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A NOVEL LOW-FRICTION SURFACE FOR BIOMEDICAL APPLICATIONS: MODIFICATION OF POLY(DIMETHYLSILOXANE) (PDMS) WITH POLYETHYLENE GLYCOL(PEG)-DOPA-LYSINE

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Abstract

Aqueous biocompatible tribosystems are desirable for a variety of tissue-contacting medical devices. L-3,4-dihydroxyphenylalanine (DOPA) and lysine (K) peptide mimics of mussel adhesive proteins strongly interact with surfaces and may be useful for surface attachment of lubricating polymers in tribosystems. Here, we describe a significant improvement in lubrication properties of poly(dimethylsiloxane) (PDMS) surfaces when modified with PEG-DOPA-K. Surfaces were characterized by optical and atomic force microscopy, contact angle, PM-IRRAS, and X-ray photoelectron spectroscopy. Such surfaces, tested over the course of 200 rotations (~8m in length), maintained an extremely low friction coefficient (μ) (0.03±0.00) compared to bare PDMS (0.98±0.02). These results indicate the potential applications of PEG-DOPA-K for the modification of device surfaces. Extremely low μ values were maintained over relatively long length scales and a range of sliding speeds without the need for substrate pre-activation and in the absence of excess polymer in aqueous solution. These results were only obtained when DOPA was bound to lysine (modification with PEG-DOPA did not have an effect on μ) suggesting the critical role of lysine in obtaining a lowered friction coefficient.

Keywords

aqueous lubrication; surface modification; DOPA; lysine; tribology

INTRODUCTION

Surface-grafted poly(ethylene glycol) (PEG)-based polymers have demonstrated several useful biointerfacial properties including protein and cell resistance [1,2], and suppression of immunogenic and antigenic activity [3,4]. Such properties are essential in surface-modifying polymers for biomedical applications.

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Lubricity is also a desirable property for biomedical applications involving moving parts, such as the artificial joint, as well as tubular devices, e.g. catheters and endoscopes [5]. End-grafting of hydrophilic polymer chains through surface-initiated polymerization of monomers, known as the "grafting from" approach [6] has been extensively investigated as an effective means to impart surface hydrophilicity and lubricity to various polymeric materials that are used for tissue-contacting devices [5,7-9]. While remarkable lubricating properties have been achieved, these methods typically require surface activation by means of chemical or physical (high energy) methods, such as UV irradiation, plasma, or corona discharge, because of the initially non-reactive, i.e., hydrophobic and/or non-polar, surface properties of polymeric materials [7,10-12].

PEG is very attractive for surface modification since it can simultaneously impart biocompatibility and lubricity to materials. The grafting of PEG chains onto polymeric surfaces can be achieved through noncovalent interaction between hydrophobic anchoring groups of PEG-based copolymers and the surfaces in aqueous solvents [9,13,14], and the application of the aforementioned "grafting-from" approach has also been reported [15-17]. Previous tribological studies involving grafting of PEG chains, including poly(L-lysine)-*graft*-poly(ethylene glycol) (PLL-*g*-PEG) [9] or Pluronic™ [13,14], onto polymeric surfaces indicated a dramatic reduction of friction forces under aqueous conditions [9,13,14,18]. Such lubricating effects are mediated by the presence of excess polymer in the bulk, whereby the region encountering tribostress and wear of the polymer layer can be rapidly replenished by adsorption of polymer from solution, and thus a "self-healing" mechanism can be activated [13]. While this characteristic could be advantageous for conditions where continuous and cyclic tribological contacts are expected, such as bearing systems [19], it makes them unsuitable for tissue-contacting devices, since the presence of "excess polymer" *in vivo* is not a viable option. Nevertheless, tribological contacts for tubular medical devices are expected to be very mild, and do not necessitate either cyclic or long-term service. Thus, a PEG layer, stably attached onto the surface, may be sufficient for the efficient lubrication of such devices.

