MECHANICAL TUNING OF ADHESION THROUGH MICRO-PATTERNING OF ELASTIC SURFACES

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Introduction

The precise tuning of adhesion properties is of great interest for a number of applications, especially when one deals with weak adhesion. Cross-linked polydimethylsiloxane (PDMS) substrates are commonly used in microfluidic systems or in "bio-inspired" surface fabrication because of their low surface energy and weak chemical reactivity which provide anti-adhesive properties **[1]–[3]**. For a number of other applications, such as protective layers of stickers for example, the adhesion of common acrylic adhesives is too low on PDMS substrates, which then need be formulated with additives reinforcing adhesion. The design of PDMS surfaces with tailored adhesive properties remains a real technological challenge. A commonly followed path relies on chemical modification of the antiadhesive coating, which usually leads to adhesion enhancement that strongly depends on the chemical nature of the adhesive.

An alternative and potentially more universal solution based on microstructuration has been proposed and has started to be investigated recently by several authors. From a theoretical point of view, Arzt et al.**[4]** have shown, using the Johnson Kendall Roberts (JKR) theory of adhesive contacts, that splitting up one contact into many smaller subcontacts increases adhesion and Persson et al.**[5]** have shown that the effective elastic modulus of a fibrillar structure is much smaller than that of the corresponding bulk material. As a result, a fibrillar structure is expected to be highly compliant, which should help in forming intimate contact. This is, of course, of fundamental importance for adhesion on both smooth and rough substrates. Later, Jagota et al.**[6]** have shown that the work required to separate a fibrillar structure from a substrate is larger than that of the same smooth material because the elastic strain energy stored in the fibrils, when they deform, is lost during pull-off. Hui et al. **[3]**, for their part, have shown that in the case of fibrillar structures the stress concentration at the crack tip is redistributed over a zone described by a characteristic length significantly larger than the cross-sectional dimensions of the fibrils. Within this zone, the fibrils are under equal load-sharing conditions. Consequently, the failure of the interface involves a simultaneous failure of all fibrils inside this zone, which is quite different from the usual crack propagation for which stress concentration favors a sequential failure of fibrils starting with the fibrils closest to the crack tip. Indeed, all of these findings are indeed along the lines of early experiments from Fuller and Tabor **[7]**: they observed that adhesion was enhanced on rough substrates, a result interpreted using two major assumptions:

- The viscoelastic properties of the rubber are essential to forming an intimate contact with a rough surface (as a result of stress relaxation).
- The substrate roughness leads to the formation of isolated contact regions during peeling.

The final stages of separation involve only isolated still-adhering zones whose associated elastic energy, built up during peeling, is lost when the contact is broken. The same type of analysis has been also performed on wrinkle surfaces by Crosby et al.

In the present article, we review our investigations of the exact role of the patterning on adhesion enhancement between a patterned surface and a commercial acrylic adhesive tape. The first part of this article will present the experimental setup, the commercial adhesive tape. The second part of the result will briefly present some results showing that different regime of adhesion modification due to a scotch tape have been evidenced. In the last part, we will focus on the regime where the deformations in the elastic substrate are dominant, with a special emphasis on the effect of the

coupling between the pattern structures when their relative distance is progressively decreased.

Experimental setup

The peel force *F* was measured with a lab-developed peel apparatus schematically presented in figure 1. The top part includes a force sensor fixed on a 45° motorized endless screw which allows 90° peeling at a velocity *V* in the range 0.5-5000 µm/s.

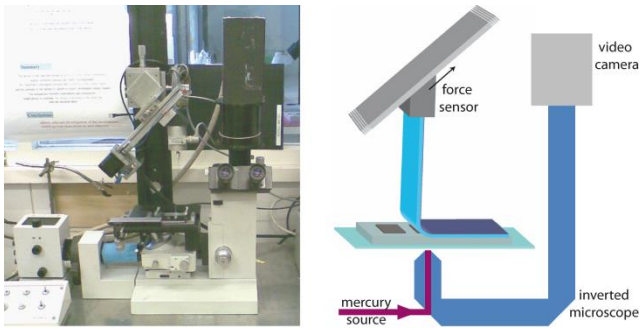

Fig.1: Picture and schematic representation of the peel experiment. Samples are put onto an inverted microscope and the peel motion is imposed by a 45° motorized endless screw coupled to motor. The peel force is measured by a force sensor attached to the peeled ribbon.

