

Reduced Frictional Resistance of Polyurethane Catheter by Means of a Surface Coating Procedure

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SYNOPSIS

Polyurethane and poly(vinyl pyrrolidone) (PVP)-coated polyurethane catheter surfaces were characterized by time of flight secondary ion mass spectrometry (TOF-SIMS) and were compared in terms of wettability and adhesion and friction properties by scanning force microscopy (SFM). Using TOF-SIMS, the presence of hard segments in the first layers of the polyurethane catheter were shown, and the presence of a PVP coating on the modified catheters was clearly identified. The PVP coating induced a hydrophilic surface after immersion of the catheters in water for several hours. When SFM experiments were carried out in water, the adhesive force developed between the PVP-coated surface and the tip became immeasurably small. Tribometric measurements along a 500-nm scan line quantified friction coefficients of 0.05 for the coated catheter and 0.50 for the native polyurethane catheter. The PVP coating on catheters provided smooth, soft, and nonadhesive surface properties, which would minimize difficulties during their insertion into the vessels of the patient. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Hydromer[®] is a poly(vinyl pyrrolidone) (PVP) crosslinked with an isocyanate. The crosslinked PVP is water insoluble but its network structure confers on it a swelling behavior in water. It has the properties of a hydrogel-like material.

Studies on the biological responses of Hydromer[®] coatings on the outer surface of polyurethane central venous catheters (CVCs) showed a strong reduction of fibrinogen and fibronectin adsorption compared to all other Hydromer[®]-free polyurethane CVCs.¹ Furthermore, protein-mediated adhesion of *Staphylococcus aureus* and *S. epidermidis* was reduced. These biological effects indicate that the PVP coating plays a role in decreasing protein-surface interactions that the native polyurethane surface does not. Furthermore, reported hydrophilic coatings, such as modified PVP, are widely used for lubricating biomaterials used for catheterization and endos-

copy,²⁻⁶ because they allow easy insertion and removal of the devices.

The aim of this work is to show how the Hydromer[®] coating can be used to modify surface features, such as the wettability, the adhesion forces, and the properties of "slipperiness," in inducing surface lubrication of polyurethane tubing. The chemical compositions of Hydromer[®]-coated and of native polyurethane catheters made of Pellethane[®] were compared by time of flight secondary ion mass spectrometry (TOF-SIMS). The hydrophilic properties of catheter surfaces were evaluated by static water contact angle measurements. Adhesion and attraction forces were measured using scanning force microscopy (SFM). Friction force microscopy was used to conduct microtribological measurements on the catheters on a microscopic scale.

EXPERIMENTAL

Catheters

Pellethane[®] 2363 (Dow Chemical Co., Ltd.) is a poly(tetramethylene oxide)-based polyurethane having

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hard segments of diphenylmethane diisocyanate and 1,4-butanediol. Catheters are generally produced by an extrusion process. Samples of single lumen (outer diameter 0.085 in.) tubings of Pellethane® and of Hydromer®-coated Pellethane® (Hydromer Inc., Whitehouse, NJ) were characterized as received, under the same conditions in which they are used in the hospital.

TOF-SIMS

TOF-SIMS spectra of the outer surface of the studied catheters were obtained by using a Perkin-Elmer PHI 7000 instrument. A 8-keV cesium ion primary beam was scanned over an area of $100 \times 100 \mu\text{m}^2$ of the catheter surface. The total ion density was on the order of 6×10^{11} ions/cm², corresponding to static conditions. A TOF analyzer with a mass range of 1–1000 amu was used to detect the secondary ions. Pulsed low energy electrons were used to neutralize the surface charges that built up during ion bombardment. Mass resolution was typically 4000. The mass range was calibrated using well-defined hydrocarbon peaks (CH_3^+ , C_2H_3^+ , C_3H_5^+).

Contact Angle Measurements

Both catheters were immersed in deionized water (MilliQ, Millipore, Kloten, Switzerland) and subsequently dried by removal of residual water from the surface with a filter paper. Immediately after drying, comparison of their wettability by water was obtained by measuring the static contact angle of a 3- μL deionized water drop. Photographs were taken 5 s after deposition of the drop.

Measurements of Surface Interaction Forces with SFM

Pieces of catheters of about 1 cm in length were glued onto holders with solvent-free epoxy adhesive. Experiments under deionized water were carried out by immersing samples in a liquid cell.

The measurements of the interaction forces between the tip of the SFM-BD2 system from Park Scientific Instruments (PSI, Sunnyvale, CA) and the catheter surfaces were performed using a 10- μm piezo scanner and a microfabricated triangular cantilever supporting an integrated pyramidal tip of Si_3N_4 (Microlever™, PSI, force constant 0.1 N/m).

