

Team 6: Fresh Kicks

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Summary

For our design we chose to address the problem of keeping white shoe sidewalls white. This is a problem that most people will be familiar with due to its personal and frustrating nature. It is one whose potential solution could have wide applications within the shoe industry but also potentially elsewhere where surface cleanliness, color preservation, or abrasion resistance is important.

White shoes get dirty for any number of reasons, most of which relate to three primary factors: material adhesion, staining, and scuffing/scratching. Material adhesion refers to the tendency for dust, dirt, and mud to stick to the shoe sidewall after exposure. This concept can be extended to anything else that a person might step in that will tend to stick to the shoe, of course. Staining refers to the absorption of grass fluid, muddy water, etc., which discolors the sidewall material. This is distinguished from adhesion in that even after the offending material or fluid is removed from the surface, a the material remains discolored. Lastly, scuffing and scratching refers to abrasion and physical penetration to various degrees that may occur to the shoe during normal use-- for example, when a shoe is accidentally bumped into a concrete step. While the abrasion alone may or may not ruin the finish of the sidewall, it will allow foreign materials to better adhere and even stain. In this sense, abrasion may be considered an indirect but important source of discoloration.

To address these problems in an economic and viable manner based on current materials technology and manufacturing processes, we went searching for those plants and animals exhibiting abilities or functions similar to what we wished to accomplish. For example, we searched for biological entities with strong adhesion resistance, self-cleaning ability, abrasion/puncture resistance, natural or structural whiteness, bright coloration, etc. After conducting a thorough search, we narrowed down our list of interesting biological candidates to those with the most potential for a real-world design and relevance to the nature of our problem. After what could be called several refining loops, wherein we discussed possible implementations using different combinations of our researched functions, we settled on the functions of the desert scorpion's cuticle and the butterfly's scales.

Our design marries the abrasion resistance and toughness of the scorpion's cuticle with the scale-detachment strategy butterfly wings use to combat adhesion. First, these functions must be summarized. The scorpion cuticle contains alternating layers of a hard, tough material and a softer, elastic material, which in conjunction protect the animal from injury or erosion due to strong desert winds carrying sand. The layers with high mechanical hardness resist abrasion and puncture, while the more elastic lower layers absorb impact energy and redistribute loads. A butterfly's wings, on the other hand, are coated with microscopic scales which serve to allow it to escape from sticky spider webs by releasing from the surface of the wing under an applied normal loading. They are very thin, in order to maintain the low weight of the butterfly's wings. As such, they are basically disposable protection.

With these functions in mind, our improved shoe sidewall, which we call Fresh Kicks, contains many white layers, within each of which is a dual-hardness/elastic modulus bilayer, which are joined together with an anisotropic mechanical bond. These layers stack from the surface of the shoe to the outside. Therefore, if the shoe sidewall is scuffed or dirtied, the wearer need only remove a layer (actually a bilayer) to expose fresh sidewall underneath. Because the layers are thin, this can be repeated for the life of the shoe. The bilayers serve to slow the rate at which abrasion occurs, thus lowering the rate of dirtying, and prevent lower layers from being prematurely punctured. The alternating, anisotropic mechanical linkage between layers will prevent multiple layers from being peeled simultaneously but will also ensure that the newly exposed surface after peeling is not "tacky" from glue, and also eliminates issues associated with the shelf life of chemical adhesives. These layered sidewalls can be manufactured in sheets from readily available materials, so that the shoe company need only cut the sheets to specification and apply them to the rest of the shoe.

We are convinced that our white shoe sidewall design is practical, feasible, economical, and will have a net positive effect on the environmental footprint of shoe materials, by reducing the rate at which people discard shoes. Fresh Kicks would also deliver convenience and satisfaction that would be marketable and would hopefully save many an unnecessary headache after accidentally stepping in a muddy puddle.

Problem Description

In terms of SR.BID, this design can be broken down into Operational Environment, Functions, Specifications, and Performance Criteria. *Operational Environment:* -In water, from rain, puddles, etc.

-In rain/dirt mix, from pasty mud to thin mud

-In dry dirt and dust

-In grass and plant matter

-On carpet, wood, other indoor flooring

-On asphalt, concrete, other synthetic outdoor surfaces

-On hot surfaces and in hot ambient conditions

-On cold surfaces and in cold ambient conditions

Functions:

-Stay white by appearance

-Provide structural properties of typical shoe sole

-Enhance attractiveness to opposite sex

Specifications:

-Must not cost significantly more than traditional white rubber (more than \sim 1.5times) to manufacture

-Must be made of environmentally friendly (preferably biodegradable) material

-Must be made of human-and-animal-safe material

-Must be made of material that does not damage surfaces

Performance Criteria:

-Sole color (in this case white) should hold so that after extended use, there is little to no visible staining or discoloration once surface mud or other debris is removed, and at expected life of sole, the maximum staining is no greater than a certain saturation -Sole should require no more cleaning than average shoes—i.e. the wearer might still have to knock off mud or other gunk, as with other shoes—but the base color will remain unchanged once this is gone, with no extra contribution needed from the wearer -Mechanical properties should be as good as those of rubber, for consistent shoe performance

-Usable life should be no less than that of regular shoe rubber

White shoe rubber presents an appealing alternative to darker colors in terms of both style and white rubber's lesser tendency to scuff and mark ground surfaces, particularly indoors. Unfortunately, it is also much more prone than darker colors to discoloration and staining from environmental factors such as grass, mud, and some man-made surfaces such as asphalt. This results in less appealing shoes after a potentially limited period of use, providing less utility for some wearers by inducing them to spend money on a new pair and toss the old ones in the trash. In addition to staining, even the temporary presence of mud or dirt on the shoe can render it highly undesirable to both the wearer and to spectators. The presence of these materials is often exacerbated by scratching and scuffing caused by normal wear, which allows these to infiltrate mechanical openings and thus accelerate the shoe-dirtying process. The main reason for the undesirability of a discolored and/or scuffed shoe is that it may render the wearer less attractive to the opposite sex. Pazda et al. have found that bright red clothing worn by females increases perceived sexual receptivity and therefore sexual attractiveness to the opposite sex (2012). It is also a widely known phenomenon that the strength of pigmentation in birds acts to mediate their sexual attractiveness, which is generally justified according to the extended-phenotype phenomenon where lack of pigmentation can be a signal for disease or ill-health. Such an explanation is likely also valid in humans, in that cleaner/brighter clothing is an indicator of greater wealth, where wealth is associated with the ability to provide for the mate and offspring.



In all likelihood, the lack of a current self-cleaning shoe design results from the lack of a short-term economic incentive to invest in one, because faster shoe wear means consumers will tend to replace them more quickly, and thus buy more over a given time period. This concern, of course, does not account for important market factors such as the portion of shoes with an enhanced design in the retail space and the retail company's market share. Additionally, the problem of improving shoe rubber in terms of its ability to hold color is not necessarily obvious, because it can be easily taken for granted.

On the other hand, there are retail products available which are manufactured by companies specifically involved in the manufacture of shoe-care products, for whom the extended lifetime of shoes will not be an economic deterrent. However, these ultimately require the user to apply a liquid solution to the shoe in the desired areas. If the shoe is only partially white, the user must control the exposure of non-white parts of the shoe to the whitening solution, as it will tend to discolor them. Therefore on the whole, the current methods for cleaning shoes and maintaining whiteness are unwieldy and must also be specifically purchased for the color white, leading to a limitation in the range of shoe colors that can be maintained with a given cleaning kit. Kiwi whitener is an example of such a solution.

Solution Description

*The highlighted solutions are the ones selected for further consideration, all others are rejected.

