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PAPER

Tunable stimulus-responsive friction mechanisms of polyelectrolyte films and tube forests†

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The pH-responsive frictional behavior of layer-by-layer assembled poly(allylamine hydrochloride) and poly(acrylic acid) multilayers is quantified in different geometric forms of a continuous planar film and anisotropic tube forests. A mechanistic change from surface adhesion dominated frictional behavior to visco/poroelasticity-governed shear occurs for the planar film upon pH-stimulus. This pH-dependent friction can be further controlled by the discrete anisotropic geometry of the tube forest, which introduces additional friction due to asymmetric deformation of the discrete bending of the tubes during lateral motion. This study provides important insights into the design of polyelectrolyte-based coatings with a wide range of controllable surface frictional properties, tuned *via* interactions between the inherent stimulus-responsive material behavior and the microgeometry of the anisotropic tube forest.

1. Introduction

Recently, frictional behaviors of polymeric materials have received increased attention. Polymer hydrogels and interfaces can incorporate a richness and complexity of friction and lubrication mechanisms, such as fluid flow, hydrophobicity, surface roughness, and molecular organization, therefore exhibiting fascinating tribological properties.^{1,2} For example, polymeric surfaces with tailored and well-controlled stimulus-responsive frictional properties hold great potential for an array of engineering and biomedical applications including drug delivery, microfluidic devices, cell culture substrates, and sensors.^{3,4} To date, systems which exhibit stimulus-responsive friction, such as certain end-grafted polymer brushes,^{5–9} polymer nanoparticles,¹⁰ and cross-linked hydrogels¹¹ (Table 1), are largely controlled by molecular-level interactions such as chain entanglements, viscous flow of solvent, charge effects, hydration, adhesion-induced stretching of adsorbed polymer chains, chain desorption, and polymer segment–segment interactions.^{1,12–18} Such materials

have been shown to undergo changes in the friction coefficient, μ (defined as the slope of the lateral force *versus* applied normal force curve), up to an order of magnitude (≈ 2 to $15\times$ for polymer brushes,^{5–9} $\approx 6.5\times$ for polymer nanoparticles¹⁰ and ≈ 4 to $5.3\times$ for macro-hydrogels,¹¹ Table 1) upon the application of stimuli such as temperature,^{5,6,11} pH,⁵ ionic strength,^{7,8} and solvent.⁹ However, the controlled tunability of surface friction including sensitivity, range, and temporal response to the external stimuli is yet to be fully realized and can be challenging through molecular-level design. Previously reported studies on non-responsive surfaces have utilized surface texturing, roughness, patterning, and fibrillar microstructures to control friction, which is primarily a contact area splitting effect.^{19–23} Here, we explore the frictional mechanisms of the stimulus-responsive polyelectrolyte multilayers and the use of a microscale tube geometry to control the frictional mechanism and magnitude. In addition to the contact area effect, the tube geometry results in a coupling between “inherent” material (molecular) responsiveness and induced deformation mechanisms associated with anisotropic shape and the discontinuous spatial distribution of material. The use of well-defined microscale geometries has potential for the tunability of surface friction through systematic variation in structural parameters, as we have demonstrated previously in indentation.²⁴

In this study, pH-dependent polyelectrolyte multilayers (PEMs) (Fig. 1a) were prepared *via* layer-by-layer assembly of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA, Fig. 1a) into continuous planar films and anisotropic substrate-anchored tube arrays or “forests”²⁵ (Fig. 1b). The PAH/PAA system undergoes a well-known “inherent”, reversible

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Table 1 Summary of literature on the surface friction responsiveness magnitudes of various stimulus-responsive polymers

Type of polymer assembly	Experiment method	Polymer materials	Experiment setup	Normal force	Stimulus response type	Stimulus-responsive friction coefficients			Response ratio, μ_2/μ_1
						Solution	μ_1	μ_2	
End-grafted polymer brushes	Lateral force microscopy (LFM)	Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) ⁵	Gold-coated spherical tip, $R \approx 5 \mu\text{m}$, $4 \mu\text{m s}^{-1}$	0–40 nN	pH and temperature	Aqueous solution (24 °C)	0.070 (pH 3)	1.060 (pH 11)	15.14
		Poly(<i>N</i> -isopropylacrylamide) ₄₈ - <i>block</i> -poly((3-acrylamidopropyl) trimethylammonium chloride) ₂₀ (ref. 6) Aggrecan ⁷	Silica spherical tip, $R \approx 5 \mu\text{m}$, $4 \mu\text{m s}^{-1}$	0–25 nN	Temperature	Aqueous solution (50 °C) 0.1 M NaCl	0.080 (pH 3)	0.680 (pH 11)	8.50
			Hydroxyl-functionalized spherical tip, $R \approx 2.5 \mu\text{m}$, $1\text{--}100 \mu\text{m s}^{-1}$ Aggrecan end-attached spherical tip (two opposing aggrecan layers), $R \approx 2.5 \mu\text{m}$, $1\text{--}100 \mu\text{m s}^{-1}$	0–100 nN	Ionic strength	NaCl aqueous solutions	0.029 (0.001 M)	0.089 (1.0 M)	3.07
End-attached polymer nanoparticles	Surface force apparatus	Aggrecan ⁸	Aggrecan end-attached spherical tip (two opposing aggrecan layers), $R \approx 2.5 \mu\text{m}$, $1\text{--}100 \mu\text{m s}^{-1}$	0–100 nN	Ionic strength	NaCl aqueous solutions	0.017 (0.001 M)	0.069 (1.0 M)	4.06
		Poly(2-(methacryloyloxy)ethylphosphorylcholine) (PMPC) ⁹	Gold-coated pyramidal tip, $R \approx 50 \text{ nm}$, $18.3 \mu\text{m s}^{-1}$	0–10 nN	Solution type	Ethanol–water solution	0.050 (100% H ₂ O)	0.25–0.45 (10% H ₂ O)	5.0–9.0
		<i>N,N</i> -diethylacrylamide nanoparticles ¹⁰	Two opposing nanoparticle layers, curvature = 2 cm, 100 nm s^{-1}	1–14 mN	Temperature	Water	0.040 (15 °C)	0.260 (30 °C)	6.50
Polymer hydrogels	Rheometer	Poly(<i>N</i> -isopropylacrylamide) (PNIPAAm) ¹¹	Two opposing macro-gels, $1\text{--}10 \text{ rad s}^{-1}$	0.2–0.8 N	Temperature	Water	0.150 (24 °C)	0.6–0.8 (37 °C)	≈ 4 to 5.3

