Published in final edited form as:

Colloids Surf A Physicochem Eng Asp. 1999 August 1; 154(1-2): 53–64. doi:10.1016/S0927-7757(98)00908-X.

Adhesion mapping of chemically modified and poly(ethylene oxide)-grafted glass surfaces

G. Jogikalmath, J.K. Stuart, A. Pungor, and V. Hlady*

Center for Biopolymers at Interfaces, Department of Bioengineering, University of Utah, Salt Lake City, UT 84112, USA

Abstract

Two-dimensional mapping of the adhesion pull-off forces was used to study the origin of surface heterogeneity in the grafted poly(ethylene oxide) (PEO) layer. The variance of the pull-off forces measured over the μm -sized regions after each chemical step of modifying glass surfaces was taken to be a measure of the surface chemical heterogeneity. The attachment of γ -glycidoxypolytrimethoxy silane (GPS) to glass decreased the pull-off forces relative to the clean glass and made the surface more uniform. The subsequent hydrolysis of the terminal epoxide groups resulted in a larger surface heterogeneity which was modeled by two populations of the terminal hydroxyl groups, each with its own distribution of adhesion forces and force variance. The activation of the hydroxyls with carbonyldiimidazole (CDI) healed the surface and lowered its adhesion, however, the force variance remained rather large. Finally, the grafting of the α,ω -diamino poly(ethyleneoxide) chains to the CDI-activated glass largely eliminated adhesion except at a few discrete regions. The adhesion on the PEO grafted layer followed the Poisson distribution of the pull-off forces. With the exception of the glass surface, a correlation between the water contact angles and the mean pull-off forces measured with the Si_3N_4 tip surfaces was found for all modified glass surfaces.

Keywords

Pull-off forces; Terminal epoxide groups; Adhesion; Modified glass surfaces

1. Introduction

Molecular contacts between two solid surfaces often result in a measurable adhesion [1–5]. When increasing tension is applied across an adhesive contact, the solids will separate either due to adhesive or cohesive failure. Many attempts have been made to understand and control the adhesion on macroscopic and molecular levels [6–9]. Biomaterials industry has a special interest in both adhesive and non-adhesive materials which will interface with complex biological systems. Many biological macromolecules, like proteins, have a tendency toward almost irreversible adsorption to materials surfaces [10]. In contrast to the ubiquitous protein adsorption to solid surfaces, cells usually do not adhere to solids nor to each other in such a non-specific manner. The absence of the non-specific adherence of cells is the result of a strong and relatively long-ranged repulsive potential between cell surfaces [11–13] which has the origin in the cell membrane polysaccharide coat, glycocalyx.

One strategy of preparing a non-adhesive material is to coat its surface with surface-grafted hydrophilic polymer chains which will perform a function similar to the glycocalyx layer. The two principal methods of the attachment of polymer chains to solid surfaces are physical adsorption and/or chemical covalent grafting [14]. The attractiveness of physical adsorption lies in the simplicity of the experimental procedure. The disadvantages of physically adsorbed coatings are the relatively poor mechanical stability of the layer, slow desorption of polymer, and redistribution and transfer of the polymer layer to another surface during contact [14,15].

The covalent grafting of polymer chains to surfaces is a suitable alternative to the physical adsorption method. The end-grafting of polymer chains can create a more stable coat whose non-adhesive property depends on the surface density of polymer chains and on the spatial uniformity of the coat. Although the use of covalent chemistry largely eliminates the problems of the layer's mechanical stability and the redistribution and transfer of molecules during the contact, some problems still remain. An uneven chemical reactivity of the substrate can cause a non-uniform polymer density. Overwhelming lateral repulsive interactions between the polymer chains in the final grafting step can create a polymer coat with a surface density insufficient for eliminating the non-specific protein adsorption or adhesion.

In order to investigate the spatial heterogeneity in grafted poly(ethylene oxide) (PEO) layers on glass surfaces as well as the origin of this heterogeneity we applied the adhesion force mapping technique using a scanning force microscope (SFM). The SFM adhesion force measurement [16–19] is a method equivalent to the wetting measurements with a particular probe liquid. The probe here is an SFM tip made of Si_3N_4 which is brought in contact with the coated surface. When the tip does not wet the surface no force is needed to remove it from the contact. On the contrary, when the tip wets the surface, a force of dewetting is required for breaking the adhesive tip–surface bond. In the case that the adhesion measurements are made in a liquid medium one also has to account for the re-wetting of both the probe and the sample after their separation from contact [20]. In the SFM adhesion experiments the adhesion force between the sample surface (subscript ₁) and the SFM tip (subscript ₂) in the aqueous medium (subscript ₃), F_{132} , is equal to the force at pull-off which, in turn, is deduced from the deflection of the cantilever at the pull-off. According to the theory of Johnson, Kendall and Roberts [21] the pull-off force is related to the work of adhesion, W_{132} :

