization information presented in the sections below refer to the polyurethane membranes. To determine the effect of reaction time and concentration of the modifier on the amount of fluorine incorporated, the reaction times were varied from two to 2- 24 hours using two different quantities of modifier, 0.2 g (3.9×10^{-4} mol) and 0.8 g (1.56×10^{-3} mol). Numbers following PUAPFD indicate both the amount of the amino alcohol used for the modification



Scheme 4. Modification of the polyurethane membrane using perfluorodecanoic acid (PFDA)

and the reaction time. For instance, PUAPFD2,2 indicates a specimen treated with 0.2 g of the amino alcohol for 2 hours, while PUAPFD8,2 indicates a specimen treated with 0.8 g of the modifier for 2 hours. To determine if fluorine could be incorporated into the polyurethane membrane without first going through the HMDI treatment, a PU specimen was treated with 0.2 g of the amino alcohol for 2 hours omitting the HMDI stage. This control was labeled PUAPFD2,2CO. The effects of heat, solvents and air-drying on the morphology of the membranes were monitored by subjecting the membranes to the same procedure but in the absence of HMDI, PFDA and APFD and the resulting controls were labeled PUSEM. To check for the stability of the modified membranes, a specimen taken from PUAPFD2,4 was boiled in doubly deionized water for 6 hours, dried and characterized.

Schemes 4 and 5 illustrate for each perfluorinated modifier the expected chemical reactions. Treatment of PU with excess MDI would give α,ω-diisocyanato-PU (PUHMDI) which would also contain some pendent isocyanate groups as



PUAPFD

Scheme 5. Modification of the polyurethane membrane using APFD

a result of reaction with some of the backbone urethane NH's (Scheme 4). The latter reaction has been previously observed during polyurethane synthesis [21]. The initial product formed upon addition of PFDA would be an unstable polymeric anhydride which would readily undergo decarboxylation to form an amide linkage. The hydrophobic perfluoroalkyl groups are expected to migrate to the surface of the membrane rendering it water-repellent. In contrast to the above reactions, reaction of the difunctional modifier (APFD) with PUHMDI might lead to some oligomerization giving a polymer with several pendent perfluoroalkyl surface groups. Even if oligomerization did not occur due to the rigidity of the preformed membrane, the difunctional modifier could still dimerize an existing polymer chain through coupling of their diisocyanate end groups in close proximity of each other. However, the material obtained remained soluble indicating that either no or very little crosslinking occurred. Preliminary GPC data on the modified materials showed a slight increase in the molecular weight of the APFD-modified membrane over that of PFDA-modified one. Further studies involving detailed molecular weight measurements and solution behavior of the modified membranes are in progress.

Infrared Studies

The transmission infrared spectra for all polyurethane samples (both treated and untreated) showed peaks at 3320 cm^{-1} due to hydrogen-bonded N-H, 1733 cm^{-1} due to free C=O and at 1703 cm^{-1} due to hydrogen-bonded C=O. With the exception of PUHMDI which showed a strong peak at 2250 cm^{-1} due to the NCO group, transmission IR could not be used to distinguish one membrane from another. The absence of the NCO peak in the modified samples suggests that the isocyanate groups have reacted. However, the transmission IR spectra of the PUPFDA and PUAPFD samples did not show the C-F stretching frequency expected in the 1400 - 900 cm^{-1} region. Multiple internal reflection (MIR) infrared spectra of the modified samples, in contrast, showed the C-F stretching frequency at ca. 1184 cm^{-1}. In addition, there was an enhancement in the intensity of the urea C=O peak around 1615 cm^{-1} in all PUAPFD samples. This is an indication of not only the successful attachment of HMDI to the polyurethane membrane but also the involvement in the reaction of the NH_2 groups. The PUPFDA, however, showed an enhancement in the free C=O peak around 1733 cm^{-1}. The results are consistent with the reactions outlined in Schemes 4 and 5.

X-ray Photoelectron Spectroscopic Studies

The XPS scans for the polyurethane samples are presented in Figure 2. PUMeOH showed the expected peaks due to C_{1s} (~284 eV), N_{1s} (~349 eV) and O_{1s} (~523 eV) while PUHMDI showed an additional peak that we attributed to Sn_{3d} (~ 485 eV) from the stannous octoate catalyst. Both PUPFDA and PUAPFD showed F_{1s} (~680 eV) in addition to C_{1s}, N_{1s}, Sn_{3d} and O_{1s} peaks.

