Experiment 19

The Chemistry of Sticky Things

The Task

The goal of this experiment is to create and investigate the properties of a variety of sticky materials.

Skills

At the end of the laboratory session you should be able to:

- use a spring balance correctly.

Other outcomes

- You will observe the difference between wetting and non-wetting.
- You will measure the pull-off forces for different adhesives.
- You will create your own polymer slime and putty.

The Assessment

You will be assessed on your ability to maintain a clean workspace and your diligence and effectiveness at cleaning up all your equipment at the end of the experiment.

Introduction

A general feature of sticky materials is their capacity to bind two surfaces together. All adhesives share a number of common properties:

a) They are liquids or easily deformable solids such as greases, pastes or putties. The ability to flow under modest pressure is important to ensure that the contact area between the surface and the adhesive is high.

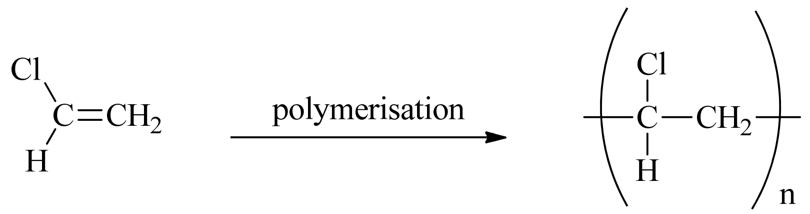
b) They contain polar molecules. Molecules with either –OH or –NH_2 groups are common amongst adhesives. An adhesive molecule must be capable of forming strong attractive interactions with a variety of surfaces and with other molecules of the same species. Polar interactions are among the strongest non-covalent interactions. There are glues, (*e.g.* the two-part epoxies) in which covalent bonds are formed between molecules in the glue, however, the molecules in these glues are still polar.

c) They are either viscous to begin with or undergo some transformation that increases their viscosity. An adhesive needs to have a high viscosity for two reasons. The first, and most fundamental, is that much of a glue's binding ability comes from the work required to get it to flow. The second benefit of high viscosity is that, when applied to a non-horizontal surface, the glue will stay put long enough for the surfaces to be pushed together, rather than simply flowing downhill, away from where it is required.

In this experiment you will explore the capacity for a number of materials to wet various surfaces and, through the control of their viscosity, to work as adhesives.

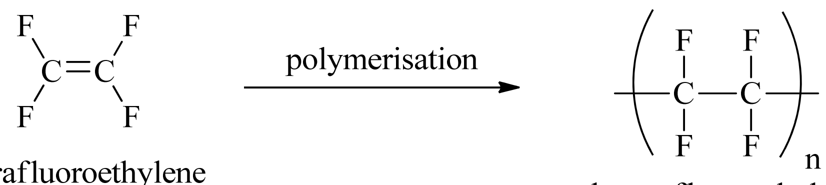
Polymers

Polymers are a component of many adhesives. They are high molecular weight materials composed of many thousands of similar repeating units. Varying the substituents on the repeating units alters the properties of the polymer to suit specific applications.



vinyl chloride

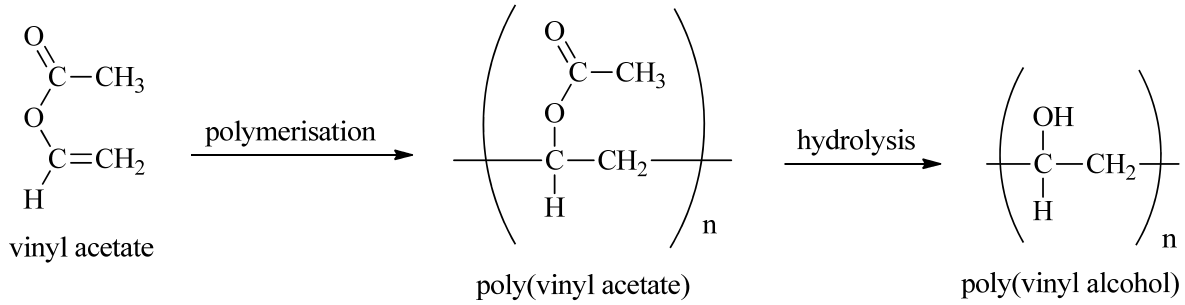
poly(vinyl chloride)
(PVC)



