

Uses of Epoxy Resins

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Preface

This book is, I believe, the first attempt to describe in a comprehensive way the techno-economic background to the use of epoxy resins. This task has not been easy, however, because of the vast number of different industries that use these resins, but to the author at least, this variety also makes epoxy resins a much more-interesting group to study than many of the 'work-horse' thermoplastics.

This is not an exhaustive study of all uses for epoxy resins, and inevitably some uses have been omitted altogether. Again, because of limitations of space, it has not been possible to consider all important end-uses in the depth that perhaps they warrant. For example, automotive primers and can linings are given only brief consideration.

The book is addressed to the reader without an extensive chemical knowledge and will, I hope, be of interest to all who are concerned with materials or in cost savings. Throughout the book units of force are given in both lbf/in² and in SI units such as MN/m². The reader will recall that $1 \text{ lbf/in}^2 = 6.895 \text{ kN/m}^2$. In converting lbf/in² into SI units I have therefore adopted the approximation $1 \text{ lbf/in}^2 = 7 \text{ kN/m}^2$ and therefore $1000 \text{ lbf/in}^2 = 7 \text{ MN/m}^2$.

One difficulty in making a study of this nature is the lack of authoritative and detailed reports in the published literature on the economic considerations that underlie the use of epoxy resins in a particular situation. It has therefore been necessary to seek the views of resin manufacturers and end-users on the total set of considerations that lead to the choice of an epoxy composition for a particular job. I therefore wish to thank all of the many individuals and organisations that generously gave me their time. They are too numerous to mention individually, except that I particularly wish to record my gratitude to CIBA-Geigy for their help.

However, the book would not have been written at all without the generous help and cooperation of the Shell Group of Companies. I

have been able freely to consult Shell International Research, and have had great assistance from both Shell International Chemical Company and Shell Chemical Company U.K. To all of these organisations and to the individuals in them I now express my thanks. In particular, I wish to thank Fred Parmenter for his continued encouragement and valuable suggestions.

Behind many authors there is often a long suffering family. To Brenda and to Sarah and Selina I wish to dedicate this book, for putting up with it for a further two years.

W.G.P.

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SECTION I

General

1 Introduction

The amounts of epoxy resins manufactured and consumed are insignificant in comparison with polyethylene, polypropylene and polystyrene. Even when resins such as polyesters and polyurethanes are considered, the amounts of epoxy resins produced are smaller. But in terms of complexity of technology, variety and breadth of application, epoxy resins are surely superior to all other plastics and resins. There is hardly an industry in which these resins are not used. They find applications in electrical and electronic devices and oil wells, in space satellites and stained glass windows, on roads and bridges and in computers, in skis and in supersonic aircraft. They form the basis of high-performance paints which are used on ships, automobiles and as food can linings. They are used in the factory, the artist's studio, the laboratory and in the home.

Epoxy resins can be used as adhesives, sealing compounds, casting resins, dipping compounds, moulding powders, paints and varnishes, powder coatings, flooring and anti-skid surfacings and as the resin matrix in reinforced composites. When in these various forms they can be manipulated by hot or cold spraying, brushing, roller coating and all the other paint application methods, knifing, dipping, pouring, high- and low-pressure compression moulding and injection moulding. The reasons for this diversity of applications lie in the fundamental characteristics of the resins. Thus, during cure, no volatiles or other by-products are formed and volumetric shrinkage is very small — of the order of 1–2 per cent. The fully cured epoxy resin systems have the well-known properties of outstanding adhesion to many substrates, chemical resistance, toughness, mechanical strength and high electrical resistance. Many variations of these properties can be achieved by adjustments in the formulation used.

It is the aim of this book to give existing users of and newcomers to the resins, and all those with an interest in materials, a review of the wide range of uses of epoxy resins, and wherever possible to show why epoxy resins were chosen rather than another material. In some

instances, new uses for the resins might be suggested to people who know them well, and others may be encouraged to experiment with epoxy resins where they have not used them before. On another level, the book might give an insight into the way in which an extremely versatile product can enter into and become accepted by a host of dissimilar industries.

BASIC EPOXY RESIN TECHNOLOGY

This section gives a brief, non-technical account of some of the basic concepts underlying epoxy resin technology and touches on the complexities of formulating epoxy systems. A more comprehensive and technical account of these matters has been given elsewhere by the author¹.