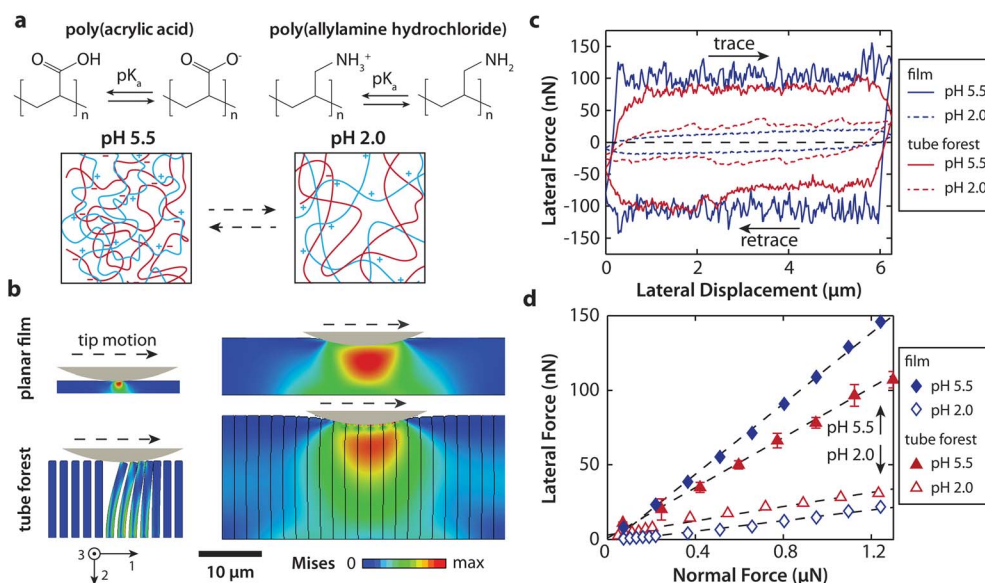


Fig. 1 Frictional behavior of PAH/PAA multilayers measured *via* lateral force microscopy using a hydroxyl-terminated self-assembled monolayer (OH-SAM) tip ($R \approx 22.5 \mu\text{m}$) in aqueous solutions, pH = 5.5 (0.01 M NaCl) and 2.0 (0.01 M HCl). (a) pH-induced molecular-level interactions of PAH and PAA. (b) Von Mises stress distribution of the PAH/PAA film and tube forest during lateral scanning at both pH 5.5 and 2.0 under $\approx 1 \mu\text{N}$ applied normal force and $10 \mu\text{m s}^{-1}$ rate. (c) Typical lateral signal loops measured at $\approx 1 \mu\text{N}$ applied normal indentation force over a $6.25 \mu\text{m}$ lateral displacement at $10 \mu\text{m s}^{-1}$ rate. (d) Friction force as a function of normal force at $10 \mu\text{m s}^{-1}$ lateral displacement rate, together with the corresponding least-squares linear regression fit ($n = 10$ different locations from three samples, mean $\pm$ standard deviation, or the standard deviations are smaller than the size of the data symbols if not shown). Frictions at zero normal forces (y -axis intercepts) are smaller than 4 nN ($\approx 3 \text{ mV}$ of the AFM lateral force signal), lower than the detection limit of the instrument ($\sim 10 \text{ mV}$).

material response from a highly cross-linked, ion-paired network wherein a majority of the carboxyl ($-\text{COOH}$) groups on PAA and the primary amine ($-\text{NH}_2$) groups on PAH are ionized at pH 5.5, to a much more swollen, highly hydrated network with fixed positive charges at pH 2.0 (Fig. 1a).^{25,26} The cylindrical tube geometry exhibits a combination of compression, bending, buckling, and twisting deformations²⁷ that can be modified by geometric design (Fig. 1b), in contrast to the behavior of planar films which undergo the classical Hertzian contact-induced multiaxial stress and strain.²⁴ Atomic force microscope-based lateral force microscopy (LFM)⁷ (Fig. 1c) was carried out on samples submerged in pH-adjusted aqueous solutions using microscale spherical colloidal tips on both the fibrillar tube forest and the planar film PAH/PAA PEMs. The spherical tips were chemically functionalized with a hydrophilic, neutral self-assembled monolayer to minimize electrostatic interactions and hydrophobicity, and consequently, the normal hysteresis adhesion-induced friction at zero normal loads. During the LFM experiments, the indentation depth, normal and frictional forces were simultaneously measured and the friction coefficient, μ , was determined as a function of pH. Finite element analysis (FEA) was then utilized to incorporate the time-dependent mechanical behavior and microscale geometry of the PEM, to quantitatively predict the measured frictional properties, and to probe the contribution of different mechanisms to the measured friction at different pHs.

2. Materials and methods

Poly(allylamine hydrochloride) (PAH) (M_w 70 000) (Sigma-Aldrich) and poly(acrylic acid) (PAA) (M_w 90 000, 25% aqueous

solution) (Polysciences) tube forests (20 bilayers) and a multi-layered planar film (70 bilayers) were assembled at pH 7.5 and 3.5 polyelectrolyte solutions using the previously described layer-by-layer assembly technique.²⁵ The film thickness, H_{film} , was measured to be $2.09 \pm 0.07 \mu\text{m}$ (mean $\pm$ standard deviation) at pH 5.5 and $8.27 \pm 0.52 \mu\text{m}$ at pH 2.0 *via* selected film removal and contact mode AFM imaging. The pH-dependent tube forest dimensions are: at pH 5.5, inner diameter $d_{\text{in}} = 0.36 \pm 0.11 \mu\text{m}$, outer diameter $d_{\text{out}} = 1.17 \pm 0.18 \mu\text{m}$, and height $H_{\text{tube}} = 12.17 \pm 0.57 \mu\text{m}$; at pH 2.0, $d_{\text{in}} = 0.48 \pm 0.25 \mu\text{m}$, $d_{\text{out}} = 1.81 \pm 0.29 \mu\text{m}$, and $H_{\text{tube}} = 18.01 \pm 1.03 \mu\text{m}$, where the average tube center-to-center distance is $1.8 \pm 0.3 \mu\text{m}$ ($n \geq 100$), measured *via* fluorescence microscopy (Fig. S1†).²⁴

