Photoinduced and self-initiated grafting of 2-methacryloyloxyethyl phosphorylcholine to poly(ether-ether-ketone): Effects of inorganic salt for shortening the graft polymerization time

Kazuhiko Ishihara[1], Taro Shiojima[1], Masayuki Kyomoto[1,2]
[1]Department of Materials Engineering, The University of Tokyo, Tokyo, Japan
[2]KYOCERA Medical Corporation, Osaka, Japan

Statement of Purpose: Poly(ether-ether-ketone)(PEEK) is one of the super-engineering plastics and expected to substitute metals and ceramics due to its excellent mechanical properties. We demonstrate the fabrication of highly hydrophilic and biocompatible nanometer-scaled layer on the surfaces of PEEK by photoinduced graft polymerization of 2-methacryloyloxyethyl phosphoryl-choline (MPC) without using any photoinitiators [1, 2].The hydrophilic and smooth more than 100-nm-thick poly(MPC)-graft layer caused a significant reduction in the sliding friction of the bearing interface because the thin water film and hydrated poly(MPC) layer that were formed acted as extremely efficient lubricants, so called fluid-film lubrication (or hydration lubrication). The fluid-film lubrication suppressed the direct contact of the counter-bearing face with the PEEK to reduce the frictional force. Thus, the poly(MPC)-graft layer is expected to significantly increase the durability of the bearings. In this study, we examined the effects of inorganic salt additives with various concentrations in polymerization system on graft polymerization rate of MPC from the PEEK surface.

Methods: The PEEK was immersed in the MPC aqueous solutions containing NaCl of various concentrations. Polymerization was carried out at 60°C on PEEK surface under 5-min UV irradiation (360 ± 50 nm, 20 mW/cm^2). After polymerization, the poly(MPC)-graft-PEEK surface was washed with clean solvent to remove monomers and free polymers. Poly(MPC)-graft-PEEK produced at various NaCl concentrations was analyzed by XPS, TEM and AFM. A unidirectional friction test was performed using a ball-on-plate machine. A 10 mm-diameter ball of SUS was used. The friction test was performed for each specimen at room temperature using a load of 0.098 N, sliding distance of 25 mm, frequency of 1 Hz and pure water for lubrication. The mean coefficients of dynamic friction were determined by averaging the measurements for five data points.

Results: Every surface analysis result revealed the surface grafting of MPC on PEEK by photoirradiation in the presence of NaCl in the solution. After grafting, the peaks ascribed to the MPC unit were clearly observed in XPS spectra. The poly(MPC)-grafting affected the surface morphologies of the PEEK. The nanometer-scale scratches attributed to the surface finishing were observed on the surfaces of the PEEK. In contrast, the surfaces of the poly(MPC)-graft-PEEK were smooth; scratches and pits were hardly observed. Moreover, we achieved for constructing an approximately 120-nm-thick poly(MPC) layer on the surface of the PEEK by addition of 2.5 mol/L NaCl in the polymerization solution with only 5-min photoirradiation. This is due to acceleration of polymerization rate of MPC in NaCl solution. The density

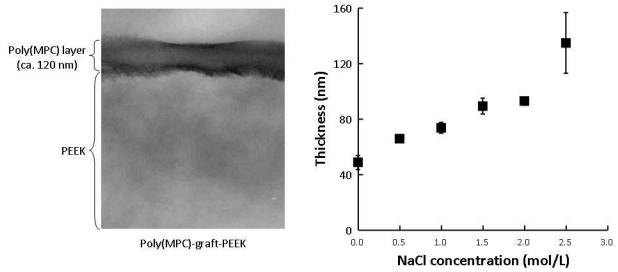

Fig. 1. Effect of NaCl concentration on the formation of poly(MPC) layer on the PEEK. TEM image shows cross-section of the specimen.

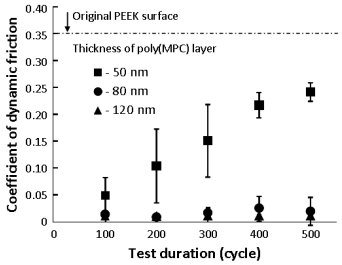

Fig. 2. Time course of frictional property of poly(MPC)-graft-PEEK with different thickness.

of the poly(MPC) layer did not change significantly with NaCl concentration. As shown in Fig. 2, the coefficient of dynamic friction of PEEK (ca. 0.35) was decreased dramatically by grafting of the poly(MPC) (ca. 0.01). That value is comparable of natural cartilage (ca. 0.02). However, it depended on the thickness of the poly(MPC) layer. Also, durability of the frictional properties depended on the thickness, more than 80-nm in thickness showed enough stability. In our previous study, it needs 60 min-photoirradiation for preparing the poly(MPC) layer on PEEK[1, 2]. Thus, we found that the addition of NaCl in the polymerization system is effective for shortening the fabrication time without adverse effect of the properties of the poly(MPC) layer.

Conclusions: Shortening of the fabrication time was successful by using an inorganic salt additive. The poly(MPC)-graft-PEEK is candidate biomaterial for developing the orthopedic devices.

References:

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Acknowledgments: This study was supported from Strategic Promotion of Innovative Research and Development (S-innovation form JST).