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1 Introduction

Michael Dornbusch

1.1 History

The history of epoxy resins began in 1854 when Berthelot first prepared epichlorohydrin by making glycerol react with phosphorus trichloride.\(^{[19–21]}\)

\[
\text{Equation 1.1: Chloromethyl oxirane (epichlorohydrin)}
\]

The next step occurred in 1891 with the first description of 2,2-bis (4-hydroxyphenol)-propane (bisphenol A) by Dianin, who produced the impure compound.\(^{[10]}\)

\[
\text{Equation 1.2: 2,2-Bis-(4-hydroxyphenyl)-propane (bisphenol A)}
\]

Sixteen years later, in 1905, Zincke in Marburg, Germany, synthesised pure bisphenol A (BPA) from acetone and phenol.\(^{[10]}\)

In 1909, the Russian chemist Prilezhaev converted numerous olefins into epoxides by reaction with peroxybenzoic acid.\(^{[8, 22]}\)

\[
\text{Equation 1.3: Preparation of epoxides, according to Prilezhaev}}^{[22]}
\]

A patent published in the same year by Horn claimed protection for a protein-based coating formulation, which was obtained by mixing epichlorohydrin and proteins, e.g. protalbin or albumose, in a ratio of 1:1 in an alcoholic solution. When
linseed oil was added to this solution, no turbidity occurred. This was probably the first patent for an epoxy-based coating formulation.

The most-commonly cited inventor of epoxy resins is Schlack\textsuperscript{[15]}, who claimed protection in his patent for I.G. Farben in 1934 for the reaction between bisphenol A and epichlorohydrin to yield epoxy resins\textsuperscript{[3, 8]}. The resins were cured with ethylene diamine. Thereafter, the coatings industry intensified its development activities in the field of epoxy resins.

Patents obtained by Castan in 1938 for the company De Trey AG, Switzerland, described the production of a resin, which was based on BPA and epichlorohydrin and was cured with phthalic anhydride. This curing process was done stepwise to yield pre-cured casting resins, which cured after application\textsuperscript{[5]}.

De Trey AG produced epoxy-based resins for dental applications\textsuperscript{[3]} but was unable to bring the products to market\textsuperscript{[18]}.

Also in 1938, Stein and Flemming from I.G. Farben patented an improved synthesis for epichlorohydrin\textsuperscript{[17]} that facilitated the commercialisation of epoxy resins by substantially boosting the yield.

In 1939, Bock and Tischbein from I.G. Farben\textsuperscript{[14]} patented the reaction between di-epoxides and polyamides and used the resulting compounds for textile applications.

A patent by Castan in 1943 described the use of catalytic quantities of bases to effect curing\textsuperscript{[6]}. In the USA in the same year, Greenlee\textsuperscript{[16]} patented the resin obtained from the reaction of BPA with epichlorohydrin and its use for coating applications, thereby laying the foundations of the industrial use of epoxy resins in that country.

Industrial production of bisphenol A from acetone and phenol started after 1945 (1946 according to\textsuperscript{[18]}\textsuperscript{[2]}. In Europe, Ciba AG developed products under patent license from De Trey AG that it sold under the trade name Araldite while, independently in the USA, the Devoe & Raynolds Company developed similar products\textsuperscript{[3]}.

Commercialisation of the resins by Ciba AG in Europe and by the US companies mentioned above led to a continuous rise in epoxy resin production after 1947\textsuperscript{[8]}.

In the late 1940s, Shell and Bakelite Co. (later: Union Carbide Corp.) commenced R&D activities in the field of BPA-based epoxy resins\textsuperscript{[18]}. At that time, Shell was the sole producer of epichlorohydrin and Bakelite was one of the largest producers of phenolic resins and BPA\textsuperscript{[18]}.

In the 1950s, BPA was also used to produce polycarbonate\textsuperscript{[2]}, and this increased global production of BPA.

