Versatile surface modification of biomaterials using biocompatible and photoreactive phospholipid polymers

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Statement of Purpose: The surface modification is important technology to improve the biocompatibility and biofunctionality of biomaterials. Usually synthetic polymers, metals and ceramics are used for preparation of biomedical devices and all of the surfaces strongly require the biocompatibility. The 2-methacryloyloxyethyl phosphorylcholine (MPC) polymers are well known to have unique properties such as excellent antibiofouling, good wettability and low friction [1]. The challenge is to bind the MPC polymers on various materials surfacees stably and easily. Herein, we propose new surface modification technology using photoreaction between the photoreactive MPC polymer and material surfaces. We designed the MPC polymer having phenylazide (PAz) groups to bind the polymer on the materials surface by UV irradiation (Fig. 1). The PAz groups are decomposed by UV irradiation to form nitrene groups, which are highly reactive radical groups. These groups are covalently bound to the alkyl groups. Thus, the MPC polymer can bind to the material surfaces through covalent bonding. The surface properties of various materials after modification were investigated.

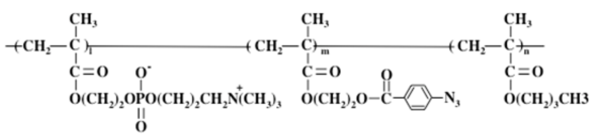

Fig. 1. Chemical structure of photoreactive MPC polymer (PMBPAz).

Methods: 2-methacryloyloxyethyloxycarbonyl 4-phenylazido (MPAz) was synthesized according to a previously reported method [2]. Poly(MPC-*co*-MPAz) (PMPAz) and poly(MPC-co-*n*-butyl methacrylate (BMA)-*co*-MPAz) (PMBPAz) were synthesized by conventional radical polymerization. Cyclic polyolefin (CPO) was obtained from Sumitomo Bakelite Co., LTd. (Tokyo, Japan). Polyethylene (PE), polystyrene (PS) and polypropylene (PP) were commercially available products. The alkyl groups were introduced on a glass (AG) and a titanium (AT) surfaces using *n*-buthyl trichlorosilane. The PMPAz and PMBPAz were dissolved in ethanol, the polymer concentration was adjusted to 0.2 wt%. The various materials were immersed in the polymer solution for 10 seconds and dried in air. Subsequently, the material surfaces were irradiated using UV lamp (254 nm, 500 uJ/cm^2, 1 min). The functional group vibrations of the PMPAz coated CPO before and after UV irradiation were examined by FT-IR/ATR. After treatment, the surface was analyzed by static contact angle measurements both by water under atmosphere and air after immersion in water.

Results: The photoreaction of PAz groups was confirmed using FT-IR/ATR. The adsorption peaks were observed on the PMPAz coated CPO substrate before and after UV irradiation. The peak at 2124 cm^{-1} was attributed to the azide group of MPAz unit. After UV irradiation, the peak was disappeared, indicating that the PAz groups were decomposed by UV irradiation. The hydrophilicity of the materials surface is related to the low friction and antifouling properties. Therefore the hydrophilicity is one of the parameters to determine the biocompatibility. Fig. 1 shows the values of contact angles by air in water on the various materials surface before and after surface modification with PMPAz and PMBPAz. In all of surfaces, high values were obtained after surface modification with PMPAz and PMBPAz. Especially, the samples except PP exhibited 180 °, that means the air bubble could not attach to the surfaces. The materials surface exhibited superhydrophilicity. The hydrophilic phosphorylcholine group is exposed in aqueous environments to reduce the interfacial free energy, thus, these results indicate successful modification of various materials with PMPAz and PMBPAz. Preliminary experiments indicated these surface treated with this technology could make inhibition of cell adhesion well.

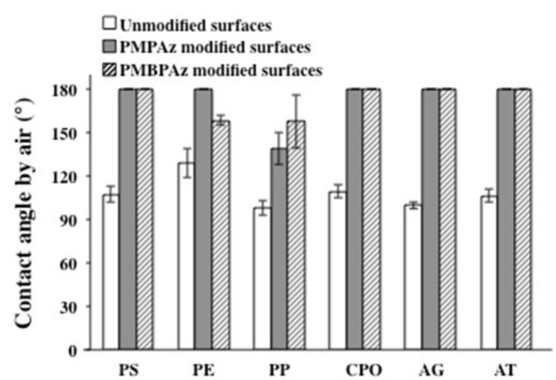

Fig. 2. The contact angles by air on the various materials measured in aqueous solution.

Conclusions: The surfaces of various materials were improved as super-hydrophilic and cell adhesion resistant surface by convenient and simple modification technique with photoreactive MPC polymers, which could bind covalently to the surface by short time UV irradiation. This technology is very convenient to apply any medical devices, which are used in clinically.

References:

1 M. Kyomoto, et al. *Biomaterials.* **2010**;31:658-668.
2 K. Fukazawa, et al. *Biosens. Bioelectron.* **2013**;40:96-101.