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The interactions of amphiphilic latexes with surfaces: the effect of surface modifications and ionic strength

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Abstract

The effect of surface modifications brought about by a polymeric stabilizer on the interactions between polymer colloid particles and various substrates in aqueous media are directly measured using atomic force microscopy. The interactions of polystyrene particles with grafted hydrophilic 'hairs' of hydroxypropyl cellulose (denoted HPC/PS), of molecular weight $\sim 10^5$, with mica, silica and graphite substrates are measured. HPC/PS is found to be compatibilized so that it will interact with both hydrophobic and hydrophilic substrates. The observed jump-to contact between HPC/PS and silica is characteristic of polymer solutions and is the result of the grafted hairy layer. Further direct evidence of HPC–substrate interaction is seen in a secondary adhesion with mica. The adhesion of the particles was found to follow the order silica > graphite > mica. The magnitudes of these interactions are rationalized in terms of the interactions of each of the substrate, core polymer and surface modification. It is concluded that the combined effects of surface roughness and hairy layer collapse due to compression give rise to the observed trend. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Adhesion; Surface interactions; Colloid probe atomic force microscopy

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1. Introduction

There is as yet insufficient fundamental scientific understanding of how the forces between latex particles and surfaces vary with particle coating (e.g. the presence of a polymeric stabilizer). Nevertheless, many commercial products such as water-based adhesives and paints rely on the interactions between coated colloidal particles and substrates for their properties. A better understanding of the effects of surface coatings on adhesive interactions would allow the continued development of existing products and also open the way to new products such as protective coatings suitable for use on seeds in broad-acre agriculture. This study extends recent work measuring the interactions that occur between individual latex particles and various substrates using atomic force microscopy (AFM) [1].

The direct measurement of the interactions between latex particles has recently been undertaken using AFM to assess the behavior of polymer colloids in relation to classical colloid theory [1]. Other studies have looked at the interactions between surfaces coated with adsorbed polymer chains [2–4], or a functional monolayer [5]. In contrast to many previous studies, the work reported here uses particles with known surface composition.

This study involves the measurement of adhesive interactions between a polymer colloid and silica, mica and graphite surfaces. The effect of ionic strength on the interactions was also determined. The observed adhesive interactions are rationalized in terms of the interactions observed in studies of other systems.

1.1. Adhesion theory

The interactions between surfaces in aqueous media are typically characterized by four distinct regions [2,5,6]: a region of zero force, a jump-to contact, a region of constant compliance and an adhesive hysteresis. Of particular interest in this study are the jump-to contact and the adhesive hysteresis. The jump-to contact is a result of the attractive forces between the surfaces becoming strong enough to give a region of mechanical instability, suddenly drawing the surfaces together. The adhesive hysteresis is due to the short-range forces between the surfaces holding the surfaces together as the separating force is increased. The peak

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force on pull-off (normalized by the radius of the particle), $F_{\text{pull-off}}/R$, is used as a measure of the adhesive strength.

It has been noted by other authors that the application of adhesion theory (in particular JKR theory [7]) has not been very successful in recent studies using polymer colloids [8,9]. The general format for the analysis follows a previously described technique [2,5,9,10], which may be reduced to the following equation

$$F^{\text{JKR}}_{\text{pull-off}}/R = -3\pi(\gamma_1\gamma_2)^{1/2} \quad (1)$$

where γ_i are the surface energies of the particle and substrate.

The influence of surface roughness has been cited as the primary reasons for the failure of this theory. Since the interactions are dependent on the radius of the probe, it is necessary that the radius be well characterized. If asperities are present on the surface then the effective radius may be greatly reduced; indeed differences of a factor of 50 between theory and experiment are not unusual [8,9]. Further, in a system with three phases (substrate, particle and water) the additional fluid–solid interfacial energies should be taken into account [10]. Consequently, the predicted values for $F_{\text{pull-off}}/R$ are often in error [8,9].

Other authors have noted that neither the magnitude of the adhesive interactions nor the relative strength of these interactions is correctly predicted by the application of JKR theory to similar systems [8].

1.2. Adhesive interactions of other systems

A number of useful results are available in the literature, although not necessarily derived directly from colloid probe AFM techniques.

