Surface Chemistry and Topography of Lotus Leaf-Like Pluronic[®]-Polyurethane: Effect on Protein Adsorption Wei Song^{1,2}, Hong Chen^{1,2*}

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Introduction: Protein adsorption, the first response after biomaterials contacting the biological environment, plays a crucial role in mediating the subsequent reactions such as platelet adhesion and in determining the final biocompatibility of biomaterials^[1]. During the past several decades, many efforts have been focused on controlling protein adsorption to biomaterials by chemical modification^[2-5], whereas fewer reports have been presented on the combination effect of surface topography and chemistry. In this paper, lotus leaf-like topography was fabricated on polyurethane (PU) surface containing Pluronic[®] as additive. The roughness and actual surface area were markedly increased by abundance micropapillae on lotus leaf-like topography while the surface chemistry and wettability were notably changed by migration of PEO chains from bulk materials to solidwater interface. Thus, the different combinations of surface chemistry and topography evidently affect the protein adsorption.

Methods : The mixture of liquid PDMS (Sylgard 184, Dow Corning) was cast on a fresh lotus leaf. After curing at RT for 72 h, PDMS was peeled off, resulting in a complementary topography of the lotus leaf. The PU solutions mixed with various mass percentages of Pluronic[®] (F127, Sigma) (0, 10, 20%) were cast on the PDMS templet and degassed 1 h at vacuum environment. After the solvent was evaporated, the films were peeled off and lotus leaf-like topography formed on PU surfaces containing different amount Pluronic[®] (designated as PU10, PU20). SEM (JSM-5610LV) was used to characterize the surface topography. Sessile droplet water contact angle and captive bubble water contact angle were measured. The adsorption of fibrinogen from buffer to lotus leaf-like surfaces was determined using ¹²⁵I radiolabeling method.

Results and Discussion: PU, PU10, PU20 surfaces with lotus leaf-like topography (PUL, PU10L, PU20L) were fabricated. The SEM micrographs are shown in Figure 1. Lots of micro-papillae with diameters around 7-10 μ m are present on the surfaces, forming the lotus leaf-like topography. Compared with PUL, some smaller nipples circled the top of micro-papillae on PU20L. The addition of Pluronic[®] into PU might cause the phase separation which is responsible for the formation of smaller nipples.

On flat surfaces, there were little differences between sessile droplet and captive bubble water contact angles, whereas on lotus leaf-like surfaces, captive bubble contact angle significantly decreased compared with that on flat ones (data not show).

Protein adsorption result is shown in Figure 2. Because of a mass of micro-papillae, the actual surface area of PUL was much larger than that of flat PU. Accordingly, fibrinogen adsorption sharply increased on PUL. However, when Pluronic[®] added, no significant difference was found between flat and lotus leaf-like surfaces. Pluronic[®] is a PEO-PPO-PEO triblock copolymer. When exposed to aqueous solution, the hydrophilic PEO chains in PU bulk are partially extended into the interface to provide PEO-rich surface^[6]. Besides, according to Wenzel's equation^[7], the lotus leaf-like topography can further enhance the hydrophilicity caused by interfacial enrichment of PEO chains. Consequently, fibrinogen adsorption on PU10L and PU20L was remarkably reduced to the same level as that on flat one. Such result suggests that protein adsorption depends on both surface chemistry and topography. Changing one of the parameters could dramatically affect protein adsorption.

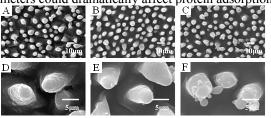


Figure 1. SEM mircographs of lotus leaf-like surface topography (A, D) PU; (B, E) PU10; (C, F) PU20

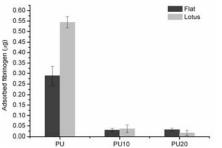


Figure 2. Fibrinogen adsorption on flat and lotus leaf-like surfaces

Conclusions: Lotus leaf-like topography was easily formed on PU surfaces containing different amount Pluronic[®]. In aqueous environment, captive bubble contact angle remarkably decreased on lotus leaf-like surfaces. Protein adsorption results suggest that adjusting the combination of surface chemistry and topography is possible to control protein adsorption.

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References: [1] Chen H, et al. *Prog Polym Sci* Doi:10.1016/j.progpolymsci.2008.07.006. [2] Chen H, et al. *Macromol Biosci* 2008, 8, 863. [3] Chen H, et al. *J Biomed Mater Res* Doi: 10.1002/jbm.a.32152. [4] Chen H, et al. *Biomaterials* 2005, 26, 7418. [5] Chen H, et al. *Biomaterials* 2005, 26, 7418. [5] Chen H, et al. *Biomaterials* 2000, 21, 683. [7] Wenzel RN. *Ind Eng Chem* 1936, 28, 988.