For the friction force measurement, a micro-spherical tip (gold coated polystyrene, end radius $R \approx 22.5 \mu\text{m}$, nominal spring constant $k \approx 14 \text{ N m}^{-1}$, Novascan) was functionalized with a neutral, hydrophilic, hydroxyl-terminated self-assembled monolayer (OH-SAM) by 24 h immersion in 3 mM 11-mercaptoundecanol ($\text{HS}(\text{CH}_2)_{11}\text{OH}$, Sigma-Aldrich) ethanol solution. For each state, friction forces were measured for at least 30 different scan locations on more than four samples over applied normal forces of $0\text{--}1.5 \mu\text{N}$ at $1\text{--}100 \mu\text{m s}^{-1}$ lateral displacement rates in aqueous solutions at both pH 2.0 (0.01 M HCl) and 5.5 (0.01 M NaCl). The sample-to-sample variation was found to be smaller than the location variation within each sample (one-way analysis of variance, $p > 0.05$), data measured under the same experimental condition are therefore pooled. The compressive indentation depth at a given normal force was determined by simultaneously monitoring the cantilever deflection and z -piezo displacement of the AFM. The improved wedge calibration method^{7,28} was employed to quantify the friction forces in the units of nN from the half-width

of each of the lateral force signal loops (Fig. 1c). The lateral linearity ratio (friction coefficient) μ was then calculated as the slope of frictional *versus* applied normal indentation forces using least squares linear regression for each lateral displacement rate, pH and sample geometry (planar film *versus* tube forest). Two-way analysis of variance was applied to test the effects of displacement rate, pH and sample microstructure, where all of these factors were found to significantly affect μ ($p < 0.001$). For the tube forest, at pH 5.5, for each $L = 6.25\ \mu\text{m}$ lateral scan loop at all the tested lateral scan rates, given the maximum indentation depth D_{max} at $1.5\ \mu\text{N}$ the applied normal force was $\approx 300\ \text{nm}$, the tip-sample contact radius r_{max} was thus $\approx 3.7\ \mu\text{m}$ ($r_{\text{max}} = \sqrt{R^2 - (R - D_{\text{max}})^2}$), and contact area A_{max} was $\approx 90\ \mu\text{m}^2$ ($A_{\text{max}} = \pi r_{\text{max}}^2 + 2r_{\text{max}}L$). At pH 2.0, given $D_{\text{max}} \approx 1.5\ \mu\text{m}$, the maximum contact area was $A_{\text{max}} \approx 300\ \mu\text{m}^2$. Assuming each tube occupies $1.8 \times 1.8\ \mu\text{m}^2$ area, the measured frictions therefore result from the interactions of a large assembly of tubes (≈ 25 tubes at pH 5.5, ≈ 95 tubes at pH 2.0) during the scanning, and the experiment provides reasonably homogenized effective mechanical responses for the tube assemblies.

Finite element analysis (FEA) was conducted on the planar film and discrete tube forests to predict the friction behavior caused solely by the viscoelasticity of PAH/PAA during lateral scanning *via* the rigid spherical tip ($R = 22.5\ \mu\text{m}$). A normal force of $\approx 1.0\ \mu\text{N}$ is instantaneously applied to the indenter; subsequently a lateral displacement of $3\ \mu\text{m}$ is imposed at different sliding rates from $1\ \mu\text{m s}^{-1}$ to $100\ \mu\text{m s}^{-1}$ under a constant normal force. The tangential surface friction coefficient between the tip and sample surfaces, μ_{S} , was specified to be frictionless and 0.10, with no overclosure for pH 5.5 and 2.0. The film and discrete tubes are represented by plane strain elements with clamped bottom surfaces and modeled as isotropic viscoelastic materials using a Prony series model where the material constants and relaxation times were determined from the force relaxation behavior of PAH/PAA measured previously (Fig. S2†).²⁴ Values of the geometric parameters, including film and tube heights, tube diameters and center-to-center distance, were taken as the average values determined by AFM and fluorescence microscopy experiments.²⁴

3. Results and discussion

Fig. 1d shows that in the range of the applied normal force, a linear dependence of frictional *versus* applied normal force was

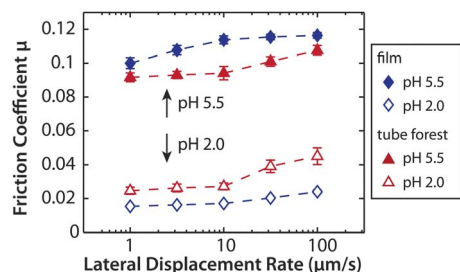


Fig. 2 Friction coefficient μ of the PAH/PAA film and tube forest as a function of the lateral displacement rate at pH 5.5 and 2.0 ($n \geq 30$ different locations on more than four samples, mean $\pm$ 95% confidence interval (CI), or the 95% CI are smaller than the size of the data symbols if not shown).

observed under all the tested conditions for both the planar film and tube forest PAH/PAA PEMs, thereby obeying the classical Amonton's law. This linearity, and hence, the friction coefficient μ , was found to be highly repeatable over roughly ten loading cycles at the same location in the normal force range of ≈ 0 to $1.5\ \mu\text{N}$, suggesting no permanent disruption of the PEM molecular structure or the microscale geometry during the experiment. This observation is consistent with the indentation behavior of the PAH/PAA PEM, where up to $2\text{--}3\ \mu\text{N}$ indentation force introduced negligible plastic deformation (*data not shown*). This PEM structure is not permanently disrupted by shear due to the presence of ionic cross-links between PAH and PAA, which is unlike the case of adsorbed, uncross-linked polymers that are able to undergo shear-induced permanent conformational changes and desorption.²⁹ The absence of any abrupt change in the linearity of the data (Fig. 1d) suggests constant deformation mechanisms over the applied normal force range studied for all the tested conditions. In the absence of tip-sample normal surface hysteresis/adhesion, as previously measured *via* nanoindentation (Fig. S3†), friction forces at zero normal forces were found to be negligible at all the tested states (Fig. 1d), suggesting the absence of substantial normal adhesion-induced friction. The frictional response of PAH/PAA PEM was found to be highly dependent on the pH-stimulus (Fig. 1c and d) and lateral displacement rate (Fig. 2) for both the tube forest and planar film (Table 2). The pH-dependent frictional responsiveness ratio ($\mu_{\text{pH}5.5}/\mu_{\text{pH}2.0}$) ranged between 2.4 and 6.5 (Table 2).

