

## INTERRACTION FORCES BETWEEN POLYMER-COATED GLASS SURFACES

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### ABSTRACT

We have investigated and measured the intermolecular forces between two layers of guar gum, a naturally occurring polysaccharide, adsorbed to glass using a Particle Probe AFM. To our knowledge, no work on the interactions of adsorbed guar gum using any force sensing technique has been previously reported. In this work a glass particle with a nominal diameter of 20 $\mu$ m was glued to a silicon cantilever to construct a particle probe surface apparatus. The polymer was allowed to adsorb onto two glass surfaces, i.e. the glass particle and a flat glass plate, and data are presented to describe the evolution of the adsorbed polymer layer with time. Scans were carried out at 0.33 Hz corresponding to approach and separation velocities of approximately 260 nms<sup>-1</sup>. On approach of the surfaces at partial surface coverage of the polymer, either repulsive steric interactions or weak attractive bridging interactions were seen. On surface separation, a long-range attraction occurred, as bridging polymer chains were pulled apart. During the partial surface coverage experiments, the adhesion and attractive interactions decreased as the adsorbed polymer layers evolved. When a stable equilibrium layer was achieved at full surface coverage, the system displayed a repulsive steric behaviour starting at a relatively large interaction distance, ~300 nm. A marked hysteresis was observed upon surface separation at full surface coverage indicating disruption of the developed adsorbed polymer layer.

**Keywords:** interaction forces, atomic force microscope, adsorbed polymer layers, glass surfaces.

### INTRODUCTION

Polysaccharides have many different applications in industry. They are valuable in foods as additives, in pharmaceuticals and cosmetics, as well as many other industrial and consumer applications. Being natural polymers they are relatively cheap and easier to buy compared to synthetic polymers. They are biodegradable and so are preferred from an environmental point of view. But most importantly they have specific properties that make them attractive for their application. Guar gum is a high molecular weight, naturally occurring polysaccharide, derived from the seed of the guar plant *Cyamopsis tetragonoloba* [1]. The polymer structurally consists of a linear chain of a polymannose backbone randomly substituted with a D-galactose side chain on approximately three out of five mannose units, as is shown in Figure 1. The backbone is joined by  $\beta$ -D-(1 $\rightarrow$ 4) linkages.

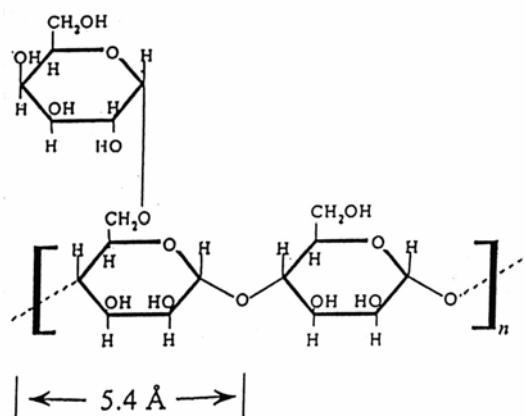


Figure 1: The chemical structure of guar gum [2].

Guar gum is one of the most extensively used polysaccharide polymers in both food and industrial applications. This is due to its high thickening efficiency, good compatibility, wide availability and low cost. It is commonly used as a stabilizer and thickener in the food industry, its hydrogen-bonding properties play an important role in the paper and mining industry, and its viscoelastic properties governs its applicability in oil well fracturing. While there have been extensive rheological [3-5] and numerous adsorption studies [6-8] of guar gum, little is known about the actual structure and organization of the molecules in solution and on surfaces. However, the existence of aggregates in guar solutions has been widely accepted [9]. A recent study [2] has indicated that these aggregates appear to be an inherent part of guar solutions and their presence is most likely to be due to the ability of guar molecules to form both inter- and intramolecular association complexes. Intermolecular force measurements could provide better understanding of the behaviour of this polymer, which may lead to improved application in industry.

