

# ON THE ORIGINS OF ADHESION IN PAPERMAKING SYSTEMS

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## ABSTRACT

The purpose of this study was to investigate the effect of polyelectrolytes on the adhesion forces between polyelectrolyte-coated surfaces and to relate the observed phenomena to the performance of dry strength additives in papermaking systems.

The adhesive properties (pull-off forces) between polyelectrolyte-coated surfaces in air were determined as a function of the polymer charge density and the number of contacts. We found strong adhesion energy for model systems coated with polymers of the highest (cationic) charge density, which suggests that electrostatic surface-polyelectrolyte-surface bridges are the main cause of the adhesion. At low charge density another force contribution due to entanglement of polymer chains gives rise to a significant contribution to the adhesion forces. The disruption of the contact leads to irreversible changes in the adsorbed layers when either the number of electrostatic bridges formed is large or when entanglement effects are important for polymers with a relatively low binding strength to the surface. These results are discussed in terms of our current understanding of development of dry strength in fiber systems.

## INTRODUCTION

Dry-strength additives are water-soluble materials, most of which are macromolecules containing electrically charged groups (polyelectrolytes). Polyelectrolytes are also used in industry as additives to control colloidal stability and adhesive properties of surfaces.

Cellulosic fibers possess a self-adhesive quality, allowing them to bond to each other after they are suspended in water and then dried in contact with each other. A typical fiber within a paper sheet crosses about 20 to 40 other fibers [1], and such contacts determine many of the overall physical properties of paper. The chemical and physical nature of inter-fiber bonds, formed in the absence of added polymers, have been reviewed by others [2–9]. Some of the key mechanical approaches to increasing inter-fiber bond strength within a paper sheet include increased refining of the fibers [10–11], more intensive or longer pressing of the paper web [12–13], and, in some cases, taking steps to limit the shrinkage of the resulting paper as it is being dried [14–16].

Despite fibers' own capacity to adhere to each other, still a large proportion of paper grades are manufactured with chemicals to enhance the strength of inter-fiber bonds in the resulting product. Some of the most widely used classes of products are cationic starch [17–35] and medium-mass acrylamide copolymers [36–51]. Guar and related gum products [52–58] and carboxymethylcellulose (CMC) [59–61] are also well-known for their ability to increase paper dry strength when they are added to the furnish.

Additional key motivations for using polyelectrolytes to enhance dry strength are: (a) the need to achieve paper strength goals with less fiber material [62]; (b) allow use of lower-cost fibers with less bonding ability, as in the case of some recycled fibers [28, 44, 46, 49]; (c) make it possible to use more mineral filler, not only to save cost, but also to improve paper's optical characteristics and smoothness [24, 27, 46]; (d) achieve paper strength goals with less refining energy, a strategy that also can help avoid excessive loss of caliper (thickness at a given mass per unit area) and avoid excessive loss of freeness [39, 46] and, (e) overcome certain quality problems such as linting, low internal bond, or inadequate stiffness to meet grade requirements [68].

Most polymers used in papermaking can be described as water-loving macromolecules of medium to high molecular mass [2–4]. Davison [3] listed hydrogen bonding ability as one of the most universally characteristic features of dry strength additives. In certain cases dry-strengthening performance of polyelectrolytes has been found to increase with molecular mass, at least up to the range of about 100,000 grams per mole [40, 69–70]. Reynolds and Wasser [43] reported that the best dry-strength performance was obtained when linear acrylamide-based polymers were in the range between

about 100,000 and 500,000 Daltons. The practical upper limit of molecular mass usually is related to such factors as ease of handling of the chemicals. Also, at molecular masses above about 2 million Daltons, water-soluble polymers tend to have an increasing ability to flocculate suspended matter, making them more suitable as retention aids [71] rather than as strength additives.

The relative benefits of cationic polyelectrolytes tend to be reduced under conditions that do not favor efficient adsorption onto fiber surfaces. For instance, high electrical conductivity of the water, due to the presence of salt ions, can limit the ability of fibers to take up cationic starch [72–74]. Cationic polyelectrolytes having a higher charge density have been shown to be more effective in such situations [32]. In terms of dosage levels, it is known that little additional improvement in strength often is observed when the addition amount is increased above about 1 to 2% [17, 22, 31, 75], which is a typical range for the adsorption capacity of papermaking furnish solids for additives like cationic starch.

In situations where the amounts of anionic colloidal materials in the furnish are relatively low, the effectiveness of cationic polyelectrolytes tends to be maximized when the macromolecules have a low, but finite cationic charge density [50, 69]. It has been reported that the dry strength of the paper increases with decreasing charge density of the polymer [76], presumably due to increased polymer-polymer interpenetration and due to increased viscoelastic losses that occur during the rupture of the paper sheet under strain. For example, Park and Tanaka [50] found that a cationic acrylamide copolymer having a cationic charge density of 0.6 meq/g (approximately 10% charged groups) was more effective than a similar copolymer having a charge density about five times larger. Such results are also consistent with factors that maximize the adsorbed amount of cationic polymers onto negatively charged surfaces.

An opposite trend, but one which still is consistent with the importance of efficient adsorption of the polymer, prevails when the content of anionic colloidal materials in the furnish is high. Low-charge cationic polyelectrolytes products often show little benefit under such conditions. This loss of effectiveness has been attributed to neutralization of the cationic character before most of the molecules are able to attach themselves onto the fibers and other solids in the furnish [44]. By contrast, higher-charge cationic polyelectrolytes have been reported to have a greater tolerance for the same adverse conditions, consistent with a greater ability to adsorb.

Mechanical, chemical, and rheological (viscoelastic) contributions have been used to explain the way by which polyelectrolytes increase paper strength. Within each of these contributions there are various possible

interpretations, at the molecular level, for the role of polyelectrolytes and the mechanisms inherent to the development of adhesive forces. In any given case it is likely that several factors act simultaneously and therefore there is no way to arrive easily to clear-cut interpretations or cause-effect relationships. Here we will focus on only one such aspect that according to published evidence is judged to be essential for paper strength development, namely, the increase of adhesion due to chemical and physical bonding.

During the past years surface force measurements have been used to investigate the interactions between polyelectrolyte-coated surfaces in aqueous solutions [77–80]. From such studies knowledge has been generated pertaining the polyelectrolyte charge density [80,81], ionic strength [82–84], substrate characteristics [85–87], order of addition of polyelectrolytes, and other factors [88–89] that influence the adsorbed layer structure and the resulting surface forces. The shear forces between polyelectrolyte-coated surfaces have also been quantified [90]. Conversely, very little fundamental work has been done on the adhesion between polyelectrolyte-coated surfaces in air.