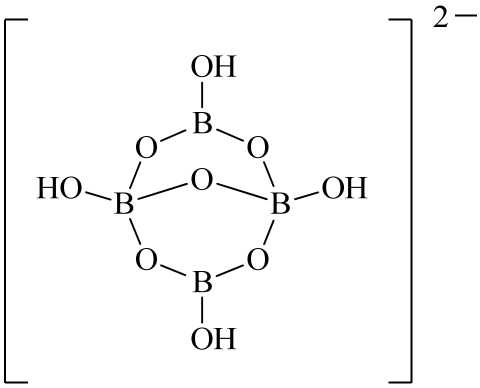
tetrafluoroethylene

polytetrafluoroethylene
(PTFE or Teflon)

In this experiment you will use poly(vinyl alcohol). It is produced commercially by the hydrolysis of poly(vinyl acetate). Poly(vinyl alcohol) is soluble in water as a result of the hydrophilic alcohol groups attached to the polymer backbone. The average value of n for the poly(vinyl alcohol) used in this experiment is at least 2300.



Cross-linking of the polymer chains is another way in which the properties of the polymer can be modified. It effectively increases the molecular weight of the molecules and results in a material with a more rigid structure. Borax can be used as a cross-linking agent. The molecular formula of borax is usually given as $Na_2B_4O_7{\cdot}10H_2O$ for historical reasons, but, as it contains Na^+ and $[B_4O_5(OH)_4]^{2-}$ ions, its formula is more sensibly given by $Na_2[B_4O_5(OH)_4]{\cdot}8H_2O$.



Structure of the $[B_4O_5(OH)_4]^{2-}$ anions present in borax

The cross-links are formed when the anions react with the hydroxyl groups of the polymer to form one of two types of bonds. The elimination of water would produce strong covalent bonds. Alternatively, the formation of relatively weak hydrogen bonds, that break and reform under flow, produces a 'viscoelastic gel' with interesting physical properties.

Glucose and Starch

Glucose is the most common organic molecule in Nature. It is metabolised by the body to produce energy and also forms many different polymers, such as cellulose and glycogen. The representation of glucose shown in Figure 1 shows the buckled nature of the 6-membered ring and the orientation of the H and OH groups attached to the ring. The carbon atoms are numbered according to a standard convention.

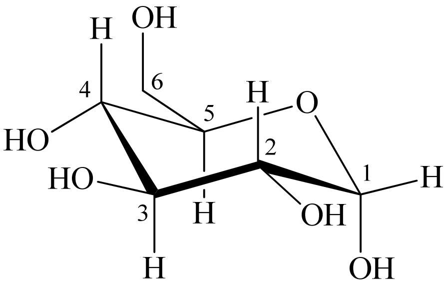


Figure 1: The glucose monomer unit.

Starch is a naturally occurring polymer of glucose, derived from plants. It occurs as granules that vary in shape and size, depending on their origin. Intact starch granules are insoluble in cold water, but hot water causes the granules to swell until they burst. (Heston Blumenthal and other chefs utilise the various properties of starch granules in their cooking of "perfect" chips and roast potatoes.) Starch consists of two fractions: amylose and amylopectin.

Amylose is water soluble and consists of chains of between 1000 - 4000 glucose units. C1 of one glucose unit is linked, via an oxygen atom, to C4 of the next glucose unit.

Amylopectin is insoluble in water and there are up to 1,000,000 glucose units per molecule. As well as the usual C1-C4 linkage found in amylose to give chains of about 25 glucose units, there is the occasional C1-C6 link that results in extensive cross-linking.

Spring balance

A spring balance is a device used to measure force in newtons (N). A newton is equivalent to 1 kg m s^{-2}. For example, the force due to gravity exerted by an object is given by its mass (in kg) multiplied by the acceleration due to gravity (9.8 m s^{-2}). In this experiment you will use a spring balance to measure the force you need to apply to break the adhesive interactions between a glue and a solid substrate.

