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Adhesion between oppositely-charged polyelectrolytes

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The adhesion between a grafted polyelectrolyte layer (brush) and a gel of an oppositely charged polyelectrolyte has been measured as a function of applied pressure, and the interface has been traced using neutron reflectometry. The interface (in aqueous medium at pH 6) between the (polycationic) brush and the (polyanionic) gel has a limited pressure-dependence, with a small amount of deformation of the interface at the brush-gel contact. Brushes with a dry thickness of up to 13 nm exhibit weak adhesion (measured using a mechanical force tester) with an adhesive failure when the gel is detached. Thicker brushes result in the gel exhibiting cohesive failure. Reversing the

geometry, whereby a polycationic brush is replaced with a polyanion and the polyanionic gel is replaced with a polycation reveals that the pH-dependence of the adhesion is moderately symmetric about pH 6, but that the maximum force required to separate the polycation gel from the polyanion brush over the range of pH is greater than that for the polycation brush and polyanion gel. The polyanion used is poly(methacrylic acid) (PMAA) and polycations of poly[2-(diethyl amino)ethyl methacrylate] (PDEAEMA) and poly[2-(dimethyl amino)ethyl methacrylate] (PDMAEMA) were used.

Keywords: acid-base interactions; polymers; novel adhesives; pressure-sensitive; surface roughness/morphology.

Subject classification codes: include these here if the journal requires them

1. Introduction

Adhesion between polymer interfaces has attracted considerable interest, partly due to its industrial importance [1, 2]. The use of 'smart' materials for adhesive applications has become an area of some significant effort [3]. Charged polymers are of particular importance in the field of adhesion because of the possibility of using an environmental stimulus, such as salt, temperature, or pH to control the adhesion *in situ*, including the ability to reverse the adhesion of a system that has already bonded [4, 5, 6, 7, 8, 9]. A true environmentally switchable adhesive system should be able to detach spontaneously as the relevant environmental parameter is changed, but for practical purposes a sufficient reduction in the adhesion might suffice.

Aqueous adhesion involving charged polymers is controlled by a number of parameters beyond pH or the ionic strength of the medium, such as the applied load or compression [6, 7, 8], the time during which the load is applied [8], the relative speed at which the two surfaces are separated [8], temperature [4], and layer thickness [6]. The origin of the adhesion between the polymers is likely to have different mechanisms depending on the materials used, and in many cases more than one might contribute to the adhesion. These mechanisms would include the interdigitation of components so that one layer becomes entangled in the other [10, 11, 12], hydrogen bonding at the interface between the polymers [13, 14, 15, 16, 17], and electrostatic effects [18]. Some conclusions about the mechanisms can be made by comparing

the pH dependence of the adhesion between oppositely charged polyelectrolytes with that between two similar polyelectrolytes [19]. In that work, the frictional adhesion between two grafted polyelectrolytes was measured using friction force microscopy. Such grafted layers are frequently called polymer brushes [20, 21]. It was concluded that the adhesion between oppositely charged polyelectrolytes of poly(methacrylic acid) (PMAA) and poly[(2-dimethylamino)ethyl methacrylate] (PDMAEMA) is largely due to electrostatic interactions and van der Waals forces, with the latter dominating when only one component is charged and the former when both polymers are charged. Another possibility is that the free polyelectrolyte chains can interpenetrate (interdigitate) across the boundary, as has been described for neutral chains [11]. Such a mechanism was not considered in the FFM measurements [19] because it is inappropriate for a brush-brush system, but it was dismissed on the basis of neutron reflectometry data for a system of oppositely charged polyelectrolytes [7].

Previous experiments investigating the adhesion between two polyelectrolytes of differing charge, whilst useful, are not completely general and different mechanisms are likely to apply for different systems. The mechanisms listed above include electrostatic interactions, hydrogen bonding, van der Waals forces, and morphological properties, including chain entanglements. In this work the adhesion between PMAA with two similar polycations (PDMAEMA and poly[(2-diethylamino)ethyl methacrylate], PDEAEMA) is considered. Neutron reflectometry is used to reveal the pressure dependence of the interfacial profiles of PDEAEMA brushes in contact with a PMAA gel. The adhesive behavior of PDEAEMA and PDMAEMA in contact with PMAA is presented using mechanical testing data.

2. Experimental

2.1 Brush synthesis

All brushes were grafted from silicon wafers purchased from Prolog Semicor (Kiev) with the following characteristics: diameter, 50 mm; dopant p-type boron with orientation (100) cut to within 1°; and thickness, 4000 ± 50 μm. The surfaces used for PDMAEMA brushes were cleaned by washing with acetone and toluene. They were then rendered hydrophilic by exposure to a UV ozone lamp for an hour. An initiator layer could be deposited directly onto such surfaces and this was achieved using a solution of 1.5 μl/ml (11-(2-bromo-2-

methyl)propionyloxy)undecyl trichlorosilane (the initiator) in dry toluene. The resulting substrate was therefore ready for PDMAEMA brush synthesis. A different procedure was used for growing PDEAEMA and PMAA brushes. The silicon substrates were cleaned using the RCA method [22], before immersion in a 2% (v/v) solution of ethanol and 3-aminopropyltriethoxysilane (APTES) (Aldrich: Dorset, UK; 98%) for 10 min. The substrate was then rinsed with ethanol, dried under nitrogen, and annealed under vacuum at 120°C for 30 min. The substrate was then immersed in a solution of 3 mmol α-bromoisobutyryl bromide (Aldrich, 98%), and 3 mmol triethylamine (Aldrich, 99%) in 90 ml dichloromethane (Aldrich, 99%) for 30 min. The initiator-coated substrate was finally rinsed with dichloromethane and ethanol before drying under nitrogen.

Atom transfer radical polymerization (ATRP) was used for all brush syntheses [23, 24]. The activating catalysts for polycation syntheses were copper(I) chloride (Aldrich, 99%) for PDMAEMA brushes and copper(I) bromide (Aldrich, 99%) for PDEAEMA. CuCl was purified before use by stirring overnight in glacial acetic acid before being filtered and washed with ethanol and diethyl ether a few times and then left to dry under vacuum. Copper(II) bromide (Aldrich, 97%) was used as the deactivating catalyst. The ATRP ligand for polycation brush synthesis was 2,2'-bipyridyl (bipy; Aldrich, 99%). The solvent for DEAEMA brush synthesis was a mixture of deionized (DI) water and methanol, whereas DI water and acetone was used for synthesizing PDMAEMA brushes. CuBr, $CuBr_2$, bipy, acetone, methanol, DI water, 2-(dimethylamino)ethyl methacrylate (DMAEMA; Aldrich, 98%), and 2-(diethylamino)ethyl methacrylate (DEAEMA; 99%, Aldrich) were all used as received. Solid species were degassed for between 10 and 30 min, whereas liquids were purged under nitrogen for 20 min.

The synthesis of PDMAEMA brushes was carried out using a procedure described previously [7]. The ATRP reaction is performed in a tightly sealed 200 ml flask which had been degassed under nitrogen for 20 min. The reagents were added into the flask in the following order: firstly the species in the solid state, 0.210 mmol of CuCl, 0.0062 mmol of $CuBr_2$, and 0.4802 mmol of bipy. These were stirred and degassed for 10 min after which 5.3 ml of acetone and 0.5 ml of DI water were added. Finally 0.0213 mol of the DMAEMA monomer was added. The solution was left for an hour at room temperature in a nitrogen environment to allow equilibration between the catalyst and the ligand. Afterwards the reaction solution was added to an airtight glass cell containing the silicon wafer functionalized with the

4

initiator layer. The reaction was performed at 35°C, which yielded a measured polymer growth rate of 1.6 nm/h.

