Oily nanocoatings

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Tribological performance of molecular thermoplastic elastomeric films grafted onto a silicon surface was enhanced by adding a minute amount of paraffinic oil, which was adsorbed by the rubber matrix. The nanocomposite films show bimodal distribution of the surface elastic modulus, caused by the nanodomain structure. Minute amounts of oil, trapped within the rubber phase after evaporation, modified the nanotribological properties of these layers. We observed a significant decrease of the friction coefficient by 40%, along with a lower elastic modulus of the rubber phase. We suggest that under high shear stresses and sliding velocity, oil molecules can be compressed out of the bulk to the surface, facilitating instant local lubrication of the contact area.

KEY WORDS: nanotribology; nanocoatings; oil lubrication; scanning probe microscopy

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 [1–3]. A variety of molecular films have been proposed for this purpose [1,3–11]. Recently, we proposed a nanocomposite elastomeric layer grafted to silicon surfaces as a wear-resistant molecular layer [12–16]. As a means to enhance the performance of these coatings, we proposed to exploit either a hard capping layer or their saturation with paraffinic oil or other low-molar weight lubricant. The latter approach may provide a natural mechanism for self-healing of nanocomposite coatings and the creation of local, instantaneous lubrication, facilitated by diffusion from the protective layer within the contact area.

In this publication, we report preliminary results on the enhancement of the nanotribological performance of elastomeric monolayers of a tri-block copolymer, which was recently developed [13,14] by adding paraffinic oil that can swell the chemically identical rubber matrix, due to the compatibility of their chemical structures (figure 1). We expected that the presence of oil within the monolayer and its surface redistribution under local mechanical stresses generated within the contact area would modify the nanomechanical and nanotribological response of the oil-containing polymer monolayer.

2. Experimental

As a nanocomposite layer, we used poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS), (Kraton, Shell) chemically grafted onto a silicon wafer surface. A self-assembled monolayer with epoxy terminal groups was used as a binding interface (figure 1) [17,18]. Paraffinic oil, $C_{15}H_{32}$ (Aldrich), was used as a lubrication additive. The grafted SEBS layers were saturated in oil vapor. Several droplets of paraffinic oil and a sample silicon wafer with grafted SEBS were placed separately in a test tube. The test tube was divided into two chambers with a neck and sealed for the desired time. The oil content within the SEBS monolayer was monitored by means of FTIR spectroscopy and ellipsometry. Surface morphology and nanotribological properties were studied with scanning probe microscopy (SPM). More details of the experimental results devoted to the kinetics of oil diffusion will be published elsewhere [19]. The surface distribution of the elastic modulus and the friction properties of the ultrathin polymer layers were measured according to procedures described earlier [20–23].

3. Results and discussion

Paraffinic oil should be fully compatible with the ethylene–butylene rubber phase of the copolymer due to similarity of their chemical structures. Indeed, as we observed, the bulk SEBS material could be easily swollen in oil up to 600% and retained its composition for a long time both in the bulk state and within polymer films (for details, see [19]).

The spherical nanodomain morphology of a dry SEBS monolayer, as revealed by SPM imaging, is presented in figure 1 and discussed in detail elsewhere [13,14]. This morphology remained clearly visible, even for the layers with a large initial amount of added paraffinic oil (figure 2). The oil content within the SEBS layer after saturation within oil vapor was monitored with ellipsometry and varied from 10 to 70%. The surface morphology of the SEBS layers with the highest oil content looked a bit fuzzier than the layers with low oil content and the dry layer (figures 1 and 2). Under dry ambient conditions, the oil tended to evaporate from the SEBS layer within several hours after specimen preparation with only a residual amount ($<4\%$) being detected

