ChemSumer

Sticky Situations: The Wonders of Glue

By Linda Shiber

For many of us, the allure of glue peaks during early elementary school. We eat it as a forbidden delicacy, we use it to create seasonal construction paper crafts, and some of us may even use the colored varieties to spice things up. After, say, second grade, most individuals forget about glue. The initial fascination evaporates, and, instead, we begin taking the sticky stuff for granted. In actuality, however, glue deserves far more attention. It comes in many forms, is derived from surprising sources, and fulfills a plethora of functions.

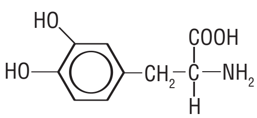
Creatures that stick and sticky stuff from creatures

What do mussels, fish, and geckos have in common? They all have the ability to stick, or become sticky. The most impressive member of this group is the mussel. Mussels spend their lives permanently attached to rocks in the ocean. It's a stressful life—they're constantly bombarded by harsh waves, yet they don't get washed away. Their secret? Well, the key to the mussel's tenacity is a gluey secretion called byssus, which originates from glands in its "foot". University of California at Santa Barbara researcher Herbert Waite discovered that these glands secrete two materials: resinlike proteins and hardening substances. When the two mix and contact water, they harden, forming a bond that is able to oppose thousand-pound forces. The hardening process is where all of the interesting chemistry comes in.

WILKER GROUP AT PURDUE UNIVERSITY

Mussel adhering to a sheet of polytetrafluoroethylene (Teflon).

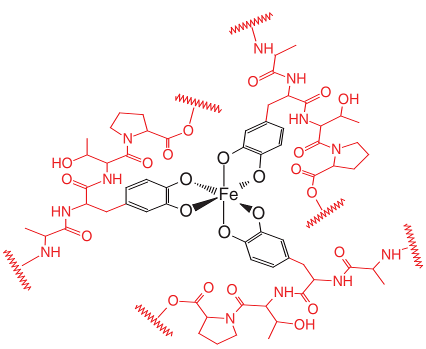
Before the glue hardens, the molecules in the byssus are in the form of polymer chains that have side groups made of DOPA, or dihydroxyphenylalanine.



dihydroxyphenylalanine (DOPA)

Polymer chains are simply long chains of molecules that are covalently linked together. Why is DOPA important? Well, in its oxidized form, it is involved in the cross-linking between the protein chains of the mussel glue, creating a meshwork that binds the mussel to its rock. Cross-linking is important for making the glue stick to itself and to the surfaces to which it is adhering. However, the DOPA cross-link story doesn't end here. Mussel glue contains a remarkably high concentration of iron, and Jonathon Wilker at Purdue University wanted to find out why. Research done by Wilker in 2004 revealed that mussels use iron that is in the surrounding water to join the byssus molecules together via their DOPA side chains, forming this cross-linked framework. It turns out that each iron atom can bind three DOPA side chains.

When the iron-DOPA linked molecules are exposed to oxygen, the complex forms radicals. Radicals are extremely reactive substances, and in this case, their reactivity is responsible for internal cross-linking of the glue and for connecting the glue to surfaces. The end result of the process is a strong, waterproof adhesive that keeps mussels on the rock of their choice for life.



Each iron atom binds to three DOPA side chains.

Fish glue

Although mussel glue is impressive for its sheer strength, it only serves the purposes of the mussel. Other animal-derived glues have been used by humans for serving their own needs. Fish glue, as an example, is prepared by heating the skin or bones of certain types of fish in water. Extra-pure fish glue may be manufactured from swim bladders. The protein-based substance was patented in the 1750s, and it is still used today for various tasks. Fish glue is special because it bonds well to leather and can be easily removed with hot water or steam (without damaging the bonded surfaces). These qualities make it a good candidate for, interestingly, pipe organ restoration and repair. Pipe organs rely on leather for the pneumatics, which control how much air is expelled from the pipes when a key is depressed. More specifically, when an organist presses a key, an electric current travels through a cord to valves that open to specific increments, controlling the air that leaves the pipes and, in turn, the sound that's produced. Leather is used on the valve disks, the gaskets, and the pneumatics. These leather components inevitably wear out and require replacement. Fish glue is the choice when one must reaffix new leathers, because when they deteriorate (after 50 years or so), the glue can be removed without causing damage to the instrument.