Force-versus-distance curves were obtained by recording the lever deflection during approach and separation of the sample as a function of sample displacement. When the sample approached close to the tip, the latter was slightly attracted and came into contact with the surface of the sample. When

the sample was retracted from the tip, a pronounced attractive interaction was usually registered before the tip and the sample separated. The sample position was defined as equal to zero when the cantilever was in contact and parallel to the surface. The forces that evolved during the displacement of the sample were calculated from the lever deflection values. The lever deflection values were multiplied by the lever force constant and divided by the slope of the advancing linear repulsive part of the force-versus-distance curve of a freshly cleaved mica, analyzed in the same conditions.⁷

F_{att} , the attractive force, represents the force on approach measured as the tip is brought into contact with the surface sample; and F_{adh} , the adhesive force, quantifies the force needed by the lever to break the adhesion between the tip and the sample during withdrawal of the sample.

Microscopic Scale Tribometry with SFM

Microfriction measurements were made with the SFM tribometer (AST CSEMEX) developed by the Swiss Center for Electronics and Microtechnology Inc. (Neuchâtel, Switzerland). Experiments were carried out using a triangular Si_3N_4 tip supported by a rectangular cantilever having a normal and lateral force constant of 0.05 and 500 N/m, respectively (OMCL series, Olympus Optical Co., Tokyo, Japan). The samples were scanned under water and phosphate-buffered saline (PBS) solution along a 500-nm line at a scanning speed of 1 Hz, and the applied normal force was increased and decreased periodically. The difference between the lateral force measured during the back scan and that measured during the forward scan corresponds to the frictional force between the tip and the sample surface. The values of the friction coefficient were calculated from the slope of the linear dependence obtained by plotting the friction forces versus applied normal forces on the samples.^{8,9} Because all the measurements were carried out under the same conditions (same levers, laser beam adjustments, and solution conditions), the values of the friction coefficient obtained for both catheters and glass as reference substrate can be compared.

RESULTS AND DISCUSSION

TOF-SIMS Characterization

SIMS proved to be a valuable method for analyzing the composition of polymer surfaces, for instance for detecting the enrichment of the surfaces with additives or undesirable contaminants.¹⁰ The tech-

nique allows major fragments of surface compounds to be identified and has the potential to give detailed information on the molecular structure of the outermost polymer surface layers that is difficult to achieve with other techniques like electron spectroscopy for chemical analysis (ESCA).^{11,12}

Figures 1 and 2 show the positive ion SIMS spectra in the 0–240 amu range for uncoated and PVP-coated catheters, respectively. Table I suggests possible ion assignments for the peaks in the positive ion spectrum of a Pellethane® catheter surface. Structures for these ions and their relationship to the polymer chain were identified according to Hearn et al.,^{13,14} Newman et al.¹⁵ and Tyler et al.¹⁶ All the peaks characteristic of the Pellethane® spectrum can also be found in the Hydromer® spectrum. The main fragments corresponding to the soft segments constituting the polyurethane surface are observed for both polymers at 55 ($C_4H_7^+$, $C_3H_3O^+$), 57 ($C_4H_9^+$), 71 ($C_4H_7O^+$), 73 ($C_4H_9O^+$), 127 ($C_8H_{15}O^+$), and 145 amu ($C_8H_{17}O_2^+$). Peaks located at 42, 77, 91, 106, 150, 165, and 223 amu can be assigned to the hard segment fragments $C_2H_4N^+$, $C_6H_5^+$, $C_7H_7^+$, $C_7H_8N^+$, $C_8H_7NO_2^+$, $C_{13}H_9^+$, and $C_{14}H_{11}ON_2^+$, respectively. The presence of such fragments confirms that there is no pronounced surface

segregation of polyurethane blocks. Hard blocks may be dispersed in the soft matrix at the first layers of Pellethane®, although the soft segments having a low surface energy are expected to cover or to predominate at the surface. This phenomenon was already observed by Hearn et al.¹⁴ and Affrossman et al.¹⁷ using SIMS. However, it should be noted that SIMS (like other vacuum techniques) probes the composition of the surface under ultrahigh vacuum (UHV) conditions. These results are not necessarily typical for a corresponding surface in contact with water or biological environments, because more or less rapid surface rearrangements following introduction of samples in the vacuum chamber have been demonstrated for many polymers.¹⁸ Nevertheless, the main conclusions deduced from this analysis, regarding the specific differences between coated and uncoated catheter surfaces, should still be valid.

