

표면개질에 의한 소수성 및 친수성 폴리우레탄의 피브리노겐 흡착

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Fibrinogen adsorption to hydrophobic and hydrophilic polyurethanes
by surface modification

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I. INTRODUCTION

A study of protein adsorption is important in understanding blood response to materials and developing blood compatible polymers. In particular, fibrinogen is known to be a protein of high surface activity so that plays a leading part to result into thrombus formation. However, Cooper et al. reported that some sulfonated polyurethane(PU) exhibits a high affinity for fibrinogen but a enhanced thromboresistance(1). It is also known that fibrinogen exhibits the initial behavior of transient adsorption and the displacement by trace proteins, which has been called "Vroman effect"(2-4).

In this work, the adsorption behaviors of protein, especially fibrinogen to perfluorodecanoic acid(PFDA) grafted PU (PU-PFDA), poly(ethyleneoxide)(PEO) grafted PU (PU-PEO) and further sulfonated PU (PU-PEO-SO₃), which were reported to be more antithrombogenic(5,6), were investigated and discussed from results obtained by adsorption-kinetic and adsorption-isothermal data.

II. MATERIALS AND METHODS

The methods of surface modification of highly hydrophobic PU-PFDA, hydrophilic PU-PEO1000, and negatively charged PU-PEO1000-SO₃ have been previously described(5,7) as shown in Fig. 1.

The surface of PU(Pellethane) beads was treated

with hexamethylene diisocyanate(HMDI) to yield PU-HMDI having free isocyanate groups. PFDA was attached onto the surface via the -NCO groups of PU-HMDI to obtain PU-PFDA. PU-HMDI also was grafted with PEO(MW=1000) to have PU-PEO1000. Propane sultone(PST), a sulfonation reagent, was further reacted with the hydroxyl end groups of PU-PEO1000 to produce PU-PEO1000-SO₃.

Each of the three different PU beads was first contacted with bovine plasma containing ¹⁴C-labeled fibrinogen as a function of adsorption time or plasma concentration. Sample was then rinsed with PBS solution and placed in 2% SDS solution for 2 days, and the surface concentration of fibrinogen was determined by counting the radioactivity.

III. RESULTS AND DISCUSSION

On the whole, initial adsorption of fibrinogen onto the surface was increased with increasing of adsorption time and plasma concentration, but after the plateau is reached, its adsorption amount was in inverse proportion to them. The adsorption amount of fibrinogen onto PU-PEO was much less than that onto PU to confirm a characteristic effect of PEO grafted. However, PU-PEO-SO₃ exhibited a considerably increased fibrinogen adsorption to compare with PU-PEO, where the first adsorption was nearly same regardless of plasma concentration and adsorption time as shown in Fig. 2.

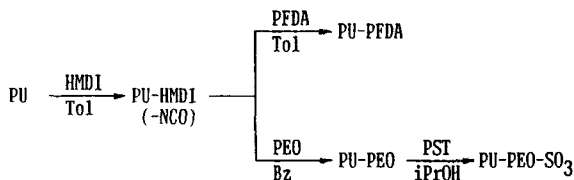


Fig. 1. Modification scheme of PU surfaces.
HMDI = $\text{OCN}(\text{CH}_2)_6\text{NCO}$, PFDA = $\text{CF}_3(\text{CF}_2)_8\text{COOH}$,
PEO = $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, PST = $(\text{CH}_2)_3\text{SO}_3$

This may indicate a specific and high affinity between sulfonate groups and fibrinogen.

Fig. 3 shows typical adsorption kinetics for fibrinogen from 0.6% plasma on modified PU surfaces. All the surfaces indicated the Vroman effect only at about 0.6% plasma concentration, however the displacement by other plasma protein such as contact phase clotting factors was relatively low. Therefore, it is thought that the Vroman effect depends strongly on the surface properties of materials, plasma concentration, and adsorption time.

After the equilibrium state, the amount of fibrinogen adsorption on modified PU surfaces was decreased in the following order: PU-PFDA > PU > PU-PEO1000-SO₃ > PU-PEO1000.

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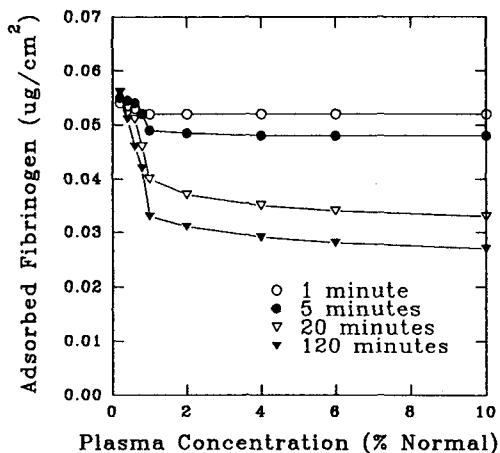


Fig. 2. Adsorption isotherms for fibrinogen on PU-PEO1000-SO₃.

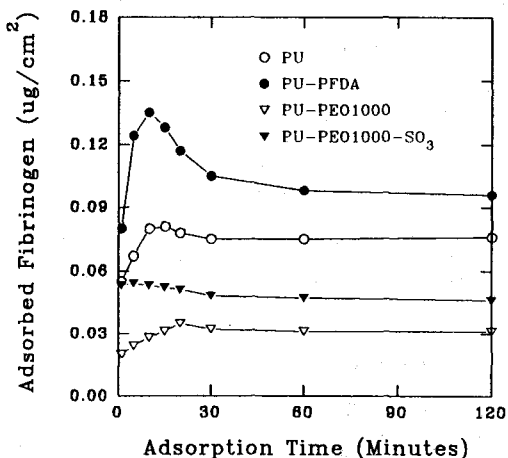


Fig. 3. Adsorption kinetics for fibrinogen from 0.6% plasma.