The theories explaining adhesion phenomena are often complex, as they usually relate the process of bond-forming and bond-breaking that are very different in nature [91]. Pioneering work by Johnson, Kendal and Roberts [92] and Derjaguin and collaborators established some basis for understanding the influence of molecular forces on adhesion between solid bodies, especially for the case of an elastic particle and a rigid substrate [93–97]. The effect of contact deformations on the adhesion of particles has also been considered [98]. Nevertheless, dissipation effects and rate dependent adhesion has been little discussed [99].

The case of adhesion between fibers with adsorbed layers of polymers is even more difficult to characterize and understand due to the complex nature of fiber surfaces (topography and chemical heterogeneity, etc.), let alone the case of fiber networks and composite structures in paper sheets.

For the reasons explained above, in this study we consider simplified (model) systems. By measuring interaction forces between polyelectrolyte-coated surfaces, we aim to obtain data that enables us to better interpret the adhesion forces in papermaking systems. The measurements were conducted with the surface force apparatus and the atomic force microscope. Since the adhesion in air between surfaces depends on the atmospheric conditions such as the relative humidity or the presence of organic vapors [100], we worked under controlled humidity and temperature conditions.

The effect of the polyelectrolyte charge density on the development of adhesion was the focus of our experiments. The adhesion forces between two polyelectrolyte-coated surfaces and between one polyelectrolyte-coated

surface and one bare surface were measured, and issues related to interaction forces after multiple surface contacts were also considered.

## MATERIALS AND METHODS

The polyelectrolytes used in this investigation were random copolymers of uncharged acrylamide (AM) and positively charged [3-(2-methylpropionamido)propyl] trimethylammonium chloride (MAPTAC). By balancing the ratio MAPTAC/AM in the (radical) copolymerization process, macromolecules with different charge densities (percentage molar ratio of cationic monomers) were synthesized and kindly provided by the Laboratoire de Physico-Chimie Macromoléculaire (Paris). In Table 1 a list of the studied polyelectrolytes along with their charge densities (or cationicity,  $\tau$ ) and molecular weight is provided. For convenience, the polyelectrolytes are referred to as “AM-MAPTAC-X” where X is a number which indicates the respective percentage charge density (e.g., AM-MAPTAC-100 is poly(MAPTAC), with no AM units). Note that in this study both low and high charge density polyelectrolytes were considered.

**Table 1** Charge density ( $\tau$ ) and molecular weight of the investigated polyelectrolytes

Polyelectrolyte	$\tau$ , %				MW, mol/g
	Theoretical	Elemental Analysis	Potentiometry	NMR	
AM-MAPTAC-1	1	0.5	1	–	900 000
AM-MAPTAC-10	10	10	9	8.9–9.5	1 000 000
AM-MAPTAC-30	30	31	31	24.2–25.6	780 000
AM-MAPTAC-100	100	99	95	–	480 000

### Substrate preparation

Muscovite mica from Reliance Co. (NY) was used as substrate. Before any experiment, pieces of mica were cleaved several times on both sides in a laminar flow cabinet until an adequate thickness was obtained. All the employed tools were previously cleaned and protective clothing and gloves were worn to minimize contamination of the high-energy mica surfaces.

Adsorption of the studied copolymers of AM-MAPTAC onto oppositely charged mica planar surfaces was allowed in aqueous solutions at pH 5 at

20 °C. In a typical experiment an aqueous solution of the polymer (at 0.1 or 20 ppm concentration) was freshly prepared by dilution with pure water of ca. 700 ppm polyelectrolyte stock solution. Freshly cleaved mica pieces (5 × 2 cm) were then immersed in the solution (contained in a 25 mL glass beaker) for ca. 6 h during which equilibrium adsorption is reached. At the end of this period the substrate was withdrawn from the polymer solution and immersed in a large vessel filled with pure water in order to remove any non-adsorbed polymer. Previous studies have demonstrated that the polyelectrolytes adsorb strongly to most oppositely charged surfaces (e.g. silica, mica, gold) and that no detectable desorption takes place upon immersion of the polyelectrolyte-coated substrate in pure water [81, 87, 101, 102]. To reduce the risk of Langmuir-Blodgett deposition at the three-phase line, the respective liquid surface was aspirated (using a Pasteur pipette connected to a water-jet pump) prior to any substrate transfer between the air and the liquid phases. Finally, the substrate was placed vertically inside a glass hood in a laminar flow cabinet and left to dry overnight. The water used in all experiments was obtained by using a Milli-Q Plus 185 unit.

### **Atomic force microscopy**

Imaging of adsorbed polymer on mica was accomplished by using a Nano-scope III MultiMode™ scanning probe microscope (Digital Instruments, Santa Barbara, California). The tapping mode imaging technique was used to study the sample's topography by probing the surface with an oscillating tip. In this mode a piezo stack excites a cantilever vertically, causing the tip to oscillate near its resonant frequency [103]. Close to the sample surface the tip tends to be deflected due to its interaction with the surface material. However, the amplitude of the oscillation is kept constant by a feedback loop that adjusts the vertical position of the sample (using a piezoelectric tube on which the sample is mounted). The vertical position of the scanner (z) at each (x,y) location is thus used to reveal the topographic image of the sample surface.

The probe used in the experiments consisted of 125 μm-length, single-beam cantilever and a tip (5–10 nm nominal radius of curvature) as an integrated assembly of single crystal silicon produced by etching techniques (TappingMode etched silicon probe model TESP). The spring constant and resonant frequency are reported by the manufacturer to be 20–100 N/m and 290–346 kHz, respectively.

Before imaging, the substrate was cut and gently pressed onto a sticky tab on a 15 mm diameter metal disk that then was attached to a magnetic sample holder on the piezoelectric scanner (Model AS–12V, “E” vertical MultiMode

SPM scanner). The polyelectrolyte-coated surfaces were imaged in dry air, since the use of ambient conditions may introduce a layer of adsorbed water molecules on the sample surface that gives rise to extra capillary forces between the tip and the sample (which may interfere with the AFM experiment) [104, 105]. In order to achieve controlled relative humidity and temperature, nitrogen from a humidity generator (Model RH-100, VTI Corporation) was flowed continuously through the instrument head (where the sample and probe are enclosed). The temperature and relative humidity were set in all cases at 20 °C and ca. 0 %, respectively.

