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PLASTICS TECHNOLOGY

Tutorial

Part 2

Tutorial is conformed to a State education standard in the direction 240100 – "Chemical technology" and the program "Polymer science and technology".

The tutorial describes plastics based on polymers obtained by polymerization, polycondensation and on chemically modified polymers (preparation of monomer, polymerization or polycondensation, properties, processing and applications).

The tutorial is designed for the masters studying the disciplines "Chemistry and physics of macromolecular compounds", "General chemical technology of polymers", "Plastics technology".

Prepared by the Department of Plastics technology.

Учебное пособие соответствует Государственному образовательному стандарту по направлению 240100 – «Химическая технология» и программе «Наука о полимерах и технология».

В пособии описаны пластмассы на основе полимеров, получаемых путем полимеризации, поликонденсации, и химически модифицированные полимеры (подготовка мономера, полимеризация или поликонденсация, свойства, переработка и применение).

Предназначено для магистров, изучающих дисциплины «Химия и физика высокомолекулярных соединений», «Общая химическая технология полимеров», «Технология пластмасс».

Подготовлено на кафедре технологии пластических масс.

Contents

Preface

One of the fastest changing fields today is the field of plastics as new polymers are synthesized, new uses are found, and existing processes and products are modified and improved for ecological needs, better economics, and better values.

What makes plastics the most versatile of all materials is the ease with which they can be given any desired shape and form. Molding and fabrication processes, however, vary depending on the type of polymers to be processed and the end products to be made.

In this tutorial, plastics have been broadly divided into three categories, namely, plastics based on polymers obtained by polymerization, plastics based on polymers obtained by polycondensation and plastics based on chemically modified polymers. The first group of polymers was reviewed in the tutorial "Plastics Technology" (part 1). The second group of polymers includes epoxy and phenolic resins, aminoplastics, heterochain polyesters, polyamides and polyimides, etc. The third group of polymers includes chemically modified polymers of unsaturated hydrocarbons, polymeric alchohols, cellulose plastics and other polymers and polymeric combinations that play special and often critical roles in diverse fields of human activities.

1 CONDENSATION POLYMERIZATION

In this form of polymerization, initiation and termination stages do not exist and chain growth occurs by random reaction between two reactive groups. Thus in contradistinction to addition polymerization an increase in reaction time will produce a significant increase in average molecular weight. An increase in temperature and the use of appropriate catalysts, by increasing the reactivity, will also increase the degree of polymerization achieved in a given time.

In the case of linear polymers it is often difficult to obtain high molecular weight polymers. The degree of polymerization $\overline{x}$ will be given by

$$\overline{x} = \frac{\text{No. of available for reaction}}{\text{No. of groups not reacted}}$$

If p, the extent of reaction, is the fraction of groups that have reacted, then

$$\overline{x} = \frac{1}{1-p}$$

Thus when 95% of the groups have reacted (p = 0.95) the degree of polymerization will be only 20.

Even lower molecular weights will be obtained where there is an excess of one reactive group, since these will eventually monopolize all the chain ends and prevent further reaction. The presence of monofunctional ingredients will have similar effects and they are sometimes added deliberately to control molecular weight.

It is to be noted that only one condensation reaction is necessary to convert two molecules with values of $\overline{x} = 100$ to one molecule with $\overline{x} = 200$. A similar reaction between two dimers will produce only tetramers ($\overline{x} = 4$). Thus although the concentration of reactive groups may decrease during reaction, individual reactions at later stages of the reaction will have greater effect.

As with addition polymers, molecules with a range of molecular weights are produced. In the condensation of bifunctional monomers

$$\frac{\overline{x}_w}{\overline{x}_n} = (1+p)$$

where $\overline{x}_w$ and $\overline{x}_n$ are the weight average and number average degrees of

polymerization respectively. Thus as the reaction goes towards completion the ratio of the degrees of polymerization and hence the molecular weights approaches 2.

