

## **Environmental AFM as a Probe of the Morphology, Viscoelasticity and Lubricity of Crosslinked Hydrophilic Biomedical Coatings**

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We explore the morphology and tribo-mechanical properties of polyacrylate catheter coatings variably UV-crosslinked (1,4- butanediol diacrylate), as prepared and following variable tribological history under aqueous immersion (to mimick stresses during catheter deployment) to assess the lubricity and durability of coatings. A rich surface morphology is revealed over micro- to nano-scales, strongly dependent on both the extent of crosslinking and subsequent macrotribological processes. Submicron defect structures resulting from the sponge-coating deposition process include shallow (nm's) circular depressions hundreds of nanometers across ("cheetah spots") and much deeper/narrower "pinholes"; from the UV curing we find deep but larger in diameter "craters" plus "fissures" running between the deep holes and craters. The deepest defects exhibit modified behavior, as sensed in multiple AFM modes sensitive to dissipative properties (friction, adhesion, phase), consistent with these defects extending to the substrate, the Pebax catheter tube.

Contact-mode "rippling", a form of wear due to shear forces during raster scanning by the tip, is a strong function of UV curing up to moderate curing times (10 seconds) but only weakly from moderate to long curing times (10-50 seconds). Examples of this phenomenological behavior are contrasted in Figure 1 for the cases of 5 and 10 second curing times. Slowly mapped AFM nanoindentation measurements are used to interrogate changes in both elastic and dissipative properties (i.e., viscoelasticity) of the coatings as a function of the above UV curing as well as subsequent aqueous macro-tribological history. Such nanomechanical responses are further explored under variable humidity and temperature (heated sample). A highly reproducible solvent-induced glass-rubber transition is identified over a narrow range of relative humidity (Figure 2), and found to be shifted to higher humidity on coatings that are "over cured" (50 seconds compared to 5- and 10-second curings). These 50 second UV coatings are also found to be nonlubricious in the macrotribological tests. In the process of exploring humidity cycles, dramatic irreversible transformations in coating morphology are fortuitously discovered, whereby many of the defects present from sponge coating and UV curing are largely "healed".

Fast force-curve mapping mode is use for (i) zero-wear, high-resolution imaging (including imaging before/after ripple-inducing scanning as shown in Figure 1), wherein the smallest dissipative domains in tip-sample adhesion images become even smaller for higher UV curing times, thus suggesting sensitivity to the size of cooperatively rearranging regions in the glassy state; and (ii) quantifying glass-rubber transition, sensed in stiffness and adhesion images as a function of sample temperature.

Broadly, this study demonstrates (1) technologically relevant and scientifically rich phenomenology over scales ranging from tens of microns to tens of nanometers; (2) connections of nanoscale dissipative behavior to macroscale properties; and (3) the complementarity that multiple AFM methodologies [1] afford in analyzing lubricious hydrophilic coatings as are important to biomedical device technologies. This follows similar work on drug-eluting biomedical device coatings [2].