Epoxy resins, also known as epoxide or ethoxyline resins, contain the epoxy group which is the chief centre of their reactivity. When manufactured, the resins are either liquids or solids and contain, on average, two epoxy groups per molecule. In this physical state, the resins are thermoplastic, that is, they can be repeatedly softened by heat and hardened by cooling. In fact, some epoxy resins are almost pure organic chemicals.

However, the essential feature of epoxy resin technology is the conversion of the resin into a hard, infusible three-dimensional network in which the resin molecules are crosslinked together by means of strong covalent bonds. This conversion can be termed polymerisation, but is more commonly called curing or hardening of the resin. The reagents that bring about this change are known as curing agents or hardeners, these terms being completely interchangeable. It is in this cured form that the resins are almost always used: in the uncured, 'non-crosslinked' state they are of limited use.

Curing is an irreversible change and once the resin has been cured it cannot be recovered again in its original form. Cure can be slowed down, stopped or speeded up, but it cannot be reversed. Hence epoxy resins fall into the category of thermosetting polymers, which, once polymerised, cannot be re-used by melting and reprocessing. Continued heating of a thermoset merely leads to softening and eventually degradation and breakdown of the material.

In practice, cure is brought about simply by mixing the resin and curing agent, the two materials sometimes being dissolved in a

suitable solvent. Once this mixing has occurred, a point of no return has been reached; cure begins and proceeds at a rate dependent upon factors such as temperature and the reactivities of the resin and curing agent towards each other. Some curing agents will react with the resins at room temperature or below, while others require heat to effect the polymerisation. The curing reaction is exothermic, that is, heat is evolved during the crosslinking process, which causes an increase in the temperature of the system. This is often called 'exotherm', and can reach high levels, perhaps 150–200 °C or above.

The temperature level reached in any particular example will depend not only upon the reactivity of the resin and curing agent, but also upon the temperature of the reactants and of their surroundings, that is, upon the rate at which polymerisation is occurring and the rate at which the heat evolved is being dissipated to the surroundings. Clearly, the ratio of the surface area to the mass of the reactants is important, as a large surface area would allow more heat to be dissipated compared with a smaller surface area for the same mass. This situation occurs if a mixture is being used as an adhesive rather than for casting purposes.

In practice, care is taken to ensure that the increase in temperature of a bulk mixture of resin and curing agent is not excessive. In the absence of such control, bubbling, cracking, charring and even complete degradation of the resin could occur in severe cases.

The time taken from the initial mixing of the resin and curing agent to the point when the viscosity of the mixture has become so high as to render the mix unusable is called the 'pot life' of the system. This time is therefore the practical working life of the mix, during which the material must be applied to the job concerned. To a large extent, the pot life is influenced by the same factors that affect the exotherm, and pot lives can vary from a few seconds to several weeks, such is the wide range of possibilities with epoxy resin formulations. The pot life is also dependent upon the intended application of the system; thus a viscous mixture may still be pourable into a mould but would not be suitable for glass-fibre impregnation in a laminating process.

The simple resin—curing agent combination alone seldom provides a material with all the properties required for use in a given application, and other materials must be added so as to modify the properties of the cured resin or to make it cheaper. The correct choice of the types and amounts of the different components of an epoxy

formulation is a fairly precise, difficult and important task because the final properties and eventual performance of the system depend upon it. The various classes of materials that can be added to the resin and curing agent combination are:

- (1) Diluents.
- (2) Inert fillers and pigments.
- (3) Flexibilisers.
- (4) Fire retardants.
- (5) Resinous modifiers.
- (6) Cure accelerators.
- (7) Reinforcements.

Some modifying materials frequently perform more than one function at the same time; thus a diluent might also be a flexibiliser or a cure accelerator. The classification does, however, provide a convenient basis for discussion.

Diluents

Diluents are liquids used to reduce the viscosity of the mixture. They can react chemically with the curing agent and resin, or be non-reactive, and are used in small amounts, generally of the order of 5- 10 parts per 100 parts (w/w) of resin.

Inert fillers

Inert fillers have a variety of functions, but are chiefly used to make the system cheaper and to modify the physical and mechanical properties such as thermal conductivity and expansion, hardness and compressive strength. Other fillers are used to impart thixotropy to the mixture, that is, to thicken the mix so that it will not run off inclined surfaces but will flow when stirred.

Flexibilisers

Cured epoxy resins are usually hard but brittle solids. If a tougher, more flexible material is required, which is better able to withstand mechanical stressing or thermal shock, the epoxy system may be modified in one of two ways:

- (a) Long, flexible molecular chains may be incorporated into the network during cure. This is achieved by using a flexible epoxy resin, curing agent or reactive additive.
- (b) Long-chain molecules that remain unreacted after cure of the resin may be incorporated into the system. This effect, which is often regarded as plasticisation rather than flexibilisation, is achieved with non-reactive additives.