1.2.1. Cellulose–cellulose interactions

Recent work by Rutland et al. [11], Carambassis and Rutland [12] and Holmberg et al. [13] with insoluble cellulose particles using AFM reported a jump-to contact attributed to protruding hairs.

The behavior of (soluble) HPC in water has been studied by viscometry by Suto et al. [14]. It was found that a 0.1 mol dm^{-3} NaCl electrolyte was a better solvent than water, implying that the chains would be more extended in solution than in pure water. Suto et al. [14] postulated that this effect may be due to reduced hydrogen bonding between segments of an HPC chain. The screening effect of the salt reduces the strength of hydrogen bonding interactions, allowing solvent–HPC interactions to dominate the inter-segment interactions, making the electrolyte a better solvent.

1.2.2. Polystyrene latex–latex interactions

There is considerable difficulty in obtaining data for the interactions of 'pure' polystyrene as initiator fragments are often present on the surface of the latex giving the particle either positive or negative charge.

The interactions between polystyrene latexes have been measured in previous studies [1,15,16]. These interactions were found to be dominated by surface charges at most separations, although some van der Waals attraction was observed at short distances. These short-range attractive interactions were observed as a jump-to contact in the AFM [1,15] and the formation of doublets in electrophoretic studies [16]. Longer-range interactions were also observed; however these were influenced by the presence of dissolved gases and vanished on thorough degassing of the solutions used [15].

1.2.3. Polystyrene–silica interactions

Direct polystyrene–silica interactions are difficult to measure as the charge–charge interactions usually associated with such measurements normally predominate, as seen, for example, in the preliminary work undertaken in this study. Eliminating the charge on a latex particle is quite difficult as a surface charge is usually imparted during synthesis, either by incorporation of charged initiator fragments or addition of an ionic stabilizer.

It is, however, possible to make uncharged polystyrene chains, if not an uncharged latex. This has been implemented in the adsorption of polystyrene onto silica from decalin solution [17] using a 'vinyl hexane' end group on the polystyrene chain. This study indicated that polystyrene had some affinity for the silica substrate, although it was easily displaced by contaminants.

Another study of the interactions between polystyrene and silica looked at the adsorption of polystyrene chains onto a porous silica gel [18]. It was found that the roughness of the surface had a large influence on the stability of the adsorption, which was attributed to chains becoming entangled inside the pores on the surface.

1.2.4. Polystyrene–graphite interactions

Work has been performed with polystyrene latexes and graphite substrates showing evidence of van der Waals attractions at short distances [19,20]. It has also been argued that direct π-orbital interactions between compounds with significant aromaticity can lead to attractive forces [21].

1.2.5. Polystyrene–mica interactions

The interactions between polystyrene and mica may be inferred from grafting experiments. In these experiments, an initiator group was substituted onto the mica surface and a polymer bead grown around the graft site [22,23]. It was seen in this experiment that the polystyrene does not wet the mica surface but remains roughly spherical until such time as the graft density is so high that a film is able to form. The implication of this observation is that the polystyrene–mica interactions are unfavorable in comparison to polystyrene–polystyrene interactions. Other studies have looked at the adsorption of polystyrene chains onto a mica surface [24,25]. As with the silica interactions, the use of a θ-solvent for the polystyrene was required to prevent mica–solvent interactions dominating.

Recent studies of polystyrene–mica interactions by Biggs and Spinks [9] have been performed using colloid probe AFM with large applied loads. The polymer colloids in these experiments were prepared using suspension polymerization; however no details of the initiator or stabilizer systems used or the nature of the particle surface were provided. While the results concerning the magnitude of the interactions cannot be used in this study, the effect of the higher loads used by the stiffer cantilevers (around 100 times stiffer than those used here) are quite useful.

The effect of the applied load was found to be quite significant [9]. This was justified by viscoelastic deformation of the polymer particle allowing the removal of asperities on the surface and increasing the contact area. Biggs and Spinks noted that a polystyrene particle under the loads used in this study would not undergo a viscoelastic deformation, thus making the effect of any asperities more significant to the measured interactions.

1.2.6. Influence of surface roughness

It is generally accepted that surface roughness, in particular roughness of the colloidal particle in AFM work, acts to reduce the adhesive interactions by reducing the effective contact area [8,9]. This reasoning is only applicable where the surfaces are rigid enough not to undergo significant deformation. The loads used in the experiments reported here are not sufficient to flatten the asperities in the substrates or in the polystyrene [8,26]. Using higher loads, e.g. with a stiffer cantilever [9], or a more easily deformable material will not reduce the contact area.