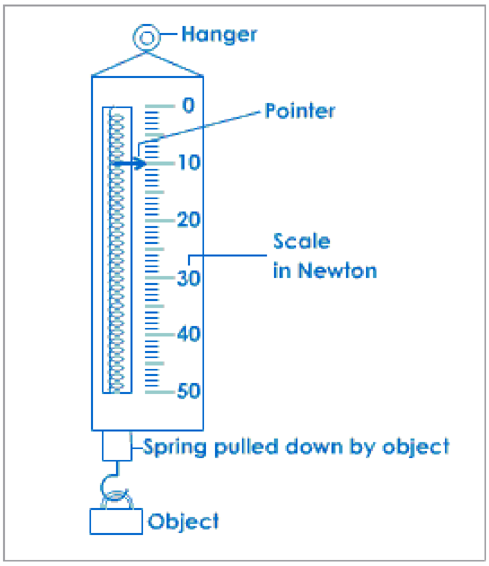


Figure 2: A diagram of a spring balance.

The balance is held at the top by the hanger and the object that you want to measure is attached to the hook at the bottom of the balance. This hook is attached to a spring, which measures the force. The spring has a pointer attached to it, which is used to read the force in newtons from the calibrated scale.

Wetting Surfaces

A liquid will wet a solid if the attraction between the liquid molecule and the surface is greater than the attraction between the liquid molecules themselves. Measuring the degree to which a liquid wets a surface is, in principle, straightforward, although in practice it is very sensitive to surface contamination and roughening.

The idea behind measuring wetting ability is to observe carefully the shape of a liquid drop on the surface as shown in Figure 3. A liquid that wets a surface well will spread out on the surface, resulting in a low contact angle. A liquid that does not wet a surface will 'bead' and produce a high, spherical droplet with a large contact angle, as in the case of water on a Teflon-coated surface.

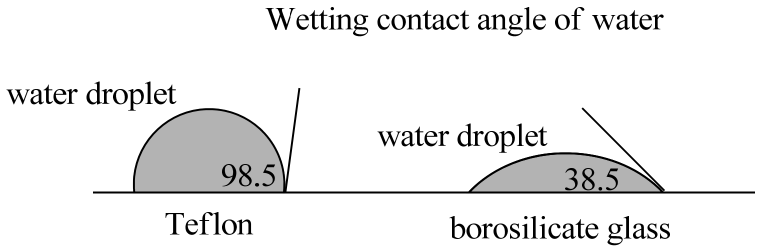


Figure 3: Examples of the shape of water drops on different solid surfaces.

Safety

Chemical Hazard Identification

starch (wheatened cornflour) – non-hazardous

vaseline – non-hazardous

paraffin oil – non-hazardous. Use safe work practices to avoid eye or skin contact and inhalation.

glycerol – non-hazardous

detergent - non-hazardous

poly(vinyl alcohol) - non-hazardous

borax - hazardous. Irritant, moderate toxicity.

Risk Assessment and Control

Low risk.

Boron compounds are toxic if ingested (especially for ants).

There are no special hazards associated with this experiment

Waste Disposal

Dispose of all of your solid waste in the bin.

Plastic pipettes are single use only. Dispose of them in a rubbish bin. **Don't put them in the locker drawer.**

Experimental

This experiment is to be carried out in pairs.

Part A Droplet shape

In this part of the experiment you will examine the shape of liquid droplets on surfaces for 4 liquids and 4 surfaces. The four different surfaces are:

- glass - use a black tile which has a glass-coated surface
- wood - use a paddle pop stick
- metal - use the handle of a nickel spatula
- plastic - use a plastic square supplied.

(A1) **In your logbook**, construct a table in which to record your observations with the four liquids (oil, water, water+detergent and glycerol) along the top of your table and the four surfaces (glass, wood, metal and plastic) down the side.

(A2) Record the shape of the droplet for each liquid/surface combination using the three categories, A, B and C, depicted in Figure 4. A droplet is described as "A" - non-wetting - if the height is greater than the contact radius. It is classified as "B" - intermediate wetting - if the height and contact radius are similar, and it is classified as "C" - the strongly wetting case - if its height is much smaller than the radius of the drop's contact area.

