

Super Glue: The Superman of the Adhesive World

By Martin Antensteiner

Imagine that you are heading to your car on your way to work. You open the car door and sit down only to notice that something doesn't quite feel right. You examine your seat for the source of your discomfort and notice a large tear in the upholstery! You now face a dilemma: fixing your upholstery in an inexpensive and appealing way. The answer is cyanoacrylate adhesives, commonly referred to as super glue. Many of us know the strength and speed at which super glue bonds almost any two surfaces together, but few of us have ever considered what it's made of, or what gives it that well-known adhesive quality.

Two kinds of cyanoacrylate glue are common today, poly(ethyl-2-cyanoacrylate) and poly(methyl-2-cyanoacrylate). Their chemical names appear foreign and intimidating at first glance, but just as new land appears foreign to any explorer, understanding the structure and inner workings of the unknown will remove this trepidation. Cyanoacrylate glues are actually polymer chains comprised of thousands of repeating units called monomers. Monomers, meaning one-part, represent exactly one repeating unit in the glue. Polymers, meaning many-parts, are long chains comprised entirely of monomers. Think of a Marti Gras bead necklace. Each bead is identical and they all connect together in massive chains. Just as the beads alone can't function as a necklace, the monomers by themselves do not have very many uses. The union of the monomers into chains is what eventually gives glue the power to hold two materials together.

Monomers bind together in polymer chains through a process called polymerization. This process exploits a key trait among monomers, the double bond. Drawing two lines between atoms, as seen in Figures 1 & 2, is how double bonds are represented in chemical structures.

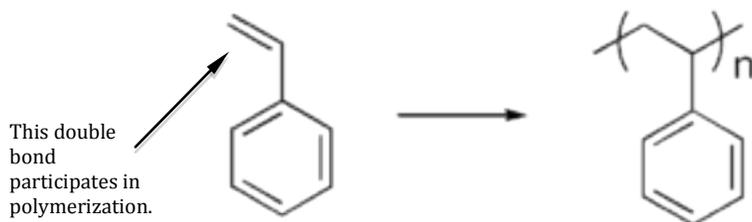


Figure 1. The chemical structure of styrene as a monomer (left) and as part of a polymer (right). The subscript "n" represents how many monomers are in that chain. (Source: Google Images)

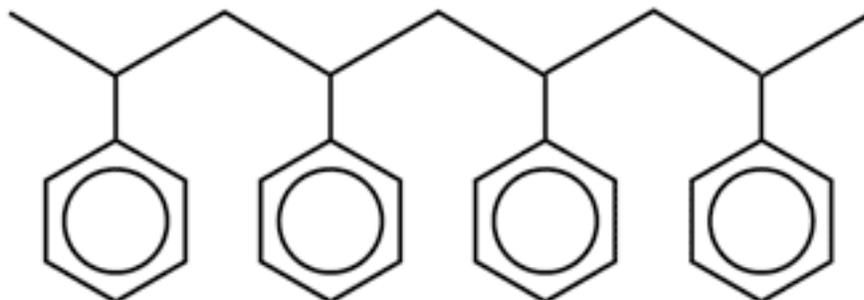


Figure 2. The chemical structure representation of four units of a polystyrene chain. The circles in the 6-member rings are another way to represent the three double bonds in the 6-member rings of Figure 1. (Source: Google Images)

These double bonds are more reactive than any other part of the monomer and make perfect candidates for bonding. Chemists have discovered that it's possible to force monomers to attach to one another using these bonds. For example, in polystyrene, the double bond in Figure 1 is replaced by a single bond in Figure 2 as the monomer connects to other monomers on either side of that bond. Here we can see how the 6-member ring remains unaffected throughout the process.

Though cyanoacrylate glues contain the same type of double bond that causes styrene to polymerize, super glues are unique in that moisture alone will start polymerization. The double bonds in cyanoacrylate glues eagerly react with any form of anion, which is a molecule that carries a negative charge. The most common initiator for super glues is water, or more specifically, the hydroxyl ions within water, represented by OH^- . This means that any hint of water will cause the monomers found in super glue to immediately form the intertwining polymer chains that we know as "dry glue." Once an anionic polymerization reaction has begun, it will stop only when all monomers have been consumed or a foreign substance interferes.

