Chemical Engineering
#Session C4

SELF-HEALING STRUCTURES: NISSAN'S SCRATCH SHIELD PAINT

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Abstract—

A miraculous modern technology in the field of material science engineering is self-healing structures. A self-healing structure is a material that acts as the human body does; it repairs inflicted damage. When a scratch is made on the surface, the material heals itself by one of three methods.

Three common forms of self-healing materials are capsule-based, microvascular, and intrinsic [1]. The three different strategies have been developed in an attempt to give non-living materials the ability to heal on their own. Capsule based methods involve a capsule containing a self-healing agent and the material outside containing a catalyst. When a break occurs, a capsule near the damaged area breaks and a reaction occurs between the catalyst and agent that heals the fracture [2]. The microvascular system gives the material a network of channels that contain the healing agent. The same reaction occurs as did with the capsule method, but multiple healings can occur at the same location [2]. The intrinsic materials have a characteristic to self-heal that only needs to be activated by some stimulus in the environment [3]. In most cases, this is heat [4].

Applications of the self-healing materials range from medical advancements to paint and iPhone cases [5]. Nissan has collaborated with a local Japanese university to find the perfect scratch resistant paint. The final product is known as Scratch Shield and is available on many Nissan models [5]. Nissan's Scratch Shield paint has withstood many trials, but their latest innovation, the iPhone case, hasn't had the best of luck [6]. With the phone case still in a trial period there is room for improvement.

In this paper, we will discuss the various properties of self-healing structures and the advantages and disadvantages of Nissan's scratch shield paint.

Key Words—Paint, Polymer, Polyrotaxane, Scratch Shield, Scratch Resistant, Self-Healing, Self-Repair

INTRODUCTION: SELF-HEALING STRUCTURES

One cut in a circuit can put the lights out on an entire string of Christmas lights. A single break at the base of a building may eventually send the structure down. A puncture in a space craft could cause disaster for astronauts. Not a day goes by that the average human being does not drop, scratch, or break something. Although a single scratch or break in a structure may seem like a minor issue, it can often be a difficult fix and cost a great deal of money. Wouldn't it be nice if every blemish made to an object could magically reform back to its original shape? This is the idea that is being worked on for self-healing structures. Within the past couple of decades, material scientists have been doing a great deal of research on this phenomenon. The idea is to come up with methods and mechanisms that act as the human body does. Whenever one is scratched or cut, the body immediately takes action to heal the wound. Likewise, when a lobster or crab has a break in their shell, their exoskeleton quickly begins working on repair. If only buildings, cars, electric circuits, and cell phones could have this same healing process, an unimaginable amount of time and money would be saved. The quest to find a perfect self-healing material is currently a tremendous component of research for material science engineers.

Self-healing structures are constantly being updated with technology, and new strategies to build a self-healing material are surfacing each day. With the work of polyrotaxanes—and sometimes heat—structures are capable of mending themselves back to their original shape and filling in the gaps formed by scratches [7]. Depending on the size of the scratch, the healing process can take as little as a few minutes or as long as a few weeks [8]. Many different strategies have been developed and each is a work in progress. There are downfalls to many approaches, but the scientific community is getting very close at finding an answer. The hopes are that with a combination of these strategies and new ideas, the perfect self-healing material will someday be discovered.

Scratch shield paint was Nissan's attempt at a self-healing material. Nissan has applied the concept to their car paints to eliminate scratches from here on out. Nissan's paint has been able to withstand the tests of many. But is this paint the perfect self-healing material? Nissan believes so…