In the case of trifunctional monomers the situation is more complex. From the schematic diagrams (Figure 1) it will be seen that the polymers have more functional groups than the monomers.

(a)   (b)   (c)
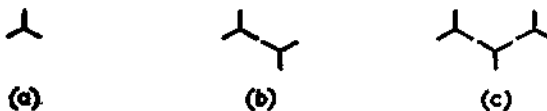
Figure 1

It is seen that the functionality (no. of reactive groups = f) is equal to $n+2$ where n is the degree of polymerization. Thus the chance of a specific 100-mer (102 reactive groups) reacting is over 30 times greater than a specific monomer (3 reactive groups) reacting. Large molecules therefore grow more rapidly than small ones and form even more reactive molecules. Thus "infinitely" large, cross-linked molecules may suddenly be produced while many monomers have not even reacted. This corresponds to the "gel point" observed with many processes using thermosetting resins. It may in fact be shown that at the gel point with a wholly trifunctional system $\bar{x}_w = \infty$ whilst $\bar{x}_n$ is only 4.

Appendix - A note on molecular weight averages and molecular weight distribution

A mass of polymer will contain a large number of individual molecules which will vary in their molecular size. This will occur in the case, for example, of free-radically polymerized polymers because of the somewhat random occurrence of chain termination reactions and in the case of condensation polymers because of the random nature of the chain growth. There will thus be a distribution of molecular weights; the system is said to be polydisperse.

The molecular weight distribution may be displayed graphically by plotting the frequency at which each molecular weight occurs against that molecular weight (or more practically the frequency within a narrow molecular weight band). When this is done certain characteristics may be established. These include:

(1) A measure of the central tendency of the distribution. While this could be expressed using such statistical terms as a mode or median an average (mean) molecular weight is more useful; but see below.

(2) The breadth of distribution. It is common to refer to polymers having a narrow- or a broad-molecular weight distribution. While this could be quantified in terms of statistical parameters such as standard deviation, mean deviation or inter-quartile range, such data is seldom made available by the polymer supplier and is also of somewhat limited value if the distribution deviates significantly from being symmetrical.

(3) The symmetry of the distribution. As pointed out in the previous section on condensation polymerization, large polymer molecules can grow rapidly, particularly where there are trifunctional monomers. This can lead to a positively skewed distribution, i.e. a distribution with a long high molecular weight tail. Other polymerization methods may leave a significant amount of unreacted monomer which would give a negative skew.

(4) The modality of the distribution. In the example given in the previous sentence the distribution would probably have two peaks or modes, one corresponding to the monomer molecular weight and the other related to an average polymer molecular weight. Such a bimodal distribution can also occur if two polymer samples of different average molecular weight are blended together. Trimodal, tetramodal, pentamodal distributions, and so on, could similarly be envisaged.

While breadth, skewness and modality of a distribution are all of some interest the most important parameter is the average molecular weight. This however can be defined in a number of different ways. Conceptually the simplest is the number average molecular weight, invariably given the symbol $\overline{M}_n$. This is essentially the same as the arithmetic mean molecular weight where the sum of the weights of all the molecules are divided by the number of molecules. This is the same as saying that $\overline{M}_n$ is the sum of the product of the number fraction of each molecular weight (n_i) times the molecular weight (M_i) i.e.

$$\overline{M}_n = \sum n_i M_i$$

For some purposes this average may be less useful than the weight average molecular weight defined by $\overline{M}_w$ which considers the fraction by weight of each molecular size i.e.

$$\overline{M}_w = \sum w_i M_i$$

This can best be explained by taking a somewhat extreme

theoretical example. Let us consider a tiny sample of polymer consisting of 1 molecule with a molecular weight of 100000 and 999 molecules with a molecular weight of 100. In this case the number average molecular weight will be

$$(0.001) \cdot (100000) + (0.999) \cdot (100) = c.199$$

However, a moments consideration makes clear that over half the mass of the polymer consists of the molecule with the molecular weight of 100000 and that this would have an important influence on the properties of the polymer mass not reflected in the number average figure which is in any case totally unrepresentative of any of the molecules. In this case the weight average molecular weight will be

$$(100000/199900) \cdot (100000) + (99900/199900) \cdot (100) = c.50125$$

While this example shows an extreme difference in the two molecular weight averages, the other extreme is where all of the molecules have the same size, i.e. they are said to be monodisperse. In this case the two averages will have the same value.

