

# DELIVERABLE

## D 2.1

### **The Developed set-ups based on shaft-loaded blister test and peel test**



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## The Developed set-ups based on shaft-loaded blister test and peel test

The ESPCI is developing adhesion tests well adapted to the constraint of adhesion in or under water<sup>1</sup>. The initial plan in the proposal was to focus on the peel test in wet conditions and the shaft-loaded blister test which is also designed to test adhesion in the presence of some water and for very long contact times. However the type of materials synthesized by the ESR's in the different groups (coacervate adhesives, hydrogels) and the synthesized surface modifications (hydrophilic and amphiphilic brushes and microgels) are not adapted to these geometries and we have decided instead to focus on two adhesive tests that can function fully underwater and that are more adapted to test viscoelastic fluid adhesives.

Namely we have developed

- 1) An adhesion test, based on using a rheometer with two parallel plates and applying a displacement normal to the sample. The rheometer is already available at ESPCI and the key challenge here is to develop the experimental protocol and to define the experimental geometry. The key advantage of the setup is to be able to test the adhesive properties of a thin, fluid or solid, viscoelastic layer at different temperatures with a rapid temperature switch. This type of test will be essential to test the capabilities of injectable hydrogels and coacervates to switch state from an injectable fluid to an adhesive solid.
- 2) A specially designed setup<sup>1</sup> to carry out probe tack tests either in air or fully underwater. This design has two advantages: it adapted to modify surface chemistry (at least on one side of the two contacting surfaces) and is equipped with contact visualization capabilities that can be used to analyze the debonding mechanisms. The temperature of the test can be controlled by there is more inertia and a change takes time. This setup is ideally suited to probe the adhesion between a soft gel and a hard surface previously functionalized.

### a) Developing a Temperature-Controlled Probe Tack test on a Rheometer

Injectable hydrogels based on thermoresponsive copolymers, especially those with a Lower Critical Solution Temperature (LCST), are promising candidates for a number of biomedical applications, including bioadhesion, which is defined as the process whereby natural or synthetic polymers are brought into contact with biological tissue for elongated periods of time. The appeal of these products lies in their thermo-responsiveness; thus, it is of critical importance to look into their behavior and properties below and above the transition temperature.

Normally, one method to measure the adhesion of soft matter is the probe-tack test<sup>2</sup>, where, the surface of the solid probe is first brought into contact with the sample (thin adhesive layer coated on a rigid substrate) and applies a given compression force, followed by measuring the force as detachment is applied at a constant debonding speed.

The area under the normalized force-displacement curve provides useful information about the adhesive properties of the thin adhesive layer (its work of adhesion, failure mechanism, etc.). One can also follow the *in situ* debonding of a sample through a camera, that can help to associate different debonding mechanisms with different curve shapes achieved. A schematic representation of the test procedure as well as the curve usually obtained for soft adhesive layers with a probe tack test is given in Figure 1.

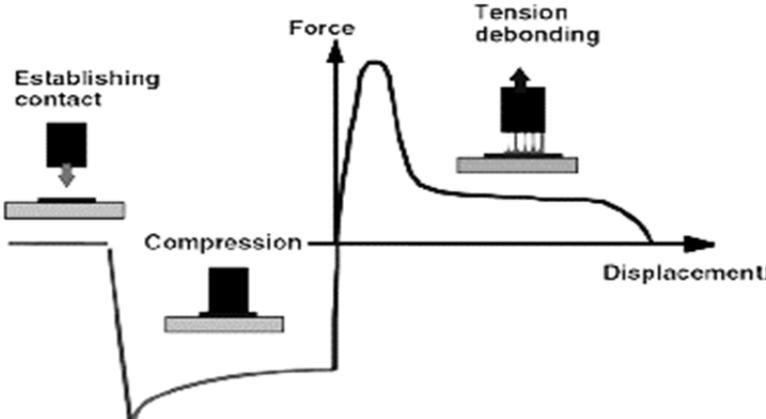


Figure 1: Schematic of the probe tack test as a function of time (that can be converted into displacement).

The Probe tack test is a versatile tool that enables us to look into a sample's adhesive properties and failure. However, an accurate and responsive (fast) control of the temperature is not easily feasible on our standard setups available at the ESPCI.

Yet, for samples in which physical properties can vary largely in response to changes in temperature, it is desired to perform such tests in a finely temperature controlled manner. To do so, we have been trying to develop an analogous experiment on a rheometer that offers a fine control over temperature, while it can be programmed to exert compression or tension comparable to the tack set-up. The rheometer based set-up is shown in Figure 2 below.

