Preparation of Siloxane−Urethane Coatings Having Spontaneously Formed Stable Biphasic Microtopograpical Surfaces

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Since materials interact with their environment primarily through their surfaces, understanding and controlling the composition and topography of a material's surface are of utmost importance. Adhesion, appearance (e.g., gloss), tribological, and haptic properties as well as biocompatibility are all affected by the surface topography and chemical composition of the surface of a material.[1,2] Because of the recognition of the important role topography plays in interactions with biological systems, there has been an increasing interest in development of methods for preparing polymer surfaces having defined topographical features. In thin films of polymer blends or block copolymers, microphase separation expressed at the surface of the polymer films results in microtographical surface features.[3,4] Selective removal of one of the component phases by solvation[5] or degradation[6] can also be achieved. Domain size and orientation can be controlled by electric fields in copolymers,[7] by polymer-on-polymer stamping,[8] and by guided phase separation from deposition of a binary polymer blend onto a chemically patterned substrate.[9] Hyperbranched fluoropolymers have been found to form self-assembled surface topographies after cross-linking with difunctional poly(ethylene glycol) or poly(dimethylsiloxane) (PDMS).[10] Surface phase separation has also been observed in a PDMS system cross-linked with a fluorinated silane.[11] PDMS elastomers having well-defined microtopographical features have been prepared by contact molding and have been shown to inhibit settlement of fouling organisms.[12−14]

The surface of a solvent-cast block or graft copolymer system is composed predominately of the lowest surface energy component. This is especially the case in copolymer systems composed of PDMS segments. Numerous studies of the surface composition of PDMS block and graft copolymer systems have shown that PDMS predominates on the surface even at low bulk concentrations, due to its low surface energy relative to other organic polymers.[15−22] This feature can be exploited to create tough, low surface energy polymers such as PDMS−polyurethane block or graft copolymers that may be useful as easy-release coatings for combating marine fouling. However, upon exposure to an aqueous environment, the surfaces of copolymers of PDMS and polyurethane rearrange as the more hydrophilic polyurethane components migrate to the surface, displacing the hydrophobic PDMS.[23−25]

In this communication, we describe the synthesis of a cross-linked PDMS−polyurethane thick film coating that spontaneously phase separates to form microtopograpical surface domains, composed primarily of PDMS, surrounded by a polyurethane matrix.

Table 1. Compositions of Coating Formulations Prepared[26]

formulation	wt % PDMS	wt % PCL	wt % XIDT
A	30.0	15.3	54.7
B	20.0	21.0	59.0
C	10.0	26.7	63.3
D	0.0	32.3	67.7

To design tough coatings having stable low surface energy surfaces, we have been exploring the synthesis of cross-linked PDMS−polyurethane systems. In a cross-linked system, the hydrophobic PDMS-rich surface that is formed in air is likely to be constrained against rearrangement upon exposure to an aqueous environment. Three PDMS−polyurethane formulations with 10, 20, and 30 wt % PDMS and one control polyurethane were prepared, as illustrated in Table 1. The composition consisted of a hydroxy functional poly(dimethylsiloxane) (PDMS), a trifunctional polycaprolactone polyol (PCL), and a polyfunctional isocyanate based on isophorone diisocyanate (XIDT).[26] Coatings were cast from a solution of these reactive oligomers in a solvent blend, and the formulations also contained a catalyst (dibutyl tin diacetate) and a pot-life extender (2,4-pentanedione). Since PDMS has a much lower surface energy than the polyurethane, the PDMS was expected to stratify to the coating surface during film formation and cross-linking, resulting in a polyurethane coating having a smooth, low surface energy PDMS outer layer with a tough polyurethane sublayer. Indeed, tapping mode AFM studies of the 20 and 30% siloxane−urethane coating compositions (A and B) showed very smooth surfaces fully covered by PDMS, illustrated in Figure 1b. The polyurethane control containing no PDMS (D) also had a feature-free surface. However, we found that formulation C containing 10% PDMS remarkably yielded a microstructured surface with discrete domains as shown in Figure 1a. These domains have an average diameter of 1.4 μm and a height of ca. 50 nm. A planar view of this surface is also shown in Figure 3a. Interspersed between the larger domains are numerous smaller domains as well. The size distribution of the larger domains is fairly uniform. While it may be assumed that the domains are primarily composed of PDMS, the domain sizes are much larger than expected if they were composed solely of the 1000 g/mol PDMS block. Thus, these domains apparently consist of a mixture of the PDMS as well as some of the polyurethane components. This is consistent with a recent study of PDMS−polyurethane block copolymers by Sheth et al., which indicated that in systems containing low MW PDMS oligomers (900 g/mol) there is substantial phase mixing of the PDMS block with the polyurethane.[27]