High resolution scans of the C_{1s}, N_{1s}, O_{1s}, Sn_{3d} and F_{1s} regions enabled us to obtain the surface compositions presented in Table 1. A decrease in percent surface carbon in going from PUMeOH to PFDA- and APFD-treated samples was accompanied by a corresponding increase in percent surface fluorine composition (0% for PUMeOH, 23 - 36% for PUPFDA and 37 - 41% for PUAPFD) confirming the slightly higher efficiency of the amino alcohol (APFD) as a fluoroalkylating agent than the monofunctional acid (PFDA). The observed ratios of fluorine to carbon suggest that (1) the coverage with fluoroalkyl groups was

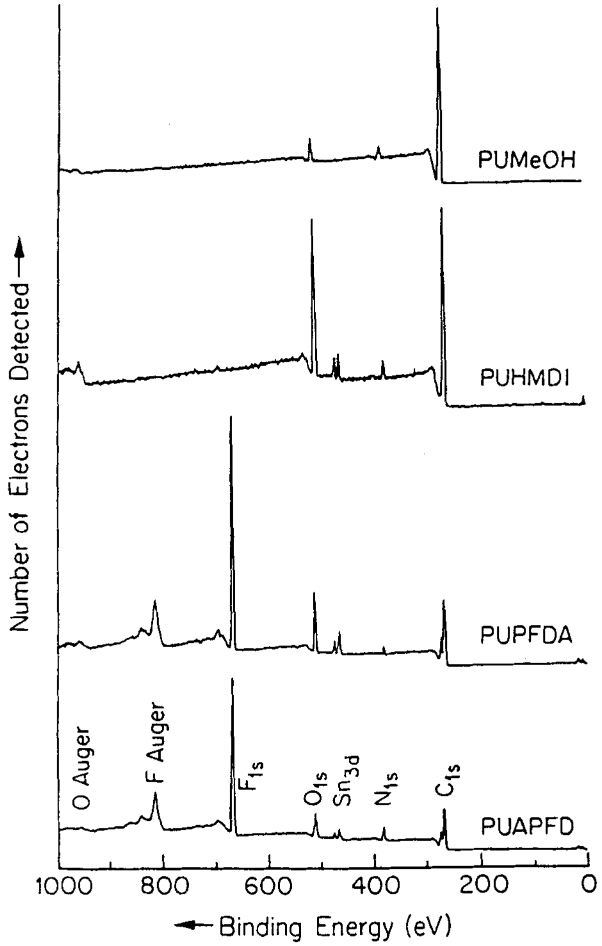


Figure 2. XPS scans for the various polyurethane membranes.

higher in PUAPFD than in PUPFDA (F/C = 0.91 and 0.74, respectively), and (2) both the treatment time and the quantity of amino alcohol had no significant effect on the amount of fluorine incorporated (F/C = 0.81 - 0.91 for all PUAPFD samples).

Representative high resolution scans of the C_{1s} regions for both the original and treated samples are presented in Figure 3. The fluorinated samples showed peaks due to CF_3 and CF_2 in addition to the hydrocarbon C-C, ether C-O, amide N-C=O and carbamate N-CO-O groups of PUMeOH and PUHMDI. The specimen used to check whether or not HMDI was required for the modification

TABLE 1. Surface Composition by XPS for Various Polyurethane Membranes

SAMPLE	C_{1s}	N_{1s}	Sn_{3d}	O_{1s}	F_{1s}	N/C	F/C
PUMeOH	89.4	4.1	-	6.5	-	0.05	-
PUHMDI	73.3	3.7	0.9	22.2	-	0.05	-
PUPFDA2,2	46.7	1.6	1.2	15.8	34.6	0.03	0.74
PUAPFD2,2	44.0	6.1	0.6	9.2	40.1	0.17	0.91
PUAPFD2,4	44.4	6.0	0.6	8.9	40.2	0.14	0.91
PUAPFD2,6	44.9	7.4	0.7	10.3	36.7	0.16	0.82
PUAPFD2,8	45.6	6.4	0.5	8.7	38.8	0.14	0.85
PUAPFD2,10	45.9	7.3	0.5	9.0	37.3	0.16	0.81
PUAPFD2,12	44.6	6.1	0.6	8.1	40.6	0.14	0.91
PUAPFD2,24	44.7	7.1	0.6	9.0	38.6	0.16	0.86
PUAPFD2,2CO	74.3	3.5	-	20.3	2.0	0.05	0.03
PUAPFD2,4C1	49.4	7.0	0.2	12.2	31.2	0.14	0.63
PUAPFD8,2	45.8	7.5	0.5	8.2	38.0	0.16	0.83

