

Triplex molecular layers with nonlinear nanomechanical response

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The molecular design of surface structures with built-in mechanisms for mechanical energy dissipation under nanomechanical deformation and compression resistance provided superior nanoscale wear stability. We designed robust, well-defined trilayer surface nanostructures chemically grafted to a silicon oxide surface with an effective composite modulus of about 1 GPa. The total thickness was within 20–30 nm and included an 8 nm rubber layer sandwiched between two hard layers. The rubber layer provides an effective mechanism for energy dissipation, facilitated by nonlinear, giant, reversible elastic deformations of the rubber matrix, restoring the initial status due to the presence of an effective nanodomain network and chemical grafting within the rubber matrix. © 2002 American Institute of Physics. [DOI: 10.1063/1.1486267]

The technology known as micro- and nanoelectromechanical systems (MEMS and NEMS) provides batch-produced microsensors, microgears, microengines, membranes, and actuators.¹

The incorporation of motion with a sustained, reliable long-living contact of mating surfaces is a challenging issue.^{2,3} For nanoscale systems, precise design of molecular surfaces, which allow for selective and controllable interfacial interactions, is critical in making them capable to sustain nanoscale contact stresses.^{4,5} Currently, the most efficient way to design well-controlled molecular surfaces is in the form of self-assembled monolayers (SAMs).^{6–8} This approach was implemented for controlling the interfacial properties of various microfabricated solid surfaces.^{9–11} The nature of the nanoscale contact interactions for such surfaces has been widely debated over the years.^{12–14} The origin of mechanical energy dissipation was related to atomic interlocking, breaking, and formation of chemical bonds, the formation of conformational defects, heating phenomena, interfacial slippage, and collective tilting of the molecules.^{15–22}

Recently, we proposed a molecular design of well-defined nanoscale surfaces that include a highly elastic, reinforced rubber interlayer chemically grafted in between the solid substrate and a hard top layer.²³ We suggested that such a combination will provide an effective mechanism for energy dissipation, facilitated by reversible elastic deformations of the chemically grafted/reinforced rubber matrix, enhanced by capping with the top hard layer, which prevents the penetration of solid asperities through the compliant layer (Fig. 1). Such “triplex,” multilayered surface structures, with total thickness not exceeding several tens of a nanometer, can be fabricated via a combination of a directed multistep self-assembly with UV irradiation, as is described

in detail elsewhere.²⁴ Here, we report the surface nanotesting of these triplex structures, which, indeed, indicates that superior wear stability can be achieved which is not merely several percentage points better than the stability of conventional SAM modified surfaces, but, in fact, can be orders of magnitude better.

Figure 1 shows the step-by-step assembly of the triplex, mutually grafted, surface nanolayers with a total thickness of 20–30 nm beginning with a bare silicon surface functionalized with an epoxy-terminated SAM.²⁴ The cartoons illustrate the microstructure of each layer, and the scanning probe microscopy (SPM) images display the nanoscale surface morphology.²⁵

The micromechanical testing of each individual layer showed that the top hard layer possessed an elastic modulus of 2 GPa (typical for hard plastic), while the rubber interlayer was highly compliant with an elastic modulus of 10 MPa (typical for reinforced rubber). The elastic modulus of the epoxy-terminated SAM was estimated to be about 1 GPa. The overall elastic modulus of the stiff [100] silicon surface was 190 GPa.

To test the nanomechanical behavior of the surface, we used nanomechanical probing with a sharp SPM tip. The contact radius estimated from Hertzian mechanics was in the range of 1–10 nm. The double spring model with a variable spring constant was used to reveal the depth profile of the elastic modulus variation as has been discussed elsewhere.^{26–28} Briefly, for the current value of the elastic modulus at a specific indentation depth, the Hertzian model gives

$$E_i = \frac{3}{4} (1 - \nu^2) \frac{k_n}{R^{1/2}} \frac{z_{\text{defl},i,i-1}}{h_{i,i-1}^{3/2}}, \quad (1)$$

where indentation depth $h = z_{\text{pos}} - z_{\text{defl}}$; z_{defl} is a measured vertical deflection of the SPM cantilever; z_{pos} is the vertical displacement of the SPM piezoelement; k_n is a cantilever