A common characteristic of super glues is that they become rigid and unyielding after they have dried, which could dissuade you from using them to patch your upholstery. Therefore, one of the most important properties of cyanoacrylate glue is what's referred to as the glass transition temperature. It is the temperature at which the glue becomes malleable, just as there is a temperature when a turkey removed from the freezer becomes soft. This temperature is governed by the flexibility of the monomer side groups: the more flexible the group, the lower this temperature. Side groups are parts of a monomer that do not become directly bonded to another monomer in a polymer chain. This characteristic is often used to distinguish polymers that behave in similarly, such as methyl and ethyl cyanoacrylate.

As seen in Figures 3 & 4, ethyl cyanoacrylate has one more carbon on the far right side of its structure than methyl cyanoacrylate.

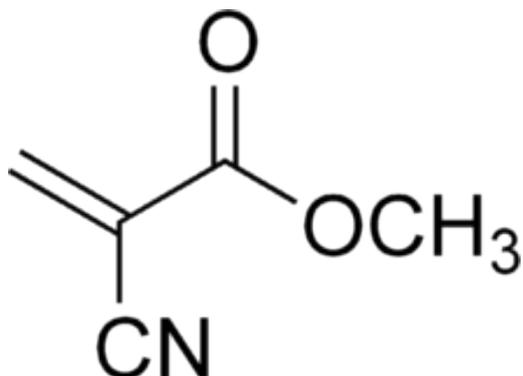


Figure 3. The chemical bond structure of poly(methyl-2-cyanoacrylate)
(Source: Google Images)

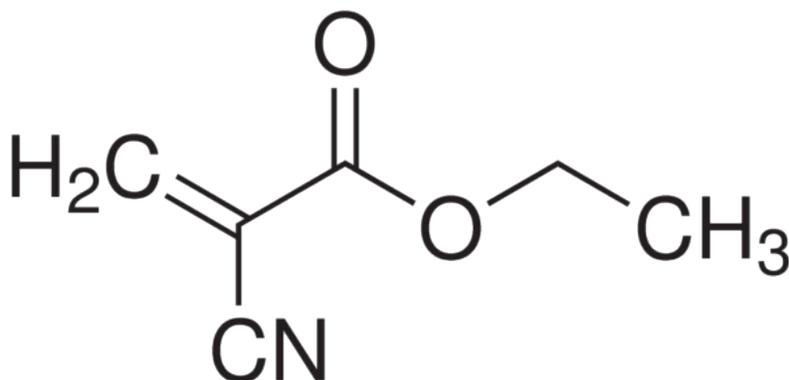


Figure 4. The chemical bond structure of poly(ethyl-2-cyanoacrylate)
(Source: Google Images)

The extra carbon in ethyl cyanoacrylate provides more flexibility to the monomer, just as a longer pencil eraser is more flexible than a short one. Methyl cyanoacrylate, with this shorter side group, remains rigid at slightly higher temperatures than ethyl cyanoacrylate. This gives it a wider range of applications at higher temperatures. Since methyl cyanoacrylate remains stiffer at higher temperatures, it is ethyl cyanoacrylate that will best repair your upholstery without causing continued discomfort from a rough seal. It is the disparity in the working temperatures, as a result of chemical structure, that forms the main difference between ethyl and methyl cyanoacrylate.

When we purchase super glue at any convenience store, we usually receive small tubes with a fine tipped, thoroughly sealed nozzle. Inside, we assume there is a clear, thick liquid with an acrid odor that will adhere to anything on contact. What's inside is more interesting than that. Within every tube of super glue resides the monomer, of either ethyl or methyl cyanoacrylate, supplemented with various chemicals in miniscule amounts that prevent the glue from curing before the seal is

removed. These chemicals work by sealing out moisture and temporarily inhibiting the anionic polymerization process. When we squeeze the tube and apply the monomers to a surface, water (or another anionic substance) initiates the reaction. In industry applications, chemicals exist that are added to a reaction to halt its progress. For domestic applications, such agents can manifest in the form of dirt, dust, and other foreign contaminants. This is why instructions always recommend thoroughly cleaning the surface before using the glue.

Despite knowing a few characteristics of super glue, we still fear the predicament that results from inadvertently gluing our fingers together or, even worse, to another part of our anatomy. But how exactly is this colorless paste capable of animating such a fear? Super glue adheres to our skin because it is not nearly as smooth as it seems (Figure 5). The roughness of our skin's surfaces unlocks the secret of super glue's amazing ability to transform our hands into flippers.

