Surface Modification of Silicone Rubber with Poly(ethylene glycol) Hydrogel Coatings

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Received 19 June 2003; accepted 5 November 2003

ABSTRACT: Hydrogel coatings of monoacrylated poly(ethylene glycol) (PEG) methyl ethers of different molecular weights were attached to silicon rubber surfaces and crosslinked with hexanediol diacrylate or ethoxylated trimethylolpropane diacrylate by UV polymerization. The wetting, evaluated with the water contact angles, correlated with the surface oxyethylene chain density, which was evaluated with the ESCA >C—O—/—CH_2— ratio obtained from the C(1s) peak. As measured by the ESCA N(1s) peak, bovine serum albumin formed very thin protein adsorbates on the PEG-coated surfaces. A strong correlation was found between low protein adsorption and a high >C—O—/—CH_2— ratio of the PEG-coated substrate. The PEG-coated silicon rubber also demonstrated very low cell and platelet adhesion. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1486–1492, 2004

Key words: silicons; rubber; hydrogels; coatings; proteins; adsorption; adhesion

INTRODUCTION

For many years, silicone rubber has been investigated as a biomaterial for the production of medical devices, such as artificial heart and prosthetic heart valves,[1] breast implants,[2] ophthalmologic devices (including ocular lenses,[3,4] scleral buckling implants for retinal detachment surgery,[5] and drainage implants for glaucoma[6]), artificial noses, ears, and chins in maxillofacial reconstruction,[7] artificial skin,[8–10] rubber esophagi,[11] biosensors,[12,13] temporomandibular joints,[14] catheters,[15,16] and kidneys.[17] The stability, toxicity, hydrophobicity, tissue response, and oxygen permeability of this material have been reported in many articles.[18–20] Although silicone rubber has excellent bioinertness, softness, and stability, serious problems arise when silicone devices are implanted for a long time.[21–24]

Because the body recognizes as foreign hydrophobic biomaterials such as silicone rubber, they stimulate inflammation and fibrosis, the latter process generating a fibrous capsule that isolates the biomaterial. The capsule not only impairs the implant's ability to function by producing a physical barrier between the implant and the surrounding tissues, but it also contracts and causes further complications.[25] Hydrogel[26]and collagen[27,28] coatings have been reported to reduce fibrosis around biomaterials implanted in animals. In many cases (membranes, ocular lenses, etc.), surface hydrophilization is desirable for combining the stability of hydrophobic silicone rubber with the advantages of hydrophilic materials and for providing good wetting by physiological liquids.[1,20]

A suitable surface modification could extend the biomedical applications of silicone rubber.[23,24,29] Poly(ethylene glycol)s (PEGs) are often used for polymer surface modification to improve biocontact properties. In some previous publications,[32–39]we have described the preparation of PEG-coated poly(vinyl chloride), polyethylene, poly(methyl methacrylate), and natural rubber (NR) surfaces that have shown excellent protein repellence. In this article, we describe a silicone rubber surface modification with a hydrogel coating containing pendant oxyethylene (OE) chains, prepared by the photopolymerization of monoacrylated methoxy PEG with OE chains of different lengths and structures. The chemical composition of the modified surface and its protein adsorption were investigated with ESCA. Because of the experimental problems involved in the measurement of the surface tension of hydrophilic swelling films, we used water contact angles only to study the hydrophobic–hydrophilic character of the surfaces.

EXPERIMENTAL

Materials and chemicals

The silicone rubber samples were prepared by injection molding after the vulcanization of poly(dimethylsiloxane) (PDMSO; Siloprene LSR 2070, GE Bayer Silicones). They were cleaned by sonification for 30

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Contract grant sponsor: National Scientific Fund of Bulgaria; contract grant number: K-1004/00.

Journal of Applied Polymer Science, Vol. 92, 1486–1492 (2004)

min in a 1:1 ethanol/water mixture and were dried in an air flow.

