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Epoxy Resins

Fundamentals and Applications

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Fundamentals and Applications

Foreword

Hardly any class of resins is more widely used in the coatings industry than that of epoxides. Therefore, anyone who works with coatings needs a good overview of this topic.

This book seeks to provide that very knowledge from three aspects:

First, it surveys the historical development of epoxy resins, from the first synthesis in the 19th century to the first patents for epoxide compounds in coatings to industrial scale production of resins based on bisphenol A. Chapter 1 also proposes a unique nomenclature based on DIN standards for avoiding the proliferation of terms used for epoxy resins in the coatings industry.

Second, the book contains a compilation of the chemical properties of the epoxy (oxirane) group, of polymers containing epoxy groups and of polymers produced with epoxy groups (phenoxy resins). Chapter 2 presents the chemistry of the epoxy group, i.e. a characterisation of the three-membered ring, followed by the chemistry that is facilitated by this functional group and that is actually used within the industry. Finally, it examines the production and characterisation of polymers, both with and without epoxy groups, along with their curing reactions.

A comprehensive overview of all the possible reactions of epoxy groups is provided, with the focus on reactions that are relevant to coatings. Modern methods of characterising the compounds, such as NMR, IR and NIR spectroscopy are explained on one hand, while all the typical key parameters used in industry and based on corresponding DIN and ISO standards are presented on the other.

The third aspect is coating agents and how they are used in industry.

Chapter 3 covers the general use of epoxy resins and phenoxy resins. Sections 3.2 to 3.5 discuss the state of the art regarding the use of epoxy resins in industrial areas such as corrosion protection, flooring, powder coatings, can and coil coatings, as well as offering sample coating formulations and discussing the property profiles of the resulting coating surfaces. The topic of can coatings, in particular, includes a detailed discussion of the toxicological properties and current legislation on the use of resins based on bisphenol A.

Chapter 4 deals with trends in the epoxy resins market. Among the topics here are new applications, alternative compounds for BPA in food packaging, and new trends in the coatings industry.

This book will serve not only as a reference book on the chemistry of epoxides and their properties, but also as a monograph on the industrial coatings applications of epoxy resins, both with and without epoxy groups. It will therefore prove useful to students, developers and industrial users alike.

Düsseldorf, December 2015

Michael Dornbusch



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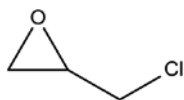
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1 Introduction

Michael Dornbusch

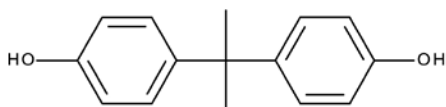
1.1 History

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



Equation 1.1: Chloromethyl oxirane (epichlorohydrin)

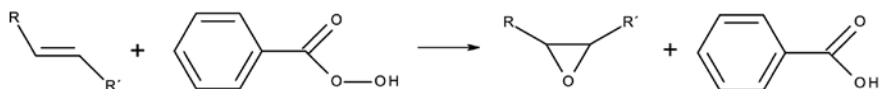
The next step occurred in 1891 with the first description of 2,2-bis(4-hydroxyphenyl)-propane (bisphenol A) by *Dianin* ^[2], who produced the impure compound ^[10].



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].



Equation 1.3: Preparation of epoxides, according to Prilezhaev^[22]

A patent published in the same year by *Horn* ^[9] 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*^[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^[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^[5].

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

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

In 1939, *Bock and Tischbein* from I.G. Farben^[14] patented the reaction between diepoxides 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^[6]. In the USA in the same year, *Greenlee*^[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^[18])^[2]. In Europe, Ciba AG developed products under patent licence from De Trey AG that it sold under the trade name Araldite while, independently in the USA, the Devoe & Reynolds Company developed similar products^[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^[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^[18]. At that time, Shell was the sole producer of epichlorohydrin and Bakelite was one of the largest producers of phenolic resins and BPA^[18].

In the 1950s, BPA was also used to produce polycarbonate^[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^[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^[8] 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^[8].

One of the oldest applications is that of internal can coating^[8]. 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^[8].

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 multi-layer boards^[1].

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^[8].

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^[1], 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^[18] 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 dicyclohexylamine (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*.

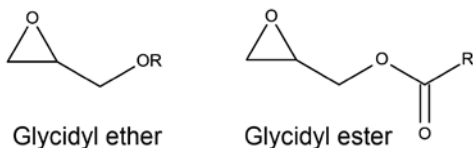
1.3 Terms and markets

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].



Equation 1.4: Typical oxirane compounds found in epoxy resins

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.