This frictional behavior of both the film and tube forest can be attributed to a number of mechanisms, all of which are coupled to the inherent molecular-level responsiveness described previously (Fig. 1a): (1) the non-specific, non-covalent probe tip-surface interactions and/or adhesion-induced stretching of adsorbed polymer chains at the tip-sample interface,¹³ which for the tube system is modified by contact splitting and bending, buckling deformations, (2) an asymmetric stress field within the deformation zone at the back and front of the spherical tip during lateral loading, introduced by the visco/poroelastic time-dependent relaxation of PAH/PAA (Fig. 3), and lastly, (3) for the discontinuous, anisotropic tube forest, an asymmetric material distribution during deformation (controlled by the tube geometry) (Fig. 1b) due to the lateral displacement induced bending of the tubes, which is absent in the case of continuous planar films.

3.1 Stimulus-responsive frictional behavior and mechanisms of the planar PAH/PAA PEM film

The planar PAH/PAA PEM film exhibits a significantly higher friction in the ionically cross-linked structure at pH 5.5 ($\mu \approx 0.10\text{--}0.12$) compared to the charged, highly hydrated and swollen structure at pH 2.0 ($\mu \approx 0.015\text{--}0.024$). 2D isotropic, viscoelastic finite element simulations were utilized to simulate the LFM experiments and to investigate the frictional mechanisms of the PAH/PAA PEM planar film (see Methods, Fig. 3). The time-dependent material constants were determined from the force relaxation behavior of PAH/PAA measured previously.²⁴

At pH 5.5, the planar film exhibits a dramatic relaxation in indentation (with a time constant of 1 second for $\approx 95\%$ force relaxation calculated from a five-element viscoelastic model, Fig. S2†) due to extensive breaking/reformation of ionic cross-

Table 2 Summary of pH-dependent frictional responses of the PAH/PAA polyelectrolyte multilayer film and tube forests measured *via* lateral force microscopy ($n \geq 30$ scan locations, mean $\pm$ standard deviation)

Friction coefficient μ		Lateral displacement rate ($\mu\text{m s}^{-1}$)				
		1	3.16	10	31.6	100
$\mu_{\text{pH}5.5}$	Film	0.100 ± 0.007	0.108 ± 0.006	0.114 ± 0.005	0.115 ± 0.004	0.116 ± 0.004
	Tube forest	0.092 ± 0.007	0.093 ± 0.006	0.094 ± 0.011	0.101 ± 0.008	0.108 ± 0.008
$\mu_{\text{pH}2.0}$	Film	0.015 ± 0.001	0.016 ± 0.001	0.017 ± 0.001	0.020 ± 0.002	0.024 ± 0.002
	Tube forest	0.025 ± 0.008	0.026 ± 0.009	0.027 ± 0.008	0.039 ± 0.014	0.045 ± 0.019
$\mu_{\text{pH}5.5}/\mu_{\text{pH}2.0}$	Film	6.51 ± 0.64	6.64 ± 0.48	6.66 ± 0.43	5.68 ± 0.51	4.84 ± 0.50
	Tube forest	3.72 ± 1.47	3.54 ± 1.47	3.46 ± 1.27	2.58 ± 0.96	2.39 ± 1.08

links. FEA simulations, which assume a frictionless tip-sample contact (surface friction coefficient, $\mu_s = 0$), predict a viscoelasticity-induced friction coefficient of about 0.0046 ($10 \mu\text{m s}^{-1}$ lateral displacement rate) to 0.019 ($1 \mu\text{m s}^{-1}$ lateral displacement rate), which are roughly 5 to 20% of the measured μ values

(Table 2).^{30,31} Inclusion of a surface friction coefficient, $\mu_s = 0.10$, results in a net friction coefficient $\mu \approx 0.11$ at a lateral displacement rate of $10 \mu\text{m s}^{-1}$ (Fig. 4a), which more closely approximates the experimental data. Hence, FEA simulations predict that the majority of the friction for the PAH/PAA film at

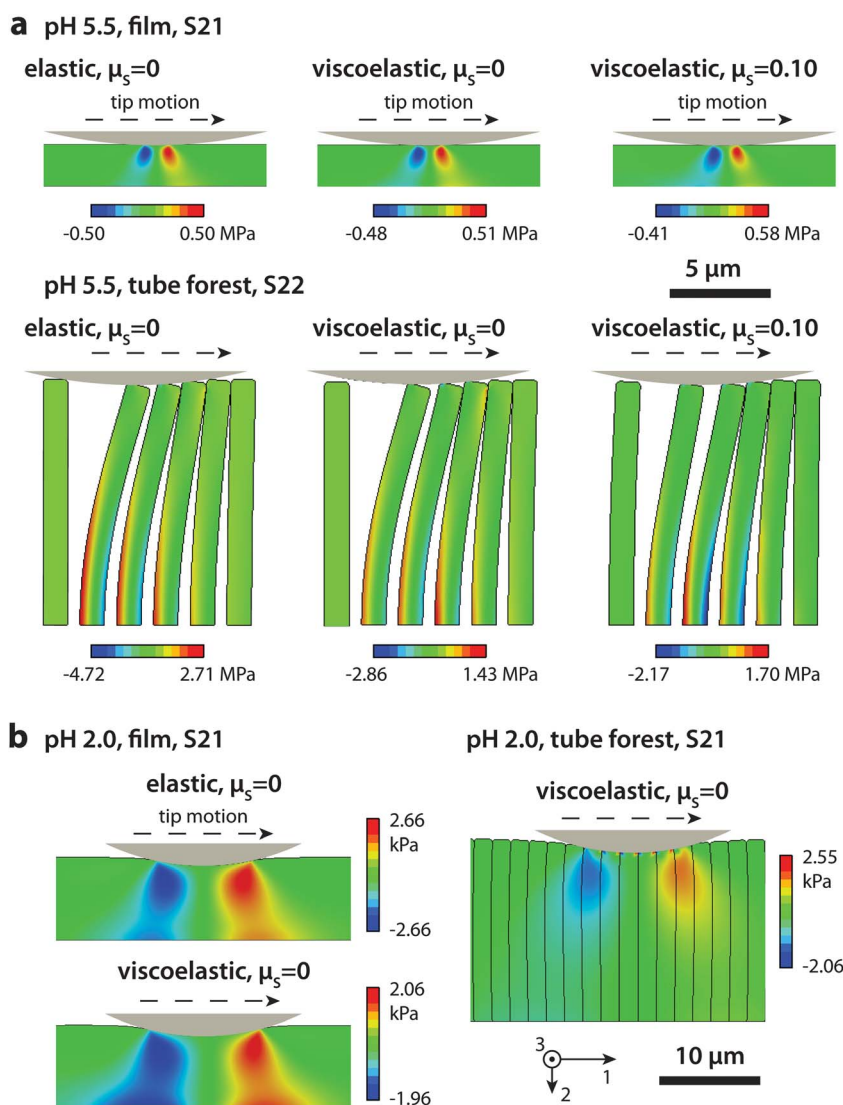


Fig. 3 Finite element analysis (FEA) prediction of the frictional behavior of the PAH/PAA multilayer planar film and tube forest under $1 \mu\text{N}$ normal indentation force at $10 \mu\text{m s}^{-1}$ lateral displacement rate ($R = 22.5 \mu\text{m}$) assuming either elastic or viscoelastic deformation. Stress distribution (a) at pH 5.5, S21 for the film and S22 for the tube forest with and without tip-sample surface frictions ($\mu_s = 0.10$ and 0 , respectively) and (b) at pH 2.0, S21 for both the film and tube forest without tip-sample surface frictions ($\mu_s = 0$).

