ChemMatters (ISSN 0736–4687) is published four times a year (Oct., Dec., Feb., and Apr.) by the American Chemical Society at 1155 16th St., NW, Washington, DC 20036–4800. Periodicals postage paid at Washington, DC and additional mailing offices. POSTMASTER: Send address changes to *ChemMatters Magazine*, ACS Office of Society Services, 1155 16th Street, NW, Washington, DC 20036.

Subscriber Information
Prices to the United States, Canada, and Mexico: $14.00 per subscription. Inquire about bulk, other foreign rates, and back issues at ACS Office of Society Services, 1155 16th Street, NW, Washington, DC 20036; 800-227-5558 or 202-872-6067 fax. Information is also available online at http://chemistry.org/education/chemmatters.html.

Question From the Classroom

By Bob Becker

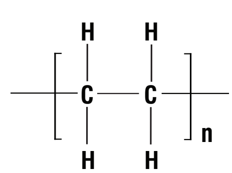
JUPITER IMAGES

Q: Lately, in chemistry class, we have been learning all about polymers. Our teacher shot some Silly String across the room, and we read an article from *ChemMatters* about how SuperBalls are made from polymers. So we know that polymers are fun, but what can they do that really matters?

A: A better question might be what CAN'T they do? From clothing to medicine to cars to computers ... you name it ... it's probably made from—or made better by—polymers. As you have learned, polymers are long-chain molecules of repeating molecular units, sometimes hundreds of thousands or even millions of units long. That may seem long, but longer still is the list of applications for which polymers have been used in every imaginable field.

One field that has gotten a lot of press lately is the war in Iraq. Consider the following examples that illustrate how polymers are used for more than just fun and games.

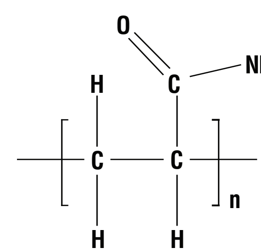
Dyneema. This ultra strong, light-weight polymer is reported to be 15 times stronger than steel (and up to 40% stronger than Kevlar, the polymer of which bullet-proof vests have traditionally been made). Body armor and flak jackets incorporate these polymers, along with ceramic plates to help protect soldiers and civilians from bullets and the shrapnel from explosive devices. Dyneema is the trade name of extremely long chains of polyethylene, also called high-performance polyethylene (HPPE). The extreme length of each individual molecule gives HPPE its unique properties. Its density is less than 1 so it floats on water, yet it is considered the strongest fiber in the world.



Dyneema, where $n > 100{,}000$

Kevlar. Panels made from Kevlar are being used to help armor the fleet of Humvees. Because its strength-to-weight ratio is so much greater than steel, Kevlar can offer the same protection as steel, without adding all the extra weight, which would reduce the speed and maneuverability of the vehicles. Kevlar is also used to coat the floors of Blackhawk helicopters.

Sodium polyacrylamide. Like sodium polyacrylate, the super-absorbent polymer used in disposable diapers, sodium polyacrylamide absorbs hundreds of times its weight in water. So what does this have to do with troops in Iraq? First, although helicopter pilots have been well trained to fly in all sorts of weather conditions, the desert climate is so dry that huge amounts of sand and dust get stirred up as they approach the ground. This can reduce visibility to zero, and can lead to very treacherous landings. Having a ground crew hose down the landing area with water does not work all that well. But there is something about sodium polyacrylamide that binds to dust, and sprinkling a layer of the polymer crystals over the sand, raking it in, and then hosing it down eliminates these rotorwash brownouts completely. With an estimated three out of every four helicopter accidents in Iraq and Afghanistan attributed to these brownouts, a little polymer can save a lot of lives.



polyacrylamide

What's more, sodium polyacrylamide has helped soldiers on the ground to stay cool. Chunks of this polymer have been sewn into cotton bandanas. During the scorching summer months, these are then soaked in water and draped around the soldiers' necks. As the water evaporates off the bandana, this endothermic process helps to cool down the bandana, as well as the person wearing it. The polymer inside then releases some of its absorbed water and the evaporation can continue for many more hours of cooling than a simple water-soaked bandana could provide.

A third use for this superabsorbent polymer is in self-pressurizing tourniquets. Tourniquets are nothing new; for centuries, straps have been tightened around soldiers' limbs to prevent blood loss. You see them in just about every war movie ever made. But the use of tourniquets is actually quite controversial: the restriction of blood flow often results in the loss of what otherwise would have been a healthy arm or leg. How do you apply enough pressure to minimize blood loss, but not restrict blood flow to the rest of the limb? Hemodyne (a company in Virginia) has come up with a solution: the BioHemostat is a bandage which absorbs the blood—thanks to the sodium polyacrylamide inside—and as it expands, it applies just the right pressure to stop the bleeding but not the blood flow.