Off to the glue factory …

Marine animals aren't the only sticky organisms, though. Glues are also made by boiling the hooves, hides, and bones of animals such as horses. You may have heard the saying that elderly horses are led off to the glue factory. There is some truth in it. For instance, hide glue was used in the past to make bows, glue together ceramics, and is still used today in woodworking. The glue is made by heating hides and skins in an alkaline solution containing lime ($Ca(OH)_2$), which softens and breaks down the tissue, releasing collagen. Next, the hides are run through a water rinse to remove excess lime, and hydrochloric acid is added to aid in the lime removal by neutralizing it. The resulting material, called "stock", gets heated for a specific amount of time, which allows further breakdown of the collagen into a gluey material. As this hide glue cools, it attains a gelatinous quality. When all water has been evaporated, the hide glue becomes concentrated in sheets or blocks. To use the hide glue, an appropriate amount is added to hot water, melted, and then spread onto whatever needs gluing.

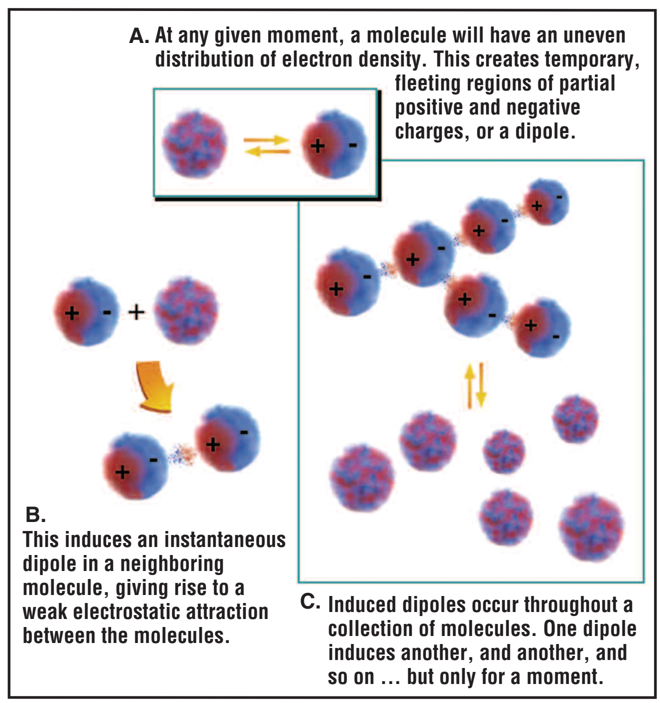
We've got geckos climbing the waals

Geckos climb on all kinds of surfaces, including ones that are completely vertical. Professor Autumn Keller and undergraduate

AUTUMN KELLER, LEWIS AND CLARK COLLEGE

students at Lewis and Clark College have discovered how the critters can defy gravity. The key to the gecko's nimble footwork are millions of tiny hairs, called setae, which are arranged on the pads of its feet. The setae each split into more tips called spatulae (amounting to figures in the billions), which are microscopic. These miniscule hairs work to hold the gecko on a surface through a mechanical approach, rather than by, say, secreting a gluey substance. The key to the geckos "stickiness", then, is something called van der Waals forces.

Van der Waals forces refer to three types of attractive forces that can exist between neutral molecules: dipole-dipole forces, hydrogen bonding, and London dispersion forces. The type of van der Waals force employed by the agile gecko is London dispersion. These are weak electrodynamic forces between molecules caused by an instantaneous, temporary dipole of one atom inducing a similar temporary dipole on an adjacent atom, causing the atoms to be attracted to one another.



Van der Waals forces.

All molecules experience van der Waals forces, but the gecko's secret is its surface area. Because there are so many setae and spatulae, the total area of the gecko's foot in contact with the surface that it's scaling can be immense, so all the tiny attractions can add up to serious stickiness.

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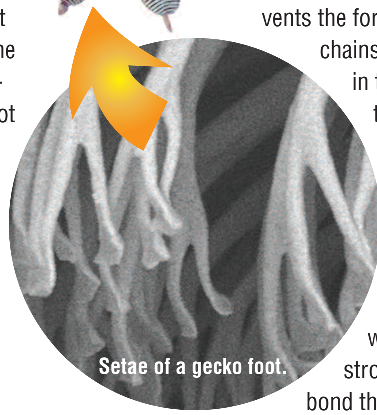
In addition to van der Waals forces, the gecko's ability to stick is attributable to geometry. When a gecko runs, its foot moves in such a way that optimizes the contact between its setae and the surface. The gecko actually pushes its foot pads down and slides them forward slightly, thereby initiating the sticking. To lift their feet back up, the angle at which the setae touch the surface is increased, and the gecko "peels" each foot off the ground.

