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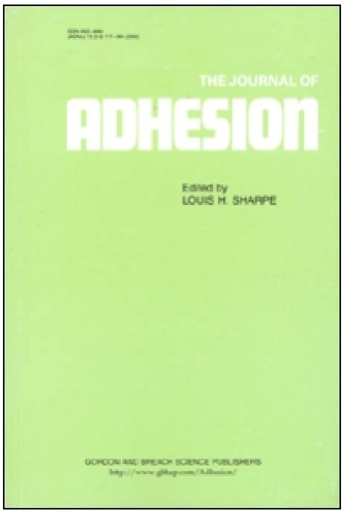

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

A New Tool for Adhesion Science: The Atomic Force Microscope

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To cite this Article Creuzet, F. , Ryschenkow, G. and Arribart, H.(1992) 'A New Tool for Adhesion Science: The Atomic Force Microscope', The Journal of Adhesion, 40: 1, 15 — 25

To link to this Article: DOI: 10.1080/00218469208030468

URL: http://dx.doi.org/10.1080/00218469208030468

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J. Adhesion, 1992, Vol. 40, pp. 15–25
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A New Tool for Adhesion Science: The Atomic Force Microscope

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(Received May 7, 1992; in final form July 7, 1992)

The recently-developed Atomic Force Microscope (AFM) has been used to study the problem of adhesive failure in an elastomer/glass system. Polymeric residues have been obtained in various conditions by peeling a polyurethane film from glass plates. Their observation with nanometric resolution reveals structures which have not been detected by the usual techniques. We present typical images which emphasize the importance of the nature of the substrate and the ageing conditions. The results are discussed in relation to the nature of the interphase and the failure mechanism. Furthermore, a particular mode of use of AFM is described to illustrate the potential of this technique as a locally-resolved spectroscopic tool.

KEY WORDS adhesion; adhesive failure; atomic force microscope; glass; interphase; peeling test; polyurethane.

INTRODUCTION

The properties of adhesive assemblies are usually studied by mechanical tests which deliver macroscopic information. Depending on technological requirements for the practical adhesive joint, various test designs (peeling, shear, torsion, cleavage, etc.) have been optimized.[1] Besides the numerical value of the failure strength, it is fruitful to characterize the behavior of the adhesive joint by its mode of failure: three classes are commonly named *cohesive*, *interfacial* and *"in a weak boundary layer"*.[2] However, beyond this rough classification, it is important to keep in mind that these tests involve microscopic properties and phenomena acting at the molecular scale; relevant chemical bonds at the interface, rheology of the polymer, structure of the interface, texture of the substrate, diffusion of impurities, are many contributions that must be investigated in detail for a complete description of adhesion.

As a result, the mechanism of failure is a rich problem which has the potential to give valuable information on the so-called "interphase"[3] between the substrate and

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the polymer bulk. In the past years, many techniques and especially spectroscopic characterizations have been used to analyze the surface after breaking.[4] Nevertheless, the problem remains almost unsolved, partly because the apparent structures at the surface may be organized at a very small scale, and heterogeneities whose dimensions (typically less than 1000 Å) are much smaller than the spatial resolution of the spectroscopic technique have not been detected yet.

In this paper, we show that the recently-developed Atomic Force Microscope (AFM)[5] has the capability to bring new and important insights into the problem of adhesion failure, precisely because it permits both the observation and the local characterization of surfaces at various scales from 5 Å to 100 μm. Ultimately, it should be possible to achieve a very detailed description of the mode of failure propagation which can lead to a complete understanding of the failure mechanism, when combined with adhesion strength measurements and spectroscopic data. To illustrate the new capabilities offered by AFM, we have chosen to present a preliminary study on a system already investigated in our laboratory by other techniques. The experiments are performed on the adhesion failure obtained by peeling an elastomeric polyurethane film from a glass substrate. Firstly, topographic images of glass surface after failure have been obtained with nanometric resolution and precise information on the location of the failure can be inferred. By modifying the nature of the substrate (industrial float-glass, silica) and the ageing conditions of the test-assembly before peeling, we have explored different mechanisms of failure: almost perfectly interfacial at one end, and within an interphase at the other end. Besides, we have used the AFM to perform local surface experiments, such as measuring short-range and long-range surface forces or probing surface hardness. This last series of experiments turns the technique into a spectroscopic tool at the submicronic scale.

