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History of the Development and Growth of Thermosetting Polymers

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ABSTRACT

Fibrous proteins are cross-linked through the disulfide linkages of cystine; animal and vegetable proteins can be cross-linked by the reaction of tannic acid, chromic acid, or formaldehyde; and natural rubber can be vulcanized by heating with sulfur. However, most thermosetting polymers are synthetic polymers. These include saturated polyesters (Glyptals) synthesized by Smith in 1901, phenolic plastics produced by Baekeland in 1907, urea and melamine plastics produced by John and Henkel in 1918 and 1935, alkyds patented by Kienle in 1933, glycol maleates patented by Ellis in 1937, and epoxy resins patented by Schlack in 1933. Many of these developments were made prior to the advent of commercial synthetic thermoplastics. However, because their fabrication is more labor intensive than that of thermoplastics, thermosetting plastics now account for less than 20% of all plastics produced. Nevertheless, over 2.5 million tons of these thermosets are produced annually and the use of these cross-linked plastics continues to grow.

Some naturally occurring proteins which have been in existence for many centuries are cross-linked through the disulfide linkages in the cystene residues. Likewise, the protein in hair has been

thermoset for centuries by the hot waving process in which the disulfide linkages in the cysteine residue are cleaved to produce unstable sulfenic acid groups. The latter produce aldehydic groups through the loss of hydrogen sulfide, and the residual aldehyde groups cross-link with the amino groups or adjacent protein molecules.

Leather, which is an equally ancient thermoset or cross-linked polymer, has been called the most historic of all useful materials. Tannin, which was used originally as the cross-linking agent, has been replaced in part by sodium dichromate [1]. Formaldehyde has been used as a cross-linking agent for the preservation of animal protein and for the stabilization of proteineous fiber.

As early as the eleventh century, the monk Theophilus discussed the use of linseed oil in paint. The oil and gum technology, of course, was based on cross-linking reactions which may not require heat but produce thermoset polymers [2]. These natural oleoresinous varnishes were replaced, to some extent, by synthetic polyesters which eventually were called alkyds.

Glyceryl tartrate polyester resins were first synthesized by Berzelius in 1847, glyceryl phthalate polyester resin by S. W. Smith in 1901 [3], and alkyd resins were produced by Kienle in the 1920s [4]. Kienle, who coined the term "alkyd" from alcohol and acid, controlled the cross-link density of these polyesters by varying the amount of unsaturated acids used as reactants in the unsaturated polyester resins.

Natural rubber (*Hevea braziliensis*) was cross-linked or vulcanized by the addition of sulfur by Liedersforff in 1832 and Charles Goodyear in 1839 [5]. The thermoset product produced by the latter, as well as by Thomas Hancock, was an elastomer. However, Charles' brother Nelson Goodyear, patented a process for heating natural rubber with a large quantity of sulfur in 1851. This thermoset product, called hard rubber or ebonite, was the first man-made moldable thermosetting plastic.

POLYESTERS AND PHENOLICS

Glyptal and Bakelite, which were synthetic thermosetting plastics, were not discovered until over three decades after Nelson Goodyear's production of hard rubber. The glyptal polyester, which is produced by the condensation of difunctional phthalic anhydride and trifunctional glycerol, was first used as a thermoset coating. However, this and other alkyds are also used as moldable thermosets [6].

Phenolic resins are now called Bakelite after Leo Baekeland, who was primarily responsible for their commercialization. The synthesis of a resin by the condensation of phenol and formaldehyde was first reported by von Bayer in 1877 [7]. Other early experimenters, such as Ter Meer [8] and Claus and Trainer [9], investigated this resin but, like many other organic chemists, lost interest because

they were not able to crystallize and characterize amorphous resinous products. However, Manasse [10] and Lederer [11] were able to separate and characterize methylolphenol which is the intermediate obtained by the condensation of phenol and formaldehyde. The Merklin and Losekam Co. attempted to market phenolic resins in 1889. Farbenfabriken Bayer patented a process for the production of methylolphenol [12] which is an intermediate product in the synthesis of phenolic resins, and Speir patented a solid with antiseptic properties which was obtained from the ammoniacal condensation of resorcinol and formaldehyde [13].

The production of cross-linked insoluble resinous products obtained by the acidic condensation of phenol with an excess of formaldehyde was reported by Claisen [14] and Kleeberg [15]. Blumer patented the soluble resins obtained by the condensation of phenol and formaldehyde in the presence of organic acids [16]. This product, called Laccain, was proposed as a substitute for shellac.

Improvements in the catalytic and noncatalytic condensation of phenol and formaldehyde were reported by Henschke [17], Fayolle [18], and Story [19]. Information on the unsuccessful attempts to produce useful products by the condensation of phenol and formaldehyde were recorded and available to other organic chemists whose goals were not restricted to the production of crystalline solids.

Thus a Belgian born chemist, living in Yonkers, New York, was able to produce and commercialize a thermosetting plastic which he described in his well-known "heat and pressure" patent [20]. Baekeland had previously developed Velox photographic paper, and he used the royalties from this invention to establish and equip a laboratory for the investigation of phenolic resinous products. This inventor also patented the use of a cellulosic filler [21] with acid-catalyzed [22] as well as alkaline-catalyzed phenolic resins [23].

Lebach also was granted patents on the alkaline condensation of phenol and formaldehyde [24] and the curing of these resole resins by the addition of strong inorganic acids [25]. Baekeland was granted about 400 other patents for uses of the resin which he called Bakelite. Bakelite Gesellschaft mbh in Erkner, Germany, produced these phenolic resins in 1910. The General Bakelite Co. was also established later that year in the United States.