HISTORY OF NISSAN'S SCRATCH SHIELD

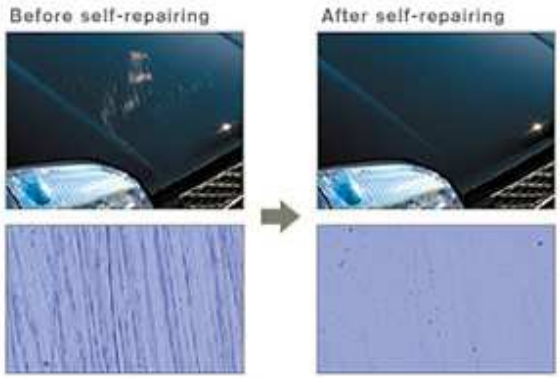
In 2009, the Nissan automotive industry, in collaboration with the University of Tokyo and Advance Softmaterials Incorporated, developed a clear coat paint that is unlike any other [8]. It is the world's very first scratch resistant and self-healing clearcoat paint [5]. Nissan is Japan's second largest automotive company by volume [5]. Advanced Materials Incorporated is based in Tokyo and is a company that handles polyrotaxanes and slide-ring gels [9]. The University of Tokyo, often times known as Todai, is a moderately large, multi-cultural university in Japan [10]. The paint which these three groups developed was originally used on the Infiniti models along with the Nissan Murano, 3702 and X-Trail [5]. Due to the success that the scratch shield paint has had on the cars, Nissan has decided to give

its license to NTT DoCoMo Incorporated [8]. DoCoMo is a mobile phone company in Japan that used the scratch shield paint on their phones. Most recently, Nissan has decided to apply their healing paint to the cases of iPhones. Due to the paint's success on Nissan cars, scratch shield paint shows a promising future.

NISSAN'S SCRATCH SHIELD PAINT

Nissan's scratch shield clearcoat is unlike any other paint. It is made of a highly elastic, flexible resin that is said to prevent or heal eighty percent of scratch marks [8]. This paint is made with a tougher coating so that scratches are much less likely to occur in the first place. When conventional paint is scratched, the polymer chains tear and the surface is permanently damaged. However, scratch shield paint contains a special slide-ring structure [5]. With this structure, polymer chains are able to scatter the tension that is put on the surface from outside forces [5]. This method keeps the surface intact so that it does not tear. Therefore, whenever the surface of a car with scratch shield paint is scratched, the chains rebound and repair themselves after contact. It is even said that a car with conventional paint will have five times the scratches than one with scratch shield paint after fifty car washes [8]. Shown below is a picture of a car immediately after being scratched, and then another picture after the scratch shield paint healed the surface.

Figure 1



Before and after effects of scratch shield paint's healing capabilities [8].

After a few short days, the scratches that were very apparent faded away because of the scratch shield paint's unusual properties.

SCIENCE BEHIND SELF-HEALING STRUCTURES

Self-healing structures often try to mimic the restoring process of the human body. The human body has an amazing quality of being able to be cut, bruised, or scraped and heal entirely on its own within a few days. When one cuts themselves, clotting agents are brought to the damaged area. Here they form a clot, then remodel and regrow the skin. This is the same idea that scientists are incorporating into self-healing methods. It is essentially as if they are making a synthetic blood clot.

There are three main types of self-healing processes: capsule-based, vascular, and intrinsic [1]. In a capsule-based self-healing process, the healing material is located within a capsule. When pressure is put on the material, the capsule bursts and the restoring process begins [1]. In the second kind, vascular (sometimes called micro vascular) healing, there are "capillary-type hollow chambers" that pump the healing agent to the damaged area when necessary [1]. Lastly is the intrinsic strategy to develop a self-healing material. The intrinsic type of healing usually involves thermoplastic materials. The thermoplastics have the intrinsic property to self-heal and do not require the addition of a catalyst, monomer, or any special treatment to the surface [3]. The bonds of thermoplastics reform through the method of heating rather than through the use of chemicals [3].

Each of these methods follows a three step process. First, a response is triggered due to the damage [1]. Then either chemical materials are transported or heat is transmitted to the affected region [1]. Lastly, the heat or chemicals help to repair the system. Each type of the three self-healing processes is different and more detailed, but this is the general process of repair.

Capsule-Based Method

In the category of capsule-based self-healing materials, the methods discovered by various scientists require the same overall theory. Most materials can be produced to contain microcapsules which carry a self-healing agent. When this agent comes in contact with a catalyst, the gap that is formed due to an external stress on the material is filled in. The catalyst is stored in material outside of the capsule while the capsule contains the healing agent. The two only combine when the capsule bursts due to the external force [2]. This is very similar to the ability of the body to clot when the skin is cut. The clot covers the damaged area and heals the skin [1].