Siloxane contaminants or additives on the polymer surfaces were indicated by the presence of peaks at 28, 147, 207, and 221 amu, typical for polydimethylsiloxanic components. Detection of this marginal siloxane content was also observed using ESCA¹ for both catheters and its amount was estimated to be about 4% (atomic percentage based on elemental contribu-

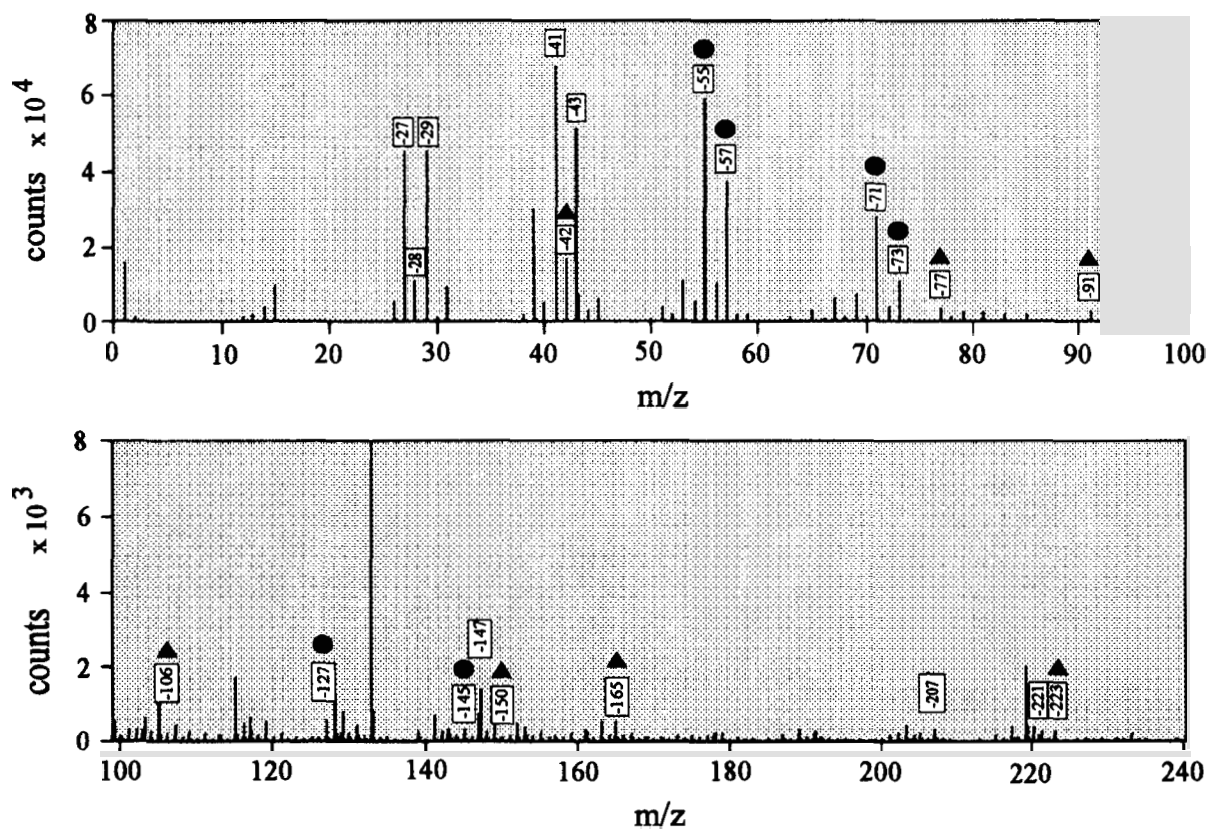


Figure 1 Positive SIMS spectrum of a Pellethane® catheter: (●) contribution of polyurethane soft segments and (▲) contribution of polyurethane hard segments.