Semiconducting organic polymers, or SOPs. A research team at MIT led by chemist Tim Swager and electrical engineer Vladimir Bulovic has designed a new line of SOPs that have the capacity to sniff out explosives with greater sensitivity than any other detection method yet developed. When ultraviolet light of just the right intensity is shined upon a film of these SOPs, the film produces laser light. But when a molecule of trinitrotoluene (TNT) binds onto the polymer chain, the laser action ceases. This effect is sensitive enough to detect TNT molecules at concentrations of only a few parts per billion. According to the researchers, new technologies for explosives sensing could help protect soldiers from improvised explosive devices (IEDs), one of the greatest threats facing Coalition Forces in Iraq. Enhancing the sensitivity of these detection systems could increase the distance at which explosives can be identified, giving the soldiers greater standoff capabilities.

Silly String. (That's right: Silly String!) Whereas SOPs may pave the way for a very high-tech IED-detection system, a much lower-tech solution comes in a can—and in a variety of bright, festive colors. This is ingenuity at its best. Before searching a building, ground troops have taken up the practice of spraying Silly String across the doorways and into each room. The IEDs are often triggered by extremely fine, nearly invisible trip wires. When the strands of Silly String land on the floor, the room is considered safe to enter. But when the strands get caught in mid air ... soldiers beware! Better living through chemistry, no doubt. If only all of the challenges in Iraq had such simple solutions.

ChemMatters®
Vol. 25, No. 2 APRIL 2007


MIGUEL CRUZ


GETTY IMAGES


MIKE CIESIELSKI


ASSOCIATED PRESS IMAGES

TEACHERS!
FIND YOUR COMPLETE TEACHER'S GUIDE FOR THIS ISSUE AT
www.chemistry.org/education/chemmatters.html.

PAINTBALL

Chemistry Hits Its Mark

PHOTOS BY MIGUEL CRUZ

Your heart is pounding as your adrenalin skyrockets. Projectiles whiz past your head as you dive for cover behind a makeshift plywood barrier. You return fire, but you know you are outnumbered. The enemy is closing in. Suddenly, you're hit. You reach for the wound. Your fingers are covered in a sticky red liquid. You have become another casualty. Fortunately, the red liquid is not blood, and the battle you have bravely fought is not actual combat—it is the exhilarating sport of paintball!

The first paintballs were fired by foresters and ranchers to mark trees and cattle. Then someone got the bright idea that it would be more fun to fire paintballs at people than at trees and cows. Thus the sport of paintball was born. From its inception in the 1980s, the sport has grown by leaps and bounds. Today, over 10 million people participate annually in paintball games. Over 1 billion paintballs are produced each year!

Although there are numerous variations, players typically attempt to capture an opponent's flag without being shot by a paintball. The first team to capture the opponent's flag and return it safely to their territory is the winner. The action is fast and furious, with a typical game lasting anywhere from 5 to 30 minutes. Sound dangerous? Other than a little bruising, it's actually safer than golf because of the protective face gear that all players are required to wear. And the game itself would not be possible without—you guessed it—chemistry!

By Brian Rohrig

Paintballs

Paintballs are a marvel of both engineering and chemistry. They must be strong enough to be fired at an initial velocity of up to 91 m/s (200 mph) without breaking, yet burst open when they hit someone without causing any tissue damage beyond mild bruising. The deformation of the paintball on contact greatly increases its stopping time, thus lessening the force (and the sting) of its impact. To accomplish this task, paintballs are made with a tough but elastic outer coating of gelatin, with a liquid center. The process by which liquids are manufactured within a gelatin shell is known as encapsulation.

Encapsulation technology originated with the pharmaceutical industry. The process involves enclosing a substance—either liquid or solid—within a thin transparent gelatin membrane. These capsules are commonly called soft gels, since they are somewhat elastic and give a little when squeezed. Soft gels are commonly used for medicine, vitamins, bath oil beads, and a variety of other applications.

Gelatin is made from denatured collagen fibers, which are derived from the skin, bones, and connective tissue of animals. The gelatin for paintballs is usually made from pig skins, which tend to make the best paintball. A plasticizer is also added to increase stability and make the gelatin more moldable. The gelatin-plasticizer ratio is formulated so as to establish the optimal balance between elasticity and brittleness, enabling the paintball to break open on impact yet not break when initially fired.

MIKE CIESIELSKI

Though technically not water soluble, gelatin does break down in water to form a colloidal gel. That is why it is so important to keep paintballs dry. Gelatin is used in a variety of foods. Jell-O, marshmallows, gummy bears, ice cream, yogurt, cream cheese, and margarine all contain gelatin. Its unique constitution helps to give foods thickness and texture. And it provides the perfect medium to keep the paintball intact—until it hits you!