The bottom part is an inverted optical microscope allowing to visualize the peel front at micrometric scale. The sample is illuminated perpendicularly to its plane with a mercury source, through an optical fiber. Prior to each experiment, the adhesive tape (3M 600) was put into contact with the substrate, under a load corresponding to a pressure of 0.1 MPa, for 12 hours to ensure that *the adhesive fully fills the space between the micropatterns* (which can easily be checked optically, due to the refractive index matching when intimate contact between the substrate and the adhesive is attained).

Soft Patterned PDMS substrates were produced by classical molding techniques using a silicon wafer with an etched resist layer as a mold. This mold was obtained with standard electronic lithography techniques: a thin layer of a positive resist (MicroChem PMMA 950k) was spincoated onto a silicon wafer and its thickness fixes the height *h* of the pillars. This resist layer was then locally exposed to an electron beam (30kV, 13nA) in a FESEM (Zeiss SUPRA 55VP). The desired pattern was first design with DesignCAD Express V16.2 and the FESEM was controlled with NPGS V9.0.190 to write the pattern. After irradiation, the exposed parts of the resists was develop in MIBK:IPA solution (3:1) during 60 sec under agitation. PDMS replicas were obtained by pouring in this mold a millimeter thick layer of PDMS mixed with a crosslinker (Sylgard 184, Dow Corning), curing at 50 °C for 24 h, and finally peeling off the crosslinked PDMS elastomer from the mold. The patterned PDMS elastomer films were finally fixed on a pretreated (UV-Ozone) glass plate. The elastic modulus of the films, E=1.8±0.1 MPa, has been measured by a JKR test [8]–[10].

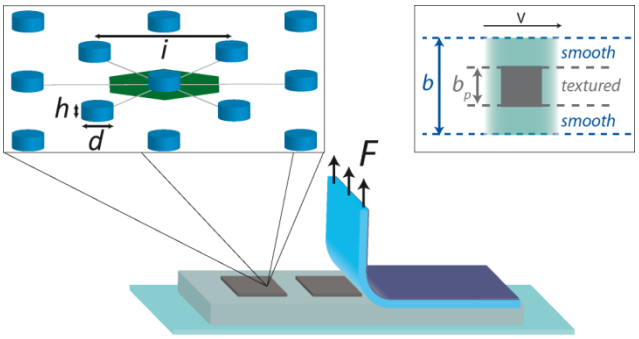

Fig.2: Schematic view of the geometry of a peel sample: the acrylic adhesive in contact with a patterned substrate is peeled at 90°. The width of the contact *b* is 19 mm and the width of the patterned area b_p is 8 mm, which means that, as shown in the right insert, when the peel front sweeps the patterned zone of the substrate, the peel force results from both smooth and patterned contact

Hard patterned surfaces were made of optical cement. The optical cement is much harder, with a Young's modulus of 1.6 GPa (Summer Optical information). The details of the experimental procedure for hard substrate fabrication can be found in Lamblet et al [11], [12].

On a typical elastomer patterned surface, three succesive zones (8 mm by 8 mm) were patterned, and separated by non patterned zones (5 mm), as shown schematically in figure 2, so that the peel force on both smooth and patterned surfaces could be measured on the same sample.