This reaction heals the material very efficiently, but there is one major error to this approach. If there is another crack in the same area as a previous damage, there will no longer be a capsule available to break. Therefore, no reaction can occur to reform the material [11]. This process is very similar to the chemical process that makes a glow stick glow. Upon the bending of a glow stick, you hear a cracking. This cracking is the sound of capsules bursting, and the glow is a result of a reaction between the chemicals released and

the chemicals outside of those capsules. Glow sticks can only be used once because at the end of the use, the capsules have been broken.

This method can also be seen in a variety of other applications. For example, microcapsules are mixed into paint pigment to make the paint self-healing. It is also applied to delicate electric circuits and computer parts. Whenever a self-healing electric circuit is cut, a connected light bulb will turn off. However, microcapsules break and fill in the cracks of the circuit with the healing material. A few minutes after the crack begins filling, the light bulb is again able to turn back on. This process saves companies time and money so that they do not have to fix every cut that is applied to their circuits.

Microvascular Method

As a response to the not always perfect capsule-based approach to creating self-healing materials, scientists have worked to develop a new strategy mimicking the cardiovascular system of the human body. The body has the amazing quality of healing itself with the ability of blood to reach every part of the body due to its cardiovascular system. When the skin is cut, blood immediately comes to the surface and clots over the cut [1]. This process was attempted with the capsule-based system, but a major fault was the ability to heal the same spot multiple times.

This new microvascular system within materials supplies a self-healing agent to wherever damage may occur. This self-healing agent reacts with the catalysts in the material to swell like a blood clot to heal the damaged area. There is an outside source supplying the healing agent to the vascular network, and when a break occurs, the liquid self-wicks to the location of damage to repair itself [2]. However, this is not the best approach to having a material self-heal. This could not be applied to very large or very small scale materials, or materials that move such as computer screens. The necessity of the material to stay on a mechanism that supplies the vascular circulation does not make these materials very practical. A positive aspect of this system, though, is that once the material is healed by the microvascular method, the material is often much stronger than it was originally.

An example of this method is portrayed through a video made by Byte Size Science [1]. In this video, a large foam block breaks under too much pressure. A machine that is attached to this foam block begins pumping a healing material into the crack of the block. Only five minutes after this crack is filled, the structure is healed and can hold more pressure than originally [1]. Although not always convenient, the microvascular method is much more effective. This being said, though, it is still not a “perfect” self-healing method.

Intrinsic Method Dealing with Thermoplastics

The last category of self-healing materials contains materials with the intrinsic ability to self-heal. These materials are intrinsic because they do not require the addition of a catalyst or healing agent, and they also do not require any surface treatment [3]. Thermoplastics are lab produced polymers that have their own ability to repair due to their polymer link makeup. They are called thermoplastics because they require only the addition of heat to repair. This is a very good approach to developing a material that can be used for more practical reasons.

There are two basic thermoplastics: those that require the addition of heat, and those that through damage create their own heat [4]. Both types follow the same basic processes to reform when cracked. In the recent past, thermally reversible reactions have been studied and it has been discovered that cross linking covalent bonds can be reformed at high temperatures once they are broken [3]. This occurs because the matrix of the material contains many weak bonds. These bonds are brittle and the cross-linked polymers will break extremely easily. These bonds, however, are thermally reversible due to Diels-Alder reactions. The Diels-Alder reaction is basically a reaction that forms covalent bonds which ultimately heal any crack to a thermoplastic material [4].

The simple thermoplastics that require the addition of heat to heal follow the steps exactly as described above. The thermoplastics that create their own heat have a little more to their healing processes. Projectile punctures to certain thermoplastics can produce enough heat to heal immediately upon the projectile exiting the material. A material like this is special because it virtually seals itself as soon as the projectile leaves [4]. An example that exemplifies this is military fuel tanks. Military fuel tanks are at risk for bullet punctures, and if this were to occur, the oil held inside would escape. If these tanks were made out of thermoplastics, the hole created by a bullet would close immediately, due to the heat transferred to the material upon contact [4]. The oil would not spill because the hole would essentially never be exposed.