Synthetic polymers containing DOPA and lysine (K) have a strong affinity for many surfaces 20-23 and may be useful in biomaterial tribosystems. The presence of L-3,4-dihydroxyphenylalanine (DOPA) in mussel adhesive proteins is believed to be critical for their impressive interfacial properties [24]. Thus, the objective of this study was to determine if application of PEG-DOPA-K (Figure 1) to PDMS surfaces results in an improvement in the grafting of PEG chains, and hence aqueous lubrication properties with biomedical relevance. We have chosen PDMS as the tribopair for three reasons. Firstly, PDMS can represent silicone-based polymeric materials that have already found a broad range of biomedical applications [25], and can further represent the broad class of hydrophobic polymeric materials used for tissue-contacting devices. Secondly, tribological interactions involving elastomers, either on one or both sides of the contact, typically yield mild contact pressures, analogously to the application of tissue-contacting devices. Thirdly, many previous PEG-based copolymers have been tested with tribopairs involving PDMS [13,14], and thus these can be directly compared with PEG-DOPA-K for their lubricating efficacy. To this end, we have selected two other PEG-based copolymers for comparison, PEG-DOPA and Pluronic™, both of which are known to adsorb readily onto hydrophobic surfaces. The comparison with PEG-DOPA, which is identical to PEG-DOPA-K except for the absence of lysine is, in particular, expected to reveal the role of lysine in the lubricating behavior.

MATERIALS AND METHODS

Tribopairs

Poly(dimethylsiloxane) (PDMS) elastomer was used for both pin and disk, as previously described [14]. Briefly, the base and curing agent were thoroughly mixed in a 10:1 ratio (w/w) and ensuing bubbles generated from mixing were removed by vacuum. Tribopairs consisting of hemispherical pins (6 mm diameter) and flat disks (30 mm diameter, 5 mm thickness) were fabricated in polystyrene 96-well cell-culture plates and a custom-machined aluminum mold, respectively [14].

Synthesis of PEG-DOPA-K and surface modification

N-carboxyanhydrides (NCAs) of DOPA (diacetyl-DOPA-NCA) and lysine (Fmoc-K-NCA) were prepared, [26]. Briefly, methoxy-PEG-NH_2 (PEG-NH_2, MW 5,000 Da) was dried by azeotropic evaporation with benzene and further dried in a desiccator for 3h. Ring-opening polymerization of NCA was performed by dissolving PEG-NH_2 in anhydrous THF at 100 mg/ml, purging with argon, and adding a 6M excess of undiluted diacetyl-DOPA-NCA and Fmoc-K-NCA. The reaction mixture was stirred at room temperature for 5 days under exclusion of water vapor. The peptide-modified block copolymers were purified in succession with diethyl ether, cold methanol, and again diethyl ether. Peptide-coupled PEG was dissolved in anhydrous DMF at a concentration of 50 mg/ml and sparged with argon for 10 min. Pyridine was added to make a 5% solution and stirred for 15 min with argon bubbling. The mixture was rotary-evaporated to remove excess pyridine and precipitated in diethyl ether. The crude polymer was further purified by dialysis (MWCO > 3,400 Da) for 4 hours and lyophilized to yield PEG-DOPA-K (Fig. 1).

Lysine content was verified by ^{1}H NMR. The DOPA content of the block copolymers was determined using UV absorbance of polymer solutions in 12.1 mM HCl at the maximum absorbance wavelength of the catechol (λ_{max} = 280 nm) [27]. Solutions containing known concentrations of free DOPA amino acid were used to construct the calibration curve.

Tribopairs were incubated in 1 mg/ml PEG-DOPA-K in 0.6M K_2SO_4, 0.1M N-morpholinopropanesulfonic acid (MOPS), pH 9.0 for 18h at 50°C. Following modification, tribopairs were rinsed with ultrapure water and blown dry with nitrogen.

For some comparison tests, samples were incubated overnight in other PEG-containing copolymers, 1 mg/ml PEG-DOPA (MW of PEG is 5,000 Da) [20] or 1 mg/ml Pluronic™ P105 (molecular formula EO_{37}-PO_{56}-EO_{37}, i.e. MW of PEG chains are 3,250 Da, according to the manufacturer) [13] under identical conditions to those described previously.

Contact Angle

Static water contact angle (Ramé-Hart, Netcong, NJ) was measured before and after modification with PEG-DOPA-K.

Atomic Force Microscopy (AFM)

Topographic images of PDMS surfaces were obtained in air by tapping-mode AFM (Asylum MFP-3D, Santa Barbara, CA) with silicon cantilevers (f = 280 kHz). The film thickness of PEG-DOPA-K on PDMS was measured from the height difference between modified and unmodified regions on the same sample.

Gel Permeation Chromatography (GPC)

Multimer formation in solution was detected by overnight incubation of PEG-DOPA-K and PEG-DOPA in 0.6M K_2SO_4, 0.1M MOPS, pH 9.0 at 50°C. GPC analysis was performed on

this solution using multi-angle laser light scattering (Wyatt Technology, Santa Barbara, CA) in a mobile phase consisting of 0.1 M NaCl, 50 mM PO_4^-, and 0.05 % NaN_3.