In 1955, a cross-licensing agreement among the four US producers of epoxy resins saw Dow Chemical Co. and Reichold Chemicals Inc. enter the market when they joined the patent pool\textsuperscript{[18]}.
In the 1960s, the range of epoxy resins on the market surged dramatically. Ciba AG produced epoxidised o-cresol-novolak resins, Dow Chemical Co. offered epoxidised phenol-novolak resins, Shell introduced multiply epoxidised tetra-functional phenols and Union Carbide entered the market with multiply functionalised epoxides in the form of triglycidised p-aminophenols\[18\].

Also in the 1960s, Ciba AG in Europe and Union Carbide in the USA established industrial production methods for the epoxidation of olefins with peracetic acid by the Prilezhaev reaction. Ciba AG launched cycloaliphatic epoxy resins onto the market in 1963, following these up with additional products in 1965 based on licences obtained from Union Carbide\[18\].

Finally, in the 1970s, Ciba-Geigy AG developed epoxy resins based on hydantoin and Shell developed resins based on hydrated bisphenol A, but both product groups had little success on the market\[18\].

The hormonal activity of BPA, now considered a toxicological property, has a historical background, too\[4\]. The British chemists Dodds and Lawson\[11, 12\] were searching in 1936 for chemicals that would make suitable replacements for natural oestrogen in medical treatments.

A bio-assay revealed that bisphenol A was a substance with a weak oestrogenic effect. It was then discovered that derivatives such as diethylstilbestrol\[13\] were much more potent and so BPA never found use as a drug\[7\]. These results have since been confirmed several times\[4\], but there is controversy surrounding the implications.

### 1.2 Applications for epoxy resins

Outstanding properties, such as resistance to humidity and chemicals, good adhesion to numerous substrates, and good mechanical properties combine to make epoxy resins versatile construction materials and coating agents\[18\].

Applications for epoxy resins can be divided into three areas:

- Coatings
- Adhesives
- Construction materials.

A rough overview of these is given below.

#### 1.2.1 Coatings

The best known application in this area is likely to be that of heavy duty corrosion protection (see Section 3.2)\[8\]. Major examples here include shipbuilding, offshore, and engineering structures, such as bridges, with solvent-borne, water-borne and solvent-free coatings, cured with various amines, being used in all areas\[8\].
The automotive industry uses resins based on epoxy-amine adducts that have been produced from epoxy resins (see Section 3.1.3). Resins bearing amine groups can be protonated and the resulting cationic particles deposited by means of cathodic polarisation on a workpiece and cured with blocked isocyanates at 170 to 190 °C, i.e. they can be covalently crosslinked. This cathodic electrodeposition coating (or E-coating) process provides the corrosion protection found on modern car bodies (see Section 3.1.3).

Another important application area is that of powder coatings (see Section 3.4). When epoxy resins are combined with suitable hardeners, such as dicyandiamide (DICY) (see Section 2.1.1), acid anhydrides (see Section 2.4.2), phenol novolaks (see Section 2.4.1) or polyisocyanates (see Section 2.1.1), the outcome is thermosetting powder coating systems that possess outstanding properties.

One of the oldest applications is that of internal can coating. Owing to their strong yellowing, these epoxy-resin-based coatings are also called “gold coatings” (see Section 3.5) and are cured with cresol resols at elevated temperatures.

Epoxy resins are also successfully employed in specialty applications, such as UV-curable epoxy resin systems (see Section 3.1.2) in UV-curable solder resists and protective coatings for printed circuits, especially for fine-line and multilayer boards.

This list could be continued indefinitely, not only as regards applications for epoxy resins but also combinations with other resin types. Foremost among these are alkyds etherified with epoxies, polyacrylic resins that react with the OH groups of the epoxy resins, and amino resins, such as melamine, which are able to react with epoxy resins in different ways.

### 1.2.2 Construction materials

Applications in construction materials can also be divided into two main groups, the first of which combines epoxy resins with other materials (fibres) to make construction components. The other uses epoxy resins in electrical and electronic engineering.