Hexanediol diacrylate (HDDA) was acquired from Union Chemie (Belgium); 2,2-hydroxy-2-propiophenon (HPP) and acrylic acid were obtained from Merck, F.R.G. Methoxy PEGs with molecular weights of 550, 1900, and 5000 were acquired from Aldrich Chemical Co., Inc. (United States), and ethoxylated trimethylolpropane [TMP$(EO)_{20}$] was obtained from Perstorp AB (Sweden). PEG monoacrylates were synthesized as described, in detail, in ref. 32.

Crystallized and lyophilized bovine serum albumin (BSA; Sigma Chemical Co., United States), prepared by Cohns method IV, was dissolved and diluted to 1 wt % in phosphate-buffered saline (0.01*M* KH_2PO_4 and 0.15*M* NaCl, pH 7) and was stored at +4°C less than 24 h before use.

Deionized water was used when solutions were made and rinsing was performed.

Sample preparation

Mixtures were used to prepare PEG coatings with the following compositions: 0.002 mol of monomethoxy PEG monoacrylate; 0.0006, 0.002, or 0.006 mol of HDDA; 0.0002 mol of HPP; and 1:1:1 (w/w/w) toluene/ethanol/ethyl acetate (used as a solvent). To maximize the ethylene oxide chain content in the coating deposited on the silicone rubber substrate, we varied the molar ratio of PEG acrylate to HDDA. The compositions are labeled with the molar ratio of the OE adduct to HDDA. The solvent had the following properties: it was a good solvent for the acrylated OE adduct, it spread on the substrate surface, and it had suitable volatility for obtaining smooth and uniform film formation. Each mixture was diluted in the solvent to a final dry content of 1 wt %. A 1% solution was applied to a silicone rubber surface with a spiral-rod applicator. The film was allowed to dry and was then UV-cured (Fusion System, United States) in a two-step cure procedure, which is described in detail in ref. 32. Afterward, it was rinsed twice with deionized water. It was assumed that only stable adhering PEG remained on the silicone surface.

Protein adsorption

Samples (10 mm × 14 mm) were exposed to 50-mL magnetically stirred (200 rpm) solutions in the following order: (1) equilibration of the samples in a pure buffer for 1 h, (2) exposure to a 1% BSA solution for 1 h, (3) desorption by bathwise exposure to a fresh buffer three times for 15 min, and (4) rinsing for 10 s in deionized water for the release of excess salt. It was assumed that only irreversibly adsorbed proteins remained on the surfaces after this treatment.

Cell adhesion

Samples (3 cm × 3 cm) of PEG 5000 coated NR latex films, which were first ethanol-sterilized, were exposed to 75-mL suspensions (1,000,000 cells/mL) of a fibroblast cell culture. The suspensions were allowed to settle onto the substrates for 1 h, and the substrates were transferred to solutions of sense fetal calf serum and incubated at 37°C up to 48 h. The surfaces were inspected and photographed with an optical microscope.

Platelet adhesion

This test was performed as described in ref. 40 with fresh citrated human blood. The density of the platelet coating was observed with an optical microscope and photographed.

Instrumentation

The wetting of the PEG-coated surfaces was characterized by the advancing water contact angle measurement with a model A 100 goniometer (Rame Hart, Inc., United States).

ESCA

A Leybold Heraeus ESCA instrument (Al Kα, excitation energy = 1486.6 eV) was used for surface analysis. The operating conditions were always set to 13 kV and 14 mA. The sample orientation was normal to the direction of the entrance of the hemispherical electron energy analyzer of the spectrometer. Complete spectral scans and detailed recordings of the main peaks were made for each sample at 6×10^{-9} Torr. The binding energy (E_B) scale was fixed by the assignment of E_B = 285.0 eV to the —CH_2— carbon (1s) peak. On the basis of this reference peak (called C1 in the figures) and according to previous studies,[41–43] the carbon chemical shifts for different oxygen-containing groups were C2 (>C—O— from hydroxyl, hydroperoxide, ether, or alkyl ester, ΔE_B = 1.5 eV), C3 (>C═O from carbonyl or amide, ΔE_B = 3.0 eV), and C4 (—COO— from carboxyl or the corresponding ester, ΔE_B = 4.2 eV). The areas of the different peaks were computed graphically from the spectra and were corrected with Scofields relative cross sections:[44] σ/C(1s)/ = 1.00, σ/O(1s)/ = 2.93, and σ/N(1s)/ = 1.68.