The most direct way of measuring the intermolecular interaction force between two macroscopic bodies is to position them close together and measure the force by the deflection of a spring as a function of separation. This enables direct measurement of intermolecular forces such that the nature and range of the force law (force as a function of separation) can be obtained. However, the challenge comes in measuring very weak forces at very small intermolecular or surface separations, which must be controlled and measured at nanometric resolution. The Atomic Force Microscope (AFM) has recently been used for the measurement of intermolecular forces [10-12]. Prior to this, the Surface Force Apparatus (SFA) was the most significant tool for direct study of surface forces [13-14]. A wide selection of polymeric systems has been investigated; most of these studies concern the effects of adsorbed polymers on the forces between two solid surfaces [15-19]. There are also several studies on polysaccharide systems [20-21]. These recent force-sensing techniques have made it possible to observe and measure polymeric phenomena such as steric interactions, polymer bridging and the evolution of polymer surface coverage. To our knowledge however, no work on the interactions of adsorbed guar gum has been reported. This preliminary study focuses on measurement of the interaction forces between glass surfaces in dilute aqueous guar gum solution using a modified atomic force apparatus called the Particle Probe AFM. Using this system we directly measured the interaction forces between two adsorbed guar gum layers covering the glass surfaces in electrolyte medium and investigated the kinetic effects of the adsorption process.

## MATERIALS AND METHODS

### Particle Probe AFM

This custom built apparatus was constructed in our laboratories [18] based on the principles of the commercial AFM, for the sole purpose of studying the surface forces of adsorbed polymer layers at nanometre length scales and nanoNewton forces in a variety of media. A schematic drawing of the apparatus is shown in Figure 2.

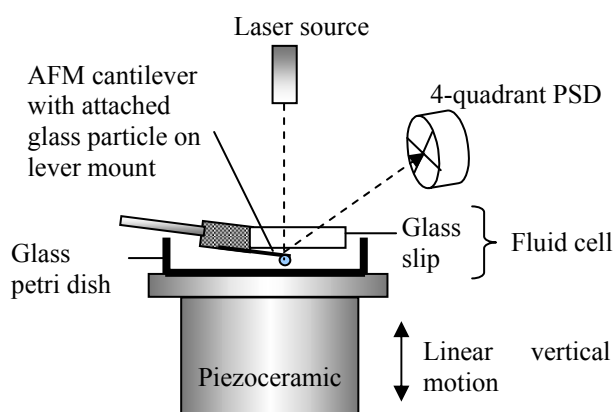


Figure 2: A schematic drawing of the Particle Probe AFM (not to scale).

The fundamental method used follows that of [10] with the original AFM. A glass particle probe was glued to the end of a flexible cantilever, which was used to sense the force. This glass particle acted as a substrate to which the polymer would adsorb. The cantilever was attached onto a lever mount that was kept stationary throughout the experiment. The second substrate, a readily available glass surface (petri dish) was positioned on to a piezoelectric ceramic tube (type PZT-5H, Morgan Matroc, U.K.) where the probe-surface separation could

be controlled to nanometer resolution by raising or lowering the surface towards the probe. This was done by subjecting the piezo to an electric field driven from an amplified signal generator (Thandor TG501-RS Ltd, U.K.), which causes the piezo to expand or contract linearly with the voltage. This approach allowed any desired signal and speed to be applied to the driver. Usually a saw tooth voltage of  $\sim 0.33$  Hz was applied so that each 'approach and separation' cycle would last  $\sim 3$  s. Interaction forces are continuously detected and recorded during surface approach up to hard contact and subsequent surface separation. The change in height of the piezo, which is effectively the probe-surface separation, could be determined by knowing the piezo expansion factor per unit voltage input. Interferometric calibration of the piezo yielded a displacement constant of  $2.5 \text{ nmV}^{-1}$ . Calibration of the equipment is based on two assumptions: a) zero force is obtained when the probe is well away from the surface and free from any interaction; b) the region of constant compliance (when the detector signal moves linearly with the drive voltage during hard surface contact) was used to determine zero separation.