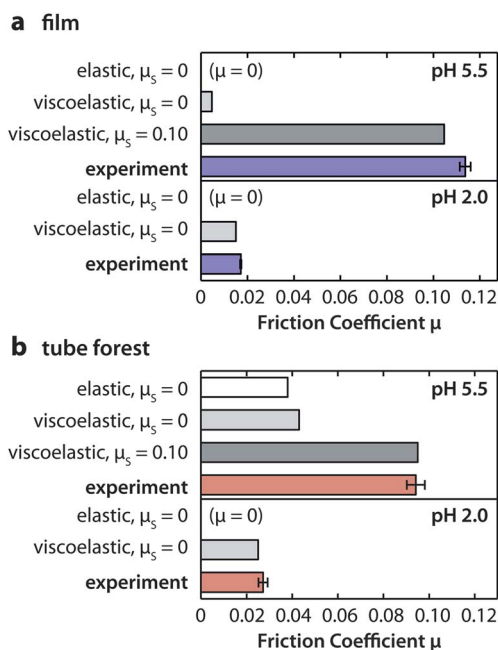


Fig. 4 Comparison of finite element analysis (FEA) predicted friction coefficients assuming different deformation mechanisms and experimentally measured values at $10 \mu\text{m s}^{-1}$ lateral displacement rate at both pH 5.5 and 2.0 ($n \geq 30$ different locations on more than four samples, mean $\pm$ 95% confidence interval for experiment data), (a) planar film and (b) tube forest.

pH 5.5 originates from tip–surface interactions ($\approx 95\%$ of μ) with a secondary contribution ($\approx 5\%$ of μ) from viscoelasticity (Fig. 4a). The surface friction may originate from tip–sample surface interaction-induced stretching of adsorbed (for example, by van der Waals chain interactions) polymer chains at the tip–sample interface,¹³ further suggested by the observed prominent “stick-slip” behavior,³² *i.e.*, the resistance to elastic deformation and shear arising from adhesion between nano-asperity surfaces,³³ as shown in the fluctuations of lateral force signals at $\approx 1 \mu\text{N}$ normal force (Fig. 1c). FEA simulations provide additional information on the local continuous, multiaxial and Hertzian-like stress distributions. For a frictionless tip sliding on an elastic film, the shear stress (S21) exhibits a symmetrical stress distribution between the deformation regions located near the back and front of the probe tip (Fig. 3a); however, when the viscoelasticity is included in the film, S21 demonstrates an asymmetrical stress distribution even for a frictionless tip (Fig. 3a and S4a†), and such an asymmetry is amplified by surface-dominated friction (Fig. 3a). Consequently, the asymmetric shear stress breaks the symmetric Hertzian-like von Mises stress distribution for indentation on elastic films (Fig. 1b and S4a†).

In comparison, the planar film at pH 2.0 exhibits the absence of “stick-slip” behavior in the lateral force *versus* displacement data (Fig. 1c), likely due to the presence of net positive charges ($-\text{NH}_3^+$ on PAH) and the fluid-like hydration sheath surrounding these charges, which can serve as a lubricating layer to reduce surface friction with the neutral hydroxyl-functionalized probe tip.^{30,31} In combination with the effect of less hydrophobicity and stronger electrostatic repulsion at pH 2.0, the friction response transitions from the stick-slip behavior at pH

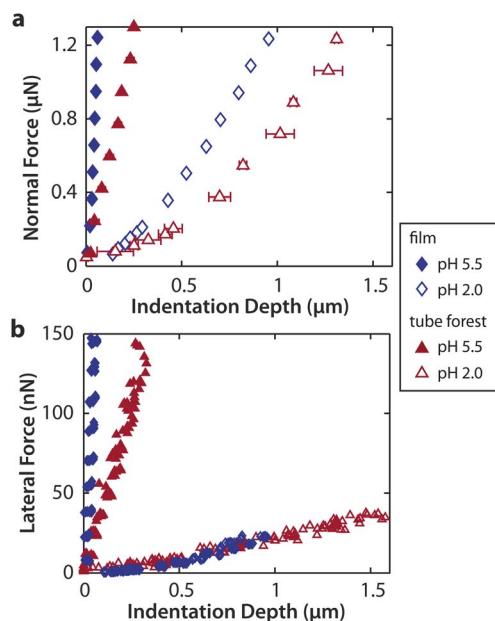


Fig. 5 Friction and corresponding indentation behavior of PAH/PAA multilayers measured *via* lateral force microscopy using a hydroxyl-terminated self-assembled monolayer (OH-SAM) tip ($R \approx 22.5 \mu\text{m}$) in aqueous solutions, pH = 5.5 (0.01 M NaCl) and 2.0 (0.01 M HCl) at $10 \mu\text{m s}^{-1}$ lateral displacement rate. (a) Applied normal force *versus* measured indentation depth ($n \geq 10$ locations from three samples, mean $\pm$ 95% confidence interval). (b) Friction force *versus* indentation depth, each data symbol represents one lateral scan. The observations at other rates are similar.