Optical microscopy

Modified and unmodified PDMS surfaces were imaged *en face* by optical microscopy using a Zeiss Axiovert 135 microscope equipped with a CCD camera (ORCA-ER, Hamamatsu, Japan).

X-ray Photoelectron Spectroscopy (XPS)

Survey and high-resolution XPS spectra were collected on an Omicron ESCALAB (Omicron, Taunusstein, Germany) configured with a monochromated Al Kα (1486.8 eV) 300W X-ray source, 1.5 mm circular spot size, a flood gun to counter charging effects, and operating under ultrahigh vacuum ($<10^{-8}$ Torr). The takeoff angle, defined as the angle between the substrate normal and the detector, was fixed at 45°. Substrates were mounted on sample studs by means of double-sided adhesive tape. All binding energies were calibrated using the C(1s) carbon peak (284.6 eV). Analysis consisted of a broad survey scan (50.0 eV pass energy) and a 10-min high-resolution scan (22.0 eV pass energy) at 90-110 eV for Si(2p), 275-295 eV for C(1s), 390-410 eV for N(1s), and 525-545 eV O(1s). High-resolution spectra were acquired and used to calculate atomic composition.

Polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS)

A thin film of PDMS (ca. 30 nm thickness) was spin coated onto gold substrates[28]. The thin film was then modified with 1 mg/ml PEG-DOPA-K in buffer. After 1h or 18h of modification at 50°C, samples were rinsed with ultrapure water and dried with nitrogen. High-resolution polarization-modulation infrared reflection-absorption spectroscopy on a Bruker IFS 66v IR spectrometer, equipped with a PMA37 polarization-modulation accessory (Bruker Optics, Germany), was employed to determine the presence of PEG-DOPA-K films on the PDMS surface. The interferogram from the spectrometer's external beam port was passed through a KRS-5 wire-grid polarizer and a ZnSe photoelastic modulator before reflecting off the sample surface at an angle of 80° and being detected with a liquid-nitrogen-cooled MCT detector. Typically, 1,024 scans of multiplexed interferograms were collected with 8 cm^{-1} resolution and processed with OPUS software (Bruker Optics, Germany).

Pin-on-disk tribometry

Lubricating properties of PEG-DOPA-K on PDMS were characterized by testing apposed pairs in a pin-on-disk geometry (CSM, Neuchâtel, Switzerland) in HEPES buffer [1314]. Briefly, the load was controlled by dead weight and the sliding speed by a motor underneath the disk. Frictional forces generated during sliding contact were monitored by a strain gauge and measured as a function of speed (0.00025 – 0.1 m/s) at fixed load (1N, unless otherwise mentioned) or rotations (up to 200) at fixed speed (0.0005 m/s) and load (1N, mean Hertzian contact pressure = 0.36 MPa) [14]. For these measurements, the average friction over a defined number of rotations (20) was obtained at each speed. Generally, the friction forces in the initial few rotations showed a characteristic change ("running in" behavior) yet exhibited a steady kinetic friction force, F_k, after no more than 5 rotations. For μ-versus-speed plots, the latter half of the total number of rotations (11^{th} to 20th) was averaged in order to eliminate the "running-in" effect. Long-term friction measurements for 200 rotations or more, were also conducted at fixed speed (0. 0005 m/s) and load (1N).

RESULTS

Film thickness, wettability, and gross morphology

Surface modification of PDMS with PEG-DOPA-K was confirmed on both macro and micro scales. Wettability (water contact angle) measurements showed increased hydrophilicity of PDMS after PEG-DOPA-K modification (<15°, Fig. 2B) compared to before (109°, Fig. 2A). Optical micrographs (Fig. 2CD) indicated a fairly uniform layer of PEG-DOPA-K (Fig. 2F) while AFM micrographs showed some heterogeneity, with a layer thickness on the order of 0.5-1 μm compared to unmodified samples (Fig. 2E).

XPS

Differences in chemical composition between bare and PEG-DOPA-K modified PDMS surfaces were evident by XPS analysis. XPS spectra indicated the presence of increased N(1s) (+2.1%), increased C(1s) (+4.8%), and decreased Si(2p) (−4.1%) after adsorption of PEG-DOPA-K onto the PDMS surface (Fig. 3 and Table 1). Spectra of modified samples showed the presence of a N(1s) peak at 399.7 eV, which was not observed in the spectra of unmodified (control) PDMS surfaces and was attributed to the peptide in adsorbed PEG-DOPA-K. Further, a diminished Si(2p) signal, representative of the silicon present in PDMS, was also noted after modification.

