Part I: Shoe Repair

Recently the soles of my Nike Air Total Package basketball sneakers have begun to peel away from the “upper” part of the shoes. As seen in Figure 1, the Phylon\(^1\) (foam ethylene vinyl acetate (EVA))\(^2\) midsoles and solid rubber\(^1\) (blend of synthetic and natural rubber)\(^2\) outsoles are separating from the relatively porous leather uppers because of adhesive failure.

I wish to extend the life of these shoes by either adhering both the midsole and outsole to the upper or adhering just the outsole to the upper. The former, although it will require additional work, is more desirable because it is a more complete repair. However, Phylon soles are quite difficult to bond.\(^8\) One effective bonding method includes extensive solvent wiping, followed by applying a UV-activated primer, followed by the application of a two-component polyurethane adhesive. The other effective method is to first flame treat the Phylon, then apply an isocyanate primer, and finally use a two-component polyurethane adhesive.\(^8\) Both of these methods are too involved and expensive for the level of repair I am willing to do. As such I will only attempt to bond the rubber outsole to the leather upper.

The biggest obstacle to this job is joining a porous surface to an impermeable surface. For the porous uppers, the adhesive is expected to penetrate into the material favoring mechanical adhesion. Conversely, the non-porous rubber soles favor chemical adhesion and often—because of their low surface energy—both chemical (e.g. halogenation) and mechanical (e.g. roughening) surface preparations are required. The difficulty lies in finding an adhesive that can bond by both mechanisms of adhesion to the different types of surfaces all while meeting the service requirements of the shoe.\(^8\)
In Part One of this paper, I intend to review five commonly available adhesives (Original Shoe Goo®, Rhino Glue™, Instant Krazy Glue®, The Original Super Glue®, and Gorilla Glue®) to determine which will be most suitable for the job. When choosing an adhesive with which to repair my shoes, I will factor in not only bonding capabilities, but also prices and ease of application. To identify which of these adhesives would be ideal for the job, I first need to determine what qualities the adhesive must possess in order to suit the shoe’s use as casual shoes subjected to occasional running and walks across muddy fields. The adhesive’s failure annoys me most when water gets between the insole and outsole of the shoes, wetting my socks and feet from below. As such, the adhesive I choose has to be waterproof and approved for outdoor use.

In addition, the adhesive must be able to (1) securely bond to rubber and leather as well as (2) tolerate the rigors of everyday walking and running, a requirement that demands sufficient strength and flexibility. Finally, the adhesive should be easy to apply, with a dry-time fast enough to avoid clamping if possible.

Using these criteria, I can begin to evaluate the five possible adhesives. Super Glue, Krazy Glue, and Rhino Glue all come from the cyanoacrylates chemical family, specifically ethyl cyanoacrylate. This is favorable to methyl cyanoacrylate for the bonding of rubber because the larger molecule size leads to a more flexible adhesive. These cyanoacrylates are single-compound liquids that contain an acidic stabilizer, which keeps the adhesive from polymerizing. This stabilizer is neutralized and the adhesive is cured by polymerization when the adhesive comes in contact with surface moisture. This curing process does not release any byproducts.

Cyanoacrylates will bond to most surfaces (they are especially good for nonporous surfaces), but have trouble bonding to silicones, polyolefines, some fluoroelastomeres, and to glass. Also, because of the acidic stabilizer in the cyanoacrylates, these adhesives sometimes have trouble bonding to surfaces that are naturally acidic like paper and leather because stabilizer has trouble neutralizing. However, the cyanoacrylate products reviewed claim they can bond with leather and therefore contain an additive which can convert surfaces into a species that neutralizes the acidic stabilizer. Rhino Glue’s manufactures specifically claim that their glue has been altered to better adhere to porous surfaces like leather. Cyanoacrylates are also brittle, have poor impact resistance, and have poor peal strength, all qualities that are undesirable for shoe repair.
Cyanoacrylates do, however, have a very fast cure time, which makes them quick and easy to apply. To apply a cyanoacrylate adhesive one simply cleans the surface of oil, dirt, and the like, spreads a thin layer of glue, and then holds the glued surfaces together for between 30 seconds to 2 minutes. Because the glue cures almost instantly and doesn’t expand much upon curing, a clamp is not needed. Any of these three cyanoacrylate adhesives would be fair candidates to glue the outsole to the upper, where there is less impact and flexure than on the bottom of the shoe. Although this would not be an ideal repair, water would no longer get in the shoe and wet my foot from below and that is certainly an upgrade from the shoes’ current condition.