$$F_{132} = -1.5\pi RW_{132} \quad (1)$$

where R is the effective radius of the SFM tip. The work of adhesion, W_{132} , depends to the interfacial energy between the sample and the SFM probe, γ_{12} , the sample and the aqueous medium, γ_{13} , and the SFM probe and the aqueous medium γ_{23} , respectively:

$$W_{132} = -\gamma_{12} + \gamma_{13} + \gamma_{23} \quad (2)$$

which is equal to:

$$W_{132} = W_{12} - W_{13} - W_{23} + 2\gamma_3 \quad (3)$$

The first three terms on the r.h.s correspond to the works of adhesion in vacuum and the fourth term is equal to the work of cohesion of the aqueous medium, W_{33} . The works of adhesion, W_{13} and W_{23} , are, in principle, experimentally accessible quantities from the

contact angle measurements; thus by using the combination of the pull-off force and contact angle measurements, one can determine the work of adhesion in vacuum between the unknown sample and the SFM tip probe, W_{12} . Assuming that the contribution of the SFM probe surface energy to W_{12} remains unchanged, any variation of W_{12} is assigned to the variation of the surface energy of the sample, γ_1 , i.e. to the chemical heterogeneity of the surface.

From the experimental design point of view, however, one would prefer several SFM probes of different surface chemistry, or different liquids or various combinations of the two, in order to solve for the unknown in Eq. 3. Some research groups have already demonstrated a multi-probe approach in determining the single bond forces [22,23], including the receptor-ligand bonds [24–26]. Others have used the differences in the pull-off and friction forces to detect the contrast between patterns of different surface chemistries [27]. This so-called chemical force microscopy technique has demonstrated, so far, its confirmatory rather than predictive character [27,28].

In order to study the origin of surface heterogeneity in the grafted PEO layer the spatial mapping of pull-off forces has been performed after each chemical step used in modifying glass surfaces with PEO. The chemistry steps involved the silanization of a glass surface by γ -glycidoxypolytrimethoxy silane (GPS), the hydrolysis of the terminal epoxide groups into hydroxyl groups, the activation of the hydroxyls with carbonyldiimidazole (CDI) and finally, the attachment of α,ω -diamino poly(ethyleneoxide). The spatially-resolved adhesion measurement was performed by repetitiously making and breaking contacts between the SFM Si_3N_4 tip and the modified glass surface in a raster-like fashion over a selected surface area. Both the adhesion maps composed from the individual pull-off forces and the histograms of forces were used to analyze the uniformity of surface layers after each modification step.

2. Materials and methods

2.1. Materials

The silane reagent, GPS was obtained from Hüls/United Chemical Technologies (Bristol, PA). 1,1'-carbonyldiimidazole (CDI) was purchased from Aldrich (Milwaukee, WI). Glycine-p-nitroanilide (g-pNA) was purchased from Sigma (St. Louis, MO). Chromatographically pure bisamine-PEO (Mw 3500 Da) was from Shearwater Polymers (Huntsville, AL). All buffers and reagents used were fresh and of a high quality commercial grade. Toluene (glass-distilled Omni-Solv) from EM Science (Gibbstown, NJ) contained less than 0.01% residual water. All deionized (DI) water used was subject to reverse osmosis filtering and UV treatment, and had a conductivity of less than 20 mS. Glass coverslips were obtained from VWR Scientific. Coverslips were carefully handled and stored either in glass staining jars or supported by ceramic slide holders (Thomas Scientific) or a clamping holder fabricated from Teflon and designed specifically for this purpose. Glass beads (5–50 μm diameter, Duke Scientific, Palo Alto, CA) were used in quantitative analysis of epoxide surface groups.

2.2. Chemical modifications of glass surfaces

Step 0: glass coverslip surfaces were submerged in piranha solution (70% H_2SO_4 :30% H_2O_2) for 15 min and subsequently rinsed thoroughly with DI water. After drying in a vacuum desiccator, the surfaces were further cleaned with oxygen plasma (200 mTorr, 50 W) (Plasmod, Tegal Corp.) for 2 min.

Step 1: immediately thereafter, the surfaces were placed in a reaction vessel to which was added 1% (v/v) GPS and 0.2% (v/v) triethylamine in dry toluene (adapted from ref. [29]).

The vessel was equipped with a CaCl_2 drying tube and was suspended in a water bath, where it was heated to 70°C for 8 h, stirred overnight at room temperature, and heated another 8 h before washing with toluene and acetone. The GPS–glass surfaces were then dried in vacuum overnight for curing.

