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Tribological properties of cross-linked oleophilic polymer brushes on diamond-like carbon films

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ABSTRACT

Surface-initiated atom transfer radical copolymerization of hexyl methacrylate (HMA) and 3-ethyl-3-oxetanylmethyl methacrylate (OxMA) was carried out on the surfaces of block- and ring-type steel pieces covered with silicon-incorporated diamond-like carbon (DLC-Si) in order to generate an oleophilic copolymer brush layer at the outermost surface. The sample was then immersed in a 1% BF_3OEt_2 solution to form cross-linkages between oxetane groups in the polymer brush chains. The thickness of the polymer brush layer was confirmed to be 50 nm through transmission electron microscope images of the focused ion beam (FIB)-fabricated cross section. The friction properties of the composite films were evaluated using block-on-ring tests under a load of 49 N (130 MPa), using a base oil at 353 K for 30 min. Although the brush layer was partially scratched from the substrate surface during the friction test, the polymer brush-immobilized DLC-Si exhibited a low friction coefficient of 0.02, while the friction coefficient of the non-modified steel substrate was 0.12. It is supposed that the oleophilic polymer brush was swollen in the oil to form a stable lubrication layer, thus preventing the direct contact of the DLC-Si substrate. The dependency of the tribological properties on normal load, sliding velocity, wear depth, and the silicon content of the DLC-Si substrate was also investigated.

1. Introduction

Diamond-like carbon (DLC), which has an amorphous carbon structure, is one of the most promising known solid lubricants as a result of its low abrasion, low friction, and chemical resistance properties [1–4]. Since the mid-1980s, DLC films have attracted much interest from both the industrial and scientific research communities. However, DLC films also possess some disadvantages, such as a high residual compressive stress and a high fragility in humid or aqueous environments [5]. These problems can be addressed by doping the DLC films with metal or non-metal atoms. In general, a DLC film is formed on a substrate surface by the chemical vapor deposition (CVD) method, combined with various plasma and ion-sputtering. By using a mixture of metal halide gas and hydrogen-based gas in the CVD process, metal-doped and non-metal-doped DLC can be obtained. For example, DLC that is exposed to a mixture of tetrachlorosilane, methane, hydrogen gases produces silicon containing DLC (DLC-Si) films, which exhibits low friction and a high wear resistance under an ambient atmosphere [6–11]. Hokkirigawa and coworkers reported that the DLC-Si film exhibited a stable friction coefficient with respect to the sliding velocity, and a high wear resistance in automatic transmission fluid [12].

However, additional reduction of the friction coefficient of DLC-Si is required for the tribo-elements on the surface of the power transmission used in conjunction with a fluid lubricant under higher contact pressures. One possible solution is the surface modification of DLC-Si with organic molecules [13], which would improve its surface affinity with a fluid lubricant and form a stable hydrodynamic lubrication layer on the DLC-Si surface, resulting in a low friction coefficient. Herein, we propose surface-tethered polymers with a high graft density and well-defined structure, so called “polymer brushes” [14,15], which have garnered much attention recently since they also possess low friction

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characteristics [16–20].

Over the last decade, various types of well-defined, high-density polymer brushes have been prepared through surface-initiated controlled radical polymerization (CRP). Such brushes are grown from the surface initiating sites that are immobilized on solid surfaces or substrates through covalent bonding. As a result, the brush chains are strongly anchored and hard to detach from the substrate, even in a good solvent or under conditions that impose a large shear deformation. Therefore, polymer brushes with a nanometer-scale thickness can act as an efficient lubricant against friction.

In principle, densely grafted polymer chains within an ideal solvent stretch outward from the substrate surface in order to reduce their interaction with other polymer chains, and avoid chain overlap. The state of chain stretching is also determined by the osmotic pressure, since the osmotic pressure affects the polymer conformation and elastic restoring force of polymer chain. When two opposing, polymer brush-covered surfaces are brought into contact with one another in a good solvent, they typically repel each other as a result of the excluded volume effect among polymer segments, which can suppress the mutual interpenetration of the two compressed brushes. This phenomenon is the classical lubrication mechanism for the efficient lubrication of solvated polymer brushes, based on repulsive steric forces [21]. The reduction of frictional forces between solid surfaces bearing polymer brushes was first reported by Klein and coworkers [22] using a surface force balance, and they also reported that the polyelectrolyte brushes could act as efficient lubricants between mica surfaces in an aqueous solution. Spencer et al. have reported that not only a hydrophilic brush in water, but also a oleophilic polymer brush revealed significant reduction in friction coefficient in oil environment [23].

However, wear resistance of the polymer brush is not sufficient for friction under a high normal load around 100 MPa. Polymer brushes are eventually worn out by friction, thus producing a high friction coefficient as a result of the exposure of the bare substrate. Therefore, the wear resistance applications of polymer brush are not sufficient for practical use under load-bearing conditions.