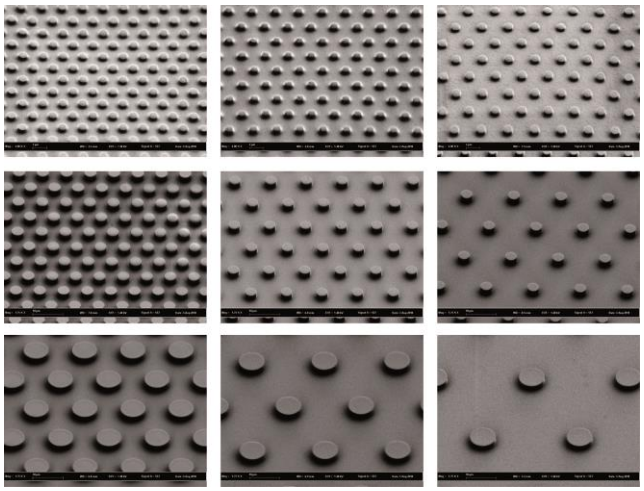

Fig.3: Examples of patterned surfaces. The height is 2.2µm for all pictures. For the first line, pillars diameter is 1.5µm and the spacing is from left to right 3, 3.5 and 4. For the second line, pillars diameter is 4µm and the spacing is from left to right 8, 12 and 16. For the third line, pillars diameter is 8µm and the spacing is from left to right 16, 24 and 32.

The acrylic adhesive was a commercial tape (3M600). Its width *b* is 19 mm, the thickness of the adhesive layer is 17 µm and that of the backing is 40µm. The storage modulus E'=0.02 MPa and the loss modulus and *E*''=0.005 MPa of the acrylic adhesive have been measured using dynamic shear experiments at 24°C and at a frequency of 0.1 Hz[12].

The patterned can be characterized by the pillars diameter *d*, the height *h* and the distance between two pillars *i*. All these lenghtes are micronic as seen in fig. 3.

One has to notice that the width of the adhesive tape is larger than that of the patterned zone on the substrate. Then, as shown schematically in the right insert in figure 2, when the peel front reaches the patterned zone of the substrate, the contact is mixed, and the peel front sweeps both patterned and smooth areas so that the measured peel force includes these two contributions.

Texturation induces an adhesion enhancement

A typical curve for the peel force as a function of the position of the peel front, either on a smooth or a mixed textured and smooth part of the substrate is reported in figure 4.

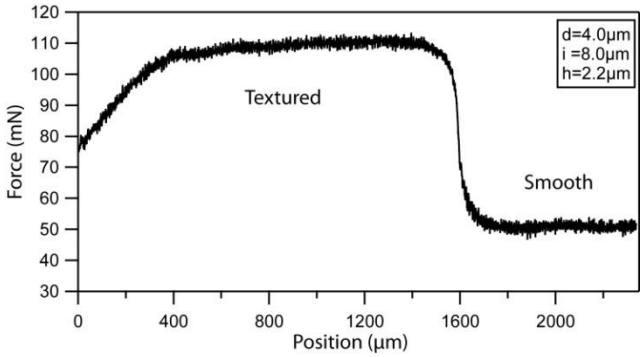

Fig. 4: Peel force versus position on textured and smooth interface.

A neat increase of the peel force is observed when the peel front sweeps the patterned zone of the substrate, with a measured force typically twice that obtained on the fully smooth surface. In order to analyze the results and evidence the role of the patterning in providing enhanced adhesion, we chose to discuss the data obtained on the patterned substrates in terms of effective adhesion energy, i.e. the energy to be paid to unbind a unit area of adhesive tape :

$$G = \frac{F_p}{b_p}.$$

Where F_p is the force due to the patterned zone and b_p the lateral size of the paterned zone. For that, we precisely calculated the part of the force due to the smooth part of the tape. On the contrary the adhesion energy on the smooth substrate will be $G_s=F_s/b_s$.

Because the adhesive has invaded the channels between the pillars, the real area of contact is larger than the apparent one. Knowing the dimensions of the pillars, this surface enhancement can easily be estimated. We assume that the pillars are perfect cylinders and that the pattern remains non deformed inside the contact. The surface increase per unit area is:

$$\frac{\Delta S}{S_s} = \frac{2\pi}{\sqrt{3}}\frac{dh}{i^2} = \frac{2\pi}{\sqrt{3}}\left(\frac{d}{i}\right)^2\frac{h}{d}$$

The relative increase of surface $\Delta S/S_s$ is a complex combination of the aspect ratio of a pillar, h/d , and of the aspect ratio of the pattern, d/i. A simple increase of the adhesion energy due to a geometrical effect will simply lead to a relative increase of adhesion $\Delta G/G_s=\Delta S/S_s$.