Step 2: the terminal epoxide groups were first hydrolyzed and then derivatized with a CDI crosslinker to make the amine-reactive glass surface. The hydrolysis was achieved by immersing the surfaces in a 100 mM NaCl solution adjusted to pH 4 with 10 mM HCl, and heating to 70°C for 30 min, followed by rinsing with DI water and drying in vacuum [30].

Step 3: the surfaces carrying terminal hydroxyl groups (i.e. HGPS–glass surfaces) were then immersed in a solution of 20 mg CDI per 10 ml p-dioxane, which was stirred at room temperature for 1 h [31]. They were then rinsed with dioxane and acetone and dried. The CDI-activated glass (i.e. CDI–glass surfaces) were stored in a dry atmosphere until further use to avoid hydrolysis of the imidazole groups.

Step 4: in the final surface modification step the CDI–glass surfaces were placed in a small volume of 50 mM carbonate–bicarbonate buffer (pH 9.5) with 10 mg PEO-bis-amine/ml and 11% (w/w) K_2SO_4 [31,32]. This mixture was heated at 60°C for 18 h, then rinsed with buffer and DI water to make a NH_2 –PEO–glass surface.

The glass beads were chemically modified in the same way as flat glass surfaces, the only difference being that the beads were washed using a Millipore (Bedford, MA) vacuum filtration system while sitting on a Durapore 0.65 μm pore size filtration disk. These disks were compatible with all solvents used except acetone, which was not used to wash the beads in this step. The overall scheme of chemical reactions used in modifying glass surfaces with PEO is shown in Fig. 1.

2.3. Surface characterization

The water contact angles of modified glass surfaces were measured using the sessile drop method and a goniometer (Rame-Hart). Several 5 μl droplets of double distilled water were placed randomly on each glass surface and contact angles were measured. The XPS spectra were measured using a Hewlett-Packard 5950B ESCA instrument. XPS spectra were obtained for clean glass, GPS and PEO derivatized surfaces. The elemental analysis was performed by recording a wide scan XPS spectra, taken from 0 to 1000 eV. The atomic percentages were calculated by adjusting the area under each elemental peak with its Scofield cross-section [33]. Chemical binding information was sought in the C1s (carbon) narrow scan spectra, measured over a range of 20 eV. Deconvolution of the C1s spectra was performed by means of a curve-fitting program. An electron flood gun was operated at 10 eV to minimize the surface charging effects.

Quantitative determination of the surface epoxide groups was carried out using GPS-modified glass beads. A 10 μM solution of g-pNA in acetone was reacted with 2 g of GPS-modified glass beads in a closed vial at 80°C for 4 h. The beads were rinsed well with acetone and vacuum dried, then weighed for surface area determination. To cleave the p-nitroanilide (pNA), 10 ml of 4 N NaOH was added to the beads and stirred for 2 h. The absorbance of the pNA/NaOH solution was measured at 410 nm using a Perkin-Elmer Lambda 6 UV/VIS spectrophotometer. The concentration of pNA was calculated using its extinction coefficient, $\epsilon_{410\text{nm}} = 8.8 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$. The total number of cleaved pNA in solution was divided by the total surface area of the beads to determine surface density of reactive groups.

2.4. Adhesion mapping

A commercial SFM (Explorer, Topometrix) was used for mapping of the adhesive force in the layer imaging mode. All adhesion measurements were performed in double distilled water. A silicon nitride tip (nominal radius of curvature, $R=50$ nm) integral to a triangular SFM cantilever was employed as an adhesion probe. The adhesion mapping comprised 2500 (i.e. 50×50 sites) consecutive force–displacement cycles made on 5 by $5 \mu\text{m}^2$ (or 10 by $10 \mu\text{m}^2$) sized areas. In this way, the pull-off force was probed every 100 nm (or 200 nm) apart. The maximal load in each cycle was ≈ 5 nN. The resulting set of the force–displacement curves was analyzed using a custom-written computer program which extracted the magnitude of the force at pull-off just before the cantilever returned to its resting position. The forces were calculated using the nominal spring constant, $k_s=0.05 \text{ Nm}^{-1}$. The 50 pN resolution in the pull-off force measurements was determined by the total displacement made in each cycle and the number of layered images taken by the microscope.

