Chemistry

Cyanoacrylate: The Super Glue

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Having been asked to write a STEM article, I thought about a variety of topics, until I settled on something which, in my opinion, neatly encompasses almost all aspects of STEM. I chose superglue, which acts using complex chemistry, and is now used increasingly in the world of technology and engineering. Superglue is a $400 million industry with industrial, medical, and household uses; it has had, and still has a dramatic effect on the world today.

In 1942, Dr Harry Coover Jr. was working at Kodak Laboratories experimenting to synthesise optically clear plastics for use in gun sights during World War II. His work was with a group of chemicals called cyanoacrylates, but he found that they stuck to everything that he touched, so he decided to abandon the substance. Later, in 1951, working at Eastman Kodak, Dr Coover oversaw a research team attempting to make a heat-resistant coating for jet canopies. One of his research students, Fred Joyner, spread ethyl cyanoacrylate (now the main constituent of superglue) between two lenses to examine it with a refractometer,

to measure the refractive index, and hence determine the purity of his sample. He found that the two lenses became stuck very strongly together. Coover then saw the potential of the substance as an adhesive. Superglue was finally put on the commercial market in 1958 by Eastman Kodak and was not popular for use until the 1970s.

Cyanoacrylate has the general chemical formula is $CH_2=C(CN)CO_2R$, with R representing an organic molecular group. As a simple explanation of how they work: due to the highly polar nature of the nitrile (CN) and ester (RCOOR) groups, these compounds polymerise quickly on any basic surface, especially in the presence of water. They polymerise with the repeat unit of structure in fig. 1, in the way depicted by fig. 2.

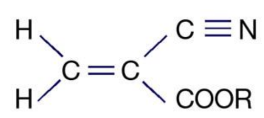


Figure 1: Monomer

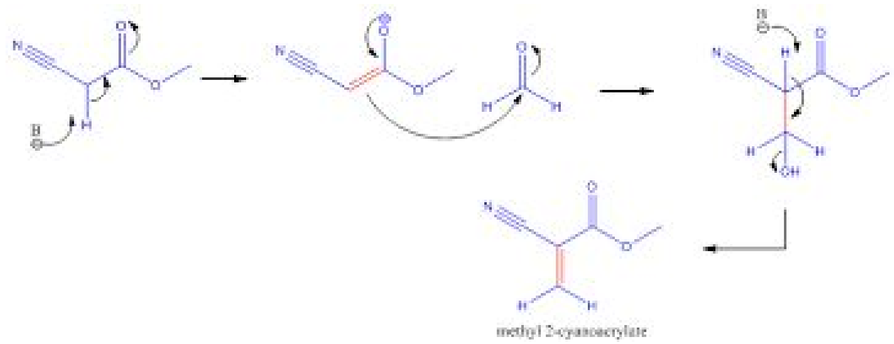
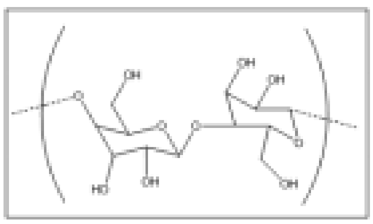


Figure 2: Polymerization

As a slightly more in depth explanation, in three steps, cyanoacrylate forms a very strong bond via a nucleophilic chain polymerisation reaction: when it is first squeezed out of the tube, the initiation step occurs. This is when an OH ion (from a water molecule, acting as a nucleophile due to it being electron rich) breaks the C=C double bond (the OH^- ion is attracted as one of the carbons in the C=C is partially positive, an electrophile – due to resonance of the nitrogen and oxygen atoms in the cyanoacrylate molecule). One of the carbon atoms forms a new bond with the OH ion, and an anion on the other side of the bond is formed. Secondly, during the propagation step, the anion formed bonds to another cyanoacrylate monomer at the C=C double bond, forming a C-C single bond and another anion which can bond to another cyanoacrylate forming a polymer chain. The termination step occurs when there are no more cyanoacrylate monomers, and thus you are left with a polymer, poly-cyanoacrylate, a strongly bonded solid. Even the driest surfaces have enough water to begin the reaction, so it can glue almost anything. To ensure that the reaction does not start in the tube, the tube contains hydroquinone acting as a radical inhibitor. The formulated adhesive also contains some other property-modifying additives.

