Some fundamentals of adhesion in synthetic adhesives

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Abstract

Various adhesion mechanisms that have been understood in the field of synthetic adhesives are described and these are linked with situations relevant to fouling issues. The review mainly deals with mechanical aspects of adhesion phenomena, with an emphasis on the role of the elasticity of the bodies, called substrata, attached by adhesive. The consequences of thin film geometry of the adhesive material are described, such as various heterogeneous deformations upon traction. The importance of the bonding process is discussed, as well as some examples of non-wetting surfaces. Some basic ideas of fracture mechanics are provided and in particular, the behavior of layered systems is discussed. Rolling sticky objects and peeled (flexible) adhesive tapes display similar mechan- isms and it is shown how they differ from the normal separation of rigid bodies. Some issues directly related to fouling issues are also discussed, such as forces and torques acting on shells, the advantages of gregarious settlement behavior and concepts for fouling release and antifouling.
Keywords: adhesion mechanisms; synthetic adhesives; the bonding process; non-wetting surfaces; fracture mechanics; fouling issues.

THIN FILMS

Synthetic adhesives are usually soft, essentially incompressible materials that do not flow. They are used in the form of thin films of typically 100 m m in thickness. Their adhesive properties are often tested in a controlled test that mimics the typical situation of two solid bodies linked by an adhesive. In the so-called probe-tack geometry, introduced by Zosel (1985), a flat, solid punch, called the probe, is brought into contact with an adhesive film deposited on a rigid substratum. After a certain contact time, the force is recorded while the probe is being pulled away (Figure 1a). Because the adhesive material is almost incompressible, pulling the solid bodies apart causes a strong convergent deformation and thus a strong resistance to separation, i.e. to good adhesion. Furthermore, because the resistance of the adhesive is so important, the deformability of the entire system, and in particular the compliance of the machine itself may play a role. Elastic energy is stored for some time, until the adhesive gives way and causes a sudden separation, as discussed in a specific geometry by Francis et al. (2001). Sudden separation is possible when instabilities develop in the bulk of the adhesive material so as to relieve much of the stress. Such instabilities have been observed directly during separation in a modified version of the probe-tack test (Lakrout et al., 1999) and shown to fall into two main categories, viz. fingering instabilities and cavitation. Both types of instabilities are driven by the need for relieving the stress.

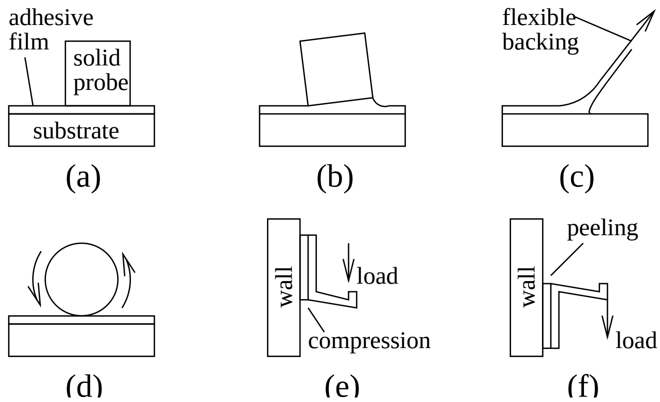

FIG. 1: Influence of substratum flexibility on adhesion. Normal separation of rigid bodies (a) is slightly stronger than tilting (b) and much stronger than peeling (c). Rolling (d) is similar to peeling in the separation region. The usual design of adhesive hooks (e) avoids the tendency to peeling that would be induced by the finite flexibility of the material in other geometries (f).

When air fingers protrude from the edge of the sample towards the center, they bring atmospheric pressure well into the sample and thus relieve the negative pressure that has developed near the center due to the applied traction. In the case of purely viscous liquids, this is the well-known Saffman- Taylor instability (Saffman et al., 1958). Cavitation also relieves stress since the

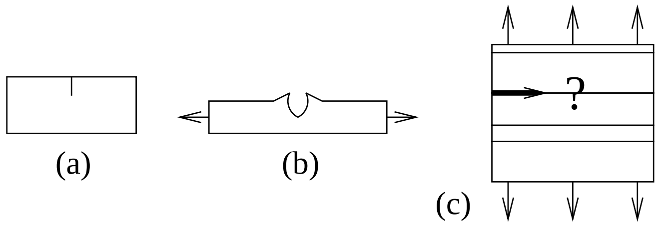

FIG. 2: Adhesion phenomena and fracture mechanics. Elastic band with a notch at rest (a) and under tension (b). In a layered system under traction (c), contrasts in the elastic properties and thicknesses of the different layers may cause the fracture to migrate from its initial location to another one, either within a material (cohesive rupture) or at the interface between them (adhesive rupture).