PM-IRRAS

Reflective PM-IRRAS was applied to qualitatively determine the presence and chemical composition of the PEG-DOPA-K layer on thin-layer PDMS. PEG-DOPA-K modification on thin-film PDMS (on a Au substrate) was initially performed for 18h, however PM-IRRAS spectra indicated saturated reflection (Fig. 4A), i.e., the polymer layer was too thick to allow measurements by PM-IRRAS. Bands associated with Si-O (1,100 cm^{-1}) and Si-CH_3 (1,265 cm^{-1}) chemical species from PDMS were not observable when high amounts of PEG-DOPA-K were deposited (Fig. 4A). When the modification time was reduced to 1h, a thinner film of PEG-DOPA-K accumulated on the PDMS thin film surface. PM-IRRAS analysis revealed distinct amide bands at 1,650 and 1,540 cm^{-1} in the polymer-associated spectrum. (Fig. 4B).

Pin-on disk tribometry

PEG-DOPA-K coating resulted in extremely low friction at self-mated sliding contacts between coated PDMS surfaces when tested in a pin-on-disk geometry. PEG-DOPA-K-modified PDMS tested over the course of 200 rotations (~8m in total distance) (Fig. 5A), at fixed speed (0.0005 m/s) and load (1N), maintained an extremely low average friction coefficient (0.03±0.00) compared to that of bare PDMS (0.98±0.02) (Fig. 5A). The lubricating effect by PEG-DOPA-K surface modification represents a 33-fold reduction in μ values compared to bare PDMS. While the remarkable lubricating effect of PEG-DOPA-K ($\mu \leq 0.03$) was reproducibly observed in sliding contacts up to 200 rotations, extended measurements up to 1,000 rotations revealed a gradual increase in μ, commencing between the 300^{th} to 500^{th} rotation, with μ reaching 0.1 to 0.3 by the end of measurements (data not shown). During shorter experiments carried out as a function of speed (20 rotations at 0.00025 – 0.1 m/s, 1 N), PEG-DOPA-K was found to reduce μ by 42-fold compared to bare PDMS (Fig. 5B) with a slight increasing trend with increasing sliding speed. Similarly effective lubricating properties were observed from the measurements carried out under 2 N and 5 N (data not shown). Meanwhile, the other PEG-containing polymers, such as PEG-DOPA and Pluronic™ P105, did not reveal any noticeable lubricating effect, and resulted in higher friction forces compared to bare PDMS.

GPC

Formation of PEG-DOPA-K multimers in solution was monitored by performing GPC of PEG-DOPA-K solutions incubated under conditions identical to the surface modification reactions (0.6M K_2SO_4, 0.1M MOPS, pH 9.0 at 50°C). The presence of multimers at elution times ca. 60-62 min was clearly evident in the PEG-DOPA-K sample incubated at pH 9.0 (Fig. 6). Multimer formation was notably lower for PEG-DOPA and PEG-DOPA-K at pH 6.0, suggesting that both alkaline pH and the presence of lysine residues are important in forming multimers in solution under these conditions.

DISCUSSION

As was addressed in the Introduction, the aim of this work was to develop an approach to modify polymeric surfaces with PEG chains, with particular interest in improving the lubricating properties of tissue-contacting medical devices. Surface grafting of PEG chains for this particular purpose is not a trivial task since many other established methods require surface preactivation 6,29 or presence of excess polymer [19], which may not be possible for *in vivo* situations.

These results indicate substantial improvement in lubrication properties of PDMS after surface modification with PEG-DOPA-K. Modified surfaces were qualitatively characterized by contact angle, optical microscopy, and atomic force microscopy (Fig. 2A-E). Chemical composition of the modification layer was further verified by XPS (Fig. 3) and PM-IRRAS (Fig. 4) analyses. In comparison to other PEG-containing copolymers, such as PEG-DOPA and Pluronic™ P105, PEG-DOPA-K modification resulted in a 42-fold reduction in the friction coefficient ($\mu = 0.03$) over long-term tests (Fig. 5A). Additionally, an extremely low friction coefficient was maintained as a function of sliding speed, over the whole speed range employed in this work (Fig. 5B). Taken together, these results demonstrate the possibility of biomedical applications of PEG-DOPA-K surface modification for medical devices, such as catheters. In contrast, the other PEG-containing copolymers, such as PEG-DOPA and Pluronic™ P105, revealed no noticeable lubricating effect, and in contrast, slightly higher friction forces compared to bare PDMS surfaces. In addition, in preliminary studies, PEG-DOPA-K surfaces have indicated anti-fouling properties as well as decreased protein and cell attachment (unpublished data) similar to those previously reported for PEG-DOPA [20,23].