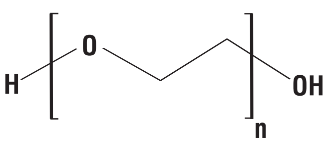
A typical paintball is 68 caliber, meaning its diameter is 0.68 inches (1.7 cm). They are also available in other sizes as well. Paintballs come in a variety of colors; some glow in the dark, others fluoresce under black light.

The first paintballs were not water soluble, since they were similar to the original formulation which was used to mark trees and cattle. When a forester marks a tree, it is important that rain not wash off the mark. The first paintball contests resulted in a lot of stained and ruined clothing, to the chagrin of many parents.

In the mid-1980s, the paintball manufacturers decided to make a water-soluble paintball. This was a daunting task, since the "paint" for the paintballs could not contain any water or else they would break down the gelatin shell. This feat was accomplished by using water-soluble compounds, but not water itself. And once paintballs became water soluble, the popularity of the sport skyrocketed.

After much research, it was determined that polyethylene glycol (PEG) would be an excellent substance for the liquid inside of a paintball.

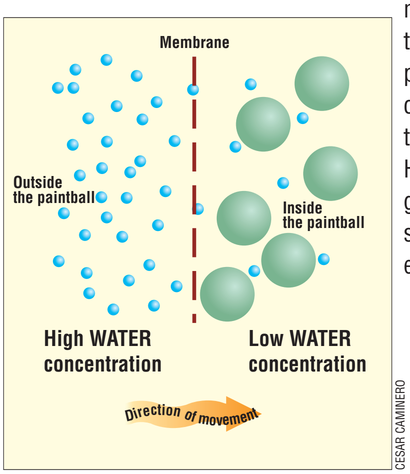
Polyethylene glycol is a tasteless, colorless, and nearly odorless compound that dissolves in water but has no effect on the gelatin shell. PEG is very viscous, meaning it flows slowly. Its thick syrupy consistency makes it perfect for use in paintballs; they have a consistency somewhat like blood when they break open.



polyethylene glycol, PEG

That's swell

If a paintball is dropped into a beaker of water, it will expand to an impressive size. Through osmosis, water will pass through the gelatin membrane and hydrogen bond with the polyethylene glycol within. Since the concentration of water is much greater outside of the paintball than inside, water will diffuse inward in an attempt to equalize the concentration of water. Water will continue to travel through the gelatin membrane until the concentration of water inside the paintball is equal to the concentration of the water on the outside of the paintball. However, as it swells the gelatin shell will break down, spilling the contents before equilibrium is reached.

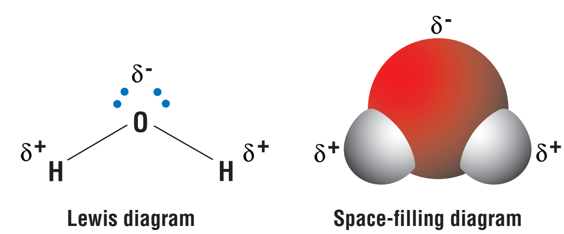


Osmosis: a paintball swells up when placed in water.

As you can see, paintballs are not really made from paint, but rather from a mixture of non-toxic food grade ingredients. The exact combination of ingredients is a trade secret but we do know that in addition to polyethylene glycol, they also contain colored food dyes, preservatives, and a thickener such as starch or wax. The ingredients within the paintball are also biodegradable, so they pose no threat to wildlife or the environment.

Bonding with your paintballs

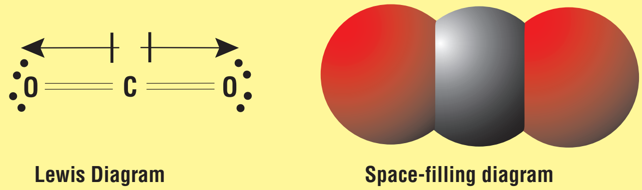
What makes paintballs water soluble? The answer lies in polarity and hydrogen bonding. Water is a polar substance that has distinct regions of positive and negative charge. Water's polarity is due to the differences in electronegativity between oxygen and hydrogen. Electronegativity, as defined by the late American chemist Linus Pauling, is "the power of an atom in a molecule to attract electrons to itself." Oxy-



Two representations of water, showing regions of partial charges.

Are all molecules with polar bonds polar?