We recently reported that partially cross-linked ion-containing polymer brushes were effective for improving wear resistance and low friction coefficient in water [24]. Copolymer brushes containing some functional groups, such as epoxy and oxetane, have the potential to initiate ring-opening polymerization in the brush layers to form 2-dimensional cross-linked thin films. In addition, the improvement of wear resistance can be expected by the use of the cross-linked copolymer brushes [25,26].

In this study, an oleophilic copolymer brush containing an oxetane group was prepared by surface-initiated CRP and a subsequent ring opening reaction, thus producing an oleophilic cross-linked organic layer on a DLC-Si surface, which is a practical tribomaterial in the automobile industry. The combination of the cross-linked polymer brush and a DLC-Si will likely improve the lubrication properties and wear resistances of sliding surfaces under conditions where lubrication oil is present.

2. Experimental

2.1. Materials

Block- and ring-type steel specimens were prepared by Toyota Motor Corp. (Aichi, Japan) and were covered with DLC-Si layer by the vapor deposition process. Silicon content in DLC-Si layer was 7, 14, 32, and 45%. Thickness of DLC-Si was 2.7 μm. Surface roughness of the steel and DLC-Si were 0.18 and 0.20 mRz 94JIS, respectively. Test pieces of DLC-Si were cleaned through exposure to ultraviolet rays (λ = 172 nm) under vacuum for 10 min under reduced pressure (30 Pa). Copper(I) bromide (CuBr, Wako Pure Chemicals) was purified through successive washing with acetic acid and ethanol, and dried under vacuum. Anisole, n-hexyl methacrylate (HMA), and ethyl 2-bromoisobutylate (EB), which were purchased from Tokyo Chemical Inc. (TCI), were distilled before use. (−)Sparteine (Nacalai Tesque) was distilled under reduced pressure, and subsequently stored as an anisole solution. 3-Ethyl-3-oxetanylmethyl methacrylate (OxMA) was synthesized from methacryloyl chloride and 3-ethyl-3-oxetanylmethanol, and purified by distillation. The synthesis of (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane (BHE) has been described in previously published work [27,28]. The surface initiator, BHE, was immobilized on a DLC-Si substrate through the chemical vapor adsorption method [29]. Boron trifluoride diethyl etherate (BF_3OEt_2, Aldrich) was used as received without purification. Lubrication oil was a mineral base oil with a SAE (Society of Automotive Engineers) viscosity grade “5W-30” containing paraffin, naphthene, and aromatic compounds, without friction modifier additives, supplied by Toyota Motor Co. (Aichi, Japan).

2.2. Preparation of cross-linked copolymer brushes

A typical surface-initiated atom transfer radical polymerization (ATRP) [30] was performed as follows (Fig. 1). A few test pieces of the initiator-immobilized DLC-Si and CuBr (0.125 mmol) were introduced in a separable flask with a stopcock, and dried by repeating a degassing and argon purge procedure. An anisole-based solution containing (−)Sparteine (0.250 mmol), HMA (375 mmol), OxMA (21.7 mmol), anisole (2.2 mL), and EB (0.120 mmol) was added to the catalyst. The resulting reaction mixture was degassed again through repeated freeze–thaw cycles in order to remove any residual oxygen, and subsequently stirred in an oil bath at 353 K for 36 h under argon, which simultaneously generated the copolymer brushes on the substrate and free (unbound) copolymer from EB. The reaction was stopped by opening the glass vessel to air at 273 K, and the reaction mixture was then poured into methanol in order to precipitate the free copolymer. The test pieces were washed with toluene using a Soxhlet apparatus for 12 h to remove the free polymer adsorbed on their surfaces, and then dried under nitrogen at room temperature. The number-average molecular weight and molecular weight dispersity of the resulting free copolymer, poly(HMA-*co*-OxMA), was M_n = 271,000 and M_w/M_n = 1.29, respectively, which was determined by size exclusion chromatography. The monomer unit ratio of HMA/OxMA in the copolymer was determined to be 9.0/1.0 by ^{1}H NMR. The thickness of the random copolymer brush (L) was approximately 50 nm, which was estimated by ellipsometer under ambient conditions. The graft density (σ) of the polymer brush was estimated to be 0.12 chains nm^{-2} by the following equation:

$$\sigma = d\,L\,N_A\,10^{-21}\Big/M_n \quad (1)$$

where d and N_A are the assumed density of the bulk polymer at 293 K and Avogadro's number, respectively.

The copolymer brush-tethered DLC-Si pieces were further immersed in a 0.5% BF_3OEt_2 dichloromethane solution under dry argon for 1 h in order to initiate the ring-opening reaction of the oxetane groups, forming linear ether linkages between the brush chains. Fig. 1 illustrates the schematic view of the cross-linked copolymer brush on the DLC-Si surface and its chemical structure.

2.3. Friction measurement using a tribometer

The friction properties of the polymer brush films were