Adhesion enhancement on hard surfaces

We have first studied the enhancement of adhesion $\Delta G_p= \Delta G – Gs(\Delta S/S_s)$ in order to evidence a potential non trivial geometrical enhancement of adhesion on hard substrates (fig. 5) [12]. We have studied at different peeling velocities, the effect of the height of the pillars for a given pattern geometry (d =2 μm and i=4 μm).

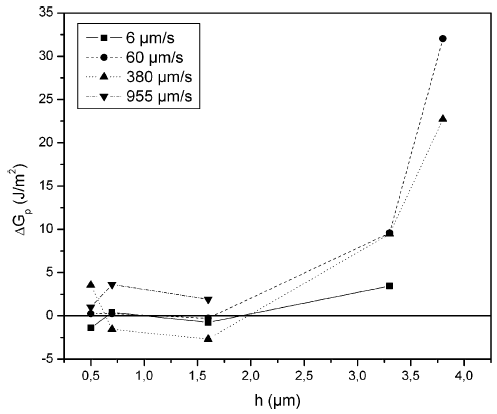

Fig. 5: Non trivial part of the adhesion energy on hard patterned surfaces.

We observed that almost the patterning does not affect the adhesion energy when the pillars are smaller than 4 µm.

Adhesion enhancement on soft elastic surfaces

We have then studied the enhancement of adhesion $\Delta G_p = \Delta G - Gs(\Delta S/S_s)$ in order to evidence a potential non trivial geometrical enhancement of adhesion on soft substrates (fig. 6) [12]. We have studied at different peeling velocities, the effect of the height of the pillars for a given pattern geometry (d =2 μm and i=4 μm).

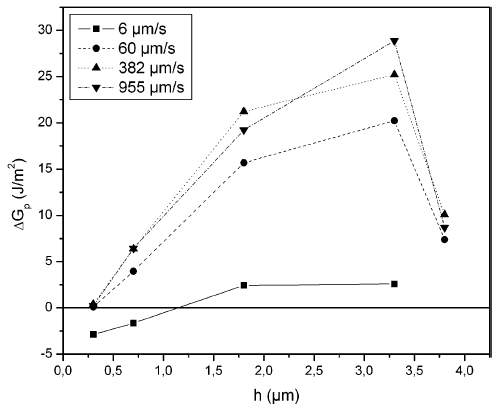

Fig. 6: Enhancement of the peel energy measured on a PDMS elastomer patterned with micropillars versus the pillar height h for different peel velocities

By varying the geometry of the pillars, for an hexagonal array of micropillars with a spacing i, a height h and a diameter d, two regimes of adhesion enhancement have been identified: for relatively low aspect ratio of the cylindrical pillars, (h/d<1.5), soft patterned substrates are more efficient than rigid ones in enhancing adhesion, pointing out the role of the deformation of the pattern; for pillars with higher aspect ratio, only rigid patterned surfaces do enhance adhesion. Then the only possible contribution to the energy dissipation comes from the enhanced viscoelastic losses in the adhesive layer.

Systematic study of the adhesion enhancement on soft elastic surfaces

A systematic investigation of the exact role of the characteristic dimensions of the patterning on adhesion enhancement, focussing on the regime where the deformations in the elastic substrate are dominant has been performed (fig. 7) and discussed in [13].

