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Polymers

by Joseph Alper

In the 1800s, anyone who was anyone owned a pool table, complete with hand-crafted ivory billiard balls. This meant trouble for African elephants, whose tusks commanded a handsome bounty. The largest flawfree tusks were made into billiard balls; less perfect tusks became bracelets, combs, and piano keys. Predictably, ivory hunters soon decimated the elephant herds that roamed the plains of Africa and the jungles of Asia, and the manufacturers of billiard balls became alarmed at the diminishing supply of their raw material.

By 1863, the ivory shortage had become critical. This prompted officials at Phelan and Collender, a billiard ball manufacturer in New York, to sponsor a competition. The prize was $10,000 to the first person who developed a satisfactory synthetic ivory. A young printer in Albany, N.Y., John Wesley Hyatt, heard about the contest and, with his brother Isaiah, set out to win the prize. The Hyatts never received the prize money, but their efforts led to a discovery that would change the world. They invented celluloid, the very first plastic.

Celluloid

This substance was like nothing ever seen before. In many ways it resembled ivory. It was smooth, hard, and wear-resistant, and it could be carved. But when heated, celluloid took on the consistency of candle wax and could be pressed into molds or rolled into sheets. This was a tremendous advantage for manufacturers. Instead of carving each piece of solid raw material into an intricate shape, they could make the shape just once—as a mold—then turn out thousands of perfect copies.

Celluloid caught on quickly. It was used to make combs, dentures, and window curtains for early automobiles. Demand for the wonder material was so high that in 1871 the Hyatts formed Celluloid

Manufacturing Co., which later became part of Celanese, now one of the world's largest chemical manufacturers.

Totally man made

Forty-four years later, in 1907, the American chemist Leo Baekeland invented the first totally *synthetic* plastic, which was not based on materials from nature. With very little modesty he called it Bakelite. Like the Hyatts, Baekeland was searching for a material to replace a natural product, in this case shellac, which was obtained from the secretions of the Indian *lac* bug. Like any good scientist, Baekeland started his quest by searching through the chemical literature.

It was a reported failure that attracted his attention. Thirty-five years earlier, the German chemist Adolf von Baeyer had mixed phenol, a commonly used disinfectant, with formaldehyde and obtained a hard, insoluble mass that ruined laboratory equipment because it could not be removed once it had formed. To most chemists, this was an outcome to be avoided at all costs, but not to Baekeland.

He decided to investigate this reaction further and found that phenol and formaldehyde would react at room temperature to form a new material—a plastic solid that could be put into a mold and heated to give a hard, insoluble solid. This was Bakelite, the first polymer deliberately created from "scratch" in the laboratory. It was such a good material that today, more than 75 years later, it is still used to make many molded objects such as automobile distributor heads, insulators for power lines, and knobs for radios.

Polymers

Other synthetic materials followed on the heels of Bakelite's success, and today we are surrounded by thousands of polymer products. Our clothes are polymers, from nylon or cotton undergarments to polyesterblend wash-and-wear shirts to acrylic sweaters. At picnics we eat with plastic forks, drink from styrofoam insulating cups, pour soft drinks from plastic bottles, and wrap our food in clear films. Polymers are used in personal computers and ball point pens, disposable diapers and bullet-proof vests.

What are these ubiquitous materials with so many forms and functions? All polymers are giant molecules, made up of many units called monomers. The word *polymer* comes from the Greek words *polys,* meaning many, and *meros,* meaning part. Likewise, monomer means single part. For example, polyethylene, familiar to us as clear bags, is made by bonding together many monomer units of ethylene molecules, $CH_2=CH_2$, as shown in Figure 1. A typical polyethylene chain can contain 10,000 to 20,000 repeating ethylene units and have a molecular weight of 280,000 to 560,000.