	Biological Solution	Why Selected or Rejected
1	Desert Scorpion	The alternating hard and soft shell layers as a mechanism for abrasion resistance are ideal because this is not mutually exclusive with other surface properties. (Han et al., 2010).
2	Earthworm	The mechanism which resists dirt adhesion is an electric potential difference which draws moisture from the soil to create a water layer between the skin and the environment. It would be impractical to have shoes which maintained a water layer around the sole. (Zu 2006).
3	Brown Algae	The honeycombed layers which resist tearing would be more effective in the top half of the shoe, but we decided to focus on keeping the soles of the shoes looking like new. (Denny, 2002).
4	Butterfly Wing Nanostructure	The nanostructure repels water, so it beads up and carries dirt away. This passive self-cleaning is selected as a strong possibility for our shoe design. (Zheng, 2006).
5	Pitcher Plant	The anisotropic microstructure is both hydrophobic & oleophobic, making it super non-stick. It is uncommon to find a surface with both properties, so it is an interesting one to consider. (Bohn, 2004).
6	Hetereoterid Bugs	Hydrophobicity. Rejected because of redundant function.
7	Arthropod Molting	Arthropods are able to shed a single outer cuticle through molting, leaving a new pristine layer underneath. It's ability to generate one cohesive layer with little to no downtime makes it a good potential source
8	Parrot Feathers	Resist Bacterial Degradation of pigments. Rejected as bacteria doesn't seem to be our primary source of staining or color degeneration.
9	Butterfly Wing Scales	Resist Adhesion. Selected for durability in most directions, but use of layering and anisotropic weakness in the normal

		direction to permit simple shedding of adhered particles.
10	Argentus Butterfly	Structural Color. Rejected for other, similar, structural color approaches which maintain/ create whiteness.
11	Marble Berry	Structural color. Accepted because tight coils of cellulose make it ultra brightly colored and ultra hard. Uses a phenomenon known as Bragg Reflection to cause constructive interference.
12	Horse Hooves	The hierarchical structure of horse hooves uses concentric tubes of keratin to strengthen the overall structure against the large compressive forces generated when the horse walks. These tubes also slow crack propagation through the hoof, but these properties are dependent on a very small tube diameter which is likely impossible to manufacture, so this solution is rejected.
13	Crane Fly	The crane fly has thousands of hair like projections extending from its wings and legs, which utilize surface tension and contact angles to create a superhydrophobic surface. While this is a valuable trait, due to the pitcher plant's ability to repel both polar and nonpolar compounds, the structure was rejected.
14	Pumpkin	Due to its contoured geometry and waxy cuticle, the pumpkin is able to prevent the adhesion of dirt and mud to the pumpkin's fruit and stem structures. This method, however, relies on a waxy outer coat which could potentially wear off or be rendered ineffective in the event of a fracture, so this solution is rejected.
15	Dung Beetle	The texture of the dung beetle' shell gives it the ability to resist soil adhesion. Much like the gecko, the beetle's shell is covered in microscopic setae which act to provide its surface function. However, in the beetle's case these setae result in a reduced contact area vs. the nominal area of the shell, which means that adherence of foreign materials is reduced rather than enhanced. The beetle's setae protrude at a different angle to those of the gecko, and are characterized by a higher stiffness. This higher stiffness reduces their deformation and ultimately results in a lower contact area. Rejected for manufacturing difficulty.
16	Kenyan Sand Boa	The outer scales of the Kenyan sand boa are very resistant to abrasion due to their high β -keratin content, which gives them a high mechanical hardness value. These are layered over

		progressively more flexible (less hard) layers of scales, so that while the combined scale layers provide an effective barrier to abrasion they also allow flexibility and movement. Rejected in favor of scorpion's similar mechanism in non-scale form.
17	Cabbage Butterfly	The butterfly's wings give them high reflectance and as a result, white coloration. It has been found that white butterfly wings contain very little pigmentation, but are arranged in an array of ribs and beads which very effectively diffuse light to make them appear white. In fact, the beads in particular are primarily responsible for giving the wings their white appearance. Rejected due to non-necessity and difficulty of manufacture in final product.
18	Cicada Wings	The cicada's wings exhibit self-cleaning behavior due to the nanopillar array that covers them, which lowers the contact area between water droplets and the wing surface and allows them to slough off the wing, carrying dirt with them. Rejected due to similarity to nanostructure of butterfly wings.
19	Cyphochilus Beetle	The wings of the cyphochilus beetle give it a brilliant white appearance. This is due to its wing scales' aperiodic, random network of internal filaments, which scatter light very effectively. These scales have the advantage of giving very effective whiteness in spite of being significantly thinner than standard printer paper. Rejected due to non-necessity and difficulty of manufacture in final product. Rejected for manufacturing difficulty.
20	White's Tree Frog	The frog secretes a sticky mucus on its feet to provide some degree of adhesion. This mucus comes off as the frog walks carrying with it any dirt attached to the bottoms of the feet. Its an interesting self-cleaning mechanism. Rejected due to the necessity of secreting a mucus-like substance.
21	Stonefly Larva	This burrowing insect is densely covered in small hairs, even on its eyes! The hairs are so dense that it essentially keeps any dirt particles from ever touching the actual body of the insect. Rejected due to infeasibility of manufacturing and high risk of breaking hairs from human walking.

22	Salvinia Fern Leaf	The leaf has small hair-like structures around it. The outer edge of these hairs are extremely hydrophilic, and the lower parts (near the leaf) are super hydrophobic. When in water, the water immediately pulls to the tips of the hairs, leaving a thin film of air between the tips and the leaf itself like a force field. Rejected since this mechanism is limited to wet environments.
23	Polynesian Box Fruit	The box fruit is so tightly covered and the covering is so dense that the fruit can stay in water for 2years and then still be good on the inside, and able to grow. The simple mechanism is the ability of the outer shell to be tightly shut and consist of materials that won't allow water or dirt to pass through in any manner. Rejected for its requirement of a hard and dense material and is only good at keeping things out.
24	Camels	The nictitating membrane of the camels eye (also found in some other mammals and reptiles) acts as a protecting layer. The membrane can swipe across pushing away any dirt and debris on the eye. The interesting part is that this "3rd eyelid" can be held shut and still allow vision since its translucent. The mechanism is a cover that can be pulled over when needed to avoid damaging the inside, and then pulled away when no longer needed. Rejected since the requires a material that may tear during walking and storing the cover when not in use maybe a hassle.

Solution Description: Butterfly Wings



Figure 1. SR.BID of Butterfly Wings

Butterflies have powerful flying muscles and some of the largest wings in the insect kingdom. Flight is essential to their survival, not just to forage for food, but also to escape predators who may be attracted by these large, colorful targets. Butterflies' finely tuned systems are very sensitive to the buildup of dirt on their wings, so it is important that they automatically stay clean over their potentially 1 year lifespan, when operating in an environment of airborne particles such as pollen and dirt. Since they make their habitat among flowers and other plants, their environment is often moist, dewy, or even rainy. A major danger for insects of this size is spider webs, which can be fatal to most insects if they run into the sticky threads, but even if they do manage to escape, it requires much struggling and flapping to break free before the spider can reach them.

Butterflies have adapted to maximize their fitness in their particular operational environment. Their large wings are optimized not only for the motion of flight, but also to stay clean and maintain their flight efficiency. They accomplish this through hydrophobic self cleaning, similar to the lotus plant. Nanoridges cover the surface of their wings, reducing the effective surface area for contact with water and surface contaminants. Dirt particles remain on the tops of these nanoridges, so do not get embedded into the surface. Likewise, moisture beads up on the tops of these ridges and rolls off, carrying the raised dirt particles with it. A performance comparison with the wings of other insects shows significantly less particle adhesion on butterfly wings, even with the tiniest pollen particles (Watson et al., 2012).

Another important function for the butterfly's survival in its operational environment is the ability to quickly and easily to spider webs. It accomplishes this by not getting stuck to the sticky silk at all. Each wing surface is covered with millions of microscopic scales which contain the nanostructure described above and also give the butterfly its brilliant colors. Approximately 600 scales are found in one square millimeter, at a single layer only 150 nanometers thick. When a butterfly flies into a web, it seems to simply slide off and fly away, unlike other insects which become stuck and entangled. This is because it leaves its scales behind and flies free.

The scales are attached through a "peg-and-socket" system in which wing stalks attach directly into angled sockets on the wing (Figure 2). Due to the directionality of sockets, a force applied perpendicular to the scale will cause the scale to move in the socket, but to remain intact. By introducing a force normal to the socket, however, the scale will readily come free, allowing the butterfly to make a quick escape by canting its body accordingly (Zhang et al. 2006). The scales, however, do not regenerate, and "spider web scars" can be seen on butterfly wings, so if enough scales are lost in a lifetime, the wings' rigidity and resistance to tearing may reduce over time. However, butterflies possess so many of these tiny scales that the mechanism is highly effective for most individuals. Experiments comparing healthy butterfly wings with denuded wings showed that wings with scales had 2 to 6 times lower adhesion force to spider silk (Eisner et al., 1964).