EXPERIMENTAL

The substrates that we have used are industrial float-glass from Saint-Gobain Vitrage France and mechanically-polished amorphous silica (quality 124) from W.Q.S., Germany. Polyurethane films (thickness≈0.76 mm) are made by extrusion starting from polymer grains provided by S.N.P.E., France. Films are joined to the substrate by hot-pressing at 12 bars and 140°C. In the same process, the film is backed with a sheet of cotton cloth. Before preparing the test-assemblies, all substrates are cleaned with water and rinsed with ethanol. Their lateral dimensions are 10 cm × 5 cm. The ageing process of test-pieces is performed in a wet (100% R.H.) and hot (70°C) environment for different periods of time. Afterwards, polyurethane strips 13 mm wide and 100 mm long are peeled at an angle of 90° with an Instron test machine at a constant velocity of 20 mm/mn. The peeled glass surface is examined by Atomic Force Microscopy, using a commercial instrument from Park Scientific Instruments (U.S.A.).

In previous studies,[6] the same surfaces were characterized using various techniques: wettability measurements, ellipsometry, reflection FTIR spectroscopy and Scanning Electron Microscopy (SEM). The results established in Ref. (6) may be summarized as follows. Amorphous silica and float-glass exhibit distinct behavior with respect to adhesion of polyurethane. For the former, the peeling force remains constant (60 N/cm) whatever is the ageing time from 0 to 14 days. For the latter, when the ageing process is extended, the peeling force decreases monotonically from about 90 N/cm, reaching zero after 14 days of ageing. In the case of silica, FTIR detects a very small amount of polyurethane which is not observable by SEM. The situation is quite different for float glass: when the ageing time increases, ellipsometry and FTIR data show that the mean thickness of the polymeric residue grows. Correlatively, SEM reveals an heterogeneity which becomes more and more pronounced with ageing time. Moreover, spectroscopic techniques[6] give strong indications for a kind of ordering of the PU near the silica surface. It is important to note that in all cases, and whatever the substrate, wettability measurements show that some organic residue covers most of the surface although no characterization of this layer has been given so far.

The full description of the AFM technique can be found in the literature.[7] Basically, a sharp tip attached to a micro-cantilever of known stiffness is placed close enough to the surface so that any surface-tip interaction induces a bending of the cantilever. Consequently, the deflection of the cantilever is a direct measure of the force between the tip and the surface and can be used to construct an image when scanning the tip position. The most common mode of operation is called "repulsive" and corresponds to a contact of the tip to the surface; in this case, the topography of the surface is easily recorded with a lateral resolution of a few Angströms. Other experiments using the same instrument can be implemented: one of them is to record the force between tip and surface as a function of their distance when the tip is moved back and forth ("force profile"). This can be used to identify the nature of the area underneath the tip, especially when the force profile has been proved to be a signature of the material,[8] and even to map the surface by using various kinds of local properties.[9,10] Finally, it is important to emphasize that, among the near field microscopies, this imaging technique is the only one that is applicable to insulators and has the potential to reveal details at the atomic scale, as well.

RESULTS

The AFM experiments were performed on the samples mentioned above within a few days after the peeling test. In order to compare the peeled and the bare substrates, a thin Mylar sheet was used to prevent the adhesion of the PU film on part of the substrate. For all samples, several images were recorded on different locations in order to verify the reproducibility of the observed features. In order to characterize the corrugation quantitatively, we measured the surface roughness, defined as the root mean square (rms) of the height deviation to the mean flat surface. Obviously, this quantity is a spectral parameter and strongly depends on both the scan size and the rate of digitization.[11] We have chosen to calculate the roughness on a 5000×5000 Å^2 surface with 256×256 points. As already reported,[12] the atmosphere side of bare float glass exhibits a roughness of 2 Å, a value compatible with X-ray reflectivity measurements;[13] this reveals float glass as one of the smoothest

