

Elastomeric Materials

Because rubber plants occur naturally in only a few out-of-the way places around the world—such as Malaya, South America, and Indonesia—attempts to create synthetic materials with the useful properties of rubber began a century and a half ago. The many investigations eventually resulted in a variety of new elastomeric materials and also laid the basic foundations for polymer chemistry. Chemists finally succeeded in synthesizing the actual rubber molecule in the late 1950s, but by that time other elastomers had found broad applications in worldwide technology and industry.

The synthesis of rubber from other raw materials could not begin until the basic chemistry of the substance was better understood. In 1826 in England, Michael Faraday made one of the first chemical analyses of natural rubber, interpreting its molecular formula as C_5H_8 . With this knowledge, many other hopeful researchers attempted to build synthetic rubber molecules that could be produced easily and inexpensively. In 1838 in Germany, F.C. Himly was able to obtain a volatile distillate from natural rubber, and in 1860 in England, chemist C.G. Williams went further and distilled natural rubber into three parts, oil, tar, and “spirit” (the volatile fraction). He named the “spirit” isoprene.

The next step was to see if isoprene could be synthesized from readily available raw materials and then converted back into rubber. In France, Georges Bouchardat used hydrogen chloride gas in 1875 in a prolonged distillation of isoprene, which yielded a rubberlike substance. This was one of the first synthetic elastomers ever created.

In 1882 in England, W.A. Tilden produced isoprene through the destructive distillation of turpentine, rather than any raw material that came from natural rubber. He reported that, after storage or through the action of chemical agents, his specimens of isoprene changed into a material that resembled rubber.

The search for substitutes for natural rubber did not make major progress until researchers stopped trying to reproduce the exact chemical composition of rubber, and instead concentrated on synthesizing materials with similar properties.

Such rubbery materials, with chemical structures very different from rubber, required a more general designation, though: “Elastomer,” a contraction of *elastic* and *polymer*, was defined as a substance

that can be stretched at room temperature to at least twice its original length and, after being stretched, rapidly returns to approximately its original length when the stress is removed.

For a material to exhibit elastomeric properties, it must have long threadlike molecules, flexibility in the molecular chain to allow stretching and coiling, and some form of chemical or mechanical bonds between the molecules. Petroleum has been the most important raw material for creating synthetic elastomers; some synthetic rubbers also use potatoes and grains (and the alcohol produced by them), coke, limestone, salt, and sulfur.

Germany and Russia, who had no ready access to plantation rubber, began to work in earnest on the problem at the turn of the century. In 1901 I. Kondakov produced a rubberlike substance by heating dimethylbutadiene with potash; and in 1910 S.V. Lebedev polymerized butadiene (which he had obtained from ethyl alcohol made out of potatoes) into an acceptable elastic material.

In the United States, Kyrides and Earle at the Hood Rubber Company synthesized dimethylbutadiene and polymerized it into synthetic rubber; David Spence of the Diamond Rubber Company synthesized isoprene from turpentine, then prepared synthetic rubber in a pilot plant.

One “failure” in the search for synthetic rubber was Silly Putty.

Hoffman and Harries in Germany, and Mathews and Strange in England, independently studied the polymerization of butadiene, isoprene, and dimethylbutadiene. They discovered how to prepare synthetic elastomers from these base materials by using metallic sodium as a general polymerizing agent. During World War I, while Germany was under a naval blockade, 2,300 tons of “methyl rubber” were manufactured by this process—“Methyl H” as a substitute for hard rubbers and “Methyl W” for soft rubber applications. Shortages forced the use of dimethylbutadiene as the base material, rather than the more satisfactory butadiene or isoprene. Methyl rubber proved to be a poor substitute for natural rubber, and it was abandoned immediately after the war.

In the late 1920s in Germany, Staudinger laid the foundations of basic polymer chemistry, and a boom in synthetic elastomers occurred. In the United States, with ample supplies of natural rubber, interest in developing synthetics waned. However, some companies showed increasing interest in developing elastomeric materials with particular physical and chemical properties for special applications that needed, for instance, greater chemical resistance or greater solvency than natural rubber.

The first such special elastomer, polysulfide rubber, better known by the trade name of Thiokol[®], was marketed in 1930 by the Thiokol Chemical Corporation. J.C. Patrick discovered Thiokol in 1920 while trying to prepare a new antifreeze from ethylene dichloride and sodium polysulfide; instead, he found a new rubbery substance that was not marketed until a decade later. While Thiokol has a much lower tensile strength than natural rubber, it also shows excellent resistance to organic solvents such as gasoline, and it resists weathering and gas permeation over a wide range of temperatures.