2. Experimental

Force measurements were undertaken using the technique of chemical force microscopy [5,27,28]. This involves attaching a single particle to the cantilever, using an adhesive and a micromanipulator. The polymer colloids were synthesized as part of this study using the technique of dispersion polymerization [29,30]. This polymerization technique synthesizes latex particles with a grafted polymeric stabilizer on the particle surface.

2.1. Dispersion polymerization

HPC/PS latexes were synthesized using a dispersion polymerization technique described by Lok and Ober [30]. Ethanol (absolute, CSR), 2-methoxyethanol (99.3%, Aldrich), hydroxypropyl cellulose (HPC, MW 100,000 nominal, Aldrich), styrene monomer (99% + , Fluka) and benzoyl peroxide were used as supplied. The HPC stabilizer (1.75 g) was dissolved in ethanol (175 ml) and 2-methoxyethanol (250 ml) under nitrogen in a 500 ml cylindrical reactor. The reaction mixture was held at 65 °C and stirred using an impeller stirrer at 300 rpm for 30 min. Benzoyl peroxide (3.0 g) dissolved in styrene (75 ml) was added and the temperature maintained for a further 2 h. At this time, the temperature was raised to 75 °C for a further 22 h. At the conclusion of the polymerization reaction, the particles were separated from the ethanol/2-methoxyethanol dispersant by centrifuging, before redispersing the particles in Milli-Q water (Millipore).

2.2. Surface preparation

Muscovite mica (Probing and Structure, Qld, Australia) and monochromator grade ZYH graphite (Advanced Ceramics, OH, USA) were cleaved immediately prior to use. Glass microscope coverslips (Mediglass, Australia) washed with copious amounts of Milli-Q water (Millipore) were used as the silica substrates.

2.3. Ionic strength effects

The ionic strength measurements were performed in KNO_3 (min. 99%, Merck) solutions freshly prepared with Milli-Q water (Millipore). A number of experiments were performed with each probe at different ionic strengths. The ionic strength was varied from 10^{-4} to 10^{-1} mol dm^{-3}.

2.4. Chemical force microscopy

The AFM used in this study was a Multimode AFM with a Nanoscope III controller (Digital Instruments Inc., Santa Barbara, CA, USA). An 'E' scanner (14 μm × 14 μm × 2 μm) was used for all measurements. All measurements were undertaken inside a commercially available fluid cell (Digital Instruments).

The cantilevers used in this study were silicon nitride type NP cantilevers (Digital Instruments). The stiff cantilevers (100 μm in length, nominal spring constant 0.58 N m^{-1}) were used for all experiments. The spring constant of the cantilevers was measured using the technique of Cleveland et al. [31]. Polymer particles (prepared as described before) were mounted on the cantilevers using the method described by Ducker et al. [2,32,33] using Epikote 1004 epoxy resin (Shell) to glue the particles to the cantilever tip. Colloid probes were examined by both optical and scanning electron microscopy (SEM).

The frequency at which force curves were collected was 1 Hz (the adhesive curve was found to be independent of the frequency of measurement from 0.1 to 10 Hz) and did not display large noise levels due to hydrodynamic drag [2,6,9,34]. Experiments were performed with a 600 nm scan size. The total deflection from initial contact to the maximum applied load was 200 nm, thus maintaining a systematic loading force and contact time across all experiments; these conditions were used because the adhesion may be a function of the applied force [9,34].

3. Results and discussion

3.1. Dispersion polymerization

The HPC/PS particles synthesized were found to be 6.4 μm in diameter (from optical microscopy and SEM). The particles were seen to be reasonably monodisperse in size. Although the surface roughness of these particles was not characterized by AFM, SEM images of the probes indicated that the surfaces were considerably smoother than those produced by suspension polymerization reported elsewhere [9].

For the hydroxypropyl cellulose (HPC) stabilized/styrene system used here, the actual species stabilizing the particles in the system is poly(styrene-*g*-HPC); it has been reported that under similar conditions, ~25% of HPC chains are grafted to the polystyrene substrate [35]. Furthermore, previous fluorescence quenching experiments indicated that only ~75% of the HPC chains associated with the particle are found on the surface of the particles [36]. The remaining chains are inaccessible to aqueous fluorescence quencher as it was imbibed into the particles.