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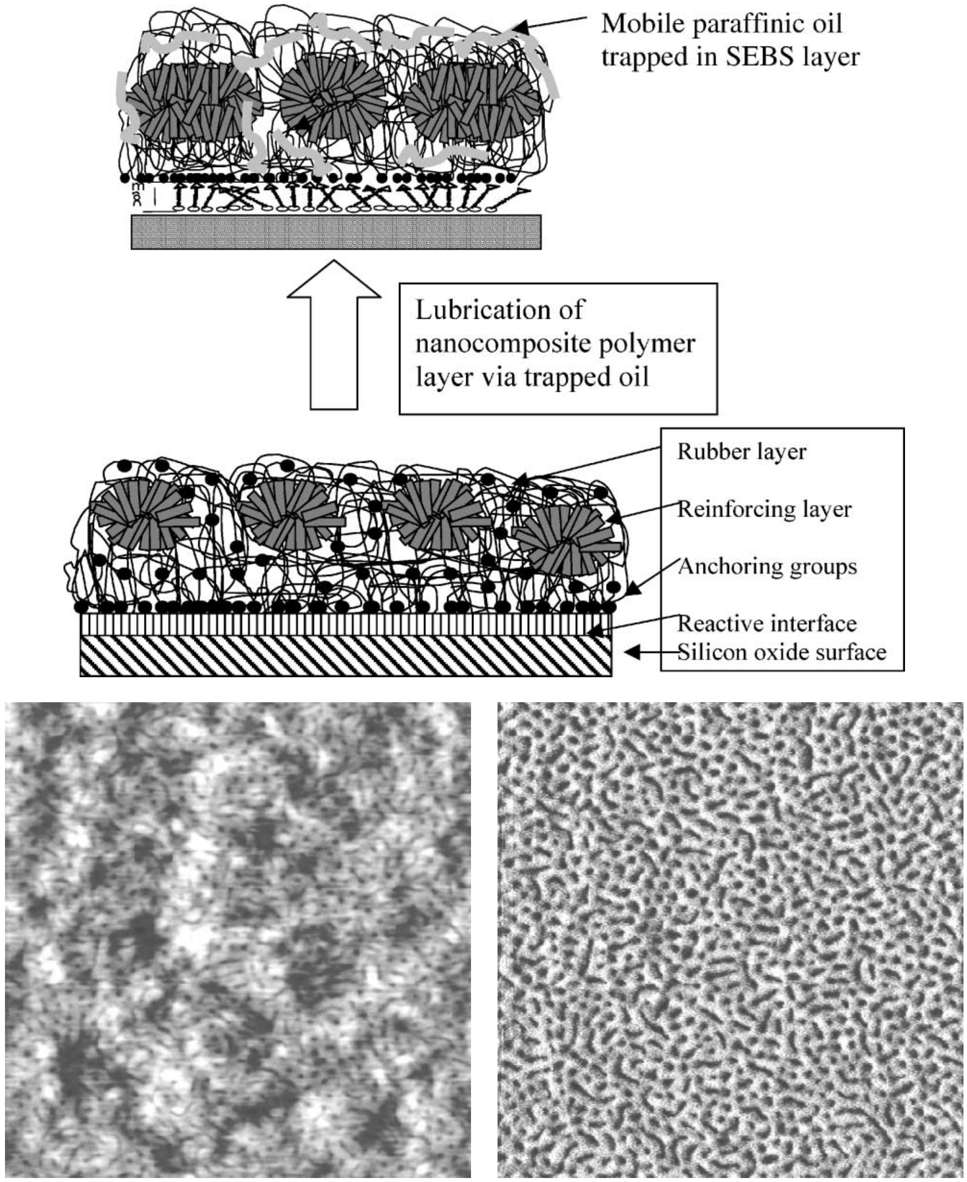

Figure 1. Microstructure of a SEBS molecular layer grafted onto an epoxy-terminated surface (center). Hard blocks are presented by dark gray spheres and the soft rubber matrix contains anchoring groups shown by black dots [13]. The SEBS film with the paraffinic oil is presented on the top. The paraffinic molecules entrapped in the rubber matrix of the SEBS layer are shown by light gray curved rods. Bottom: SPM height (left) and phase (right) image of grafted SEBS film of 8 nm thickness; scan size $1 \times 1\ \mu$m, height scale 5 nm, phase scale 15°. The nanodomain structure of the film is clearly seen in both topography and phase images.

after one day. The rate of oil evaporation from the SEBS layer was measured as three times lower than for a free oil surface [24,25]. This indicated that the mobility of the oil phase was severely restricted when the chain molecules were trapped within the rubber matrix, as will be discussed in detail elsewhere [19].