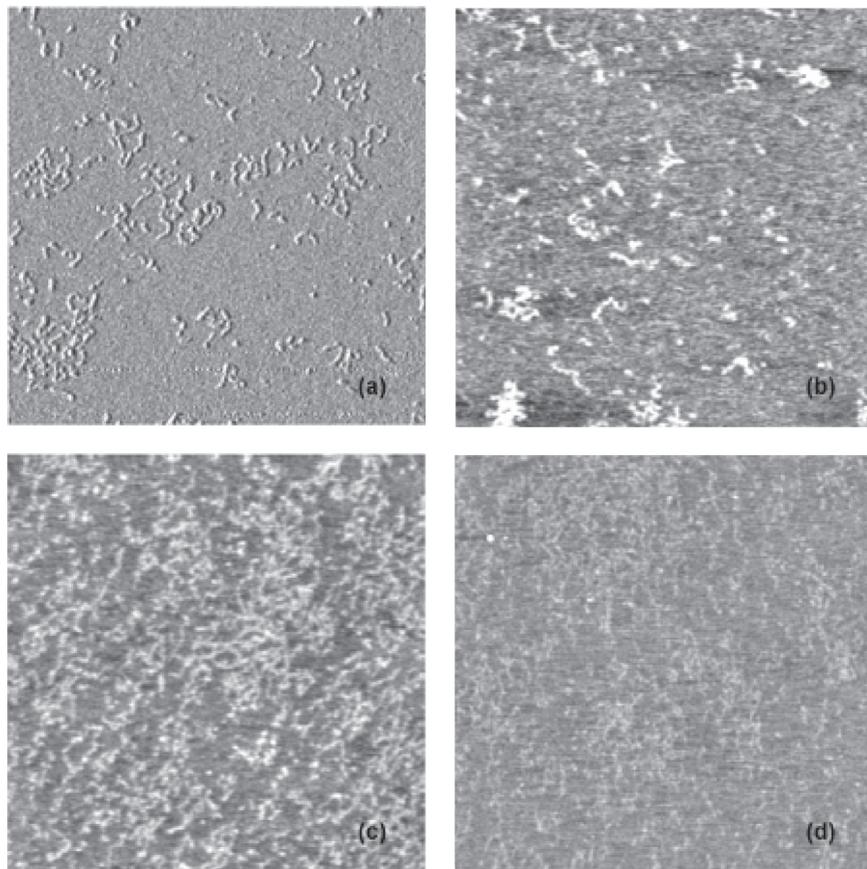
### **Surface force apparatus, SFA**

A surface force apparatus, Mark II model [106], was used for the measurement of adhesion forces. The mica substrate surfaces were glued onto optically polished half cylindrical silica discs using Epon 1004. The surfaces were mounted in the measuring chamber in a crossed cylinder configuration and the adhesion force and zero contact was determined. The measured force in crossed-cylinder geometry is, according to the Derjaguin approximation [107], equivalent to the force between a sphere (with the same radius as the geometric mean of the cylinder radii) and a flat surface, provided that the radius of the surfaces ( $\approx 2$  cm in our set-up) is much larger than the range of the surface forces. This condition is fulfilled in our setup.

The relative humidity in the measuring chamber was controlled to be close to zero by placing a beaker with  $P_2O_5$  within the sealed chamber. Next, the surfaces were removed from the measuring chamber and immersed in a beaker containing an aqueous 20 ppm polyelectrolyte solution and no added extra salt. The polyelectrolyte was allowed to adsorb for one hour before the surfaces were transferred into a beaker of water and then immediately removed and dried with a gentle stream of dry nitrogen gas. The samples were remounted in the measuring cell and allowed to equilibrate with the  $P_2O_5$ -dried atmosphere for 30 minutes prior to determination of the adhesion force. To avoid excessive shearing a relatively stiff double cantilever spring was employed. The spring constant, ca. 7500 N/m, was accurately determined after each experiment. The surfaces were separated slowly, and the negative load was increased step-wise until the surfaces jumped apart. Thus, unlike Ruths and Granick [108] in their work on surfactant and polymer coated surfaces, we did not attempt to study the effect of the rate of separation on the adhesion force.

The surface separation and the shape of the surfaces were determined using white light interferometry. White light is directed perpendicularly from below towards the surface, and multiply reflected between the silvered

backsides of the mica surfaces. Only wavelengths that interfere constructively will be able to exit from the optical cavity. Fringes of equal chromatic order, FECO, are generated and analyzed in a spectrometer. From the shape and the position of the FECO the surface separation and the shape of the surfaces can be determined.



**Figure 1** Tapping mode image (0%RH) of adsorbed polyelectrolyte on mica after equilibrium adsorption in 0.1 ppm bulk polymer concentration (scan range  $1 \times 1 \mu\text{m}^2$ ): (a) AM-MAPTAC-100; (b) AM-MAPTAC-30; (c) AM-MAPTAC-10; (d) AM-MAPTAC-1.

## RESULTS AND DISCUSSION

### Polymer adsorption

Tapping mode AFM images in air of adsorbed copolymers of AM and MAPTAC on mica from solutions with polymer concentration of 0.1 ppm are shown in Figure 1. The low polymer concentration used in these experiments was chosen so as to avoid surface saturation and allow the resolution of “individual” adsorbed polymer chains. From large scan images it was noticed that the AM-MAPTAC-100 polymer adsorbs uniformly on the mica surface. However, as the polyelectrolyte charge density was reduced, the number density of adsorbed molecules increased and some “aggregates” (or “patches”) of polymer molecules were formed. The measured apparent chain thickness of ca. 0.2–0.7 nm is in agreement with a very flat adsorbed layer structure. Furthermore, it was noticed that the AM-MAPTAC-1 copolymer has a smaller “thickness” (ca. 0.2 nm) compared to that of AM-MAPTAC-100 (ca. 0.5–0.7 nm). This observation is consistent with a “bulkier” AM-MAPTAC-100, as anticipated from the molecular structure of this polymer.

The increase in the adsorbed amount for polymers of lower cationicity is explained by the fact that in such cases more polymer units are needed to compensate the surface charge. This observation is corroborated by XPS quantitative measurements on similar systems [81] (see Figure 2). We note that when surface forces are measured, the polyelectrolyte-coated mica surface appears uncharged at a given polyelectrolyte concentration, even though experimental results clearly show that the charges of the adsorbed polymer, for the low charge density polyelectrolytes, are not sufficient for neutralizing the mica lattice charge. The reason is that small ions, mainly  $\text{H}_3\text{O}^+$ , are also adsorbed to the mica surface. The ion exchange occurring upon polyelectrolyte adsorption can be quantified by considering the charge neutralization condition:

$$\sigma_0 + \sigma_p + \sigma_s + \sigma_d = 0 \quad (1)$$

where

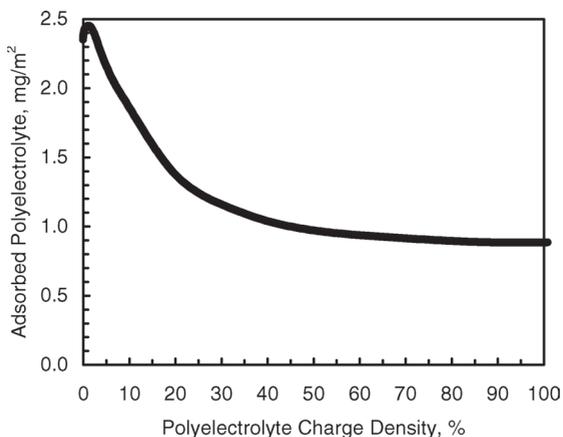
$\sigma_0$  = the lattice charge of mica, 0.338 C/m<sup>2</sup>,

$\sigma_p$  = the charges of the adsorbed polyelectrolytes,

$\sigma_s$  = the charges due to the presence of small ions in the adsorbed layer and

$\sigma_d$  = the net charge in the electrical double-layer, which is close to zero after polyelectrolyte adsorption.