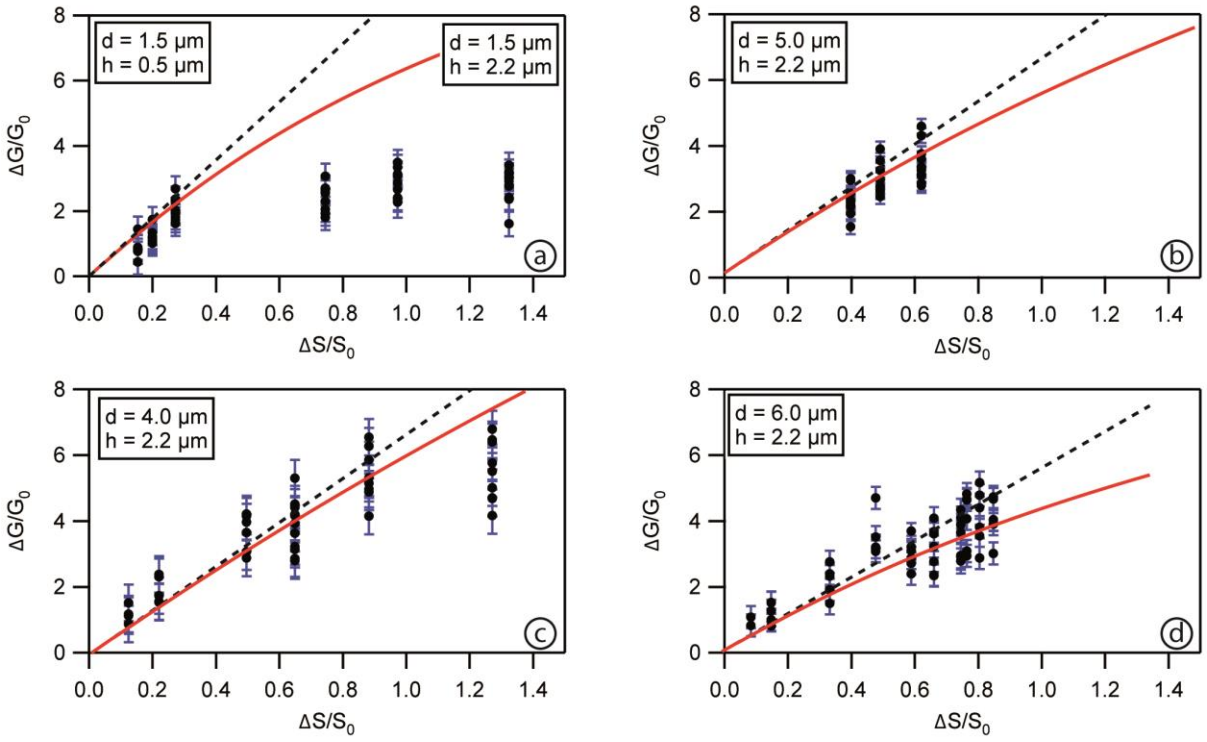

Figure 7: Evolution of the normalized enhancement of peel energy due to patterning as a function of the normalized increase of surface, for different diameters and spacing of the pillars. All data are obtained with pillars of height *h*=2.2µm, except the three series of data on the left hand part of curve 5a, for which the height has been decreased to 0.5 µm. The geometric characteristics of the pillars are all specified on each curve, and for each curve, the spacing *i* is varied to change the normalized increased area. All the data are well above the simple geometrical increase of adhesion which. Comparison between calculated enhanced normalized peel energy and experiments (data yet shown in figure 5): analytical prediction for independent pillars (dash line) and numerical (full line) model for pillars coupled through the deformations of the elastic underlying substrate.

Our systematic study has shown again a non-trivial increase of the adhesion energy. The adhesion enhancement associated to the patterning was essentially attributed to the elastic deformation of the substrate (pillars plus underlying PDMS film). We first proposed to calculate this elastic energy of deformation as a function of the aspect ratio of the micropillars assuming that the pillars are acting independently of each other. Three contributions can be distinguished: each micropillar is bent and stretched, and the substrate itself can be deformed under the effect of the local peel force transmitted through the micropillar.

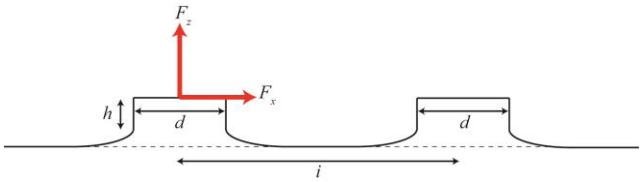

Fig.8: Definition of parameters used in the mechanical analysis.