The answer is no; in some cases, the polarity of the bonds is effectively cancelled. Consider a CO_2 molecule. Oxygen is more electronegative than carbon, so the covalent bond between the two atoms is polar. This is called a polar covalent bond; the O-H bond in a water molecule is also polar covalent. The polar nature of this bond is indicated by the arrow (+⟶) in the figure below. But the linear nature of the CO_2 molecule dictates that, overall, the molecule is nonpolar. That's because while one oxygen atom is drawing bonding electrons toward itself, the oxygen atom on the other side of the molecule is doing the same thing; the net effect is that they cancel each other out. That makes CO_2 a nonpolar molecule.



Two representations of CO_2, showing an overall nonpolar molecule.

So when predicting the polarity of a molecule, the shape must be considered. Often, molecules that are symmetrical will be nonpolar even if polar bonds are present.

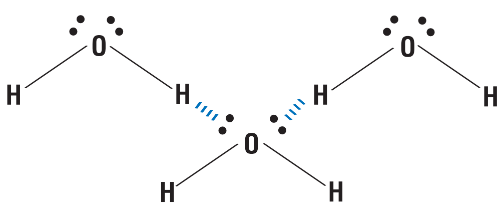
MIGUEL CRUZ

gen is more electronegative than hydrogen, so it attracts electrons to itself more strongly than does hydrogen. For a water molecule, this creates a region of partial negative charge (δ^-) on the side of the oxygen atom, and a region of partial positive charge (δ^+) on the side of the hydrogen atoms.

Because of the shape of the water molecule, these polar bonds make the molecule polar overall.

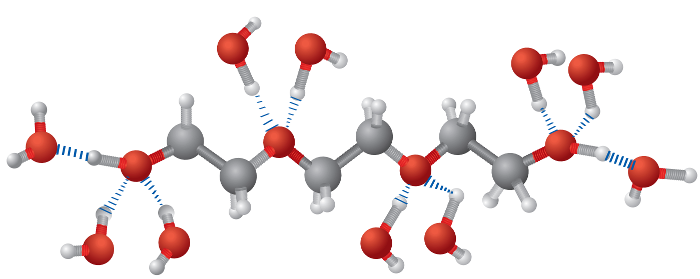
Polar molecules are attracted to other polar molecules. This attraction is due to the positive side of a polar molecule being attracted to the negative side of another polar molecule. This attraction is the basis of the intermolecular bonding that may occur when one substance dissolves into another. This tendency is summed up nicely in the principle "like dissolves like," meaning that polar substances dissolve in other polar substances.

We can take a closer look at the interaction between water and polyethylene glycol molecules. The oxygen atoms in the polyethylene glycol chain each have two nonbonding electron pairs. The partial positive charges around the hydrogen atoms in water are attracted by these



Hydrogen bonding between water molecules.

nonbonding electrons. This particular type of intermolecular attraction is called a hydrogen bond. Hydrogen bonds occur when a hydrogen atom attached to a small, highly electronegative atom (typically F, N, or O) is in the vicinity of an atom with nonbonding electron pairs. Although not as strong as covalent or ionic bonds, hydrogen bonds are the strongest of the intermolecular forces. The hydrogen bonds between water molecules are responsible for its unusually high boiling point.



Hydrogen bonding (blue lines) between polyethylene glycol and water. Hydrogen bonds are about 1/15th the strength of a covalent bond. Red = oxygen atoms, grey = carbon atoms, and white = hydrogen atoms.

The dyes used in paintballs are also polar and water soluble. The polar nature of the polyethylene glycol enables these water-soluble dyes to be dissolved within the paintball. We can't show you the structures of the dyes because they are proprietary—that means a closely guarded secret. But the colored dyes and the polyethylene glycol are water soluble, so today, when a paintball combatant returns from the field of battle and her clothes are splattered with paint, they simply need to be thrown into the wash and they will generally come out clean—though it may take more than one washing!

Magic markers

The firing instruments used to shoot the paintballs have come a long way since the game began. Known as markers rather than guns, they have evolved from hand-cocked, single-shot pistols into rapid-firing, high-precision instruments. The "marker" term arose from the first use of paintballs, which was to mark trees and cattle. The term also gives the sport of paintball a less violent image.

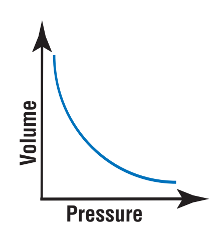
JUPITER IMAGES

The markers come in a variety of makes and models—from pistols to semiautomatic rifles. Some models can fire 100 paintballs at 30 per second using a single 12-gram CO_2 cartridge. Extra large hoppers (the storage chamber that holds the paintballs before they are fired) can hold up to 250 paintballs. Fully automatic models are available, but these are prohibited on most playing fields. There are even paintball "landmines" that will spray paint all over whoever is unfortunate enough to step on one.