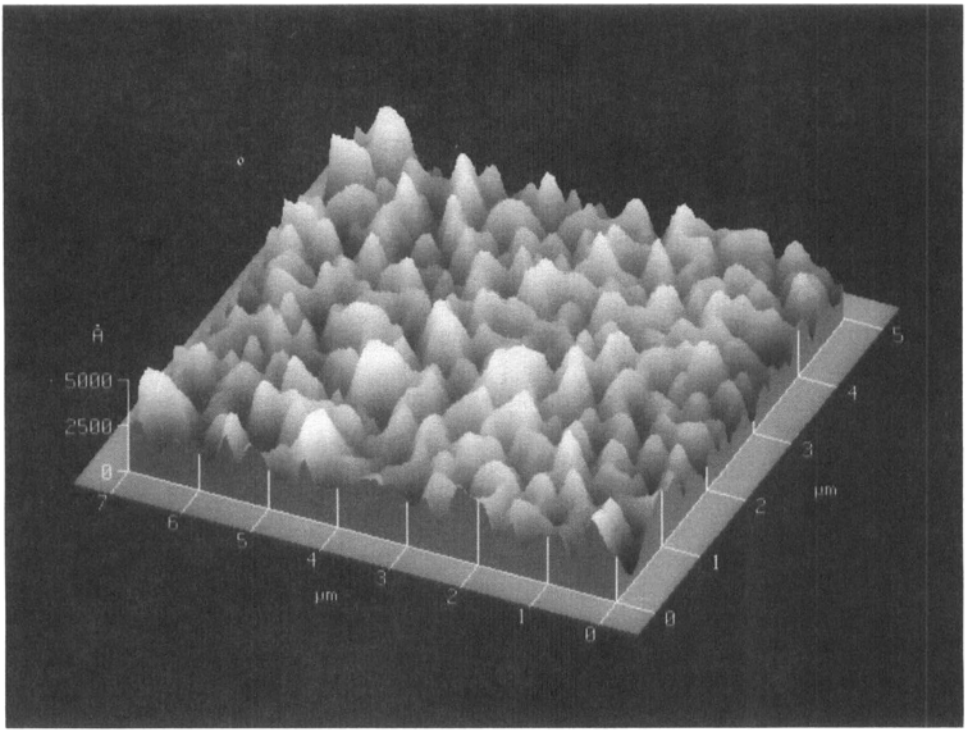
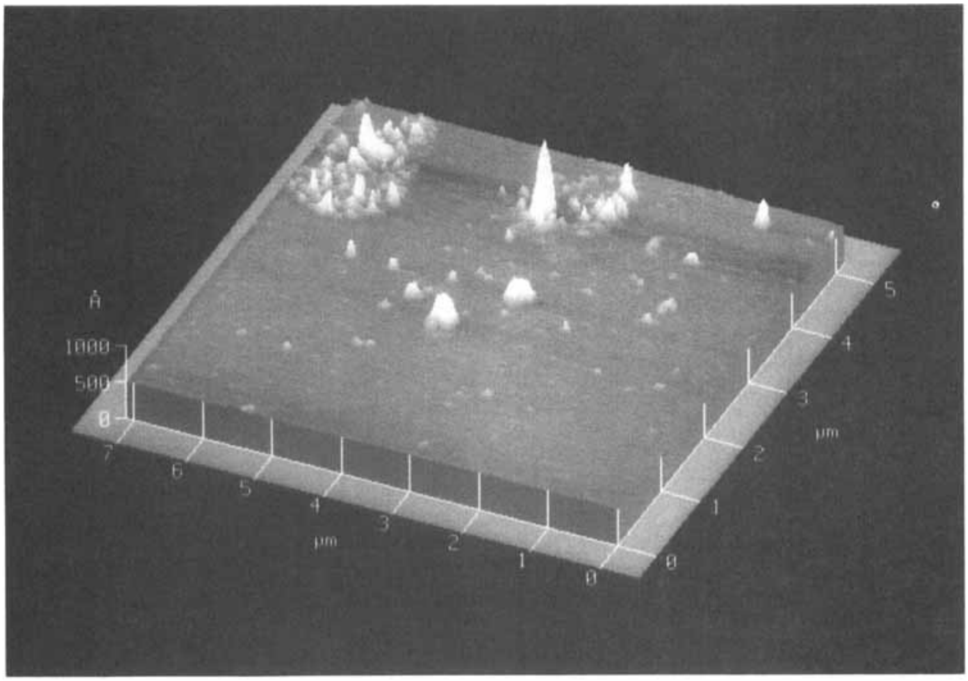