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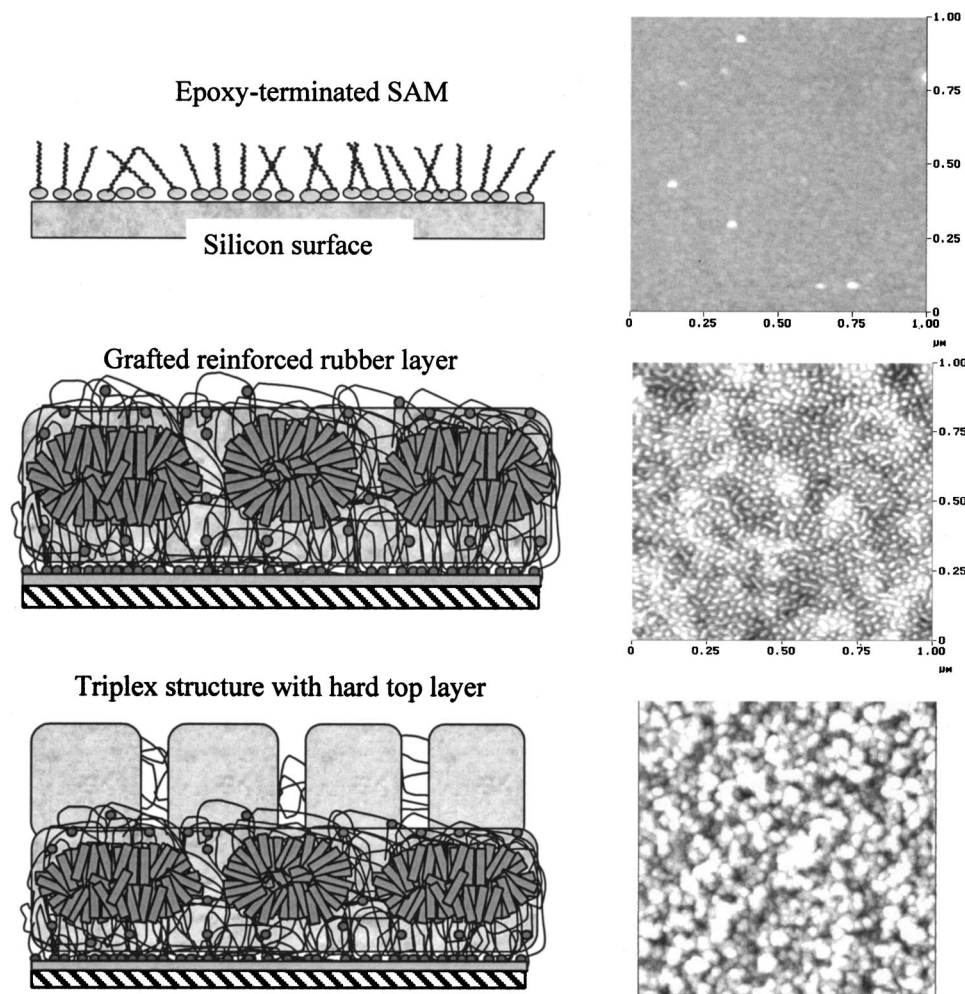


FIG. 1. Step-by-step assembly of trilayer surface structures with three molecular layers with different elastic properties: epoxy-terminated SAM, grafted rubber layer with nanodomain structure, and trilayer structure (from bottom to top). Corresponding surface topographies ($1 \times 1 \mu\text{m}$ surface area for all layers) show the atomically smooth surface of the epoxysilane SAM (microroughness is 0.2 nm), nanodomain morphology of the grafted rubber layer from triblock copolymer (microroughness is 0.3 nm), and the topmost photopolymerized layer with fine grainy morphology (microroughness is 5 nm).

spring constant; R is the tip radius; ν is the Poisson ratio; and $i, i-1$ refer to the adjacent tip displacements derived from a force–distance curve. In addition to the conventional Hertzian approach, the double-layer contact mechanics model was used to account for cooperative deformation of two layers with different elastic moduli.²⁹

The elastic response, indeed, confirmed the hard layer/compliant layer/hard layer mechanism at work, which was to be expected for the well-defined triplex structure (Fig. 2). The nonlinear response was most pronounced for the trilayer structures with similar thicknesses of rubber and hard layers and a well-developed grainy microstructure.³⁰ We believe that the hard grains play a mediating role in the transfer of mechanical stresses to the compliant interlayer and that they facilitate the mechanism of interfacial slippage during lateral motion, which assists low surface adhesion.³¹ Indeed, surface adhesion of the sandwiched layer is significantly (2–3 times) lower than for the rubber layer.³⁰

The wear resistance of the triplex coatings was tested under conditions of the mesoscale contact (contact radius about $10 \mu\text{m}$). This involved the contact of a steel ball and local pressures/velocities comparable with that of conventional MEMS operating conditions. In this method of wear testing, a sharp increase of the friction forces indicates detrimental surface failure. Experimental data are shown for the trilayer surface structures in comparison with a bare silicon surface, and the grafted rubber interlayer (Fig. 3). Also shown in this experiment for the purpose of comparison is

the data for alkylsilane SAM,³² which is a common molecular lubricant for polysilicon surfaces of MEMS (Fig. 3).⁵ At the low local pressure of about 660 MPa both the trilayer structure and the 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 3000 cycles.