Another synthetic elastomer, polychloroprene, better known by its trade name of Neoprene[®], was first marketed in 1931 by E.I. du Pont de Nemours & Co. It was discovered by J.A. Nieuwland, a professor of chemistry at the University of Notre Dame, assisted by W.H. Carothers (creator of nylon) and Elmer K. Bolton. Scientists in the Soviet Union also manufactured polychloroprene, which they called “Sovprene.”

Neoprene is manufactured from acetylene, made from coal, limestone, and water. It has a high tensile strength and resilience, good tear resistance, and good resistance to oil, oxygen, and ozone. Neoprene is used to manufacture gloves, tubes, hose, belts, gaskets, and some extruded mechanical parts.

Researchers in Germany were successful with their Buna rubbers, introduced commercially in 1935, made from sodium polymerization of butadiene and styrene. (The name “Buna” comes from butadiene and the chemical symbol for sodium, Na.) Butadiene-styrene rubber, known as Buna-S, is the most widely used synthetic elastomer and has physical characteristics very similar to natural rubber. It ages well and has good abrasion and crack resistance, though it has low strength (unless reinforced with fillers such as carbon black), low resilience, and low tear strength.

Another buna rubber used in Germany, Buna-N or nitrile, was introduced to the United States in 1937. Highly resistant to oil, nitrile is used in seals and gaskets and

HISTORICAL NOTE

other places where the rubber comes in contact with hot oils, for example the rollers in printing presses and hoses used for oil products.

The United States began manufacturing butadiene-styrene synthetic rubber when, in World War II supplies of natural rubber were cut off from the Far East. The U.S. synthetic elastomer industry had been insignificant, but at the time of the blockade only about 1 million tons—or one year's supply—of natural rubber existed in the country. The synthetic rubber industry had to begin producing almost overnight, achieving 800,000 tons per year. While improvements in the process were made during wartime, the U.S. government retained the same butadiene-styrene manufacturing methods until the end of the war to avoid confusion.

Butyl rubber (polyisobutylene) was discovered in 1937 by R.M. Thomas and W.J. Sparks, and introduced to the market in 1943 by the Standard Oil Company. Butyl rubber has become popular because of its resistance to vegetable oils, oxygen, and

ozone. It has a low gas permeability, and besides good resistance to acids and other chemicals harmful to natural rubber, butyl rubber is light in color, nontoxic, elastic, odorless, and has good electrical insulation properties. Disadvantages include its stiffness at low temperatures and sensitivity to contamination during processing (even small amounts of other rubbers or plasticizers will interfere with proper vulcanization). Butyl rubber is used for inner tubes, protective clothing, and window strips in automobiles.

Not until 1956 was natural rubber first synthesized in the laboratory. H.J. Teas and R.S. Banduski announced that they had formed small samples of natural rubber molecules out of acetate by using enzymes obtained by centrifuging latex from the rubber plant.

By this time, though, the development of the petrochemical industry had brought about so many different synthetic elastomers that natural rubber was no longer so important to everyday life and for growing industries. By the way, one "failure" in the

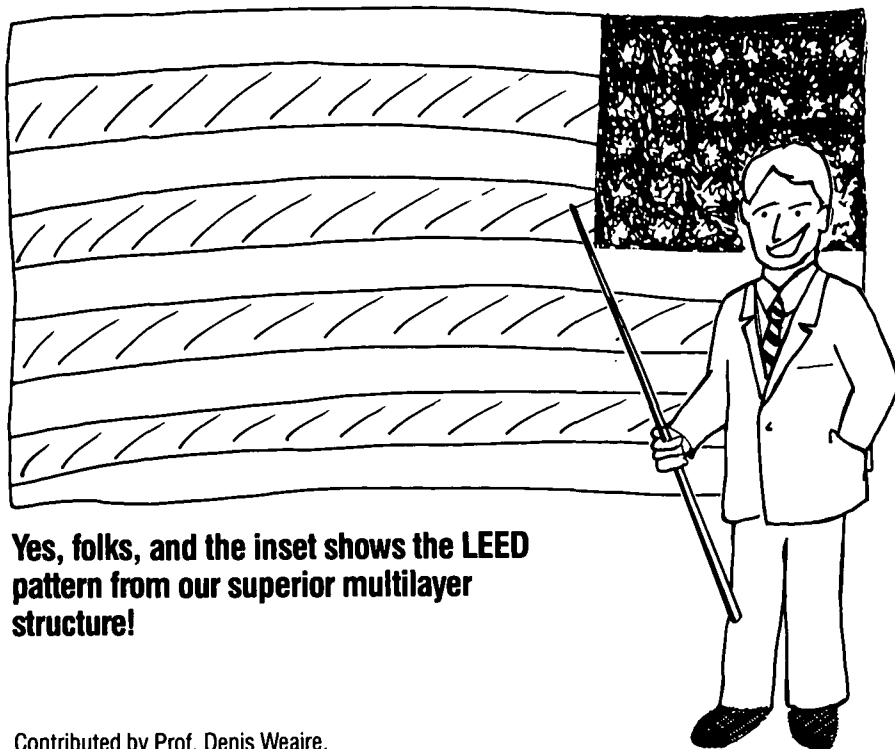
search for synthetic rubber was the development of the elastomer known as Silly Putty®, a popular children's toy for four decades now.