5.5 to more of a lubricated behavior at pH 2.0 (Fig. 1c). As a result, the friction forces are expected to be dominated by the time-dependent visco/poroelastic effect due to the asymmetric stress distributions in the deformation zones at the back and front of the tip. FEA modeling confirms this mechanism and predicts a viscoelasticity-induced friction coefficient of ≈ 0.015 at $10 \mu\text{m s}^{-1}$ assuming a frictionless contact, which is similar to the experimentally measured values of μ (Fig. 4a). Interestingly, although PAH/PAA exhibits a smaller percentage of force relaxation in indentation at pH 2.0 than pH 5.5,²⁴ the viscoelasticity-induced friction is similar to or even slightly greater in magnitude than the pH 5.5 case because of the longer time constant (≈ 3 seconds for $\approx 70\%$ force relaxation, Fig. S2†) and, furthermore, the more compliant nature leads to a greater indentation depth during shear (Fig. 5a). However, this increase in viscoelastic friction is not large enough to offset the reduction in surface friction relative to pH 5.5. As a result, a ≈ 5 – 6.5 fold net decrease in μ was observed for the planar film when changing the pH from 5.5 to 2.0 (Fig. 2).

3.2 Stimulus-responsive frictional behavior and mechanisms of the PAH/PAA PEM tube forest

Similar to the planar films, the PAH/PAA PEM tube forests also exhibit significantly higher friction in the ionically cross-linked contracted structure at pH 5.5 ($\mu \approx 0.092$ – 0.11) compared to the charged, hydrated and swollen structure at pH 2.0 ($\mu \approx 0.025$ – 0.045) (Table 2).

At pH 5.5, the values of μ are slightly lower for the tube forests compared to the planar film (≈ 0.10 to 0.12) (Fig. 2 and Table 2). Under these conditions, the tubes are initially (zero load) not in contact with each other ($d_{\text{out}} \ll$ tube center-to-center distance) resulting in “contact area splitting,” a spatially heterogeneous material distribution and opportunity for more compliant deformation mechanisms induced by the anisotropic geometry such as discrete bending and buckling of the tubes.²⁴ Hence, the normal and lateral forces are much lower for the tube forests at the same indentation depth (Fig. 5a), consistent with the previously reported nanoindentation experiment.²⁴ FEA modeling for the $10 \mu\text{m s}^{-1}$ lateral displacement rate predicts $\mu = 0.043$ for $\mu_{\text{S}} = 0$ (frictionless contact, Fig. 3a) and 0.095 for $\mu_{\text{S}} = 0.1$ (Fig. 3a and 4b), where the latter is similar to the experimental observation. The contribution of surface friction at pH 5.5 for the tube forest is reduced to $\approx 60\%$ of μ relative to the planar film (≈ 80 to 95%) due to contact splitting (Fig. 4b), which results in the indenter tip being in contact with less material and the tubes exhibiting asymmetric bending, providing a new, additional source of friction (Fig. 3a). Indeed, the FEA simulations reveal that the other 40% contribution to μ originates from an asymmetric distribution of the PAH/PAA tube material and stress around the center of the spherical tip, since the tubes ahead of the probe tip undergo significant bending deformations^{34,35} compared to the tubes behind the probe tip (Fig. 3a). This observation reveals a significant friction mechanism for fibrillar structures even in the absence of surface friction or visco/poroelasticity. FEA simulations also reveal that the indented tubes undergo different bending configurations for the tip-sample contact with surface friction coefficients $\mu_{\text{S}} = 0$ and 0.10 (Fig. 3a) and similar bending deformed configurations after lateral sliding (Fig. 1b, 3a and S4b†). At pH 5.5, lateral bending and compression resistance upon shearing of the tubes result in an effective friction coefficient of 0.038 even when the material is purely elastic (the absence of rate dependence), which is close to the viscoelastic tubes (0.043) (Fig. 4b). The rate dependence of PAH/PAA is hence not a major contributor to its shear resistance for the tube forest at pH 5.5, similar to the case of the film but for different reasons: the film friction is dominated by surface friction and the tube friction has the additional contributions from asymmetric tube bending. Fearing *et al.*²³ observed an increase in friction for a fibrillar morphology of stiff polypropylene fibers in comparison with their solid film, where they indicate the increased friction was due to increased surface area of the fibrillar geometry. Our system shows a decreased effective surface area contact that leads to lower surface friction which offsets the additional friction contribution from the asymmetric bending of the tubes, and therefore lowers the net friction for the tube forest.

For the tube forest at pH 2.0, μ values (≈ 0.025 to 0.045) were observed to be greater than those for the planar film (≈ 0.015 to 0.024) (Fig. 1d and 2, Table 2). At pH 2.0, swelling of the PAH/PAA network increases the tube cross-sectional area thereby resulting in inter-tube contacts and stress transfer between adjacent tubes.²⁴ Hence, the tubes do not discretely bend and the indentation behavior is similar to that of the continuous film (Fig. S5†),²⁴ which supports the inter-tube contact hypothesis. In the FEA model, the neighbouring tubes are bonded together to share the same displacement, and thus the bonded tube forest behaves like a continuous film (Fig. 1b and 3b). In

addition, the film experiences greater substrate constraints given the finite film thickness with $H_{\text{film}} < H_{\text{tube}}$. Both the FEA model (Fig. 1b and 3) and experiment (Fig. 5a) show a larger indentation depth for the tube forest than the film under the same normal indentation force, consistent with our previous indentation experiment.²⁴ However, at the same indentation depth, similar frictional forces were observed for the film and tube forest (Fig. 5b). Therefore, mainly owing to the smaller substrate constraints effect, the net friction coefficient μ is higher for the tube forest relative to the film in experiments and FEA simulations. In the absence of surface friction, the FEA modeling yields a friction coefficient μ (≈ 0.025 at $10 \mu\text{m s}^{-1}$) similar to experimentally observed values (Fig. 4b), suggesting that surface friction contributes negligibly to the measured friction in this highly charged state at pH 2.0, similar to the film. As a result of different shear deformation mechanisms for the tube forest compared to the film at both pHs, the decrease in μ when changing the pH from 5.5 to 2.0 is ≈ 2.5 to 3.5 fold at 1 – $100 \mu\text{m s}^{-1}$ lateral displacement rates, which is lower than the planar film (Fig. 2).

3.3 Rate dependence of the frictional behavior

The friction coefficient, μ , also shows dependence on the lateral displacement rate over the tested rate range (1 – $100 \mu\text{m s}^{-1}$, Fig. 2). At pH 5.5, since the material rate-dependence has minor contribution to the friction for both the tube forest and film, this rate dependent friction is likely to be mainly governed by the rate dependent nature of the stick-slip frictional behavior. The greater stick-slip induced friction at higher rate therefore overshadows the viscoelasticity-induced friction. In comparison, at pH 2.0, the rate-dependence is mainly governed by the visco/poroelastic material behavior of PAH/PAA. Utilizing the relaxation behavior of PAH/PAA measured by nanoindentation, FEA also predicts an increase in μ with increasing lateral displacement rate for both the film and tube forest at pH 2.0. Under each of the pH conditions, the friction mechanisms of the PAH/PAA tube forest and film are expected to remain the same over the range of applied lateral displacement rates.