To further verify the nature of the domains and the surrounding material, nanoindentation measurements were conducted on the microstructured siloxane−urethane surface and also on the control polyurethane surface under the application of the same threshold force value of 20 μN. Depth of indentation at peak load ($h_{\max}$) over the microdomains was considerably higher (179.5 ± 3.7 nm) than the surrounding area (83.6 ± 1.8 nm). The $h_{\max}$ value obtained on the pure polyurethane surface was 78.3 ± 10.4 nm, close to the value obtained for the matrix of the microstructured surface. Thus, the higher indentation depth indicates that the micro-

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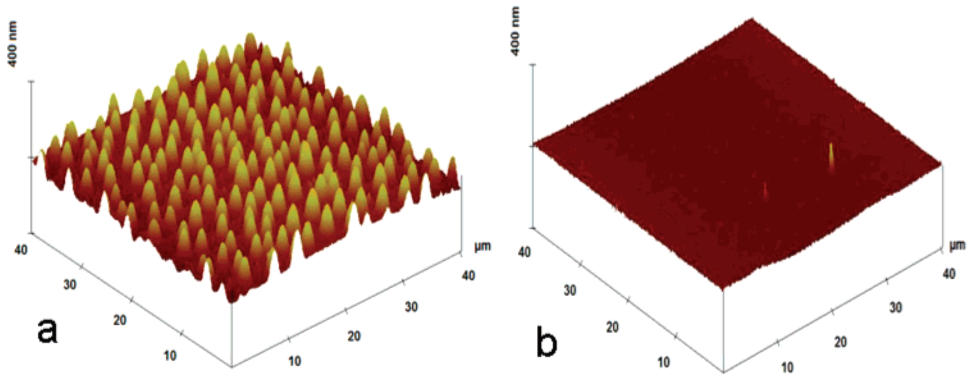

Figure 1. Tapping-mode AFM image of (a) coating C and (b) coating A.

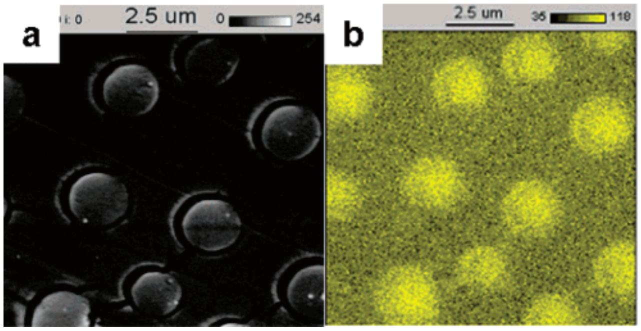

Figure 2. (a) SEM image and (b) Si map of coating C.

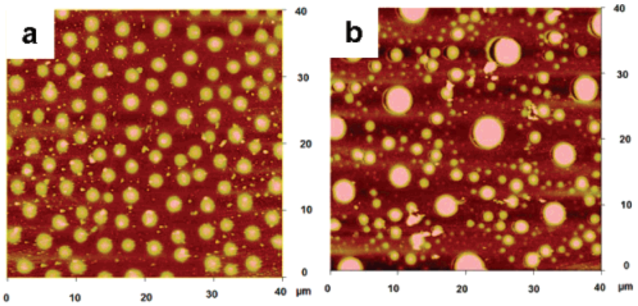

Figure 3. Topographical tapping mode AFM images in air of coating C (a) before water immersion and (b) after 2 weeks of water immersion.

domain modulus is significantly lower than that of the surrounding material, and thus the microdomains are primarily composed of PDMS, while the surrounding material consists of polyurethane containing little or no PDMS.

SEM imaging of the surface also verified the microstructured nature of the polymer surface (Figure 2a). Energy-dispersive X-ray mapping of silicon indicated that the microstructured domains formed at the surface were rich in silicon as shown in Figure 2b. In contrast, SEM imaging and Si mapping over a featureless siloxane—urethane coating (formulation A) revealed that silicon was uniformly distributed over the surface.

Preparation of the coating composition was repeated several times to ensure that it could be successfully reproduced. In addition, to verify that the surface domains did not consist of unreacted PDMS on the surface of the coating, the coating was treated with toluene, which would dissolve unbound PDMS oligomer. AFM studies indicated that, while the domains swelled, they were not removed and thus are covalently bound to the network.