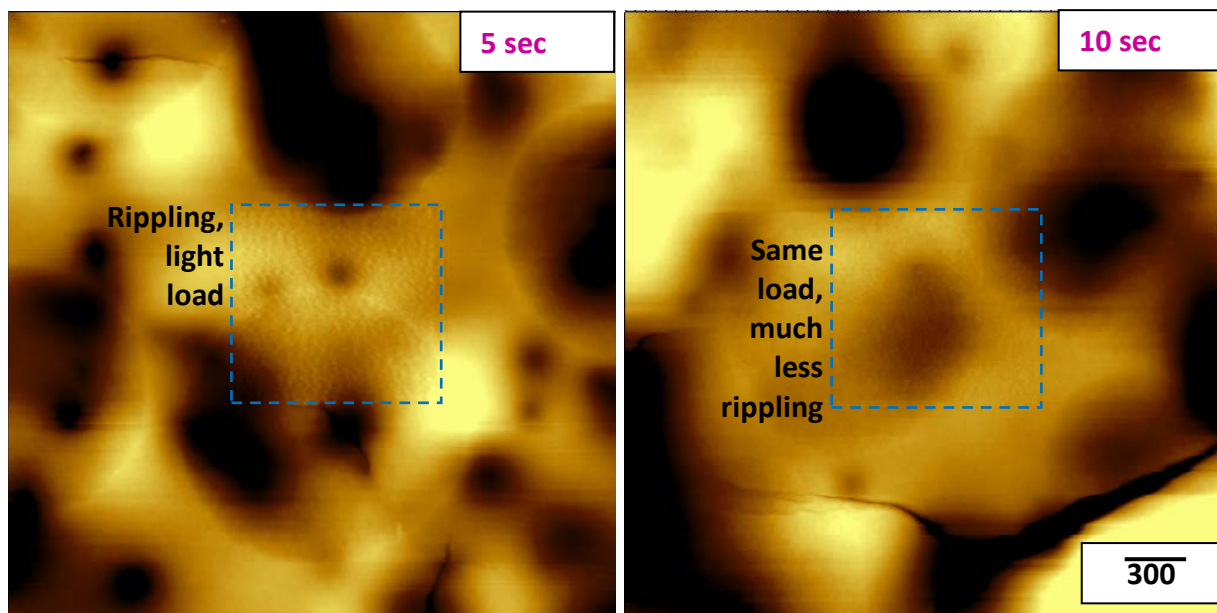


FIG. 1. Height images acquired in fast force-curve mapping (Bruker PeakForce QNM) comparing nanoscale rippling on 5-and 10-second UV-cured coatings from preceding contact mode scanning.

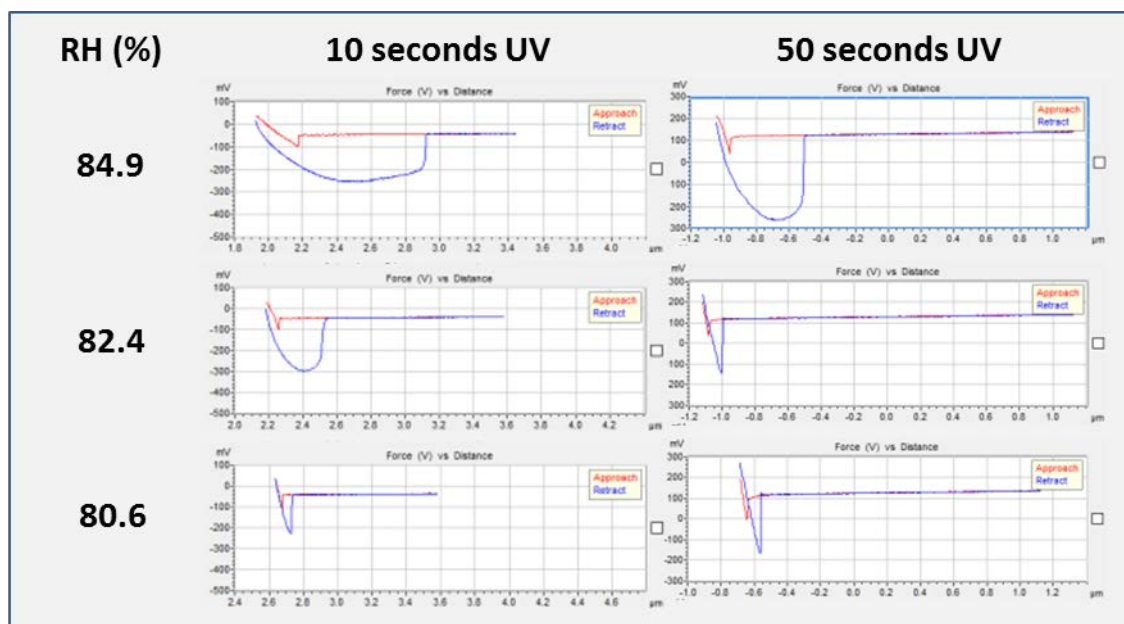


FIG. 2. Humidity-dependent, raw force versus Z cycle plots (same scales) of coatings following different times of UV curing. Glass-rubber transition occurs at higher humidity for longer curing time.

References

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 [2] G. Haugstad and K. Wormuth, “Nanomechanical Characterization of Biomaterial Surfaces: Polymer Coatings that Elute Drugs”, in *Industrial Applications of Scanning Probe Microscopy*, ed. D. Yablon, (Wiley, 2013).