The synthesis of PDEAEMA brushes was carried out using a procedure described elsewhere [25]. The solvent mixture, composed of 8 ml of methanol and 2 ml of DI water, was added to 54 mmol of DEAEMA. CuBr (0.9 mmol), CuBr$_2$ (0.3 mmol), and bipy (2.5 mmol) were subsequently added. The solution was stirred and degassed under nitrogen for 30 min and then transferred into a sealed cell glass container that contained the initiator-coated silicon substrate and left at room temperature for 24 h. Finally, the substrate was washed with methanol and ethanol and then dried under a nitrogen stream. For neutron reflectometry experiments, in order to determine contrast between the brush, gel, and aqueous environment, deuterated DMAEMA (Polymer Source: Dorval, Canada) was used. The (ellipsometric) dry thickness of the PDEAEMA brush was 27.8 ± 0.1 nm.

The synthesis of PMAA brushes followed a procedure described elsewhere [26]. A mixture of 0.061 mol of *tert*-butyl methacrylate in 0.059 mol of 1,4-dioxane was prepared. PMDETA (0.479 mmol) and CuCl (0.050 mmol) were added to this solution. After degassing, the solution was transferred into a cell containing the silicon substrate and left overnight inside an oil bath at 50ºC. The resulting poly(*tert*-butyl methacrylate) brush was hydrolyzed to PMAA by immersing the substrate inside a solution of 1,4-dioxane (10 mL) and *p*-toluene sulfonic acid (0.38 g) for 24 h at 100ºC. Finally, the PMAA brush was washed with 1,4-dioxane and ethanol and dried under a N$_2$ stream. The dry thickness of the PMAA brush as measured by ellipsometry was 32.2 ± 0.2 nm.

2.2 Gel synthesis

Both PDEAEMA and PMAA gels were synthesized using the relevant monomer (DEAEMA or methacrylic acid) and 2,2'-azobis(2-methylpropionamide) dihydrochloride (AMPA; Aldrich, 98%) as initiator. PMAA gels were made in DI water and PDEAEMA gels in a mixture of DI water and methanol. *N,N'*-methylene bisacrylamide (MBA; Aldrich, 98%) was used as the crosslinking agent for PMAA and ethylene glycol dimethacrylate (EGDMA; Aldrich 98%) for PDEAEMA. The methacrylic acid (Aldrich, 98%) was distilled under vacuum before use.

Different compositions of PMAA gels were made for their interaction with PDEAEMA and PDMAEMA brushes. For gels that were used for experiments with PDMAEMA brushes, two

solutions were initially prepared: one containing 0.80 mol of methacrylic acid mixed with 6.35 mmol of MBA (with a yield of approximately 123 monomers per crosslink), and the other containing 8 ml of DI water and 4.76 mmol of AMPA. When the two solutions were completely dissolved, they were stirred together for 20 min under nitrogen. The solution was then transferred to an airtight glass mold that had been degassed for 1 h under nitrogen. The reaction was performed for 45 min in a preheated oven at 90°C. After the reaction was completed, the hydrogels were placed in water and then washed in acid and then under basic conditions to remove any residual starting materials, and finally equilibrated to the required pH. For gels that were used for experiments with PDEAEMA brushes the compositions used were 0.55 mol methacrylic acid (1.4×10^4 monomers per crosslink), 0.23 mol AMPA 0.01 mmol, and 0.04 mmol MBA in 10 ml DI water. After mixing, the degassed solution was transferred into a special sealed glass container and then placed inside an oven for 2 h at 70°C. After cutting the PMAA gel into hemispherical pieces, it was then washed with copious amounts of water to remove any residue that had not reacted. The hemispherical hydrogels were stored in DI water. Equilibration at the required pH was performed before the experiments. The very different crosslinking densities of the PMAA and PDEAEMA gels allowed for comparable moduli, which is necessary for comparative experiments such as these.

For the neutron reflectivity experiments, flat sheets of PMAA hydrogels were required in order to maintain good contact with the PDMAEMA brush layer. The synthesis was therefore performed on a glass Petri dish of 7 cm radius, and afterwards the gel was divided into disks of 3.5 cm diameter.

For the PDEAMA gel, a solution containing 2.9 mmol AMPA, 7.9 mmol EGDMA, and 0.20 mol DEAEMA in a mixture of methanol (50 ml) in water (30 ml) was stirred and degassed for 30 min and then transferred into a special degassed glass container, which had a removable glass base that contained hemispherical holes of 4 mm diameter. The glass container was then placed inside an oven at 70°C for an hour. The polycationic gel so formed was cut into hemispherical pieces and stored inside DI water to be used later in the adhesion experiments.

2.3   Neutron reflectometry

Neutron reflectometry measurements were performed by using the time-of-flight EROS reflectometer of the Orphée reactor at the Laboratoire Léon Brillouin. The neutrons were collimated to a wavelength range of between 0.3 and 2.5 nm. The neutron beam was collimated to 3.9 mm to ensure that the beam footprint was focused onto the sample. Two angles were used in order to increase the range of neutron wave vector. For the experiments the gel was gently pressed onto the brush in a specially designed Perspex® sample cell. Care was taken to avoid contact with the cell during alignment of the beam. In these experiments, as in those of the earlier experiments [7], the neutrons were incident on the brush through the silicon substrate. This was necessary because of the large incoherent scattering of water. The disadvantage of this sample geometry is that, for thin brush layers, there is no total reflection ($R = 1$), which can be a useful means to normalize the data. A D_2O interface with silicon in the same sample cell was therefore used as a control in order to normalize the data. The exact normalization factor could then be obtained through fitting the data. The brush volume fraction profiles were obtained by optimizing the scattering length density and thickness of an increasing series of layers to minimize χ^2 as described previously [27].

2.4   Mechanical testing

For adhesion measurements, two different set-ups were used. For experiments between a PDMAEMA brush and PMAA gel, the experiments were performed in a liquid cell situated between a lamp and a high resolution camera (M125, Leica: Mannheim, Germany). The gel was observed from the side. The liquid cell consists of a 300 ml glass square container where the substrate is placed to equilibrate under known pH solution. The hydrogel is brought in contact to the disk and pulled off by a micromanipulator (Model DC300 1R, World Precision Instruments: Berlin, Germany) connected to a 100 g force transducer (World Precision Instruments). The micrometer is set to a velocity of 20 μm/s (1.2 mm/min) in both the loading and unloading stages. The experimental procedure consists of clamping the disk in the glass support and leaving the solution to equilibrate for 2 h; after which the hemispherical gel is clamped onto a Perspex® support and brought into contact with the wafer until a force of 20 mN, is reached. The gel and the wafer are left in contact for 15 min and then the gel is pulled until it is detached from the surface.

For experiments investigating the adhesion of PDEAEMA and PMAA a mechanical tester (Texture Analyser TA.XT*plus*, Stable Micro Systems: Godalming, UK) was employed to

perform the pull-off experiments by bringing a hemispherical piece of the hydrogel in contact with an oppositely charged polyelectrolyte brush in distilled or DI water. The tester comprises a mechanical probe which is used to fix the hemispherical gel inside its plastic jacket and a platform on which the brush substrate is placed. The mechanical probe brings the hydrogel in contact with the polymer brush surface (**Figure 1)**. The mechanical tester was set to apply 0.5 N on the interface between the gel and brush interface. The interface was illuminated with a lamp and side-view images of the interface were taken using a camera. The applied force studied here was therefore substantially greater than the 20 mN used for the PDMAEMA brush samples, although the basic experiment was the same. The gel was left in contact with the brush at an applied force of 0.5 N for 2 min before being retracted at a speed of 50 mm/min.