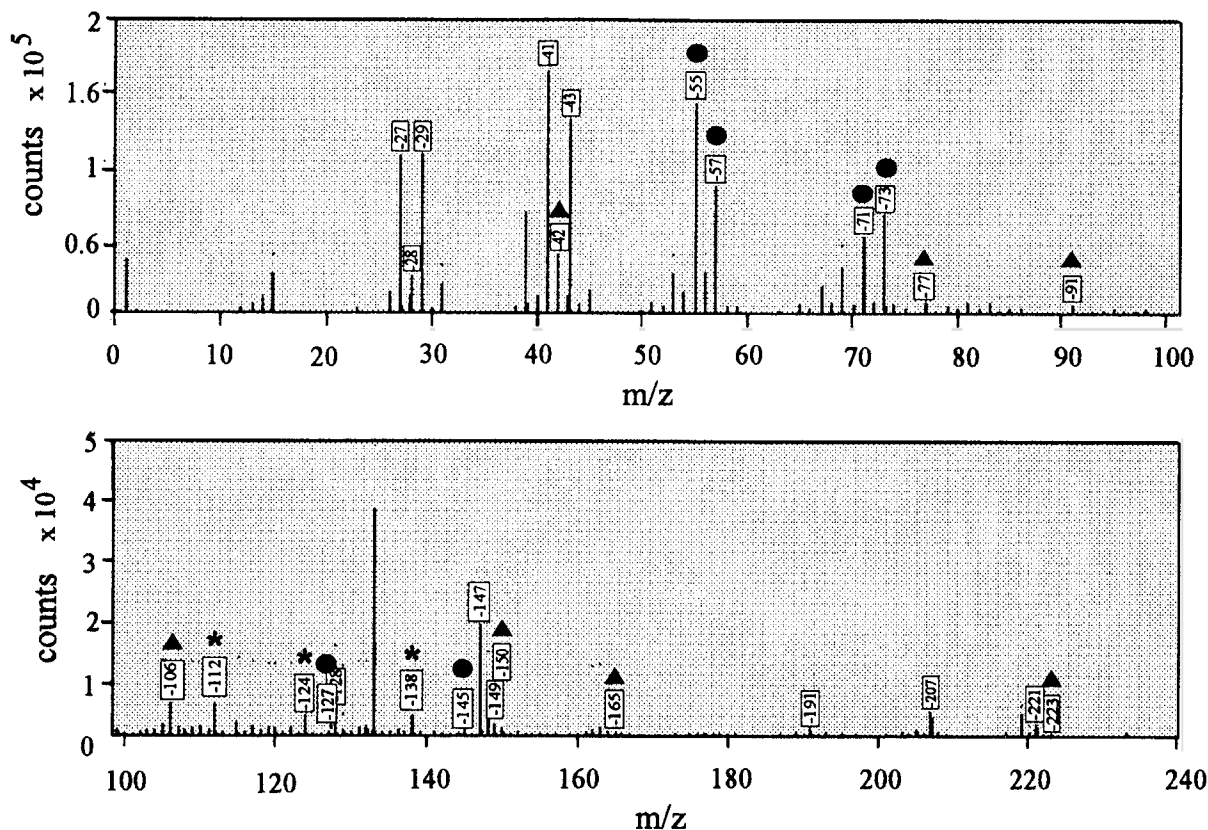


Figure 2 Positive SIMS spectrum of a Hydromer® catheter: (●) contribution of polyurethane soft segments, (▲) contribution of polyurethane hard segments, and (*) contribution of PVP.

tion of carbon, oxygen, nitrogen, and silicon). The nonattributed peaks may be due to amide waxes, which are generally used as a processing aid in the extrusion of polyurethane tubings,¹⁹ or antioxidant additives.¹⁶

The Hydromer® spectrum is presented in Figure 2. It is interesting to note that the relative intensity of peaks attributed to fragments of hard segments is higher for the Hydromer®-coated polyurethane than for the native material. It seems that this type of segment is more concentrated in the surface layers of the Hydromer®-coated catheter. Segment rearrangement may occur because of the presence of the PVP coating, which modifies the hydrophilicity of the interface and favors the presence of the more hydrophilic hard units. Migration of the hard segments toward the surface after contacting the hydrophilic environment was previously observed using ESCA.²⁰

The obvious changes in the Hydromer® spectrum were the appearance of peaks reflecting the presence of PVP. They were localized at 112, 124, and 138 amu attributed, respectively, to $C_6H_{10}NO^+$, $C_7H_{10}NO^+$, and $C_8H_{12}NO^+$. In addition to the siloxanic fragment attributed to the 207 amu, the assignment of this peak to the ionized dimerized vinylpyrrolidone, $C_{11}H_{15}N_2O_2^+$, might also be proposed


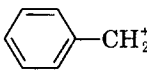
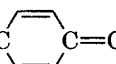
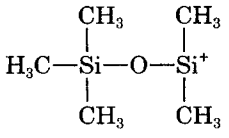
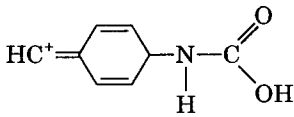
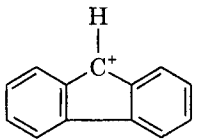
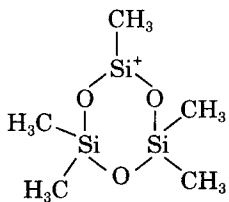
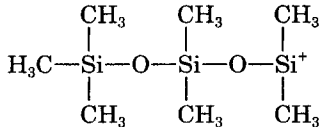
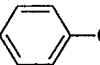

(Table II). Because characteristic mass fragments of the Pellethane® were also detected in the Hydromer®-coated catheter, the layer of PVP was either very thin, that is, below the depth of information in static SIMS (typically two to three layers), or alternatively does not form a continuous film on a molecular or microscopic scale.