Very high frictional forces between sliding contacts of two PDMS surfaces in an aqueous environment (Fig. 5A) are ascribed to the strong hydrophobic adhesive forces [14], and surface-grafted PEG chains on PDMS surface are known to provide surface hydrophilicity necessary for aqueous lubrication [13,14]. In addition, the load-carrying capacity may be improved by the repulsion between two opposing surfaces bearing PEG chains in good solvents (water), arising from the osmotic pressure developed within the solvent-laden, brush-like polymer chains [14,25]. The Pluronic™ block copolymer employed in this work is expected to be immobilized through the hydrophobic interaction between the PPO block and PDMS surfaces. However the exact nature of the interaction between PEG-DOPA, PEG-DOPA-K, and PDMS is unknown at this time. Since all tribological measurements in this work have been performed under aqueous buffer solution with no excess polymers, the lubricating performance directly indicates the stability of each PEG-based polymer layer.[19] Experimental results suggest that interactions between PEG-DOPA and Pluronic™ P105 and PDMS surface are too weak to withstand the tribological stress under the given conditions, while previous experiments revealed effective aqueous lubrication properties in the presence of excess polymers in the bulk solution [13].

The molecular structure of the PEG-DOPA-K coating is likely to be comprised of both adsorbed single chains of PEG-DOPA-K and oligomers that have polymerized through their peptide endgroups (Fig. 7). Under the alkaline conditions employed during surface modification, catechol side chains of DOPA residues readily oxidize to yield quinones that are capable of further reacting with other DOPA residues [30,31] and with primary amines [24,32] to form oligomers of PEG-DOPA-K, both in solution (Fig. 6) and on the surface (Fig. 7). Although further studies will be needed to fully understand the impact of PEG-DOPA-K polymerization on tribological properties, we can speculate that polymerization of the peptide anchors could enhance the stability of the polymer coating towards shear between the sliding surfaces. An interesting observation was that PEG-DOPA-K coatings performed much better than PEG-DOPA coatings (Fig. 5), suggesting a role for the lysine residues in lowering the friction coefficient. This effect could be manifested during formation of the coating, anchoring of the coating to PDMS, or possibly in altering tribology-relevant chemical characteristics (charge, hydrophilicity, etc.) of the coating.

Lubricious biocompatible aqueous tribosystems are desirable for tissue-contacting medical devices, such as catheters, endoscopes, and angioplasty balloons. The modification of PDMS surfaces described here is a simple, thermally activated dip-coating procedure, which results in highly effective lubrication properties. Although the lubricating effects of the coating were eventually reduced after many rotations (~1,000, equivalent to 25m in length), in its current form the coating may be suitable for single-use medical devices. In the future, it would be useful to further elucidate the lubricating properties of PEG-DOPA-K on other relevant biomaterial surfaces and to study the biological response of modified surfaces. Incorporation of other PEG-based copolymers and/or varying the DOPA:K ratio in future studies may provide further insight into the mechanistic basis for the reduction in friction.

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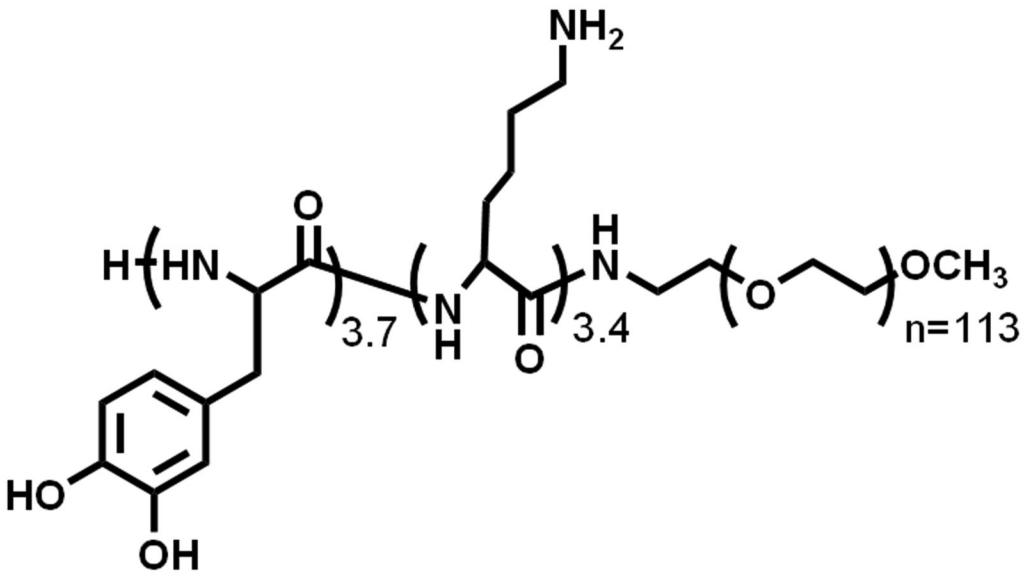