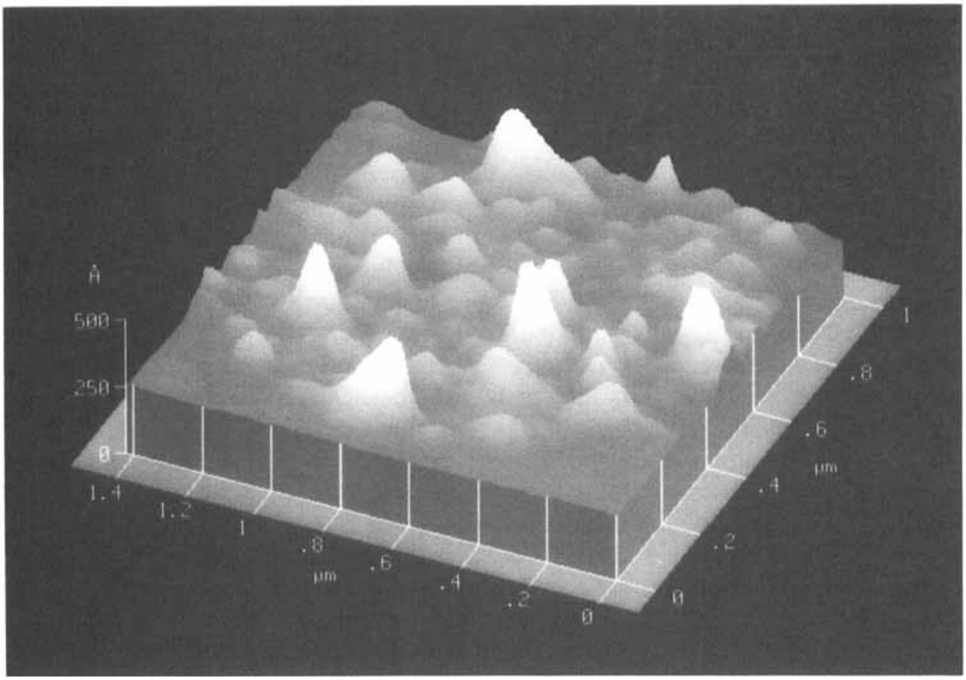
FIGURE 1 Failure surface of a 2-day-aged PU/float glass assembly. The vertical scale is magnified in order to show the corrugation.

manufactured surfaces. For the polished silica that we used, this parameter reaches 4 Å, a difference which is significant within the experimental error. Figure 1 shows a typical failure surface for a 2-day-aged PU/float glass assembly. Although the mean plane remains parallel to the bare substrate, at least at the 100 μm scale, the corrugation of the surface indicates that the fracture of PU is inhomogeneous at the submicronic scale: the surface exhibits a multitude of bumps, more or less connected, the heights of which are in the range 1000–4000 Å. However, the diameter of the bumps is not widely distributed but centered around 3000 Å.

Figure 2a displays the image obtained when no ageing of the assembly is performed. Although SEM observations predict that a homogeneous surface is to be found, small and randomly distributed islands of polymer residue are observed on this image. Note that the small size of these islands (about 1 μm diameter and 200 Å height) may explain why they have not been detected by other techniques. As shown in Figure 2b, which is an image taken at a smaller scale, the structure of each island appears similar to the one of Figure 1 but with bumps of different characteristic size, *i.e.* a diameter centered around 800 Å. Between the islands, the roughness is 6 Å or so, a value unambiguously larger than the one of bare float glass. This last result indicates that some organic material remains on the substrate. Because FTIR spectroscopy indicates a mean thickness (*i.e.* integrated over the size of the infrared beam and, consequently, including the contribution of the islands discussed above)



(a)



(b)

FIGURE 2 (a) Failure surface of a non-aged PU/float-glass assembly. The roughness value measured between the bumps shows the presence of a thin polymeric residue. (b) Enlargement of the island on the back left corner of Figure 2a.