For the second test, the local pressure reached 1.2 GPa, which was much higher than the yield strength of a vast majority of polymeric materials. Under these severe loading conditions, the wear resistance mechanism was controlled by the ability of the surface to self-heal and restore itself, rather than by direct elastic resistance of the surface. Indeed, all reference surfaces failed almost immediately (Fig. 3). Alkylsilane SAM failed after 900 cycles. Finally, the trilayer surface structure showed a much higher wear stability, and was worn down only after 3000–3500 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.³⁰

This result demonstrates that the focused molecular design of multilayer surface structures with built-in additional mechanisms for mechanical energy dissipation and modu-

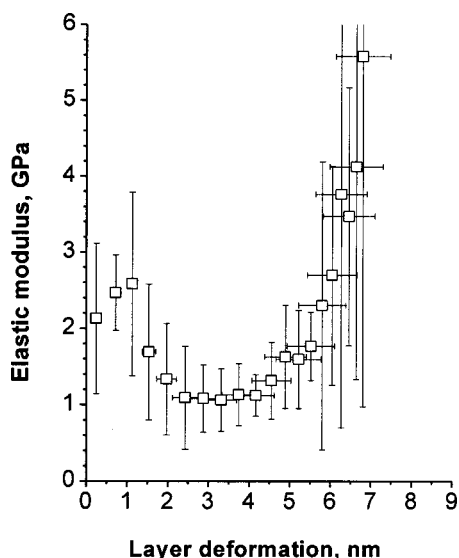


FIG. 2. Depth profiles of the elastic modulus for the trilayer structures showing the modulated elastic response with a higher apparent modulus for small and high compression rates (total thickness of the layer is 16 nm, top layer is 7 nm). Bars show the standard deviation for an array of 30 profiles obtained at different surface locations.

lated compression resistance provides wear stability superior to that of conventional SAMs, which is the current choice for molecular lubrication of microdevices.

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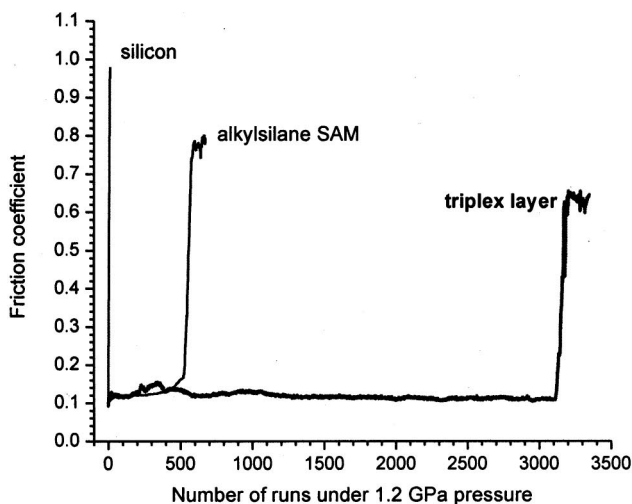
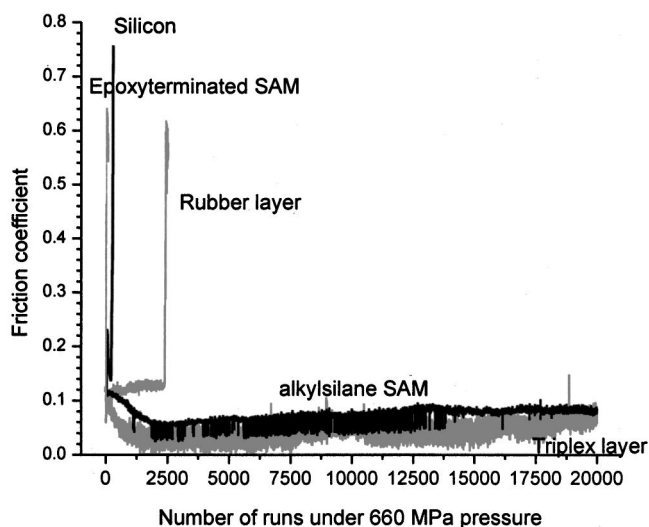


FIG. 3. Friction coefficient of various surfaces against a steel ball vs a number of reciprocal sliding cycles for different surfaces obtained with a microtribometer at low (top) and high (bottom) normal loads (alkylsilane SAM from C₁₆ alkyl chains is described in Ref. 32).

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