

## Technical Insight

### **The History of Tomorrow's Materials: Protein-Based Biopolymers**

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How to reduce our dependence on fossil fuels? Plastics derived from renewable resources are one part of the answer. Engineering viable biobased materials contributes to a more sustainable future economy. Additionally, many biobased materials are biodegradable as well as renewable, offering an outlet for overflowing solid-waste streams. Plastics based on soy protein are one promising class of renewable, biodegradable materials. Although agriculture-based plastics have been around for over a century, they were largely forgotten after the advent of synthetic, fossil-fuel-based polymers. This article revisits the literature left to us by early-20th-century engineers who made protein-based plastics from casein and soy protein on an industrial scale, and recounts early research on and applications of biopolymers such as casein and soy protein-based plastics.

### **Lessons From History**

Hidden in an early-1900s townhouse on Ursula Street in Essen, Germany, is the world's largest collection of plastic items. Owned by Ulrich and Ursula Kölsch, the collection houses tens of thousands of articles, all numbered and placed on shelves from floor to ceiling throughout the ground-floor flat. With each item perfectly catalogued, the collection is an exceptional archive dating to the 1840s. We see not only the development of plastics, but also how this unique material helped in the development and change of design and aesthetics. The Kölsch collection shows us how, in the first 80 years of the plastics industry, products were made exclusively of biopolymers, most from renewable resources such as cellulose, casein, shellac, and ebonite. Here and there we stumble upon items made of plastic materials that most of us have never heard of, such as Bois Durci and kopal resin. However, these materials helped shape what is today the plastics industry.

For example, Bois Durci, an early plastic that dates to the 1850s, is a mixture of sawdust, usually of a hardwood such as ebony or rosewood, and blood or egg. The sawdust was mixed with vegetable oils and mineral or metallic fillers, and the blood with a gelatinous substance diluted in water. The dry and wet components were mixed and compressed into finished parts in a steel mold held in a steam-heated screw press.

A number of items in the Kölsch collection have the word EBENA stamped on their bottoms. These items, most of which are decorative Art Deco bowls, containers, boxes, lamps, radios, and clocks, are made of a mixture of wood fiber, pigments, and a fossilized tree resin called kopal. Found in the forests of Africa, kopal is the inland counterpart of amber, which is found in the North Sea and Baltic Sea. Between 1921 and 1931, the EBENA factory in Wijnegem, Belgium, was the only manufacturing facility to produce kopal products. After EBENA

closed in 1931, expensive fossilized resins such as kopal and amber were forgotten as molding materials, except for perhaps a few jewelry applications.

Casein, discussed in detail below, is a milk protein obtained via acidification or enzymatic action. The resulting curds can be dried, molded, and treated with a hardening agent to yield commercial plastic. Casein had its heyday as a commercial plastic in the early 1900s, the same period when many other items in the Kölsch collection were produced.

Another material found among the items in the Kölsch collection is soy protein-based plastic. Soy protein can easily be isolated from soybeans and molded. Soy plastics, which for a short period were used in automotive knobs and even body panels, never saw the widespread adoption predicted by Henry Ford in the 1930s. World War II sent his dream of “growing a car like a crop” into oblivion.

The recent revival of interest in these materials makes the story of their discovery and development relevant and instructive. The great success of petrochemical-based polymers from WWII through the present is testament to the versatility, economy, and durability of such synthetic materials. However, the indestructibility that for decades made petrochemical-based synthetics so desirable has increasingly become a liability. Over 25 million tons of plastic entered the municipal solid waste stream in the U.S. in 2001. This nonbiodegradable plastic waste accounted for over 11% of the municipal solid waste in the U.S., up from 1% in 1960.<sup>1</sup>

Incinerating plastics can cause toxic air pollution; plastic litter is unsightly. Thus, with continued use of nonbiodegradable petrochemical-based polymers, issues arise concerning health, the environment, and aesthetics. The expanded use of renewable, biodegradable biopolymers would alleviate the problems associated with disposal of nonbiodegradable polymers. In addition, the increasing monetary and political costs of American and European dependence on foreign sources of oil make sustainable, domestically grown resources a desirable alternative.

### **Casein Plastics**

The use of casein in non-food applications dates to the second century BCE, when the Egyptians used it to bind pigments in paints, and casein has been used as an adhesive from the 18th century onward.<sup>2</sup> The first patents for making plastics from casein were granted in 1885 and 1886, in Germany and the U.S., respectively.<sup>3</sup> However, these patents made no mention of any hardening agent; the patented material easily biodegraded, and no useful products are known to have resulted. Though an undesirable property a century ago, easy biodegradation is a desirable property in some applications today. In Germany the demand for white “blackboards” (circa 1897) led to Adolf Spitteler’s serendipitous discovery of casein.<sup>2,3</sup> One night in 1897, as the story goes, Spitteler’s cat knocked over a small bottle of formaldehyde. The formaldehyde dripped from the chemist’s counter into

the cat's milk dish on the floor. When Spitteler returned to his laboratory the next morning, he found that the spilled formaldehyde had caused the milk to curdle, turning it into a hard horn-like substance, much like celluloid. In fact, his cat had just invented the first semi-synthetic plastic since cellulose. Spitteler then began experimenting with cheese curds and formaldehyde, and he found that the milk protein was rendered water-insoluble when it sat in a formaldehyde solution for extended periods of time.<sup>2</sup>