Assuming that this elastic energy stored by the deformations of the pillars and of the underlying substrate is completely lost when the peel front passes, the peel energy should become [14]:

$$G = G_s\left(1 + \frac{\Delta S}{S_0}\right) + \frac{F^2}{E}\left(\frac{32}{3\pi}\frac{h^3}{d^4} + \frac{2}{\pi}\frac{h}{d^2} + \frac{4}{\pi^2}\frac{1}{d}\right)\frac{2}{\sqrt{3}i^2}$$

The first terme in the right hand side term is the geometrical effect of the paterning, which increases the surface of contact between the substrate and the adhesive. The second term in the right hand side term of equation is the additional contribution due to the deformations of the elastic patterned substrate which can be divided in (fig. 8): the bending energy of the pillars, the streching energy of the pillars and the elastic deformation of the substrate below the pillars. This elastic term is proportional to the square of the applied force F^2. This force needs to be better identified in order to go further in the modeling.
It seems reasonable to identify the force F_s as the critical pull-off force needed to separate the adhesive-pillar interface on the upper surface of each pillar, in view of the optical observations of the detachement between the adhesive and the patterned substrate. The question is then to precisely determine the pull-off force at rupture on the top of the pillar. Inspired by the literature [15]–[19], we proposed to write the critical force at detachement as:

$$F_c = \beta G_s \pi d$$

where β is a numerical factor and the chosen characteristic length is proportional to the diameter *d* of pillars.

Replacing the value of the critical force in equation, one obtains a complete expression for the relative increase of peel energy:

$$\frac{\Delta G}{G_s} = \left[1 + \frac{\beta^2 G_s}{Ed}\left[\frac{32}{3}\left(\frac{h}{d}\right)^2 + \frac{4}{\pi}\frac{d}{h} + 2\right]\right]\frac{\Delta S}{S_s}$$

All contributions related to the deformation of the patterned substrate, gathered in the second term inside the bracket of the right hand side of equation, appear inversly proportional to the diameter of the pillars. The bending contribution gives and additional square dependence in the aspect ration, *h/d* of the pillars, the substrate deformation only linearly with this aspect ratio, while the stretching is of course independent of it. The relative increase of adhesion energy is thus predicted to increase linearly with the relative increase of surface for independent pillars, but with a slope bigger than the value one resulting from the simple geometrical effect of increased area of contact.

If this analysis is correct, i) the comparison between equation and experiments should allow one to determine the rupture criteria between the adhesive and the top of the pillars, all data being described with the unique fitting parameter β. ii) we shall observe a linear dependency of $\Delta G/G_s$ with $\Delta S/S_s$.

Indeed we observed that for low $\Delta S/S_s$, it was possible to fit all the experimental data with the same numerical factor $\beta \sim 1 \pm 0{,}1$.

At $\Delta S/S_s$ larger than 0.6, a clear discrepency between the theoretical model and the experimental data has been evidenced. Since the model assumes that the deformation of the pillars are independent, it is clear that this model should be invalid at large fraction coverage of the pillar. A full model taking into

account the coupling between the pillars as been performed in [13]. It is far beyond thte scope of this review to present the model which as nevertheless been compared to the experimental data in fig. 7.

Conclusion

By investigating in a systematic manner the efficiency of surface micro-patterning in enhancing the adhesive strength at PDMS acrylic adhesive interfaces and comparing different diameter and spacing between pillars, we have shown that the peel energy increases first linearly with the surface increase resulting from the patterning. This linear increase is not indicative of a trivial effect of increasing the area of contact between the adhesive and the patterned substrate, associated to the patterning, but can be quantitatively accounted for introducing the elastic deformation of the pillars, which is lost at detachment between the adhesive and the substrate, when the peel front passes. Two regimes of elastic deformation of the patterned substrate have been identified, depending on the aspect ratio of the pattern. When the cylindrical pillars used in the present study are far enough from each other (typically for distances between pillars larger than three times their diameter), the pillars behave independently of each other, and, for the relatively low aspect ratio pillars used, three kinds of elastic deformations contribute approximately equally to the peel energy: bending energy, stretching energy of each cylindrical pillar and deformation energy of the underlying elastic substrate. When the distance between pillars is decreased, the coupling between pillars, due to the coupling of the deformation field in the underlying elastic substrate leads to a saturation of the peel energy with the increase in surface of contact between the adhesive and the substrate.

Our investigations show that, by varying the size of the pattern, it is possible to tune the level of adhesion at PDMS acrylic adhesive interfaces. The enhancement of adhesion due to such patterning is purely elastic, and ruled first by the deformability of the patterned substrate, i.e. independent on the exact chemistry of the adhesive, and second by a rupture criteria on the top of the pillars which should remain sensitive to the chemistry of the adhesive.

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