Figure 2. Butterfly wing scales and sockets close-up

Solution Description: Dung Beetle Cuticle

The dung beetle feeds in large part on animal feces or dung, meaning that its ability to do so is of primary importance for it survival. In order to collect dung on which to feed, the beetle employs the strategy of shaping the material into a sphere and rolling to a location where it can be stored for long-term consumption. While it is in the process of collecting and shaping the dung, the beetle relies on the anti-adhesive property of its cuticle to prevent the dung from sticking to itself and hindering its movement and efficiency.

Dung beetle cuticles are hydrophobic in nature, allowing mud, dung and other wet soillike substances that come in contact with them to compact into balls and fall off without sticking. They achieve this function with an embossed surface texture on their pronotum, clypeus and elytra. This texture raises the cuticle's apparent contact angle to a range of roughly 91 to 106.5 degrees, with an average value for this angle being 97.2 degrees (Tong, Sun, Chen & Zhang, 2005).

Structurally, the cuticle is covered in convex domes. Due to the size and shape of the domes, the surface wetting condition can be considered to be homogeneous, meaning that the water in contact with the surface comes into contact with both the domes themselves and the surfaces between the domes. By making this assumption, we can characterize the surface contact angle with Wenzel's model, which states that the apparent contact angle θa is given by

 $\cos \theta a = r \cos \theta o$

where θo is the intrinsic contact angle of the surface and *r* is the surface roughness factor, or ratio of actual surface area to apparent surface area. In general, an apparent contact angle $\theta > 90^{\circ}$ will produce hydrophobic behavior, while a $\theta < 90^{\circ}$ will produce hydrophilic behavior. By interpreting this relationship we can see that the apparent contact angle for a surface with intrinsic contact angles of greater than 90 degrees can be increased by increasing the surface roughness ratio, which was inferred to be the case for the behavior of the dung beetle's cuticle (Tong, Sun, Chen & Zhang, 2005). Therefore, the convex domes are partly responsible for the cuticle's function.

For the above equation to be valid in this case it must further be inferred to be a low surface energy (intrinsically hydrophobic) material, giving it its high intrinsic surface angle. Both of these properties combined result in water beading on the cuticle rather than dispersing and wetting, meaning that the weight of the beaded water will tend to pull the water off of the cuticle when elevated to a critical angle, and thus preventing the accumulation of wet mud and dung (Tong, Sun, Chen & Zhang, 2005).

Solution Description: Desert Scorpion

Scorpions rely on a hierarchical structure which combines hard, laminated layers and soft layers of media and connective tissue (Figure 3). While the hard layer resists sharp, cutting forces, the soft layers help dampen the energy released by particle erosion. These layers can be broken down into the epicuticle, the exocuticle and endocuticle. Each layer is comprised of sublayers made up of individual sheets between 0.2 and 0.3 micrometers thick. The epicuticle or

hard layers, is comprised of 0.3 micrometer sheets which together make up about 11 micrometers of the total cuticle. It consists of four non-lamellate sublayers. The exocuticle serves as intermediate connective barrier between the epicuticle and endocuticle and is comprised of a non-lamellar layer sandwiched between two lamellar ones. It makes up a total of 20 micrometers of the total cuticle. Finally, the endocuticle makes up the remaining 65 micrometers and is comprised entirely of softer lamellate layers of decreasing thickness from 5.5 micrometers to 1 micrometer toward the center of the body. While the non-lamellate layers offer minor offer the resistance to sharp force, the majority of impact strength comes from the lamellate (plate-like) structures found in the exocuticle and endocuticle. (Polis, 1990).



Figure 3. Diagrammatic representation of the cuticle of *Hadrurus arizonensis: endo*, endocuticle, consisting of severallamellae separated by membranes; *epi*, epicuticle (comprising *c*, cuticulin layer; *dh*, dense homogeneous layer; *oe*, outer epicuticle; *om*, outer membrane); *exo*, exocuticle (comprising *he*, hyaline exocuticle; *ie*, inner exocuticle; *me*, mesocuticle). Relative thicknesses are approximately to scale, except that the epidermis is disproportionately enlarged. (Polis, 1990).

Additionally, miniscule ripples on the scorpions back change the trajectory of particles flowing over the back of the scorpion eliminating some of the damaging contact by creating an air cushion over the scorpion's back. Flow patterns in these grooves effectively create an "air cushion" effect but increase fluid turbulence leading to a change the flow field, and thus the particle motion patterns. This leads to an overall decrease in the number of particles impacting this surface. There is additional decrease in the flow velocity, decreasing the speed at which particles impact these exoskeleton, compared to a non-grooved surface. These factors combine to decrease the overall effect per impact of a given particle on the cuticle (Han et al., 2012).

The desert scorpion's success, however, is dependent upon the "coupling" of the cuticle layering with the groove structure. The groove structure alone, only accounts for about 32% of the total protection. Additionally, tests have shown, that abrasion resistance is heavily dependent of the variant nature of the exocuticle, alternating between hard and soft layers. Only in the presence of all of these factors, is abrasion resistance maximized (Han et al., 2012).

Solution Description: Marble Berry

In the forests of Mozambique, Ghana, and Tanzania there is a berry that researchers claim as the most brightly colored living organism. This berry features a striking blue-purple iridescence and maintains this color long after the plant has actually died. As the researchers note, "Uniquely in nature, the reflected color differs from cell to cell, as the layer thicknesses in the multilayer stack vary, giving the fruit a striking pixelated or pointillist appearance." The unique structure of the fruit (a microscopic layering of rotated fibers) makes the berry incredibly hard. This durability of color seems quite promising for our application. An additional note is that it attains its color not from pigment (like many larger creatures) or from hard to manufacture nano-scales, but from an alternate method.

Each cell wall of the berry is created from layers of fibers. The layers of these fibers are stacked on top of each other in a helical fashion, where the grain of the fibers is rotated by a certain angle. Light passing through this helix of fibers causes constructive <u>Bragg reflection</u> which increases the reflectivity and appearance of certain wavelengths. The curvature of the helix determines the wavelengths being made most apparent. The equation for the maximum reflected wavelength is: in a Bragg reflection organization is:

$$\lambda = p * 2 * n$$

Where n is the index of refraction, n, for cellulose is 1.53, and p is the periodicity of the layered structure, meaning that it is the minimum distance between two layers whose fibers are aligned in the same manner. The marble berry for instance has a typical periodicity of 145 nm, resulting in an expressed wavelength of around 445 nm which makes sense given its predominantly blue color. In the marble berry, the periodicity changes slightly between each cell giving it the overall specular, or pointillist appearance. In manufacturing one can use this formula to select for the expression of other colors. To express the white color, we can mimic other creatures that structurally display bright whites which achieve this through a randomization of selected wavelengths.



Fig. 2. Anatomy of *Pollia condensata* fruit. (A) SEM image of the fruit surface showing smooth cuticular layer. (B) TEM cross-section showing three distinct tissue zones: (1) an outer epicarp of 3–4 layers of thick-walled cells, (2) an intermediate region of 2–3 layers of tanniniferous cells, and (3) a zone of thin-walled cells. (C) TEM of a single thick-walled cell from layer 1. (D) TEM of the cellulose microfibrils that constitute the thick cell wall in layer 1. The red lines highlight the twisting direction of the microfibrils. (E) (Left) Scheme showing a wedge of an LH helicoid with the arched pattern exposed on the oblique face (adapted from ref. (24)). (*Right*) Circularly polarized beams of light, with \vec{k} the wave vector of the light. The handedness of the transmitted and reflected light depends on the handedness of the helicoid. Here, light transmitted through the structure (\vec{k} pointing down) is LH circularly polarized, while the reflected light (\vec{k} pointing up) is RH. (F) 3D representation of the orientation of cellulose microfibril assembly and a transmitted circularly polarized beam.





The unique properties of this fruit give it the ability to reflect more polarized light than any living organism that has ever been observed. It can reflect 30% of the light as a manufactured, silvered mirror, is able. As Vignolini et al note, "This is the highest reported reflectivity of any biological organism including beetle exoskeleton (2, 5), bird feathers (29) and the famously intense blue of Morpho butterfly scales (2)." The researchers of this berry also provide a good reference paper that addresses the manufacture and applications of such arrays of microfibrils.