From measured double-layer force before adding the polyelectrolyte it is possible to determine the effective mica surface charge. In 0.1 mM KBr one

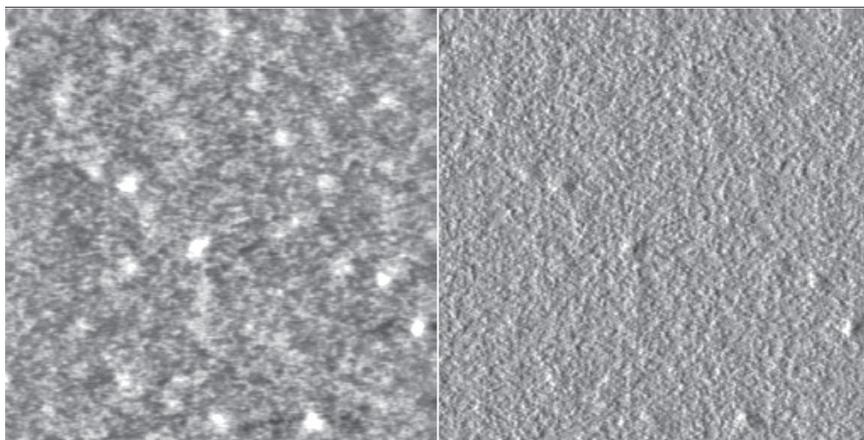


**Figure 2** Plateau adsorbed amount for copolymers of AM-MAPTAC of different charge densities on mica.

typically obtains a value of  $0.004 \text{ C/m}^2$ . The difference between the mica lattice charge and the effective charge is due to small ions accumulated next to the surface.

In all cases adsorption of the cationic polyelectrolyte resulted in desorption of small cations from the mica surface, and more so the higher the charge density of the polyelectrolyte. Further, in the case of AM-MAPTAC-100 some negatively charged ions (counterions to the polyelectrolyte) are incorporated in the adsorbed layer. This is a result of the recharging of the surface. Similar analyses of the ion exchange occurring at the solid-liquid interface due to protein adsorption have been carried out by Norde and Lyklema [109–110] and by Blomberg et al. [111].

One of the tapping mode images (for adsorbed AM-MAPTAC-10 on mica) after equilibrium adsorption at a higher polymer concentration (20 ppm) is displayed in Figure 3. It is evident that at this concentration the surface became almost fully saturated and inter-chain and intra-chain entanglements took place. It was observed that at high charge density the polymers adsorbed more uniformly, whereas at lower charge densities more disordered structures were predominant. Thus, the presence of polymer aggregates or “patches” occurs more often as the charge density is reduced.



**Figure 3** Tapping mode image (0%RH) of adsorbed AM-MAPTAC-10 polyelectrolyte on mica after equilibrium adsorption in 20 ppm polymer solution (scan range  $1 \times 1 \mu\text{m}$ ). Left: height images. Right: phase image.

### **Adhesion measurements in dry air**

For soft, large, homogeneous and elastic surfaces in a crossed cylinder geometry the pull-off force ( $F$ ) normalized by the geometric mean radius ( $R$ ) is related to the interfacial energy ( $\gamma$ ) as [92]:

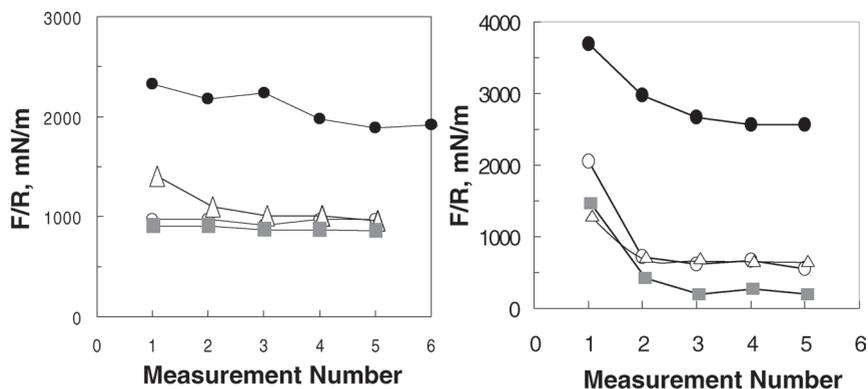
$$F/R = 3\pi\gamma \quad (2)$$

where it has been assumed that the contact between the surfaces is ideal, i.e., not associated with any excess free energy (e.g., due to surface roughness). This last assumption is hardly ever valid, and even for such smooth substrates as mica the pull-off force reported in the literature varies considerably [112]. This is partly due not only to the fact that the relative orientation of the mica crystal in the two surfaces plays a role [113], but also due to adsorption of water vapor and small amounts of other contaminants [112]. Further, Equation (2) is valid only under equilibrium conditions, i.e. rate-dependent viscoelastic effects invalidate the equation. We note that the setup used in the SFA consists of a layered system, glass-glue-mica, which complicates the adhesion mechanics as discussed by Sridhar et al. [114]. The normalized pull-off forces measured between mica surfaces in dry air in our laboratory typically falls in the range 800–1200 mN/m, consistent with the values reported by Christensson for the same conditions [112]. During the separation process the

contact radius,  $r$ , of the flat surface region decreases, and at the point of separation the value of  $r/r_0$  decreased to a value of 0.6–0.7, where  $r_0$  is the contact radius under zero load. This is in agreement with predictions based on the JKR-theory [92].

The normalized pull-off forces measured between two mica surfaces coated with a preadsorbed polyelectrolyte layer are shown in Figure 4 (left). The polyelectrolytes were adsorbed outside the measuring chamber, and therefore it was difficult to determine the absolute layer thickness with high accuracy (this is because the zero contact between the surfaces is determined on different positions). However, we observed the expected trend, i.e., a reduction in layer thickness with the adsorbed polyelectrolyte charge density ( $< 1$  nm for AM-MAPTAC-100 compared to 2–3 nm for AM-MAPTAC-1).