J. W. Aylsworth, who was chief chemist for Thomas A. Edison, used cresol instead of phenol for the production of resinous materials [26]. He found that novolak resins produced by the acid condensation of an excess of cresol or phenol with formaldehyde could be cured or cross-linked by heating with hexamethylenetetramine [27]. Aylsworth formed the Condensite Corp. of America for the production of phenolic resins but was forced to obtain a license from the General Bakelite Co.

Another company named Redmanol Chemical Products Co. was formed to produce phenolic resins developed by Dr. L. F. Redman at the University of Kansas. When Baekeland refused to grant a license to Redmanol, that company acquired control of Condensite Corp. of America which had previously acquired the license to make phenolic resins.

The three competing companies were combined to form the Bakelite Corp. in 1922 and this firm was acquired by Union Carbide and Carbon Corp. in 1939. Several other firms now produce phenolic resins and molding powders. Over 700 thousand tons of phenolic resins and molding compounds were produced in the United States in 1978.

AMINOPLASTICS

The condensation of urea and formaldehyde was described by Tollens in 1884 [28], and mono- and dimethylolurea were isolated by Einhorn and Hamburger in 1908 [29]. The first patent on urea-formaldehyde adhesive was granted to an Austrian chemist named John [30]. Other patents on urea resins were issued to the German chemists Goldschmidt and Neuss [31] and the Austrian chemists Pollak [32] and Ripper [33]. Rossiter introduced the first commercial urea resin under the trade name of Beettle resins in 1926 [34].

Carlton Ellis was granted additional patents on urea resins in 1933, and Toledo Scales sponsored a project at Mellon Institute for the development of urea molding compounds called Plaskon. Unlike the dark-colored phenolic resins, the cellulose-filled urea plastics were colorless. Over 500 thousand tons of urea resins were produced in the United States in 1978.

Although melamine was isolated by Liebig in 1834 [35], almost a century passed before resins produced by the condensation of melamine and formaldehyde were produced commercially. A patent for melamine-formaldehyde resins was granted to Henkel [36] in 1935, and these resins were described in greater detail by Gans in 1941 [37].

American Cyanamide produced cellulose-filled melamine-formaldehyde molding compounds in 1937. These colorless plastics were sold under the trade names of Cymel and Resimene. Over 90 thousand tons of melamine resins were produced in the United States in 1978.

UNSATURATED POLYESTER

Berzelius prepared glyceryl tartrate in 1847 [38], Smith prepared glycerol phthalate resins in 1901, and these glyptal resins were patented in the United States in 1914 [39]. The preparation of glycol maleate was first reported by Vorlander in 1894 [40] but the first commercial unsaturated polyesters were unsaturated oil-modified polyesters called alkyds [41].

Patents were granted to Kienle for these oil-modified polyesters [42] in 1933. This patent was assigned to the General Electric Co. Many other firms produced alkyd resins after the Kienle patent was

declared invalid in 1935. Over 250 thousand tons of alkyd resins and molding compounds were produced in the United States in 1978.

The polymerization of allyl acrylate was reported in 1873, and a patent for the copolymerization of diallyl succinate and vinyl acetate was granted in 1940 [43]. Commercial polymers produced by the polymerization of diallyl phthalate and diethylene glycol bis(allyl carbonate) are available under the trade names of Dapon and CR 39.

Carothers described techniques for the production of glycol maleate [44], and Ellis was granted a patent for the copolymerization of a prepolymer of this ester dissolved in vinyl acetate [45]. The volatility of these solutions was decreased to some extent by using styrene instead of vinyl acetate, and the inherent brittleness of these resins was overcome by reinforcing with silane-treated fiber glass [46].

The original hand lay up techniques for making reinforced polyester laminates have been replaced to some extent by filament winding, pultrusion, bulk molding (BMC), and sheet molding (SMC) techniques. The flame resistance of these resins has been improved by the use of halogenated anhydrides and by the addition of halogenated organic compounds and aluminum trihydrate (ATH). Over 500 tons of unsaturated polyester resins were produced in the United States in 1978.

EPOXY RESINS

Patents were granted to American plastic engineers MacIntosh and Walford for diepoxide plastic compositions obtained by the reaction of epichlorohydrin and cresol or phenol in 1920 [47]. The Swiss chemists Schlack [48, 49] and Castan [50] and the American chemist Greenlee were granted patents in the 1930s for the production of diepoxides from the reaction of epichlorohydrin and bisphenol-A [51].

These prepolymers, which have been called ethoxylenes, are now called epoxy resins. Caston cross-linked these polyethers by heating them with phthalic anhydride [52]. Dicyanodiamide and ditolylguanidine were also used as cross-linking agents, and patents were granted for the use of amines and reaction products of dimerized fatty acids and aliphatic polyamines (Versamids) [53].

Cross licensing agreements for the many patents issued have been arranged among Devoe and Reynolds, Ciba-Geigy, Shell, American Marietta, Dow, Reichhold, and Union Carbide. The trade names of Epon and Araldite are used to describe the epoxy resins sold by Shell and Ciba-Geigy, respectively. Over 140 thousand tons of these resins were sold in the United States in 1978.

Cycloaliphatic epoxy resins are produced by peracid epoxidation of unsaturated cyclic hydrocarbons by Union Carbide [54], and epoxy acrylates, called vinyl esters, are sold by Dow under the trade name of Derakane [55].

Since molding of thermosetting plastics is more labor intensive

than that of thermoplastics, most of the recent developments have been in the field of the more widely used thermoplastics. However, because of improvement in molding techniques and the use of automated in situ polymerization, interest in thermosetting resins has continued. More than 2.5 million tons of thermosetting plastics are used annually in the United States and the use of these plastics continues to grow.

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