Fire retardants

Techniques employed to improve the fire-retardant properties of the cured resins mostly involve the incorporation of bromine or chlorine atoms into the system, usually by utilising halogenated epoxy resins or chlorinated curing agents. Certain fillers and diluents are also valuable in this respect.

Resinous modifiers

A wide range of other resins will react chemically with the epoxy resins to form a modified or 'alloyed' polymer system. Common examples are the combinations of epoxy resins with phenolic, urea melamine, polyester, polyurethane, silicone, vinyl and nylon resins. These systems have enhanced properties in certain respects over the properties of the individual, separate resins.

Other resins, although not reacting chemically with the epoxy resins, are also used to cheapen and alter the properties of the unmodified epoxy resins. Important examples are the addition of coal-tar pitch to yield epoxy paints with much improved water resistance, and petroleum-derived bitumens to cheapen anti-skid road surfacings.

Cure accelerators

Certain simple substances can increase the rate of reaction between the epoxy resins and some curing agents, and wide variations in the rate

of cure can be achieved by the addition of small amounts of catalyst. For example, phenol causes the rate of reaction between an epoxy resin and a simple aliphatic amine to increase by several orders of magnitude.

Reinforcements

These are inert, fibrous materials whose prime purpose is to increase the strength of the system. Glass and metal fibres are widely used, the glass being in fibrillar form or woven into a cloth or mat and the metal fibres being used as discrete fibres or whiskers. Carbon fibres are also now becoming important. The whole subject of polymeric composite materials is based on the combination of a resin matrix with a fibrous reinforcement, and epoxy resins play an important part in this particular technology.

It can be seen, therefore, that what is generally referred to as an epoxy resin is more properly a carefully formulated mixture of ingredients. The correct formulation of these ingredients is a skilled task and much of epoxy resin technology consists in the successful development of formulations 'tailor made' for a particular application.

HISTORY OF THE DEVELOPMENT OF THE RESINS

Work on diepoxides was mentioned in patents in the late 1920s and early 1930s, but the beginning of today's epoxy resin technology is taken by many to be the patent of Schlack of IG Farben², whose application date was December, 1934. This patent was primarily concerned with the production of polyamines but mentions polyglycidyl ethers of diphenylolpropane (DPP). It does not, however, acknowledge these glycidyl ethers as resins. The first patent so to acknowledge the resinous characteristics of these substances appears to be that of Moss^{3, 4}, whose application date was December, 1937.

Work was also being carried out in Switzerland and in 1938 Castan⁵, a Swiss chemist employed by the dental products manufacturers De Trey Frères of Zürich, filed a patent, to be followed by a second in 1943⁶. These two patents described the

Introduction

production of diglycidyl ethers and esters, including a resin based on DPP and ECH (epichlorohydrin), and polymerisation of these resins with acid anhydrides such as phthalic anhydride, and organic and inorganic bases including amines.

Attempts in the early 1940s to market Castan's products as casting resins for dental use failed, and the patents were subsequently licensed to CIBA A.G. of Basle (now CIBA-Geigy). At the Swiss Industries Fair in 1946, this company demonstrated the use of an epoxy resin adhesive, Araldite type I, to bond light alloys and at the same time offered samples of an epoxy casting resin to four Swiss electrical companies. This introduction of the resins to industry can be taken as the beginning of the commercial exploitation of these remarkable materials.

Parallel with this European activity, the paint company Devoe and Raynolds in the U.S.A. had been working with Shell Chemical Corporation to develop epoxy resins suitable for the surface coatings industry. This led to a long series of patents by Greenlee and co-workers of Devoe and Raynolds, the first being filed in September, 1943⁷. The work by Greenlee covered methods of preparing the higher molecular weight DPP-ECH resins⁸⁻¹¹ and important ways of modifying the resins or combining them with other materials to form surface coatings. Outstanding amongst these methods were the esterification of epoxy resins via both their hydroxyl and epoxide groups to form drying or non-drying resin esters¹² and the combination of epoxy resins with phenolic^{13, 14} or amino resins^{15, 16} to produce stoving finishes. While this basic work was being carried out, the Shell researchers were investigating a vast range of possible curing agents for the resins, monoepoxide compounds as reactive diluents and other possible modifications to the resin-curing agent combination¹⁷⁻²². Shell obtained licences to the Devoe and Raynolds patents and began to market a range of liquid and solid epoxy resins under the name Epon in the U.S.A. and Epikote in all other countries, principally to the surface coatings industry. These early resins were based on DPP and ECH and they continue to be the most important class of epoxy resins throughout the world.