3. Results and discussion

3.1. Contact angles and surface analyses

The results of the water contact angle measurements performed after each surface modification step are shown in Table 1. The clean glass surface had a very low contact angle of $6^\circ \pm 3$, and would ideally be expected to be fully wettable by water. The GPS–glass surfaces had water contact angles of $47^\circ \pm 5$, whereas HGPS–glass surfaces which carry terminal hydroxyl groups instead of the epoxide group displayed water contact angles of $35^\circ \pm 4$. The activation of the hydroxyl group with CDI imparts some polar character to the surfaces due to the imidazole group: CDI–glass surfaces had contact angles of $31^\circ \pm 4$. The NH_2 –PEO–glass surfaces showed contact angles of $\approx 20^\circ$. The atomic percentages of elements determined by XPS analysis are also shown in Table 1. In the case of a clean glass surface the presence of some carbon, 6 at. % in this case, is typical for slight surface contamination. The narrow-scan XPS spectrum of a GPS–glass surface C1s region (not shown here) showed three different types of carbon species: 56.2% of aliphatic carbon, 36.4% of ester carbon (C–O) and a 7.5% of carbonyl carbon (C=O). The C1s spectrum for NH_2 –PEO–glass surface displayed two peaks with the binding energies consistent with aliphatic and ether (C–O–C) carbon. The ratio of ether to aliphatic carbon was ≈ 1 , a rather low value for grafted PEO chains. For a different immobilization scheme [32], we found the ratio of ether to aliphatic carbon could be as high as 9. This implied that the PEO grafting protocol used in this study did not result in a dense PEO layer.

The g-pNA assay used to determine surface coverage of epoxide groups on the GPS–glass surfaces showed an average of 0.35 epoxides/ nm^2 from three experiments; a value which was $\approx 10\%$ of the number of SiO_2 surface silanol groups [34] thus suggesting that a large number of the epoxide groups may have been hydrolyzed prior to the g-PNA analysis.

3.2. Adhesion force maps and histograms

The spatial adhesion map and the pull-off force histogram for a 10 by $10 \mu\text{m}^2$ clean glass surface are shown in Fig. 2. The pull-off force contrast in adhesion map images was adjusted to range between 0 nN (white pixel in the upper left corner of each image) and 15 nN (black pixel in the upper left corner of each image). Note that in all other adhesion map images (Figs. 3–6) the contrast was set between 0 nN and 10 nN and that these two pixels were not included in force histograms. For the clean glass surface the mean pull-off force of 8.35 nN and the variance (i.e. squared standard deviation, σ^2) of 2.5 nN^2 was calculated from the best fit of a normal distribution to the pull-off force histogram.

The GPS–glass surface adhesion maps of 5 by 5 μm^2 and 10 by 10 μm^2 areas and the respective pull-off force histograms are shown in Fig. 3a and b, respectively. The silanization of the glass surface with GPS resulted in an overall lower adhesion of the SFM probe: the two mean pull-off forces were 3.85 nN (Fig. 3a) and 3.75 nN (Fig. 3b) and the respective variances were in both cases equal to 0.55 nN^2 based on the normal distribution fits to the experimental data. The spatial distribution of the adhesion (Fig. 3) showed randomly distributed low adhesion sites (bright pixels). The chemical origin of the low adhesion sites was unknown.

Once the epoxide groups of the GPS–glass surface were hydrolyzed into hydroxyls groups (HGPS–glass), the pull-off force map showed a much larger variation on both 5 by 5 μm^2 (Fig. 4a) and 10 by 10 μm^2 (Fig. 4b) scales. The respective pull-off force histograms appeared to be skewed and could not be fitted with a single normal distribution. The fits required at least two normal distributions which differed both in the mean pull-off force and the variance. When measured on two different surface areas the population of lower adhesion sites had a mean pull-off force at 4.05 nN (Fig. 4a) and 3.70 nN (Fig. 4b), respectively. The respective FWHM widths were 2.3 nN (0.9 nN^2 variance) and 2.4 nN (1.05 nN^2 variance). The sites with higher adhesion showed the mean force at 5.0 (Fig. 4a) and 4.85 pN (Fig. 4b) with a narrower FWHM widths of 1.30 nN (0.3 nN^2 variance) and 1.40 nN (0.35 nN^2 variance), respectively. The ratios of the lower to higher adhesion site numbers were computed from the areas below the two normal distributions. The ratios for the two imaged areas were quite similar: 2.20 for the 5 by 5 μm^2 area (Fig. 4a) and 2.14 for the 10 by 10 μm^2 area (Fig. 4b).

The pull-off force histograms were very reproducible between the two different surface areas. The mean pull-off force of the HGPS–glass sites population described with a lower adhesion normal distribution (3.9 nN, Fig. 4) was similar in magnitude to the mean pull-off force of GPS–glass surface (3.8 nN, Fig. 3). Similarity between the mean pull-off forces suggested that there is a common chemical group present on both the GPS– and HGPS–glass surfaces that is responsible for the adhesion. One possibility is that the hydrolysis of the GPS epoxide group was incomplete so that there are some residual epoxide groups still present on the HGPS–glass surface. This appears to be in contradiction to the low epoxide surface density determined using the glass beads and g-pNA method. Also, the respective variances of the GPS–glass and HGPS–glass histograms were, however, quite dissimilar (i.e. 0.55 nN^2 vs. 1.0 nN^2).