Nanomechanical testing of dry and oil-containing layers revealed differences in their elastic response (figure 3). The histogram of the surface distribution of elastic modulus revealed its bi-modal character. As was concluded after fitting the experimental data with two peaks, the main maximum was located around 120 MPa and another maximum with a lower area appearing as a shoulder was found at a higher value of elastic modulus of about 280 MPa (figure 3). The presence of two contributions on this histogram reflected the nanocomposite nature of the layers with different mechanical properties of hard nanodomains being embedded in the compliant matrix. Only the high-resolution nanomapping applied in this work (a single pixel of 15 nm across was smaller than the interdomain distance of about 30 nm [13,14]) revealed the different elastic responses possessed by the hard domains and the rubber matrix. Absolute values obtained in this work were close to those reported earlier for similar SEBS films and also obtained from the Hertzian analysis of the force–distance curves [26]. Both values represented an overestimation of the actual layer modulus due to an unaccounted contribution from a stiff silicon substrate. Complete analysis should exploit a model of

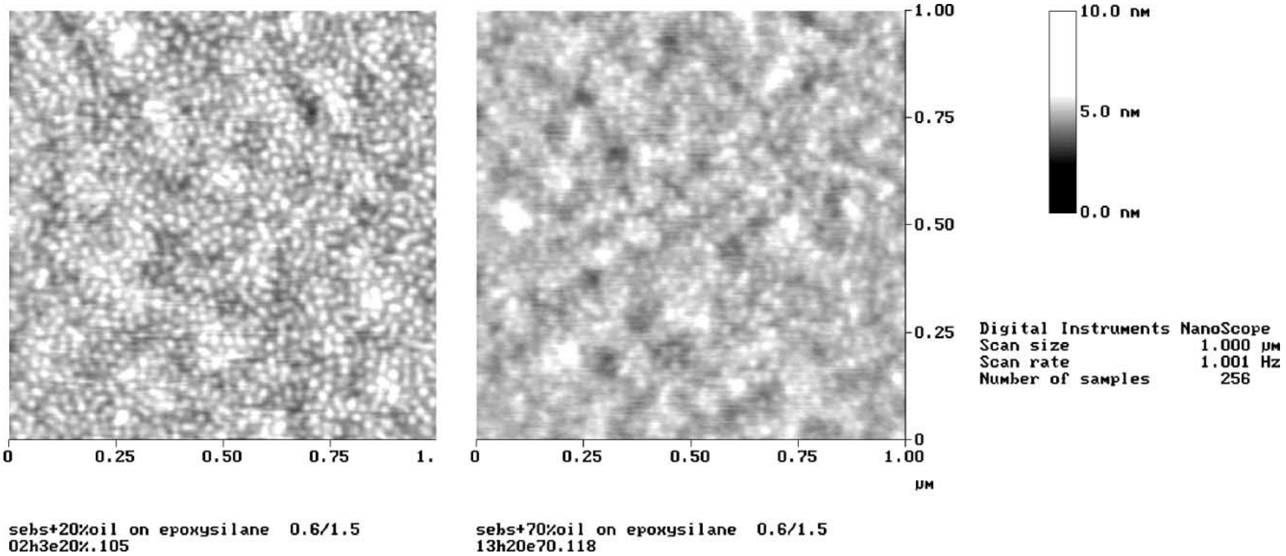

Figure 2. SPM images of the SEBS films saturated with 20% oil (left) and 70% oil (right). Scan size is 1×1 μm, height scale is 10 nm.