Solution Description: Pitcher Plant

The pitcher plant is known for its ability to trap insects in its pitcher. The plant grows mostly in Asian tropic, and around islands in the Indian and Pacific Ocean. The environments are usually very humid, with warm days and cool nights. The plant is a climbing plant with one

stem, and makes use of tendrils to hold onto things. The pitchers can occur higher up or near the ground on the same plant.

The function of the plant that is of interest is its ability to trap insects. Typically insects land on the peristome (near the mouth of the pitcher) and then as they move towards the interior they simply slip and fall into the pitcher which is filled a digestive acid that drowns the insect and breaks it down chemically. This is accomplished through a unique slippery surface that is both wettable and anisotropic due to waxiness. The outer peristome surface is built of a microstructure with radial ridges created by overlapping cells. It is basically like a series of steps that lead to the inside. The inner waxy surface is always slippery, keeping insects that fell in from crawling out. Most insect capture occurs when the peristome is wet. In a study with ants, it was found that the surface is more slippery when wet. This is attributed to the fact that the water rolls down and inward in the direction of the ridged, steplike cells, and so pulls with it anything on the surface. Of 100 ants that visited the plant, 82 fell in! This is very successful as it gives the plant an 82% capture rate. In addition, parts of the plant are hydrophobic and oleophobic to prevent virtually any form of sticking to it. This enhances its ability to trap, since the stickiness of many insects' feet are made useless. The slippery surfaces are very crucial to the pitcher plant's ability to obtain nutrients to survive.

Problem-Solution Analogy

Desert Scorpion

Problem Target	relation Biological Source: Dese Scorpion	
 Operational Environment Airborne contaminants Moisture exposure Impact forces from walking and running Exposure to dirt, grass stains, chemical stains 	 similar different different partial overlap 	 Operational Environment Airborne contaminants Dry, arid climate Impact forces from particles blown in high winds 4 Exposed primarily to sand
Functions1Collects dry particles2Collects dirt/ mud3Scuffs and Cracks	1 similar 2 similar 3 same	Functions1Ripples create a change in flow field to deflect particles2Ripples create a change Sein flow field to deflect particles3Prevents erosion
 Specifications Non-toxic Manufacturable Requires no cleaning by user Sustains walking forces Surface coating (or lack of) has no impact on structural integrity Surface reapplication should be possible 	 same different same same different same 	Specifications1Non-toxic2Organically grown3Air-cushion prevents dirt from adhering4Soft connective tissue layer absorbs energy impact energy5Hard, laminated cuticle to resist ploughing and cutting6Cuticle Regeneration
Criteria 1 Must last minimum 1 yr, up to 3,000 steps/day	1 different	Criteria 1 Must last lifespan (up to 25 years

Although at first look, it appears that there are many more "differences" than "sames" in our analogy chart, the overlap occurs in the key functions for our design. This hints at a good

potential for pursuing a bio-inspired design in this direction. The desert scorpion shell is a good analogy for abrasion resistance and cleanliness, because the scorpion must perform these same functions in a very extreme environment. With wind speeds up to 70 miles per hour, blowing sharp sand particles at the scorpion's cuticle, it must withstand forces equal or greater than that seen in everyday shoe use. In addition, its ability to resist sharp and impact forces, make it an effective method for dealing with both particulate impacts and compression forces from walking. The shell is also flexible, distorting to distribute compression forces, just like the sneaker. They are extremely effective at dealing with loose dirt particles, and are able to last the scorpion's lifetime of 25 years.

Conversely, the scorpion is a poor analogy because of its limited environment and additional surface elements do not translate well to the shoe. The scorpion lives in a desert environment which sees very little rainfall and thus very little clumping muds and clays. Thus, the surface has not been tested for the resistance to these types of substrates and may or may not show resistance to them. Additionally, scorpions have a very unique groove structure across their carapace to which creates an "air cushion", decreasing impact angle, impact force, and total number of impacts. While the shell itself will maintain most of its impact strength, its overall performance may not be as good as that of a scorpion shell.

Problem Target	relation Biological Source: Butte Wings	
 Operational Environment 1 Dirt, dust, mud 2 Moisture exposure 3 Impact forces from walking and running 4 Exposure to grass stains, chemical stains 	 similar same different different 	Operational Environment1Airborne contaminants2Exposure to dew, etc.3Most motion is in flight4Risk of adhesion to spiderwebs
Functions 1 Collects dry particles 2 Collects dirt/ mud	1 same 2 same	Functions1Self-cleans, anisotropic2Resists adhesionScales
Specifications1Non-toxic2Manufacturable3Requires no cleaning	1 same 2 different 3 same	Specifications1Non-toxic2Organically grown3Passive self-cleaning

Butterfly Wings

4 5 6	by user Sustains walking forces Surface coating (or lack of) has no impact on structural integrity Surface reapplication should be possible	4 5 6	different different different	4 5 6	Sustains forces during flying, scales only fall when stuck to webs Loss of scales makes wings prone to tearing No scale regeneration
Criter 1 2	ria Must last minimum 1 yr, up to 3,000 steps/day Must not add > 5 mm thickness to sole sidewall	1 2	different similar	Criter 1 2	ia Must last lifespan (up to 1 year) Thickness 150 nm

The properties of butterfly wings share numerous similarities with the defined problem of keeping shoes looking new. Cleanliness is essential to butterflies' survival, however the insects live in habitats full of dust and other pollen, as well as multiple sources of moisture. Shoes are worn in dusty environments, where maintaining cleanliness is not as necessary but also desirable, and shoes must be water resistant since they experience puddles, moist dirt, etc. during outdoor use. Often, dirt on shoes comes in the form of mud which can become caked on and difficult to remove after it dries. Butterfly wings resist adhesion to almost any kind of other surface, and can be used to address this problem in shoes. A shoe has several design requirements for which butterfly wings can inspire a solution. The designers wish to develop a solution which is non-toxic, which of course living organisms are. The shoes should be self-cleaning without effort from the user, much like butterfly wings. Any solution that is developed should not appreciably add to the thickness of the sole, and since butterfly scales are only 150 nm thick, the basic principles may be applicable.

However, butterflies and shoes also have several differences. Butterfly wings are organically grown by nature, where materials are cheap, but developing thin manmade layers is challenging from a manufacturing perspective. A shoe design should last a minimum of 2 years to justify the cost to the consumer, with an average 3,000 steps per day for casual wear, which transmit high impact forces from walking and occasional running. In contrast, butterflies only live up to 1 year, and most forces on the wing come from flight, when the scales are not very likely to be brushed or knocked off. One disadvantage of the biological system compared to the problem definition is that the loss of scales may reduce the strength of the butterfly's wings, while the surface coating of shoes should have no impact on their structural integrity.

Marble Berry

Problem Target		relation		Biological Source: Marble Berry
Opera 1 2 3 4 5	ational Environment Airborne contaminants Moisture exposure Heat Changes Impact forces from walking and running Exposure to mud, grass stains, chemical stains	1 2 3 4 5	similar same Not as significant for shoe different Same	 Operational Environment Airborne contaminants Exposure to dew, etc. Heat Changes Little Motion Exposure to weather, mud, grass
Funct 1 2 3	tions Resists dry particles Resists dirt/ mud Bright Coloration	1 2 3	same similar same	Functions1Very Hard2Little known about adhesion resistance3Structural light for increased brilliance
Speci 1 2 3 4 5 6	fications Non-toxic Sustainable Ingredients Manufacturable Requires no cleaning by user Sustains walking forces Surface coating (or lack of) has no impact on structural integrity	1 2 3 4 5 6	same Same different same same same	 Specifications Non-toxic Sustainable ingredients (cellulose) Organically grown No Self Cleaning motion Durable Eye Catching External fruit shell protects seed
Criter 1 2	ria Must last minimum 1 yr, up to 3,000 steps/day No surface reapplication	1 2	same same	 Criteria Protect Seeds (for several years) Maintains appearance after cellular death of fruit.