Coatings intended for immersion in aqueous environments must not rearrange or reorient in order to maintain their performance properties. To study the stability of the microstructured surface, tapping mode AFM images were made after 2 weeks of water immersion and are shown in Figure 3. The PDMS domains, while they changed in size and size distribution, did not disappear. The mean diameter of the domains was 1.4 μm before water immersion and after water immersion the mean diameter of the larger domains in Figure 3b was 3.82 μm. The fact that some domains were able to grow in size indicates that there is some degree of mobility of the polymer on the surface of this coating. Water can plasticize the polyurethane matrix and allow diffusion of PDMS-rich polymer from domain to domain.

While the polymer composition is a major factor, another controlling factor for the formation of microstructured surface domains is the solvent composition used in the coating formulation. The solvent composition plays a role in the initial compatibility of the components during mixing and also influences the point of phase separation during curing as the solvents evaporate at different rates. Three different solvents—EEP (ethyl ethoxy propionate), MAK (methyl *n*-amyl ketone), and BA (butyl acetate)—in a ratio of 38:17:45 comprised the solvent composition of the formulations listed in Table 1. Formulation C was repeated using EEP, MAK, and BA in a ratio of 43:12:45. This formulation again resulted in a coating having isolated microdomains on the surface with a similar average size. However, as shown in Figure 4, the microdomain structure of this coating was much more stable after water immersion than when the previous solvent composition was used. The microstructured surface domains of this coating only showed a change in mean diameter of 0.17 μm. The use of a slower evaporating and more polar solvent blend perhaps provides the system with more mobility during the cross-linking process and results in a more stable surface structure.

In summary, a unique siloxane—urethane composition was identified that results in the spontaneous formation of a stable microtopographical biphasic surface structure. This is the result of a complex set of conditions being met such that PDMS-rich domains phase separate during the film formation process and restrict the ability of the PDMS to fully cover the surface of the coating. Further exploration of the many variables that affect surface domain formation and domain size is required in order to fully understand and control this system.

This system demonstrates that it is possible to generate stable microstructured surfaces without using multistep templating and molding methods to create surface

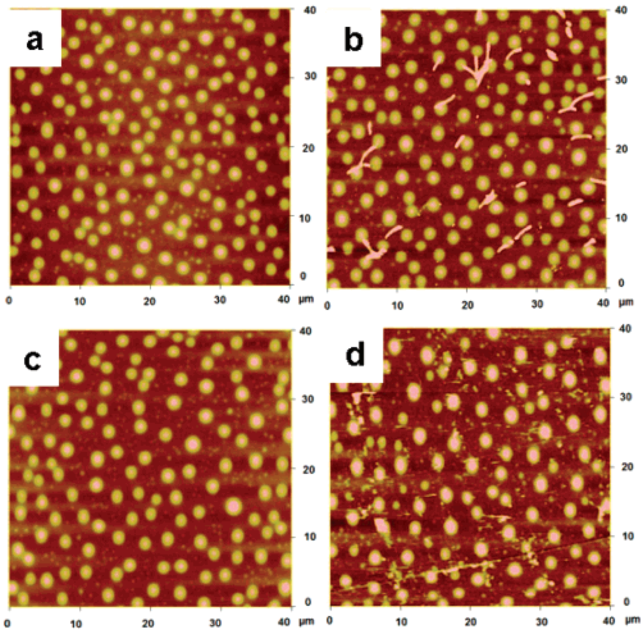

Figure 4. Topographical AFM images of microstructured coating surface prepared using formulation C with solvent combination EEP:MAK:BA = 43:12:45 (a) by tapping mode in air before water immersion, (b) by tapping mode in air after water immersion, (c) by contact mode under water before water immersion, and (d) by contact mode under water after water immersion.

topographical features. Thus, this approach has a number of significant advantages, namely, the elimination of a separate patterning step and the consequent ability to prepare and apply microstructured coatings over a large area. Since this system makes use of readily available materials, this is also a commercially viable approach.

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Supporting Information Available: Detailed information on synthetic and analytical procedures used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(26) PDMS: α,ω-bis[3-(2′-hydroxyethoxy)propyl]poly(dimethylsiloxane) from Chisso, M_n = 1000 g/mol. PCL: Tone 0305 from Dow Chemical, hydroxyl equivalent weight = 180 g/equiv. XIDT: triisocyanurate of isophorone diisocyanate from Rhodia, isocyanate equivalent weight = 342 g/equiv. Further experimental details are available in the Supporting Information.
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