Markers all operate on the same basic principle—using compressed gas to launch a paintball. Gases can be readily compressed because there is so much space between the molecules. When the marker is cocked, a paintball falls from the hopper into the barrel. When the trigger is pulled, a quick blast of compressed gas is released directly behind the paintball, propelling it forward at an initial velocity up to 91 m/s.

It's a gas

The most common gas used in paintball markers is compressed CO_2. The CO_2 within a gas canister is at an extremely high pressure—around 800–850 psi (pounds per square inch). At this pressure, however, CO_2 will actually liquefy. So, within the high-pressure confines of a gas cartridge, much of the CO_2 will typically exist as a liquid. The liquid is actually responsible for controlling the pressure of the CO_2. As long as there is



Boyle's Law

some liquid present, the pressure of the gas in contact with the liquid will remain constant. The pressure of the gas will equal the vapor pressure of the liquid. Thus, the pressure of the CO_2 will stay constant for each shot; if there were no liquid present, releasing the gas would decrease the pressure of the remaining gas. However, if the marker is fired many times in succession, the pressure will temporarily drop since it takes some time for the liquid CO_2 to vaporize and restore the pressure.

The vapor pressure of CO_2 at room temperature is about 60 times atmospheric pressure. To prevent a canister from exploding under high pressure, CO_2 tanks are fitted with a copper burst disk that is made to pop off if the pressure exceeds a safe level. This varies between 2200 psi and 2800 psi, depending on the manufacturer.

When a small amount of this gas is released, it expands greatly, since it is now under much less pressure. Boyle's law states that the volume of a gas is inversely proportional to its pressure, so long as the temperature is held constant. Inversely proportional means that when one factor decreases, the other increases. When the volume of a gas goes down, its pressure goes up. Likewise, when the pressure decreases, the volume increases.

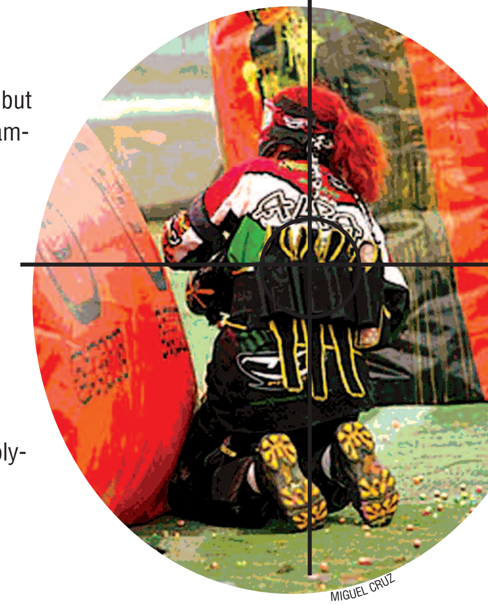
The paintball is propelled forward by the increase in the volume of the CO_2, which is due to the decrease in pressure the gas experiences as it leaves the cartridge and enters the firing chamber. The only thing standing in the way of the expanding gas is the paintball, which is launched effortlessly through the air.

Just do it.

The sport of paintball is highly addictive. Serious players can spend hundreds, or even thousands, of dollars on high-tech gear. There are numerous organized leagues and tournaments in nearly every state and in countries around the world.

Even the U.S. Army is getting into the game; they have made an arrangement to sponsor the Long Island Big Game, to be held May 19–20, 2007, in New York. Organizers expect over 2000 players, and the game will feature tanks, a helicopter, missions, and prizes.

A few bruises are a small price to pay for a sport that not only is immensely entertaining, but also teaches strategy, builds teamwork, and provides great exercise. And if that upcoming chemistry test is stressing you out, there is no better way to relieve that stress than by heading to the woods with some friends and blasting each other with spheres of brightly colored gelatin-encapsulated solutions of pigment used polyethylene glycol!



MIGUEL CRUZ

Can you find the density of a paintball?

Paintballs come in various sizes, but a typical paintball will have a diameter of 1.7 cm and a mass of 3.1 grams. Can you determine the density of a paintball? The formula for the volume of a sphere is $4/3\ \pi\ r^3$. The formula for density is m/v.

You can find the answer on page 20.

Ten tips from tourney players

Get in shape: It's a physical sport. Eat well, stay active, and cut bad habits such as smoking.

Protect yourself: Cover up with appropriate gear to prevent bruises or a blood clot.

Know the rules and abide by the do's and don'ts. Be a good sport.

Learn to shoot with either hand. This increases your mobility.

Be unpredictable: Make yourself a harder target for the competition.

Prepare: Study the game and walk the field. Pack your gear the night before.