The molecular weight ratio $\overline{M}_w / \overline{M}_n$ can thus be considered as a crude measure of the breadth of the molecular weight distribution and is often used for this purpose.

One further point might be made here. Although the example illustrates the difference between the two types of molecular weight average, the weight average molecular weight in this example cannot be said to be truly representative, an essential requirement of any measure of central tendency. In such circumstances where there is a bimodal, i.e. two-peaked, distribution additional data should be provided such as the modal values (100 and 100000 in this case) of the two peaks.

1.1 Epoxy Resins

The epoxy resins are characterized by the possession of more than one 1.2-epoxy group (I) per molecule. This group may lie within the body of the molecule but is usually terminal.

$$\begin{array}{c} O \\ / \backslash \\ -CH-CH- \end{array}$$
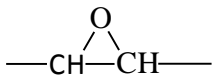
(I)

The three-membered epoxy ring is highly strained and is reactive to many substances, particularly by with proton donors, so that reactions of the following schematic form can occur:

$$\overset{\displaystyle O}{\overset{\displaystyle /\backslash}{-CH-CH-}} + HX \longrightarrow \overset{\displaystyle OH}{\overset{\displaystyle |}{-CH-CH-X}}$$
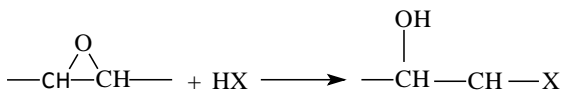
Such reactions allow chain extension and/or cross-linking to occur without the elimination of small molecules such as water, i.e. they react by a rearrangement polymerization type of reaction. In consequence these materials exhibit a lower curing shrinkage than many other types of thermosetting plastics.

There is, quite clearly, scope or a very wide range of epoxy resins. The non-epoxy part of the molecule may be aliphatic, cycloaliphatic or highly aromatic hydrocarbon or it may be non-hydrocarbon and possibly polar. It may contain unsaturation. Similar remarks also apply to the chain extension/cross-linking agents, so that cross-linked products of great diversity may be obtained. In practice, however, the commercial scene is dominated by the reaction products of bis-phenol A and epichlorohydrin, which have some 80-90% of the market share.

In the early stage of their development the epoxy resins were used almost entirely for surface coating and developments in this field are to a large extent due to the works of S.O.Greenlee and described in a number of patents. These included work on the modification of epoxy resins with glycerol, the esterification of the higher molecular weight materials with drying oil acids and reactions with phenolic and amino resins.

Before World War II the cost of the intermediates for these resins (in most cases epichlorohydrin and bis-phenol A) would have prevented the polymers from becoming of commercial importance. Subsequent improvements in the methods of producing these intermediates and improved techniques of polymerization have, however, led to wide commercial acceptance.

By the beginning of the 1980s world capacity for epoxy resins reached about 600000 tonnes per annum but at this time plant utilization was only about 50-60%. Thus with a global consumption of about 10 million tonnes per annum for thermosetting plastics, epoxy resins had a share of about 3%. Western Europe and the USA each had about 40% of the market and Japan a little over 10%. This situation has not greatly changed since then; but by the late 1990s the world market for epoxy resins had risen to about 750000 t.p.a.

About half of epoxy resin production is used for surface coating applications, with the rest divided approximately equally between electronic applications (particularly for printed circuit boards and

encapsulation), the building sector and miscellaneous uses. In tonnage terms consumption of epoxy-fibre laminates is only about one-tenth that of polyester laminates, but in terms of value it is much greater.