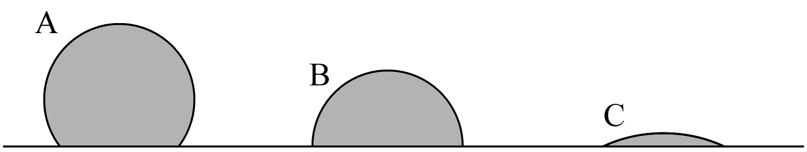


Figure 4: Three categories of droplet shape

For your logbook:

What difference did you observe between the non-polar oil and the polar liquids water and glycerol?

What effect did adding the detergent have on wetting?

Part B Gelation of poly(vinyl alcohol) with borax

In Part A you saw the effects of different strengths of intermolecular forces on the interaction between a liquid and a solid substrate. In this part of the experiment you will investigate the effects of cross-linking, a chemical means of modifying the strength of intermolecular interactions.

(B1) Weigh out 2 g of poly(vinyl alcohol) into a clean dry 100mL beaker (Skill 3.1 Part B).

(B2) Take 25 mL of deionised water in a 100 mL beaker and warm it to approximately 90 °C on a magnetic heater/stirrer hot plate.

(B3) Keep the beaker on the hot plate and, while stirring continuously with a wooden stirrer (paddle pop stick), slowly sprinkle the poly(vinyl alcohol) from step (B1) on the surface of the water. This procedure prevents the formation of a sticky mass of polymer that is difficult to dissolve. Stir until the polymer is *completely* dissolved. (This is very important!)

(B4) Cool the solution and then pour into a polystyrene cup. Add 5 mL of borax solution and stir the mixture vigorously with the wooden stirrer.

(B5) Knead the gel formed into an elastic ball in the palm of your hand. Observe what happens when you stop applying pressure to it.

For your logbook:

Describe the appearance and behaviour of your slime. What happened when you stopped applying pressure to your ball of slime? Did it maintain its shape?

Based on the chemical structures of poly(vinyl alcohol) and borax given in the Introduction suggest a possible structural formula of your cross-linked slime.

Part C Silly Putty

In Part B you investigated a so-called “viscoelastic” polymer system, with intermolecular forces modified by cross-linking. Now you will look at starch, a naturally occurring polymer consisting of linked glucose monomer units.

Solid starch consists of starch granules. In this part of the experiment you will investigate how the viscosity of a suspension of starch depends on the amount of starch added to water and on applied stress.

Because this part of the experiment involves the use of large amounts of starch and water, and can be particularly messy, you will do it as a group project with your demonstrator. Your demonstrator will call you all together to do it at an appropriate time.

(C1) Together with your demonstrator mix water and starch in a volume ratio of 1:1 in a plastic bowl by slowly adding water to the starch.

(C2) Pour some into your hand. **Record its flow behaviour in your logbook**.

(C3) Punch the mixture in the bowl with your clenched fist (Don't be afraid.). **Record your observations in your logbook**.

The behaviour you have observed with starch is known as *dilitancy*, *i.e.* a stress-induced increase in viscosity. In contrast to the slime you looked at in Part B of the experiment, the stress-induced change in viscosity you observed for the starch suspension or "silly putty" isn't due to any intermolecular forces between the starch granules. To understand its origin, carry out the following simple analogy in pairs at your bench.

(C4) Take out a pencil and hold it up vertically, resting one end on the bench. Place your finger on the top of the pencil and press down (*i.e.* apply a force) so that it stays in a vertical position. You shouldn't support the pencil in any other way.

(C5) Remove the pressure from the top of the pencil by taking your finger off quickly. Record in your logbook what happens to the pencil.

For your logbook:

The behaviour of the pencil is analogous to the behaviour of the silly putty. If possible, now explain the difference in viscosity of the silly putty when punched and when picked up slowly in the fingers.

Part D Adhesion between surfaces: Measuring the peel-off force

One standard measure of the strength of adhesion is to measure the maximum force required to peel a flexible material from a solid surface (as shown in Figure 5). In this part of the experiment you will use a spring balance to measure this peel off force.