The presence of the modified PVP on the Pellethane® catheter was previously identified by ESCA.¹ It was barely detectable by a modest increase in nitrogen percentage compared to that of the native polyurethane catheter. However, a substantial amount of oxygen was observed and attributed to the trapping of water molecules in the Hydromer® network. SIMS has a smaller sampling depth, which provides a better surface sensitivity than ESCA, and is therefore more specific in determining the detailed molecular structure of polymeric surfaces and thin films.

Contact Angle Measurements

Figure 3 shows water contact angle values for catheters in both their native and "wet" states after different periods of storage in water. The contact angle for a Pellethane® catheter is about 85° and appears

Table I Possible Assignments for Positive Ion Fragments from Pellethane® Catheter

Mass (amu)	Ion Assignment	Structure
27	$C_2H_3^+$	$H_2C=CH^+$
28	$[Si]^+$	Si^+
29	$[C_2H_5]^+$	$H_3C-CH_2^+$
41	$[C_3H_5]^+$	$H_2C=CH-CH_2^+$
42	$[C_2H_4N]^+$	$H_2C=C=NH_2^+$
43	$[C_3H_7]^+$	$H_3C-CH_2-CH_2^+$
55	$[C_4H_7]^+$	$H_3C-CH_2-CH=CH^+$
	$[C_3H_3O]^+$	$H_2C=CH-C\equiv O^+$
57	$[C_4H_9]^+$	$H_3C-CH_2-CH_2-CH_2^+$
71	$[C_4H_7O]^+$	$H_2C=CH-CH_2-CH=OH^+$
73	$[C_4H_9O]^+$	$H_3C-CH_2-CH_2-CH=OH^+$
77	$[C_6H_5]^+$	
91	$[C_7H_7]^+$	
106	$[C_7H_8N]^+$	$H_2N^+=C$  $C=CH_2$
127	$[C_8H_{15}O]^+$	$H_3C-CH_2-CH_2-CH_2-O^+=CH-CH_2-CH=CH_2$
145	$[C_8H_{17}O_2]^+$	$H_3C-CH_2-CH_2-CH_2-O-CH_2-CH_2-CH_2-CH=OH^+$
147	$[C_5H_{15}OSi_2]^+$	
150	$[C_8H_8NO_2]^+$	
165	$[C_{13}H_9]^+$	
207	$[C_5H_{15}O_3Si_3]^+$	
221	$[C_7H_{21}O_2Si_3]^+$	
223	$[C_{14}H_{11}ON_2]^+$	H_2N  $-CH=$  $=N^+=C=O$

to remain fairly constant up to about 8 days of immersion in water. This indicated that the polyurethane surface rearrangement was very slow and,

therefore, that the surface migration of hydrophilic components, such as the hard segments, was not detectable by contact angle measurements. Fur-

thermore, in this period, the migration to the surface of extractable additives, contaminants, or low molecular weight chains did not affect the wettability and could in fact have prevented the hard segments from reaching the surface. Chen and Ruckenstein²⁰ showed that the interfacial free energy of commercial polyurethanes decreases only after 30 days in water, resulting from the increase of the polar component of the surface free energy. However, results of their ESCA experiments indicated that rearrangement of segments occur after 14 days of immersion in water. Keeping the Pellethane[®] catheter immersed in water for only 8 days may not be sufficient to notice structural surface modifications. The slowness of the rearrangement may be imputable to the presence of an interfacial free energy gradient along the surface layers generated by water-extractable materials, which creates a shear stress opposed to the motion of the hard segments.²⁰

The Hydromer[®] catheter exhibited a hydrophobic behavior in a dried state, with a high contact angle of about 90°. This value was reduced by 50% within less than 3 h of immersion and decreased rapidly to reach a complete wetting by water (0°) after 70 h. The entrapped water molecules in the swollen polymer network conveyed significant hydrophilic properties and allowed reorganization of the hydrophilic groups at the surface. Such behavior was already observed with hydrogels of poly(2-hydroxyethyl methacrylate), which showed high water contact angles at the gel-air interface and low angles after immersion in water.²¹ It has been proposed that hy-

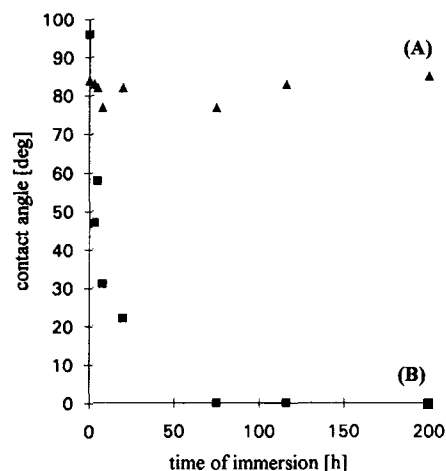


Figure 3 Measurements of water contact angle (degrees) versus time of immersion in water (h) on (A) Pellethane[®] and (B) Hydromer[®] catheters.