Scientists claim that the marble berry achieved its brilliance through co-evolution with animals to achieve an attractiveness that aids in its dispersion. Similarly humans have evolved cultural signifiers, such as brightly colored, stainless shoes, which demonstrate status and power. The apt portions of the analogy connecting the abilities of the marble berry and the shoes are both of their desired properties for hardness, water, and stain-resistance. On top of this are eyecatching light reflective abilities. The operational environments are quite similar for both of the items, a similar pressure, elevation and exposure to dirt, with the difference in that the shoes will face more impact forces from walking and running. Functionally, as previously mentioned the analogy is apt since they both strive for immaculateness, and their performance criteria are quite similar in terms of durability of brightness.

Dung	Rootla	Cutic	10
Dung	Deelle	Cunci	e

Problem Target	relation	Biological Source: Dung Beetle Cuticle
 Operational Environment 5 Dirt, dust, mud 6 Moisture exposure 7 Impact forces from walking and running 8 Exposure to grass stains, chemical stains 	5 same6 same7 different8 different	 Operational Environment 5 Muddy environments/dung 6 Exposure to moisture in mud and dung 7 Only significant forces produced during flight 8 Must not adhere to mud or dung
Functions3Collects dry particles4Collects dirt/ mud	3 same 4 same	Functions3Self-cleans4Resists adhesion
 Specifications 7 Non-toxic 8 Manufacturable 9 Requires no cleaning by user 10 Sustains walking forces 11 Surface coating (or lack of) has no impact on structural integrity 12 Surface reapplication should be possible 	 7 same 8 different 9 same 10 different 11 same 12 similar 	Specifications7Non-toxic8Organically grown9Passive self-cleaning10Sustains forces during flying11Hydrophobic surface texture not shown to be structurally important12Cuticle is periodically shed and regrown
Criteria 3 Must last minimum 1 yr, up to 3,000 steps/day 4 Must not add > 5 mm thickness to sole sidewall	3 similar 4 similar	 Criteria 3 Must last between molts 4 On the order of .005mm thickness

Though, the dung beetle is not used as a primary source of inspiration for this particular design, it serves as an additionally apt analogy to the target problem. The dung beetle spends most of its time in an environment that is frequented by shoes, and it also naturally wicks away dirt and mud, which is important for keeping a shoe white. The dung beetle achieves this function through a relatively straightforward mechanical surface structure which would likely be manufacturable and not interfere with the appearance of the shoe (Tong, Sun, Chen & Zhang, 2005). On the other hand, the beetle's cuticle does not provide oleophobicity or exceptional protection from abrasion and impact, all of which would be desirable in the final product. Similarly, the cuticle will stain permanently if staining does occur, which is a prime concern when addressing how to keep shoe sidewalls white.

Problem Target	relation	Biological Source: Pitcher Plant
Operational Environment1Dirt, dust, mud2Moisture exposure3Impact forces from walking and running4Exposure to grass stains, chemical stains	 similar same different different 	Operational Environment1debris2humid environmentsand rainfall3insects landing on it4exposure to larger animals
Functions1Resists dirt/dry particles2Resists water/mud	1 different 2 different	Functions1Resists insect adhesion2wetting makes it more slippery
Specifications1Non-toxic2Manufacturable3Requires no cleaning by user4Sustains walking forces5Surface coating (or lack of) has no impac on structural integrity6Surface reapplication should be possible	 different different different similar different similar 	Specifications1Filled with acid2Organically grown3No self-cleaning4Sustains insect impacts5wet surface enhances slippery surface6surface mostly slippery when made wet
Criteria 1 Must last minimum 1 yr, up to 3,000	1 similar 2 different	Criteria 1 lasts life of the plant 2 slippery feature works

Pitcher Plant

2 Surface reapplication	steps/day 2 Surface reapplication		better when wet
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The pitcher plant is a good and bad analogy. The surface is very slippery, so very little will stick to it, including oils, dirt, and insects. In translating this to our problem the slick surface would provide a great mechanism for keeping dirt and mud from sticking to the shoe in the first place. On the other hand, the slippery surface may also be dangerous to the wearer if it's too slippery! Most consumers would probably not want to leave wet footprints as they walk around, either.

Arthropod Molting

Problem Target	relation	Biological Source: Desert Scorpion
 Operational Environment Airborne contaminants Moisture exposure Impact forces from walking and running Exposure to dirt, grass stains, chemical stains 	 similar similar different partial overlap 	Operational Environment1Airborne contaminants (dragonfly and/or scorpion)2Underwater3Protection during new
 Functions 4 Cohesive peelable bilayer layer 5 Reveals new version of the layer 	4 same 5 similar	 Functions 4 Generates a single removable layer 5 New layer keeps animal protected but may require hardening
Specifications7Non-toxic8Manufacturable9Peels easily with mechanical forces10Leaves pristine layer underneath11Can be done on the go12Surface reapplication should be possible	 7 same 8 different 9 different 10 same 11 similar 12 similar 	Specifications7Non-toxic8Organically grown9Molting fluid used to loosen the cells allowing peeling10Doesn't damage or peel the layer underneath11Requires minimal down time12Cuticle Regeneration

Criteria 13 Must last minimum 1 yr, up to 3,000 steps/day	13 different	Criteria 13 New layers are generated every several weeks or months

In nature, there are several solutions to the problem of shedding a uniform layer that no longer serves the necessary purposes it was designed to serve. In the case of arthropods, this process is called molting. Arthropods, including crabs, lobsters, and dragonflies all opt to shed their exoskeleton rather than attempting to expand the outer shell itself. Molting is a good analog for the Fresh Kicks problem in the sense that it does efficiently remove a single outer layer without damaging or removing any of the layers below it. Nature's solution, however, is practically infeasible in a non-living system. To molt, arthropods first separate the outer layer from the epidermis through a process called apolysis. This may be done through intentional abrasion and damage to the outer shell or simply through a series of intentional movements designed to loosen the outer layer. From there the arthropods secrete a "molting fluid" into the gap between the old exoskeleton, and the newly forming one (Krishnakumaran, A. & Schneiderman, H.A.). It is this fluid which, through hydrostatic pressure (among other factors) makes the release of the exoskeleton possible. To complete the molting process, the arthropod the reabsorbs the molting fluid and then shucks the outer shell.

When addressing the problem of clean shoes, or any micro-scale bilayer for that matter, the controlled release of finite amounts of fluid between layers ranges from an expensive improbable solution to a complete impossibility. While using water or another readily available solution comes to mind, this drastically increases the probability of undesired delamination. Due to this, we opted to exclude molting technology from our possible biological solutions and instead focus on systems that required an outside force to induce removal, thus increasing the wears control over layer removal.

Visual Representation



Figure 6. Visual representation of Fresh Kicks

Mechanistic Explanation

Our design draws inspiration from the scorpion and butterfly wings. Fresh Kicks were designed to keep your shoes looking new for a longer period of time. This was accomplished through a layered material that shoe manufacturers could attach to the shoe sole sidewalls during the manufacturing process in the same manner they currently attach sidewalls. To help evaluate our idea quantitatively and qualitatively, we additionally designed a real-world prototype shoe to test. Since we do not have access to cellulose nano-crystals or EVA processing equipment, we respectively used similar, yet lighter-duty, materials consisting of cellulose tape and spongy duct-tape. These were combined in hard-soft bi-layers and wrapped around the existing white walls of one part of a new pair of shoes. Material and temporal constraints limited us to a total of twenty peel-able layers (instead of the targeted 100) in the prototype model. The alternate shoe was left unmodified to serve as a "control" shoe. The shoes were then subject to many days of normal wear, and many days of accelerated dirtying.



Figure 7. Prototype "Fresh Kick" constructed from bilayers of hard cellulose outer-tape and resilient, thick duct-tape inner-tape.