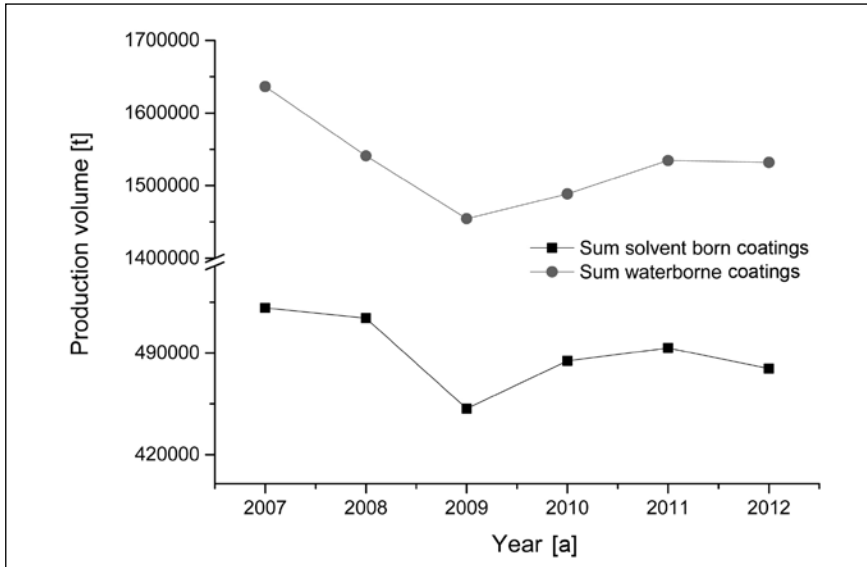


Figure 1.1: Production volumes for waterborne and solvent-borne coatings in Germany^[25-27]

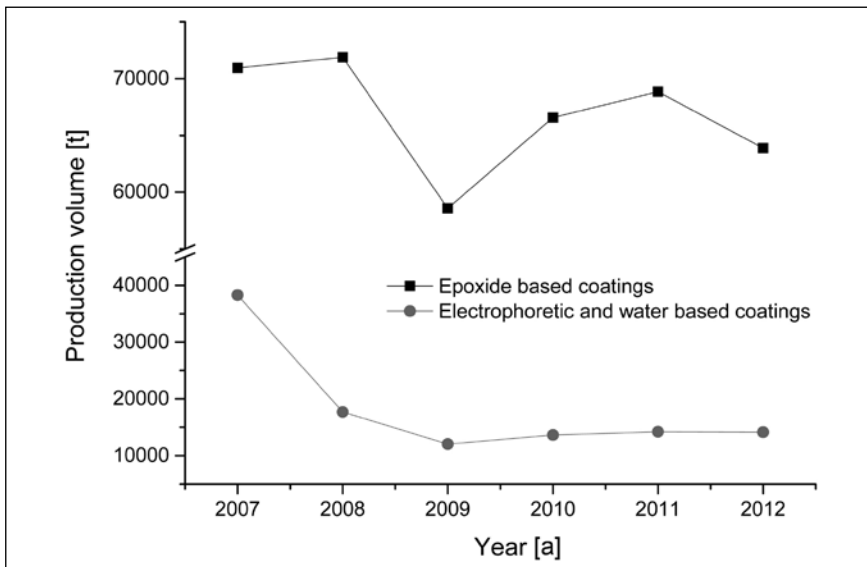


Figure 1.2: Production volumes for epoxy resins in Germany^[25-27]. No data are available for the year 2010.

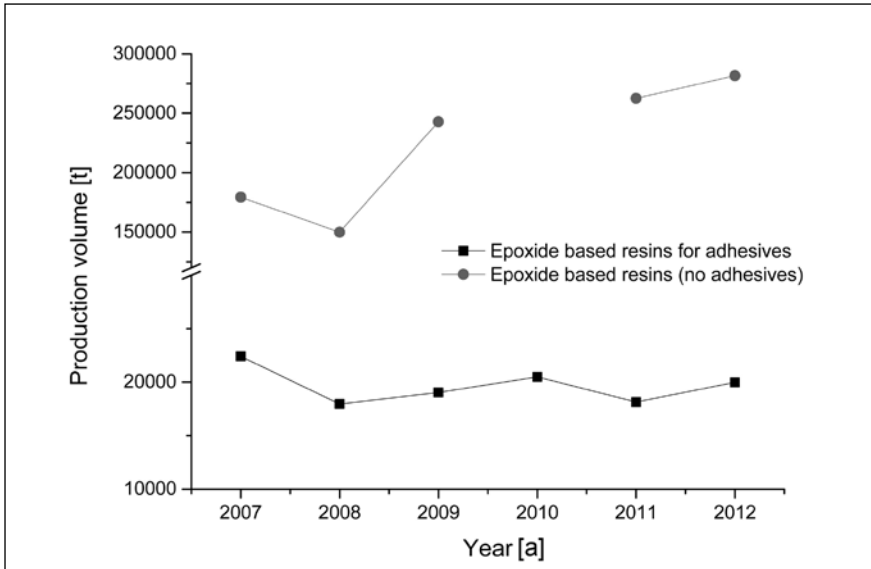


Figure 1.3: Production volumes for epoxy-based coatings and electrophoretic and waterborne coatings in Germany^[25-27]

The global epoxy resins market was forecast to increase to 1.93 million metric tons by 2015, according to a 2010 study by Global Industry Analysts Inc. (European Coatings journal, 10-2010).