For AM-MAPTAC-100 the pull-off force measured during the first separation cycle was very large, 2300 mN/m, i.e., about twice as large as between the uncoated mica surfaces. This strong increase in adhesion cannot be explained by an increase in the van der Waals force, since the refractive index of mica is higher than that of the polymer. We suggest that the reason for this



**Figure 4** The normalized pull-off force as a function of the number of times the surfaces have been separated from each other at a given contact spot. The measurements were carried out in dry air. Filled circles represent AM-MAPTAC-100, open circles AM-MAPTAC-30; filled squares AM-MAPTAC-10 and, open triangles AM-MAPTAC-1. The plots on the left correspond to symmetric cases, i.e., represent the situation with both mica surfaces being coated by a layer of the respective polyelectrolyte and the plots on the right represent the asymmetric cases, i.e., pull-off forces between one mica surface coated with cationic polyelectrolyte and one bare mica surface. In all cases the polyelectrolytes were adsorbed from a 20 ppm aqueous polymer solution.

higher adhesion is bridging, i.e. once the surfaces are in contact the conformation of the adsorbed polymers may change to allow the segments of the same polymer to bind to both surfaces. This change in conformation is entropically driven. We note that the charges on the MAPTAC-polymer are located 0.7–0.8 nm away from the backbone, and by a simple rotation the charged groups may change their position in space by 1.5 nm. This flexibility is likely to facilitate the bridging process.

When the pull-off force is measured repeatedly at one and the same contact position, a decrease in adhesion with the number of measurements is observed. However, for AM-MAPTAC-100 the adhesion force remains high, and the lowest value obtained, after 10 measurements, was 1700 mN/m (data not shown). The decrease in adhesion force is interpreted as an indication that some polymer molecules are stretching out during the separation process. When the bridges are broken, the polyelectrolytes collapse back onto the surfaces but they are unable to find an equally flat conformation as prior to separation (a slight increase in layer thickness, by some 0.5–1 nm is observed). The increased layer thickness makes formation of bridges slightly more difficult during the subsequent contact, which explains the reduction in adhesion force. Upon separation the radius of the contact region decreased until  $r/r_0$  was in the range 0.65–0.75, which is slightly larger than the value of 0.63 expected from JKR-theory. It was also noted that the contact area did not shrink in a continuous fashion with increasing negative load, but rather the contact radius decreased in a stepwise fashion related to stick-slip friction behavior and adhesion hysteresis [115].

Additional experiments were carried out using one mica surface coated with the polyelectrolyte and one bare mica surface (Figure 4, right). For AM-MAPTAC-100 the pull-off force measured during the first separation is very high, about 4000 mN/m. The large value of the adhesion force is explained by extensive bridging between the polyelectrolyte-coated surface and the bare mica surface. Again, the adhesion force decreased with the number of contacts and reached a plateau value of 2600–2700 mN/m and the layer thickness increased by 0.6–0.8 nm. These results give strong support for the view that as the surfaces are separated, polymer molecules are transferred from the polyelectrolyte coated surface to the initially bare surface, and as a result the number of bridges formed is reduced. We note, however, that the adhesion force remained higher than that between two mica surfaces coated with AM-MAPTAC-100,. Therefore, it is clear that the surfaces should be less than fully covered with polyelectrolytes for maximum adhesion.

The pull-off forces for AM-MAPTAC-30 (symmetrical case) was significantly smaller than for AM-MAPTAC-100 and it was independent of the number of measurements at a given spot. This indicates that the number of

bridges formed was significantly less and thus the layer was not disturbed by the measurement. This observation can be explained by the fact that less charged segments were present and that the uncharged segments constituted a steric barrier counteracting the reformation needed in order for a polymer chain to cross from one surface and bind to the other. In fact, the adhesion force observed between AM-MAPTAC-30 coated mica surfaces was rather similar to that between two bare mica surfaces, indicating that the van der Waals forces were sufficient to account for the observed adhesion. We note that the contact radius of the flat region decreased until the ratio  $r/r_0$  reached a value of 0.7–0.8, at which point the surfaces jumped apart. This is slightly larger than predicted by JKR-theory. One may speculate that this is due to the discontinuous decrease in contact radius during the separation process and thus related to stick-slip friction.

For the AM-MAPTAC-30 asymmetric system (Figure 4, right) the adhesion during the first separation was significantly higher, 2200–2100 mN/m, than between two AM-MAPTAC-30 coated surfaces (symmetric case). This demonstrates that a significant number of bridges were formed. The pull-off force after several contacts was lower for the asymmetric case compared to the case of two AM-MAPTAC-30 coated surfaces. When inspecting the FECO fringes after the first separation it was noted that the contact region no longer appeared absolutely flat. Clearly, the redistribution of polyelectrolytes between the two surfaces resulted in formation of a less homogeneous coating, and the increased surface roughness contributed to the relatively low value of the adhesion force. The value of  $r/r_0$  decreased to a value of 0.6–0.4, slightly lower than expected by JKR theory. The tendency was that the contact radius decreased to lower values with increasing number of separations, i.e. with increasing roughness of the polymer layer. A smaller than expected contact radius at the point of separation in air has also been observed for surfaces coated with uncharged polymers.

The results for AM-MAPTAC-10 were qualitatively similar to those obtained for AM-MAPTAC-30. In the symmetrical case the adhesion forces were lower than those observed for the polyelectrolytes of higher charge density, i.e., the bridging mechanism became less important as the charge density of the polyelectrolyte is decreased. The decrease in contact radius prior to the jump out was found to be consistent with predictions of the JKR-theory for the symmetric system. However, for the asymmetric system it was observed that, just as for AM-MAPTAC-30, the contact became less homogeneous with increasing number of contacts and the value of  $r/r_0$  decreased to lower values than expected from JKR-theory.

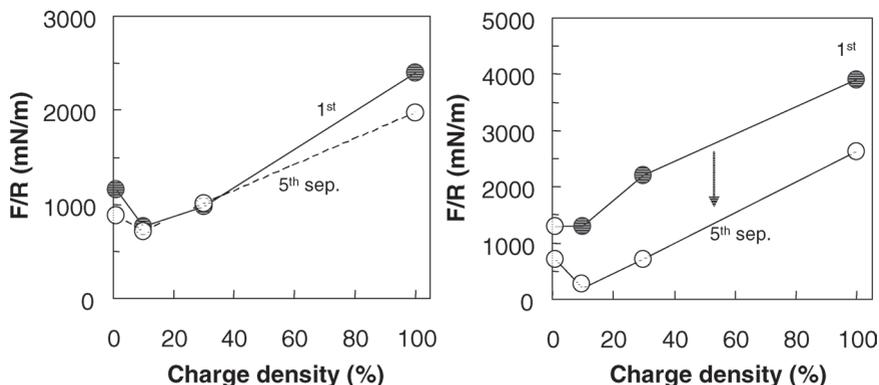
For the symmetric case of AM-MAPTAC-1 we observed an adhesion force that was significantly larger than for the case of AM-MAPTAC-10. Further,