One problem is that, due to the reactivity of the substance, always ready to polymerise, it can cause rapid, and dangerous reactions. For example, cotton is made up of largely cellulose. As you can see from the structure of cellulose, just a note on the structure here (literary designer's job) it has many OH^- groups, which can initiate the polymerisation reaction of cyanoacrylate. In fact, only a trace amount of cotton is needed to initiate the reaction, which is extremely exothermic and often the cotton will catch fire, so be careful!



Cellulose

As I have mentioned, cyanoacrylate has a variety of uses, above and beyond the domestic uses that we know about. One example of this is cyanoacrylate fuming, which is a forensic science technique that uses the vapours of super glue to develop latent fingerprints used since the 1970s. The fuming is performed in a developing chamber (as oxygen inhibits the polymerisation process) using ethyl cyanoacrylate and water, which results in a white polymeric layer forming over the ridges of the print after about two minutes. The reason why it only forms on the ridges is because eccrine sweat makes up the ridges on the fingerprint, and therefore there must be something in the eccrine sweat that initiates the anionic polymerisation reaction. Possible initiators are amino acids, water, and sodium lactate, though the exact mechanism is unknown. This method is especially useful as it can show trace amounts of exocrine secretions such as blood and sweat without corrupting or destroying them, so that they can also be used for DNA testing. In addition, this method makes a fingerprint semi-permanent so that it can be dusted and tape-lifted various times without being ruined.

But one of the most ground-breaking uses of the substance has been in medicine. In

1966, cyanoacrylate spray was said (by Harry Coover) to have been used in the Vietnam War as an easy portable method to reduce bleeding in wounded soldiers until a hospital visit was possible. Then, in the early 1970s, and potentially before, it was said to have been used for mending bone and tortoise shells. What I should point out at this stage is that the cyanoacrylate that I am talking about in the medical context isn't that which you would find in your toolbox, but instead, it is one formulated for medical use. During the Vietnam war, various formulations were tested however none were approved as they had potential to irritate the skin. In 1998, the US Food and Drug Administration (FDA) approved the first medical adhesive, Dermabond (2-octyl-cynoacrylate). The versions that we use today are less toxic than that which we keep in our toolbox and have plasticizers to make them more flexible. There are three main forms of cyanoacrylate that we use in a medical sense today: 2-octyl-cyanoacrylate (Dermabond, SurgiSeal); n-2-butyl-cyanoacrylate (Histoacryl, Indermil, GluStitch, GluSeal, LiquiBand); and 2-ethyl-cyanoacrylate (Epiglu). The standard 'superglue' is made of ethyl 2-cyanoacrylate.

Many people have these forms of cyanoacrylate in their first aid kit, as it is ideal for the closure of the two sides of clean minor cuts, such as knife cuts or paper cuts. It has many benefits including: drying fast to stop the bleeding, staying in place for a long time and by the time it wears off the cut is typically healed, keeping dirt and air out of the cut and reducing scarring.

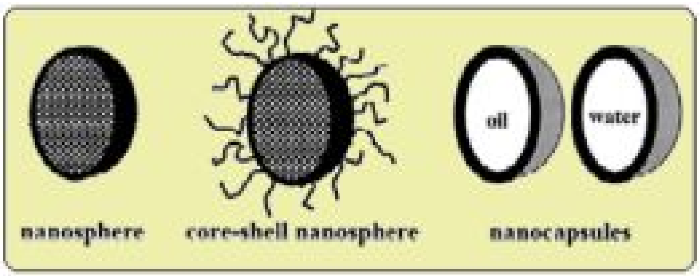
Other domestic uses include stringed-instrument players forming protective finger caps with cyanoacrylates. This isn't the only time that they are used in music. They are now commonly used to bond the pads of clarinets, saxophones, and oboes, as well as producing the shiny finish on string instruments such as guitars, as they are considered to have acoustic benefits to the wood. They are also being used by rock climbers to repair damage to skin on their fingertips. Although the glue isn't toxic and will wear off quickly, applying large quantities of glue and its fumes directly to the skin can cause chemical burns, and this is just one of the safety issues...