3.4 Interplay between geometry and frictional mechanisms

As demonstrated by the PAH/PAA film and tube forest, a number of factors can affect the frictional mechanisms and magnitudes of μ for polyelectrolyte layers, including the surface interaction, modulus, time-dependent viscoelasticity and geometry. All these factors can be varied to control the contribution from different frictional mechanisms and quantitatively tune the values of μ . (1) For example, surface friction is directly related to the stresses at the effective tip-sample contact area. For the same tip-sample interactions μ_{S} , a larger effective contact area and a higher contact stress result in greater surface friction, as is the case for the PAH/PAA film *versus* the tube forest (Fig. 3a). The tube forests exhibit lower net μ than the film due to the smaller effective tip-sample contact area despite the additional friction contribution from asymmetric material deformation. (2) Substrate constraints also affect the contact profile. For the same viscoelastic material properties, weaker constraints result in greater indentation depth and larger contact area, and therefore higher friction from both surface interaction and viscoelasticity-

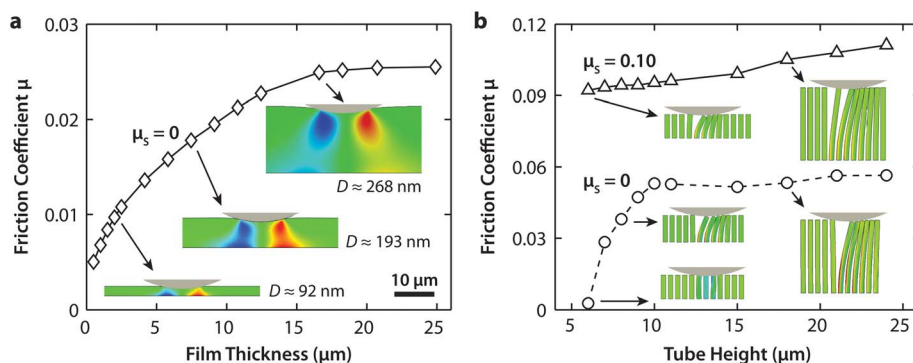


Fig. 6 Finite element analysis (FEA) prediction of the friction coefficient for the planar film and tube forest geometries and corresponding stress contours (S21 for the film, with the corresponding normal indentation depth, and S22 for the tube forest) at 1 μN applied normal force. (a) Viscoelasticity-governed friction as a function of film thickness, demonstrated by the material properties of the PAH/PAA film at pH 2.0 ($10 \mu\text{m s}^{-1}$). (b) Asymmetric material deformation induced friction as a function of tube height, demonstrated by the material properties of the PAH/PAA tube forest at pH 5.5 ($10 \mu\text{m s}^{-1}$), where the tube outer diameter $d_{\text{out}} = 1.2 \mu\text{m}$ and center-to-center distance $w = 1.8 \mu\text{m}$.

induced shear. For instance, for PAH/PAA at pH 2.0, the tube forest, with greater thickness (height), shows weaker effective indentation resistance than the film, and therefore, higher viscoelasticity-induced friction (Fig. 3b and S5†). However, for materials that display similar relative viscoelastic relaxation, the friction coefficient does not depend on the modulus, because the weaker shear and compressive resistance cancel out when calculating μ . For the PAH/PAA film, the viscoelasticity-induced friction from the film is much greater at pH 2.0 (lower modulus) than at pH 5.5, despite the stronger viscoelastic relaxation. It should be noted that, in this particular case, the higher friction at pH 5.5 relative to pH 2.0 is because of the greater surface friction μ_s at the net neutral state that offsets the increase in μ due to viscoelasticity. (3) Lastly, the microscale geometry, as shown for the tube forest at pH 5.5, can introduce additional friction mechanisms due to contact splitting and asymmetric material deformation, further affecting the measured friction.

Utilizing all these factors, design of the polyelectrolyte layers with different geometries can provide quantitative control over the friction mechanism and magnitude at each responsive state, allowing stimulus-responsive mutability of the friction coefficient μ . As predicted by finite element analysis, for the planar film geometry, the viscoelasticity-governed friction coefficient μ increases with increasing film thickness (Fig. 6a) due to weakening of the substrate constraint effect. When the film thickness is increased to a relatively large value so that the indentation depth $D \ll H$, the substrate constraint effect becomes negligible and the value of μ reaches a plateau. For example, for the film at pH 5.5, this substrate constraint effect is negligible given the much higher indentation modulus, and consequently, $D \ll H$ within the tested force range. For the tube forest geometry, the height of single tubes plays a dominant role in determining the friction coefficient. When the tube diameter and the distance between neighboring tubes are kept constant and the aspect ratio of the individual tube increases from 5 to 20 (*i.e.* the height of the tube increases from $6 \mu\text{m}$ to $24 \mu\text{m}$, Fig. 6b), for the tip-sample friction $\mu_s = 0$, the deformation of tubes experiences a transition from a compression dominated deformation to bending dominated deformation, where the friction coefficient increases rapidly due to the bending of tubes during sliding. With the further increase of the tube height, the friction coefficient

increases slightly and reaches a plateau. However, for the tip sample friction $\mu_s = 0.10$, the friction coefficient of tube forest increases slightly with the tube height and is around 0.10, which indicates the dominating effect of tip-sample surface friction.

4. Conclusions

In summary, one important observation emerging from this study is that the friction coefficient μ and underlying mechanisms of the polyelectrolyte system can be altered by both the external material stimulus (solution pH) and the micro-scale geometry, such as the tube forest *versus* the planar film. This result suggests stimulus-responsive polymers as a viable candidate for designing coatings with dynamic frictional behavior upon changes in external stimuli such as temperature^{5,6,11} and pH.⁵ The external stimuli can result in tunability of both the magnitudes of the friction coefficient μ and the underlying friction mechanisms, such as the transition from “stick-slip” dominated surface friction to viscoelasticity-induced shear resistance, as demonstrated by the pH-responsive PAH/PAA planar film. This responsiveness in the frictional behavior can be further controlled by a variety of geometrical factors. For example, the tube outer diameter, d_{out} , center-to-center distance, w , and aspect ratio of the tubes can be varied to induce friction behaviors related to different deformation mechanisms. As demonstrated by the tube forest model system, when the majority of the tubes are not in initial contact ($d_{\text{out}} \ll w$), the additional compliance from tube bending/buckling can (1) decrease the friction coefficient μ (pH 5.5) due to the reduction in the material in contact with the probe tip and (2) increase μ due to the addition of discrete, asymmetric tube bending and buckling deformation mechanisms. When the tubes are in initial contact upon swelling ($d_{\text{out}} \approx w$), the additional asymmetric mechanisms are absent, and other factors such as changes in the influence of substrate constraints due to changes in the film thickness/tube height now govern the changes in μ (at pH 2.0). For a tube forest with a smaller d_{out} , or a larger w , than the presented system, the tube bending/buckling effect can still take place in the more swollen state as well, thereby changing μ at pH 2.0. Hence, the vertical coating thickness (film or tube forest), the tube geometry, and the areal distribution can be used to tailor changes in the friction coefficient with changes in pH. All these