a slight decrease in the pull-off force with increasing number of separations was observed. The decrease in adhesion force was accompanied by an increased inhomogeneity of the contact region. Clearly, unlike the situation with AM-MAPTAC-30 and AM-MAPTAC-10, but similarly to AM-MAPTAC-100, we now have material transfer between the two surfaces. Due to the low charge density of the adsorbed polymer, this cannot be explained by formation of electrostatic bridges. Rather we suggest that the layer for the low charge density AM-MAPTAC-1 is less compact than for the other polymers. This promotes the possibility of chain interpenetration and entanglement between the two polymer layers. During the separation process, even though it is carried out slowly, the polymer layers do not have time to disentangle but the chain interlocking contributes to viscoelastic losses that increase the measured adhesion. The resulting material transfer process is facilitated by the relatively low affinity between AM-MAPTAC-1 and the mica surface due to the low number of electrostatic bonds between the surface and the polyelectrolyte.

For the asymmetric system, AM-MAPTAC-1 coated mica vs. bare mica, the adhesion during the first separation is lower than for the other polyelectrolytes. This observation is consistent with a lower number of electrostatic bridges formed. However, material transfer still did occur due to attractive interactions between the uncharged acrylamide segments and the bare mica surface. This was clearly observed as an increase in layer thickness and a less homogeneous contact region with increasing number of separations. The adhesion force after the first separation was higher than between one AM-MAPTAC-10 and one bare mica surface. We attribute this to an increased importance of viscoelastic losses due to chain entanglement.

The effect of charge density on the adhesion between one polyelectrolyte-coated surface and one bare mica surface is summarized in Figure 5 (lower curves). In this case the adhesion between the two surfaces decreased with the number of contacts for all polyelectrolytes studied, and this is attributed to material transfer from the polyelectrolyte-coated surface to the initially bare surface. We further suggest that the relatively low decrease in adhesion force for polymer of low charge density is due to a relatively large contribution of polymer entanglements to the adhesion force.

We note that in our experiments the polyelectrolyte with the highest charge density increased the adhesion in air the most whereas the opposite trend is observed when polyelectrolytes are used as dry-strength additives. This may be due to several effects. First the charge density of mica is larger than that of the pulp fiber, which leads to a decreased importance of electrostatic bridges in the latter case. Further, in our case the polyelectrolyte layer was preadsorbed and the surfaces dried before they were brought into contact. On the



**Figure 5** The normalized adhesion force between two polyelectrolyte-coated surfaces (symmetrical case, upper graph) and between one polyelectrolyte-coated surface and one bare mineral surface (asymmetrical case, lower graph) measured during the first (filled circles) and fifth (open circles) separation as a function of the charge density of the polyelectrolyte. The polyelectrolytes were adsorbed from a 20 ppm aqueous polymer solution.

other hand, in real papermaking systems these additives are added to the paper furnish (fiber suspension) which is subsequently dried in the drier section (after water removal in the forming and press sections). Thus when paper is made the fibers are dried in a condition of close proximity between each other due to surface tension and capillarity effects. In this case there are much larger chances for the adsorbed polymer layers to interpenetrate and interlock. As a result, the viscoelastic losses during the eventual course of paper rupture are expected to be much larger in the latter case.

Such experiments can also be carried out with the surface force apparatus, and we note that studies with the SFA have shown that the adhesion between model cellulose surfaces that are brought into contact in water and subsequently dried is larger by a factor of three than the adhesion between dried cellulose surfaces [116]. This is due to increased chain interpenetration that increases the viscoelastic losses occurring during the separation process.

In the case of fibers unrecoverable energy loss accompanying cycles of straining and release has been attributed to bond breakage and elastic effects in the vicinity of local detachment sites [117]. The loss was found to be proportional to changes in the optically bonded area. Though such evidence is consistent with the proposed mechanism, a very high proportion of the energy required to break a sheet of paper is consumed in stretching and

bending of fibers, and most of this energy is completely lost when rupture occurs. Such elastic energy, which gets released during local detachment events when paper is stretched, has the potential to distort any analysis of the contribution of dry strength additives to inter-fiber bonding energy.

### **Effect of the surrounding medium**

There are several molecular contributions to the adhesion force. The van der Waals attraction is always present, and this force contribution is about a factor of five larger in air than in water. This is a consequence of the fact that the difference in dielectric properties of the surface and air is larger than between the surface and water.

A second contribution comes from formation of electrostatic surface-polyelectrolyte-surface bridges. This effect increases with the number of bridges formed and the strength of each bridge. Since the electrostatic force is reduced when the dielectric constant is increased, the strength of each electrostatic bridge will be higher in air than in water. On the other hand, the mobility of the polyelectrolyte chain will be higher in contact with water as compared to the case of contact in air, which may favor formation of more bridges in water. Furthermore, the polyelectrolyte layer swells in water and this will oppose the formation of surface-polyelectrolyte-surface bridges.

A third contribution arises from bridges formed by uncharged segments. This contribution is considerably smaller in water since in this case both the surface and the acrylamide units have to be dehydrated in order to form a mica-acrylamide bond.

A fourth contribution arises from entanglement effects. The more open layer structure in water favors chain interpenetration, but it also makes it easier for the chains to disentangle during the separation process. It is difficult to a priori state if this effect will be more important in water or in air since (in an intricate way) it will depend on the structure of the polyelectrolyte layer, chain relaxation rate and the deformation rate during rupture of the adhesive joint. Some recent work on uncharged polymers has shown that the solvency of the polymer chain greatly influences the role of chain interpenetration for the adhesion between polymer-coated surfaces in liquid media [99, 118].

The experimental observation is that the adhesion force is significantly stronger in air than in water, much more so than expected from consideration of only van der Waals forces. This is the case also for hydrophilic surfaces such as mica without any polymer coating, and this is related to the hydration of the surface that reduces the interfacial tension. The adsorption of AM-MAPTAC-100 on mica surfaces increases the adhesion force in water significantly, and this has been related to bridging [82]. However, the adhesion

between AM-MAPTAC-100 coated surfaces in air is significantly stronger, providing evidence that this force contribution is even stronger in the low dielectric media due to the increased strength of each electrostatic bridge.

The adhesion force in water, just as in air, decreases with decreasing poly-electrolyte charge density. This is partly due to a decreased importance of electrostatic bridges but also due to the development of a steric repulsion between the surfaces in water as the charge density of the polyelectrolyte is decreased. This, in turn, is related to the hydration of the polymer segments for which water is a good solvent.