These thermoplastic materials are a very good strategy toward creating self-healing materials because they are quite reliable. There is no need to worry about when a catalyst or monomer may become unstable or if the material can heal multiple times. The thermoplastics are beneficial because they are resistant to solvation. Due to this resistance, there is less importance put on the environment. They also can be healed multiple times in the same area [3]. The one downfall to thermoplastics is that they cannot withstand projectile velocities that are too high and close.. The stress of the bullet can sometimes be too much for the material to withstand [3].

The intrinsic method can be seen through the research that was carried out by NASA scientists on thermoplastics. NASA focused on making their space crafts and military planes essentially bulletproof. With the intrinsic method and a focus on having a high level of tensility, NASA was able to create planes and space crafts that would heal bullet

punctures almost immediately after contact. The material has much more tensile strength meaning that it could withstand much more stress per unit area [1]. Whenever a bullet is shot at the space craft, the bullet penetrates the wall, the material is pulled along with the bullet, and then the structure closes back in on itself [1]. The key component to this process is how the bullet raises the temperature of the wall during penetration. The walls of these space crafts are thermoplastics. Whenever a bullet punctures the wall, polymer strands are broken. The heat created then acts as a catalyst and brings the polymers back together faster [3]. This is no different than the idea of melting plastic to form a mold or welding metal. The heating of these materials makes the bonds between polymers connect and form. NASA's technology can quickly heal a puncture wound that was caused by a bullet flying five kilometers per second [1].

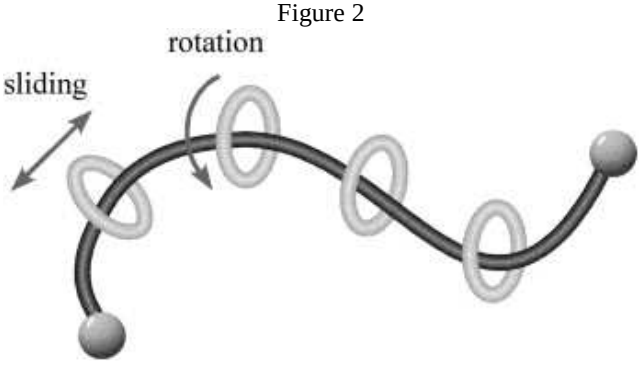
SCIENCE BEHIND NISSAN'S SCRATCH SHIELD PAINT

Every self-healing material is made of compounds and polymers specific to the researcher or company that has developed the material. Nissan has its own recipe for their self-repairing paints that is kept under lock and key. With Nissan's inability to release every ingredient to their healing paint, it is only possible to research the main components of scratch shield paint. Nissan's self-healing material consists of a network of polymers. These polymers are slide-ring structures of polyrotaxanes which give a lot of elasticity to the paint. Due to the slide-ring structure, this method of healing is intrinsic. Scratch shield paint heals itself because of its own properties rather than an addition of a healing agent. Another ingredient in Nissan's recipe is chitosan. Chitosan is a form of chitin, a polysaccharide found in marine crustaceans. When UV light reacts with chitosan, the healing process of the scratch shield paint begins. These three components are the main ingredients of the scratch shield paint and give it its physical properties.

Polyrotaxanes

Polyrotaxanes are considered a part of supramolecular chemistry. Whenever polymers have polymeric assemblies of monomers without any covalent bonding, they are considered supramolecular polymers [12]. Since these are non-covalent interactions, the bonds are formed through hydrogen bonds or Van der Waals force [12]. A polyrotaxane is an example of a supramolecular polymer. To form a polyrotaxane, a linear polymer goes through a number of cyclic molecules and the ends contain a bulky end group [12]. The purpose of these end groups is to restrict the cyclic molecules. These molecules can slide and rotate on the chain but they are unable to move off due to the end groups. The picture below is an accurate depiction of a polyrotaxane:

Figure 2

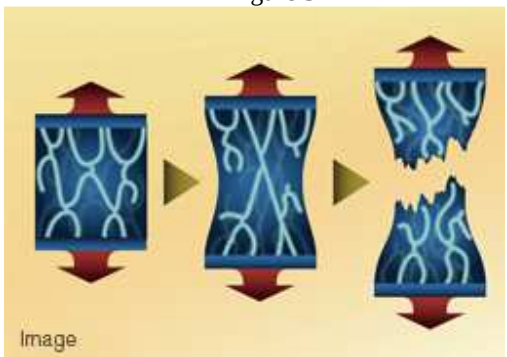


This is a typical polyrotaxane. It consists of a polymer string with cyclic molecules, trapped by bulky end groups [13].

Slide-Ring Structure

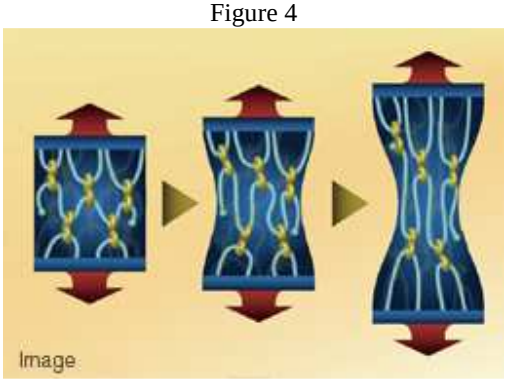
One of the most important components of scratch shield paint is its slide-ring structure. Slide-rings are formed by the cross-linking of cyclic molecules [12]. Two of these cyclic molecules bond together to create a figure-eight-like shape and they slide along a polymer chain [12]. This sliding reduces local stress on the surface as the double-loops of cyclic molecules act as pulleys [12]. This pulley-like structure gives the material much more elasticity so that it can move without tearing. The figure below depicts the different outcomes of stress put on conventional paint and stress that is applied to scratch shield paint with slide ring technology:

Figure 3



This is a visualization of the tearing of polymers of conventional paints [14].

Figure 4



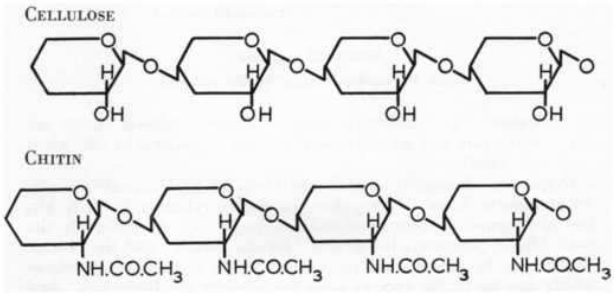
This is a depiction of the slide-ring structure of the polymers in scratch shield paint [14].

In Figure 3, which portrays conventional paint, it is seen that whenever the polymer chains are in a static state, they are likely to tear under force [14]. However, when slide-ring technology is incorporated, the stress put on the surface is dispersed. The cyclic molecules slide to withstand the impact and then they slide back to their original positions. Whenever the cyclic molecules rebound, the outer appearance goes back to normal and there is no longer damage to the surface [13]. The slide-ring structure of the polymers in scratch shield paint gives an added elasticity to the structure of the paint. This elasticity protects the polymer makeup of the material from permanent damage, and with the help of other components in the paint the scratches soon disappear forever.

Chitin/Chitosan

Among the components that Nissan has released as being in their scratch shield paint is chitin. Chitin is a hard, white, inelastic polysaccharide that can be seen all over the place in nature [15]. Chitin is commonly compared to cellulose in that they are both common polysaccharides that slightly resemble each other. Cellulose contains a string of repeating units of carbons and oxygens with some hydroxide groups coming off the strand. In chitin, some of the hydroxide groups contain acetamido groups. This is the only difference in their structures [16].

Figure 5



These two chains are the structural formulas of cellulose (top) and chitin (bottom) [17].

Cellulose has commonly been given more attention than has chitin due to the easier extraction process of cellulose. A downfall to the use of chitin is the difficulties that arise when attempting to extract it. Chitin is most easily taken from the exoskeletons of crustaceans, but this is still not an easy process. The chitin is not water-soluble, so the chitin cannot be extracted by those means. The substance containing chitin is treated with many compounds in order to remove the chitin [16].