The AFM cantilever deflects or bends when any interaction forces are present. These nanometer deflections were monitored by using optical beam deflection [22]. Here a laser beam was directed onto the end of the cantilever tip and the reflection of the beam was monitored by a split, four-quadrant, position-sensitive detector (PSD). This allowed both the lateral and vertical spot motion (i.e. the twisting and bending of the cantilever) to be determined. In order to work in liquids, a glass slip was attached to the lever mount, which provided a stable solvent interface, and hence a clear laser optical path. The PSD (SPOT-9D) and the signal amplifiers (301-DIV, 30 kHz) were both obtained from Optilas U.K. Ltd. The laser was a 3mW diode laser ( $\beta$ -TX) with additional optics (Vector Technology Ltd, U.K.). The resultant data were captured into Snapshot, a commercial software running on an IBM compatible personal computer (PC) using a commercial data acquisition card (PCL812PG) obtained from Advantech, U.K. All processing thereafter was performed on a Microsoft Excel spreadsheet to produce force-separation curves. Vibration is a common problem to all AFM force sensing techniques. Due to the sensitivity of the cantilever to even nanometer disturbances, the effects show up quite clearly in the produced signal. For this apparatus, a pneumatic Anti Vibration (AV) table was used to isolate it from acoustic noise sources. Also to minimize noise interference due to light, the apparatus was kept covered throughout an experimental run. Further extensive description of the apparatus, calibration and experimental techniques can be found elsewhere [18].

## Sample Preparation

The glass petri dishes (Bibby Sterilin Ltd, U.K.) were rigorously cleaned in an ultra-sonic bath for several hours with a dilute RBS (surfactant) solution (Chemical Concentrates (RBS) Ltd, U.K) then thoroughly rinsed with Nanopure water (resistivity  $18 \text{ M}\Omega$ ) and finally dried under a laminar flow hood and dust free conditions. The glass probes (BDH, U.K.) were spherical particles with a nominal diameter of  $20 \mu\text{m}$ , which were also cleaned in a similar manner. The commercial cantilevers used for these experiments were triangular silicon nitride Type B AFM cantilevers (Topometrics, U.K). The manufacturers supplied a quoted spring constant range of  $0.04$ - $0.35 \text{ Nm}^{-1}$  and lever dimensions of  $180 \mu\text{m}$  length and  $40 \mu\text{m}$  width. However, direct calibration of the cantilever spring constant using the resonance shift technique [18] yielded a value of  $0.034 \text{ Nm}^{-1}$ . The probe was attached to the cantilever using standard araldite (Evode Ltd, U.K). The araldite was inert in the polymer solution hence there was no contamination of the system. All other chemicals were B.D.H analytical grade material and were used as received. Guar gum powder (WG-32) was obtained from Halliburton (USA) and was used as received. The molecular weight of the polymer is unknown, but typically natural guar has a molecular weight in the range of  $500,000$  to  $5,000,000$ . A known amount of guar gum powder ( $100 \text{ ppm}$ ) was dispersed in a known amount of  $0.1 \text{ M NaCl}$ , magnetically stirred for an hour and refrigerated overnight to ensure full hydration. The cold environment was necessary to prevent the polymer from being degraded by bacteria. Prior to use, the dilute polymer solution was allowed to reach room temperature, stirred and filtered once using grade 1 Whatman filter paper to remove any microgel particles from the guar solution.

## Force–Separation Measurements

The cleaned glass petri dish and cantilever arrangement is called the fluid cell as shown in Figure 2. Note that the cantilever is positioned at a slight angle to ensure that only the particle probe would be in contact with the polymer layer during surface approach. The fluid cell was carefully mounted on top of the piezo and carefully aligned so that the laser beam was directed onto the tip of the cantilever. Further alignments were made to direct the laser beam reflection onto the center of the PSD face. Once everything was in position, no more adjustments were made during an experimental run unless otherwise stated. Initially an aqueous solution of  $0.1 \text{ M NaCl}$  (without polymer) was introduced into the fluid cell and force-separation measurements were made. This was to

examine a clean system and provide a control for comparison between the system with and without polymer. Note that to ensure that the liquid interface was sufficiently covered by the glass slip, the working solution volume was  $\sim 25$  ml. Next, all of the electrolyte solution was replaced with a dilute solution of the polymer dissolved in 0.1M NaCl. A kinetic study was performed where the guar gum was allowed to adsorb to both surfaces and force-distance measurements were taken after several elapsed time intervals. All the interactions were measured at the same site throughout the experiment and the probe was kept immersed in the solution at all time. All experiments were carried out at room temperature ( $25 \pm 2^\circ\text{C}$ ) and measurements were performed at a speed of 0.33 Hz, which corresponds to  $\sim 260 \text{ nms}^{-1}$ .