Figure 1.
Chemical structure of PEG-DOPA-K. The average number of DOPA units and lysine units is 3.7 and 3.4, respectively. It should be noted that DOPA and K residues are statistically distributed.

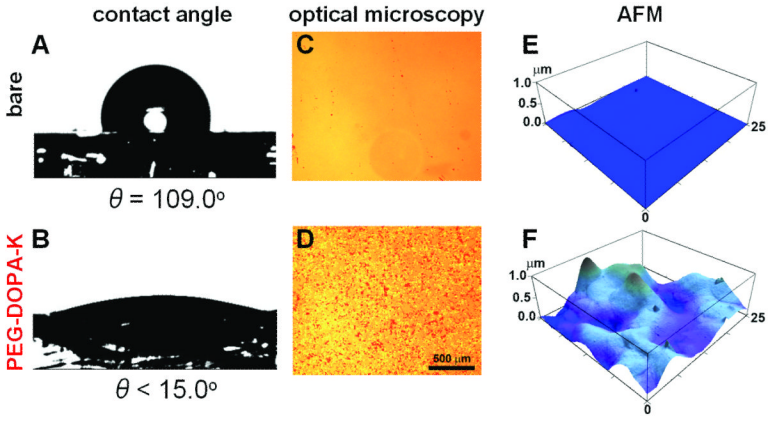

Figure 2.

Wettability and gross morphology of **(A, C, E)** bare and **(B, D, F)** PEG-DOPA-K modified PDMS surfaces by **(A, B)** contact angle, **(C, D)** optical microscopy, and **(E, F)** atomic force microscopy (AFM).

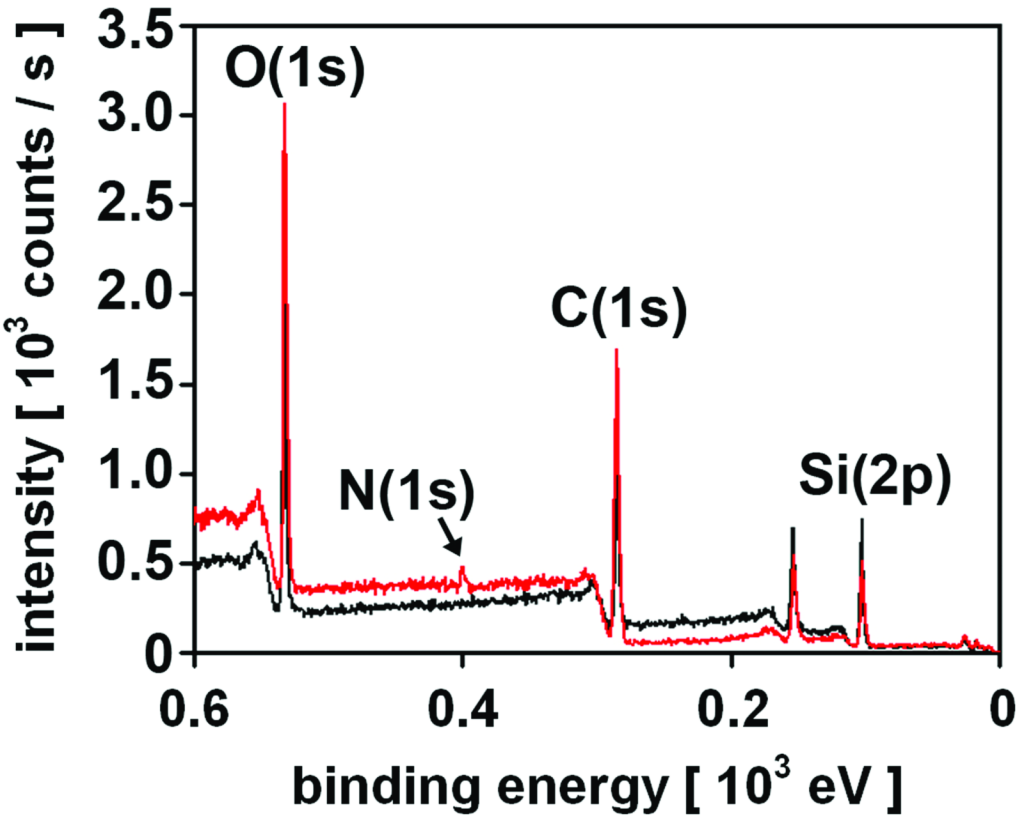

Figure 3.
XPS chemical composition analysis of bare (black) and PEG-DOPA-K (red) modified PDMS samples.