RESULTS AND DISCUSSION

PEG hydrogel coatings on silicone rubber

In Figure 1 are presented ESCA survey spectra of bare (curve 1) and PEG 1900 coated (curve 2) PDMSO. The spectra of PEG 550, PEG 5000, and TMP$(EO)_{20}$ coated

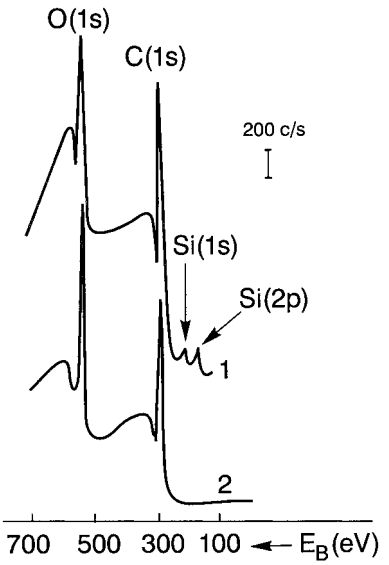

Figure 1 ESCA survey spectra of (1) bare PDMSO and (2) PEG 1900 coated PDMSO.

silicone rubbers were similar, and so they are not shown here. Two characteristic ESCA peaks of PDMSO, Si(2p) at E_B = 101.4 eV and Si(2s) at E_B = 153 eV,[41] presenting on curve 1 in Figure 1 are missing in curve 2. Evidently, they were effectively attenuated by the PEG hydrogel coating, which formed a sufficiently thick and coherent layer, despite possible swelling of the substrate, diffusion of HDDA (the hydrophobic HDDA component diffused more easily than PEG into the substrate polymer), and more dense in-depth crosslinking than on the substrate surface. The thickness of the photocured hydrogel coating was greater than the ESCA sampling depth (typically 3 nm for polymers[46]), and so the substrate Si(2p) and Si(2s) signals were extinguished. The C(1s) and O(1s) spectra of different 1:1 PEG/HDDA coatings (PEG molecular weights of 5000, 1900, and 550) and of $TMP(EO)_{20}$ coatings are shown in detail in Figure 2. The —C—O— peak (C2) in the C(1s) signal is predominant for PEG 1900, PEG 5000, and $TMP(OE)_{20}$. The results of the deconvolution of these peaks are given in Table I.

To maximize the OE chain content in the PEG coating deposited on PDMSO, we varied the PEG/HDDA molar ratio. The relative intensities of the characteristic groups of the PEG coatings, containing HDDA in different molar ratios, are also given in Table I. The >C—O—/—CH_2— intensity ratio as a function of