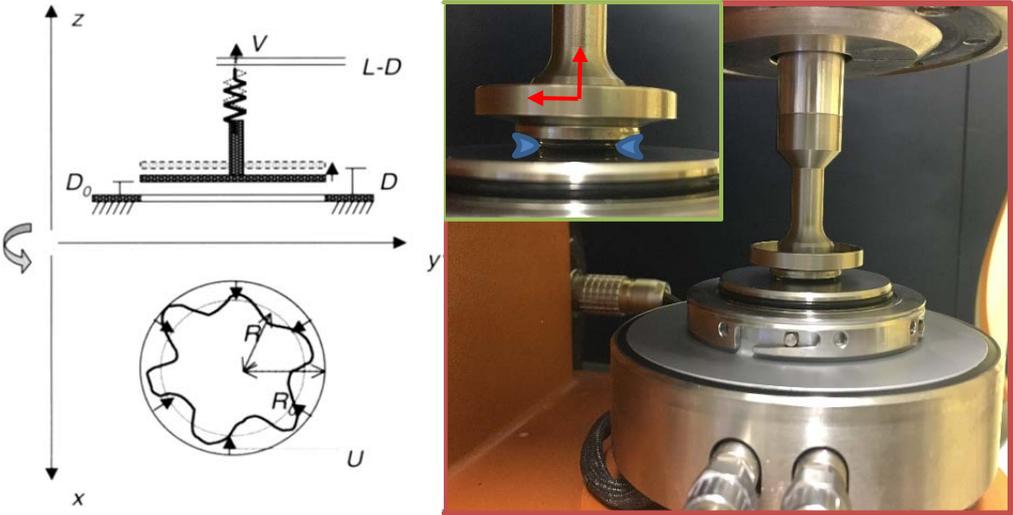


Figure 2: Schematic and definition of the characteristic distances of the geometry during the test and image of the setup at the ESPCI.

So far, ESR 5 (Mehdi) has been working on fairly simple materials with more or less well-known properties, such as Newtonian fluids (Silicon oil) or commercial products (hair gel) to assess the reproducibility of the experiments. Also, previous works in our lab offered simple models to correlate the applied force with the distance between the gaps. For a given sample, with well-defined properties, these predictions can be employed to investigate the reproducibility of the experiments. The following equations predict the Force as a function of the geometrical and the material parameters of the experiment for a Newtonian or for a Yield-stress fluid, respectively<sup>3</sup>.

$$F = \frac{3 \pi \eta R_0^4 D_0^2 V}{2 D^5}$$

$$F = \frac{2 \pi R_0^3 D_0^{3/2} \sigma_y}{3 D^{5/2}}$$

where  $F$  is the pull-off force,  $R_0$  is the initial radius of the thin adhesive film,  $D_0$  is its initial gap (or adhesive film) thickness and  $D$  is the thickness of the gap as a function of time.  $\eta$  is the film viscosity for the Newtonian fluid and  $\sigma_y$  is the yield stress of the fluid.

As it can be seen, the relationship between force and displacement depends on the type of fluid (viscosity, yield stress) as well as the test procedure (speed, initial gap, plate diameter).

This setup provides curves of normalized nominal stress vs normalized strain curves. First trials with these simple fluids give reproducible results and are promising. The sample preparation still requires some attention and a new set of plates with a lower diameter is being manufactured but these improvements should be solved in the next few weeks.

We might also try to add a camera to the set-up while maintaining its advantages, to enable online monitoring of the samples. In our early experiments, we have achieved reasonably reproducible results, but more experiments are needed in order to come up with a well-established test procedure that can be used to study a variety of soft adhesive samples in a reliably reproducible manner.

## b) Adhesion test for thick gels on functionalized surfaces

The prototype probe tack setup to measure adhesion underwater<sup>1</sup> consists in a specially designed sample holder that can maintain a typically 1 mm thick gel sample (thinner is possible) on a glass-bottom recipient while a cylindrical probe can make and release a contact.