Spitteler and his business partner Ernst Krische secured several patents in 1899 and coined the trade name "Galalith," from the Greek words for milk (gala) and stone (lithos). Casein-formaldehyde soon was being produced and utilized in numerous applications across Europe. By 1915, European manufacturers of casein had found a viable method of making high-quality casein plastic. Dry casein could be slightly moistened with water, and then processed into a plastic by applying pressure and shear, as in a heated extruder.<sup>4,5</sup> Water was added to casein resins as a plasticizer prior to molding. Water enhanced processability,<sup>3</sup> but resulted in greater shrinkage and warpage as the material dried. The same gains in processability could be achieved by using a 10% borax solution in place of the water.<sup>5</sup> This reduced shrinkage, but the finished material still absorbed large amounts of moisture and was subject to significant warpage. This shortfall was addressed by "hardening" the casein plates and rods in a 40% formaldehyde solution, rendering them water-insoluble.<sup>5</sup> Even so, the water absorption of casein was approximately 20%–30%.<sup>3</sup>

The development of casein in the U.S. proceeded more slowly than in Europe. It was not until 1919 that the first casein plastic that was up to European quality standards was made in the U.S.<sup>3</sup> Even then, the industry in the U.S. did not advance for several reasons: climatic differences meant the European processes could not be copied in a straightforward manner in the U.S., the long and costly process was not easily transferred to faster processing in automatic machines, and the scrap could not be reworked, so 50% waste was not uncommon. All this made competition with established materials more difficult.<sup>3</sup>

In 1929, P.C. Christensen added aluminum stearate, a water-soluble aluminum salt, to the resin and produced a nonhardened plastic rigid enough to be worked in automatic machines; and the alum casein scraps were easily reworkable, greatly reducing waste.<sup>3</sup> In 1926, 55% of the world's buttons were made of casein.<sup>3</sup> Worldwide casein production increased from 10,000 tons in 1930 to 60,000 in 1932.<sup>3</sup> However, buttons, belt buckles, and jewelry remained the main products in which casein could be used, pending a method of reducing the absorption of water from humid air.<sup>3</sup> But casein plastic still required hardening in formaldehyde, making its manufacture a long and costly process. The hardening and subsequent

drying could take anywhere from two weeks to a year, depending on the thickness of the part.<sup>6</sup>

In 1938 in Utica, New York, USA, a tannery was ordered to shut down because it was polluting a local stream. William S. Murray, a prominent Utica politician and chemist, obtained a 30-day stay and found a method of solidifying the waste runoff, thereby protecting the stream. He applied the same methods to the skimmed milk being discarded by a nearby powdered-milk plant. By changing the natural milk sugar to aldehyde in the presence of casein, he found a method of casein plastic production that eliminated formaldehyde hardening.<sup>7</sup> He secured a patent, but World War II prevented any further development of his promising new process.<sup>8</sup> The continued use of phenol formaldehyde and widespread adoption of synthetic plastics during and after WWII drastically curtailed the use of casein,<sup>2</sup> which is produced at a minimal level today.

### **Soy-Protein Plastic**

Soybeans were introduced to the United States from Asia in 1804. They were grown more as a curiosity than a substantial crop until World War I, when concerns about vegetable-oil shortages made the oil-rich soybean an attractive crop.<sup>9</sup> The success of extruded plastics from casein in the early 1900s spurred research into other agricultural sources for plastics, including soy protein.<sup>10</sup> By 1913, patents had been issued in Britain and France for preparing plastics from soy protein.<sup>11</sup> The first U.S. Patent for soy-protein plastics was issued to Sadakichi Satow in 1917.<sup>12</sup> Satow used a wet process, analogous to that for casein. It involved a long hardening period in formaldehyde, and since drying took place after shaping, the final products were susceptible to warping, shrinking, porosity, and water absorption.<sup>13</sup> These drawbacks prevented any commercialization of Satow's patent.

In the 1920s and 1930s there was a significant drive to help American farmers by making industrial products from agricultural byproducts, known as the chemurgy movement. Chemurgy attracted a lot of intellectual and monetary capital, most notably from Henry Ford and Thomas Edison. These titans used their financial, research, and manufacturing resources to encourage the production of industrial goods from agricultural byproducts. Ford spearheaded an effort to utilize soy meal and protein in making parts for automobiles. In 1930, he laid out his vision to his lieutenants at the Ford Motor Company. A yearlong survey of crops with potential industrial applications revealed that soybeans were the most promising candidate. By 1932 the company had planted 8000 acres of soybeans, an acreage that would increase to 12,000 by 1936.<sup>14,15</sup>

Ford developed a process to prepare molded plastics using soybean meal, which contains 48% protein, hardened with formaldehyde. These soy-formaldehyde parts

absorbed more than 20% moisture by weight, causing severe warping and cracking. Phenolic resin, known to be water-resistant, was mixed with soy-formaldehyde resin to make a more water-resistant plastic. These thermoset phenolic-soy-formaldehyde plastic parts were filled with 30% wood flour; they were cheaper to produce than straight phenolic resin parts, weighed less, and did not require costly surfacing or finishing.<sup>15</sup> In 1936, one million Fords each had 15 lbs of soy-plastic parts—in gearshift knobs, window frames, electrical switches, horn buttons, and distributor caps—using over 3 million lbs of oil-free soybean meal.<sup>15</sup> This was in addition to 5 lbs per vehicle of soybean oil used in foundry sand cores and enamel.