Like the butterfly's layered scales that fall off, our design allows for a simple method of cleaning shoes. If you get dirt/mud/stains on any part, simply peel off that layer and you have a new one below. Essentially the layers are stacked together and sold as one thick sheet. The thicker the sheet the longer lasting it will be. A typical sheet will consist of about 100 layers, at with a total thickness of about 2.5 mm (with each layer half the thickness of a piece of packing tape) so as not to affect the aesthetic appearance of the shoe by noticeably increasing the sidewall thickness. The layers are held together in an orientation similar to "Post-It" notes coupled with

the directional style adhesion of the butterfly. The general idea is that each layer is offset from the layer below, which ensures that pulling one layer does not cause the others to peel off as well. In order to successfully achieve this, an adhesive will be used to hold the layers together in a similar fashion to a roll of packing tape, except the perforations between layers will be staggered. When the layer is pulled, the sticky adhesive comes off, leaving no residue on the lower layer. The alternating and staggered location of peeling points as well as the directionality of the starting pull allows the pulling action to only occur in specific alternating directions. This concept faced some concern as to its viability and the possibility of accidental de-lamination, but in testing our simple prototype we found that the dimensional reduction encountered with specific, alternated tear-off points lead to simple targeted removal by the user with no unwanted peeling, including during dirtying and abrasion testing. Through our prototype we also discovered that the optimal location for the peeling locations would be situated within the instep of the shoe since this area encounters the least amount of direct, environmental impact.



Figure 8. Testing the interaction and immaculation of our prototype by selectively peeling off a single, dirtied layer.

Each entire layer will be removed each time. Basically, after each peel cycle there is a clean new looking shoe! The butterfly with its scales only removes scales in the affected areas. This may seem great in that only the "damaged" parts are removed. However, over time the biggest flaw in this is the loss of uniformity. One part may become 30 layers thick and less than an inch next to it the shoe may still have 80 layers, with each layer about .025 mm thick would be noticeably uneven. Since different areas of the shoe go through different levels of wear, after time the front of the shoe will look thinner than the sides or back. The instep area would

probably look the thickest. This uneven look takes away from the visual and logistic appeal of the shoe and therefore contrasts the entire purpose of having Fresh Kicks.

In addition to layering, butterflies are also great at avoiding adhesion to almost everything. We considered utilizing its hydrophobic nature but turn away for better alternatives. In a detailed analysis, it was found that trying to mimic the butterfly in this regard would be much more difficult and expensive to do. The development of such a material conflicted with the goal of making very thin and peelable layers.

Pulling off layers is great to get rid of stains and dirt, but our design also address resistance to abrasion. Modeling the scorpion's exoskeleton, each individual layer of the sheet is actually a composite which consists of extremely hard particles embedded within a softer, more elastic epoxy-like substance. This hard-soft difference helps spread and diffuse impacts and even point loads. The hard material is concentrated towards the top of each layer and gradually diffuses down through the soft portion. The harder material prevents direct damage from scraping and abrasion, whereas the softer layer acts disperses impact so that cracks, etc. do not propagate through the shoe.

For application of a product containing 100 layers, the top 99 would be removable. The last layer would be semi-permanently affixed to the shoe sidewall, with the potential to install a fresh application of Fresh Kicks if the customer wishes to continue using the the shoe after the 99 layers are used. Conservatively assuming that the wearer wishes to refresh his or her shoes once a week, a single application will last nearly 2 years. This means that even if the shoe is discarded after 100 layers have been used, the environmental impact of discarded shoes can be cut in half, assuming the average first-world consumer replaces casual shoes every year.

The product can also easily be manufactured in different colors to appeal to a broader market and be implemented with more shoe styles. Early consumer surveys indicated that customers would even be interested in multicolored layers, so that your shoes can take on a new personality every time you peel off a composite EVA-cellulose nanocrystal bilayer! The possibilities are nearly endless.

Materials and Manufacturing Considerations

Two main components make up our design:

- 1 An elastomer composite that provides:
 - a resilience by dissipating impact energy
 - b resistance to abrasion and impact
 - c a barrier to fluids and foreign particles that cause staining and dirtying
- 2 An adhesive that selectively binds the bilayers together, so that the wearer can manually peel off a single layer at a time and no residue is left on the outer surface of the layer below.

The initial version of our design included a hierarchical layering as a direct translation from the scorpion cuticle, consisting of a hard outer coating over a softer material. However, we

discovered many complications and additional considerations required with this design. The following specifications describe the hard and soft layers as distinct components joined together, and the adhesive as a third material, but the discussion which follows explains the adjustments made to the design in its current version.

1) Hard outer layer for abrasion/fluid resistance

The outer layer will be based on organic cellulose. It provides promising mechanical properties, including extremely high Brinell hardness and modulus of elasticity (Young's modulus), as well as manufacturability when in the form of cellulose nanocrystals. Its four-box analysis is given below.

Functions	Material Properties/Constrai nts/Costs
-Provide structural integrity (min ~10 MPa yield stress, equivalent to rubber) -Display brightness (high reflectance %, near that of marble berry, ~60%) -Provide abrasion resistance (between 30 and 120 Rockwell R Hardness, dimensionless) -Provide fluid resistance	-Be manufacturable -Cannot be too heavy -Must not be toxic -Low environmental impact in both production and disposal -Cheap to manufacture in bulk
Operational	Performance
Environment	Characteristics
-Exposed to various	-Prevent blemishing
surfaces, materials,	for minimum 1 week
climates while	of daily use
walking in	-Stay permanently
indoor/outdoor	bonded to sub-layer
situations	for duration of life of
-Permanently bonded	shoe (~2 yrs)
to resilient/spongy	-Stay temporarily
inner layer and	bonded to adhesive
temporarily bonded to	layer until wearer
adhesive layer	requires removal (min
-Subjected to impact	life of shoe)

2) Resilient layer for energy dissipation

The impact resistant sublayer will provide a means of volumetrically dissipating impact energy, which makes biodegradable EVA (ethylene-co-vinyl acetate) a prime candidate, since it is already an ideal material used in shock absorption, flexibility, and comfort in athletic shoes.

Functions	Material Properties/Constrai nts/Costs
-Provide structural integrity (min ~10MPa yield stress, equivalent to rubber) -Provide impact absorption (low modulus of elasticity (MPa), high yield strength (MPa)) -Maintain comfort characteristics of a traditional casual shoe	-Be manufacturable -Cannot be too heavy -Must not be toxic -Low environmental impact in both production and disposal -Cheap to manufacture in bulk
Operational Environment	Performance Characteristics
-Permanently bonded to both stiff/hard outer layer and adhesive layer -Subjected to fatigue stresses from walking	-Prevent blemishing for minimum 1 week of daily use -Stay temporarily bonded to adhesive

3) Adhesive layer for interlayer attachment

Our adhesive material will be that used in common medical tape, due to its having a strong unpeeled adhesive shear strength while being highly peelable (low normal adhesive strength) and doesn't leave a sticky residue.

Functions	Material Properties/Constrai nts/Costs
-Ensure firm bond between layers during daily wear (high bonding strength, Pa) -Allow for user removal (moderate peeling strength, Pa)	-Manufacturable -Extremely thin -Non-toxic -Low environmental impact in both production and disposal -Cheap to manufacture in bulk
Operational Environment	Performance Characteristics
-Wet/ dusty environments -Fatigue stresses from flexing of shoe	-Maintain stickiness in wet and dusty conditions -Maintain flexibility in shoe -No residue left on hard layer below

As mentioned at the beginning of this section, the distinct hard and soft bilayer presented several problems. We initially determined that the 3 different materials (hard, soft, and adhesive) would have relatively independent properties as shown in the four-box method above, but would still need to be compatible with each other for manufacturing and should function together as a single part. Because we specify a desired low-range Young's Modulus for the elastic layer and a relatively high Young's Modulus for the hard layer, we had to consider the trade-offs between Young's Modulus and cost. Our optimization analysis in CES EduPack showed little difference in the cost for rubbers versus cellulose-based harder substances, such as wood. That said, it was important to recognize that as the stiffness of the outer layer is increased, there is roughly a proportional increase in the stiffness of the shoe sidewall as a whole; for a high enough value of stiffness, this could mean that the flexibility of the shoe sole could be compromised, rendering it unwearable.

In the initial version of the design, we elected to use cellulose for our abrasion-resistant outer layer, biodegradable EVA for the more elastic inner layer, and medical tape adhesive for the interlayer adhesive. Each fulfills the criteria for the effective functioning of its mechanism.

In particular, the EVA offers mechanical properties known to function well for shoe wear (flexible, lightweight, durable), while the outer cellulose layer offers the ability to tune its mechanical properties based on the amount of filler in the final product. We will incorporate the BioMoGo technology developed by Brooks, a running shoe company, into the EVA layer. BioMoGo is simply EVA with a non-toxic, natural additive mixed into the rubber which encourages anaerobic bacteria to consume the rubber once it is in a landfill. This reduces the degradation time from over 1000 years to just 20 years, and the material properties of EVA which make it so attractive as a material in shoes are virtually unchanged (Zarda, 2008).