The other hypothesis is related to the mechanism of hydrolysis of the GPS–glass surface epoxide groups. It has been shown that two populations of primary hydroxyls are produced by acid hydrolysis of GPS epoxide group on chromatographic silica gels: C(5) primary hydroxyl as a major product and a C(6) primary hydroxyl coupled to a C(5) secondary hydroxyl (i.e. terminal diol) as a minor product [35,36]. In this case the appearance of the HGPS–glass adhesion sites with higher pull-off forces is probably related to the terminal diol group, i.e. to the combination of C(6) primary hydroxyl with a C(5) secondary hydroxyl present at 1/3 of the sites. The two hydroxyls can participate in two hydrogen bonds which are likely contributing to the adhesion. The HGPS–glass adhesion sites (Fig. 4) with lower pull-off forces are, according to this hypothesis, related to the terminal C(5) primary hydroxyl groups. One recognizes that the siloxane bond network (i.e. Si–O–Si–O–Si) is also susceptible to acid hydrolysis which can lead to the removal of the whole GPS moiety. However, neither of the two populations of the HGPS–glass surface sites showed the magnitude of pull-off forces similar to the pull-off forces found for clean glass (mean pull-off force=8.35 nN) thus ruling out the possibility that the acid hydrolysis of the GPS–glass surface has resulted in the exposure of the glass surface.

The spatial distribution of the pull-off forces on HGPS–glass surfaces showed an appearance of macroscopic regions with different pull-off forces (Fig. 4a and b). Similar regions were also found in the spatial map of the pull-off forces measured on the CDI–glass surface as shown in Fig. 5. The histogram of CDI–glass pull-off forces was fitted with a single normal distribution with a peak at 2.95 nN and a variance of 1.10 nN². This mean pull-off force was lower than any mean pull-off force found on the preceding surface chemistries. The CDI (Fig. 1) is known to react with a hydroxyl group. In the case of chromatographic GPS silica gel activated with CDI it has been shown that the primary reactive group onto which CDI binds is the terminal C(5) primary hydroxyl group (H.P. Jennissen, unpublished) rather than the terminal diol (i.e. C(6) primary hydroxyl with a C(5) secondary hydroxyl). It is unlikely that CDI reacts with the silanol groups.

The adhesion maps for the NH₂–PEO–glass surfaces are shown in Fig. 6a (5 by 5 μm² area) and b (10 by 10 μm² area), respectively. The pull-off forces between the SFM probe and the PEO-coated surface have been largely eliminated after the polymer grafting step. The two histograms of pull-off forces showed a force distribution similar to the Poisson distribution model with mean pull-off forces of 0.30 nN (Fig. 6a) and 0.15 nN (Fig. 6b). In the case of the 10 by 10 μm² map (Fig. 6b) the mean pull-off force and its variance were equal in magnitude (0.15) as expected for the Poisson distribution model. The spatial adhesion map (Fig. 6b) showed that the adhesion was localized to a few discrete regions of the surface. The pull-off forces in the 5 by 5 μm² spatial map (Fig. 6a) showed overall larger forces yet, their magnitude was much smaller when compared with other surface chemistries (Figs. 2–5). For the adhesion results shown in Fig. 6a the mean pull-off force (0.30 nN) had the variance of 0.15 nN².

3.3. Spatial variation of surface heterogeneity

The summary of the mean pull-off forces and respective variances measured for all surfaces is given in Table 2. Using the contact angle measurements and the Young–Dupré equation one can calculate the two works of adhesion, W_{13} and W_{23} and then combine these results with the JKR expression for the pull-off force (Eq. 1) in order to calculate W_{12} . Hence, the variance of the pull-off forces for a given surface can be interpreted as a measure of variation of surface energy. However, the use of the water contact angles is not without problems as they depend on the extent of the adsorption of the water vapors to each tested surface as noted previously by Zisman [37]. Furthermore, the contact angles of fully wettable surface do not reflect the balance of interfacial forces and, in this case, Eq. 3 becomes an inequality. The Si₃N₄ surface is thought to be very similar to the silica surface upon contact with water [38]. The adhesion between the clean glass and the Si₃N₄ tip is the case in which both surfaces are water wettable and water contact angle measurements can not be used to find either W_{13} or W_{23} . The literature data on glass surface energy is inconsistent; a reasonable estimate of 275 Jm^{−2} has been justified by Iler [39] although much smaller values have been reported as well [19,40]. The observed 8.35 nN pull-off force between glass and the Si₃N₄ tip agrees well with the results of Hoh et al. [38] who showed that the lowering of the solution pH increases the magnitude of the pull-off force. The work in this study has been done in water at pH around 5.5–6. Glass surfaces may exhibit a variation in surface composition due to the presence of other alkali oxides. In addition, the high energy of this surface drives its contamination which also may contribute to the pull-off force variance.