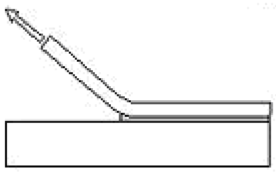


Figure 5: Arrangement for a peel off measurement.

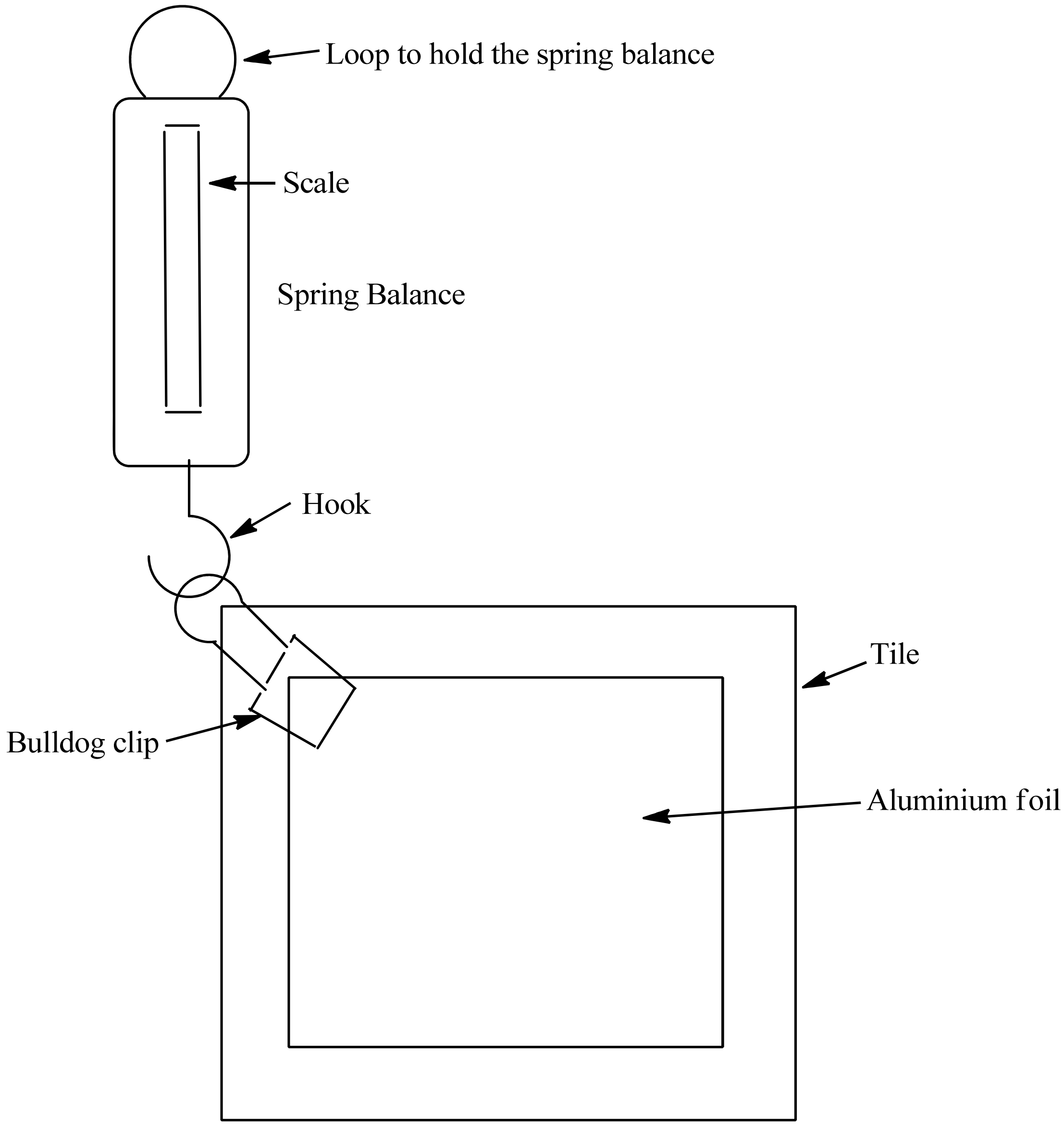


Figure 6: Diagram of the set-up for measuring the peel-off force.