Up until recently, chitin had only been thought of as a structural polysaccharide found in the exoskeleton for only structural reasons. New research has been conducted and concludes that chitin has many more properties that can help with many problems.

The properties of chitin that can be extremely helpful are its non-toxicity and fiber forming ability [16]. New applications have been developed in the medical field due to these properties. When someone is badly injured and needs stitches, thread made from chitin could be used because chitin would biodegrade in the body. When a severe burn occurs to the skin, artificial skin would have to be used to protect the exposed areas from germs. Chitin artificial skin has been developed to protect the exposed body and it has had wound healing abilities. This ability to heal wounds has been demonstrated in the armed forces as well. Chitin bandages are used to stop bleeding immediately upon contact by the paramedics in the armed forces [16].

With the many new applications of chitin focusing on medical needs, it is odd to think that it is a component of scratch shield paint. Scratch shield paint has a main goal that is very similar to that of the stitches and bandages: to heal. Scratch shield paint simply heals a nonliving object rather than a lobster or victim of war. Chitosan is the form of chitin used in scratch shield paint, and it uses UV light to activate its healing processes [18]. This is a source of conflict with the effectiveness of a self-healing material needing UV light, but it is very convenient for cars, which mostly sit in the sun all day.

SCRATCH SHIELD PAINT APPLIED TO IPHONES

Due to the successful outcome of the scratch shield paint on Nissan's cars, Nissan decided to expand its efforts away from the automotive industry. Apple's iPhones are a very popular phone right now. However, these high tech phones are notorious for shattering when dropped from only a few feet. Applying a clearcoat of scratch shield paint to an iPhone case changes the imminent disastrous future of a cracked screen. These upcoming iPhone cases are compatible with the iPhone 4 and 4s [7]. These cases are

likely to make iPhones life-proof for they possess very special features. Since the cases are coated with Nissan's scratch shield paint, they will be self-healing to scratches. Also, due to the gel-like, rather than glossy, surface, the cases will be much more scratch resistant, so that scratches are unlikely to form in the first place [5]. These covers are also made from ABS plastic (containing acrylonitrile, butadiene, and styrene), which is a protective material widely used in the automotive industry [5]. Unlike other cases, Nissan's new iPhone case will be tighter fitting and more rigid so that it is easier to hold. At the moment, the iPhone cases are still in the initial rounds of testing. Although many aspects of the case have proven positive, the cases still need some work before they can be released out into the market.

THE NEGATIVE SIDE OF SCRATCH SHIELD PAINT

Although there are many positive sides to Nissan's scratch shield paint, a magical all-healing paint is simply too good to be true. It has been proven that this paint works, but does it always? Scratch shield paint requires UV rays to self-heal [19]. This is quite the inconvenience during the winter months or in regions of little sunlight. It also makes it harder for the scratch on an iPhone case to go away. A car is often out in the sun for hours, but it is not often when someone leaves an iPhone sitting out in the sun. Also, if the scratch goes so deep that it breaks the bonds within the clearcoat, there is no way of fixing the paint job [19]. No amount of polishing and waxing can fix a scratch that breaks the bond of the clearcoat.

There are many YouTube videos hitting the web on the effectiveness of scratch shield paint. In a video linked on a website critiquing Nissan's scratch shield, the process of healing a scratch on a car that is coated with the healing paint is documented. The reality is that the paint works fine on the car. This is evident because there were no longer scratches visible at the end of the test [19]. Another video tests the ability of the iPhone case to heal. There is little success with the trial, but it may have been the fact that the scratch was made very deep [6].

Many car detailers' beliefs are contrary to the scratch shield paint. Although this paint is not very expensive, it is extremely difficult to work with. Unlike regular car paint, the scratch shield paint swirls when applied and does not fix the scratch. Although the paint may work for smaller scratches, it is definitely still a major work in progress.