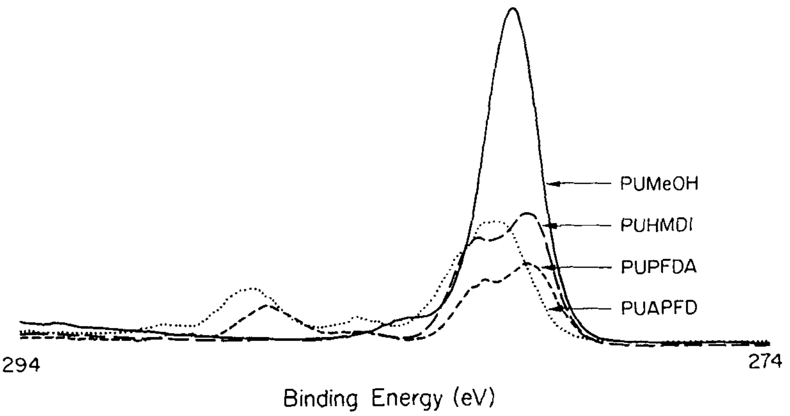


Figure 3. C(1s) High energy resolution scans for the polyurethane membranes.

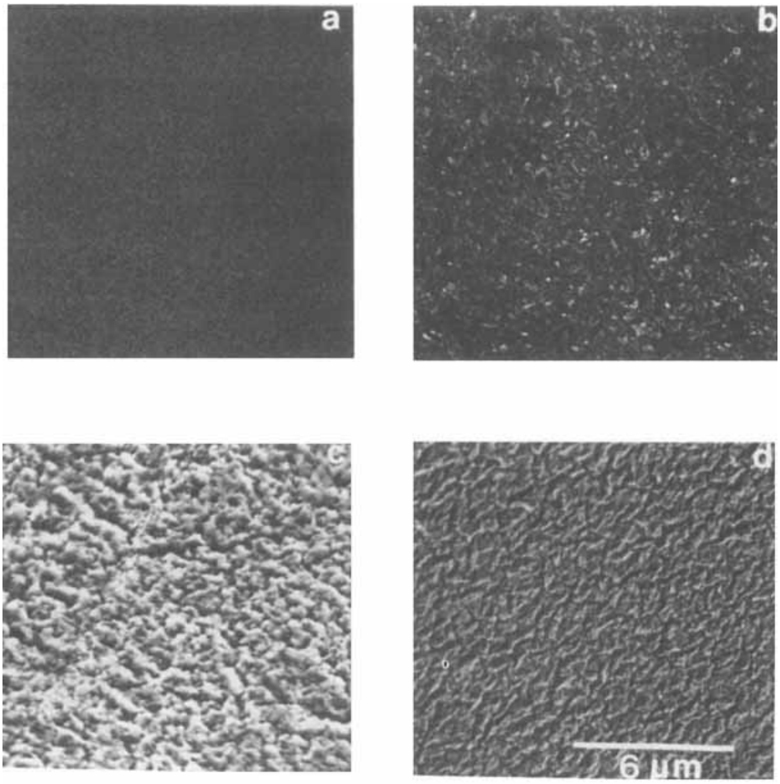


Figure 4. SEM micrographs for the polyurethane membranes: (a) PU; (b) PUHMDI (c) PUPFDA (d) PUAPFD.

(PUAPFD2,2CO) had only ~2% fluorine incorporated after treatment for 2 and 24 hours, respectively, indicating that HMDI indeed increased considerably the amount of fluorine incorporated onto the polyurethane membrane surface. PUAPFD2,4C1, the specimen used to check for the stability of surface fluorine, had approximately 31% fluorine after boiling in doubly deionized water for 6 hours showing that the surface of the modified material is durable.

Scanning Electron Microscopy

Figure 4 shows representative SEM micrographs for the different polyurethane membranes. Examination of the micrographs revealed differences in the morphologies of the treated and untreated samples. The PUHMDI (4b), PUPFDA (4c) and PUAPFD (4d) showed some surface roughness which was absent in PU (4a) or PUMeOH. The surface roughness was more pronounced for PUPFDA

TABLE 2. Contact Angle Data for Various Polyurethane Membranes[a]

	Dynamic Contact Angles				Static Contact Angles
SAMPLE	Hexadecane	Water			Water
	Θ_{adv}	Θ_{adv}	Θ_{rec}	Θ_{adv}-Θ_{rec}	Θ_s
PU	92° (2)	89° (1)	72° (3)	17°	97° (5)
PUMeOH	95° (2)	91° (2)	46° (4)	49°	-
PUPFDA2,2	92° (1)	104° (3)	56° (3)	48°	98° (3)
PUAPFD2,2	93° (6)	102° (2)	51° (5)	51°	112° (5)

[a] Standard deviations in parentheses.