Whilst the properties of the cross-linked resins depend very greatly on the curing system used and on the type of resin, the most characteristic properties of commercial materials are their toughness, low shrinkage on cure, high adhesion to many substrates, good alkali resistance and versatility in formulation.

Preparation of resins from bis-phenol A

The first, and still the most important, commercial epoxy resins are reaction products of bis-phenol A and epichlorohydrin. Other types of epoxy resins were introduced in the late 1950s and early 1960s, prepared by epoxidizing unsaturated structures. The bis-phenol A is prepared by reaction of the acetone and phenol.
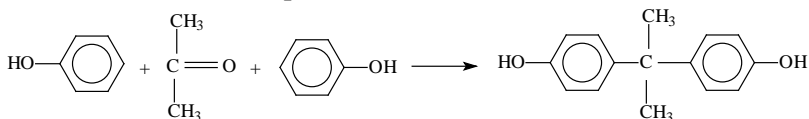
Since both phenol and acetone are available and the bis-phenol A is easy to manufacture, this intermediate is comparatively inexpensive. This is one of the reasons why it has been the preferred dihydric phenol employed in epoxy resins manufacture. Since most epoxy resins are of low molecular weight and because colour is not particularly critical the degree of purity of the bis-phenol A does not have to be so great as when used in the polycarbonate resins. Bis-phenol A with a melting point of 153°C is considered adequate for the most applications whilst less pure materials may often be employed.

Epichlorohydrin, the more expensive compound is derived from propylene by the sequence of reactions shown in Figure 2.

Figure 2

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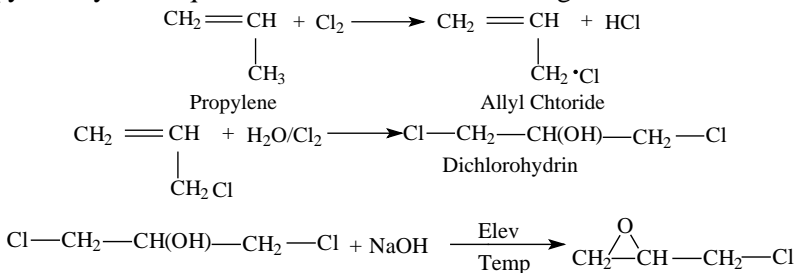
It will noticed, that the initial steps correspond with those used in the manufacture of glycerol. The material is available commercially at 98% purity and is a colourless mobile liquid.

Many of the commercial liquid resins consist essentially of the low molecular weight diglycidyl ether of bis-phenol A together with small quantities of higher molecular weight polymers. The formation of the diglycidyl ether is believed to occur in the manner shown in Figure 3, the hydrochloric acid released reacting with the caustic soda to form sodium chloride.
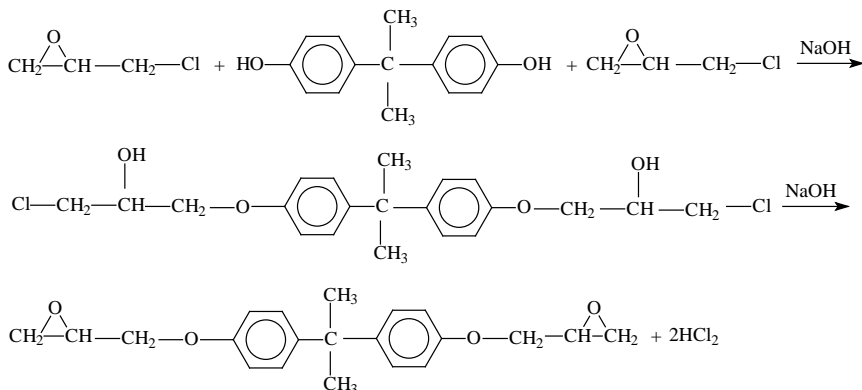
Figure 3

The diglycidyl ether has a molecular weight of 340. Many of the well-known commercial liquid glycidyl ether resins have average molecular weights in the range 340-400 and it is therefore obvious that these materials are composed largely of the diglycidyl ether.