THE FUTURE OF SELF-HEALING STRUCTURES

The study of self-healing structures is still a very new science and technology. Although the perfect design has yet to be discovered, great leaps have been made in this field of research. Even though Nissan's scratch shield paint has a few flaws, it is still usually able to repair itself and it maintains the "new car" look for longer. Once a material is designed that is able to heal every scratch and mark made, the opportunities for the application of this material are endless. Self-healing structures may one day be incorporated in everything from eyeglasses to microwaves and sporting goods to buildings. These materials are already being applied to car paint and electric circuits. Considering the clearcoat paint is fairly inexpensive, it may eventually be applied to just about every object.

SUSTAINABILITY

Sustainability is a very important aspect of every type of engineering. It is crucial that when creating new designs and products, their impact on the environment is taken into account. Self-healing structures are extremely beneficial to the environment. When a surface heals itself, there is no necessary repair to be done, and the product does not need to be disposed of. With these structures, products last longer and create less waste.

The website for EPA (Environmental Protection Agency) describes how sustainability is important in ensuring that the earth will "always have the water, materials, and resources to protect human health and our environment "[20]. A big factor today in deciding whether or not to adopt a new process or design is determining how that process or design affects the environment. The self-healing materials described in this paper will benefit the environment greatly. These materials will last longer, resulting in less toxic waste in our landfills. With less toxins in our environment, we ensure that the earth will prosper for many more years to come.

Scratch shield paint and many other self-healing materials are great resources to our environment. If these materials begin to be used widely across the world, waste can be reduced drastically. Many everyday objects that we use are disposable and do not last long without breaking. Light bulbs, for example, are a common household item. Light bulbs do not last long at all and need to be changed a few times a year. If the light bulb's filaments did not break, or could constantly heal any damage, new bulbs would not have to be produced and bought several times per year. Although light bulbs are very small objects, they create an unimaginable amount of waste which causes great harm to the environment.

Self-healing materials are being developed for applications in which a material needs to or is able to last longer, and therefore be replaced less often. This idea is very similar to recycling bags. Many supermarkets are selling reusable bags in order to reduce the waste from plastic bag usage. Plastic bags are very disposable, and usually break after one use. The new reusable bags last longer and therefore create less waste in the environment.

The reusable bags are like the self-healing materials, and the plastic bags are like the regular materials. Both the self-healing materials and the reusable bags are very helpful to sustaining a pollution free environment. Less waste in landfills leads to less harmful chemicals from the waste in our environment.

Trash that sits in landfills decomposes in the dirt. The decomposition of plastics and electronics can release many harmful toxins into the soil and air which are very unhealthy for plants, animals, and humans alike. Many activists around the world even say that the chemicals released by this decomposition process are causing cancer and global warming. These are very serious matters, and many scientists and environmentalists are searching for ways to prevent this destruction. These problems of wastes and toxins can be avoided with the use of self-healing materials. Self-healing structures can be applied to nearly anything, including electronics. When a part is damaged in a computer, or an electric circuit is broken, the part or circuit typically has to be thrown away and a new part bought. With self-healing structures, though, the computer part or circuit can fix the damage done, rather than being thrown into a landfill and taking up valuable space. This healing process saves great time and money. It also creates a much smaller amount of waste which is undoubtedly beneficial to our environment.

CONCLUSION: SELF-HEALING STRUCTURES

Technology today is focused mainly on improving lives, and making everyday life more convenient. One way that scientists are attempting to make life easier is through the creation of self-healing materials. A self-healing material would eliminate the worry of being careful not to scratch or crack a material. A self-healing circuit could save so many computers from being thrown in the trash. If very sensitive, expensive hardware contained self-healing technology, millions of dollars could be saved.

The self-healing structures that have been fully developed so far include capsule-based materials, microvascular materials, and intrinsic materials. The capsule-based and microvascular systems mimic processes that the human body completes to protect itself from damage. These are all quite amazing advances in technology, but none are foolproof. Nissan has attempted to make their car paint and iPhone case out of their scratch shield material. There is little proof for or against their new invention, but nonetheless it is a step in the right direction. Maybe years from now self-healing materials will be commonplace.

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