The medical tape adhesive was selected for its high shear adhesion and relatively low normal adhesion. It was identified as the best option because it is relatively inexpensive, easy to remove, and although not entirely nontoxic, it will exist in such small proportion compared to the rest of the product that we hope its environmental impact will be negligible. The adhesive has a shelf life of approximately 2 years, which should satisfy the needs of our design, and is stable over a range of temperatures and in the presence of moisture.

The cellulose material for the hard layer was the main source of complications with the initial version of our design. The distinct bilayer concept borrowed from existing technology that was then integrated into our design. A Southeast Asian tape manufacturing company, Louis Tape, offers a biodegradable cellulose tape which is both transparent, allowing us to select any color for the EVA layer, and very highly adhesive due to the natural rubber-based adhesive. We had hoped that the rubber adhesive on the cellulose tape would serve to bond it to our soft EVA layer. It should be noted that this adhesive was distinguished from the medical tape adhesive. The rubber adhesive accomplishes the permanent joining of the hard and soft layer to comprise the bilayer, while the medical tape adhesive functions as the removable, low-effort, residue-free adhesive between the discrete bilayers of the Fresh Kicks design. This would however increase the thickness of each bilayer, which partly decreases the economy of our design in terms of materials and also the number of layers which could be offered to customers with each application of the product.

Another major problem with this concept is the hydrophilicity of cellulose. Cellulose nanocrystal technology is fairly cutting-edge and not yet familiar to the materials world, but it is known that exposure to water will essentially disintegrate the molecular structure of the material. This can be avoided by laminating the cellulose layer to seal it off from moisture, but if the lamination lacked the same abrasion resistance as the rest of the design, it would become ineffective if scratched slightly during normal wear of the shoe.

Considering these challenges, we have since found research and received advice from experts in the field showing that a composite will fulfill our desired functions while avoiding several complications associated with a distinct hierarchy of two joined materials. Since cellulose nanocrystal requires a substrate or epoxy to form a continuous solid anyways, we first considered embedding the nanocrystals on the surface of the EVA layer during the manufacturing process before the EVA cures fully. Our research showed that a better alternative would be to actually mix the cellulose nanocrystals into the EVA material so that it was evenly

distributed. While at first this seemed like it would not provide the desired properties described above with the alternating hard and soft layers, we consulted a materials science professor who confirmed that the mixing of functions we are trying to achieve has been accomplished with similar composites, such as dispersed aluminum oxide particles greatly increasing the hardness of copper, while allowing it to remain ductile. Although this is a departure from the biological inspiration of the scorpion, it still incorporates the basic principles of combining materials with different properties to achieve a) impact force dispersion through elasticity and b) abrasion resistance through hardness.

Further potential for improving this design would be to explore other ways of joining the layers besides simple tape-like adhesives. One recommendation we have received is to use hydrogen bonding between layers. An example of this type of bonding is window clings or car stickers, which don't actually use an adhesive and are easily removable yet fairly sturdy while they are attached. We must research this idea more to determine which changes if any would be required to our design, and whether the concept is feasible for the materials and manufacturing constraints. If it is possible to implement hydrogen bonding between layers, we would be able to further reduce the thickness and materials cost of each layer, thus improving the design's environmental friendliness and feasibility as a mass consumer product.

Quantitative Assessment



Figure 9. Force-resistance diagram

We decided that since shoes experience a range of abrasive and impact forces from normal daily use, the protective layer should not fall off automatically, but rather be peeled off by the user. This also prevents accidental littering. We take the thickness of a single bilayer to be .05 mm, the approximate thickness of packing tape. If an added thickness of 5 millimeters is allowed around the sidewall of the shoe soles, 100 protective layers can be applied to each shoe. If the user "cleans" his or her shoes by removing a single layer once a week, a single application can last ensure like-new soles for 2 years. The designers also hope to offer a re-application of the product which can be purchased and applied separately after the initial application has been exhausted.

Using the mathematical basis for the resistance of the scorpion shell, its impact resistance can be explained through the following equations. Based on the ratios found in the equations, it becomes apparent that material choice significantly influences erosion protection for a given system. A smaller elastic modulus generates a larger impact force, as well as a longer shock duration leading to a deeper indentation. (Han, Z.) This method of erosion resistance, coupled with the highly elastic materials of a shoe wall, lends itself to an effective system to decrease abrasion. 1

pmax is

radius of impact particle elastic biggest

$$p_{\max} = 1.2R^{2} \rho_{1}^{0.6} \frac{1}{\left[\frac{1-v_{1}^{2}}{E_{1}} + \frac{1-v_{2}^{2}}{E_{2}}\right]^{0.4}} U^{1.2}, \qquad (8)$$

$$T = 5.15R \rho_{1}^{0.4} \frac{\left[\frac{1-v_{1}^{2}}{E_{1}} + \frac{1-v_{2}^{2}}{E_{2}}\right]^{0.4}}{U^{0.2}}, \qquad (9)$$

$$t = 1.3R \rho_{1}^{0.4} \left[\frac{1-v_{1}^{2}}{E_{1}} + \frac{1-v_{2}^{2}}{E_{2}}\right]^{0.4} U^{0.8}, \qquad (10)$$

(8)

the biggest impact force of particles; R is particle; ρ_1 is density of particle; U is speed of particle; v_1 , v_2 is Poisson ratio of (9) and target; T is shock duration; E_1, E_2 is modulus of particle and target; t is the indentation depth (Han, Z.)

We use the materials given above

in our materials assessment section to determine the particle size to create a given indentation depth, where the particle size is p_max, using equation (8). For the sake of simplicity, we limit our analysis to comparing the effectiveness of the materials we use in our design to the materials present in a scorpion's cuticle with respect to limiting abrasive indentation depth, according to the equation below

where for ratios greater than 1 our design is more effective than scorpion cuticle at resisting abrasion.

It is sufficient to say that if our design is at least as resilient to environmental abrasion as a scorpion's cuticle, it will withstand the rigors of shoe wear. Such an assumption can be made considering that abrasive forces while walking will be similar to those encountered by a scorpion in a harsh desert environment, at least as particulate abrasion is concerned. Impact forces may be of significantly greater magnitude in a shoe - for example, if the wearer kicks the edge of a stairstep - but the basis of our bilayer is EVA, which has already been widely shown to be a robust shoe material in the structural sense. Qualitatively, the impact resistance of scorpion cuticle suggests that a layered structure will tend to enhance impact-resistance of a given material, meaning that layered CNC/EVA and EVA will likely be more robust under impact than EVA alone.

For our calculations we use available material property values of EVA, carbon nanocrystals, material representative of scorpion cuticle (Han, Z.), and silica (sand), where EVA and CNCs represent our design and silica represents the impacting particle.

We find:

Etotal for our composite:

 $0.0636 \times 10^{9} \times \frac{150 \times 10^{9} \left(1 + 200 \times 0.44\right) + 200 \ 0.0636 \times 10^{9} \ 0.2}{150 \times 10^{9} \ 0.2 + 0.0636 \times 10^{9} \ (200 + 0.44)}$

= 1.9865774217563101923122269344912265336302175092... \times 10¹⁰

(considering only about 5 significant figures)

Numerator using Poisson's ratio for CNC (ignoring constants in equation for pmax):

$$= \frac{1}{\left(\frac{1-0.35^2}{302 \times 10^9} + \frac{1-0.44^2}{19.8 \times 10^9}\right)^{0.4}}$$

=

13933.953

Denominator:

$$\frac{1}{\left(\frac{1-0.35^2}{302\times10^9}+\frac{1-0.38^2}{2.12\times10^9}\right)^{0.4}}$$
= 5706.631

Numerator using Poisson's ratio for EVA (ignoring constants in equation for pmax):

$$\frac{1}{\left(\frac{1-0.35^2}{302\times10^9}+\frac{1-0.2^2}{19.8\times10^9}\right)^{0.4}}$$
__13051.094

So, for the two numerator/denominator ratios we have 2.44 and 2.29, respectively. Using both available Poisson's ratios independently due to the lack of the ability to mathematically combine them, our material still outperforms scorpion cuticle. In reality our material would probably fall between the above values.