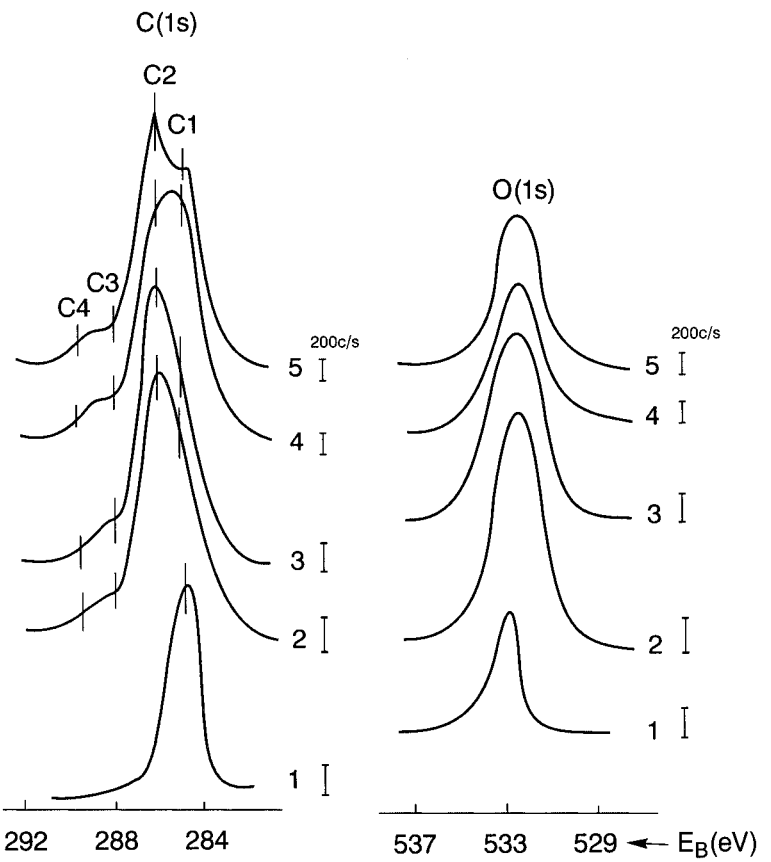

Figure 2 C(1s) and O(1s) peaks of (1) the bare PEG substrate surface, (2) PEG 500, (3) the PEG 1900 coated substrate surface, (4) the PEG 550 coated substrate surface, and (5) the $TMP(EO)_{20}$ coated substrate surface. The molar ratio of PEG to HDDA was 1:1.

TABLE I
Cross-Section Corrected Relative Intensities of Characteristic Groups for Acrylated PEG Coatings on Silicon Rubber Substrates

	>C—O—/—CH_2—	—COO—/—CH_2—	O(1s)/—CH_2—
PEG 550			
(1:1)	0.85	0.16	0.64
(2:1)	0.78	0.10	0.43
(3:1)	0.52	0.08	0.28
PEG 190			
(1:1)	1.68	0.24	1.25
(2:1)	1.74	0.18	1.20
(3:1)	1.55	0.20	1.53
PEG 5000			
(1:3)	1.40	0.28	0.92
(1:1)	1.75	0.24	0.98
(2:1)	1.85	0.25	1.36
(3:1)	1.25	0.13	0.64
$TMP(OE)_{20}$	1.71	0.17	0.76
$TMP(OE)_{20}$/PEG 1900 (1:1)	1.89	0.22	1.20
$TMP(OE)_{20}$/PEG 5000 (1:1)	1.92	0.21	1.34

these molar ratios is explicitly shown in Figure 3. The surface density of the OE groups showed a maximum for an optimum molar ratio of approximately 1:1–2:1. Molar ratios lower than the optimal ratio demonstrated poor wetting (discussed later), whereas higher ratios resulted in the dissolution of the coatings due to high swell stresses and low degrees of crosslinking. The maximum surface density of OE was higher for molecular weights of 1900 and 5000 than for a molecular weight of 550. The surface density of OE increased when HDDA was exchanged for $TMP(OE)_{20}$, which was also difunctional. The data from ESCA C(1s) and O(1s) peaks for such coatings with a 1:1 molar ratio of PEG 1900 or 5000 to HDDA (Table I) confirmed this suggestion.