drophilic groups turned to the bulk side of the gel when the sample was exposed to air, whereas they migrated to the surface when the interface became more polar. The mobility of chains may be enhanced by the presence of water, which acts as a plasticizer in hydrogel-like polymers.²² An explanation proposed by Etzler²³ was based on a statistical model for the water structure near the solid interface. The author argued that the probability of hydrogen bonds for water was higher when the water molecules were near the interface. Thus, the more the polymer is swollen, the more water molecules are present and

Table II Possible Assignments for Positive Ion Fragments from Hydromer[®] Coating

Mass (amu)	Ion Assignment	Structure
112	$[C_6H_{10}NO]^+$	
124	$[C_7H_{10}NO]^+$	
138	$[C_8H_{12}NO]^+$	
207	$[C_{11}H_{15}N_2O_2]^+$	

able to bond other water molecules at its surface, rendering the polymer surface more wettable.

Measurements of Surface Interaction Forces

Other surface features, which are of primary importance for the use of catheters, are the adhesion and attraction forces developed between the sample surface and a surface host. They can be quantified by SFM by measuring the forces during approach, contact, and retraction of the SFM tip from the surface. Figures 4 and 5 show force versus distance curves recorded on the Pellethane® and Hydromer® catheter in air and in water.

In air [Figs. 4(A), 5(A)] the shape of the curves was similar, although Hydromer® exhibited a higher adhesive force. Generally, when the experiments were done in air, forces were intensified by the adsorbed liquid layers resulting from capillary condensation. The thin adsorbed water layer created a meniscus between the tip and the surface that participated in the attraction and adhesion. Thus, it

was expected that the more hydrophilic surface exhibited higher values of F_{att} and F_{adh} .²⁴⁻²⁶ However, measurements of static contact angle showed that the Hydromer® is highly hydrophobic in air. The high pull-off force of about 200 nN needed to break the contact between the tip and the Hydromer® surface, could be due to the softness of the coating that tends to embed the tip.

In water, two types of curves for each polymer surface were recorded. The adhesive force between the Pellethane® catheter and the tip was increased by about 25% when experiments were carried out in water [Fig. 4(B,C)] with respect to the measurements in air. This can be linked to the migration of low molecular weight chains to the surface in water. Figure 4(C) shows surprising lever deflections when the sample and the tip come into contact. It seems that the tip was first subjected to a repulsive force due to a top-most soft layer or charged layer on the surface and then was attracted after having penetrated this layer. However, the soft layer did not influence the retraction motion and the value of adhesion force of

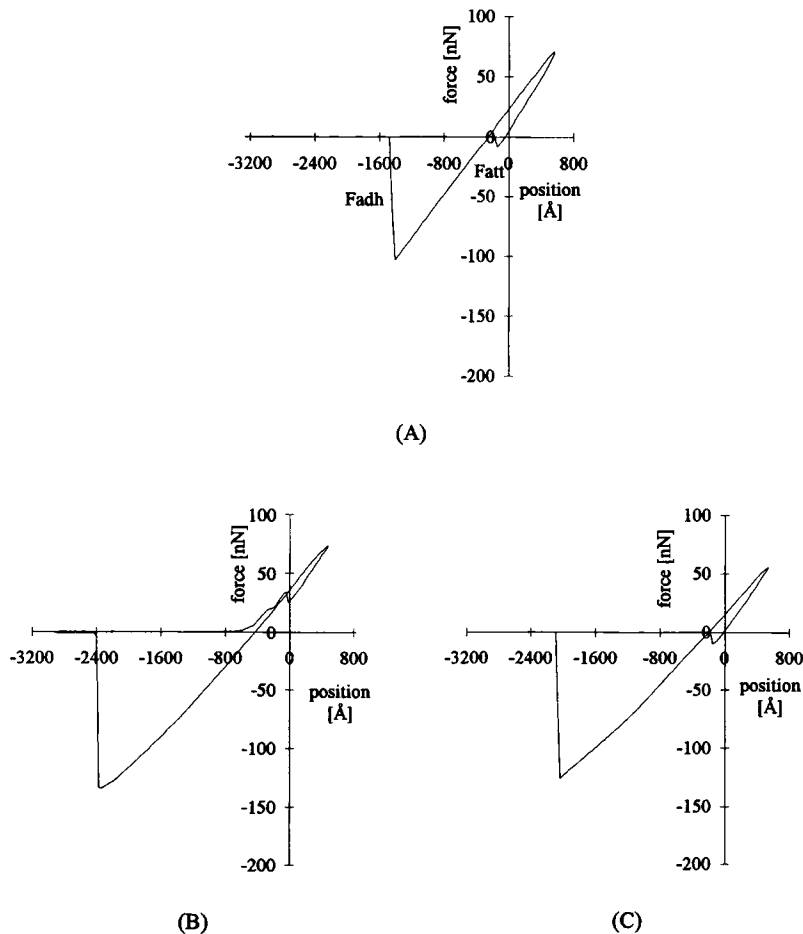


Figure 4 Force versus distance curves of Pellethane® catheter (A) in air and (B,C) in water.

