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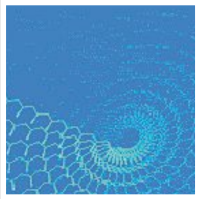

Polymer and Colloid Highlights

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Lateral Deformability of Polymer Brushes by AFM-Based Method

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The application of lateral force microscopy (LFM) on chain end-grafted polymer assemblies (or polymer 'brushes') can provide a measure of the lateral deformability of the grafted chains. This parameter has a fundamental importance when dynamic objects like cells or bacteria interact with polymer brush coatings on implants, scaffolds for tissue engineering or antifouling surfaces. Brush lateral deformability is investigated by studying the morphology of friction-loops obtained by LFM. Specifically, hydrated brushes show 'tilted' friction-loops between scanning-direction reversal and steady sliding (Fig. 1a).[1] The tilted zone of the loops is caused by the lateral deformation of the swollen brushes when subjected to a sliding probe under load. The observed degree of tilt is correlated with the brush swelling ratio and the chain length of the grafted polymer (brush thickness).

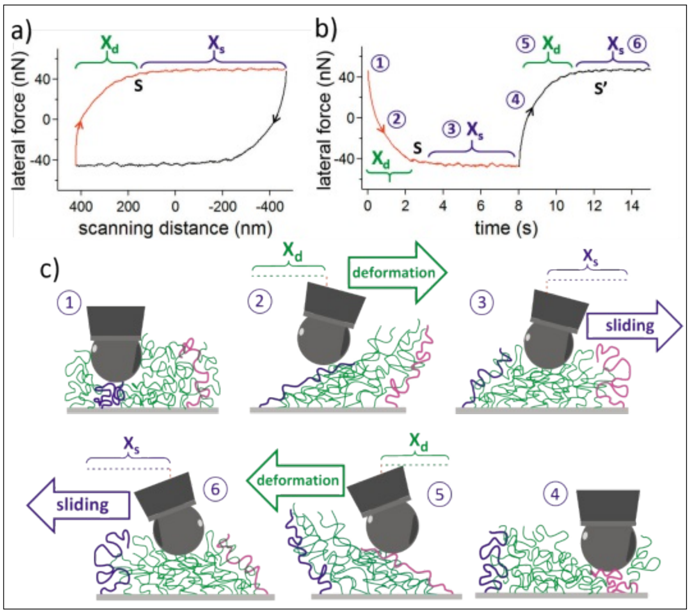

Fig. 1. A representative friction-loop obtained by LFM on POEGMA brush (a, b). The schematics in (c) exemplify brush-probe interactions during the recording of a friction-loop.

In Fig 1a, a representative friction-loop recorded on 50-nm-thick poly(oligoethylene glycol)methacrylate (POEGMA) brushes is reported together with the corresponding friction-vs-time plot recorded during the loop (Fig. 1b). Static friction at the compressed POEGMA brush (position '1' in Fig. 1b and 1c) causes an initial tilting of the loop ('2', corresponding to a scanning distance X_d). This tilt corresponds to the lateral deformation of the brushes that are bent and stretched by the scanning probe. Steady sliding was attained when the shear force exerted by the probe overcomes the spring force by the deformed brush (point S followed by section '3' corresponding to scanning distance of X_s). After scanning-direction reversal (position '4'), the compressed brush is laterally deformed in the opposite direction ('5') until sliding finally occurs (S', followed by '6').

A variation of brush thickness (tethered-chain length) reflects a change in the extension of the tilted-loop section before the occurrence of steady sliding (Fig. 2a).

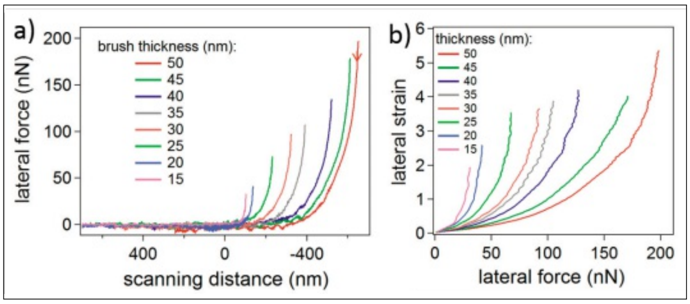

Fig. 2. (a) Single-traces from friction-loops recorded on POEGMA brushes presenting different dry thickness and the corresponding lateral strain-vs-lateral force profiles (b).

Normalization of the scanning distance corresponding to the tilted portion of the loop (X_d) by the equilibrium swollen thickness of the POEGMA brush, provides the brush lateral strain as a function of the recorded lateral force (Fig. 2b). When this measurement was plotted for increasing brush dry thicknesses a progressive increment of brush lateral strain is found (Fig. 2b).

Polymer brushes under shear forces can be laterally deformed well beyond their equilibrium conformation. This arises from the coiling of the polymer chains within a brush assembly, which do not extend further then 10% of their fully stretched length.[2,3] Therefore, the estimated lateral strain exceeds the equilibrium 'length' for all the brush thicknesses studied (lateral strain >1). Longer grafted chains can be laterally deformed to a larger extent compared to shorter ones and for a given applied shear stress. Hence, thicker polymeric grafts yielded higher lateral strain or 'deformability' compared to thinner ones.

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