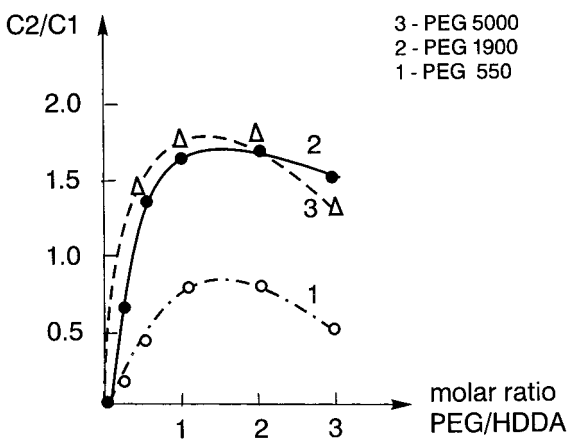

Figure 3 >C—O—/—CH_2— (C2/C1) intensity ratios from carbon (1s) signals as a function of the molar ratio of PEG to HDDA for (1) PEG 5000, (2) PEG 1900, and (3) PEG 550 coatings applied to PDMSO.

Contact angles

Because of the experimental problems involved in the measurement of the surface tension of hydrophilic swelling coatings, we only used the water contact angle to qualitatively study the swelling kinetics and the hydrophobic–hydrophilic character of the studied surfaces.

Time-dependent water contact angles (Fig. 4) showed that swelling occurred on all coatings attached to silicone rubber, as indicated by the slow attainment of the contact angle equilibrium, that is, a 5–12° decrease in 5–15 min. Figure 4 shows that the equilibrium contact angles varied with both the PEG molecular weight and the PEG/HDDA molar ratio. The measured contact angle decreased as the >C—O—/—CH_2— ratio increased (Table I).

Coatings containing PEG 5000 (Fig. 4) or $TMP(OE)_{20}$ (Fig. 4, dashed curves) generally showed the lowest equilibrium contact angles. For 3:1 PEG 5000/HDDA and 3:1 PEG 5000/$TMP(OE)_{20}$ coatings (Fig. 4, curves 4 and 5, respectively), complete wetting was observed, and for that containing excess HDDA (i.e., a molar ratio of 1:3), the contact angle was 18°. The low contact angle measured for our hydrogel coatings was also due to contributions from the surface roughness, swelling, and capillary forces in the porous structures.

Protein adsorption

The results of the deconvolution of the carbon C(1s), oxygen O(1s), and nitrogen N(1s) spectra of the bare PDMSO substrate and the PEG hydrogel coatings on the same substrate after BSA adsorption are given in Table II. The peptide group, —CO—NH—, showed up in both the C(1s) and N(1s) peaks. The N(1s) spectra