## RESULTS AND DISCUSSION

All interaction forces are presented as  $\text{Force}/2\pi R$  according to the Derjaguin approximation [23]; the force normalised in this way effectively gives the interaction energy per unit area. This allows interaction forces to be compared even if different sized particle probes are used.

### Bare glass surface

Figure 3 shows the results of interactions measured between bare glass surfaces in pure electrolyte medium without adsorbed polymer, i.e. a clean system. On approach of the surfaces, there are no detectable interactions until  $\sim 14$  nm surface separation, where a gradually increasing attractive force starts to occur. Subsequently, the probe becomes unstable as the force gradient exceeds the spring constant resulting in a rapid 'jump in' of the probe towards contact with an attractive energy of  $\sim 10 \mu\text{Nm}^{-1}$ . Beyond this the force rises rapidly and linearly indicating the surfaces moving together in hard contact. Note that the slight scatter in the data is likely to be vibration from ground noise transmitted by the lower glass surface, which shows up in the signal during hard contact.

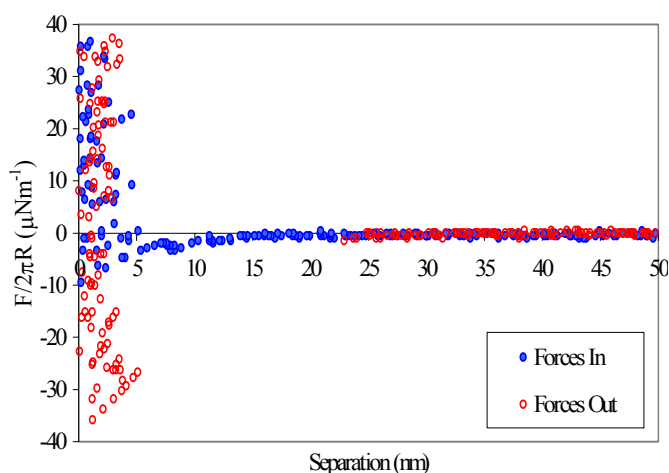


Figure 3: Force-separation data for interactions between bare glass surfaces in pure electrolyte solution (0.1M NaCl) without polymer.

On separation, the surfaces remain attached until an energy of  $\sim 30 \mu\text{Nm}^{-1}$ , whereupon the probe is rapidly released, with a sudden 'jump out' to a surface separation of  $\sim 23$  nm. However, within the scatter of the data, it can be seen that the probe appears to move slightly away from hard contact at  $\sim 15 \mu\text{Nm}^{-1}$  until it reaches a separation of  $\sim 5$  nm at  $\sim 30 \mu\text{Nm}^{-1}$  before the sudden 'jump-out'. This behaviour is thought to be due to the particle rolling on the surface under pressure [18] and if this is the case, then the adhesion value stated here is not strictly correct. Nevertheless, these results demonstrate that in a pure electrolyte system, there is expected to be no detectable interaction of bare surfaces at large surface separation. But as the surface separation decreases, an attractive interaction rapidly increases at short-range, consistent with the van der Waals theory.

## Guar adsorbed on glass

The fluid cell was filled with dilute polymer solution (100 ppm guar dissolved in 0.1M NaCl) to allow polymer adsorption onto both surfaces. A kinetic study was performed where the force-separation measurements were taken after several elapsed time intervals. Note that the times and magnitude of forces quoted should only be taken as a guide because the characteristic features of the profiles shown may occur at slightly different times and magnitudes for repeat runs. This implies that the adsorption rates are sensitive to certain conditions not under direct control in these experiments, such as surface separation and temperature. As mentioned before, vibration is a common problem to all AFM force sensing techniques. For this apparatus, an Anti Vibration (AV) table was used to isolate it from acoustic noise sources. However, we observed that the addition of the guar gum polymer led to fluctuations in the interaction profile, which did not occur in pure electrolyte. This could be due to disruption of weak long-range entanglements in the solution. The effect was reduced as the glass surface was raised towards the glass probe i.e. by decreasing the surface separation. Also, the effect was always noticed to be less severe after many hours of adsorption. In certain cases, the force profiles are slightly ambiguous due to the argument raised above. This makes it difficult to be absolutely certain where the onset of any interactions occur.