The first modification reaction of the glass surface with GPS decreased its wettability (Table 1) as well as the pull-off forces (Table 2, Fig. 3). The GPS–glass variance was smaller than that of clean glass indicating thus that the surface has become energetically more uniform. The next hydrolysis step, however, resulted in an increase of the surface heterogeneity (Table 2, Fig. 4). The two populations of sites, each with its own distribution of pull-off

forces, probably reflect the difference in adhesion between the terminal C(5) primary hydroxyl group and the C(6) primary hydroxyl coupled to a C(5) secondary hydroxyl group (i.e. terminal diol). The reaction with the CDI caused the surface heterogeneity to diminish again (Table 2, Fig. 5) indicating that both sites have reacted with the CDI, perhaps to a different extent that could not be resolved by the adhesion measurements. Both the mean pull-off force and the water contact angle of the CDI-glass surface became lower.

According to the XPS analysis the final reaction of PEO grafting has not resulted in a dense 'brush'-like polymer layer. Nevertheless, very small pull-off forces with a Poisson-like distribution were observed in the adhesion maps. While the large fraction of the surface showed zero pull-off forces (i.e. below 50 pN), some distinct regions of the PEO layer showed slightly larger adhesion. The molecular origin of these adhesion sites remains unclear. At least two different hypotheses can be formulated about these sites. The first is that the localized adhesion is due to the PEO surface density variations which, in turn, are due to the underlying spatial heterogeneity of the CDI reactive groups used to covalently graft PEO chains. The heterogeneity in adhesion maps was observed on different scales on the surfaces with the preceding chemistries (Figs. 2–5): from smallest observable regions separated by 100 nm to μm -sized adhesion regions. The discrete adhesion regions on the PEO surface, however, do not appear to follow the same macroscopic geometry found in the HGPS- and CDI-glass adhesion maps.

The second hypothesis relates the localized adhesion to the regions in which the terminal amino group of the NH_2 -PEO is exposed to the SFM probe and contributed to the measured pull-off force. According to this hypothesis the same terminal amino group of PEO is either bound to the surface or buried in the PEO layer everywhere else on the surface. The covalent grafting of the bisamine-PEO has been performed under conditions of excess PEO in solution (10 mg PEO-bis-amine/ml) and in 11% (w/w) K_2SO_4 solution which was used to decrease the solvent quality for PEO chains. While the first condition favors the terminally attached grafting of the PEO chains, the high K_2SO_4 concentration could, through the collapse of the PEO chains bring both amine ends of PEO chains closer to the reactive surface residues.

4. Conclusions

Two-dimensional mapping of the adhesion pull-off forces has been used to study the origin of surface heterogeneity in the grafted PEO layer. The variance of the pull-off forces recorded over the μm -sized regions was interpreted as a measure of the chemical surface heterogeneity. Four chemical steps used showed different effects on the distribution of the pull-off forces. The attachment of (GPS) to glass decreased the pull-off forces relative to the clean glass and made the surface more uniform. Subsequent hydrolysis of the terminal epoxide group resulted in a larger surface heterogeneity which was modeled with two populations of the terminal hydroxyl groups, each with its own distribution of adhesion forces and variance. The activation of the hydroxyls with CDI healed the surface to a certain degree and lowered its adhesion, yet the variance remained rather large. Finally, the grafting of the α,ω -diamino poly(ethyleneoxide) chains to the CDI-activated glass largely eliminated adhesion except at a few discrete regions. The very low adhesion of PEO followed the Poisson distribution of the pull-off forces.

With the exception of the glass surface, the water contact angles correlated with the mean pull-off force measured with the Si_3N_4 tip. The reason for this is most likely the similarity between the two probes used, water and Si_3N_4 tip, which probed to a larger degree the same polar types of interactions. The actual chemical nature of the surface heterogeneity remains rather elusive and could be postulated only in the case where an independent information

about chemical surface species was available. A more specific chemical information about the surface heterogeneity is expected to be obtained using the probes with different surface chemistries (or different liquids).

Acknowledgments

The authors gratefully acknowledge the discussion with H.P. Jennissen and D.W. Grainger. This work was supported by The Center for Biopolymers at Interfaces, University of Utah (G.J., J.K.S.) and the NIH grant HL44538.