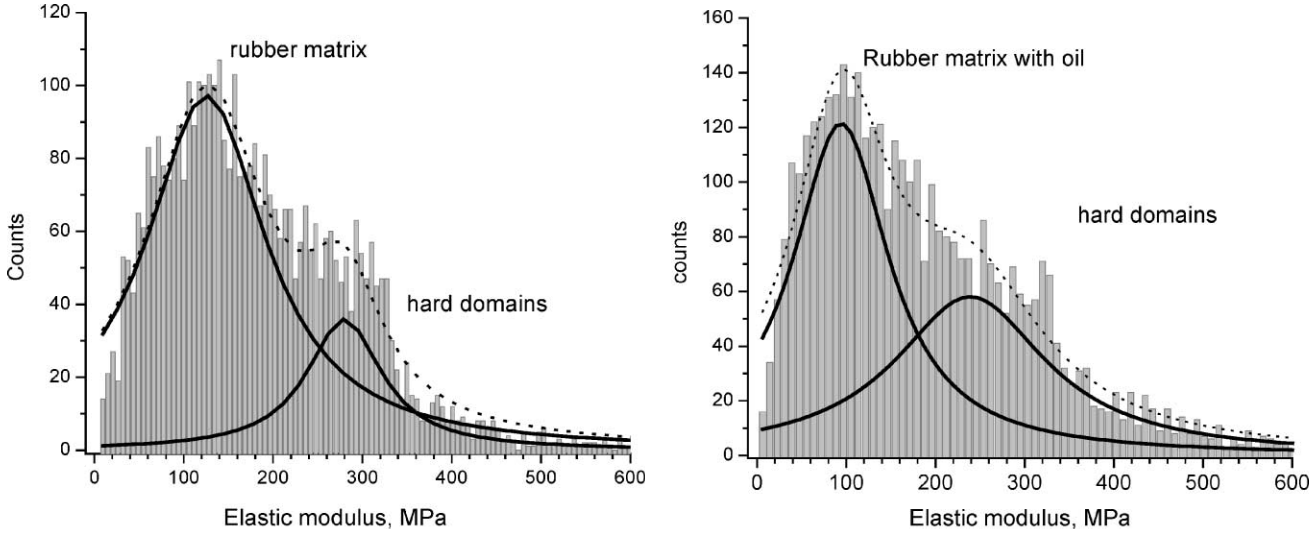

Figure 3. Surface distribution of the elastic modulus obtained from micromapping of a dry SEBS film (left) and a SEBS film containing the residual oil (right). Solid lines show the result of fitting (total, dotted line) of the distribution functions with two Lorentzian functions (thick lines).

the layered elastic solid, in order to account for the actual soft layer-stiff substrate configuration [27,28]. This model is currently under development.

Comparison of the surface distribution of the elastic modulus for dry and oil-containing layers (figure 3) demonstrated that the nanodomain structure, with a bimodal distribution of nanomechanical response, was preserved after paraffinic molecules were added to the SEBS layer. The surface histogram for the layer with trapped oil showed little change of the apparent elastic modulus for hard domains (240–250 MPa or within 10–12% of the initial modulus) but a much larger decrease of the apparent elastic modulus of the rubber matrix (30–40% decrease). This serves as an indication that the oil molecules are mainly located within the rubber phase.

Addition of paraffinic oil affected the frictional characteristics of the elastomeric layer as well (figure 4). Loading

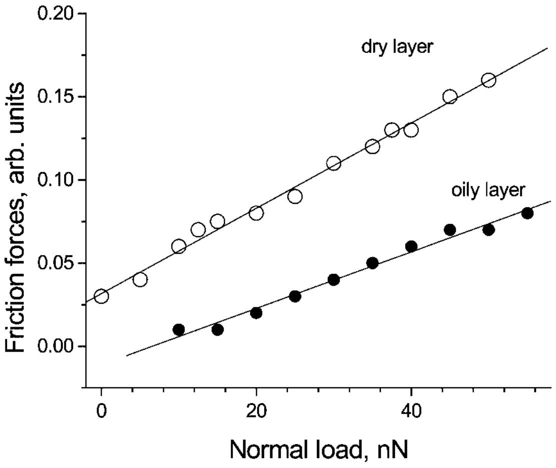

Figure 4. Friction forces (volts) *vs.* normal load as measured for a dry SEBS film (○) and an oil-containing SEBS film (●).

curves obtained for both dry and oil-containing layers under identical conditions (identical probe, scanning velocity, scanning size, and the range of normal loads) demonstrated that the friction coefficient at low normal loads (calculated as a slope of a linear approximation) was much lower for the oil-containing layer (about 40%). Adhesive forces were also much lower for the oil-containing layer, as is clear from differences in the extrapolation of friction signals to a zero level (figure 4).

4. Conclusion

In conclusion, we demonstrated that the saturation of the nanocomposite elastomeric monolayer with paraffinic oil resulted in significant reduction of the friction forces and compression elastic moduli along with the preservation of the original nanodomain microstructure. An obvious cause for the observed changes of the nanotribological properties was the presence of paraffinic molecules trapped within the crosslinked rubber matrix. The oil molecules can serve as lubrication of the local area of the mechanical contact (layer–asperity) *via* the mechanism of contact-pressure-driven expulsion and surface diffusion. We suggest that under high shear stresses and sliding velocities, this mechanism can provide the localized lubrication in the contact area that facilitates lower friction. The initial state of the compliant coating can be restored after unloading the affected surface area. However, to implement this unique property of the compliant, oil-saturated nanocoatings, fine tuning of the internal diffusion and mobility of long-chain molecules under shear stresses should be carried out. This is the subject of further studies. In particular, we are currently considering longer-chain molecules with hindered diffusion and a tendency to crystallize at room temperature [19].

Acknowledgments

This work is supported by The National Science Foundation, CMS-9996445 Grant, and Grant M01-C03 from the Department of Commerce through the National Textile Center. The authors thank Dr. V. Gorbunov and Professor S. Chizhik for helpful discussions and assistance.

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