In the late 1950s and early 1960s, other types of resin began to appear in the manufacturers' catalogues, including epoxidised novolacs and other polyfunctional epoxy resins, resins derived from halogenated DPP for flame retardancy and resins to impart flexibility to castings. Greenspan and co-workers of the Food Machinery

Corporation, U.S.A., reported on resins derived from the epoxidation of polyolefins and a range of these resins was brought to the market. The research teams of Union Carbide Corporation (Philips and co-workers) and CIBA, Basle (Batzer, Ernst, Fisch, Porrett *et al.*) investigated very many cycloaliphatic diepoxides, and market development was commenced with a small number of selected products.

The period from the mid-1960s to the early 1970s saw the continued development of new types of epoxy resins and curing agents. Increased interest was shown in the various types of cycloaliphatic resins, especially in view of their good anti-tracking properties and resistance to ultra-violet light. The glycidyl esters of the three phthalic acids, which also show these same attractive properties, were offered commercially, and development work continued on the high molecular weight linear phenoxy resins. The regular appearance in the literature of new curing agents continued unabated. One noteworthy event among the many was the marketing of a polymercaptan curing agent, which, when used with an accelerator, would cure resins at an acceptable rate at 0 °C.

Equally important, the exploitation of the outstanding properties of epoxy resin systems in an ever-growing number of uses has continued. It is difficult to select individual applications for particular mention, but the development of electrodeposited epoxy primers, epoxy powder coatings, filament-wound epoxy-glass circuit-breaker tubes, epoxy transfer moulding powders, epoxy flooring and adhesives all deserve special mention. Useful reviews, occasioned by the twentieth anniversary of the commercial introduction of epoxy resins, have also been published on the progress of epoxy technology, and mention a number of other applications which are dealt with in later chapters of this book.

Undoubtedly, the future remains bright for epoxy resins. Much has happened since the early days when CIBA and Shell, in the late 1940s and early 1950s, first began to manufacture and market these new and versatile materials. Many more manufacturers have since begun to produce the resins, and this trend will certainly continue. However, it is undoubtedly true that the continued development and exploitation of epoxy resins requires the resources of major world-wide companies, which will limit the number of manufacturers who are really able to play a significant part in this future activity.

COMMERCIAL BACKGROUND

Since the 1950s, epoxy resin production and sales have steadily increased, and in the last 10 years the world market has grown on average by at least 10–15 per cent per annum. At present, in the early 1970s, the total world-wide sales are about 150 000 tons, and probably one third of this total is accounted for by sales in the U.S.A., about a half in Europe, and much of the remaining amount in Japan. In the U.K., sales in 1972 were about 10 500 tons. At least 95 per cent of the epoxy resins sold is of the one basic type – the diglycidyl ethers of diphenylolpropane. These epoxy resins, manufactured from epichlorohydrin (ECH) and diphenylolpropane (DPP; also known as bisphenol A), have always been the ‘work-horses’ of the epoxy resin business, and no doubt will continue to be so for many years to come. One important reason for their initial popularity was that DPP was and probably still is the cheapest suitable aromatic dihydroxy compound available. The DPP–ECH resins also offer a very attractive range of properties which clearly have met customer needs over the last 25 years. The remaining 5 per cent of epoxy resins sold includes the cycloaliphatics, glycidyl esters and amines, epoxidised olefins and the specialised glycidyl ether resins such as the brominated types and the epoxy novolacs.

An analysis of sales, in 1965 and 1972, by end-use for the U.K. market is given in *Table 1.1* and shows that the surface coatings industry still dominates the market as the major consumer of the resins. Electrical and electronic uses have contracted although they are still major outlets. Other uses individually remain a relatively small proportion of the total tonnage, although they probably play a more important part in the overall earnings picture for the resins. This situation has not altered markedly over the last 15 years, and the continued flow of new developments, especially from Shell in the coatings field, will ensure that the pattern does not change rapidly in the near future.

Naturally, the end-use patterns of sales in other countries are not identical with that for the U.K., but in most major markets the surface coatings industry remains a major consumer of the resins. The resins are now manufactured in most industrialised countries of the world. In Western Europe alone there are at least fourteen different companies producing the resins, and in addition there are plants in most East European countries. The early pioneering