

Synthesis and Tribological Behavior of Nanocomposite Polymer Layers

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We report results on microtribological studies of chemically grafted nanoscale polymer layers of different architecture with thickness below 30 nm. We have fabricated the molecular lubrication coatings from elastomeric tri-block copolymers and tested two different designs of corresponding nanocomposite coatings. We observed a significant reduction of friction forces and an increase of the wear stability when a minute amount of oil was trapped within the grafted polymer layer. These polymer gel layers exhibited a very steady friction response and a small value of the coefficient of friction as compared to the initial polymer coating. A polymer "triplex" coating has been formed by a multiple grafting technique. The unique design of this layer includes a hard-soft-hard architecture with a compliant rubber interlayer mediating localized stresses transferred through the topmost hard layer. This architecture provides a non-linear mechanical response under a normal compression stress and allows additional dissipation of mechanical energy via the elastic rubber interlayer.

Keywords : Boundary lubrication, paraffinic oil, nanocomposite coatings, triplex coating, microtribological properties.

1. INTRODUCTION

Further miniaturization of microelectromechanical systems requires the development of robust molecular coatings for the enhancement of their surface nanomechanical and nanotribological properties under ambient environmental conditions [1, 2]. Recently, we have proposed using nanocomposite elastomeric layer grafted to a silicon surface as a wear resistant molecular layer [3, 4].

In this publication, we report preliminary results on the enhancement of nanotribological performance of elastomeric monolayers from tri-block copolymer by either adding paraffinic oil that can swell chemically identical rubber matrix or capping with top hard layer (for the concept sketch, see Figure 1).

2. EXPERIMENT

For fabrication of a compliant layer of 8-10 nm thickness, we used poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] (SEBS) (Kraton, Shell) chemically grafted to a silicon wafer surface as described in detail elsewhere [5, 6]. For oil treatment, paraffinic oil, C₁₅H₃₂ to C₂₄H₅₀ (Aldrich) was used as lubrication additive. For the triplex coating, both compounds, 1,6-hexanediol dimethacrylate (HDM) and photoinitiator 4-(dimethylamino) benzophenone (PI) (Aldrich) were used as received. The fabrication procedures have been described in detail elsewhere [7].

3. RESULTS AND DISCUSSIONS

Figure 1(b) illustrated the SPM topographical images of the grafted polymer gel layers with paraffinic C24 oil. The grafted polymer films possess uniform, smooth, and homogeneous surface with only a few aggregates observed over surface areas of tens micrometers across (microroughness of 0.2-0.4 nm). For polymer layers exposed to long-chain oils, globular aggregates were detected. The highest surface concentration of aggregates was observed for the highest

molecular weight paraffinic oil C24. The lateral size of surface aggregates is within 400-500 nm. That this is related to the crystallization process of paraffinic oil with low melting points during cooling from 60°C to room temperature that results in the formation of paraffinic crystals.

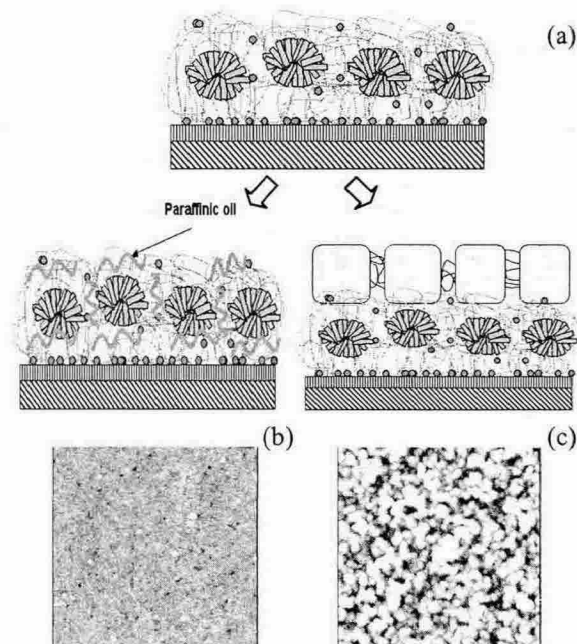


Figure 1. (a) Microstructure of nanocomposite/reinforced elastomer layers, (b) SPM topographical images of the grafted polymer gel layers with paraffinic C24 oil and (c) topmost photopolymerized layer of triplex coating. Scan size is 1×1 μm, light tapping mode.