Firstly, skin injuries may occur where parts of the skin are torn off. Secondly, cyanoacrylate is toxic, the fumes from cyanoacrylate are a vaporized form of the cyanoacrylate monomer that irritate the sensitive mucous membranes of the respiratory tract. They are immediately polymerised by the moisture in the membranes and become inert. These risks can be minimized by using cyanoacrylate in well-ventilated areas. About 5% of the population can become sensitised to cyanoacrylate fumes after repeated exposure, resulting in flu-like symptoms. Cyanoacrylate may also be a skin irritant, causing an allergic skin reaction. Finally, fibrous materials such as cotton, leather or wool can result in a powerful and rapid exothermic reaction. The heat released may cause serious burns or release irritating white smoke.

In hospitals, studies have confirmed that cyanoacrylate can be safer and more functional for wound closure than traditional suturing. The adhesive is superior in time required to close wounds, incidence of infection, reductions in percutaneous (through the skin) injuries from suture needles, which would in turn also reduce the risk of transmission of infectious diseases, and cosmetic appearance. They can be effectively used as a sealant to any part of the body where there is no tension, even now as closure to head and neck surgery. It has therefore had a revolutionary impact in medicine.

Some other uses of cyanoacrylate in hospitals are: embolization to control abnormal bleeding; haemostasis to stop bleeding; the apposition (closure) of wound edges; a sealant and reinforcement of surgical anastomosis (connection or opening between two things that are normally diverging or branching); the list goes on. Furthermore, it is now being used in dentistry – it has been used in free gingival grafting, apicectomy, root sectioning, and bonding of fractured tooth fragments.

The final aspect of medicine that I would like to look at is the delivery of medicinal drugs to specific targets in the body using nanospheres. This idea first came about in 1980. A nanosphere is a hollow, spherical cyanoacrylate polymer either filled with an active drug, or with an active drug adsorbed on its surface.

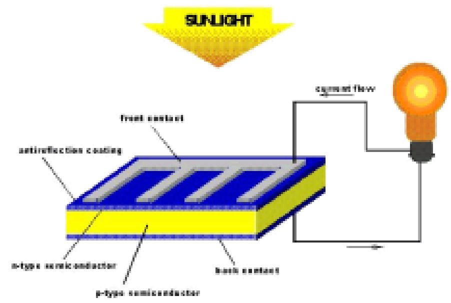


They can then be administered either orally, or intravenously. One way of loading them is soaking them in a solution of the drug, which results in surface absorption. You can also electrostatically bind to the anionic polymer, then initiate the polymerisation reaction so that the rug is trapped inside the nanosphere. This has benefits that it is trapped inside the nanosphere until it arrives at the target location, when it binds to polar substrates and the amino acids initiate the reaction. It could be used for chemotherapy to attempt to reduce the side-effect profile, as it will no longer kill off living cells. There are two issues with this form of treatment. Firstly, as the polymers degrade, they become increasingly more toxic, however toxicity decreases as chain length increases. Polyalkylcyanoacrylates are used as our cells can cope well with their breakdown products, their fast degradation kinetics, meaning that they don't get overloaded with toxins. Secondly, the rate of release of the drug must be monitored carefully. If the release time is too fast the patient can receive too high a dose in too short a time – this can be very dangerous. The aim is to release 70% of the drug within 60 minutes of the nanoparticle arriving at the site, and then in the following 120 minutes to release the remaining 30% of the drug. This use of cyanoacrylates is also of interest as it can be used to let drugs go through the blood

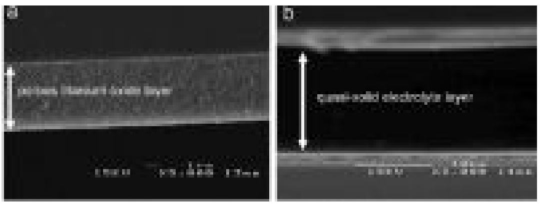
brain barrier, the mechanism by which they do this is currently unknown. This is very important because the failings of a lot of medicines is their inability to penetrate the blood-brain barrier to enter their site of action. This application may be able to be used in the treatment of illnesses such as brain cancer.