Communicate with team members. Tournament players yell at each other constantly.

Practice: Simple drills can improve your aim.

Be safe: Always wear your mask, listen to the ref, and follow the rules of the field.

Always treat a marker as if it is loaded.

REFERENCES

Chemical Institute of Canada.

http://ncwsnc.cheminst.ca/articles/1994_paintballs_e.html (accessed Feb 2007). Paintballs and Canadian National Chemistry Week.

Enotes.com. http://science.enotes.com/how-products-encyclopedia/paintball (accessed Feb 2007). How paintballs are made.

Madpaintballer.com. http://www.madpaintballer.com/make_paintballs.php (accessed Feb 2007). How to make paintballs and more.

Brian Rohrig teaches at Jonathan Alder High School in Plain City, OH. His most recent *ChemMatters* article, "NASCAR: Chemistry on the Fast Track," appeared in the February 2007 issue.

Retiring ld Tires

GETTY IMAGES

By Donald Jones and Helen Herlocker

You're walking through a city neighborhood and suddenly—what's this?—you're bouncing and springing along the sidewalk. You look down, and the pavement is some vibrant shade of brown or red—no graffiti, cracks, or chalked messages. Nice! Pedestrians with tired feet are giving it rave reviews. Tree roots can bend it but not crack it. What is it? It's one of the new rubberized surfacing materials generated from old tires. And the good news is that we're not going to run out of that source any time soon.

Presently, approximately 300 million used tires are generated annually in the United States alone. In the early 1990s the growing stockpiles of scrap tires reached as many as 3 billion, with at least another 240 million adding to the problem every year. Although limited uses were found for about one-quarter of them, the others remained, layer upon layer, in surface storage sites and landfills. There, they collected stagnant water and housed disease-spreading insects and rodents. Worst of all, they frequently caught on fire.

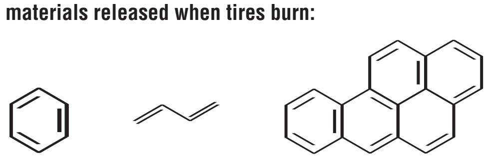
Burning ring of tire

Actually, why not burn them? Just ask anyone who has been anywhere near a burning heap of tires; they will tell you that you don't want to go there. Thick solid tires, unlike granular coal or liquid petroleum, burn slowly, releasing black clouds of noxious volatile organic compounds (VOCs). For every kilogram of tire, approximately 11 g of VOCs, 4 g of semi-volatiles, and 4 g of polycyclic aromatic hydrocarbons (PAHs)—especially dangerous carcinogens—are released into the atmosphere. Given the fact that the average tire weighs about 9 kg, you can appreciate the environmental impact of a burning heap of tires.

In February 1990, an arsonist ignited 14 million scrap tires piled outside the town of Hagersville, Ontario, Canada. The fire burned for an agonizing 17 days, caused the evacuation of over 4000 people, and cost over $10 million in firefighting and clean-up costs. A similar fire plagued Wesley, CA, in September 1999, when firefighters from several states joined local firefighters to extinguish the blaze that started in a storage site containing 5 million tires.

CA INTEGRATED WASTE MANAGEMENT BOARD-TODD THALHAMER

Some of the materials released when tires burn:



Zn Pb

benzene **1,3-butadiene** — **volatile organic compounds**

benzo[a]pyrene — **a polycyclic aromatic compound**

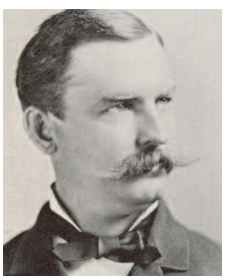
metals

Firefighters and environmental workers dread tire fires! They are especially difficult to extinguish when compared to other fires. Extreme heat liquefies the rubber, turning it into oil. With each tire generating about two gallons of oil as it burns and liquefies, a fire like the one in Ontario can release over 20 million gallons of toxic oil to either burn or leach into the soil of surrounding farmlands.

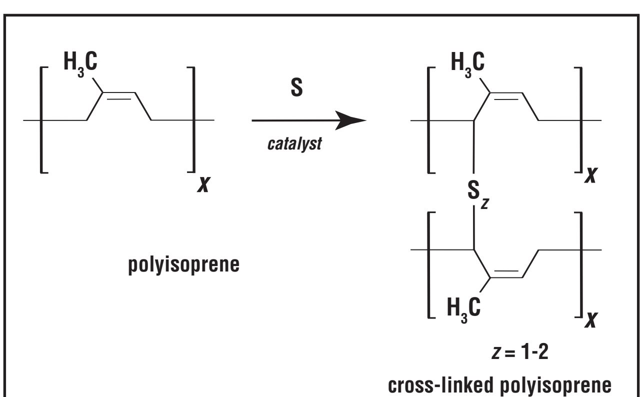
Rubber

Natural rubber, a wet sticky plant product, is an example of a polymer, a molecule in which repeating molecular subunits form chains. These chains are generally linked to one another by atomic bridges called cross-links. It's the number of these cross-links that give rubber its characteristic properties.

