

## Friction of copolymer hydrogels undergoing microphase separation

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With recent developments in soft robotics, novel stimuli-responsive soft materials are needed to control interfacial forces like friction and adhesion. Hydrogels have been a topic of interest in biotribology for decades due to their biocompatibility and extremely low coefficients of friction, and now they have also captured recent attention for applications in soft robotics. The present work is focused on tuning the microphase separation of negatively charged poly(acrylamide-co-acrylic acid) hydrogels by altering their composition. Microphase separation within the interfacial region leads to changes of the gel's interfacial structure, contact mechanics and frictional characteristics.

**Keywords (from 3 to 5 max):** hydrogels, microphase separation, friction, lubrication.

### 1. Introduction

Hydrogels have been a topic of interest in biotribology and biomimetic lubrication for decades due to their biocompatibility, extremely low coefficients of friction, and compositions similar to that of biotribosystems. Incorporation of multiple monomers in a polymer system has been known to significantly affect the hydrogel structure and lead to thermodynamically-driven microphase separations. Our goal is to leverage the microphase separation of negatively charged poly(acrylamide-co-acrylic acid) hydrogels to achieve controlled interfacial structure and frictional response.

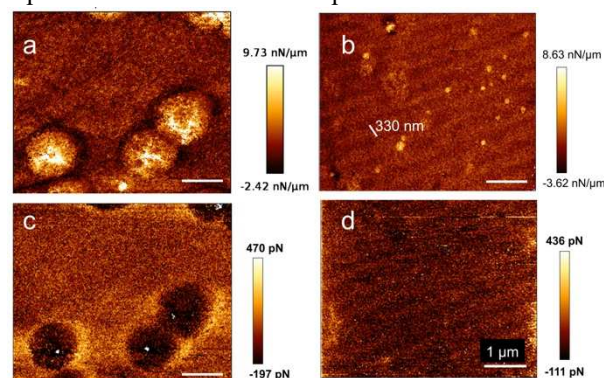
### 2. Methods

Poly(acrylamide-co-acrylic acid) hydrogels were prepared via free-radical polymerization using different mole ratios between acrylamide and partially NaOH-neutralized acrylic acid with a total monomer concentration of 8 wt%. IR spectroscopy was used to confirm the tunable composition of the hydrogels, Dynamic light scattering (DLS) to characterize their microstructure and rheology was performed to determine their viscoelastic behavior. We prepared hydrogel thin films either grafted or non-grafted to a glass substrate, in which the former ones led to significantly reduced swelling. The interfacial microstructure was imaged by Quantitative Imaging AFM. The surface maps provided height, adhesion, and elasticity using a sharp silicon unfunctionalized tip. Electrostatic force mapping in DI water using tips coated with triamino-silanes (positively charged) enabled us to gain insight into the phase compositions. Friction force and adhesion measurements were conducted by colloidal probe AFM.

### 3. Discussion

Bulk characterization using IR spectroscopy confirms the incorporation of the charged monomer in the copolymer with a concentration linearly proportional to the feed concentration. QI imaging has revealed two types of microphase separation in the interfacial region depending on the acrylic acid to acrylamide ratio ( $x$ ). At  $x=0.25$ , a micrometer-large spherical, swollen and soft phase was detected in DI water, which became more prominent with increase in  $x$  to 0.7. While Figure 1a-b reveals the surface

structure, we found spherical microdomains also present underneath the surface, although smaller and less in number, which illustrates the difference between the bulk and the interfacial microstructure. When  $x$  was further increased to 1.5, the number and size of spherical domains decreased and almost vanished, while a lamellar phase was present at  $x=1.5$  and  $x=4$  in the grafted samples. The thickness of these lamellae ranged between 200 and 300 nm, and hence, they are larger than the mesh size inferred from DLS, but reminiscent of the large Debye length in DI water. Grafting the gels to a glass substrate hindered the swelling ability of the hydrogels, thus limiting the water content. When the microgels were allowed to fully swell (non-grafted), the microphase separations became much less prominent.



**Figure 1.** Interfacial structure of hydrogels imaged by QI for AAc to AAm mass ratios of a-c) 0.67 and b-d) 4. Scale bars are 1  $\mu\text{m}$ . The images a-b) show the stiffness and c-d) show the spatially varying adhesion, since the lamella do not appear in the height image.

The control of the interfacial structure of poly(acrylamide-co-acrylic acid) hydrogels was accomplished through modulation of the acrylic acid to acrylamide mole ratio. The different microstructures arising from the microphase separation in the interfacial region also led to spatially varying adhesive and frictional characteristics of the hydrogels. To illustrate this, Figures 1c-d shows adhesion 2D maps for the same samples showed in Figure 1a-b. Note that the adhesion is smaller at the spherical domains because they are less deformable.