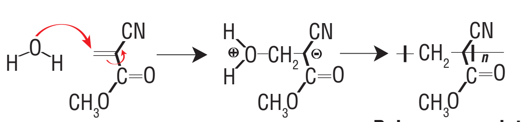


Setae of a gecko foot.

A glue by any other name

Although hide glue might be news to you, products like superglue and gorilla glue are probably much easier to recognize. Superglue comes in small containers and packs a whole lot of stickiness. The molecule responsible for its adhesive qualities is cyanoacrylate, an acrylic resin. Cyanoacrylate was discovered in the 1940s by a man named Harry Coover who was working at the Eastman Kodak company. Following his discovery of this sticky substance, Eastman Kodak began looking into alternative uses for the material. The key to cyanoacrylate glue was that it stuck to skin. Hence, research was done to see if it could be used medically to hold the tissue surrounding surgical incisions together. It could and it did. In fact, during the Vietnam War, a cyanoacrylate glue spray was used on battle wounds as a fast way to stop bleeding until the injured person was transported to a medical facility.

So how does cyanoacrylate work its adhesive magic in products like Superglue? Well, in its liquid state, Superglue's main ingredient is the monomer methyl-2-cyanoacrylate. Exposure to water (or, the trace amount of hydroxide ion present in water) causes the monomers to undergo a polymerization reaction in which they form long chains that can connect two surfaces together.



Polycyanoacrylate

Because trace amounts of moisture exist on most surfaces, Superglue cures quickly and without much coaxing. The reason that Superglue doesn't stick to the walls of its package is because an acidic stabilizer has been added. This stabilizer prevents the formation of polymer chains but is overridden in the presence of the thin layer of water molecules that coats most surfaces wherever there is moderate humidity.

Is there any way to reverse the strong, waterproof bond that Superglue makes? There are some factors that may weaken its adhesiveness. For instance, heating glued objects to a temperature greater than 180 °F, or exposing it to temperatures less than 30 °F will soften the glue or cause it to become brittle. Acetone, a substance found in nail polish removers, can also soften the bond by partially dissolving the polymer chains, making it easier for them to slip past each other.

Primates and polyurethane

Another type of human-made glue that may be familiar to you is Gorilla Glue. Gorilla Glue is used in home repairs and woodworking and is lauded for its waterproof bond. In contrast to Superglue, Gorilla Glue doesn't dry within seconds. Rather, it allows the person using it a 20-minute window in which surfaces may be shifted and adjusted to glueable perfection. What's the key to this bond? The answer is polyurethane polymers. A polyurethane polymer is a chain of molecules attached to one another via urethane links. The central reaction responsible for chain formation is between two types of monomers: a polyol (polyethylene glycol or polyester polyol) and a diisocyanate (either aromatic or aliphatic).

Depending on the type of monomers and/or catalysts used, polyurethanes have widely different properties. Although the substance is used as a glue, through variation of the polymerizing reagents and through various additives, it may acquire properties that allow it to act as a varnish or a foam. For example, using an aromatic diisocyanate monomer would create a substance with differing mechanical properties as opposed to using a linear monomer. The same variation is seen with the polyol used; a polyethylene glycol monomer produces a softer, more flexible polyurethane than a polyester polyol might.

The sticky-icky lowdown

Now that we've profiled how different kinds of glue form bonds, the next logical question is how do glues interact with the surfaces they're gluing? How does a glob of glue convince two objects to stick to it and to each other? There are several ways this can occur. The first way is pretty much common sense. Glues work mechanically by invading the pores and cracks in the two surfaces, increasing the area that becomes sticky. Sometimes, the effectiveness of glue can be increased by making the surfaces rougher. This provides the glue with plenty of crannies it can diffuse into and occupy.

Another major way that glues work is by taking advantage of electrostatic forces present on the surfaces of the objects being glued. Different objects contain molecules with varying dipole moments, which may attract them to one another. An adhesive force is created when electrons are transferred from one surface to another, creating positive and negative charges, which are attracted to one another.

It's clear that there's a lot more to glue than its sentimental role as a childhood snack. Animals make it, people make it, and it holds together so many of the items we rely upon every day. Look around. Glues are everywhere, from the natural world to the chemistry lab. It would be virtually impossible to separate our lives from them. Not that we'd want to, of course. The bottom line, then, (and pardon the pun) is that we're stuck on glue.

Period.

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Additional references can be found in the Teacher's Guide.

Linda Shiber is a freelance writer living in Louisville, KY. She is working on a medical degree and lives with her dog, Ralph.