Cyanoacrylate is being used increasingly in the developing world of design at the moment. For example, granular 3D printing methods cause the product to be powdery and fragile. They are then dipped in cyanoacrylate adhesive, which wicks into the porous model, and cures to a hard, solid piece. It leaves you with a strong, glossy surface, on a previously fragile, powdery object.

In addition, it has now been used for underwater bonding. If you put some high viscosity adhesive onto an object, then put it under water, it immediately forms a hard shell of cyanoacrylate around the globule – but the cyanoacrylate under that shell remains viable longer. Once under water, you can smash the object with the glue on, onto whatever you want to glue, so that the glue shell bursts, and the liquid inside it can bond the two components.



Cyanoacrylate has even been looked at for use in solar cells (photovoltaic cells – PV cell). In order to create a successful PV cell, there needs to be a high solar cell conversion efficiency of higher than 10%. Liquid electrolytes have been used for this reason - however, with liquids, there is always the problem of the liquid leaking from the solar cell, which poses an environmental threat. Solid electrolytes do not have this problem, but they have reduced solar cell conversion efficacy.



Cyanoacrylate has been looked at because it can exist as a gel, which is known as the quasi-solid state. Gel electrolytes have almost as high a solar cell conversion efficacy as liquid electrolytes but have a smaller risk of leaking. PV cells rely on semiconductors, which are materials whose electrical conductivity increases with increasing temperature. The way that they work is that an electron from the semiconductor is excited by sunlight (photons) into a higher energy state. An electric field forces the electron to flow around the cell in one direction until it ends up where it began, thus completing the circuit. If you look at the image below, you can see the layer structure: the bottom layer is made up of dye molecules. Photons excite electrons from the dye molecules into the electrolyte layer. The electrolyte layer is made of cyanoacrylate and tetrapropylammonium cations [N(Pr)4]+ which favours anion transfer. This means that it is easier for the electron to go from the excited dye molecules into the next layer, the titanium oxide layer. After the electron goes through the titanium oxide layer, it passes through an external circuit - this generates the current.

The electrons re-enter the internal circuit through a platinum counter-electrode. The electrons are then transferred back to the excited dye molecules through a redox reaction: $I_3^- + 2e \rightarrow 3I^-$, in which the iodide ions give back the electrons to the dye molecules which would then resume their ground state. The size of the cyanoacrylate monomer means that it is less viscous, and it gets through the titanium oxide layer easily, enabling good electron transfer. Cyanoacrylate also has an added advantage in that it displays great mechanical strength and keeps the substrates together.

Cyanoacrylate is even being used in the preservation and stabilization of objects from archaeological digs. It is used particularly for the reparation of hairline fractures and on bones which are porous, which many fossil bones are, as it penetrates and stabilizes the bone through capillary action.

In engineering, Michigan State University think that they may have invented a new type of adhesive, based on cyanoacrylate, for joining car parts together, which bonds at a variety of temperatures to a variety of materials. The bond can be reversed, so recycling of parts would be easy. Currently, research into the potential of the new glue is still in the laboratory testing phase, but they say that they may have it soon. It contains cyanoacrylate along with many other ingredients, including magnets.

Finally, cyanoacrylate has been looked at as a herbicide. When photosynthesis takes place, the photons 'excite' the electrons into higher energy states, which causes reduction reactions take place. The electron is excited via a route called the photosystem II pathway. Cyanoacrylate inhibits the growth of weeds by photosystem II pathway and consequently inhibits electron excitation.

Who knew that superglue had so many uses? Not bad considering that it was discovered by accident! But, as Harry Coover once said: 'one cannot help wondering how many potentially important inventions lie dormant in the recorded observations of scientists which at the time were judged to be irrelevant to their research objective', and concluded wisely, 'this should serve as a reminder to all of us to be open minded and curious enough to pursue unexplained events and unexplained results that may unlock new secrets and lead to new and excited discoveries in the future'.