For measurements of the elastic modulus of PMAA gels, the gel was placed in contact with a silicon surface immersed in aqueous solution at the required pH. Different loads P were applied and the contact diameter $2a$ determined. The silicon surface is slightly negatively charged or uncharged under most pH and there is no strong adhesion with the PMAA, which allows the modulus K to be calculated using the Hertz equation [28],

$$a^3 = PR/K, \tag{1}$$

where R the radius of the gel. The gradient of a plot of a^3 as a function of P reveals the modulus, since R is known. For PDEAEMA gels the modulus was calculated using an APTES-coated silicon wafer so that the positively charged gel had no additional adhesive interactions with the surface.

3. Results and discussion

3.1 *Neutron reflectometry determination of depth profiles*

Neutron reflectometry data and fits are shown in **Figure 2** for PDMAEMA brushes of 11 and 20 nm thickness as pressure is increased on the brush. The fits are of a very good quality and we can therefore be confident in the volume fraction profiles shown. The volume fraction profiles are extracted from the scattering length density profiles which is possible if there are only two components. Here, the components are brush, gel, and water which means that an unambiguous volume fraction-depth profile is impossible. However since the PMAA gel and

8

the aqueous medium have similarly small scattering length densities, it is reasonable to treat them as identical and analyze the data as for a binary system. In all samples the brush volume fraction increases from the silicon substrate over a few nm. It is likely that this at least partly reflects the initiator monolayer attached to the native oxide layer on the silicon substrate.

With no gel attached, the brushes are relatively compact and do not extend deep into the solution. These PDMAEMA brushes are therefore behaving in a similar manner to the PDEAEMA brushes in water in an earlier study [27]. As pressure is applied to the gel the behavior changes a little for the 20 nm brush (**Figure 2d**), whereby an extra layer is necessary in the fitting profile to accommodate a slightly extended region of constant volume fraction ($\varphi \approx 0.4$). The 11 nm brush (**Figure 2b**) changes very little, except for during the application of 3 kPa, where a more stretched brush is observed, but only at a small volume fraction. This may well reflect an effect of non-conformal contact between the brush and the gel at this low pressure. The changes in structure for all of the data do not necessarily mean that the brush is interdigitating into the gel; it is equally possible that the gel-brush interface is buckling and that there is a lateral structure but no interdigitation. This is possible because the gel is relatively soft, with a modulus $K \approx 170$ kPa. Alternatively, a combination of buckling and interdigitation may be possible. Despite the ambiguity, it is clear from the neutron reflectometry data that there is a thickness dependence of the structure, and it is not unreasonable to conclude that this could affect the adhesion.

To consider the thickness dependence in more detail, in **Figure 3** the volume fraction-depth profile is shown for three brushes of different thickness but under similar applied pressures. Here it can be seen that the extension of the brush into the gel gradually increases with increasing brush thickness. The thicker brushes have more capacity to extend into the gel, and the brush profile also becomes slightly broader (i.e. there is an increase in the width of the extended interface) with thickness.

3.2 *Brush thickness-dependent failure of the PMAA-PDMAEMA interface*

To test the effect of different brush thicknesses on the adhesion of the two components a mechanical force tester was used to bring the two components into contact, and then to separate them. Sample data are shown in **Figure 4**. Here both the applied force on withdrawal of the gel from the brush layer and the contact diameter are shown and their behavior are somewhat different. The contact diameter for the 31 nm brush layer reaches a plateau after ~6

s, although the force still increases. This plateau corresponds to a 'neck' forming (**Figure 5**), which does not appear in the 13 nm sample. Systems which exhibit such a 'neck' invariably end in cohesive failure at the interface, as can be seen from the optical images of the interface in **Figure 5**. The two thinner brush layers (3 nm and 13 nm) did not exhibit a 'neck' and cohesive failure did not occur (or was negligible). In the neutron reflectometry experiments, a pressure was applied, whereas the mechanical tester here applied a force of 20 mN. In fact, this force was applied over a contact diameter of ~1.3 mm in both cases, corresponding to a nominal pressure of 15 kPa, which is equivalent to that in the neutron experiments. This means that a comparison with the data of **Figure 3** is tempting, whereby the brush volume fraction profile has two distinct parts, as opposed to the more uniform structure of the thinner layer. Whilst strong conclusions cannot be drawn about the correlation between the volume fraction profile and cohesive failure with these limited data, it cannot be excluded that the brush interpenetrates the gel to some degree for cohesive failure to occur. The difference in the failure mechanisms is clear from the data in **Figure 5**. In the case of the 16.5 and 31 nm brushes, the contact between the brush and gel remains as the gel is retracted; this is highlighted on the image for the 31 nm brush. There is no such contact on the two thinnest brushes, for which adhesive failure is observed. In **Figure 4**, these can be differentiated because there is a substantial time period (between 7 and 25 s) where the contact diameter remains unchanged for the 31 nm brush, but an equivalent period is not observed for the thinner 13 nm brush.

3.3   Comparison between polycation brush/polyanion gel and polyanion brush/polycation gel

To consider whether or not the geometry (polycation brush and polyanion gel) is the determining factor in the adhesion it is necessary to reverse the roles, so that a polycation gel is used in concert with a polyanion brush. To this end pH-dependent adhesion experiments were performed on a PMAA gel in contact with a PDEAEMA brush and a PDEAEMA gel adhering to a PMAA brush. The results for these experiments are shown in **Figure 6**, both as maximum force required to separate the brush and the gel (F_m) and the work done (W_+) in separating them (the area under the force-distance curve for $F > 0$, which therefore excludes repulsive interactions).

The adhesion (force and work done) is at first glance symmetric about pH 6 for both the polycationic and polyanionic brushes. The PDEAEMA gel requires both more work and a

10

greater force to be detached from the PMAA brush at pH 6 than the PMAA gel does from the PDEAEMA brush. It is appealing to attribute this behavior to mechanical properties: here the PMAA gel has a modulus of 0.30 ± 0.04 MPa in DI water (pH 6) [9], while for the PDEAEMA, $K = 0.48 \pm 0.03$ MPa. Furthermore, the swollen gels have a smaller modulus than those that are uncharged. The PMAA gel has a modulus that changes from $K = 0.42$ MPa at pH 1 to 0.17 MPa at pH 12 [9], whilst the PDEAEMA gel changes from $K = 0.37 \pm 0.01$ MPa at pH 1 to 0.63 ± 0.02 MPa at pH 12. This means that the PDEAEMA and PMAA gels have similar moduli at pH 1, but significantly different values for the maximum force and work of adhesion at this pH. These are 3 and 8 times greater respectively for the PDEAEMA gel than the PMAA gel.

Whilst the modulus plays an important role in the adhesion (as it must, through the JKR equation) it is also important which component is swollen and which contracts. The effect of charge on the polymers is key. These brushes are expected to be swollen by the osmotic pressure of their counter-ions, and so they are unlikely to retain the charge expected for polymers in dilute solution at a given pH because counter-ion condensation will result in the denser grafted polymer layer [29]. The pK_a of a weak polyelectrolyte is necessarily measured in dilute solution. In the brush, however, the presence of nearby chains and associated counter-ions would raise the energy of the system due to the increased Coulombic energy. This energy can only be reduced by counter-ions condensing on the chain, with the result that weak polyelectrolyte brushes are not expected to be as charged as the equivalent chains in dilute solution, and also that their neutralization point is shifted relative to chains in dilute solution. There is a much greater effect of charge (and thus osmotic pressure) in the PMAA brush than in the PDEAEMA brush (these brushes are of similar dry thicknesses, and so are comparable) because the PMAA brush has the greater change in thickness. The PDEAEMA brush does not change as much in thickness (a factor of two) between high and low pH as the PMAA does between low and high pH (a factor of four) (**Figure 7**). The maximum swelling of the two gels was similar, so effects due to swelling are dominated by the brush layer. This is not surprising because a gel can swell in three dimensions, whereas a brush can do so in only one. In order to consider the possible effect of counter-ion condensation, the pH-dependent thickness of the two brushes in aqueous media was measured using ellipsometry (M-2000V rotating compensator ellipsometer, J. A. Woollam Co., Inc.: Lincoln, USA).