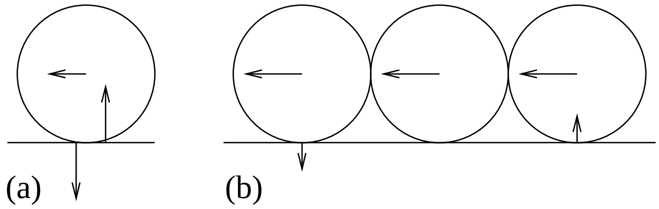

FIG. 3: Advantage of gregarious settlement. Organisms on a ships hull are subjected to a hydrodynamic force (drawn horizontally for simplicity). They transmit not only this force to the hull (not shown), but also the resulting torque (drawn as two vertical arrows). In the case of a single organism (a), the torque involves large compressive and tensile stresses when the contact region with the hull is narrow. If two or more organisms are rigidly bound to one another (b), the torque that they transmit to the hull involves much smaller stresses in the contact regions, thus impeding detachment.

growing bubbles provide some of the extra volume required by the plate separation. Since adhesive materials are usually more elastic than viscous, they are most often subject to cavitation, which involves strong deformations on the scale of the sample thickness. They almost never undergo fingering, which would involve deformations on the scale of the entire sample. When a very viscous liquid is used in this geometry instead of proper adhesive material, fingering is observed at low separation rates while cavitation occurs at higher rates (Poivet et al., unpublished observations), which further illustrates the fact that both mechanisms compete in relieving the applied tensile stress. Both fingering and cavitation involve strong deformations in the sample during separation and thus cause a large energy dissipation, ranging typically from 100 to 1000 $\mathrm{J/m^{-2}}$ for good adhesives, which is much higher than typical surface energies in the $0.01 - -0.1$ $\mathrm{J/m^{-2}}$ range.

A number of properties are associated with an adhesive. It is usually a soft material that does not flow and made of polymers whose molecular architecture may vary (cross-linked polymers, block-copolymers). It can accommodate large defor- mations in order to dissipate a large amount of energy, yet it is essentially incompressible.

The need for relieving the applied stress is so strong in the thin film geometry that if the adhesive material is too resistant, e.g. if it is very elastic, fingering and cavitation from the edge of the sample may occur at the interface, as shown by Ghatak (2000) and Shull (2000). This highlights the fact that not only the bulk of the adhesive film, but also its interfaces with the solid bodies set up during the bonding process, must resist separation efficiently.

THE BONDING PROCESS

The quality of the contact between the adhesive and the substrata results from the interplay of inter- actions at different length scales. On the molecular scale, it results generically from van der Waals interactions (Israelachvili, 1992). Surface chemical bonds (Gent et al., 1972), macromolecular interdigita- tion (Raphaël et al., 1992) or macromolecule elongation (Lake et al., 1967), however, may enhance significantly the strength of the interface for specific substratum-adhesive pairs. Surface treatments and cleaning are also essential. On the micrometre scale, solid substrates usually display some degree of surface roughness (Greenwood et al., 1966) that may reduce the degree of intimacy of the contact with the adhesive if the adhesive material is not very soft (Dahlquist, 1969; Fuller et al., 1975; Creton et al., 1996; Crevoisier et al., 1999). For very soft adhesives, however, the surface roughness of the substratum may paradoxically enhance the strength of the interface, as small air bubbles trapped at the interface may generate suction effects upon traction (Gay & Leibler, 1999b).

When seeking a bad adhesion even with good adhesives, the main strategy is to weaken the contact at the body surface, and in particular to use non-wetting surfaces, i.e. surfaces such that the gain in surface energy upon making contact with the adhesive is small. When spread on such surfaces, most liquids do not spread spontaneously but gather into droplets. On very weakly wetting surfaces, in particular on lotus leaves and on other plants and on some insect wings (Wagner et al., 1996; Barthlott et al., 1997; Neinhuis et al., 1997), millimetric drops are almost complete spheres and can easily roll. Solid surfaces were successfully designed to mimic this lotus effect and the surface design, an array of micrometer-sized poles, enhances the weak wettability achieved through chemical treatment (Bico et al., 1999).

FRACTURE MECHANICS

The mechanisms described above, by which the adhesive material undergoes heterogeneous defor- mations upon traction, involve the bulk of the adhesive film. However, as seen from a distance, the adhesive joint appears to be the interface between both solid bodies, and its deformations due to traction can be seen as a fracture propagating at this interface. In this perspective, adhesion phenomena are connected to the field of fracture mechanics. A small notch cut on one side of an elastic band (Figure 2a) illustrates a number of points. If the band is pulled gently, it stretches homogeneously except in the vicinity of the notch where it is less stretched (Figure 2b). In other words, elastic energy is stored in the material but the notch relieves some of this energy. If the band was cut further, the notch would be longer and relieve more stress. This will not happen spontaneously unless it is pulled more strongly. It will generally happen when the elastic energy released by the notch propagation is sufficient to break further bonds at the interface and propagate the fracture. This is a central concept in fracture mechanics, called Griffiths criterion (Griffith, 1920).