In 1942, 150 million lbs of extruded soy-meal plastic, made of phenol-formaldehyde, soy, and wood flour, were produced.<sup>11</sup> However, the water absorption of even these soy plastics remained high enough that products such as Ford's automotive body panels warped excessively. Still, the utility of soybeans in industrial products was a genie let out of the bottle. A 1936 article noted that the oil and meal of "soybeans are used in making paint, enamel, varnish, glue, printing ink, rubber substitutes, linoleum, insecticides, plastics, glycerin, flour, soy sauce, breakfast foods, candies, roasted beans with nut-like flavor [and] livestock feeds."<sup>14</sup>

At the same time that the Ford Company was implementing its process for producing soy-protein plastics, research into other techniques to make plastic parts from soybeans was ongoing at the U.S. Regional Soybean Industrial Products Laboratory in Urbana, Illinois. From 1936 through 1942, the lab published a steady stream of research articles on its progress in making plastics from soy meal and soy protein. One innovation was the advent of a dry process in which the soy meal in powder form was prehardened with formaldehyde before shaping.<sup>9</sup> This eliminated the post-shaping hardening step, sharply reducing production time and cost, since soy proteins needed more highly concentrated formaldehyde than casein to be hardened in a wet process.<sup>16</sup> The prehardened material was claimed to be thermoplastic because it could be shaped repeatedly.<sup>13</sup>

However, further experimentation indicated that instead of being truly thermoplastic, the prehardened soy-formaldehyde resin displayed thermoset and thermoplastic behavior, perhaps because of a long curing reaction.<sup>9</sup> Work was needed to find a soy-meal-based material that was either sufficiently thermoplastic to be injection-molded or that would thermoset completely so it could be removed from a hot die. Different hardening agents were used, formaldehyde being the most effective in terms of low-water absorption, followed by furfural and propionaldehyde.<sup>6</sup> It was also determined that hardening the soy meal at the isoelectric point of soy protein (pH 4.2–4.5) reduced the water absorption of the final parts.

The thermoplastic character of prehardened soy resin appeared only with adequate plasticization. Water was the most effective plasticizer, but the high water absorption of the molded parts made finding another plasticizer a priority. Seventy different candidates were screened, and none produced parts with better water resistance than those plasticized with water itself.<sup>13</sup> Ethylene glycol was the top-performing non-water plasticizer. Water repellents were investigated as a means of increasing the moisture resistance of the final parts.<sup>6</sup> Aluminum stearates<sup>13</sup> and oleanolic acid<sup>13</sup> were found to be the most effective at decreasing water absorption. A 1940 article explored the possibility of making laminates by coating paper with a solution of soy-formaldehyde, and then hot-pressing multiple sheets<sup>17</sup> together into a single plate. Water absorption was again found to be problematic, but it could be reduced by adding outer laminate sheets treated with phenolic resin.

One means of decreasing water absorption was to denature the protein prior to processing. Denatured soy protein is not water-soluble and cannot be plasticized by water. However, Beckel *et al.* found that denatured soy protein plasticized with formamide (a teratogen, unfortunately) could be successfully molded.<sup>18</sup> This material reportedly retained its strength and displayed little swelling or distortion when submerged in water for 48 hours and then dried. Thus, denatured, insoluble soy protein holds promise as a water-resistant plastic material. The issues raised in these early reports would prove to be the same that present-day researchers face in making a viable plastic from soy protein: a) finding ways to reduce water absorption and achieve dimensional stability; b) finding effective plasticizers that do not attract moisture or leach from parts; c) discovering a method of producing truly thermoplastic (or truly thermoset) soy protein resins; and d) understanding the effects of denaturation on processing and properties.

World War II effectively put an end to the chemurgy movement, including Ford's efforts to introduce large quantities of soy plastics into automobiles. After WWII, cheaper and better-performing synthetic petrochemical-based resins replaced soy-based and milk-based protein plastics.<sup>19</sup>

## Conclusion

From WWII through the 1980s there was little research on protein plastics. However, such research is experiencing a resurgence. Environmental concerns associated with petrochemical plastics have led to industrial and commercial interest in environmentally friendly alternatives. Environmental concerns on the part of consumers have helped biobased materials gain some acceptance despite their high cost. As research on protein-based plastics yields properties comparable to those of fossil-fuel-based resins, the adoption of these materials will become more widespread. Walking down quiet Ursula Street in Essen and through the door to the Kölsch collection is more than paying a visit to the past. It is also passing

through the doorway to a future where renewable materials will help free us from dependence on fossil fuels and will usher in a sustainable industrial age.

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