Some polymers are named after the chemical bond formed between the monomers. Polyesters, for example, are a family of polymers in which the monomers are joined by an *ester* chemical group. Polyesters can be made into strong fibers that are often woven with cotton to make wrinkle-resistant fabrics (Figure 2).

Polyamides are another family, one in which the monomers are linked by amide groups. These include nylon, used in carpets and everyday clothing, and polyaramids, a special group of extremely strong polymers used to replace steel tire cord and to make bullet-resistant vests and experimental plastic auto engines (see box, Plastic engines).

Polymers can be made from more than one kind of monomer. Bakelite, the first synthetic polymer, was made of two monomers, phenol and formaldehyde. Nylon is made from *adipic acid* and *hexamethylene diamine,* and the new plastic beverage bottles are made from *ethylene glycol* and *terephthalic acid* (see box, Making a PET bottle).

Designer polymers

Polymers have become valuable because they have such a wide variety of properties and because polymer chemists have learned much about designing polymers with specific properties. As you might expect, the chemical composition of the monomer plays an important role in determining a polymer's characteristics.

What is much more surprising is that chemically identical polymers can have dramatically different properties because of *physical* changes in the polymer structure. Polyethylene, for example, can display many different traits. Look at the many ways this substance has been put to use, each of which relies on different physical properties. It is used to make

- flexible plastic milk bottles,
- clear, stretchable food wrap,
- rigid bleach bottles,
- artificial ice for skating rinks,
- wind-blocking insulation for homes, and tough, tear-resistant paper.

It is almost as if a different material were used in each application. In fact, they are all polyethylene.

If ethylene is simply heated in the presence of the right catalyst (a compound that speeds a chemical reaction without itself being used up), the result is a polymer with very long and completely linear molecules. Polyethylene made in this manner is fairly strong and melts at about 135 °C. It is called high-density polyethylene (HDPE) and is made into products by injecting it while warm into a mold or rolling it into sheets. It is used to make sandwich bags, trash bags, and milk bottles.

Branching out

If the polymerization reaction is run at much higher temperatures and under extreme pressure, the polymer formed has shorter chains with many branches. The branches prevent the chains from packing together well; they act like stacked up dead tree branches. This is low-density polyethylene (LDPE). It is more flexible than its high-density cousin, but it is weaker than HDPE and it melts at a lower temperature. LDPE with many branches is used to coat cardboard milk cartons. With fewer branches, it makes a fine wrapping film.

If ethylene is polymerized with yet another type of catalyst, ultrahigh-molecular-weight polyethylene (UHMWPE), is formed with a molecular weight greater than 5-10 million. This polymer is so viscous that is cannot be formed readily even at temperatures much above its melting point. It is extremely abrasion resistant and is used for bearings and as plastic ice is skating rinks. Another way of manipulating polyethylene produces a tough, paper-like material, called Tyvek (see the article on p. 8).

Ivory hangs on

The polymer industry got its start more than 100 years ago with a search for synthetic ivory. Since then, scientists have developed countless polymers that have replaced ivory in most applications. Ivory piano keys have been replaced with keys of styrene-acrylonitrile. Ivory chess pieces have been replaced by ones of polystyrene. However, no single material has successfully duplicated all the properties of ivory, and some unique ivory properties have never been duplicated.

The strings on a violin are traditionally supported by an ivory bridge. Ivory is the preferred material because it is strong enough to support tightly wound strings and it also transmits acoustic vibrations well without favoring certain notes. Ivory was the only material with this combination of properties until now.

O.A. Battista, a chemist and inventor in Ft. Worth, Tex., was working on a method for recycling scrap polymers. Every year, millions of pounds of torn nylon stockings, worn-out polyester clothes, empty polyethylene milk bottles, and crushed polystyrene coffee cups go to waste. In fact, some of the properties that give synthetic polymers advantages over wood and paper in daily use become handicaps at throw-away time. When dumped into a landfill, many of these strong, insoluble substances are not biodegradable. Battista was trying to develop a method for reusing scrap polymers. Years earlier, he had found that dilute hydrochloric acid would break down the cellulose polymers in cotton and wood into small clumps called microcrystals. Microcrystalline cellulose, as this product is called, is now the most common source of fiber in high-fiber foods.