Since the energy stored depends on the elastic properties of the entire system, not only does the elasticity of the testing apparatus play a role if it is soft enough, but very non-intuitive behaviors may arise. The fracture may propagate within the adhesive film i.e. its cohesion affected, or it may take place at the interface with one of the substrates. More generally, when considering a stack of several layers from different materials (Figure 2c), the system may break upon traction or peeling. The system may choose between different fracture mechanisms (interfacial or cohesive, with further choice in a layered system). At first, it usually chooses the weakest mechanism in terms of force since it triggers separation first and thereby relieves the stress on the other possible mechanisms. In the long run, however, fracture propagation is driven by the elastic energy stored in the system under tension which must exceed the energy required by the fracture. The system thus tends to choose the separation mechanism that dissipates the smallest amount of energy per unit surface area since the fracture will then be able to propagate faster.

But, when a sheet of paper is torn out of note-pad, depending on how exactly the paper is pulled and how the note-pad is held, the sheet may detach neatly or be torn. Due to the mismatch in the elastic properties of the note-pad and the paper sheet, the fracture may propagate along a path that does not minimize the energy dissipation. More generally, in a layered system, the elastic properties of the various layers may prevent the fracture from migrating towards its energetically optimal location.

PEELING, TILTING AND ROLLING

As discussed above, separating both substrata in the probe-tack geometry is difficult because the lateral extension of the adhesive joint is much greater than its thickness (thin geometry). It is also essential that both substrata are rigid (Figure 1a). Indeed, when an adhesive tape is considered, the sticky side is the adhesive film, while the non-sticky side is the (very flexible) backing. Thus, the backing plays the role of one of the substrata. But peeling a tape off a table is quite easy because the backing is flexible and only a restricted region of the adhesive is under tension at any given time during peeling (Figure 1c). Peeling is, in general, so much easier that it is avoided as much as possible in practical situations. For instance, adhesive hooks for bathroom or kitchen utensiles are designed in such a way that the hook deformations induced by a hanging weight cause the adhesive layer to be locally compressed rather than peeled, otherwise the adhesive joint would soon be ruined (Figure 1e, f).

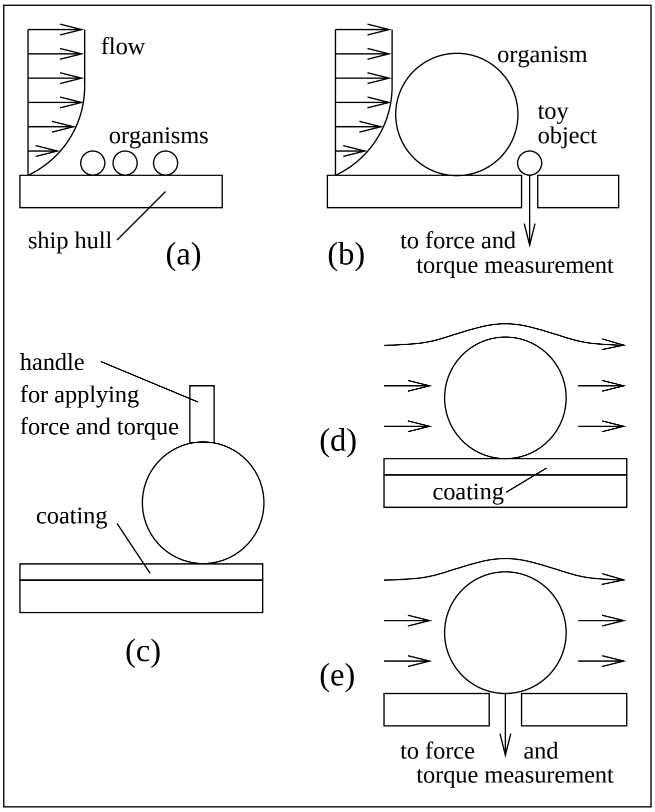

FIG. 4: Schematic comparison between ship-scale (a) and laboratory-scale experiments (b-e). The size of real organisms is some small fraction of the boundary layer under real ship conditions (a). In order for laboratory experiments to determine the hydrodynamic forces involved (which include both drag and lift) and the resulting torque transmitted to the hull, the organisms themselves should not be used. Instead, small toy objects should be used so that their size is the same small fraction of the laboratory-scale boundary layer (b). After proper upscaling of the measured stresses to the size of the organisms, fouling-release coatings can then be tested by either applying the force and torque through direct mechanical action (c) or by applying a laboratory- scale flow (d) which has been calibrated (e).