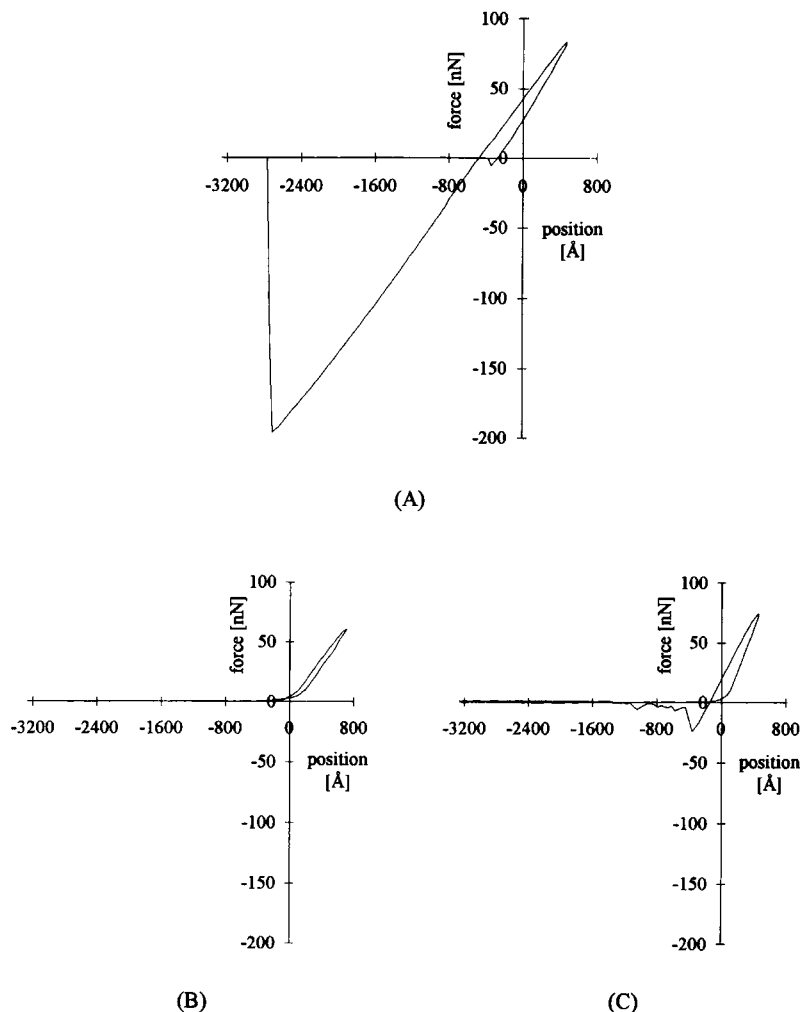


Figure 5 Force versus distance curves of Hydromer® catheter (A) in air and (B,C) in water.

about 135 nN. The fact that the migration in water of the low surface energy compounds was probably not homogeneous in the first layers and along the surface could explain the observation of two types of curves obtained on this surface.

The behavior of the Hydromer® toward the SFM tip in water was very different. The adhesive force measured in air was huge, whereas it became very small and even equal to zero [Fig. 5(B,C)] when the sample was immersed in water for about 2 h. At this time, the water contact angle of the Hydromer® surface could be estimated at about 50°. In the case of Fig. 5(C), jumps on the retraction branch occurred along a distance of 80 nm before separation of the tip and the surface. A main jump before discrete discontinuities was recorded with an adhesive force of 24 nN.