History credits New Jersey chemist Charles Goodyear for inventing a process in the mid-19th century for controlling the number of cross-links in uncured rubber. The initial result was a product much more durable and chemically resistant than the original, but would begin to deteriorate within a few days, gradually breaking down into a wet crumbly mess. Vulcanization, a chemical process named after Vulcan, the Roman god of fire, adds more cross-links by introducing sulfur at high temperatures. Along the rubber molecule, there are several sites called *cure sites*, which are particularly attractive to sulfur atoms. During vulcanization, highly reactive sulfur atoms form chain-like bridges that span from a cure site on one rubber molecule to one on a neighboring molecule.


COURTESY OF THE GOODYEAR TIRE & RUBBER COMPANY

Charles Goodyear



Vulcanization of natural rubber

Chemists have developed ways to control the vulcanization process to favor either short or long sulfur cross-links between rubber molecules. Short cross-links (1 or 2 sulfur atoms) result in a product with good heat resistance, while longer cross-links (3–8 sulfur atoms) give the rubber more elasticity and flexibility. Blends of natural and synthetic rubber (along with many other materials) can be used to make a very sturdy automobile tire that can last around 40,000 miles.

Then what?

Given the danger, public safety issues, and the negative environmental impact of costly tire fires, all but eight states have laws severely restricting the disposal of scrap tires in landfills. In some rural areas, regulations like these have led to unfortunate measures of local convenience. Streams, rivers, and hillsides are often found littered with old tires with no uses and no immediate means of disposal.

So, what do you do with hundreds of millions of old tires? Just as the problem seemed hopeless and the stockpiles were reaching a critical mass, economic reality entered the picture. The cost of virgin rubber on the world market started to rise as dramatically as the price of crude oil rose. Manufacturers began eyeing the vast and growing stockpiles of rubber tires with new interest. Today, new and creative uses for recycled tires, like the sidewalk mentioned earlier, are springing to the forefront.

Three uses for an old tire

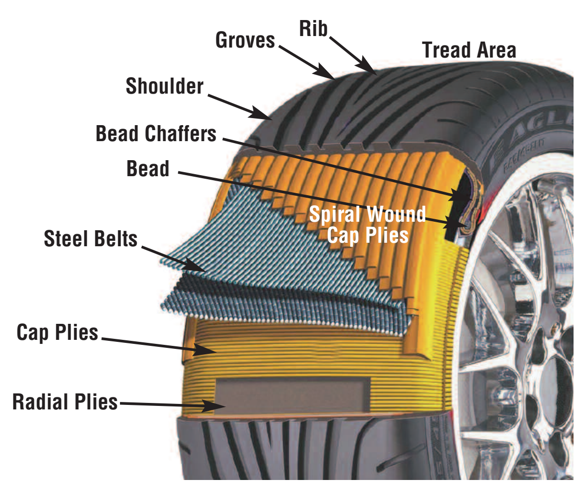
Light my tire

The first use—as fuel—may be particularly hard to believe, given all we've said about burning tires! But nearly half of the used tires generated in the United States over the past few years have become tire-derived fuel (TDF), providing energy for a variety of industrial and public utility applications. Major users include cement kilns, pulp and paper mills, electric utilities, and various industrial boilers. In all three uses the steel "bead" used to attach the tire to the rim of the wheel is removed before shredding. For some applications, whole tires, including their fabric and steel components, are used. In others, whole tires are preshredded to expose more surface area for combustion. Burned under carefully controlled conditions, the energy recovered per ton of tires is somewhat larger than that for coal and about the same as for oil—not so surprising given the largely hydrocarbon composition of vulcanized rubber.

TDF has another advantage: Under the right conditions, it is a cleaner fuel than either coal or oil. With no nitrogen content, TDF combustion results in less nitrogen oxide (NO_x) emissions into the atmosphere. Although any burning in the presence of air will result in a reaction between atmospheric nitrogen and oxygen to form NO_x, fuels like certain coals and oils bring enough of their own nitrogen to the mix to increase NO_x emissions dramatically. Oil can contribute as much as 50% of the total, and coal, as much as 80%. As for TDF, make that a zero. Burning TDF will result, however, in some SO_2 emissions, because of the sulfur introduced in the vulcanization process.