The contact and detachment can take place in air or in water and is typically between a soft swollen hydrogel (thickness ~ mm) and a hydrogel thin film or a polymer brush (thickness ~ nm) (Figure 3a). The thin film is typically chemically attached to a silicon wafer glued on a mobile stainless steel probe, which is fixed to a 10 N load cell and is

moved vertically to make contact with the soft material. Before making a contact, both surfaces need to be parallel with each other to obtain reproducible results. After a correct alignment in air, contact is made in water with an area of contact equal to that of the thin film. During the contact, the probe remains motionless at a constant pressure (of the order of 3-4 kPa) during a constant contact time to assure the formation of interactions at the interface. Finally, the probe can be pulled off at a constant debonding rate under continuous acquisition of the displacement of the probe and the force detected on it.

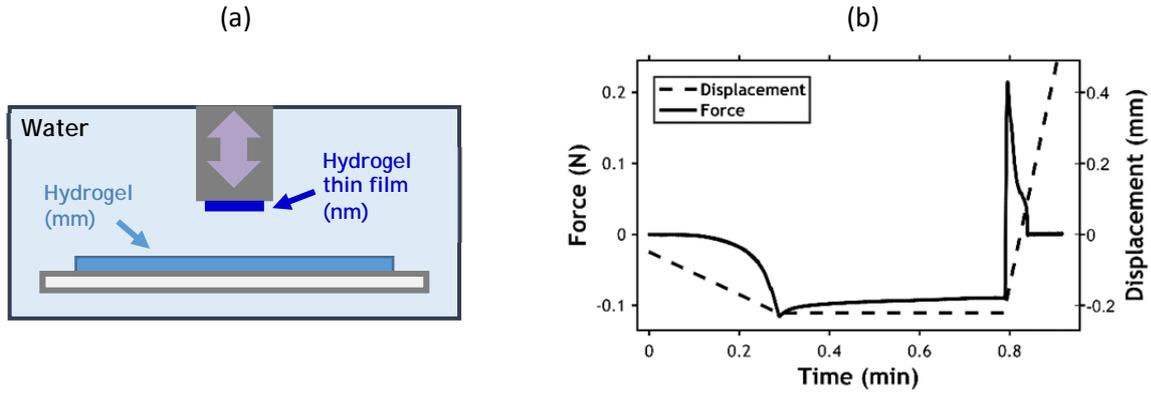


Figure 3 (a) Working principle of flat-flat contact test between hydrogel (mm) and a hydrogel thin film ( $<1\mu\text{m}$ ). The purple arrows show the direction of motion of the probe. (b) Typical raw data obtained from an underwater adhesion test between polyelectrolytes gels.

This test is used to measure the adhesion energy from the raw data of displacement and force (Figure 3b). The strain  $\varepsilon$  is obtained by normalizing the displacement by the initial thickness of the thick hydrogel  $T_0$  ( $\sim 1\text{ mm}$ ). The normalized stress  $\sigma$  is obtained by dividing the force by the thin film contact area. After calculating the stress and strain for the debonding section of the test (Force  $> 0\text{N}$ ), work of adhesion  $W_A$  is calculated as follows:

$$W_A = T_0 \int_0^{\varepsilon_{max}} \sigma d\varepsilon$$

Experimental conditions are very important for this type of test and several variables drastically affect the  $W_A$  reproducibility. The effect on the work of adhesion of some of these variables, such as contact time, contact pressure and debonding rate is well described by Sudre et al.<sup>1</sup> and their effect on the debonding curve needs to be assessed for every new system.

However, there are additional variables that are not mentioned in the paper and that are necessary to improve the reproducibility of the results.

When using this setup to measure the adhesion due to electrostatic interactions between soft hydrogels and thin films, it is recommended to:

- Make sure that the thin film is well protected during the alignment in air. If the interaction is stronger ( $W_A > 1\text{J/m}^2$ ), it is possible to break the hydrogel and

damage the thin film surface. One possible solution is to cover the thin film with a stretched layer of Parafilm® while performing surface alignment.

- Fix firmly the thick hydrogel at the bottom of the setup. There are two options with the same results in  $W_A$ : either to glue the hydrogel with a cyanoacrylate adhesive to the glass slide or to clamp it in between the glass slide and a counter plate with a hole in it (to let the probe pass through). The first option is faster and reproducible but only for equilibrated hydrogels and for short tests underwater (< 1 min). In contrast, the second could be used for longer tests but requires larger hydrogel samples.
- The surface area of the thin film should be smaller than the probe area in order to avoid hydrodynamic and bending effects when breaking the interaction between the hydrogel and the thin film.
- Avoid using non homogeneous films in the test even if is required to work with thicker films (thickness  $\sim \mu\text{m}$ ).

## References

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