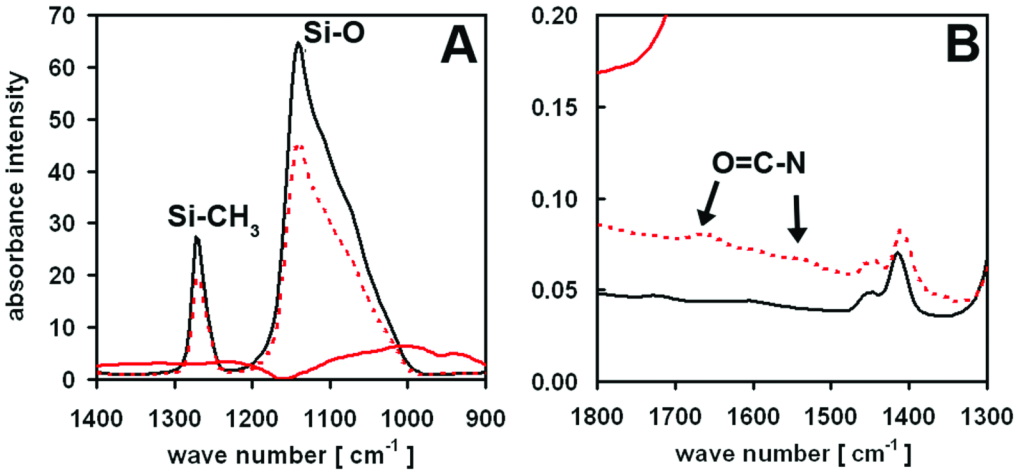

Figure 4.

PM-IRRAS chemical composition analysis of lower (--) and higher (–) amounts of PEG-DOPA-K deposited on PDMS-Au substrate (black). Bands associated with **(A)** Si-O (1,110 cm^{-1}) and Si-CH_3 (1,265 cm^{-1}) chemical species from PDMS were not observable when **(B)** higher amounts of PEG-DOPA-K were deposited and peaks associated with amide bonds were displayed.

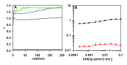

Figure 5.
Effects of surface modification on friction coefficient (□) as a function of **(A)** rotations and **(B)** sliding speed. For sliding speed measurements, the average friction over a defined number of rotations (20) was obtained at each speed. PDMS surface were left bare (black), or were modified with PEG-DOPA-K (red), PEG-DOPA (green), or Pluronic™ P105 (blue).