Wear resistance of the polymer layer was tested under conditions of the mesoscale contact (contact radius about 10 μm). This involved the contact of a steel ball and local pressures/velocities comparable with that of conventional MEMS operating conditions. Figure 2 shows the coefficient of friction calculated as a ratio of the lateral forces to the normal load as a function of the number of sliding cycles. At a low normal load of 0.3 N, the grafted polymer gel layers exposed to oils showed a performance much better than the uncoated silicon and the dry polymer film. The polymer gel layers did not show a failure or significant deterioration up to 20,000 cycles (the maximum number of cycles tested here) whereas the silicon and the dry polymer layer failed within 200 cycles and 2,700 cycles respectively.

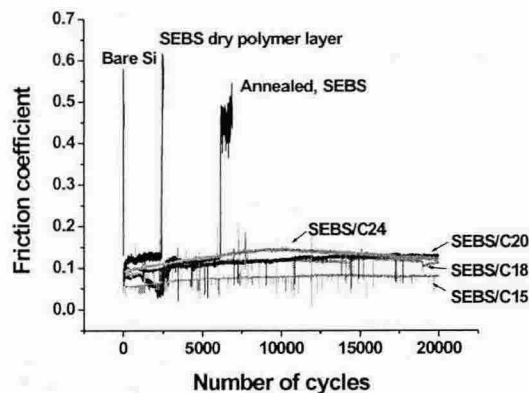


Figure 2. The coefficient of friction as a function of a number of sliding cycles for the bare silicon, dry polymer layer, annealed polymer layer, and polymer gel layers at the normal load of 0.3 N.

As the alternative approach, we designed robust, well-defined trilayer surface nanostructures chemically grafted to silicon oxide surface with effective composite modulus of about 1 GPa. The fine, grainy surface microstructure of the rigid top photopolymerized nanolayer (methacrylate-based polymer, 5-20 nm thick) possesses a combination of hard nanodomains (<50 nm across) embedded in a less densely cross-linked matrix due to internal spatial heterogeneity of these polymer networks (Figure 1(c)) [8]. The hard top layer was tethered to the compliant interlayer that, in turn, was grafted to the epoxy-terminated SAM. Such mutual interlayer tethering prevented the delamination of dissimilar molecular layers during large surface mechanical deformations.

Figure 3 shows the coefficient of friction calculated as a ratio of the lateral forces to the normal load as a function of the number of sliding cycles. At a low normal load of 0.3 N, both trilayer structure and SAM showed excellent wear stability with the friction coefficient being smaller for the trilayer surface structures (within 0.02-0.08 for both surfaces, which was several times lower than for bare silicon). The bare silicon substrate failed within only 100-200 cycles after test initiation (data were averaged over three independent measurements at various locations). The rubber layer without the hard capping of the top layer exhibited very high friction, and failed after 3,000 cycles. At a high normal load of 1.8 N (1.2 Gpa pressure), all reference surfaces failed almost immediately (not shown). Alkylsilane SAM failed after 900

cycles. Finally, the trilayer surface structure showed a much higher wear stability, and was worn down only after 3,000-3,500 cycles due to the intensive thermo-oxidation occurring in the contact area as demonstrated by Auger spectroscopy analysis of the surface chemical composition and discussed in a separate publication [7].

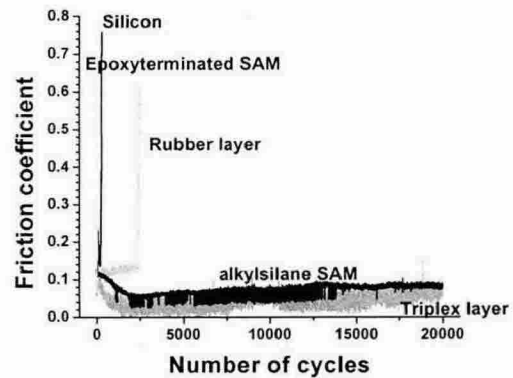


Figure 3. The coefficient of friction as a function of a number of sliding cycles of triplex layer as compared to references at the normal load of 0.3 N.

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