The thickness data were fitted to

$$l = l_2 + \frac{(l_1 - l_2)}{2} \sqrt{1 + \tanh\left(\frac{pH-\Delta_1}{\sigma_1}\right) \tanh\left(\frac{pH-\Delta_2}{\sigma_2}\right)}, \tag{2}$$

where l_1, l_2, Δ_1, Δ_2, σ_1, and σ_2 are fitting parameters. This equation is purely empirical, but it does allow a calculation of the second derivative (with respect to pH), which is zero (inflexion) at pH = 5.3 for PDEAEMA and 6.4 for PMAA. These pH values can be compared with the pK_a of the two polymers, which are 7.3 [30] and 5.7 [31] in dilute solution respectively. It is therefore clear that in both cases there is a shift compared to the pK_a, which can be attributed to counter-ion condensation.

The question of counter-ion condensation is important because at low pH the difference in adhesion between PDEAEMA and PMAA is significantly more than at high pH, where the work done in removing a PMAA gel from the brush surface is greater than that for the PDEAEMA gel. The PDEAEMA brush thickness transition has a greater shift compared to its pK_a, than that for PMAA suggesting that more counter-ion condensation occurs in the PDEAEMA which may explain why it has a lower adhesive force with a PMAA gel at low pH than the PMAA brush with the PDEAEMA gel at high pH. (This would also explain the smaller thickness change as a function of pH of the PDEAEMA brush than the PMAA brush.) Counter-ion condensation is likely when there is a large grafting density in the brush, increasing the electrostatic energy of the counter-ions. As mentioned above, there is not expected to be as much counter-ion condensation in the gels, because these can swell in three dimensions reducing the density of charges. The PDEAEMA gel swelling ratio decreases from 22 ± 4 at pH 1.3 to 3 ± 2 at pH 12.2, whereas the PMAA gel increases from 6 ± 2 to 65 ± 18 over the same range, which are changes of a factor 7 ± 5 and 11 ± 5 for the two respective gels.

It is also the case that the decrease in adhesion (for both gel and brush configurations) is slightly greater when the environment is more acidic. The origin of this behavior is likely to be related to the respective swelling of PMAA and PDEAEMA brushes; the PMAA brush undergoes a much greater collapse at low pH than the PDEAEMA brush does at high pH.

3.4   *Thermodynamic work of adhesion*

The thermodynamic work of adhesion can be calculated from these experiments assuming that the adhesion follows Johnson-Kendall-Roberts (JKR) behavior [32]. Under this formalism the work of adhesion is related to the maximum force by

$$F_m = 3\pi RW_t/2, \tag{3}$$

where W_t is the thermodynamic work of adhesion. This simple equation shows that the maximum (pull-off) force depends linearly on the radius of the gel and the work of adhesion, and is generally used for the adhesion between deformable media. As such the JKR equation is appropriate for the work described here. The JKR equation reduces to the Hertz form (**Equation 1**) in the absence of adhesion. This work of adhesion is generally presented as a function of the stress at the interface [33], because this represents the effect of the applied load at the contact line, i.e. the edge of the circular contact. Contact stresses are a longstanding problem in contact mechanics [34] and although their measurement has been of longstanding interest [2] new techniques for the in situ measurement of the stress are continually being developed [35]. The stress is given by

$$\sigma = \sqrt{\frac{3a_l K W_t}{2\pi\left(a_l^2 - a_f^2\right)}} - \frac{3K\sqrt{a_l^2 - a_f^2}}{2\pi R}, \tag{4}$$

where a_l is the radius during the application of the load, and a_f is the contact radius after the load was removed. The first term represents the effect of the load, and the second term represents a Hertzian component. When the Hertzian component is larger than the first term, the stress is compressive. This is typically the case when unloading from large loads. When the first term is the larger, the stress is tensile. This formalism requires that the gel be incompressible, and this is not the case for hydrogels under large loads. A full understanding of this limitation is lacking, but indications are that there are circumstances when it may be significant [36]. It is also notable that in the present experiments, for a given system as a function of applied load, the adhesion increased with both compressive and tensile stress. In both cases an increased load corresponds to an increased (absolute) stress. For the pH 1 results this might be considered surprising since an increased tensile stress is associated with weaker adhesion, but at pH 1 the work of adhesion increased from 2.5±0.3 J/m^2 at an applied force of 0.1 N to 8±4 J/m^2 at 2 N, an increase of a factor 3.4. The ratio a_l/a_f did not change

between 0.1 N and 2 N (a_l/a_f = 1.1) but a_l increased by 50% as the load increased. Therefore the increased work of adhesion is mainly responsible for the increase in the tensile stress with applied load at pH 1. Although the errors are significant, the trend at pH 1 (as for the other pH results) is real and the origins of this behavior would be of some interest. It is possible to speculate that the increased compression at pH 1 gives rise to increased hydrogen bonding, although this was thought to be unlikely in the case of brush-brush interactions at much smaller forces [19].

The adhesion increases with increasing stress with the pH 6 data representing the largest adhesion (**Figure 8**). The data for pH 12 show a larger adhesion than that at pH 1, which is consistent with the results presented in **Figure 6**. The results for the earlier experiments [7] are also shown for a complete comparison. The adhesion for the least adhesive system in the present work: that of the PDEAEMA brush with the PMAA gel at pH 1, which has a greater work of adhesion (2.5 ± 0.3 J/m^2 at an applied force of 0.1 N) than the most adhesive system in the earlier study (0.44 ± 0.05 J/m^2 at 60 mN [7]). These two results may reflect the role of the stress in this comparison rather than the slight dissimilarity between the two polycationic brush layers: a 16 nm-thick PDMAEMA brush subjected to a 190 kPa gel [6] with an applied force of 60 mN at pH 6 is here compared with 28 nm-thick PDEAEMA brush subjected to a 310 kPa gel with an applied force of 0.1 N at pH 1.

Given that the JKR theory describes equilibrium behavior, it would be expected that a chemical description of the components would be sufficient to describe adhesion phenomena; i.e. the work of adhesion between the same components in a given geometry should be independent of load. However, it is well known that there is hysteresis in the adhesion between soft materials; i.e. the maximum pull-off force (F_m) will yield a different (unloading) work of adhesion than that obtained during compression, i.e. the loading work of adhesion [33]. As the (compressive) stress described by **Equation (4)** increases, i.e. the stress becomes more negative, the unloading work of adhesion, which is here a proxy for the maximum adhesion (pull-off) force, increases significantly. The data presented in **Figure 8** therefore demonstrate that, even for relatively similar systems, the effect of compressive stress cannot be ignored; a system considered adhesive in previous experiments [6, 7] has a smaller work of adhesion than pH 1 values provided in the present work. Again pH 12 data do not provide as good a means of detaching the gel as those at pH 1; in fact the stress in these data is even slightly compressive.

3.5   Equilibrium considerations

A contact time of 2 min is a good proxy a physically realistic (real-world) contact, but it does not necessarily represent thermodynamic equilibrium. However, should longer contact times affect adhesive properties, they would also affect the stress at the interface, so the results presented here retain a useful generality, i.e. the work of adhesion corresponds to the stress applied. More important therefore is the rate of detachment, which should be slow enough to ensure that the system remains in quasi-static equilibrium as the gel is detached. If the gel is removed too rapidly, premature cohesive failure may occur. To test for this, the maximum adhesion force is compared against the work done (**Figure 9**). Above a retraction speed of 60 mm/min the work of adhesion decreases, although there is much less of an effect on F_m above this speed. Because both the force and work done remain unchanged for the slower speeds, it is likely that equilibrium considerations apply to the adhesion couple and thus to the 50 mm/min used in the current work. At the faster speeds this is not possible. In any case, for the measurements of W_t, it is only necessary that F_m remain constant as the probe speed is changed. A limitation of course is that any effects in regimes slower than 5 mm/min are inaccessible in the experimental geometry used here.