Based on the nominal molecular weight of the HPC, the particle number, particle radius and above grafting efficiencies, it is possible to estimate the grafting density on the particles to be ~1 HPC chain per 7 nm^2 of polystyrene surface. It is reasonable to postulate that the deformable, gel-like nature of this coverage will allow polystyrene–substrate interactions when collapsed.

3.2. Observed particle–substrate interactions

Due to the action of strong, short-range forces, which are able to keep the probe in contact with the surface [5,10,27], an adhesive hysteresis was seen in the interactions between polystyrene and each of the three surfaces studied. Following the conventions of other authors [37], any data points collected in the regions of mechanical instability (the jump-to contact and the snap-off) were removed from the data sets.

As noted in previous studies [5], measurement of the magnitude of the adhesive interaction between self-assembling monolayers often gives variability. The force curves in this study, however, were seen to be reproducible between different samples of the substrate and different colloid probes.

3.2.1. Evidence for HPC–substrate interactions

The force curves seen in some of these experiments, as shown in Fig. 1, are similar to the secondary adhesion curves described by Senden et al. [37]. A secondary adhesion occurs when a chain is adsorbed to substrate in such a way that the chain must become quite extended before the effect of this adsorption is observed in the force curve [37]. The shape of the secondary adhesion curve is in good agreement with the previous work and the interaction is at a distance consistent with the extended length of a short HPC chain, calculated as described in a later section. The secondary adhesion with mica was observed in around 5% of interactions, but was not observed with graphite or silica substrates.

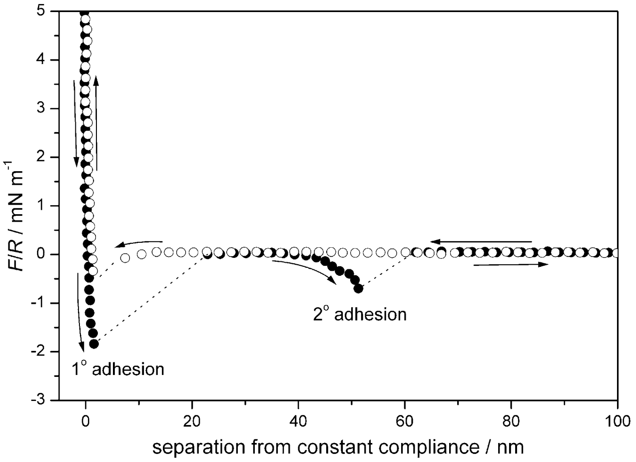

Fig. 1. The force/separation curves in a case where both a primary adhesion (marked 1° adhesion) and a secondary adhesion (marked 2° adhesion) interaction was observed. The approach curve (○) and separation curve (●) are shown, with dashed lines indicating sudden tip movements in regions of mechanical instability. This experiment was conducted with a HPC/PS probe on a mica substrate in 0.5×10^{-4} mol dm^{-3} $\mathrm{KNO_3}$ solution.

The presence of a secondary adhesive interaction presents direct evidence of the interaction of individual HPC chains with the substrate. This has important implications for the nature of the overall adhesive interaction and implies that apparently minor surface modifications are important to the adhesive properties of polymer colloids.

3.2.2. Particle–substrate interactions

Representative plots showing the relative magnitudes of the interactions with the different substrates are shown in Figs. 2 and 3. In these figures, the interactions between one particle and a number of substrates are shown. The interactions between the HPC/PS particles and a freshly cleaved muscovite mica surface were observed to be quite weak compared to the other interactions observed in this study.

The jump-to contact observed in the interactions with graphite indicates an attractive interaction exists between the surfaces at around 12 nm from initial contact (Fig. 2). The graphite substrate is significantly softer than the other materials used in this study, and in some experiments was damaged by the loads used.