Figures 4, 6 and 7 display the force-separation profiles of the adsorbed guar gum layers showing the kinetics of the adsorption process with respect to time. Shown inset are the same profiles on a larger scale. Figure 4 shows the initial measurement taken after 25 minutes of adsorption.

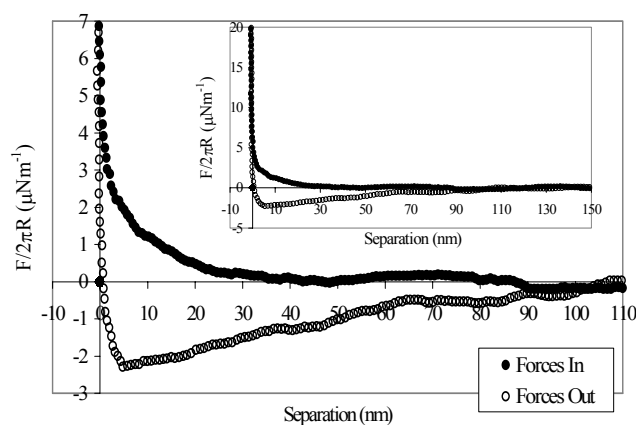


Figure 4: Force-separation data of interactions between adsorbed guar gum layers (100 ppm guar in 0.1M NaCl solution) on glass surfaces taken after 25 minutes of adsorption.

It can be seen that on approach, a definite repulsive interaction occurs at a surface separation of  $\sim 35$  nm, which rises steadily until hard contact is reached at an energy of  $\sim 5 \mu\text{Nm}^{-1}$ . A plausible explanation for the slight disturbance of the profile between 50 and 80 nm is some weak long-range entanglement in the solution. This repulsive interaction is probably due to steric effects followed by osmotic effects at smaller surface separation. When polymeric chains in a solution attach or adsorb to a surface, they dangle out into the solution where they are thermally mobile [24]. On approach of another surface, the entropy of confining these dangling chains results in a repulsive entropic force. For overlapping polymer chains, this is known as steric behaviour. As the surfaces approach even further, the concentration of polymer in the small gap between the surfaces increases. Osmotic effects create a driving force for solvent molecules to enter the region thus causing repulsion between the surfaces. Upon separation, the surfaces separate from hard contact at the zero force region but remain attached together with a maximum attraction force of  $\sim 2 \mu\text{Nm}^{-1}$  at  $\sim 5$  nm separation. From here the attractive force decreases slowly until zero force is reached when the surfaces are  $\sim 110$  nm apart. This behavior suggests that up until 5 nm the probe is stuck to the surface via the van der Waals force despite the screening layer of adsorbed polymers. Beyond this, the probe is released from hard contact but is still kept attached to the surface by adsorbed bridging polymers.

Bridging occurs when one polymer chain, already adsorbed to one surface, is able to simultaneously adsorb to an opposing surface. This can occur during surface approach whenever there are adsorption sites available on the other surface [25], either due to incomplete coverage (low adsorption density) or as sites become exposed during hard surface contact. Since the bridging chains could gain conformational entropy if the separation between the surfaces decreased, bridging gives rise to an attractive force [26]. As the surfaces are separated, the

bridging polymers would resist stretching and consequently exert a long-range attractive force. This behaviour is illustrated in Figure 5. On further separation, the bridging polymers desorb (especially when partially stretched and hence in an unfavourable arrangement), eventually releasing the probe at  $\sim 110$  nm back to zero force. Notice that the surface separation is gradual and there is no obvious 'jump out'. This observation may be attributed to the flexibility of the polymer chains, which do not resist strongly when stretched.