To measure a peel off force, attach the provided spring clip to one corner of your flexible material and then hook the spring balance to the clip, as shown in Figure 6. Pull steadily and record the highest force reading (in newtons).

But before you start collecting measurements of the peel-off force, you need to see how much they can vary depending on the rate at which you pull.

(D1) Add starch to a height of approximately 11 mm in a 100 mL beaker. Add 10 mL of glycerol to the beaker and mix into a smooth uniform slurry using a paddle-pop stick.

(D2) Use a ruler to tear your aluminium foil into 6 cm x 6 cm squares.

(D3) Uniformly spread the glycerol+starch mixture in on a clean black ceramic tile (the glazed surface is a glass).

(D4) Use your thumb to push down firmly on the aluminium, starting in the centre and moving outwards to the edge.

(D5) Now, **in your logbook**, record the maximum force when the peel-off is achieved with a steady pull rate such that the film is completely removed from the tile in 1 s, 2 s and 3 s. Remember to smooth out the aluminium foil before each measurement.

For your logbook:

What dependence did you find between the peel-off force and the rate of pulling?

(D6) Try even slower rates to see if the change in the peel off-force eventually ceases to depend on the pull rate if it is slow enough.

Part E Glues are adhesives that thicken with time

The standard strategy for glues is to have them grow more viscous with time after they have been confined between the surfaces you want to bind together. This thickening typically occurs either due to a chemical reaction forming covalent cross-links between polymer chains or due to the evaporation of solvent, resulting in an increasingly concentrated solution of adhesive molecules. The latter approach is used in craft pastes, white glue and wallpaper pastes, where the solvent is water.

In this part of the experiment you will record the change in peel off force of a water+starch mixture as a function of time.

(E1) Prepare a water+starch adhesive by taking 11 mm of starch in a 100 mL beaker, adding 10 mL of water and mixing well.

(E2) Prepare 5 identical samples of aluminium foil stuck to ceramic tiles using this water+starch mixture. Record the starting time and the required peel-off force after 1, 5, 10, 15 and 30 minutes. Use a '3 second peel off' (*i.e.* a slow peel off) to record the adhesion forces. **Record you results in a table in your logbook**

For your logbook:

Did your adhesive reach a time independent peel-off force by the end of the 30 minute period?

The increase in the adhesion strength is a result of the evaporation of water increasing the concentration of the starch+water mixture. Vaseline (also known as petroleum jelly) consists of long-chain hydrocarbons. What would you expect for the time dependence of a vaseline+starch mixture?

Part F Designing your own white-tack

The key features of temporary adhesives as used on Post-It notes and Blu-Tack are that the adhesive does not adhere to the surface it is applied to after it is pulled off (*i.e.* no mess) and also that the adhesive strength does not significantly increase with time.

Your task is to design the composition of your own version of a Post-It adhesive using any combination of water, vaseline, glycerol and starch you wish. Your goals are to produce an adhesive that provides the maximum peel-off force while

a) leaving no residue on one surface (foil or ceramic), and

b) exhibiting no significant increase in the peel-off force after 10 minutes.

(F1) First measure the peel-off force of a Post-It note. **Record the force in your logbook.**

(F2) Make use of your previous observations to identify the most likely adhesive formulae. Do not use more than 10 mL of glycerol in any of your formulations.

(F3) **Record in your logbook** all your formulations and their pull-off forces.

(F4) **Report in your logbook** the composition of your final best mixture.

Group Discussion

In Part A, which liquids produced which shape of droplet on which surface? Can you explain your results in terms of intermolecular forces? How does a detergent affect intermolecular forces?

Can you explain why the slime is able to flow in spite of the cross-links formed by borax?

Can you explain the strange behaviour of silly putty, *i.e.* the dependence of its viscosity on applied force?

Compare the peel-off forces of the post-it note you obtained in Part F with those of the other students.

Based on the peel-off forces of the different formulations you developed and the presence or lack of a residue, decide which pair produced the best formulation. Record the composition of that formulation in your logbook.