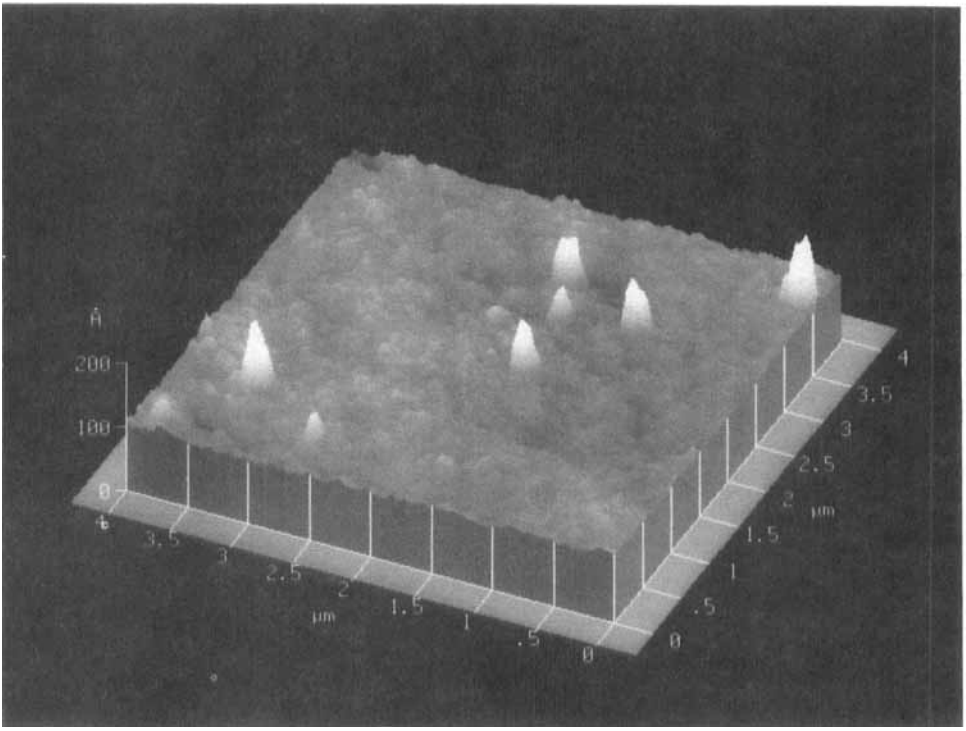


FIGURE 3 Failure surface of a 2-day-aged PU/silica assembly.

of residual polymer of the order of 10 Å,[6] we conclude that only an ultrathin residue of polymer covers the surface, which is, however, enough to explain the wettability data. For silica substrates, the analysis of experimental data shows that the topographic structure and the roughness do not depend on ageing. The failure surface for a 2-day-aged PU/silica assembly is shown on Figure 3. The surface morphology is very similar to the one observed on silica or float glass without ageing, and the roughness between the polymeric bumps is around 5 Å.

Local surface experiments have been performed by measuring force profiles at different locations of the glass surface near the border of a PU-free region where a Mylar sheet was placed in order to prevent adhesion. This area of the substrate after peeling is shown on Figure 4. Data displayed in Figure 5 are obtained by recording the deflection of the cantilever while moving the tip back and forth to the surface at location 1 on Figure 4, *i.e.* on a PU-free part of the glass surface. A typical interpretation of this type of curve is discussed by N. Burnham *et al.*[8] When the tip approaches the surface, it becomes sensitive to attractive long range forces. Point A corresponds to the characteristic "jump-to-contact" due to the mechanical instability when the tip-sample force gradient overcomes the cantilever force constant. If the cantilever is moved further (AB), the deflection is proportional to the displacement since the tip "touches" the surface. When the cantilever is withdrawn, we notice two kinds of hysteresis. One is of instrumental origin: due to the intrinsic

