Life-long Durability of Orthopedic Bearings by Phospholipid Polymer Grafting and Antioxidant Blending

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Statement of Purpose: Our ultimate goal was to optimize the surface and substrate of the cross-linked polyethylene (CLPE) acetabular liners applied to life-long orthopedic bearings such that the bearing material not only had high wear resistance, but also had high oxidative resistance. We developed an articular cartilage-based technology that allows surface modification of orthopedic bearings by using phospholipid polymer grafting, such as poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) for CLPE [1,2]. Modifying bearing surfaces with a hydrophilic layer has been reported to increase lubrication similar to that for articular cartilage under physiological conditions. On the other hand, stabilization of residual free radicals with an antioxidant such as vitamin E (VE) is necessary for preventing an oxidative degradation of CLPE substrate. Therefore, the purpose of this study is to demonstrate a surface modification with PMPC on the VE-blended CLPE; further, to investigate the effects of surface modification layer and substrate on the wear- and oxidation-resistance of the orthopedic bearings.

Methods: A bar stock of 0.1 mass% VE-blended polyethylene (GUR1020E resin) was irradiated with gamma-rays (high dose [HD]; 100 kGy) and annealed at 120°C for 12 h in N_2 gas, to facilitate cross-linking (HD-CLPE(VE)). For the control, a bar stock of polyethylene without any additives (GUR1020 resin) was irradiated with gamma-rays (50 kGy) and annealed at 120°C for 7.5 h in N_2 gas, to facilitate cross-linking (CLPE). The CLPE and HD-CLPE(VE) samples were then machined from the bar stocks and were immersed in aqueous MPC solution. Photo-induced graft polymerization of MPC was performed on the CLPE and HD-CLPE(VE) surfaces by using UV irradiation (intensity, 5 mW/cm^2) at 60°C for 90 min. All samples were sterilized using gamma-rays (dose, 25 kGy). Wear and oxidation resistances of the samples were examined by several methods. The wear resistance of liners against Co-Cr alloy femoral heads was evaluated using a 12-station hip joint simulator. Squalene absorption, after squalene soaking at 120°C for 2 h, was evaluated by Fourier transform-infrared spectroscopy. Oxidative stability (oxidation-induction time) with and without squalene absorption was evaluated by differential scanning calorimetry according to ASTM D3895. The oxidative degradation of samples subjected to accelerated aging by exposure to 80°C in air for 21 d was evaluated using FT-IR according to ASTM F2102.

Results: PMPC-grafted CLPE and HD-CLPE(VE) surfaces with a 100-nm-thick PMPC layer exhibited highly hydrophilicity and wear resistance. In the hip joint simulator test of 10 million cycles, PMPC-grafted CLPE and HD-CLPE(VE) were found to show extremely low and stable wear. Substantially fewer submicrometer-sized wear particles isolated from lubricants were found for both PMPC-grafted liners than for untreated CLPE liners.

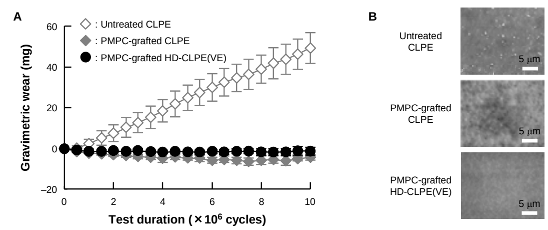

Figure 1. (A) Time course of gravimetric wear and (B) wear particles of PMPC-grafted CLPE and HD-CLPE(VE) liners during the hip-simulator wear test.

Interestingly, PMPC-grafted samples were resistant to squalene absorption, probably because of the presence of the PMPC layer; the presence of a water-fluid film and hydrated PMPC layer is the primary mechanism underlying the high oxidation resistance; water molecules in the hydration layers reduce lipid absorption, thus reducing adhesive interaction or interpenetration. The secondary mechanism is attributed to the suppressed diffusion of squalene into the PMPC layer because squalene is an insoluble molecule in the methacrylate monomer.

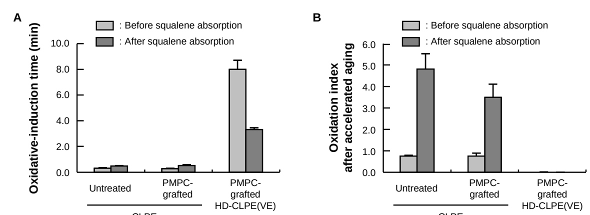

Figure 2. (A) Oxidative-induction time and (B) oxidation index of PMPC-grafted CLPE and HD-CLPE(VE).

After squalene absorption, the oxidative-induction times of PMPC-grafted HD-CLPE(VE) were significantly longer than those of the untreated and PMPC-grafted CLPE. Thus, oxidation indices of the accelerated-aged PMPC-grafted HD-CLPE(VE) were significantly lower (almost zero) than those of the untreated CLPE and PMPC-grafted CLPE, despite squalene absorption. The results of this study provide preliminary evidence that surface modification affected the extent of wear resistance and oxidative stability. This suggests that the PMPC-grafted surface and VE-blended substrate may be a promising approach for longevity of artificial hip joints.

References: [1] Takatori Y. Mod Rheumatol. 2014;11:1-6; [2] Moro T. Nat Mater. 2004;3:829-836; [3] Kyomoto M. Biomaterials. 2014;35:6677-6686.