Higher molecular weight products may be obtained by reducing the amount of excess epichlorohydrin and reacting the more strongly alkaline conditions which favour reaction of the epoxy groups with bis-phenol A. If the diglycidyl ether is considered as a diepoxide and represented as
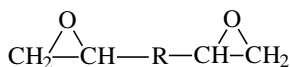
this will react with further hydroxyl groups, as shown in Figure 4.
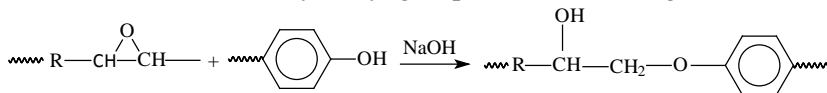
Figure 4

It will be observed that in these cases hydroxyl groups will be formed along the chain of the molecule. The general formula for glycidyl ether resins may thus be represented by the structure shown in Figure 5.

$$CH_2-CH-CH_2-\left[O-\bigcirc-\underset{CH_3}{\overset{CH_3}{C}}-\bigcirc-O-CH_2-\underset{OH}{CH}-CH_2\right]_n-O-\bigcirc-\underset{CH_3}{\overset{CH_3}{C}}-\bigcirc-O-CH_2-CH-CH_2$$
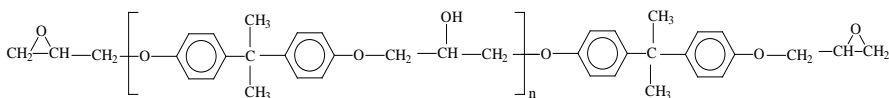
Figure 5

When $n = 0$, the product is the diglycidyl ether, and the molecular weight is 340. When $n = 10$ molecular weight is about 3000. Since commercial resins seldom have average molecular weights exceeding 4000 it will be realized that in the uncured stage the epoxy resins are polymers with a low degree of polymerization.

Table 1 shows the effect of varying the reactant ratios on the molecular weight of the epoxy resins.

Table 1– Effect of reactant ratios on molecular weights

Mol. ratio epichlorohydr in/ bis-phenol A	Mol. ratio NaOH/ epichlorohydr in	Softening point, ºC	Molecular weight	Epoxide equivalent	Epoxy groups per molecule
2.0	1.1	43	451	314	1.39
1.4	1.3	84	791	592	1.34
1.33	1.3	90	802	730	1.10
1.25	1.3	100	1133	862	1.32
1.2	1.3	112	1420	1176	1.21

It is important that care should be taken to remove residual caustic soda and other contaminates when preparing the higher molecular weight resins and in order to avoid the difficulty of washing highly viscous materials these resins may be prepared by a two-stage process.

This involves first the preparation of lower molecular weight polymers with a degree of polymerization of about three. These are then reacted with bis-phenol A in the presence of a suitable polymerization catalyst such that the reaction takes place without the evolution of by-products.

The epoxy resins of the glycidyl ether type are usually characterized by six parameters:

(1) Resins viscosity (of liquid resin).

(2) Epoxy equivalent.

(3) Hydroxyl equivalent.

(4) Average molecular weight (and molecular weight distribution).

(5) Melting point (of solid resin).

(6) Heat distortion temperature (deflection temperature under load) of cured resin.

Curing of glycidyl ether resins

The cross-linking of epoxy resins may be carried out either through the epoxy groups or the hydroxy groups. Two types of curing agent may also be distinguished, catalytic systems and polyfunctional cross-linking agents that link the epoxy resin molecules together. Some systems used may involve both the catalytic and cross-linking systems.
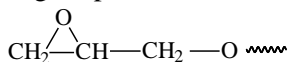
Whilst the curing mechanisms may be quite complex and the cured resins too intractable for conventional analysis some indication of the mechanisms involved has been achieved using model systems.