The interactions between thoroughly washed glass and the HPC/PS particles were considerably stronger than those measured in any of the other experiments performed (Figs. 2 and 3). The large adhesion peak made it difficult to achieve both a large constant compliance region and also observe the entire retraction curve. It should be noted that the curvature in the retraction curve for the HPC/PS–glass interactions is in part due to non-linearity in the photodiode

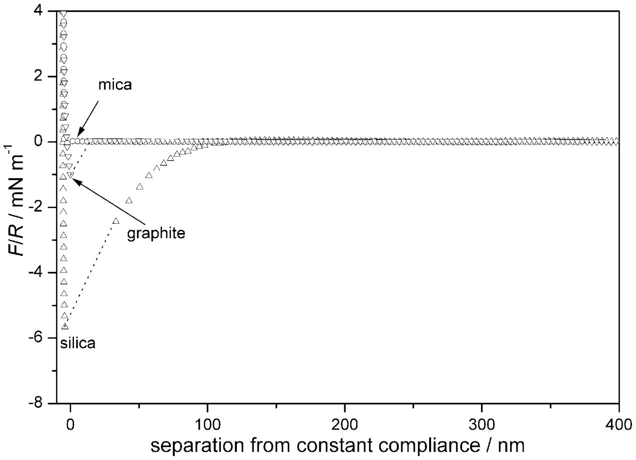

Fig. 2. The relative magnitudes of the observed jump-to contact between the HPC/PS particles and various surfaces in 0.5×10^{-4} mol dm^{-3} KNO_3 solution. The approach curves are shown for mica (○), graphite (▽) and silica (△), with dashed lines indicating sudden tip movements in regions of mechanical instability.

(the deflection here exceeds 10 V, pushing the limits of the instrument).

3.3. Effect of ionic strength on interactions

The HPC/PS particles are unusual in the context of current literature on polymer colloid AFM, as the particles do not have an inherent surface charge. This means that the interactions are not necessarily governed by the electrical double layer, but by the steric stabilizer and the bulk polymer. While some previous authors have seen repulsive forces from the compression of the electrical double layer when only one surface is charged, other authors have not observed such interactions [8]. In this study, such repulsive interactions were not observed.

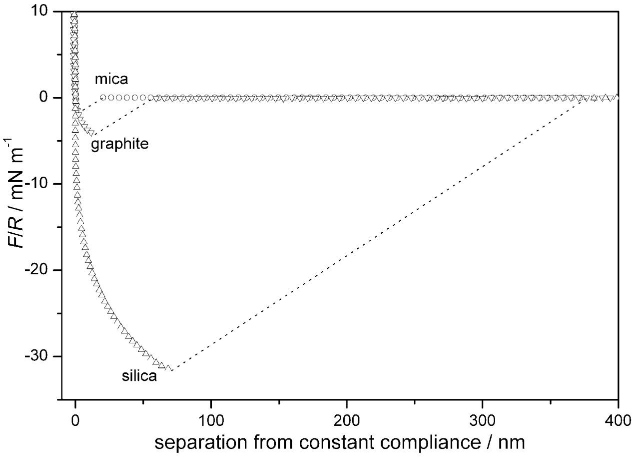

Fig. 3. The relative magnitudes of the observed adhesive interactions between the HPC/PS particles and various surfaces in 0.5×10^{-4} mol dm^{-3} KNO_3 solution. The separation curves are shown for mica (○), graphite (▽) and silica (△), with dashed lines indicating sudden tip movements in regions of mechanical instability.

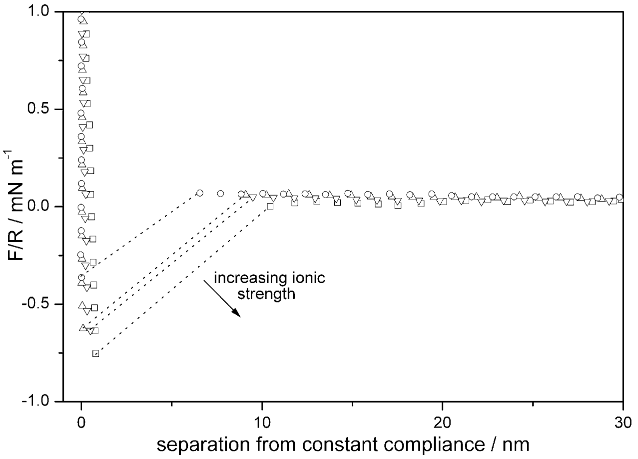

Fig. 4. The observed separation curves at ionic strengths 10^{-4} (○), 10^{-3} (△), 10^{-2} (▽) and 10^{-1} (□) mol dm^{-3}. All curves are for the interaction of HPC/PS particles with a mica substrate using a KNO_3 electrolyte. The dashed lines indicate sudden tip movements in regions of mechanical instability.