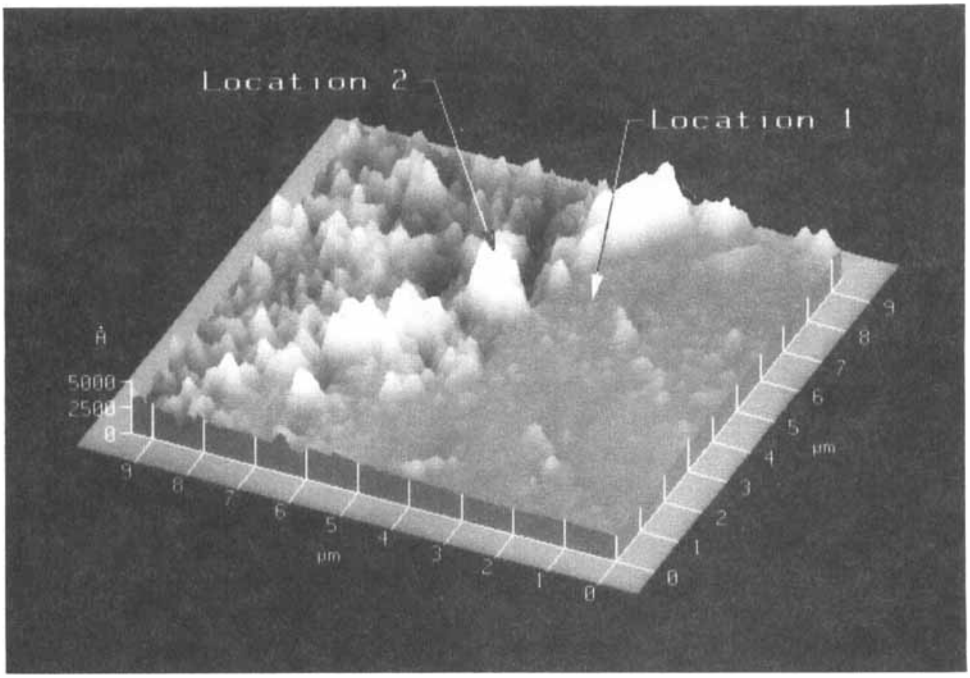


FIGURE 4 Same sample as in Figure 1 displaying a PU-free region (right-front side). Locations 1 and 2 are indicated by arrows.

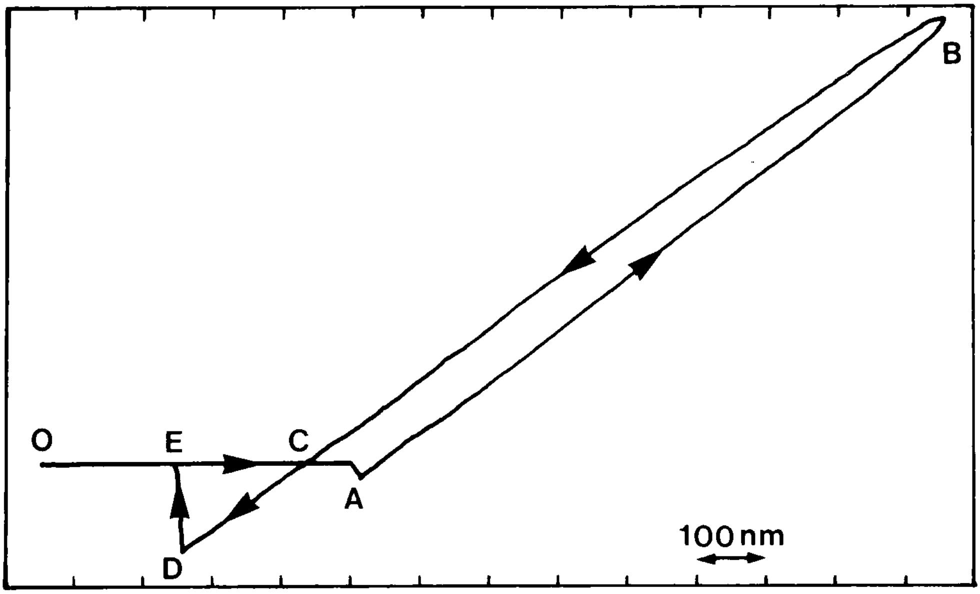


FIGURE 5 Overall cycle of the force profile performed at location 1 of Figure 4. The X-axis represents the sample position towards the tip and the Y-axis, the deflection of the cantilever (in arbitrary units). Note that the X-axis is related but not identical to the tip-surface distance.