In order for our many-layered design to work, and not fall apart, the release force between the outermost layer and the one beneath it needs to be far less than the adhesive force joining all the layers together. If not, when the user removes the outside layer, the other layers may also all peel apart, and the shoe design would fail. We have two solutions for dealing with this phenomenon, both utilizing the existing methodologies used in commercial solutions where individual layers of a laminate need to be independently removed from the whole. A primary design would use a mechanism similar to that of adhesive notes (like Post-Its). Adhesive notes use two strategies based on dimensional reduction, a) a perpendicular adhering structure, and b) the staggering of pull-off locations. A perpendicular adhering structure (like the tacky backing on a stack of post-its), could connect the edges of all the layers on either the top or bottom of a sidewall. This could be the point where the side-wall layers are attached to the ordinary sole of the shoe. This provides a collective force that is of greatest magnitude holding the sublayers together, while applying half of that force to the outermost layer. A secondary design would use alternating locations of weakness between layers, in order to provide a targeted weak point when attempting to remove a single layer.

The alternating design is what we pursued in the design of our prototype, and through many days of testing, no accidental delamination was encountered. Additionally we discovered that the opportune location for the targeted peeling perforation of the layers would be located in the instep of the shoe since this area encounters the least amount of direct, environmental impact.



Figure 10. Diagram explaining the dimensional reduction of peeling layers of a tape-like substance. (<u>http://www.agpa.uakron.edu/p16/lesson-print.php?id=how_sticky_is_your_tape</u>)



Figure 11. Convential methods to prevent accidental de-lamination (http://www.agpa.uakron.edu/p16/lesson-print.php?id=how_sticky_is_your_tape)

The location for pulling of an individual layer is always going to the be the weakest point of the layer. If the location is the same for all layers, you run the risk that a particularly located force could loosen all the layers at the same time. If you stagger the weak point, with an alternating location of perforation between each layer, the strong points of the above layer protect the

weaker points of those below. The layers could be wrapped as a continuous stip (like packing tape), but apply perforations in alternating locations as each layer is laid down.

Transfer Challenges

The design for this product primarily faces materials science challenges. Since the inspiration is drawn from an array of different micro- and nano- structures, the chief concern will be the manufacturability of the design at reasonable costs.

Scaling

There are two main scales to consider which affect our design. There is a physical scaling of the structure and the enumeration of layers. One of the inspirational structures, the scorpion's erosion resistant cuticle, has an average overall thickness of a 100 micrometers with individual layers at about 3 micrometers thick. Using comparatively new manufacturing techniques (such as those described in Habibi et al's "Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications"), and following the inspiration of the marble-berry, we can achieve brightly colored layers on this same order. Our also design incorporates the scorpion's cushioning layer into the creation of bright, erosion resistant bi-layers. With this in mind, we can safely assume a construction of at least 20 micrometers thick for the full bi-layer with adhesion.

For the amount of layers considered in the design, the scorpion has around 33, and the butterfly has only one layer of the adhesion-free scales. For long lasting protection of personal style, our product needs a layering of around an order of magnitude greater. Unlike the scorpion, we can have a much thicker overall structure, with the side soles of shoes being an average of 5 millimeters wide. Though our individual bilayers could be up to 7 times thicker, the overall paneling can be 50 times bigger, giving us 7 times more potential layers or at least 200.

Materials

As with many bio-inspired designs, the original source utilizes a quite readily available and sustainable substance, cellulose. The marble berry creates its hard exterior through the assisted self-arrangement of layers of oriented cellulose nano-fibers. While nano-technology in general is new, expensive, and difficult to create, many papers have been written about the comparative simplicity of using nano-design for the creation of self-assembled cellulose nanocrystals. As Ramirez and Dufresne point out in their article "A Review of Cellulose Nanocrystals and Nanocomposites," "Cellulose nanocrystals correspond to defect-free rod-like nanoparticles that present remarkable properties such as light weight, low cost, availability of raw material, renewability, nanoscale dimension, and unique morphology." Using this material will afford us the hardness and color-fastness of the marble-berry, while granting us the thinness of structure to create multiple redundant layers.

Performance Criteria

For sustainability of style as well as nature, we wanted our shoe sidewalls to last for at least two years. As noted in the quantitative analysis, if a person loses a layer up to once per week, the 100-200 layered walls will easily last 2-4 years. Another criteria is that the shoe-sides will be able to withstand the everyday impact of the casual shoe-wearer. Given the hardness, and erosion-resistance of our design, each layer should be able to achieve this task. Finally, stain-resistance is our final criterion, and the hardness, hydrophobicity, and shedding ability of our design presents a multi-faceted approach to conquering this exact problem.

Constraints

A primary constraint for the realization of the product will be cost. Bespoke micro- and nano- manufacturing is nearly always incurred at great cost. However, as mentioned earlier, this particular type of nanotechnology has been cited as having a far superior cost-benefit ratio. The other constraints are the construction of a lightweight, and durable material small enough to be attached to casual shoes, and it appears that the materials we aim to use are well suited for this.

Value and Comparative Assessment

In the US, the footwear industry is worth \$54 billion, with US consumers spending \$20 billion per year on shoes. According to the U.S. Department of the Interior, 300 million shoes are thrown away every year, with each pair requiring anything from 30 up to 1000 years to decompose in a landfill. The environmental impact of landfill waste from discarded shoes could be greatly reduced by a more durable, longer lasting shoe. Many people throw away shoes that are still in good, wearable condition, simply because they look dirty. The Fresh Kicks design will address this problem by allowing consumers to instantly and effortlessly clean their shoes, and keep soles looking like new for up to 2 years per application of the product. Assuming the average consumer throws away shoes after 1 year because they become dirty and start to look unattractive, Fresh Kicks can reduce the number of discarded casual shoes by a factor of $\frac{1}{2}$. The application can, with further development, become an aftermarket product which can easily be added and sized to any soles, helping buyers keep their favorite pairs looking fresh longer. Even the color can be controlled. Imagine shoes that went from blue to green to red to purple to orange every time you peeled a layer! In addition, the layers themselves are manufactured from cellulose and biodegradable EVA, resulting in a disposal but non-toxic and quickly biodegradable product. Fresh Kicks are more sustainable than current market offerings, and consumers can feel confident about saving money while having great-looking shoes for a long time!

On of the most important things to consider about our design is that it also has the potential for use in a much broader range of applications than just shoe wear. For example, possible applications include:

- keeping military and consumer vehicle and aircraft windshields and canopies clean
- keeping racing and safety helmet visors clean

• protecting and providing cleanliness for other surfaces, possibly including automobile paint finishes, table surfaces, or even solar cells

The alternative uses above almost all rely heavily on the ability to manufacture our bilayers using a transparent base material to replace traditional EVA. A polymer such as silicone, or more generally any polymer with reduced crystallinity leading to transparency and material properties suitable for our design, could be used as a transparent replacement for EVA. The racing helmets mentioned above lend themselves to our design, as clear polymer "tear-offs" are already used as protection for their visors. Our design could improve on the existing design by providing the extra abrasion resistance, and thus endurance, of the bilayer. Purely speculating, a driver might only use half of the scorpion-based "tear-offs" as compared to the current design, resulting in less waste and less likelihood of a "tear-off" becoming entangled on or ingested by another vehicle.

Military and aircraft windshields also present an interesting potential application for our Fresh Kicks design. Especially in the context of military usage, the need for a quick, effective way of cleaning those areas of the vehicle necessary for outside vision is great, given that the military operates in unscheduled, fast-moving operational environments where stopping to clean a windshield by hand may not be an option. Aircraft sometimes face similar constraints, in that they may be on-call or flying for extended periods of time, where even just the activity of cleaning a canopy may be costly in time or mission success.

Finally, there are numerous other applications where a layered protection system would be of use. One of the most obvious is the protection of phone and laptop screens, which are known for their tendency to scratch and abrade over time. Another might be the protection of various home and office surface finishes which would benefit from a scratch-resistant protective layer, such as a wooden desk surface. In any product, the use of single or multiple bilayers used for the peel-off function would be dictated by the specific function of the device and user preference, though even the single bilayer alone would provide an improvement in impact and scratch resistance over current protective film designs.

The variety and importance of possible applications for our design mean that it should not be overlooked. Fresh kicks have potential!

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