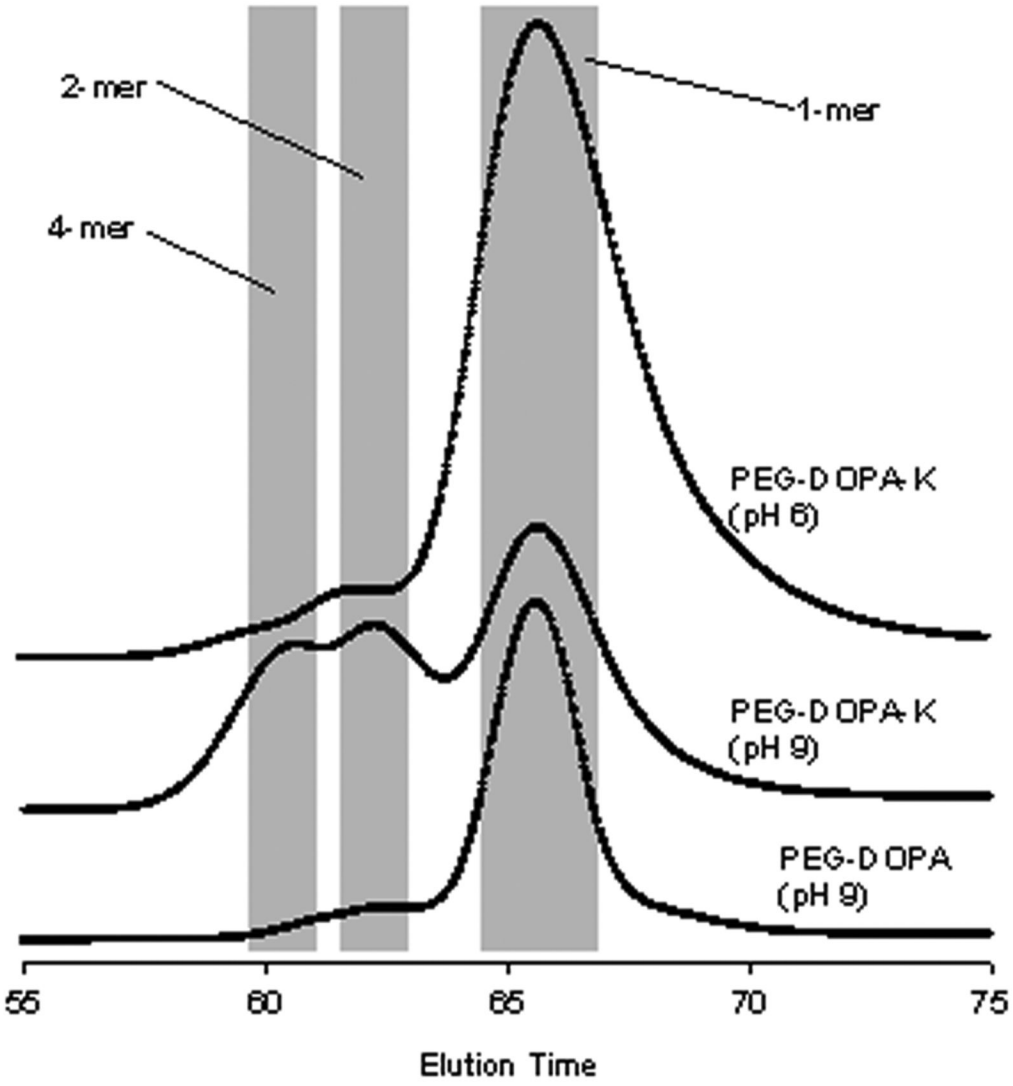

Figure 6.
Gel permeation chromatogram of DOPA-functionalized PEGs after overnight incubation in 0.6M K_2SO_4, 0.1M MOPS, pH 9.0 at 50°C.

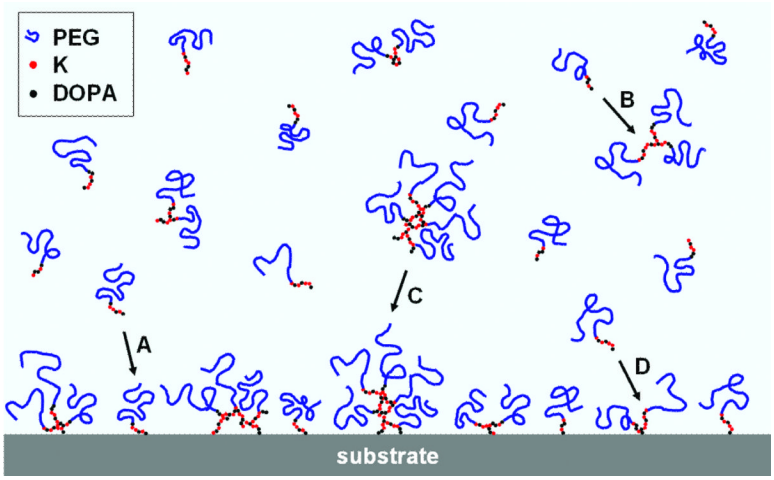

Figure 7.

Potential mechanism for PEG-DOPA-K modification of PDMS (not drawn to scale). The formation of a coating by immersion of substrate in a solution of PEG-DOPA-K can occur through several possible pathways as illustrated by arrows in the figure. Individual PEG-DOPA-K molecules can directly adsorb (graft-to) onto the substrate surface **(A**) or polymerize first with other molecules in solution **(B)** followed by adsorption of polymer clusters onto the substrate **(C)**. Alternatively, individual PEG-DOPA-K molecules may become immobilized through polymerization with surface bound molecules **(D)** in a process that resembles graft-from approaches.

Table 1

Quantitative XPS analysis of substrata

	atomic composition [%]			
substratum	**Si**	**C**	**N**	**O**
unmodifed PDMS	28.8	44.8	0.0	26.4
PEG-DOPA-K modified PDMS	24.7	49.6	2.1	23.6