Figs. 4 and 5 show the effect of ionic strength (using KNO_3 as the electrolyte) on the interactions between the particles and a freshly cleaved muscovite mica surface for the separation curves. The attractive forces between the mica and the HPS/PS particle on retraction are seen to increase in their effective strength as the ionic strength is increased from 10^{-4} to 10^{-1} mol dm^{-3}. The data for the approach curves did not show any appreciable change in behavior that could be discerned above thermal noise in the measurements.

3.4. Understanding the interactions

3.4.1. Explanation of jump-to contact

The observed jump-to contact with the mica and silica substrates is easily explained in terms of the interaction of the HPC chains with the substrate. Since the HPC chains are tethered at one point along the chain, their motion in the water is perturbed. Once the chain comes into contact with the substrate the other end is fixed as well. Continued random motions of the chain cause additional segments to become adsorbed [38]. It is postulated that the mechanism for the chain adsorption to the substrate is hydrogen bonding with the oxide groups (such as silanol groups on silica) on the surface.

It is possible to estimate a lower bound for the distance the HPC chains extend into the solution using the random flight for perturbed polymer chains in solution [39]. It should be noted that the treatment described here is for *dilute* polymer solutions [39] but the surface density of HPC grafts (around 1 chain per 7 nm^2, as calculated before) makes this an unreasonable approximation.

The distribution function of end-to-end distances is given by Flory [39] as Eq. X.8 (equation numbers referring to Flory [39]), which has a maximum in hydrodynamic

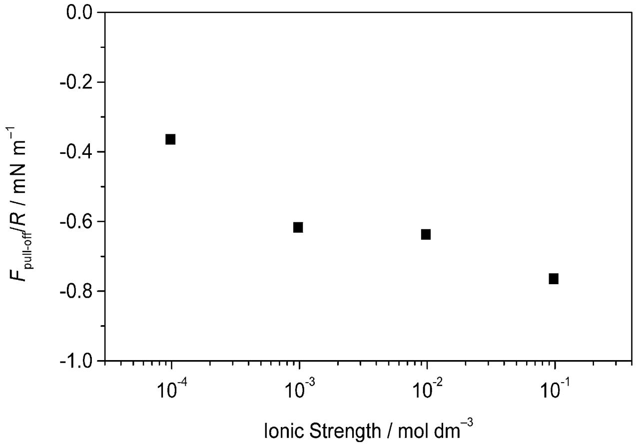

Fig. 5. The effect of increasing ionic strength on the separation curve for the interaction of HPC/PS particles with a mica substrate using a KNO_3 electrolyte.

diameter at $1/\beta$ (from Eq. X.14′) where β is the characteristic parameter of the Gaussian distribution. The parameter β is given by β_0/α (Eq. X.28) where α is the chain expansion coefficient, correcting the same parameter for an unperturbed chain, β_0. In turn, β_0 is related to the degree of polymerization and the length of the monomer unit (Eq. X.6):

$$\beta_0 = \frac{\sqrt{3/2}}{ln^{1/2}}. \tag{2}$$

The chain expansion factor, α, may be determined from the Mark–Houwink parameters using Eq. XIV.26 along with Sect. XIV-3c, which gives

$$\alpha^3 = \frac{[\eta]}{[\eta]_\theta} = \frac{K}{K_\theta} M^{a-0.5} \tag{3}$$

where K and a are the Mark–Houwink parameters for the polymer in the solvent used (in this case water) and K_θ is the Mark–Houwink parameter for the polymer in a θ-solvent at the same temperature.

As the required viscosity data for HPC are not available, the parameters for hydroxyethyl cellulose (HEC) and cellulosic polymers are used here, as shown in Table 1.

The calculated distribution of hydrodynamic diameters has a maximum of 21 nm and a standard deviation of 10 nm. From these calculations, it is reasonable to estimate that the HPC chains would extend up to ~50 nm into the water phase. As noted earlier, the HPC chains are not in dilute solution, hence excluded volume effects due to the interaction of neighboring HPC chains would tend to increase the penetration of the chains into the solution.