A few years ago, Battista noticed that when water evaporated from a suspension of microcrystalline cellulose, a hard, white block was formed. By tinkering with the evaporation process and adding small amounts of protein and calcium phosphate, both components of natural ivory, he found that he could make a material that resembled ivory in every way except two: It costs much less than natural ivory and it does not require killing elephants.

We have grown accustomed to seeing nature's materials replaced by synthetic ones. Tennis rackets are no longer made of wood, and their strings are no longer catgut. Polymers have replaced metal in cars, cotton in clothes, and wood in furniture. In recent years, medical scientists have used polymers to make artificial hearts and pills that release drugs gradually for weeks or months. These modern applications seen far removed from the nineteenth century concern over the supply of ivory. Yet, it was the near extinction of the elephant that triggered the beginning of the synthetic polymer industry. And it was a polymer chemist who finally gave the elephant back his tusks.

SIDE BARS

Plastic

Celluloid was revolutionary because it was a solid that could be made pliable and claylike for molding. Under heat and pressure, it changed from being rigid to being pliable, or *plastic.* The name of this property later came to identify an entire industry.

Plastic engines

Designers strive to make racing cars as lightweight as possible. With less inertia, a lighter car can zip through curves at high speed without skidding off the track. Amoco Chemical Company has successfully raced a Lola T-616 with a plastic engine. The Lola's earlier metal engine weighed 380 Ib, but the plastic engine weighs just 160 Ib. Much of the weight savings came from replacing the iron engine block with one of plastic and carbon fibers made by American Cyanamid. Some 50 internal parts—including piston skirts, connecting rods, and valve-train components—were molded of a *poly(amide-imide)* which Amoco calls Torlon. When the engine is operating, these parts move back and forth, changing direction as many as 300 times per second.

Parts with lower mass and inertia can change direction more easily and let the engine rev to higher speeds. The 2-L plastic engine produces 318 horsepower at 9500 rpm.

Making a PET bottle

Glass bottles for soft drinks are disappearing from the stores. After a reign of 200 years, glass soft drink bottles are being replaced by plastic ones. Plastic bottles won't break when they are dropped. Furthermore, their lighter weight makes them easier to carry and reduces transportation costs for the bottler. The material for the popular two-liter bottles is made by combining *ethylene glycol* with *terephthalic acid* to form a polyester, as shown in Figure 2. The resulting polymer is called *polyethyleneterephthalate,* or PET for short. When melted, PET can be molded into intricate shapes. To make a soft drink bottle, PET is first molded into a test-tube shaped billet. The billet is heated until soft, clamped inside a bottle-shaped mold, and blown up with hot air like a balloon. The plastic hardens quickly when it touches the cooler wall of the mold. A plastic base is glued on, a label is applied, and the PET bottle is ready to be filled.

CAPTIONS

Mark Twain and his biographer, Albert Paine, take aim at ivory billiard balls. A 1920 baby rattle molded of celluloid (bottom) shows the fine detail that was achieved with this early plastic.

Figure 1. Polyethylene is formed from ethylene gas. Brackets denote repeating unit.

Figure 2. Polyesters include many ester chemical groups (in color).

Hockey is played on plastic ice at the Brian Trottier Skating Academy in Port Washington, N.Y. The plastic material, called Glice, is high-density polyethylene coated with a thin layer of silicone oil. New to the United States, this surface is popular in Europe because it eliminates costly refrigeration.

Lightweight parts of Torlon (chemical structure below) are used in this experimental engine.

BIOGRAPHY

Joseph Alper is a Baltimore-based freelance science writer, contributing editor to Science '86 magazine, and an avid softball player.