factors can be utilized to design polyelectrolyte multilayer systems with different frictional responses upon external stimuli that hold potential for applications requiring quantitative control and dynamic surface frictional properties. Ongoing studies are probing the frictional responses of different PEM systems with a variety of microscale geometries and stimulus-responsive behaviors to provide a more comprehensive understanding of the coupling between the geometry and stimulus-responsive surface friction behavior of PEMs.

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References

- 1 J. P. Gong, *Soft Matter*, 2006, **2**, 544–552.
- 2 C. Cohen, F. Restagno, C. Poulard and L. Léger, *Soft Matter*, 2011, **7**, 8535–8541.
- 3 A. K. Bajpai, S. K. Shukla, S. Bhanu and S. Kankane, *Prog. Polym. Sci.*, 2008, **33**, 1088–1118.
- 4 M. A. Cohen Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov and S. Minko, *Nat. Mater.*, 2010, **9**, 101–113.
- 5 N. Nordgren and M. W. Rutland, *Nano Lett.*, 2009, **9**, 2984–2990.
- 6 A. Dedinaite, E. Thormann, G. Olanya, P. M. Claesson, B. Nyström, A.-L. Kjøniksen and K. Zhu, *Soft Matter*, 2010, **6**, 2489–2498.
- 7 L. Han, D. Dean, C. Ortiz and A. J. Grodzinsky, *Biophys. J.*, 2007, **92**, 1384–1398.
- 8 L. Han, D. Dean, P. Mao, C. Ortiz and A. J. Grodzinsky, *Biophys. J.*, 2007, **93**, L23–L25.
- 9 Z. Zhang, A. J. Morse, S. P. Armes, A. L. Lewis, M. Geoghegan and G. J. Leggett, *Langmuir*, 2011, **27**, 2514–2521.
- 10 X. Banquy, E. Charraut and S. Giasson, *J. Phys. Chem. B*, 2010, **114**, 9721–9728.
- 11 D. P. Chang, J. E. Dolbow and S. Zauscher, *Langmuir*, 2007, **23**, 250–257.
- 12 T. Tominaga, N. Takedomi, H. Biederman, H. Furukawa, Y. Osada and J. P. Gong, *Soft Matter*, 2008, **4**, 1033–1040.
- 13 J. Gong and Y. Osada, *J. Chem. Phys.*, 1998, **109**, 8062–8068.
- 14 N. Maeda, N. Chen, M. Tirrell and J. N. Israelachvili, *Science*, 2002, **297**, 379–382.
- 15 R. Tadmor, J. Janik, J. Klein and L. J. Fetters, *Phys. Rev. Lett.*, 2003, **91**, 115503.
- 16 A. P. Sokolov and K. S. Schweizer, *Phys. Rev. Lett.*, 2009, **102**, 248301.
- 17 L. Dai, M. Minn, N. Satyanarayana, S. K. Sinha and V. B. C. Tan, *Langmuir*, 2011, **27**, 14861–14867.
- 18 F. Goujon, A. Ghofri, P. Malfreyt and D. J. Tildesley, *Soft Matter*, 2012, **8**, 4635–4644.
- 19 J. Kwon, E. Cheung, S. Park and M. Sitti, *Biomed. Mater.*, 2006, **1**, 216–220.
- 20 M. P. Murphy, B. Aksak and M. Sitti, *J. Adhes. Sci. Technol.*, 2007, **21**, 1281–1296.
- 21 R. M. McMeeking, L. Ma and E. Arzt, *J. Appl. Mech.*, 2009, **76**, 031007.
- 22 A. Jagota and C.-Y. Hui, *Mater. Sci. Eng. R*, 2011, **72**, 253–292.
- 23 C. Majidi, R. E. Groff, Y. Maeno, B. Schubert, S. Baek, B. Bush, R. Maboudian, N. Gravish, M. Wilkinson, K. Autumn and R. S. Fearing, *Phys. Rev. Lett.*, 2006, **97**, 076103.
- 24 L. Han, L. Wang, K.-K. Chia, R. E. Cohen, M. F. Rubner, M. C. Boyce and C. Ortiz, *Adv. Mater.*, 2011, **23**, 4667–4673.
- 25 K.-K. Chia, M. F. Rubner and R. E. Cohen, *Langmuir*, 2009, **25**, 14044–14052.
- 26 J. Choi and M. F. Rubner, *Macromolecules*, 2005, **38**, 116–124.
- 27 L. Wang, C. Ortiz and M. C. Boyce, *J. Eng. Mater. Technol.*, 2011, **133**, 011014.
- 28 M. Varenberg, I. Etsion and G. Halperin, *Rev. Sci. Instrum.*, 2003, **74**, 3362–3367.
- 29 A. Feiler, M. A. Plunkett and M. W. Rutland, *Langmuir*, 2003, **19**, 4173–4179.
- 30 U. Raviv and J. Klein, *Science*, 2002, **297**, 1540–1543.
- 31 U. Raviv, S. Giasson, N. Kampf, J.-F. Gohy, R. Jérôme and J. Klein, *Nature*, 2003, **425**, 163–165.
- 32 G. A. Tomlinson, *Philos. Mag.*, 1929, **7**, 905–939.
- 33 M. T. Bengisu and A. Akay, *J. Acoust. Soc. Am.*, 1999, **105**, 194–205.
- 34 N. Nadermann, A. Kumar, S. Goyal and C.-Y. Hui, *J. R. Soc. Interface*, 2010, **7**, 1581–1589.
- 35 A. Kumar and C.-Y. Hui, *Proc. R. Soc. London, Ser. A*, 2011, **467**, 1372–1389.