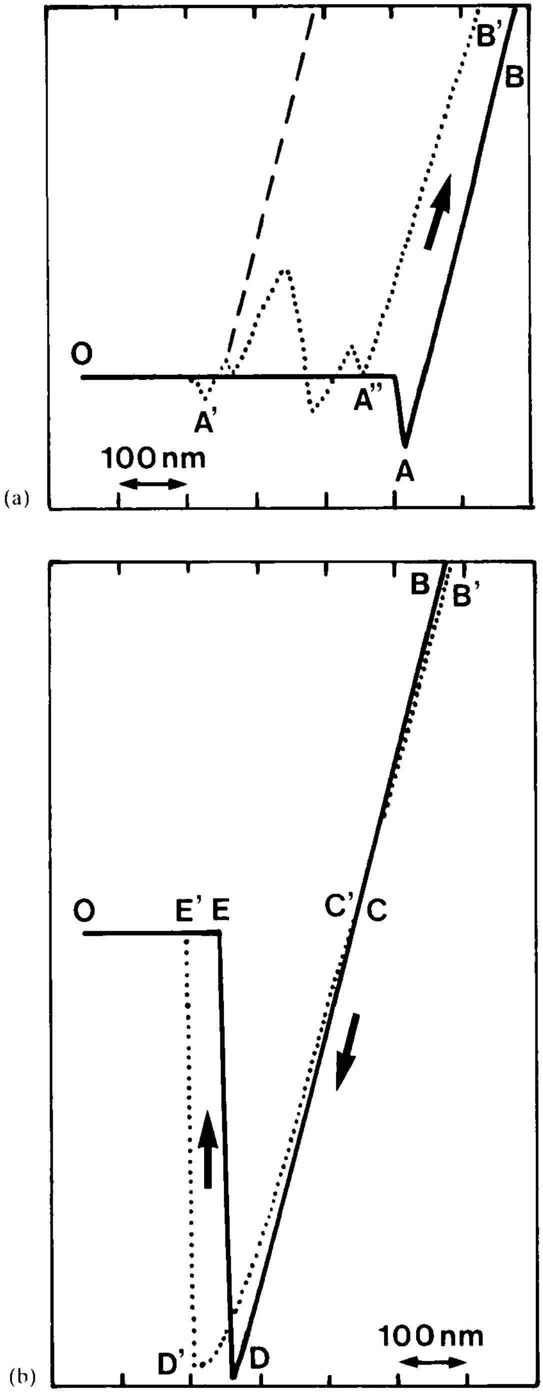


FIGURE 6 Enlarged force profiles at location 1 (full line) and location 2 (dotted line). (a) Forward trace. The broken line is drawn to show the expected trace if PU was a hard material. (b) Backward trace.

hysteretic behavior of the piezo transducer, the backward trace (BC) does not coincide with the forward trace. More interesting is the large hysteresis (CD) recorded before the system goes back to equilibrium, *i.e.* no interaction between the tip and the surface, at point E. Its magnitude is proportional to the attractive force between the surface and the tip at short range, which can be called the tip-surface adhesion force.

Due to the piezo hysteresis, it is necessary to compare independently the forward and backward traces obtained at different locations of the surface. This is done respectively on Figures 6a and 6b for location 1 discussed above and for location 2 of Figure 4 which corresponds to the top of a PU bump. As expected, Figure 6a shows that the jump-to-contact occurs earlier at location 2 (point A′) than at location 1. The height difference between points A and A′ corresponds to the height of the bump shown on Figure 4. If polyurethane was a hard material, the trace should follow the broken line. But after having started to do so, the tip begins to penetrate the PU residue when the spring force becomes higher and higher. At point A″, the tip is almost in contact with the underlying glass substrate and the trace A″B′ is nearly parallel to the trace AB obtained at location 1. During the withdrawal (Figure 6b) the return to equilibrium (E and E′) for locations 1 and 2 is almost at the same distance from the glass surface. Since jump-to-contact points A and A′ are quite different, this shows that the hysteresis due to tip-surface adhesion through short-range forces is much smaller at location 2 than at location 1. This difference could be attributed to a surface polarity lower for PU than for glass.

Although the study of dynamic effects is still under completion, we can infer that this experiment can be used to detect the presence of polymer at a very local scale.