The demand for synthetic elastomeric materials has increased each year, and new elastomers continue to be developed with physical characteristics appropriate and desirable for every application formerly dominated by natural rubber. By the mid-1970s, worldwide consumption of synthetic rubbers was nearly twice that of the natural product. The actual tonnage of natural rubber continued to increase through the 1980s, during the worldwide growth of industry, but synthetic rubbers have consistently claimed a larger percentage even though virtually all of these substitutes were completely unknown only a century before.

KEVIN J. ANDERSON.

Editor's Note: See "Rubber Stretches Over Two Anniversaries" (July 1988, p. 47) and "Large-Scale Dilatant Dynamics of Silly Putty" (February 1990, p. 69) in the MRS BULLETIN.

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In the next issue...

Guest Editor Alan R. Krauss of the Materials Sciences and Chemistry Divisions at Argonne National Laboratory turns the focus on "New Materials and New Challenges in Vacuum Technology" in a series of six articles:

"Developments and Applications of All-Aluminum Alloy Vacuum Systems" by H. Ishimaru

"Surface Preparation and Coating of Aluminum Alloys for Improved Vacuum Properties" by K. Moriyama

"Vacuum Systems for Synchrotron Light Sources" by J.N. Schuchman

"Review of Wall Conditioning and Wall Materials for Fusion Research Devices" by R.A. Langley

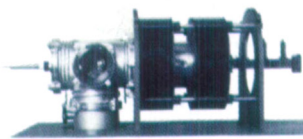
"Helium Pumping Strategies for D-T Fusion Devices" by A. Krauss, J.N. Brooks, O. Auciello, and W. Shmayda

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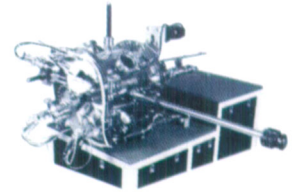


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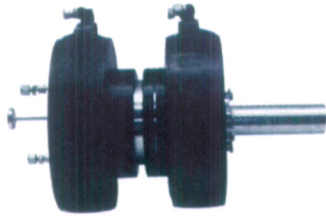
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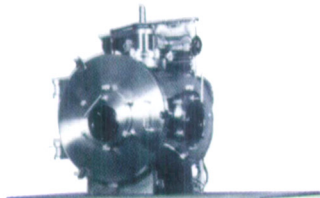


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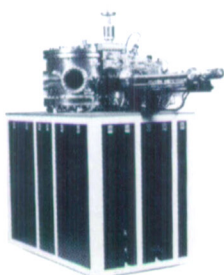
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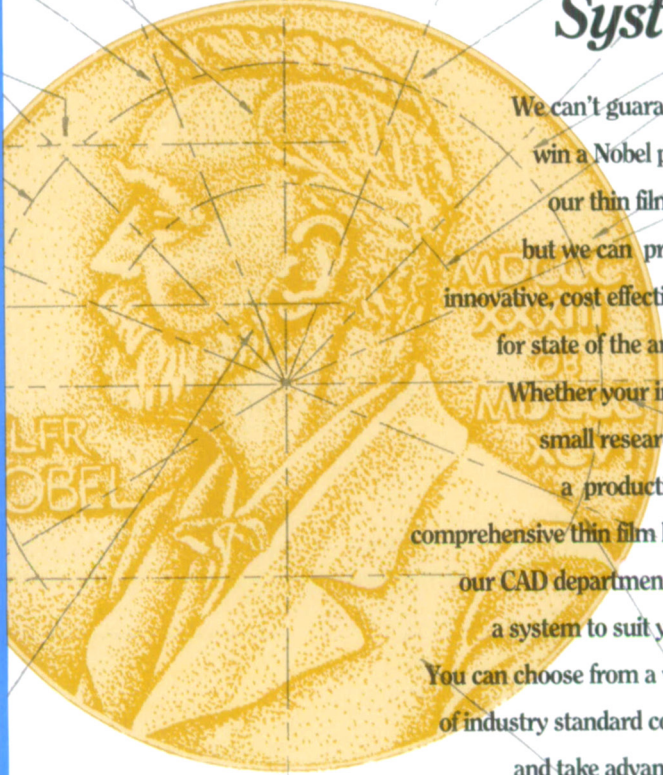


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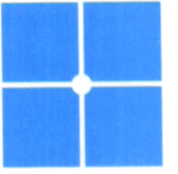
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