References

- [1]. Huntsberger JR. J. Adhes. 1976; 7:289–299.
- [2]. Kendall K. Contemp. Phys. 1980; 21:277–297.
- [3]. Kinloch AJ. J. Mater. Sci. 1982; 17:617–651.
- [4]. Israelachvili JN. Surf. Sci. Rep. 1992; 14:109–159.
- [5]. Kendall K. Science. 1994; 263:1720–1725. [PubMed: 17795378]
- [6]. Smith, JR., editor. Mater. Sci. Eng. Vol. 83. 1986. Panel Report on Interfacial Bonding and Adhesion; p. 169-234.
- [7]. Good, RJ.; Chaudhury, MK. Fundamentals of Adhesion. Lee, LH., editor. Plenum Press; New York: 1991. p. 137-151.
- [8]. Good, RJ.; Chaudhury, MJ.; Oss, CJ. Fundamentals of Adhesion. Lee, LH., editor. Plenum Press; New York: 1991. p. 153-172.
- [9]. Landman U, Luedtke WD, Burnham NA, Colton RJ. Science. 1990; 248:454–461. [PubMed: 17815594]
- [10]. Andrade JD, Hlady V. Adv. Polym. Sci. 1986; 70:1–63.
- [11]. Bell GI. Science. 1978; 200:618–627. [PubMed: 347575]
- [12]. Dembo M. Lect. Math. Life. Sci. 1994; 24:51–77.
- [13]. Bell GI, Dembo M, Bongrand P. Biophys. J. 1984; 45:1051–1064. [PubMed: 6743742]
- [14]. Fleer, GJ.; Cohen Stuart, MA.; Scheutjens, JMHM.; Cosgrove, T.; Vincent, B. Polymers at Interfaces. Chapman and Hall; London: 1993.
- [15]. de Gennes PG. Polym. Prepr. 1996; 37:101–102.
- [16]. Mizes HA, Loh K-G, Miller RJD, Ahuja SK, Grabowski EF. Appl. Phys. Lett. 1991; 59:2901–2903.
- [17]. Creuzet F, Ryschenkow G, Arribart H. J. Adhes. 1992; 40:15–25.
- [18]. Hoh JH, Cleveland JP, Prater CB, Revel J-P, Hansma PK. J. Am. Chem. Soc. 1992; 114:4917–4918.
- [19]. Kawai A, Nagate H, Takata M. Jpn. J. Appl. Phys. 1992; 31:L977–L979.
- [20]. Israelachvili, JN. Intermolecular and Surface Forces. 2nd ed.. Academic Press; London: 1992.
- [21]. Johnson KL, Kendall K, Roberts AD. Proc. R. Soc. Lond. Ser. A. 1971; 324:310–313.
- [22]. Han T, Williams JM, Beebe TP. Anal. Chim. Acta. 1995; 307:365–376.
- [23]. Williams JM, Han T, Beebe TP. Langmuir. 1996; 12:1291–1295.
- [24]. Moy VT, Florin EL, Gaub HE. Science. 1994; 266:257–259. [PubMed: 7939660]
- [25]. Florin E-L, Moy VT, Gaub HE. Science. 1994; 264:415–417. [PubMed: 8153628]
- [26]. Chilkoti A, Boland T, Ratner BD, Stayton PS. Biophys. J. 1995; 69:2125–2130. [PubMed: 8580356]
- [27]. Frisbie CD, Rozsnyai LF, Noy A, Wrigton MS, Leibler CM. Science. 1994; 265:2017–2074.
- [28]. McKendry R, Theoclitou M-E, Rayment T, Abell C. Nature. 1998; 391:566–568.
- [29]. Sanders, A. Diplomarbeit. Universität-Gesamthochschule; Essen: 1992.
- [30]. Regnier FE, Noel R. J. Chromatogr. Sci. 1976; 14:316–320. [PubMed: 956322]
- [31]. Hermanson, GT. Bioconjugate Techniques. Academic Press; San Diego: 1996.

- [32]. Lin Y-S, Hlady V, Golander C-G. Colloid. Surf. B. Biointeractions. 1994; 3:49–62.
- [33]. Andrade, JD. Surface and Interfacial Aspects of Biomedical Polymers. In: Andrade, JD., editor. Surface Chemistry and Physics. Vol. vol 1. Plenum Press; New York: 1985. p. 105-195.
- [34]. Arkles, B. Silicon Compounds: Register and Review. 5th ed.. Anderson, R.; Larson, GL.; Smith, C., editors. Hüls America; Piscataway, N.J.: 1991.
- [35]. Bayer EA, Reiners J, Nieder M. J. Chromatogr. 1983; 264:197–213.
- [36]. Zumbrink T, Demiroglou A, Jennissen HP. J. Molecul. Recog. 1995; 8:363–373.
- [37]. Zisman WA. Ind. Eng. Chem. 1963; 55:18–38.
- [38]. Hoh JH, Revel JP, Hansma PK. Nanotechnology. 1991; 2:119–122.
- [39]. Iler, RK. The Colloid Chemistry of Silica and Silicates. Cornell University Press; Ithaca: 1955.
- [40]. Zisman WA. J. Paint. Tech. 1972; 44:42–57.

Fig. 1.