This growth is being driven by such market segments as “electrical laminates” and “decorative powder coatings”. The Asia-Pacific region is the largest growth market in the world, although some plants in this region were shut down during the 2008/2009 global economic crisis.

1.4 Literature

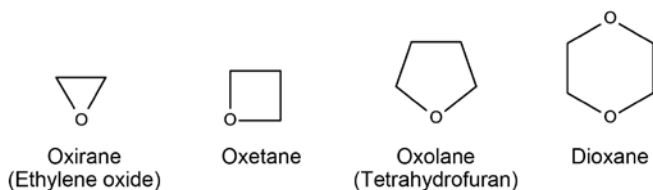
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2 Basic chemistry of the epoxy group

Michael Dornbusch

2.1 Properties and reactions of epoxy groups

Epoxides (oxiranes) are cyclic ethers that are characterised by high ring strain, which amounts to 114 kJ/mol in oxirane^[1,2] and 106 kJ/mol in oxetane^[1]. The values for cyclic hydrocarbons are in the same range: 115 kJ/mol for cyclopropane^[1] and 111 kJ/mol for cyclobutane^[1].



Equation 2.1: Important cyclic ethers and their systematic and trivial names

The ring strain results from the bond angle of 60° , which is considerably less than the normal tetrahedral carbon angle of 109.5° and the C-O-C bivalent bond angle of 110° in ethers^[7].

Small rings are stabilised by attached alkyl groups; thus the ring strain in 2-methyl-oxirane is 4 kJ/mol lower. The ring strain makes epoxides much more reactive than other cyclic ethers.

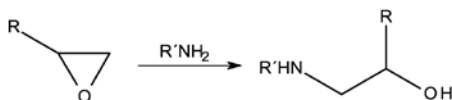
The ring strain in oxetane also enables it to react in mild conditions; its reactivity ranks between that of oxirane and open-chain ethers^[1]. In contrast, the higher homologues of the cyclic ethers are good solvents and are largely inert.

The key reactions of epoxides can be divided into two groups:

- Reactions with nucleophiles in neutral solution and
- Base-catalysed and acid-catalysed reactions

2.1.1 Reactions with nucleophiles

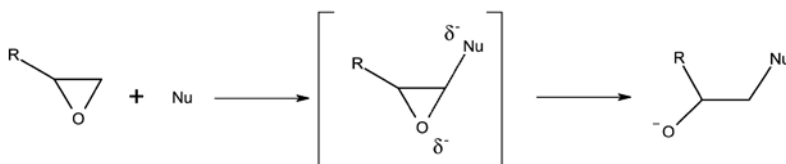
As a general rule, ethers are inert to bases, which is why they serve as solvents in numerous organic reactions. By contrast, epoxides undergo ring opening in mild conditions when attacked by nucleophiles, such as alkyl amines, in what is formally an addition reaction without elimination (see Equation 2.2).



Equation 2.2: Ring opening of an oxirane by a nucleophile

Orientation of epoxide-ring opening

In basic or neutral conditions, the nucleophile attacks the less substituted carbon atom, with ring opening and inversion in an S_N2 reaction^[1]; this creates a transition state which polarises the C-O bond, but the point of nucleophilic attack is determined by steric factors^[5].



Equation 2.3: Mechanism behind opening of the epoxide ring in a nucleophilic attack

Nucleophilic attack occurs at the less substituted carbon and only one product is generated^[2,3]. A list of important epoxide reactions in basic and neutral conditions that are of relevance to coatings technology is presented below.

Reactions with ammonia, primary, secondary and tertiary amines

Ammonia reacts with epoxides to yield mono-, di- or tri-alkanolamines, depending on the molar ratio of the reactants^[3].

The reaction of epoxides with primary amines produces in the first instance a hydroxylamine containing a secondary amine group and an alcohol group. The secondary amine then reacts with an epoxy group to produce a tertiary amine and two secondary alcohol groups^[4].

Secondary amines react in a similar way to yield tertiary amines containing a secondary hydroxyl group.