Gluing the outsole involves little risk because even if the cyanoacrylates cannot bond well with the leather, no permanent damage will be done; the shoes would be in the same condition as they are currently. Thus if I can obtain one of these three types of glue from the shop for free, they would be a risk-free first attempt at a moderate quality shoe repair. If none of them were available for free then Rhino Glue would be the best choice because of its enhanced ability to adhere to porous materials. Rhino Glue cost about $9 for a 14.2 gram bottle. This is about the same price as Krazy Glue and Super Glue. It should be noted, however, that Krazy Glue and Super Glue are also available in smaller, cheaper quantities, while Rhino Glue is not.

The next candidate, Gorilla Glue, is a member of the polyurethane family, the family of adhesives typically used for bonding soles to uppers. More specifically, Gorilla Glue is a single-component, moisture cured polyurethane adhesive. Single-component polyurethane adhesives are typically based on a polyether polyol reacted with a polyisocyanate, yielding an isocyanate-terminated polymer. These one-component adhesives cure when exposed to moisture at room temperature. This curing process results in a dried adhesive with several favorable properties including excellent flexibility even at low temperature, excellent impact resistance, and good abrasion resistance.

Unfavorable qualities of polyurethane adhesives include more difficult application than cyanoacrylates and sensitivity to moisture. However, Gorilla Glue claims to be 100%

---

+ A thin layer provides the best bond for cyanoacrylate because if the layer of glue is too thick, then the middle of the glue layer will be slow to cure because of a lack of exposure to the neutralizing bonding surfaces.
waterproof, citing having passed ANSI/HPVA HP-1-2000 Types 1 and 2, easily.\textsuperscript{10} This is a byproduct of moisture-curing Gorilla Glue. Thus, the major disadvantage for using Gorilla Glue is the difficulty of application.

Gorilla Glue is commonly applied in three steps. The first step is to prepare the bonding surfaces. This includes cleaning the surfaces of dirt and grime, roughing up the surfaces to give the glue something to “bite into,” (i.e. enhance mechanical adhesion) and dampening one surface, which will start the chemical reaction when the glue is applied. The second step is to apply a thin layer of glue evenly across the dry bonding surface. The third step is to join and securely clamp the two surfaces for several hours because the adhesive foams and expands while curing. My desire for a cheap and simple solution would probably lead to the use of duct tape for clamping, which would do a fair job. However, because of the low surface energy of rubber, abrading the surface does not sufficiently prepare the rubber for a proper bond.\textsuperscript{8} Because of this Gorilla Glue is not recommended for use on rubber.\textsuperscript{10}

That said, polyurethane adhesives are the shoe industry’s number one choice for gluing soles to uppers and, as such, proper surface preparation by some type of solvent wiping or chlorination will allow Gorilla Glue to create a very strong, flexible bond. Similar bonding difficulties exist with the porous leather, but mild scourging followed by the application of a low viscosity reactive solvent-based polyurethane primer (contain about 10% free isocyanate groups) will prepare the leather for a strong bond with the polyurethane.\textsuperscript{8}

While polyurethanes are the choice adhesives of the shoe industry, Gorilla Glue is not the ideal candidate for my repair job because of the cost and difficulty of application associated with chemical treatments and primers required to achieve a strong bond. Gorilla Glue is, however, clearly superior to the cyanoacrylates in terms of flexibility. Should a lack of flexibility cause the cyanoacrylate adhesives to fail on my shoes, I could scour the bonding surfaces and apply Gorilla Glue in hopes that the mechanical surface treatment will be sufficient to create a strong enough bond. If I should take this path a small bottle of glue will cost under $5.\textsuperscript{10}

The final candidate, Shoe Goo, is a silicon-based adhesive designed as both a waterproof sealant as well as an adhesive.\textsuperscript{11} Like other silicon-based adhesives, Shoe Goo cures at room temperature by solvent evaporation.\textsuperscript{6} To apply Shoe Goo one first cleans and roughs up the surfaces to be bonded. Next, it’s necessary to evenly spread the adhesive on each bonding
surface and allow the Shoe Goo to partially cure for 2-10 minutes. One then brings the two surfaces together carefully and applies a steady pressure to establish full contact. When these two surfaces are brought together an immediate bond forms; this makes repositioning the surfaces difficult. After holding the surfaces together for about 30 seconds, it takes between 24-72 hours of dry time before the bond is at full strength. Like with the cyanoacrylates, no clamping is necessary, which makes the application of Shoe Goo relatively easy.\(^\text{11}\)

Shoe Goo was originally designed to patch the toes of tennis shoes that tend to wear out because the toe gets dragged across the abrasive court during tennis serves.\(^\text{11}\) As such, like other silicone-based adhesives it is 100% waterproof, has good impact resistance, good flexibility, and is very weather resistant. Additionally, silicon-based adhesives bond well to both leather and rubber, seemingly making Shoe Goo the ideal choice for my shoe repair. One drawback is that Shoe Goo should be applied in a well-ventilated area. Also, the fact that Shoe Goo is advertised as a sealant first and an adhesive second is worrisome. Yet despite these minor concerns, its ease of application and favorable cured qualities make Shoe Goo my top choice for my shoe repair job. If the shop doesn’t have any Shoe Goo available, a small bottle will cost under $5.