### **Relevance to papermaking**

In this study we have employed a model substrate, mica, to mimic a much more complex material, such as cellulosic fibers. Even though some conclusions were derived, all of which are relevant in explaining the molecular mechanism of adhesion in papermaking system, any generalization should be carefully examined. There are obvious differences between the two substrates in terms of surface chemistry, topography, charge density, etc. Though the surface charge density of untreated papermaking fibers is not large [119–120], it still is useful to consider the fiber surfaces as a layer of hydrophilic, weakly negative polymers, which include tails or strands of polymer (the microfibrils) extending outwards into the solution [121]. In view of the issues explained before, it is apparent that dry strength additives present distinctive characteristics depending on the system. Some key effects typical of fiber furnishes will therefore be considered below.

The first point that needs to be stressed is the fact that in the use of polymers in papermaking, one of the major contributions to paper strength is the reinforcement and creation of bonds, as explained below. This is indeed closely related to the observations made in this study where non-electrostatic and electrostatic effects were analyzed. Changes in light scattering accompanying straining of paper have been found not to be affected by the presence of dry strength additives. The overall results suggested that these additives had its major effect on bond strength per unit of optically bonded area. Some studies related to the Page equation and the effect of dry strength additives [26] report that cationic starch additives result in a relative increase of about 40 to 50% in tensile strength in the case of unbeaten bleached kraft furnish. However, the corresponding optical analysis showed relatively little change in bonded area. In approximate terms, the cationic starch addition increased the resulting RBA value only by about 5 to 15%. One of the earliest attempts to quantify different contributions to the bonding effect of a natural gum, using the concept of relative bonded area, concluded that 60% of the

strength gain was attributed to increased bond strength, 25% to improved formation, and 15% to an increased “number of bonds” [56]. Though the definitions used in this study obviously did not conform to later conventions, the “number of bonds” term appears to represent something roughly equivalent to *RBA*. Additional reports also conclude that the effects of starch were due to changes in *bond strength per unit of bonded area* [23].

It is worth noting that many of the most effective and widely used dry strength additives have a low to moderate level of charged groups within their structure. The complexities of polyelectrolyte interactions with kraft fibers were more fully revealed by a recent work [69], that evaluated the adsorption and the dry-strengthening effects of sparingly cationic dextrans within the molecular mass range of 77,000 to about  $4 \times 10^7$  Daltons. Adsorption decreased strongly with molecular mass, consistent with the ability of smaller molecules to penetrate to a greater degree into pores in the cell wall. This effect was used to explain why, at fixed polymer dosage, dry strength improvements increased with molecular mass. However, it was also reported that the same “ultimate” tensile strength was obtained if the fibers were treated with sufficient cationic dextran, at each molecular mass, in order to compensate for the loss of lower-mass polymers into the interiors of the fibers.

One major contribution to paper strength that was not considered in this study is that of hydrogen bonding. Hydrogen bonding is widely accepted as a primary mechanism of bond development in paper [3]. The question is then what the situation is when a polyelectrolyte is added. The first type of evidence consists of the chemical composition of typical dry strength additives. As noted in the introduction, most commonly used polymers are hydrophilic, having a multiplicity of either  $-OH$  or acrylamide groups capable of hydrogen bonding. Presumably the opportunities for direct hydrogen bonding between the bare surfaces of fibers is more limited, compared to when polyelectrolytes are present. This is due to intra-molecular and intra-fiber hydrogen bonding, as well as the constraints of forming directional bonds directly between the cellulose surfaces, which can be expected to be less flexible in comparison to the adsorbed polyelectrolyte molecules in contact with aqueous solution. Additional evidence supporting the importance of hydrogen bonding when dry strength additives are used consists of the reversible nature of the polymer effects when paper is redispersed and formed again into paper.

When considering the effects of cationic polyelectrolytes, it is difficult to distinguish between the separate contributions to bonding effectiveness due to ionic bonding *versus* simply increased adsorption of the polymer resulting from charge interaction. For example, the most commonly cited reason to explain why cationization of starch increases its effectiveness is that cationic

starch retains well onto the fiber surfaces, thus increasing the opportunities for hydrogen bond formation [20]. The fact that there seems to be an optimum charge density of cationic starch to achieve dry strength [20] is consistent with this view, since it has been shown that polymer adsorption from aqueous solution onto a negatively charged surface, on a mass basis, usually is maximized at a relatively low, but finite level of cationic charge [122, 123].

At the other extreme of charge density, Linke [38] and others [124, 125] pointed out that highly charged cationic dry strength additives can be very effective in combination with fibers having a high negative surface charge density, *e.g.* unbleached kraft pulps. The systems reported in this experimental study perhaps are more representative of this latter case. However, the observation of a good performance at high cationicities could be also attributed to effects of colloidal anionic materials in the furnish. The colloidal materials are expected to neutralize cationic additives, especially those having a low charge density, so that they fail to adsorb efficiently onto fiber surfaces [125, 126].

One of the key elements that we used to explain adhesion in the studied systems was polymer interpenetration and bridging. Adhesion does not necessarily involve a “plane of contact.” Rather, one can consider a zone of interpenetration of macromolecular segments from each surface. Such interpenetration necessarily involves mixing between a surface phase and another phase, either that of an adjacent surface or an adhesive phase [4, 127–129]. In either case, the diffusion theory of bonding states that substantial adhesion between polymeric materials will occur only if there is significant intermingling by diffusion of molecular segments from both sides of the interface [128, 129]. Strong bonding tends to be found in those cases where the surface polymers not only have an optimum mobility (if the segments are too mobile, then interlocking during separation is reduced), but also in cases where there is an optimum affinity for the liquid phase (if the affinity is too high, then interpenetration is reduced due to strong polymer-polymer repulsion) [130].

Confirmation of the hypothesis that the inter-diffusion of surface polymers plays a dominant role in development of dry strength was provided recently by Pelton *et al.* [129]. Experiments were carried out with two water-soluble dextrans, both cationic, but one further modified to make it slightly hydrophobic. The two samples phase-separated in solution, showing their incompatibility. Some fibers were treated with one kind of additive, and others were treated with the other additive. Then the fibers were recombined in different ratios. Best adhesion was between like-treated fibers. Mixtures of fibers having differing hydrophobicity of their surface groups bonded more poorly, and the minimum strength was obtained at an intermediate composition of fibers treated in the two different ways.

In this study we considered the effect of van der Waal forces. Only in few reports van der Waal forces have been discussed (see for example [131, 132] and references therein), and in most cases this contribution is regarded as being too weak to make a difference in the development of dry strength. There is reason, however, not to dismiss dispersion forces. The dispersion component of force acts between all particles of matter and they tend to be especially relevant in the colloidal size range. This is important, since microfibrils at a fiber surface, filler particles, and macromolecules all can be considered colloidal in size.