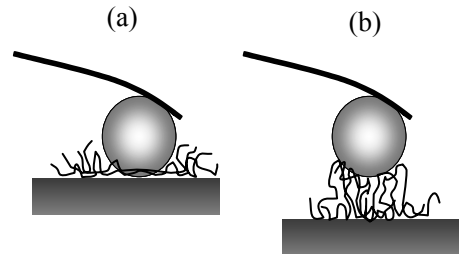


Figure 5: Illustration of probe and surface with adsorbed polymer layers, adapted from Braithwaite et al., 1997. (a) During hard contact at partial surface coverage, the polymer chains are 'squashed' together. Polymer bridging is likely to occur due to available adsorption sites on the glass surfaces. (b) During surface separation the surfaces part from hard contact but stay attached together by bridging polymer chains.

Figure 6 shows the interaction measurements taken after 7 hours of adsorption. The first thing to note is the attractive interaction that occurs upon surface approach, most likely due to polymer bridging. On close inspection of the profile on a smaller scale (not shown here), it can be seen that the attractive interaction occurs at  $\sim 66$  nm surface separation with a magnitude in the order of  $\sim 0.3 \mu\text{Nm}^{-1}$ . It is interesting that an attractive interaction was absent in the initial measurement taken after 25 minutes of adsorption. One would think that earlier in the adsorption process there would be more available adsorption sites for bridging to occur. This observation implies that the adsorption process of guar gum is a dynamic one and that these measurements were not taken at equilibrium conditions. However, the attraction is relatively weak with no obvious 'jump-in'. This indicates that if bridging does occur on surface approach under our experimental conditions, it is gradual and weak in nature. When the surfaces approach more closely, a repulsive interaction takes over, probably due to osmotic effects; this rises steadily until hard contact is reached with an energy of  $\sim 6 \mu\text{Nm}^{-1}$ . Upon separation, the surfaces immediately separate from hard contact but the interaction continues and crosses the zero force axis into the attractive region, at a separation of less than 10 nm. The fact that the interaction is in the repulsive region immediately upon separation, suggests that the adsorbed polymers are sufficiently developed to exhibit a degree of elastic behaviour.

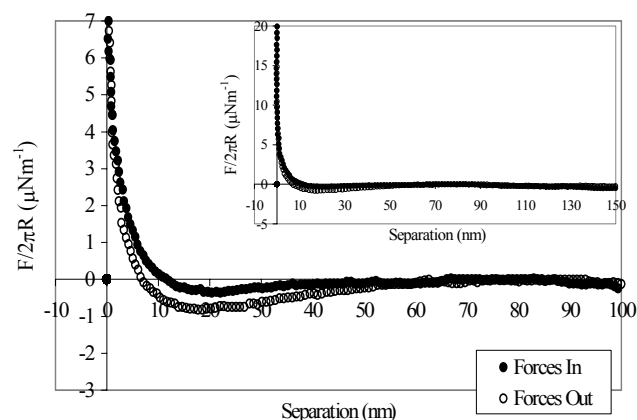


Figure 6. Force-separation data of interactions between adsorbed guar gum layers (100 ppm guar in 0.1M NaCl solution) on glass surfaces taken after 7 hours of adsorption.

This property helps push the surfaces away from each other at small surface separation. As the surfaces separate further, an attractive force due to bridging is observed, which decreases gradually until the probe is released at a surface separation of  $\sim 60$  nm. However, the depth (adhesion) and range of this attraction has significantly decreased compared to the profile in Figure 4. Decreasing adhesion and range of the attractive bridging forces indicates evolution of the polymer layer. These features can be correlated with the degree of surface coverage.

The surface coverage increases as more polymer is adsorbed, and there will be less tendency for bridging to occur due to fewer available sites. Therefore the probe is released to zero force progressively quicker with time of adsorption as can be seen by the decrease in range of attraction from  $\sim 110$  nm in Figure 4 to  $\sim 60$  nm in Figure 6. These observations strongly indicate that up to 7 hours adsorption, the glass surfaces are at partial polymer coverage.