4   Conclusion

The adhesion between oppositely charged polyelectrolytes is a complex multi-parameter problem, and the effects of some of these have been highlighted. Here the interaction between a brush and a gel has been considered. The thickness of the brush layer is a particularly important parameter. If the brush is too thin, then the adhesion is weak. Neutron reflectometry showed that the brush volume fraction profile was significantly less uniform for thicker brushes, and the volume fraction profile also changed with increased applied pressure.

The adhesion behavior is generally symmetric; adhesion weakens both at high and low pH, and the same behavior is observed if the polyelectrolytes are swapped, i.e. if a polycationic gel and a polyanionic brush combination is used. There are certain differences, insofar as the adhesion at low pH is a little less than that at high pH. This is likely to be due to the differences in the swelling of the PMAA brush with respect to the PDEAEMA brush. The same observation is made to explain why the PMAA brush adheres more strongly to the PDEAEMA brush than *vice versa*.

15

That there is less adhesion at pH 1 than pH 12 is quantified by calculating the stress at the interface. The sample at pH 1 is dominated by tensile stress, whereas those at pH 12 and 6 experience compressive stress, and also greater adhesion.

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Figure 1. Schematic diagram of the process for a polyacid gel being brought into contact with a polybase grafted polymer layer. At low pH, the brush is fully swollen but the gel excludes water and contains limited charge. At pH 6, both the brush and the gel are swollen, while at high pH the brush layer loses most of its charge and collapses to exclude water. The adhesion is maximized when both of these are charged, i.e. at pH close to 6. At this pH, the contact between brush and gel is maximized, whereas a smaller radius of contact (double arrows) is observed at the extremes of pH. The same applies for a polycation gel and polyanion brush, except that the low and high pH situations are reversed
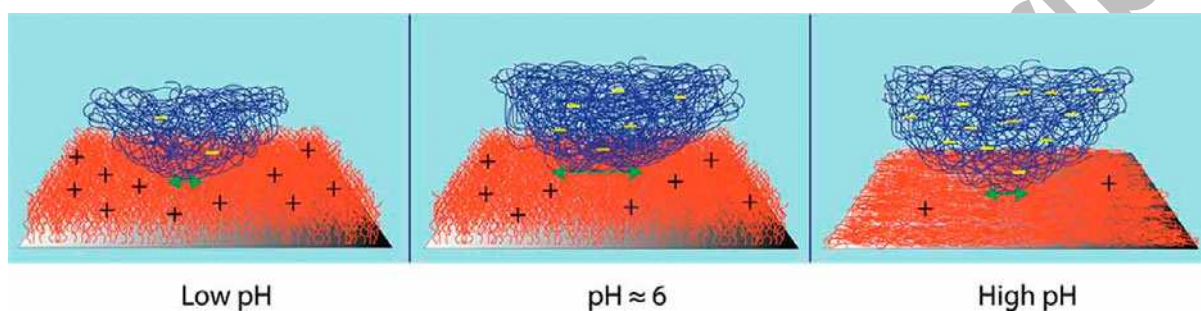
Figure 2. Neutron reflectometry data and volume fraction profiles for PDMAEMA brushes in contact with a PMAA gel in water (pH 5.8) at different pressures. (a) Reflectometry data for an 11 nm brush with (b) corresponding volume fraction profiles. (c) Reflectometry data for a 20 nm brush with (d) corresponding volume fraction profiles. The reflectometry data are shown in the Porod formalism ($RQ^4(Q)$) because this better illustrates the quality of the fits than $R(Q)$. For clarity, the neutron data are scaled by a decade for each increasing pressure; the brush data with no gel applied are unscaled
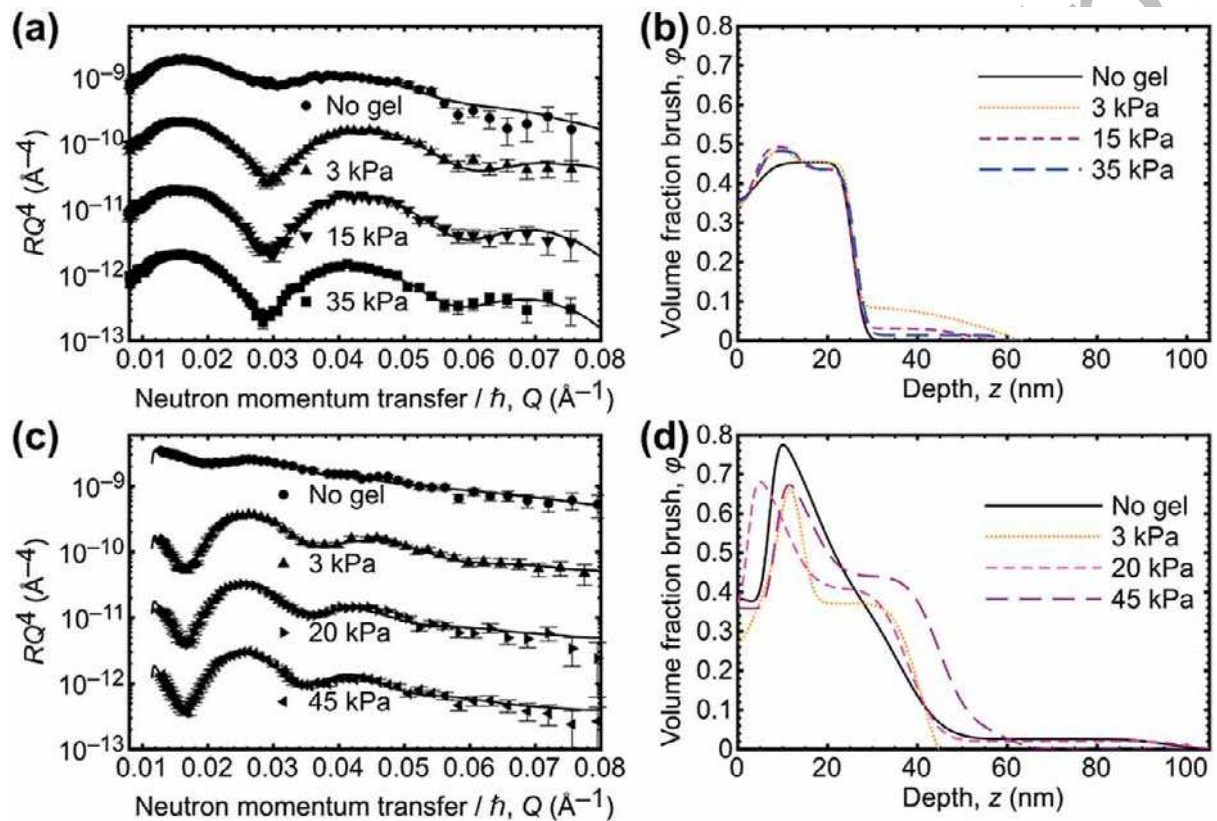
Figure 3. Volume fraction depth profiles for three brushes of different thicknesses into a PMAA gel. A similar pressure was applied in each of these experiments
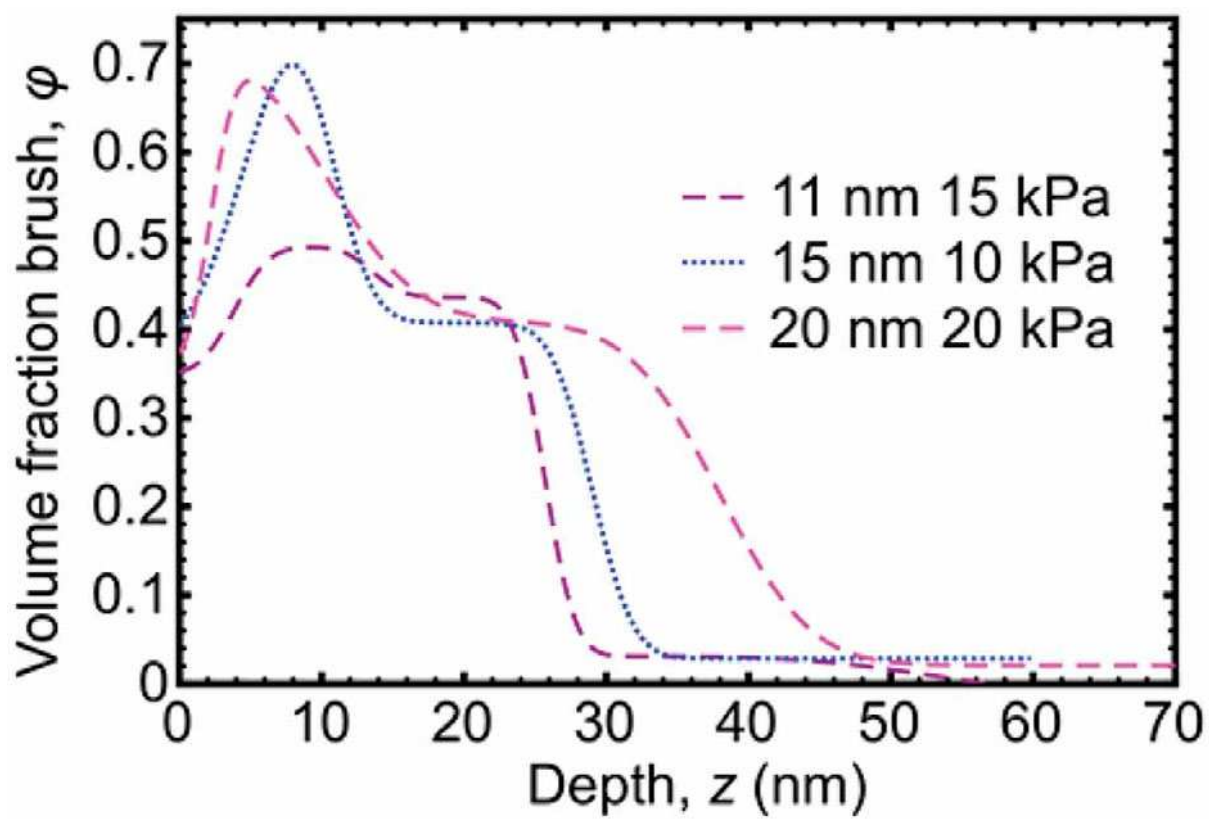
Figure 4. Force measured during retraction of the PMAA gel from the PDMAEMA brush surface along with the contact diameter (CD) as a function of time (and distance) for two different brush layer thicknesses
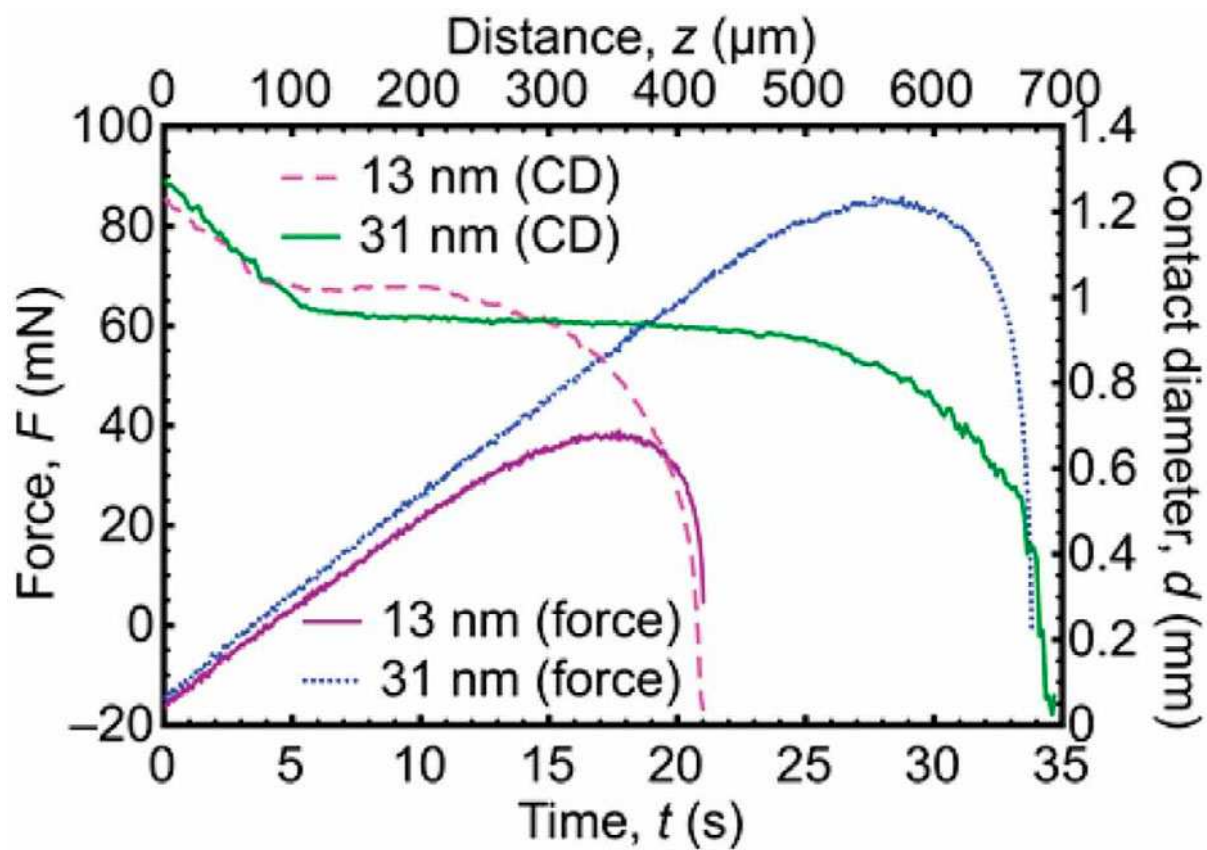
Figure 5. (Top) Photographs of a PMAA gel (K = 170 kPa) as it is detached from PDMAEMA brush surfaces for the four different brush thicknesses shown. (Bottom) The brush surface is photographed after the gel is removed. The scale bar is 1 mm, and the scale is the same in all four lower images. The contact between the gel and the brush is highlighted with an arc drawn on the (upper) image for the 31 nm brush
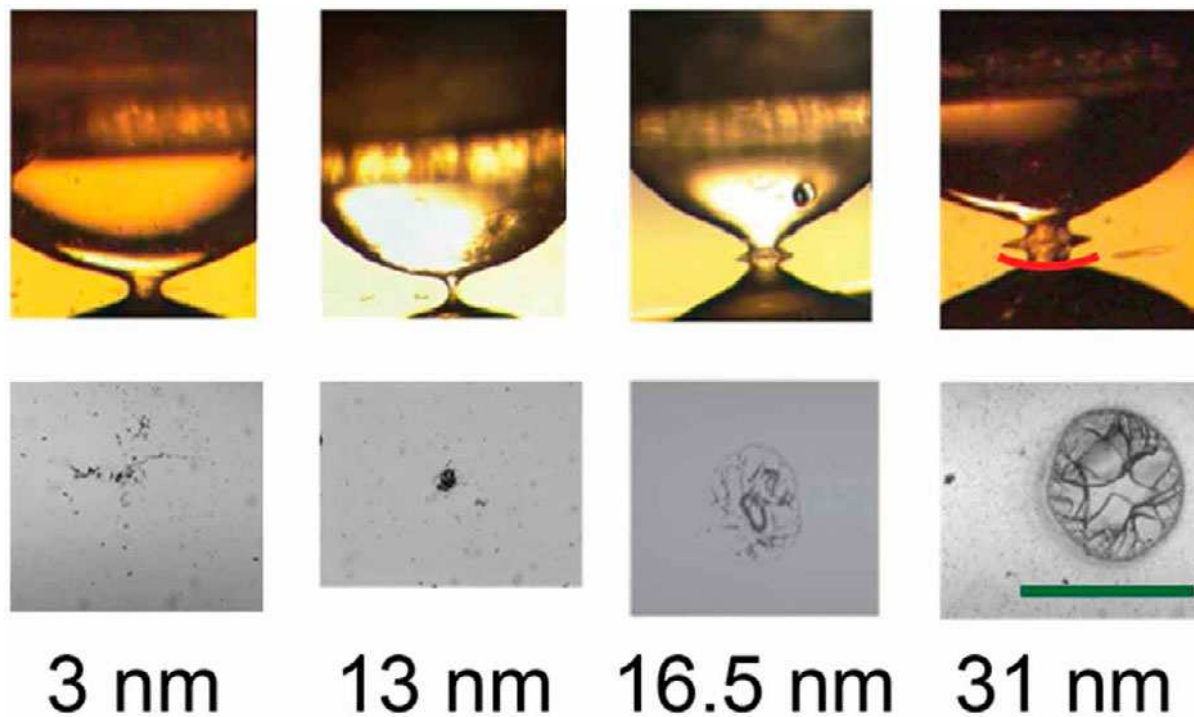