Table 1
The data used to estimate the HPC chain extension in water. In the absence of data for HPC, parameters used are for hydroxyethyl cellulose (HEC) and general cellulosic chains

Parameter	Value	Comment
Molecular weight	10^5	Nominal, as supplied
K (ml g^{-1})	9.53×10^{-3}	For HEC [40]
K_θ (ml g^{-1})	232×10^{-3}	For HEC [40]
a	0.87	For HEC [40]
l (nm)	0.79	For cellulose [39]

3.4.2. Explanation of adhesive interactions

Surface roughness and the interaction of the easily deformable hairy layer with the surface are important contributors to the adhesive interactions reported here. Other authors have noted that in the case of adhesion between hard surfaces, the effect of roughness is to reduce the effective contact area and so reduce the adhesion [8,9]. However, in this study, the hard polystyrene core has a significant layer of soft, easily deformable polymer around it in the form of the HPC layer. The effect of this layer is to *fill* the asperities in the substrate surface, *increasing* the effective contact area and giving a *stronger* adhesion. This is shown schematically in Fig. 6.

As noted earlier, the adhesive interactions between the HPC/PS particles and the mica substrate are quite weak compared to the other surfaces studied. It should also be noted that the mica surface is atomically smooth, so the effective contact surface area is small compared to a rough substrate such as glass (see Fig. 6).

In the case of the interactions of the HPC/PS particles with the graphite surface, there are a number of different factors that can contribute to the adhesion. Obviously, van der Waals forces are a significant contributor to the interaction when the particle is touching the surface. Also important are capillary forces associated with wetting the polystyrene and graphite surfaces. The surface coverage of HPC in this system is sufficiently sparse to allow the hairy layer to be compressed, exposing the underlying polystyrene and allowing graphite–polystyrene interactions to be observed. Additionally, van der Waals attractive forces and the postulated π–π interactions described elsewhere [21] could significantly increase the observed adhesion.

The adhesive interaction with silica is quite large compared to the other interactions seen in this study. It is postulated that this difference is due to the strong hydrogen bonds between the deformable hairy layer and the rough silica surface (see Fig. 6). While it is not expected that the applied loads in this study would lead to viscoelastic deformation of the particle core [9], it is expected that the HPC layer would be deformed to fill the rough silica surface giving a significantly greater surface area for HPC–silica hydrogen bonding.

Fig. 6. A schematic depiction of the interactions between rough and smooth substrates. When an easily deformable layer covers the particle, the effective contact surface area is increased, not decreased, as is the case with a hard, rigid particle.

3.4.3. Explanation of ionic strength effects

The effect on the particle–substrate interactions of changing the ionic strength is opposite to that usually observed. In general, interparticle interactions have been found to decrease in their effective range due to the increased screening of the surface charges [1]; however, 'hairy' particles have not been used in previous studies. In this case, where there is no intrinsic charge on both surfaces, another mechanism must operate.

As noted before, the introduction of salt solutions up to 0.1 mol dm^{-3} have been seen to increase the viscosity of HPC solutions [14], a property related to the extension of the chains in these solutions. Once the particle comes into contact with the substrate, the more extended chains from areas of the particle, not directly in contact with the substrate, are able to reach the substrate surface. This has the effect of increasing the number of HPC chains involved in the adhesive process, hence increasing the size of the adhesion (Fig. 7). It is interesting to note that changing the ionic strength did not make a significant difference to the jump-to contact. As the mica jump-to contact was difficult to observe in all of these experiments, it is not unsurprising that a quantitative description of this phenomenon cannot be reported here.

While there are few data from these experiments on the influence of ionic strength on the adhesion to graphite, the negligible variation observed is consistent with the above hypothesis. Since the particle–graphite interactions have their origin in polystyrene–graphite interactions, it would not be expected that the increase in solvation of the HPC would influence the adhesion significantly.

3.5. Summary of adhesive interactions

As previously noted, neither the magnitude of the adhesive interactions nor the relative strength of these interactions is correctly predicted by the application of JKR theory to similar systems [8]. The predicted $F_{\text{pull-off}}/R$ values obtained from the application of JKR theory (outlined before), along with the experimentally determined $F_{\text{pull-off}}/R$ values are summarized in Table 2.