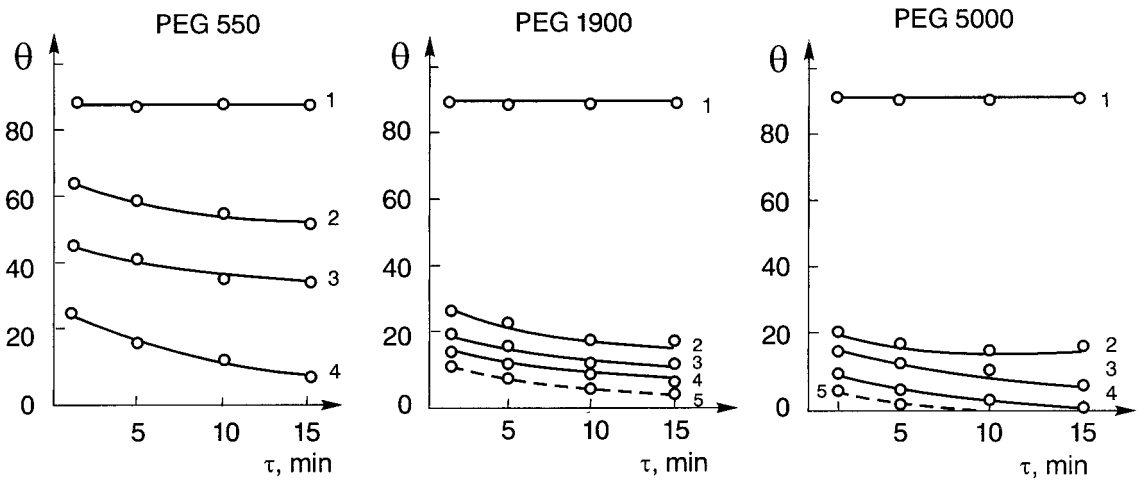

Figure 4 Wetting kinetics, expressed as water contact angles (θ), for PEG coatings applied to PDMSO. For all three graphs, sample 1 is the PDMSO substrate. The others are defined as follows: for the left graph, (2) PEG 550, 1:1, (3) PEG 550, 2:1, and (4) PEG 550, 3:1; for the middle graph, (2) PEG 1900, 1:1, (3) PEG 1900, 2:1, (4) PEG 1900, 3:1, and (5) $TMP(EO)_{20}$; and for the right graph, (2) PEG 5000, 1:1, (3) PEG 5000, 3:1, (4) PEG 5000, 1:3, and (5) PEG 5000:TMP(EO)20, 3:1.

were deconvoluted into two peaks originating from >N— groups (E_B = 400.6 eV) and >N—$^+$ groups (E_B = 402.5 eV). The total surface nitrogen content, calculated from the N(1s) peak (Table II), was relatively low for all surfaces but was much lower for the optimal PEG-coated surface.

The N(1s)/—CH_2— intensity ratio decreased as the molecular weight of PEG increased. For PEG 5000, the coating amounted to approximately 14% of the value obtained for the silicone rubber substrate; this indicated exceptionally thin protein adsorbates on the PEG coating.

Protein interactions on silicone rubber are dominated by the hydrophobic nature of the surface. As reported by Norde and Lyklema,[47] hydrophobic interactions play an important role in protein adsorption. They result in adsorption and structural rearrangement of the protein at the interphase.[48] The exceptionally low protein adsorption onto PEG-coated surfaces could be explained by the hydrophilicity of PEG, which resulted in a negligible hydrophobic driving force for adsorption. Also, a repulsive force was induced by chain interpenetrations (osmotic pressure) and elastic deformation of opposing chains. In water solutions, the protein actually came into contact with water rather than with PEG because of the strong PEG–water interaction, which led to a packaging of the PEG molecules by water.

There is a linear correlation between the surface density of OE groups, as measured by the >C—O—/—CH_2— ratio (Table I), and low protein adsorption, as measured by the N(1s)/—CH_2— ratio (Table II). $TMP(EO)_{20}$ formed a stable coating on a silicone rubber substrate, but the BSA adsorption onto this surface was considerably higher than that of PEG 1900 and PEG 5000 coatings. The formation of short loops and the entanglement of protein molecules could be the reasons for this difference.

Cell adhesion

Figure 5 presents photographs of fibroblast cells adhering to bare silicone rubber and PEG 5000 coated surfaces [Fig. 5(a)]. On both surfaces [Fig. 5(b)], only isolated cells could be seen, having an almost spherical shape, which indicated that these cells were intact

TABLE II
Cross-Section Corrected Relative Intensities of Characteristic Groups for Acrylated PEG Coatings on Silicon Rubber Substrates After the Adsorption of BSA

	>C—O—/—CH_2—	—COO—/—CH_2—	O(1s)/—CH_2—	>N/—CH_2—	>N—$^+$/—CH_2—
Substrate silicon rubber	—	—	—	0.17	0.04
PEG 550 (1:1)	0.82	0.20	0.56	0.08	0.02
PEG 1900 (1:1)	1.12	0.31	1.10	0.04	0.01
PEG 5000 (1:1)	1.69	0.33	0.90	0.02	0.01
$TMP(EO)_{20}$	1.30	0.21	0.62	0.09	0.03
$TMP(EO)_{20}$/PEG 1900 (1:1)	1.63	0.28	1.11	0.05	0.02
$TMP(EO)_{20}$/PEG 5000 (1:1)	1.67	0.27	1.25	0.03	0.02

