Significant Parameters for Protein Adsorption on Well-controlled Polymer Brush Surfaces

Tomoaki NAKANISHI,[1,2] Yuuki INOUE,[1,3] Ryosuke MATSUNO,[1,2] Madoka TAKAI,[1,2] and Kazuhiko ISHIHARA[1,2,3]

[1]Department of Materials Engineering, School of Engineering, [2]Center for NanoBio Integration (CNBI),
The University of Tokyo, Tokyo 113-8656, JAPAN, [3]JST-CREST, JAPAN
E-mail: nakanishi@mpc.t.u-tokyo.ac.jp

Statement of Purpose

Protein adsorption is the first event that occurs on materials surface when foreign materials get contact with blood. Then, platelet adhesion is introduced via adsorbed protein layers, leading to thrombosis formation. Therefore, to prevent protein adsorption is very important issue on biomaterials development. To obtain the non-biofouling property, it is necessary to understand the interaction between protein and the surface of materials. The purpose of this research is to clarify significant parameters of the surface for determining protein adsorption. Thus, it must be necessary for the surface to be defined models and for some evaluating method of protein adsorption to be clear. High density polymer brush surface via surface-initiated atom transfer radical polymerization (SI-ATRP) makes it possible to construct well-defined surface controlling chain length with narrow molecular weight distribution. Thus, we prepared well-defined polymer brush surface as a model surface. Atomic force microscopic (AFM) was used for evaluation of the surface. AFM technology makes it possible to directly measure the forces generated by protein-surface interaction in aqueous medium down to the few piconewtons (pN) range. Effects of the thickness of polymer brush layer, chemical structure and mobility of polymer chains, and the hydrophilicity of the surface on the adsorption force of protein will be discussed.

Methods

Three kinds of hydrophilic monomers; 2-methacryloyloxyethyl phosphorylcholine (MPC), 2-hydroxyethyl methacrylate (HEMA) and poly(ethylene glycol) methacrylate (PEGMA) were polymerized from initiator (BrC10DMCS)-immobilized silicon wafer by SI-ATRP. Each polymer was synthesized with the target polymerization degrees of 10, 20 and 50. The adsorption force between bovine serum albumin (BSA)-immobilized AFM tips[1)] and polymer brush surfaces was evaluated by force-versus-distance (f-d) curve in the AFM measurement mode.

Results and Discussion

Well-defined polymer surface was synthesized controlling the thickness in the range of 1-6 nm under air condition. Each polymer had the calculated chain density higher than 0.2 chains/nm^2. This result indicated that high density polymer brush surfaces were synthesized on silicon wafer. Fig. 1 shows the protein adsorption force on each polymer brush surface with different thickness of the polymer layer. Adsorption force decreased with an increase in the layer thickness in each polymer case. When the thickness of the polymer layer was thinner, the chemical structure affected the adsorption force, that is, PMPC brush layer showed the lowest adsorption force.

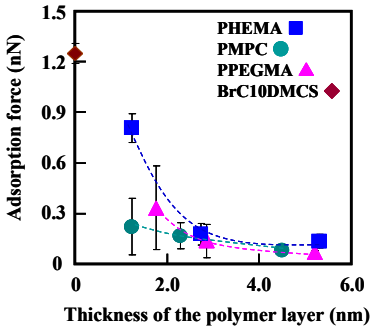

Fig.1 Protein adsorption force as a function of thickness of polymer layer

Fig. 2 shows the protein adsorption force as a function of cos (180° − θ), where θ is air bubble contact angle in water. The increase in cos (180° − θ) means the increase in the hydrophilicity. It leaded to the decrease in the adsorption force as a whole. However, adsorption force showed difference at the surface with almost the same contact angle. That is, hydrophilicity is an important but not a direct parameter to affect the protein adsorption force. It would correspond with the vertical structure of polymer brush surface in aqueous medium. Long polymer chains suppressed the adsorption force more effectively, and the vertical mobility of the polymer chains may be important to determine the adsorption force of protein.

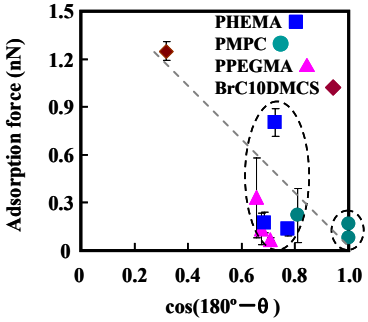

Fig.2 Protein adsorption force as a function of cos (180° − θ) (θ is air bubble contact angles in water.)

Conclusions

Hydrophilic surface tended to suppress the protein adsorption, but different adsorption force observed even the surface with almost the same hydrophilicity. Considering the thick polymer layers reduced the protein adsorption force, it was suggested that the vertical mobility of the polymer brush chains was the important factor on generation of the protein adsorption force.

References

1. Carr, P. W.; Bowers, L. D., *Immobilized enzymes in analytical and clinical chemistry*, John, Inc: New York, 1980; pp 171-173