It is seen that both the magnitude of these interactions and the relative strength of these interactions are not correctly predicted by the application of JKR theory to these systems. While roughness of the surface may contribute to this to some extent, the observed reduction in interaction strength is greater than has been seen in other studies [9]. It is important to note that in the interaction between a hard, smooth surface and a hard, rough surface, the effective contact area is reduced and so the adhesion is reduced. The persistent difficulty of accounting for surface roughness in adhesion theory is thus complicated further by the presence of easily deformable surface modifications such as a hairy layer.

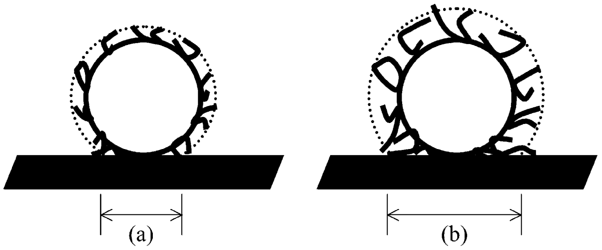

Fig. 7. A schematic representation of the effect of ionic strength on the interactions. The average thickness of the hairy layer is dotted for: (a) low ionic strength, (b) higher ionic strength giving chain extension and a larger effective contact area.

Overall, the substrate, particle core and hairy layer are all seen to have an important role in the behavior of the adhesive interactions. The interactions are represented pictorially in Fig. 8.

4. Conclusions

It has been seen that the interactions between substrates and HPC/PS particles are unlike HPC–substrate and PS–substrate interactions. It may be noted that the particles have adhesive interactions with both the hydrophobic and hydrophilic surfaces studied in this work. This may be seen with the silica and graphite interactions, where significant adhesive forces were observed. These results indicate that the overall properties of the system are an amalgam of the properties of the components: the polystyrene is responsible for the adhesion to the graphite while the HPC is responsible for the adhesion to the silica.

In these interactions, a hairy layer may increase the adhesion by increasing the effective contact area with a rough surface (e.g. with a rough silica surface). Additionally, the surface modification is observed in the secondary adhesion and the jump-to contact. The observed secondary adhesion provides direct evidence of HPC–substrate interactions and the jump-to contact with silica provides corroborative evidence of these interactions. The hairy layer may be

Table 2
The data values for the surface energy used in the calculations of $F_{\text{pull-off}}/R$. Values quoted are for ambient conditions unless specified. Additionally, the $F_{\text{pull-off}}/R$ values calculated from these surface energies using JKR theory and those obtained experimentally in this study

Material (Ref)	γ (J m^{-2})	$F^{\text{JKR}}_{\text{pull-off}}/R$ (mN m^{-1})	$F^{\text{expt}}_{\text{pull-off}}/R$ (mN m^{-1})
Mica (in vacuo) [10]	4.5	−3500	
Mica [8,10]	0.3	−900	−1.8
Graphite [8]	0.1	−500	−4.2
Silica (glass) [8]	0.35	−970	−32
Polystyrene [8]	~ 0.03		

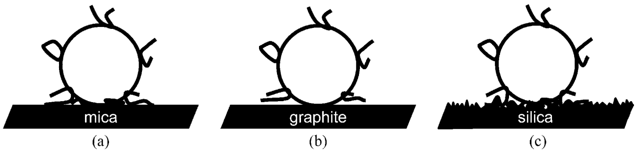

Fig. 8. A schematic of the adhesive interactions of the HPC/PS particles with the substrates studied here: (a) HPC–mica hydrogen bonding against an atomically smooth surface, (b) polystyrene–graphite van der Waals and capillary forces, (c) HPC–silica hydrogen bonding over a rough surface with a large contact surface area.

seen to act like a flocculant between the surfaces involved. The extension of the hairy layer is also evident in the increased adhesion of the particles to the substrates at higher ionic strengths.

Overall, the hairy layer used in this study gives the particles properties that are a combination of the constituent materials. The surface modifications can be involved in significant interactions with the substrate (e.g. HPC–silica); however, the coverage was sparse enough that the properties of the core may also be observed in some interactions (e.g. polystyrene–graphite).

Continued work using different surface modifications and different core polymers would be expected to yield further evidence of the composite nature of the adhesive interactions. Moreover, extension of this work to include chemically equivalent surfaces of varying roughness would also provide more information about the role of surface roughness in adhesion. The use of other substrates (e.g. cellulose, metals) and other polymers (e.g. poly(butyl acrylate), a common polymer used in paints) would also provide deeper insight.

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