Figure 6. Example force-distance curves (a) for PMAA and PDEAEMA gels being brought to PDEAEMA and PMAA brushes respectively. The maximum adhesion force (b) and corresponding work done (c) are plotted for the two different geometries (the legend is the same in both plots), whereby the gel component is the PDEAEMA and the brush PMAA, and *vice versa*. The gel was brought into contact with the brush for 2 min with an applied force of 0.5 N and then removed at a constant speed of 55 mm/min
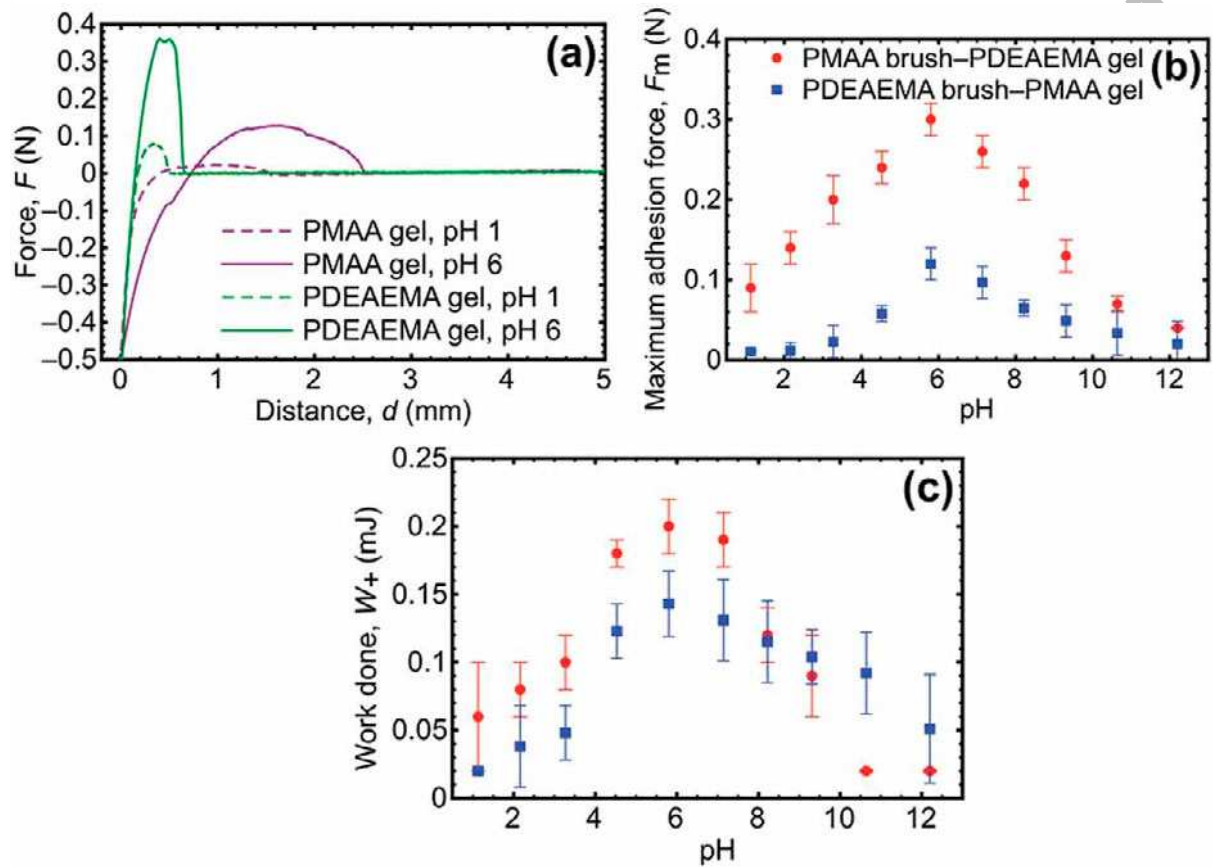
Figure 7. Ellipsometric water-swollen thickness of PDEAEMA and PMAA brushes as a function of pH. The dry thicknesses were 28 and 32 nm respectively. These solid lines are a fit to **Equation (2)** and allow a determination of the pH transition between collapsed and stretched brushes: 5.3 (PDEAEMA) and 6.4 (PMAA)
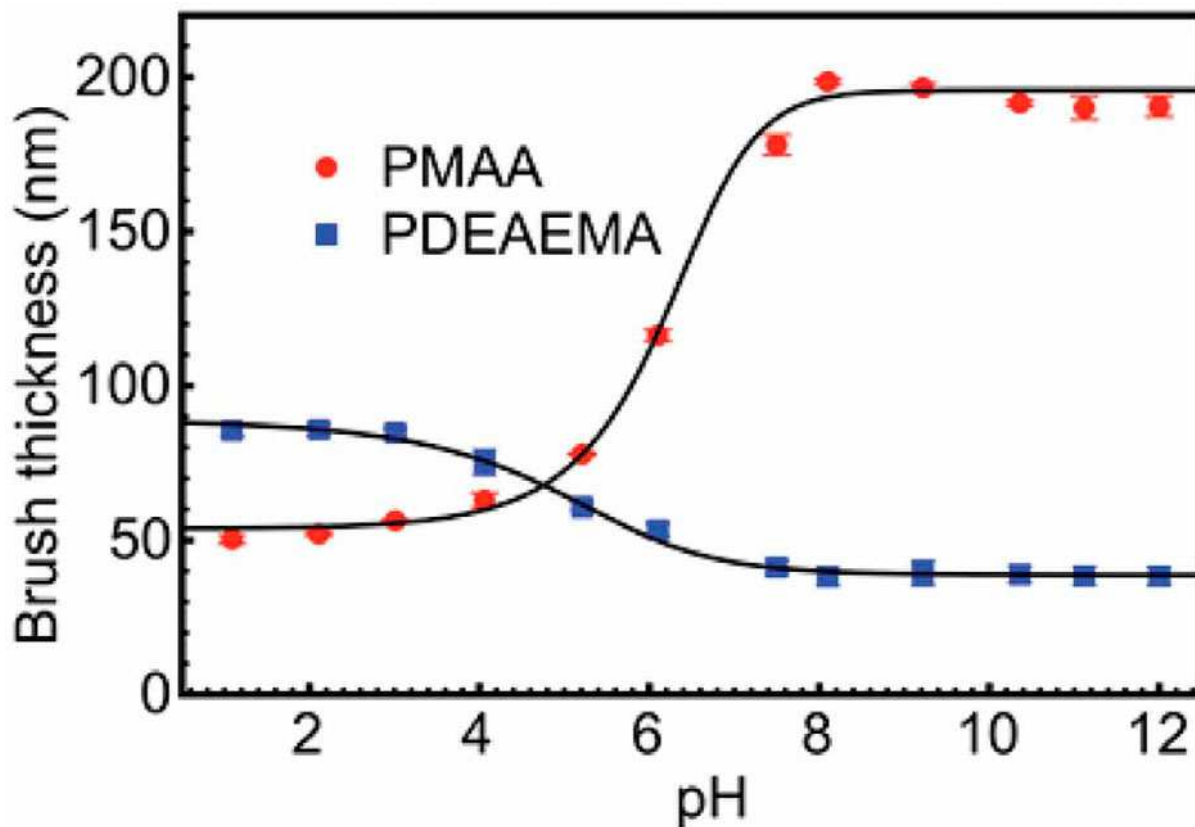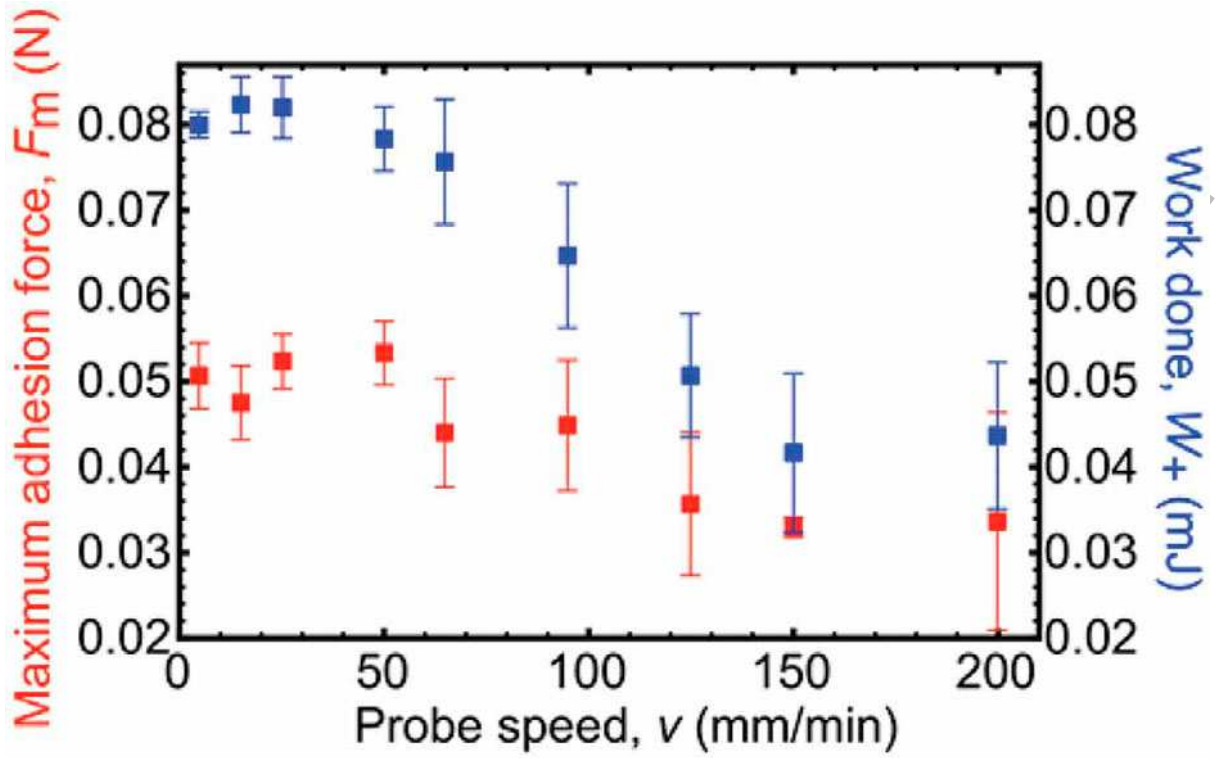
Figure 8. Thermodynamic work of adhesion for the PDEAEMA brush/PMAA gel adhesion couples measured in this experiment. The results from the earlier work [7] of PDMAEMA brushes (16 nm dry thickness) with PMAA gels are also included
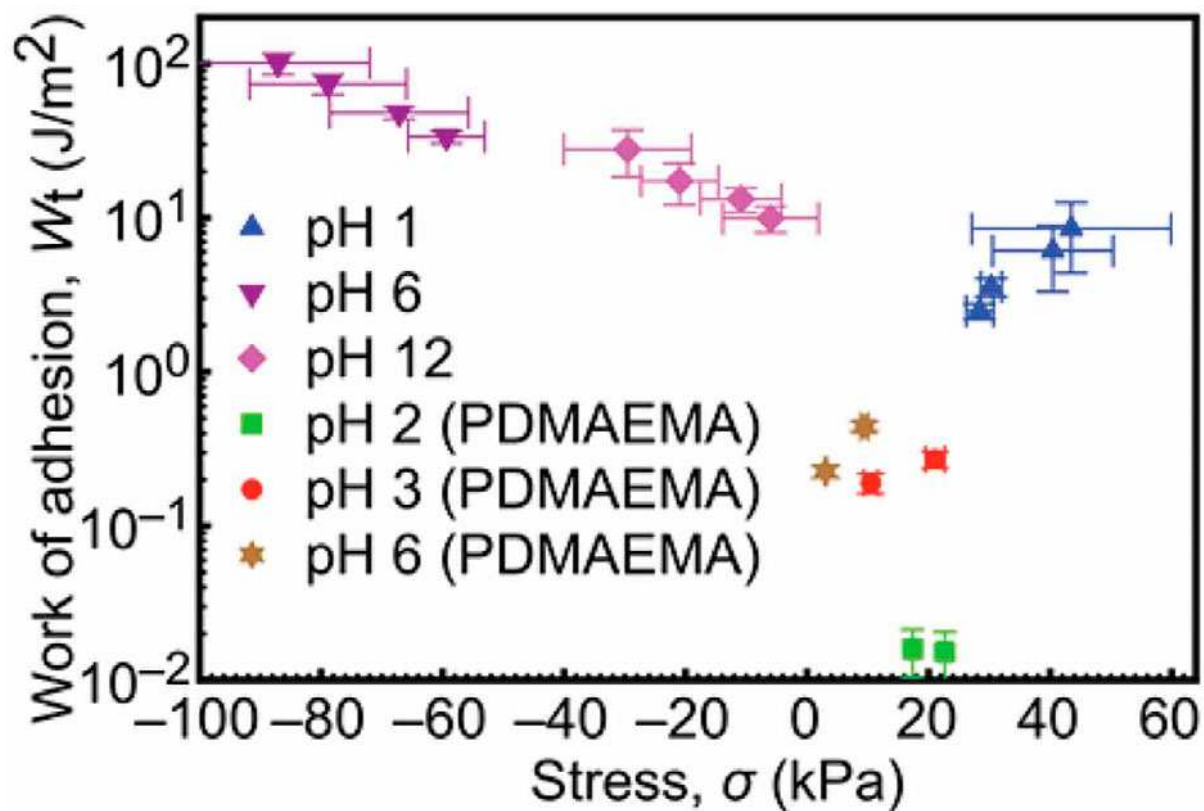
Figure 9. Maximum adhesion force and work done as a function of the probe retraction speed. For speeds above about 60 mm/min, the work done starts to decrease. A similar, but smaller effect is observed for the maximum adhesion force