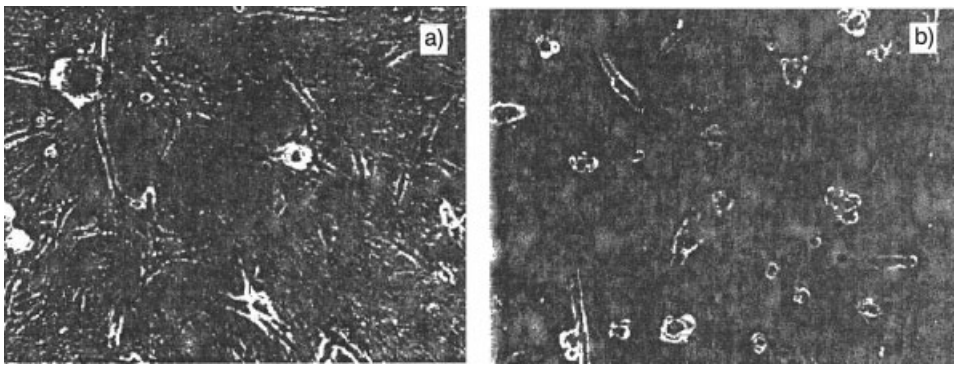

Figure 5 Optical microscopy photographs (100×) of fibroblast cells adhering to (a) a silicone rubber substrate and (b) a 1:1 PEG 5000/HDDA coating on a silicone rubber substrate.

and were not growing on the surfaces. This effect was better expressed for the PEG-coated surface, and this indicated its lower cell adhesion in comparison with that of the bare silicone rubber surface.

Platelet adhesion

Figure 6 shows optical microscopy images of platelets adhering to a bare silicone rubber surface [Fig. 6(a)] and to a PEG 5000 coating attached to a silicone rubber surface. The smaller particles shown in Figure 6(a) are platelets, whereas the much larger particles are blood cells. In comparison with the PEG-coated silicone rubber, the bare silicone rubber substrate exhibited a slightly higher affinity for platelets. The surface coating of the silicone rubber with PEG was apparently also effective for platelet repellence.

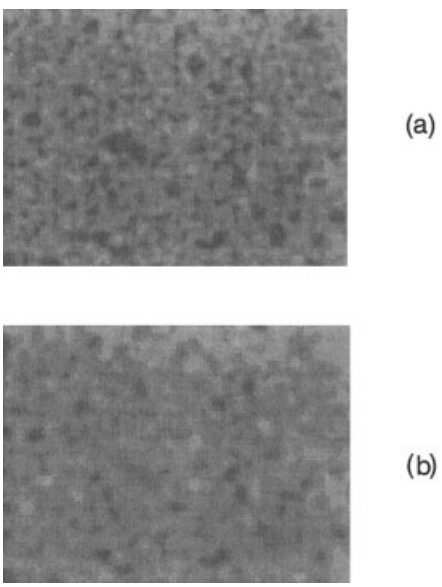

Figure 6 Optical microscopy photographs (100×) of platelets adhering to (a) a silicone rubber substrate and (b) a 1:1 PEG 5000/HDDA coating on a silicone rubber substrate.

CONCLUSIONS

The surface modification of silicone rubber by a PEG hydrogel coating made it strongly hydrophilic and reduced the protein adsorption.

A correlation between the high OE group surface density and the wettability as well as low BSA adsorption was found. The optimal molecular weight of PEG with respect to the low protein adsorption was about 2000–5000.

Branched $TMP(EO)_{20}$ was also effective in the formation of strongly hydrophilic surfaces, but the protein repellency was expressed less than that of PEG 5000 and PEG 1900 coated surfaces; this could be due to some mechanical entanglement of the protein molecules.

The negligible protein adsorption on the PEG-coated silicone rubber surfaces could be attributed to the absence of both hydrophobic and electrostatic interactions.

It may also be anticipated that PEG-hydrogel-coated surfaces will not be thrombogenic because they also demonstrate very low cell and platelet adhesion.

The author is grateful to C.-G. Gölander and S. Jönsson for constructive discussion.

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