After 16 hours of adsorption there has been remarkable development of the adsorbed polymer layers, which is evident in Figure 7. The profiles now indicate force-separation features typical of interactions between polymers at full polymer coverage on the glass surface, and the results show two distinguishing characteristics of this behaviour. The first is the very large interaction on surface approach, and the second is the marked hysteresis on surface separation. Inspection of the profiles show that on approach, a repulsive interaction is immediately felt at a surface separation of  $\sim 280$  nm. This monotonically long-range repulsive interaction, which is indicative of full polymer coverage, rises steadily until hard contact is reached with a maximum energy of  $\sim 50 \mu\text{Nm}^{-1}$ . This type of interaction is commonly known as steric repulsion. The adsorbed layers are clearly denser than during partial surface coverage; a higher force is required to reach each separation. However, it should be noted that a zero force region was not obtained in our measurement because there was interaction between the surfaces even at maximum separation.

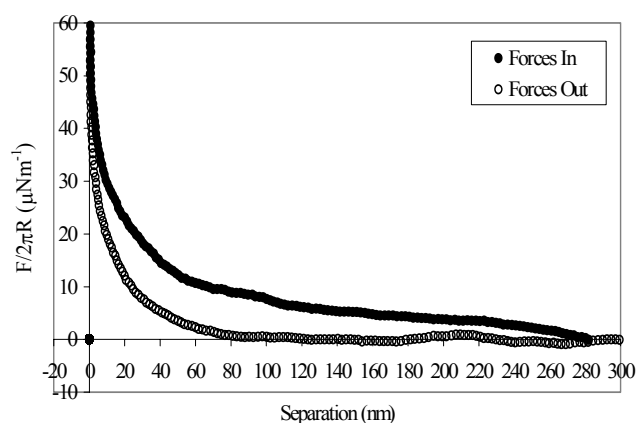


Figure 7. Force-separation data of interactions between adsorbed guar gum layers (100 ppm guar in 0.1M NaCl solution) on glass surfaces taken after 16 hours adsorption.

There have been previous reports on other systems exhibiting this behaviour [27, 20], where zero force was arbitrarily assigned as the value at the maximum downward deflection of the cantilever. If the zero force region can be achieved at maximum surface separation, then in theory the actual thickness of the adsorbed polymer layers at full surface coverage can be estimated given that the molecular characteristics of the polymer are known. The separation profile shows that the surfaces separate at an energy of  $\sim 40 \mu\text{Nm}^{-1}$ , where the force continues to decrease until there are no longer any interactions at  $\sim 80$  nm surface separation. The high separation energy indicates that the polymer layers have become much more elastic in behaviour. The marked hysteresis suggests that indentation or disruption of the elastic polymer layers may have occurred during hard contact. Note that the slight disturbance on the zero force region is possibly due to long-range entanglements.

## CONCLUSION

We have performed intermolecular force measurements on adsorbed guar gum layers to provide better understanding of the adsorption behaviour of this polymer, from a dilute polymer solution onto a solid glass surface. The kinetic study of the adsorption process clearly shows the evolution of the adsorbed polymer from partial polymer coverage to full polymer coverage on the glass surfaces. The most obvious indication of partial surface coverage is the long-range attractive interaction occurring on surface separation, which is attributed to polymer bridging due to available adsorption sites on the glass surface. As the adsorption progresses, there are fewer available adsorption sites, hence less bridging can occur. This is consistent with the observation that the depth (adhesion) and range of the attractive interactions significantly decrease after 7 hours of adsorption compared to the measurements taken after 25 minutes of adsorption.

The fact that bridging may or may not occur during surface approach implies that the adsorption process is a dynamic one and the measurements are not taken under equilibrium conditions. On closer surface approach the interactions are repulsive, probably due to steric and osmotic effects as the polymer chains overlap and the polymer concentration increases in the small gap.

After 16 hours of adsorption, the data show typical features of adsorbed polymer interactions at full surface coverage. A long-range steric repulsion is immediately sensed on surface approach and rises steadily until hard contact is reached. The adsorbed layers, which are relatively denser than during partial surface coverage, require higher forces to reach each separation. The relatively high energy of separation suggests that the polymer layers are much more elastic in behaviour and the marked hysteresis indicate indentation or disruption of the polymer layers during hard contact.

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