The main application area for epoxy resins as matrix materials is that of composites. “Composites are always the best choice when a combination of properties is needed that one material cannot provide on its own” [1]. Fibre-reinforced epoxy resins are composites which are combined, e.g. with glass-fibre reinforcements, to produce aircraft parts and blades for wind turbines, i.e. epoxy resin composites have established themselves particularly in lightweight engineering applications.

Epoxy resins are also combined with other materials like graphite, boron or Kevlar fibres to generate materials that have high-precision property profiles.
Wide-ranging applications for epoxy resins are to be found in electrical and electronic engineering.

In electronics, they serve as conformal coatings or laminating resins for the base material of printed circuit boards[1].

The printed circuit boards found in almost every electrical device consist of fibre-reinforced epoxy resins coated with copper. The epoxy resins are cured with dicyandiamide (DICY), amines or imidazoles[18].

In general, applications in electrical and electronic engineering are dominated by curing with anhydrides [1] because this kind of application benefits particularly from the low viscosity, long pot-life and low exotherm[1].

Electrical engineering has been using epoxy resins for 60 years, i.e. just after industry found applications for them. Most uses are in transformers and insulators[1]. An excellent overview of this topic is provided by Möckel and Fuhrmann in their book “Epoxidharze”[1].

1.2.3 Adhesives

A strong bond between two identical or different materials, such as metals, glass, ceramics, wood, fibres and many plastics, can be obtained with adhesives based on epoxy resins[18]. The various applications, raw materials and processes are presented in detail in Section II-2 of “Formulating Adhesives and Sealants” by Müller and Rath.

1.3 Terms and markets

1.3.1 Nomenclature

The nomenclature of epoxy resins is confusing, because different designations and colloquial terms are used in parallel.

Epoxides contain epoxy groups, i.e. three-membered rings with an ether function (see Section 2.1). The International Union of Pure and Applied Chemistry (IUPAC) and Chemical Abstracts (CA) call these oxiranes[23]. However, this systematic designation has not become widely established, especially in the coatings industry, which continues to favour the terms epoxy resins and epoxides.

Epoxides found in industry are mainly produced from epichlorohydrin, giving rise to a methyloxirane group, known as the glycidyl group. Glycidyl ethers or esters are the most commonly employed compounds thereof[23].
ISO 7142 defines an epoxy resin as a “synthetic resin containing epoxy groups generally prepared from epichlorhydrin and a bisphenol” while DIN 16945, with regard to reactivity, states that “epoxy resins are reaction resins containing sufficient epoxide groups for curing”.

The most accurate definition is given in [8], which makes reference to DIN 7728: “epoxy resins are oligomeric compounds containing more than one epoxide group per molecule”. These examples alone give some indication of the variation in definitions and nomenclatures employed.

The classification given in ISO 3673-1, which places epoxy resins into classes, is covered in Section 3.1. Finally, some resins that do not contain any epoxy groups are also called epoxides. These resins are polyether polyols, which are mainly synthesised from epichlorohydrin and BPA and which have no detectable epoxy groups in the molecule but are produced from epoxy groups [8]. This class of resins is known as phenoxy resins (see Section 2.4.1) and will be referred to as such in this book.

### 1.3.2 Markets

The growth of coatings production in Germany in the last five years is shown in Figure 1.1.

The impact of the 2008/2009 global economic crisis on coatings production volume is clearly visible, but so also is the fast recovery in the following years.

In contrast, the crisis had no visible effect on production volumes of epoxy resins for the adhesives market and for coatings (Figure 1.2). Only production of waterborne coatings (Figure 1.3) declined after 2007.

The epoxy resins market may therefore be considered stable. This stands in contrast to the German coatings market as a whole, which has declined since the turn of the millennium. Expressed differently, the coatings market needs economic growth of 2% in order for it to grow, because the coatings market has been rising more slowly than gross domestic product (GDP) since 2000 [28].

This is a German phenomenon, because the global coatings market is growing at the same rate as global GDP and so is a growth market.
Figure 1.1: Production volumes for waterborne and solvent-borne coatings in Germany[25–27].

Figure 1.2: Production volumes for epoxy resins in Germany[25–27]. No data are available for the year 2010.