In conclusion, to bond the impermeable rubber outsoles of my Nike Air Total Package basketball sneakers to the porous leather uppers of the shoes, I would use any of the five glues considered if they were freely available to me. Should any of the free glues fail, the shoes would be in no worse than current condition, because only a small area in the front of the shoe is being glued. However, should no glue be freely available to me, I would use Shoe Goo for the repair. Shoe Goo has the favorable qualities of Gorilla Glue (flexible, tough, and waterproof), but has the added benefit of easy application.
Part II: Big Dig Tunnel Failure

At about 11:01 p.m. on July 10, 2006 a passenger car was traveling eastbound in the Interstate 90 connector tunnel, in Boston, Massachusetts. The tunnel was created as part of Boston’s famous “Big Dig” project. As the vehicle neared the end of the tunnel, a section of the tunnel’s suspended concrete ceiling disconnected from the tunnel roof and fell onto the automobile and the road (as seen in Figure 2). Concrete ceiling panels and associated suspension hardware crushed the right side of the car roof under a total of about 26 tons of debris, fatally injuring the 38 year old female passenger who was riding in the front seat. Fortunately, the driver, the passenger’s husband, escaped with only minor injuries. The concrete ceiling panels were part of a suspended concrete ceiling anchored to the concrete roof with threaded bolts in epoxy-filled holes as detailed in Figure 3. The panels collapsed after the epoxy adhesive failed due to creep, causing the steel support system to detach from the tunnel roof, releasing several concrete slabs. To better understand this failure we must take a more detailed look at the epoxies that failed.

Epoxies are one of the most widely used structural adhesives. Its application in adhesive anchors (often used with threaded rods and rebar to form said anchors) has been used for over 35 years. An epoxy is a material formed by the chemical reaction between a resin and a hardener. The resin contains compounds with at least one epoxide ring (rings of two carbon atoms and one

† The use of a suspended ceiling, particularly one of concrete, was unnecessary and has since been removed.
oxygen atom), while the hardener can be comprised of a wide range of chemicals including mercaptans, amines, and amides.\textsuperscript{12} The Fast Set Powers Power-Fast epoxies used in the connector tunnel failure were amine-based\textsuperscript{+}.\textsuperscript{12}

For this epoxy, the hardener molecules contain an amine group at each edge of the molecule and the resin molecules contain an epoxide ring at each end of the molecule. When these two components are mixed, the hardener and resin begin to link in an alternating pattern as the amine groups bond with the epoxide rings. Additionally, each amine group has the ability to bond to multiple epoxide rings. This creates cross-links between the long polymer chains, preventing major rearrangements of polymer molecules. Because of its cure time, Fast Set epoxy forms a much poorer crosslink network with significantly lower crosslink density than the Standard Set variety. The extensive network of cross-links developed prevents the polymer from being melted and reformed. This feature classifies this polymer as a thermoset.\textsuperscript{12}

In addition to the hardener and epoxy resin, the overall adhesives mixture often contains some type of organic materials (with or without reactive end groups) to reduce shrinkage and cost, increase bulk stiffness and strength, and to improve gap filling. Organic compounds can

\textsuperscript{+} The Standard Set Powers Power-Fast epoxies is also amine-based.
also alter viscosity, change the rate of curing, and alter final adhesive properties. Power-Fast Set and Standard Set epoxies both contain magnesium silicate (talc) and calcium carbonate as their organic filler.\textsuperscript{12}

The stiffness of epoxy, like all polymers, is dependent on time and temperature. Epoxy responds to abruptly applied loads in a similar manner to a hard, glassy solid. However, when that load is held constant, as was the case in the connector tunnel, the polymer chains slowly rearrange and slide past each other, decreasing the stiffness of the epoxy into the rubbery region. This phenomenon of an increasing deformation subject to a constant load is called creep. The rate of creep is dependant on crosslink density, molecular structure, and temperature. Increased temperature increases the rate of creep because it increases the rate of molecular rearrangement, while increased cross-linking restricts polymer movement, decreasing the rate of creep. Thus, the Fast Set Epoxy has a much faster rate of creep than the Standard Set.\textsuperscript{12}

