# Characterization of Surface Microphase Structures of Poly(urethane urea) Biomaterials by Nanoscale Indentation with AFM

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**Statement of Purpose:** Polyurethane block copolymers are widely used in blood-contacting applications due to an acceptable level of blood compatibility and excellent physical characteristics. These properties are believed to be a result of nanoscale chemical heterogeneities that arise from the microphase separated structures of the polymers. This microphase separated structure of polyurethane has been extensively studied,[1] however, the direct relationships between chemical distribution, mechanical properties, the phase separated structure at molecular scale and the subsequent effects on protein adsorption are poorly understood. In this study we use atomic force microscopy (AFM) to probe the mechanical properties and adhesion of polyurethane materials in order to relate polyurethane copolymer chemistry and phase separation, and ultimately the activity of proteins.

**Methods:** Poly(urethane urea) films prepared from 2000 MW PTMO, MDI and EDA with 22% hard segment weight fraction were prepared by solution casting onto glass cover slips. Polymers were measured in air and aqueous (10 mM PBS, pH 7.3) environments. Atomic force microscopy was used to image the phase separated structure of polymers by tapping mode at various ratios of set point amplitude and free amplitude of oscillation ($r_{sp}$). Force imaging was used to collect 32 × 32 arrays of force curves at a scan size of 500×500 nm. Young's modulus was computed from each approaching force curve using Hertzian model[3], and adhesion forces were measured from the maximum deflection in retraction force curves.

**Results / Discussion:**

**Microphase structures of polyurethane in ambient and aqueous environments.** The separated microphase structures were observed from phase images (Fig. 1). The dimensions of the observed microphases in air are ~15–20 nm, comparable to those of adsorbed proteins. Phase images under aqueous buffer were quite different from those obtained in ambient conditions, indicating PUU materials reoriented in fluid to increase polar hard segment content at the hydrated interface, consistent with previous studies[2]. The surface remains rich in hard domains after dehydration (Fig. 1c).

**Nanomechanical properties of poly(urethane urea)**

The approaching force curves produced an indentation profile for PUU with loading force and suggested three types of distributions of hard segments in the soft matrix (Fig. 2). The indentation map illustrates the distribution of hard domains is similar to phase image, furthermore, the indentation map shows that the soft segment layer could be as thin as ~2 nm in air.

The modulus determined by the Hertzian model is the result of both soft and hard segments and the modulus map illustrates the overall microphase separated structure of PUU under buffer (Figs. 1b and 3a). The dimensions of the hard segments (~244 nm$^2$/pixel) in the modulus map is similar to the phase image, and the distribution of modulus values is found to be similar to the distribution of raw phase values. Thus the indentation measurements consistently produce a measure of separated phase structures of PUU in air and aqueous environments consistent with traditional AFM imaging but offer the opportunity to simultaneously measure adhesion (Fig. 3b).

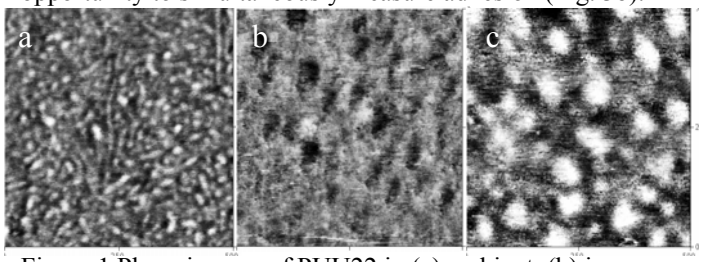


Figure 1 Phase images of PUU22 in (a) ambient, (b) in PBS , (c) after dehydrated in air. (500×500 nm)

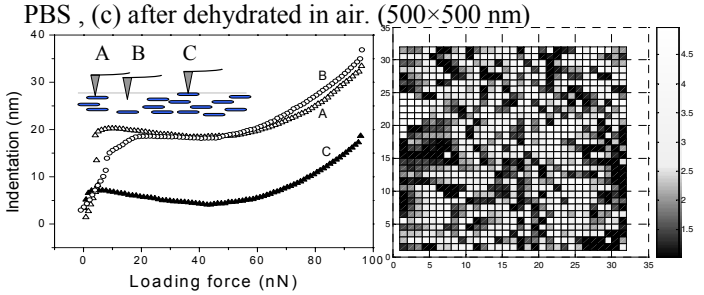


Figure 2 Indentation profile of PUU22 with loading force (left) and indentation map (right) at 10 nN force in air.

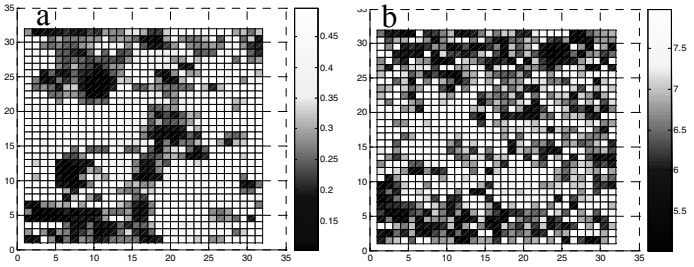


Figure 3 Modulus map (a) in GPa and adhesion map (b) in nN for PUU22 under PBS.

**Summary**: The separated microphase structure of PUU was observed in air and aqueous environments. In contrast to the structures in air, the polymer surface was rich in hard domains during hydration and after dehydration, believed to be due to water-induced structural reorientation. Nanoscale indentation measures by the AFM probe identifies the hard domains and offers insight into depth profiles. The modulus map illustrates the overall microphase separation structure and results are consistent with the observation in phase images.

**References**

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2.Agnihotri A. et al. *J. Biomater. Sci. Poly Edn*. (in press).
3. Chizhik S.A., et al., *Langmuir*, 1998, 14, 2606-2609.