

Bioinspired PDMS Elastomer Possessing High Oxygen Permeability and Protein Adsorption Resistance

Tatsuro Goda, Tomohiro Konno, Madoka Takai, and Kazuhiko Ishihara

Department of Materials Engineering, School of Engineering, the University of Tokyo

7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN.

Introduction: To obtain the high oxygen permeable, hydrophilic and protein adsorption resistant membrane is important to the medical elastomer such as artificial lung, soft contact lens, and bio-chip. We achieved it by applying the surface-initiated photo-induced radical polymerization without using any silane coupling reagents. Polydimethylsiloxane (PDMS) was grafted with bioinspired phospholipid polymer possessing phosphorylcholine unit found in the biomembrane: poly(2-methacryloyloxyethyl phosphorylcholine) (poly(MPC))¹.

Methods: PDMS was immersed in acetone solution containing benzophenone (0.1 to 10 g/L) for 1 min. The membrane was dried for 1 h under dark-vacuum condition. The PDMS coated with benzophenone was placed in the degassed MPC solution (0.25 or 0.5 mol/L) and sandwiched in glass plates. The photopolymerization on the PDMS surface was carried out using a 500 W of ultra-high pressure mercury lamp for 2 h at 30 °C without any filter. After the reaction, the membrane was washed with water and hot ethanol, and dried for 24 h in vacuum condition at 25 °C. Surface characterization was performed by XPS, ATR-FTIR and static water contact angles measurements. Single protein adsorption experiments were performed, immersed in the 4.5 mg/mL of BSA, 1.6 mg/mL of γ -globulin, 0.3 mg/mL of fibrinogen, and 2.0 mg/mL of lysozyme solutions for 8 h at 37 °C. Each sample was gently rinsed in the fresh PBS and the surface adsorbed protein was completely desorbed in 1 wt% of SDS with sonication for 20 min. Adsorbed protein amount was determined by micro BCA (Pierce, Rockford, IL, USA) technique. The oxygen permeation was performed by the electrochemical method². The polarographic cell was a cathode of platinum, and an anode of silver. The electrodes were set in the polarographic cell filled with 0.9 wt% of saline solution at 35 \pm 0.1 °C.

Results / Discussion: XPS results showed that the surface composition of N and P increased with increasing the feed concentrations of initiator and MPC monomer. Similar surface compositions were observed between 5-0.5 and 10-0.5, which indicated that free radical graft polymerization had limitations caused by recombination and dismutation. No graft polymerization was observed without initiator condition (0-0.5). The entity of ester bond (R-COO-R', 1735 cm⁻¹) in the MPC unit was confirmed by ATR-FTIR spectrum for surface modified PDMS. Static water contact angle on PDMS reduced with increasing initiator and monomer concentration, especially in the range of $x < 1$. And surface hydrophilicity of $x-0.5$ was higher than $x-0.25$ at the same initiator concentration (x). This result indicated that the water wettability and higher graft chain length was dependent on the increased MPC monomer feed concentration. Amount of non-specific protein adsorption were reduced to 20-58 % after the surface modifications. Protein adsorption was less dependent on the initiator and monomer concentrations. The oxygen permeability (Dk, barrers) of PDMS, 10-0.25 and 10-0.5 was 420, 400 and 340, respectively. PDMS membranes maintained the 80-95 % of oxygen permeability after surface modifications.

Considering the oxygen permeability of bulk water is 100 barrers, Dk of grafted membranes were still high.

Table. XPS results at a take off angles of 90°.

Code	Surface compositions (Atom%)				
	C	O	N	P	Si
PDMS	46.7	31.1	0.0	0.0	22.1
0-0.5	35.9	40.3	0.0	0.0	23.7
1-0.5	46.2	36.7	2.7	3.0	11.3
5-0.5	49.6	33.8	3.6	3.8	9.2
10-0.5	51.0	33.3	2.9	3.7	9.1
1-0.25	36.6	38.7	0.9	0.3	23.4
5-0.25	39.3	37.5	1.1	1.4	20.7
10-0.25	49.3	35.3	2.9	3.4	9.2

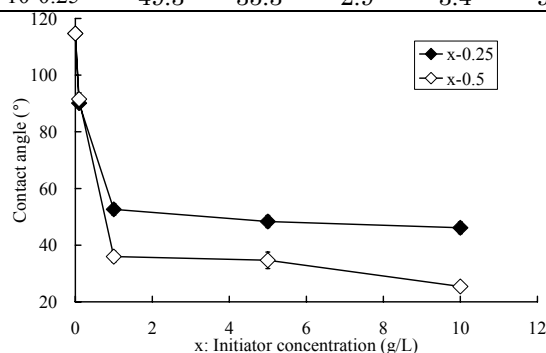


Figure 1. Relations between water contact angles on MPC grafted PDMS and initiator feed concentrations.

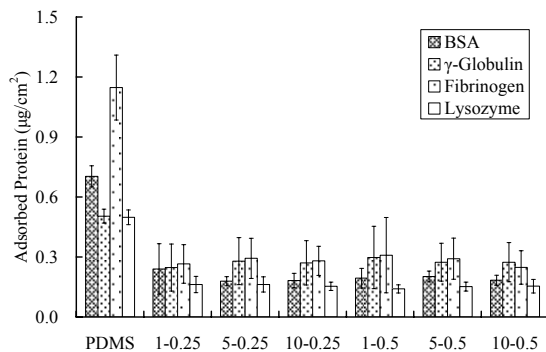


Figure 2. Amount of protein adsorption on PDMS and MPC grafted PDMS.

Conclusions: Photo-induced free radical graft polymerization by bioinspired phospholipid polymer was performed to obtain the high oxygen permeable, water wettable and anti-biofouling medical elastomer. Surface characterization performed by XPS and ATR-FTIR proved the MPC existence. Surface hydrophilicity and protein adsorption resistance were greatly improved by the MPC grafting. Oxygen permeability of PDMS was maintained after surface modification. This advanced PDMS elastomer is applicable for the biomaterials.

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References:

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- (2) V. Conpañ *et al.*, *Polymer*, 1996;37(1):101-107