The Pellethane® catheter was probably coated with one single layer of Hydromer® and the SFM imaging showed that the Hydromer® coating was homogeneous.¹ The value of adhesive force measured

on the Hydromer® catheter was different from that of Pellethane®. It emphasized that the two types of curves obtained for the Hydromer® catheter were not the consequence of coating discontinuities. Furthermore, this confirms that the detection of the polyurethane structure by SIMS was not due to the heterogeneity of the coating but to the thinness of the PVP layer, which allows observation of the native catheter surface. The differences in the two curves might be caused by a heterogeneous swelling and those in the adhesive jumps observed in Figure 5(C) might be imputable to different degrees of hydrophobicity in the first layers of PVP, confirming the presence of a different water structure in a hydrogel-like polymer.²³

Microscopic Scale Tribometry

When a solid slides over another surface, frictional phenomena are expected to be observed, which are

generally dependent on the topographical, chemical, and mechanical properties of the surfaces and on the mobility of surface components. That is why polymer lubricants are commonly used in a low viscosity form. Poly(vinyl alcohol) coatings, having a hydrogel-like structure similar to that of native articular cartilage, have been used to coat poly(ethylene) artificial joints. The friction coefficient obtained by the rotation of the specimen against a steel ball is low, about 0.02.² When swollen by water, the coating displays a slippery surface, which considerably reduces the frictional resistance during sliding against another object. The large amount of water contained in the polymer network and adsorbed at the surface participates in the fluid lubrication in enhancing enlargement of network spacings and mobility of chains.

Figure 6 shows curves of the frictional force versus normal force applied by the SFM tip on the Pellethane[®] and Hydromer[®] catheter surfaces, and on a clean glass substrate. The slopes of the plots represent the friction coefficient and are equal to 0.50, 0.05, and 0.15 (± 0.05), respectively. These values were identical in water and in PBS. The presence of salts did not influence friction force values.

The Pellethane[®] catheter exhibited a high coefficient and may have been influenced by the surface roughness (root mean square) that was measured as 29 nm with SFM on a $5 \times 5\text{-}\mu\text{m}^2$ area surface. Imaging showed numerous surface irregularities with deep cracks and crevices.¹ In spite of the inhomogeneities, measurements made at different locations on the surface gave the same value for the friction coefficient. The friction coefficient obtained for the Hydromer[®] was very low, the lateral force being almost equal to zero during the displacement of the tip on the surface. Previous SFM imaging of a Hydromer[®]-coated catheter, in a dry state, showed a smooth surface topography without depressions or mounds. The PVP coating induced a threefold lower apparent roughness.¹ For comparison, a glass substrate, which had a low roughness but no mobile chains at the surface, had a friction coefficient value intermediate between that of Pellethane[®] and Hydromer[®] surfaces.

CONCLUSION

This study demonstrated that PVP coating constitutes an effective treatment for improving wettability and frictional properties of polyurethane catheters at a microscopic scale.

With TOF-SIMS, the presence of hard segments at the surface of the untreated polyurethane catheter

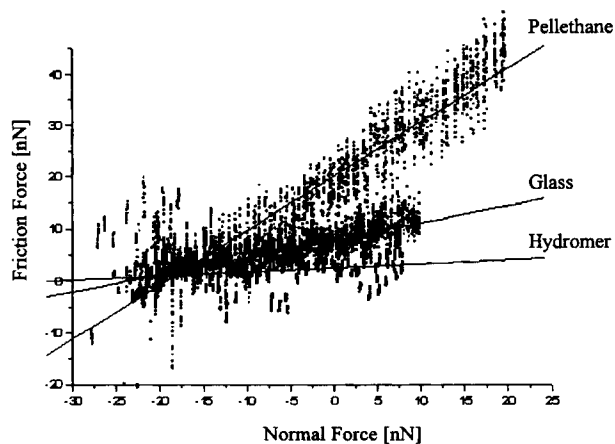


Figure 6 Friction force versus normal force in PBS on (A) Pellethane[®] catheter, (B) Hydromer[®] catheter, and (C) glass substrate.

was shown. Also, the PVP coating was unambiguously characterized with this technique. It was found that the time of immersion in water controlled the wettability of the Hydromer[®] catheter. In air, the surface was highly hydrophobic, whereas after several hours in water, the surface was totally wetted by water. This means that a prehydration may be necessary to use this biomaterial. This behavior might be interpreted by a fast reorganization of the hydrophilic groups induced by the environment or a different water structure near the interface that favors hydrogen bonds for adsorbed water molecules.

PVP coating considerably reduced the adhesive interactions measured by SFM in water and enhanced the softness of the material. Furthermore, microtribological experiments carried out by a scanning SFM tip on catheters in aqueous solution showed a very low friction coefficient for the Hydromer[®] catheter. If the friction coefficient between the sample surface and the tip is used as an indication of surface slipperiness, the PVP appears to be a good candidate for a lubricious coating, although the resistance to wear has not yet been assessed.

Combined with the fact that this polymer surface is smooth, soft, and nonadhesive in water, this biomaterial is expected to minimize the trauma to the tissues during insertion in the vessels of hospitalized patients and would induce very small perturbation in the laminar flow of blood, thereby minimizing the threat of thrombosis.

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