(Figure 4c) than for PUAPFD (Figure 4d). All PUAPFD samples showed surface roughness that did not seem to follow any particular trend with time. SEM micrographs of the PUSEM (control specimens used to check whether heat and solvent were responsible for the observed roughness) were identical to the PU micrograph shown in Figure 4a. This indicates that the observed roughness could not be attributed to temperature and solvent effects alone unless such temperature and solvent effects ensued after the HMDI and/or modifier treatments.

Wettability Studies

The wettability data obtained for the polyurethane membranes in water and hexadecane are presented as contact angles in Table 2. That the modified membranes gave higher advancing contact angles than the untreated PU is an indication of higher surface hydrophobicity. Furthermore, the static contact angles showed that APFD-modified materials exhibited higher Θ_{adv} than did both PFDA-treated and untreated samples. However, dynamic contact angles revealed that both perfluorinated systems are equally unwettable.This is surprising since the F/C ratios showed that PUAPFD had higher fluorine content than did PUPFDA. This could mean that the minimum fluorine content needed to achieve a particular level of hydrophobicity was attained with the amount of fluorine incorporated through PFDA-modification.

The elastomeric nature of polyurethane would allow optimum migration of all incorporated fluorine, no matter how small, to the surface. Alternatively, the small differences might be a reflection of the expected step-growth oligomerization (Scheme 5) not occurring to any appreciable extent due to the restricted mobility of a preformed membrane. The higher efficiency of APFD would be best realized if it were incorporated during the synthesis of the poly-urethane and the resulting modified polymer used for the membrane preparation since under such conditions the reaction outlined in Scheme 5 is expected to occur to an appreciable extent. Such a study is currently in progress.

The receding contact angles for the fluorinated membranes were lower than those for the untreated membrane in spite of the high surface fluorine content of the modified membranes. We attribute this to the roughness of the modified membrane surfaces as observed by SEM since all the samples have the same high energy CONH groups. Surface roughness tends to lower the inherent contact angle for a given surface. Furthermore, the untreated polyurethane, PU, might contain some water-insoluble additive which could have been removed during the methanol extraction, making the receding contact angle for PUMeOH significantly different from that of PU. All samples exhibited wetting hysteresis ($\Theta_{adv} > \Theta_{rec}$) which is an indication that the individual membranes are energetically heterogeneous. This is to be expected since the high energy CONH sites would be expected to interact strongly with water via hydrogen bonding. The surface heterogeneity seen in the SEM is also expected to contribute to large hysteresis. As might be expected, untreated PU with the smoothest surface showed the lowest hysteresis. All of the APFD-treated samples were equally wettable and equally heterogeneous, and seemed to have about the same hysteresis values. This is consistent with the XPS results which showed that neither treatment time nor modifier concentration had any significant effect on the amount of fluorine incorporated. The high advancing contact angles of water and hexadecane suggest that the modified microporous membranes are both water- and oil-repellent.

CONCLUSION

Modification of polyurethane membranes and their surface properties have been investigated as part of an ongoing research in our laboratories on structure-property relationships in polyurethane membranes in order to lay the ground work for protective clothing design. Two modifiers, perfluorodecanoic acid and a novel amino alcohol, 2-aminomethyl-1,1,2,3,3,4,4-H-perfluorododecanol, were compared for their fluoroalkylating ability. Conventional XPS results showed that the modified samples contained fluorine and that the amino alcohol was slightly more efficient than perfluorodecanoic acid. Both the treatment time and the amount of modifier was found to have no significant effect on the amount of fluorine incorporated. Evidence for fluorine incorporation was also provided by infrared spectroscopy (MIR) which showed the C-F stretching band around 1184 cm^{-1}. The finding that the modified microporous membranes were both water and oil repellent suggests that they may find application in protective clothing design where good liquid barrier properties are desired. Further work is in progress to understand the mechanism of the modification process and fully exploit the results reported herein. Studies on monolithic membranes where permeation by solution-diffusion mechanism can occur are also in progress.

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