Schematics of four chemical reactions used in modification of glass surfaces with terminally grafted PEO chains.

Fig. 2.

A 10 by 10 μm^2 map of the pull-off forces recorded with a Si_3N_4 SFM tip on the clean glass surface in water (top) and the histogram of pull-off forces from the same area (bottom). The contrast in the adhesion image was adjusted to range between 0 nN (white pixel in the upper left corner) and 15 nN force (black pixel in the upper left corner). The force histogram was fitted with a single normal distribution (smooth line, 8.35 nN mean pull-off force, 2.5 nN^2 variance).

Fig. 3.

Spatial distributions of pull-off forces recorded with a Si_3N_4 SFM tip on the GPS-glass surface in water. (a) A 5 by 5 μm^2 map (top) and the histogram of pull-off forces from the same area (bottom). (b) A 10 by 10 μm^2 map (top) and the histogram of pull-off forces from the same area (bottom). In both images the force contrast was adjusted to range between 0 nN (white pixel in the upper left corner) and 10 nN force (black pixel in the upper left corner). Each force histogram was fitted with a single normal distribution (shown in a smooth line, (a) 3.85 nN mean pull-off force, 0.55 nN^2 variance; (b) 3.75 nN mean pull-off force, 0.55 nN^2 variance).

Fig. 4.

Spatial distributions of pull-off forces recorded with a Si_3N_4 SFM tip on the HGPS–glass surface in water. (a) A 5 by 5 μm^2 map (top) and the histogram of pull-off forces from the same area (bottom). (b) A 10 by 10 μm^2 map (top) and the histogram of pull-off forces from the same area (bottom). In both images the force contrast was adjusted to range between 0 nN (white pixel in the upper left corner) and 10 nN force (black pixel in the upper left corner). Each force histogram was fitted with two normal distributions (smooth lines). The lower pull-off force normal distributions had the mean forces at 4.05 nN (Fig. 4a) and 3.70 nN (Fig. 4b) and the respective variances were 0.9 nN² and 1.05 nN². The higher pull-off force distributions had the mean forces at 5.0 nN (Fig. 4a) and 4.85 nN (Fig. 4b) and the variances of 0.3 nN² and 0.35 nN², respectively.

Fig. 5.

A 5 by 5 μm² map of the pull-off forces recorded with a Si₃N₄ SFM tip on the CDI-glass surface in water (top) and the histogram of pull-off forces from the same area (bottom). The contrast in the adhesion image was adjusted to range between 0 nN (white pixel in the upper left corner) and 10 nN force (black pixel in the upper left corner). The force histogram was fitted with a single normal distribution (smooth line, 2.95 nN mean pull-off force, 1.10 nN² variance).

Fig. 6.

Spatial distributions of pull-off forces recorded with a Si_3N_4 SFM tip on the NH_2 -PEO-glass surface in water. (a) A 5 by 5 μm^2 map (top) and the histogram of pull-off forces from the same area (bottom). (b) A 10 by 10 μm^2 map (top) and the histogram of pull-off forces from the same area (bottom). In both images the force contrast was adjusted to range between 0 nN (white pixel in the upper left corner) and 10 nN force (black pixel in the upper left corner). The force histograms showed a 0.30 nN mean pull-off force and a 0.15 nN^2 variance (Fig. 6a) and a 0.15 nN mean pull-off force and a 0.15^2 nN^2 variance (Fig. 6b), respectively.

Table 1

Water contact angles measured with sessile drop method and the atomic percentages of elements found on the modified glass surfaces using XPS

	Water contact angle (°)	C (at. %)	O (at. %)	Si (at. %)	N (at. %)
Glass	6 ± 3	6	63.8	30.2	0
GPS-glass	47 ± 5	46.3	36.3	17.3	0
HGPS-glass	35 ± 4	–	–	–	–
CDI-glass	31 ± 4	30.9	45.5	21.1	2.5
NH2-PEO-glass	20 ± 4	40.3	38.1	18.8	2.8

Table 2

The summary of mean pull-off forces (in nN) and respective variances found over the areas imaged (in nN²)

	Area imaged (μm^2)	Mean pull-off force (nN)	Variance (nN ²)
Glass	10 by 10	8.35	2.5
GPS-glass	5 by 5	3.85	0.55
	10 by 10	3.75	0.55
HGPS-glass ^a	5 by 5	4.05 (low) ^a	0.9 ^a
		5.00 (high) ^a	0.3 ^a
	10 by 10	3.70 (low) ^a	1.05 ^a
		4.85 (high) ^a	0.35 ^a
CDI-glass	5 by 5	2.95	1.10
NH2-PEO-glass	5 by 5	0.30	0.15
	10 by 10	0.15	0.15

^aThe histogram of pull-off forces for the HGPS-glass surface was fitted with two normal distributions.