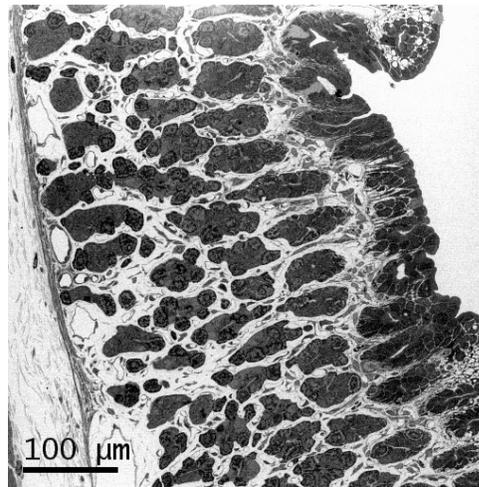


Figure 5. An Image of the cross-section of human skin taken using a serial block face scanning electron microscope (Source: www.gatan.com)

When we apply the monomer onto a surface and press the two materials to be bonded together, the individual monomers fill into every microscopic crevice on each surface. The monomers then react with the moisture inherent in the object and solidify into the final polymer. The glue can be thought of as the missing puzzle piece to the ridges on the surface in Figure 5. Once dry, this puzzle piece will not let go of the surface, even if that surface happens to be our finger. Luckily, acetone (as found in nail polish remover) contains the necessary chemical properties to dissolve the cyanoacrylate glue. Once dissolved, the glue cannot be re-used. Most surfaces remain unaffected by this method of removing the glue: a welcome relief for our fingers.

Recently, super glues have become useful in many new ways, particularly in the medical field. Lung volume reduction operations are one of the few treatments for severe cases of emphysema. Emphysema is a disease that gradually destroys the structural integrity of the lungs. Treatment operations are complex and air leaks can

arise. Stewart Horsley, MD and Joseph Miller, MD of the Emory University of Medicine found that super glue is instrumental in sealing these leaks. The process works by deflating the lung and then patching it with fibrin glue, a type of biological adhesive. A thin layer of super glue is spread over the patch and quickly covered with a layer of bovine pericardium. A bovine pericardium patch is a small section of the membrane surrounding the heart of cows or oxen. Owing to the strength of the cyanoacrylate glue, the seal would hold indefinitely.

Cyanoacrylate glues such as poly(ethyl-2-cyanoacrylate) and poly(methyl-2-cyanoacrylate) are the strongest of today's commercial adhesives. Their chemical structures coupled with their intricate properties allow them to bond to any surface where even the smallest trace of moisture exists. Capitalizing on these properties is Richard Cary, draft author of a World Health Organization report, who listed unique applications for cyanoacrylate glues including dentistry, surgery, and even fingerprinting. With such applications, it seems logical that super glue can fix our damaged car upholstery. The danger in using a product that bonds to any surface moisture is the subject of urban legends such as those written by David Emery on About.com. They tell of those who have been involved in many embarrassing situations brought on by the misuse of this wondrous polymer. Knowledge of the workings of these glues, and a bottle of nail polish remover, will prevent most mishaps from becoming permanent problems or the source of humiliation.

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Martin Antensteiner is a sixth semester junior studying the Polymer Sciences option within the Materials Science and Engineering major at Penn State University. In the summer of 2011, he worked with Dr. Erwin Vogler of Penn State on a project to determine the adhesion rates of bone cells onto various polymer surfaces. As a result of this work, he wrote a new protocol governing the use of the spectrophotometer when measuring cell concentration in solution. He has a passion for chemistry and polymers: a fact well known by his peers. He plans to enter graduate school and eventually obtain a PhD in pursuit of a career in biomaterials. Both in and away from the classroom, he lives his life by the virtues of hard work and integrity that were ingrained in him by the Boy Scouts of America and the prestigious rank of Eagle Scout.

References:

Cary, Richard. (April 12, 2005) *Methyl cyanoacrylate and ethyl cyanoacrylate*. Concise International Chemical Assessment Document 36, World Health Organization. Page 4. Retrieved from http://www.who.int/ipcs/publications/cicad/cicad36_rev_1.pdf.

Emery, David. (2012) The uses and abuses of super glue. Retrieved from <http://urbanlegends.about.com/cs/business/a/superglue.htm>.

Horsley, W. Stewart, MD and Miller, Joseph I. Jr. MD. (May 1997). Management of the uncontrollable pulmonary air leak with cyanoacrylate glue. *The Annals of Thoracic Surgeons*. Volume 63, Issue 5. Pages 1492-1493.