Engineering projects

A second broad area of use for about 20% of used tires is in civil engineering projects—projects taking advantage of the chemical stability and resilience of vulcanized rubber. For these projects, tires are shredded into tire-derived aggregates (TDA)—pieces and particles ranging in size from 2 to 12 inches depending on the intended use. The *U.S. Scrap Tire Markets 2003 Edition*, published by the Rubber Manufacturers Association, describes several applications for TDAs.



COURTESY OF THE GOODYEAR TIRE & RUBBER COMPANY

Parts of a tire.

Most of them are used as filler in landfills, where their superior properties make them useful for enhancing drainage, venting gases, closing caps, lining collection vessels, and providing additional surface cover. In addition, less costly than stone, TDAs work well in septic drain fields, where they enhance the drainage spaces for wastes. For large-scale, civil engineering projects, TDAs are valued as subgrade fill for embankments, where the existing soils are too weak for the task. You might see TDAs at work in highway construction projects as fill material behind walls and bridge abutments—projects in which the light weight, superior drainage properties, and low-cost make TDAs the best choice for the job.

Crumb rubber products

The third application for scrap tires, about 11% of them, includes a growing array of products requiring an initial and somewhat costly pretreatment to yield crumb rubber. For these applications, the steel and fabric components of the tire must be separated away, leaving the vulcanized rubber to be ground or cut to the required crumb size.

PHOTOS COURTESY OF TOTTURF.COM

Crumb rubber may be used for shock absorbing playground floors.

Imagine the logistics. It would be difficult enough to rip away the fabric and steel from one tire. But for hundreds of millions of them? The task on that scale requires knowledge of the physical and chemical properties of all of the tire components. One separation strategy begins by physically grinding whole tires into pieces of about 2 inches in diameter. These pieces are fed into a granulator where their size is reduced even further. At this stage, the remaining steel is removed by magnets, and the fibers are sifted out on shaking screens. Finally, the separated rubber is refined to the particle size required by the manufacturer.

A second method, called the cryogenic method, uses liquid nitrogen or supercooled air to freeze the ground tire stock into solid chips. A hammer mill pounds and shatters the chips, liberating the steel and fabric in the process. Then, as in the previous method, magnets and sifters remove the extraneous material, leaving exceptionally clean vulcanized rubber. By either method, clean crumb rubber is generated for any use to which costly virgin rubber is suited.

The applications and demands for crumb rubber increase every year. About one-third of it is used in the manufacture of rubber-modified asphalt (RMA), for a wide variety of surfaces. Arizona and California use most of the available RMA with growing demands in Florida, Texas, and other states. While initial production costs are high, RMA produces long-lasting road surfaces with low maintenance requirements, thereby making it cost effective in the long run. Used on highways, RMA surfaces reduce noise and shorten braking distances—features appreciated by consumers. Resilient and stable crumb rubber is attractive for surfaces under playground equipment, as a soil additive under athletic fields, and as surface material for tracks—applications with obvious human safety advantages.

Clean crumb rubber has one more obvious use, one that may eventually overtake all of the others—tire manufacturing! Presently, it constitutes a portion—about 10% in the United States—of the mix used to manufacture new tires.

Looking to the future

How far have we come toward solving the environmental problem of scrap tires? Recall that in the early 1990s there was a growing mountain of them, as many as 3 billion crowding landfills and other collection sites. Then, only about 25% of scrap tires were being reused and repurposed. Today, the news is getting better—a lot better thanks to economic realities and new industrial techniques. Today, about 80% of our annual crop of 300 million used tires will find new uses. And as for that stockpile? There are about a quarter of a billion left. Got any ideas?

What's in *your* tires?

The Goodyear P195/75R14, a popular sized tire, weighs about 21 pounds and contains:

Approximate Composition	
Carbon	85%
Ferric material	10–15%
Sulfur	0.9 to 1.25%

Making sandals from old tires!

PHOTOS COURTESY OF THOMAS J. ELPEL, WWW.GREENUNIVERSITY.NET.

How about getting 40,000 miles out of a pair of sandals? For information on how you can make your own pair of tire sandals, go to http://www.hollowtop.com/sandals.htm.

REFERENCES:

U.S. Scrap Tire Markets—2003 Edition, Rubber Manufacturers Association, 1400 K Street, NW, Washington, DC 20005 (July 2004).

EPA web site; http://www.epa.gov/epaoswer/non-hw/muncpl/tires/basic.htm. Management of scrap tires.

Kurt Reschner, http://www.entire-engineering.de/str/Scrap_Tire_Recycling.pdf. Scrap tire recycling.

Donald Jones, an active ACS member, taught chemistry at MacDaniel College in Maryland. ***Helen Herlocker***, a science writer, is a former editor of *ChemMatters*.