To summarize, oppositely charged groups on a polyelectrolyte molecule and a surface with which it is interacting are predicted to contribute to formation of bonds, though the reasons for this contribution probably overlap several different concepts that have been mentioned.

## CONCLUSIONS

Strong adhesion forces were found for systems coated with polymers of the highest cationicity, and this suggests that electrostatic surface-polyelectrolyte-surface bridges are the cause of the adhesion. At low charge density another force contribution due to entanglement of polymer chains gives rise to a significant contribution to the adhesion force. The disruption of the contact leads to irreversible changes in the adsorbed layers when either the number of electrostatic bridges formed are large or when entanglement effects are important for polymers with a relatively low binding strength to the surface.

The decrease in contact radius during the separation process was in many cases consistent with the predictions of JKR-theory. However, a smaller than expected decrease was observed in some cases and related to stick-slip friction and adhesion hysteresis occurring during the shrinkage of the contact radius. For less homogeneous layers, such as those obtained after repeated separations, the contact radius shrank to lower values than predicted by JKR-theory prior to surface-surface separation.

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## Transcription of Discussion

# ON THE ORIGINS OF ADHESION IN PAPERMAKING SYSTEMS

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*Bob Pelton*

These dry adhesion measurements are made under conditions where the polyacrylamide is a brittle polymer. Do you know the glass transition temperature of these copolymers?

*Orlando Rojas*

No, I don't. We have not measured the glass transition temperature. I note that what we did in our experiments was to first adsorb the polymer on the solid surfaces (from aqueous solution) and then the surfaces were taken out, dried under N<sub>2</sub> jet (at room temperature) and then they were re-mounted in the instrument for further measurements in a "dry condition".

*Bob Pelton*

Well, let me just make a comment here about this. We have done a lot of work looking at charge density on dry strength and we think that quaternary ammonium groups have no positive effect on dry strength. I think what might be going on here is that the moisture content in your polymers, the tackiness of them will increase with the ionic content and you may just be looking at difference on water content and difference in tackiness. You are basically bringing a polymer melt up against a hard surface.

## Discussion

Orlando Rojas

Yes, that will be true in the case of, for example, fibres where capillary forces are important during drying. In our case, we actually did not follow the typical drying process as in a papermaking system (*e.g.* to dry the surfaces while in close proximity). We were looking to understand what the effect of polyelectrolyte charge density was in the dry condition (the surfaces were dried separately and then brought into contact). I want to stress that these measurements were performed under 0% relative humidity, so I don't think there was water in the interface even though we cannot rule out the presence of difficult-to-remove, hydration water. I am sure the effect that you have just mentioned is relevant in typical systems and is coupled with contributions from entanglement, bridging, van der Waal forces, *etc.* To decouple these contributions would require some more analysis.

### Added comment:

In contrast to the observation of increased tackiness with the ionic content we would like to point out that the PE with the lowest charge density (1%) produced higher adhesion than the PE of 10% charge density. This is in contrast to the mentioned higher tackiness with increased ionic content. On the other hand this fact tends to support the observation that the presence of quaternary ammonium groups is not a key factor in the development of dry strength. We could only find some indirect support for ionic bonding contributions to dry strength – but this effect is probably better explained in terms of the higher adsorption degree. Finally, we are not sure if we could interpret tackiness as a result polymer entanglement but certainly the two are very important and also interrelated. In passing we also note that the thickness of the polymer layer decreased with increasing ionic content.

Theo van de Ven      McGill University

In your force measurements with the SFA (surface force apparatus), you used a salt concentration, I believe of  $10^{-4}$  molar. In real papermaking the effective ionic strength is probably more than 100 times that value. Can you speculate what would happen to the forces between polyelectrolytes under conditions of much larger salt concentration?

Orlando Rojas

The reason why we used very low ionic strength (typically 0.1 millimolar as

shown in some of the curves presented before) is that we want to account for the double layer forces.

By adding a small but known amount of electrolyte (in this case just 0.1 *millimolar* that corresponds to a Debye length of 30 *nm*) we know what to expect if there is any electrostatic contribution. If we use high ionic strength we are going to see a suppression of the electrostatic forces (compression of the diffuse layer) and a very short Debye length. Therefore we would not be able to see the effects of electrostatics in the total interaction force profiles.

*Theo van de Ven*

Does that mean that electrostatics is unimportant in papermaking?

*Orlando Rojas*

It is definitely important, but what we have in real systems, where salt content is high, is that the double layer, electrostatic forces are very much diminished compared to other contributing forces. You can see, for example, that in the case presented before of the low charged polyelectrolyte, the ruling interactions were steric (repulsive) forces. These steric forces in our case extend up to a distance of 100 *nm*. Note: in other cases we observed electro-steric interaction forces and, for polyelectrolytes with high cationicity charge compensation, usually reduce the electrostatic contribution relative to the total interaction force profile.

*Lars Wågberg*      KTH

I want to ask a specific question about your polyelectrolyte adsorption data. You discussed the adsorption of cationic polyacrylamide on mica and you showed that, as we expect, there is a decrease in adsorption when the charge density of the polyelectrolyte increases, and the data hence appear as electrosorption. Then you mention that for the low-charged polymers, you only reduced the charges by about about 10%. Have you any explanation for that?

*Orlando Rojas*

Yes, for the low charge density polyelectrolyte, that is, for the 1% charge density polyelectrolyte we have the highest adsorbed amount but only 10% of the surface charge of mica is neutralised. The rest of the charges are neutralised by hydrogen ions present in solution. So what we have is an ionic

## *Discussion*

exchange process at the interface, between the cationic polymer and the adsorbed counterions. Now, why we have such a low degree of neutralisation is explained by the fact that we have a large amount of polymer in a loop-and-tail type of conformation where only a small fraction of the charged groups are effective in neutralising the surface charge. In other words, there are steric constraints for further cationic groups in the polyelectrolyte molecules to reach the surface.

*Glyn Jones*      *Arjo Wiggins*

You showed on one of your slides a preference for higher adhesion if you have less than 100% coverage, but then you went on to explain that, in an asymmetric system, you have material transfer, which will then, once you repeat the test, leave you with less than 100% transfer in the system. Why is it you did not get an increase in adhesion in that system?

*Orlando Rojas*

There is continuous reduction in the adhesion when we have material transfer because in this case we have a more uniform distribution of the polymer chains between the two surfaces. So, for further contacts between the surfaces, we have fewer chances for bridging bare spaces or bare patches in the two surfaces. If you compare the symmetric case with the asymmetric case, in all situations presented, you will see that the adhesion is larger (for first contact) in the asymmetric case. This observation supports the conclusion that less than full coverage is needed to improve bridging.