Although similar to peeling at first sight, detach- ment by tilting is difficult if both the substrata are rigid. In-

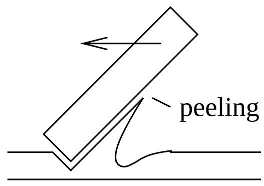

FIG. 5: Schematic separation mode of an extended rigid object (such as aggregated rigid organisms) from a coating consisting of a flexible, though weakly extensible, thin upper layer and a much softer lower layer. Deformations are magnified for clarity.

deed, tilting one object (for instance, the probe in the probe-tack geometry) involves com- pression of the adhesive film along the vicinity of one edge, and traction on the other edge and on most of the region of contact with the object (Figure 1b). Hence, tilting the object is very similar to pulling it.

Tilting becomes similar to peeling only at the point where the adhesive joint is not longer thin, i.e. if its lateral dimensions are comparable to its thickness, it is then easy. This feature is used by tropical lizards (geckoes), which can climb walls at considerable velocities. Their adhesive feet consist of a hierarchy of structures. The smallest structure is the spatula (0.2 μm in width). Adherence to the wall is important, even if it is rough, because spatulae can achieve contact with it somewhat independently of one another. However, foot removal is obviously achievable without too much effort. Because spatulae are independent, they can be tilted simultaneously and peeled away from the wall. Due to their small lateral dimension, this can be done with little effort (Autumn et al., 2000). In short, geckos use peeling on the lowest scale to lift their feet.

A round object can roll on a sticky surface, whereby a new contact with the adhesive is made at the front, while separation, similar to peeling, is achieved at the rear (Figure 1d). Because the separation dissipates more energy than is provided by the contact, a sufficient sideward force must be applied for the object to move. Experiments conducted on glass cylinders in contact with rubber (Charmet et al., 1995 and references therein) show that such rolling can occur also if the applied force has a normal component. For example, cylinders can roll both on and under an inclined rubber sheet. Similarly, marine organisms attached to a boats hull undergo a sideways force as well as a lift force (because the flow is usually in the inertial rather than viscous regime). They may thus roll if the water velocity is moderate, and they may even detach if the lift component of the force is high. If the organisms are rigid, gregarious settlement behavior hinders flow-driven detachment, since when attached together, they constitute a solid with a large lateral extension, which turns easy rolling into more demanding tilting (Figure 3).

FOULING ISSUES

Testing fouling release properties of coatings sometimes involves real-size experiments on ships, but more usually laboratory scale characterization. Hydrodynamic effects scale with dimension. In particular, boundary layers are much smaller in laboratory tests than under ship-operating con- ditions (Schultz et al., 2003), thus attached bodies should be scaled down accordingly (Figure 4a, b). The interpretation of laboratory tests therefore needs to combine information from different types of experiments. For example, small toy particles on small ships can be used in laboratory tests to mimic organisms to measure what lateral and normal drag forces and torques they undergo at various locations on the ship and at various equivalent ship speeds (Figure 4b). After proper upscaling of these forces and torques, the laboratory or small boat tests with live organisms should be performed under con- ditions where forces and torques can be reproduced (Figure 4d). These parameters can be measured if the organisms are located on small, instrumented patches inside larger panels (Figure 4e). Alternatively, if the organism under study is rigid, the forces and torques can be applied to it mechanically, in the absence of any flow (Figure 4c). If the organism is much more rigid than the coating, or, more generally, if its mechanical properties are known, its detach- ment can be mimicked with more convenient real- size toy objects with an experimental set-up that controls the forces and torques.

The mechanics of adhesion briefly described in the previous sections suggest the following direction for fouling release coatings. If an aggregate of rigid organisms on the surface is considered on a classical thin coating, the only detachment mode is tilting (Figure 3). But, if the coating is flexible in some sense, then an easier detachment mode, similar to peeling, may appear. It is suggested that a coating consisting in an inextensible, flexible, very thin upper layer and a much softer lower layer, may provide enough local compliance to accompany a tilting object and peeling away from it, thus easing its detachment (Figure 5). Such a coating may be capable of easily releasing rigid organisms.

CONCLUSION

Synthetic adhesives are efficient because they involve several mechanisms for dissipating a large amount of energy upon detachment (see reviews by Kinloch, 1996, Gay & Leibler, 1999a, and Creton & Fabre, 2002). Some of these mechanisms, and the associated mechanical aspects, have been reviewed and may enhance understanding of the settlement and release of fouling organisms and thereby lead to improvements in the design of fouling release and non-adhesive coatings.

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