DISCUSSION

These results can be interpreted within the interphase model[3] which states that the physico-chemical properties of the polymer in the neighborhood of the interface are different from those in the bulk. They depend on the overall history of the assembly and obviously have a strong influence on its mechanical behavior.

In the case of the glass/polyurethane system, previous results[6] have shown that the ageing treatment leads to a thickening of the interphase on float glass, and that the peeling force decreases when the interphase thickens. The present work not only confirms these facts but also brings new important results which may be summarized as follows: i) in any case, the structure of the peeled surface is heterogeneous at a scale of *100 to 1000 Å and ii) a polymeric residue remains on all substrates*, in agreement with the wettability experiments.

Moreover, the detailed AFM observations reported here allow us to describe the structure of these residues:

—In the case of a 2-day-aged float glass assembly (Figure 1), the failure is clearly *cohesive,* but large bumps are observed which suggest an organization of the polymer during the peeling test. A tentative explanation is that the polymer tends to form regularly-spaced fibrils when the film is torn during the peeling test. When these fibrils break, they would collapse and form the bumps that are observed.

—In the case of silica or non-aged float glass assemblies, the failure is almost *interfacial*, but it is important to emphasize that this designation is not completely correct since polymeric residues are still present. More precisely, the organization is very particular and islands of polymer emerge from a homogeneous sub-nanometric layer of PU. The morphology of the islands has close similarities to the one given for float-glass aged assemblies, but at a much lower scale which indicates that the fibrillation mechanism is less efficient for the failure propagation. However, the rest of the surface is covered with a PU layer of mean thickness less than, or of the order of, the molecular dimensions of the polymer chains. In that case, the residual polymeric material probably consists of non-connected chains which are either disentangled or broken.

These results lead us to a comparative description of the failure mechanism in the different cases which have been examined. For PU/silica and non-aged PU/float-glass assemblies, no interphase thicker than molecular dimensions exists. The cohesion energy of PU is higher than the adhesion energy; the peeling force is high and the failure is almost interfacial. On some places, however, the presence of islands of residual polymer shows that some inhomogeneity exists at the micrometer scale. It could be due to chemical impurities in the PU film or on the glass surface leading to a weakening of the polymer or a reinforcement of the interface. In the case of aged PU/float-glass assemblies, an interphase of cohesion energy lower than the adhesion energy is formed. Failure occurs by a tearing of the polymer in this interphase. The difference in the ageing behavior for glass and silica assemblies is interpreted as a chemical degradation of the polymeric chains by alkaline species present in float-glass. This is compatible with ellipsometry measurements[6] which show that the thickness of the residual PU layer increases with ageing time, as expected for a chemical process governed by diffusion. We note that the effect of ageing is more pronounced for cohesive bonds than for interfacial bonds, contrary to what is observed with structural adhesives, like epoxy, on glass.[14] But in those cases both the chemistry of the glass-polymer system and the polymer rheology are very different.

CONCLUSION

In this paper, we have pointed out that AFM experiments can provide new and unique information on interface and interphase in adhesion science. The glass/polyurethane system studied in this paper demonstrates that surface imaging at the submicronic scale as well as local surface characterization is very useful to identify the nature of the interface/interphase and the location and mechanism of failure. Inhomogeneities at very different spatial scales have been evidenced. Beyond this example, we expect that the contribution of AFM will be a real breakthrough in adhesion science.

Our results show that the accepted classification of failure is limited to practical purposes and that a more sophisticated description of adhesion is necessary: it must involve observations at the molecular scale. Undoubtedly, this will lead to a critical reexamination of the information that is obtained from adhesion tests, such as peeling tests. Of course, the experimental procedure described in this paper can be generalized to other adhesion experiments, with different geometry and various materials. For instance, we have started a study of the interphase between glass fibers and a polymeric matrix in order to achieve a better understanding of the bonding and debonding mechanisms in composite materials.

From the academic point of view, some of the results presented here open the way to new investigations in the field of the physics of fracture of polymers in the bulk material as well as near an interface. A few studies have already started in this direction in our laboratory: influence of the rate and temperature of the peeling test on the mode of failure, examination of single chains adsorbed to the substrate, etc.

Acknowledgements

The assistance of M. Simonet and F. Kazemi in the preparation of samples is appreciated. We are also indebted to P. Chartier for fruitful discussions.

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