Cured epoxy tends to be a brittle material that will fracture rather than plastically deform as load increases. Under large loads, the epoxy fractures progressively, mimicking the behavior of a softening material. Small cracks form where the epoxy is most stressed, placing greater loads on intact epoxy.\textsuperscript{12} Eventually, the epoxy fractures to a point where it can no longer support its intended load and the adhesive fails, resulting in catastrophe. This type of failure occurred in the connector tunnel because the Fast Set Power-Fast epoxy used had poor creep resistance. Had the engineers instead used the Standard Set variety of Power-Fast epoxy, which (as shown in Figure 4) has much better creep resistance, the tragic collapse would have been avoided.\textsuperscript{13}

\textbf{Figure 4:} Creep test results for test anchors installed with Power-Fast Fast Set (two upper curves) and Standard Set (two lower curves) epoxies under a 2,000-lb tension load\textsuperscript{12}
Works Cited

1. "Nike Air Total Package Men's Basketball Shoe Reviews." Nike Store. 26 Mar. 2009 <reviews.nike.com/9191/310431/reviews.htm>. This website is run by Nike. The primary purpose of this particular site is to give customers a chance to review the Nike Air Total Package Men's Basketball Show. These reviews were not used in this paper. The website also provides a description from Nike about the shoe. This description was used to determine the materials of the outsole, midsole and upper. There is no particular reason to suspect Nike of about this information. Site map unavailable.

2. "Nike Shoes Technology." Sneakerhead. 26 Mar. 2009 <http://www.sneakerhead.com/nike-brand-technology.html>. This website is run by a California-based, internet retailer of brand name sneakers. The primary purpose is to sell sneakers, but the website also has sections on sneaker history, technology, and such. The specific page explains Nike's labels for materials in common scientific terms. I have no reason to disbelieve this website as they are a member of the Better Business Bureau and stand to gain nothing from lying about what materials Phylon and Solid Rubber are made of. Site map at http://www.sneakerhead.com/site-map-main.html.

3. "Super Glue Adhesive Products." Super Glue Adhesive Products. 26 Mar. 2009 <http://superglue.supergluecorp.com/>. This website is run by Super Glue Corporation/Pacer Technology to promote and sell their adhesive products. The website was used for basic information on Super Glue. I tried to only take information from this website that was objective or something negative about the product as these facts seemed very likely to be true. Site map at http://supergluecorp.com/sitemap.html.

4. "Instant Krazy Glue." Krazy Glue. 27 Mar. 2009 <http://www.krazyglue.com/>. This website is run by the Krazy Glue Corporation to promote and sell their adhesive products. The website was used for basic information on Krazy Glue. I tried to only take information from this website that was objective or something negative about the product as these facts seemed very likely to be true. Site map unavailable.

5. "Rhino Glue - Home." Rhino Glue. 27 Mar. 2009 <http://www.rhinoglue.com>. This website is run by the Acro Corporation to promote and sell their adhesive products. The website was used for basic information on Rhino Glue. I tried to only take information from this website that was objective or something negative about the product as these facts seemed very likely to be true. Site map at http://www.rhinoglue.com/sitemap.html.


10. "Gorilla Glue - Home." [Gorilla Glue](http://www.gorillaglue.com/). 28 Mar. 2009 <http://www.gorillaglue.com/>. This website is run by the Gorilla Glue Company to promote and sell their adhesive products. The website was used for basic information on Gorilla Glue. I tried to only take information from this website that was objective or something negative about the product as these facts seemed very likely to be true. Site map at [http://www.gorillaglue.com/information/sitemap.aspx](http://www.gorillaglue.com/information/sitemap.aspx)

11. "Shoe Goo Adhesive 1108." [Eclectic Products](http://www.eclecticproducts.com/shoegoo.htm). 28 Mar. 2009 <http://www.eclecticproducts.com/shoegoo.htm>. This website is run by the Eclectic Products, Inc to promote and sell their adhesive products. The website was used for basic information on Shoe Goo. I tried to only take information from this website that was objective or something negative about the product as these facts seemed very likely to be true. Site map unavailable.

12. National Transportation Safety Board. "Highway Accident Report: Ceiling Collapse in the Interstate 90 Connector Tunnel." National Transportation Safety Board. 28 Mar. 2009 <www.ntsb.gov/publictn/2007/HAR0702.pdf>. This page contains the official accident report compiled by the National Transportation Safety Board (NTSB). The website is maintained by the NTSB. I have full confidence in this source as it was created by a government agency and cites its sources throughout. Site map at [http://www.ntsb.gov/sitemap.htm](http://www.ntsb.gov/sitemap.htm).


**Photograph Sources**