The reactivity of the epoxy ring is enhanced by the presence of the ether linkage separated from it by a methylene link.

$$CH_2\overset{O}{\overbrace{}}CH-CH_2-O\,\text{\tiny\char`\~\char`\~}$$

The epoxy ring may then be readily attacked not only by active hydrogen and available ions but even by tertiary amines. For example, with the latter it is believed that the reaction mechanism is as follows:

$$R_3N + CH_2\overset{O}{\overbrace{}}CH \text{\tiny\char`\~\char`\~} \longrightarrow R_3\overset{\ominus}{N}-CH_2-CH\text{\tiny\char`\~\char`\~}$$
$$\underset{\overset{|}{\underset{O^{\ominus}}{}}}{}$$
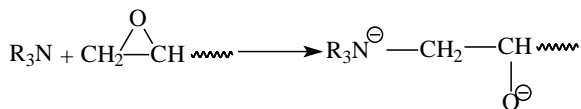
This ion may then open up a new epoxy group generating another ion which can in turn react with a further epoxy group.

$$\text{\tiny\char`\~\char`\~} CH_2-CH\text{\tiny\char`\~\char`\~} + CH_2\overset{O}{\overbrace{}}CH\text{\tiny\char`\~\char`\~} \longrightarrow \text{\tiny\char`\~\char`\~}CH_2-CH\text{\tiny\char`\~\char`\~}$$
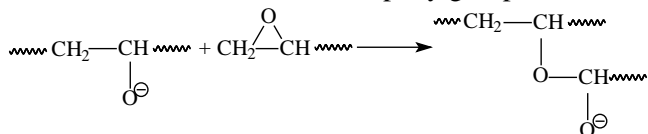
Since this reaction may occur at both ends of the molecule (in case of glycidyl ether resins) a cross-linked structure will be built up.

The overall reaction is complicated by the fact that the epoxy group, particularly when catalyzed, will react with hydroxyl groups. Such

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groups may be present due to the following circumstances:

(1) They will be present in the higher molecular weight homologues of the diglycidyl ether of bis-phenol A.

(2) They may be introduced by the curing agent or modifier.

(3) They will be formed as epoxy rings are opened during cure.

(4) In unreacted phenol-type materials they are present as impurities.

The epoxy-hydroxyl reaction may be expressed as

$$R\!-\!OH + CH_2\!\!-\!\!CH \text{ www} \longrightarrow RO\!-\!CH_2\!-\!CH \text{ www}$$
$$\underset{OH}{|}$$
$$\text{or}$$
$$HO\!-\!CH_2\!-\!CH \text{ www}$$
$$\underset{OR}{|}$$

This product will contain new hydroxyl groups that can react with other epoxy rings, generating further active hydroxyl groups, e.g.

$$CH_2\!\!-\!\!CH \text{ www} + RO\!-\!CH_2\!-\!CH \text{ www} \longrightarrow RO\!-\!CH_2\!-\!CH \text{ www}$$
$$\underset{OH}{|} \qquad\qquad O\!-\!CH_2\!-\!CH\text{www etc.}$$
$$\underset{OH}{|}$$
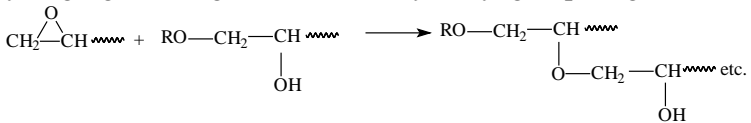
The predominance of one reaction over the other is greatly influenced by the catalyst system employed. Tertiary amine systems are often used in practice.
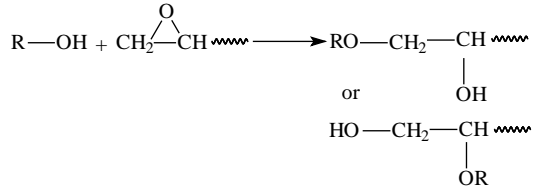
In addition to the catalytic reactions the resins may be cross-linked by agents, which link across the epoxy molecules. These reactions may be through the epoxy ring or the hydroxyl groups. Two examples of the former are:

(1) With amines

$$CH_2\!\!-\!\!CH\text{ www} + \underset{H}{\overset{NR}{H}} + CH_2\!\!-\!\!CH\text{ www} \longrightarrow \text{www}CH\!-\!CH_2\!-\!N\!-\!CH_2\!-\!CH\text{ www}$$
$$\underset{OH}{|}\quad\underset{R}{|}\quad\underset{OH}{|}$$

(2) With acids

$$CH_2\!\!-\!\!CH\text{ www} + HOOC\cdot R\cdot COOH + CH_2\!\!-\!\!CH\text{ www} \longrightarrow$$

$$\text{www}CH\!-\!CH_2\!-\!OOCRCOO\!-\!CH_2\!-\!CH\text{ www}$$
$$\underset{OH}{|}\qquad\qquad\underset{OH}{|}$$
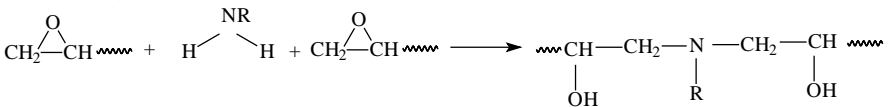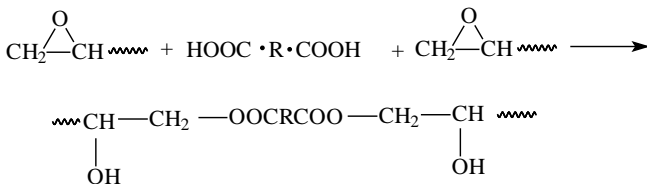
The reactions indicated above in fact lead only to chain extension. In practice, however, polyamines are used so that the number of active hydrogen atoms exceeds two and so cross-linkage occurs.

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In the case of acids and acid anhydrides, reaction can also occur via the hydroxyl groups that are present, including those formed on opening of the epoxide ring.

$$\text{\wwww}\,R \cdot COOH \;+\; HO \!\!-\!\!-\!\! \longrightarrow \text{\wwww}\,R \cdot COO \!\!-\!\!-\!\! \;+\; H_2O$$

Both amines and acid anhydrides are extensively used cross-linking agents. The resins may also be modified by reacting with other polymers containing hydroxyl or mercaptan groupings, e.g.

$$\text{\wwww}\,SH \;+\; CH_2\!\!-\!\!CH\,\text{\wwww} \longrightarrow \text{\wwww}\,S\!\!-\!\!CH_2\!\!-\!\!\underset{|}{\overset{OH}{CH}}\,\text{\wwww}$$

These various systems will be dealt with individually in the following sections.

Amine hardening systems

Amine hardeners will cross-link epoxy resins either by a catalytic mechanism or by bridging across epoxy molecules. In general the primary and secondary amines act as reactive hardeners whilst the tertiary amines are catalytic.
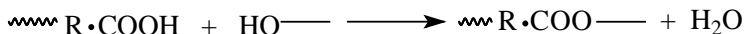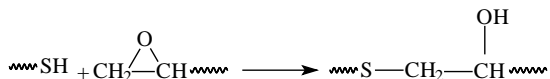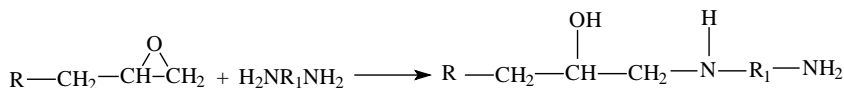
Diethylenetriamine and *triethylenetetramine* are highly reactive primary aliphatic amines with five and six active hydrogen atoms available for cross-linking respectively. Both materials will cure glycidyl ether at room temperature. In the case of diethylenetriamine, the exothermic temperature may reach as high as 250°C in 200 g batches. With this amine 9-10 pts phr, the stoichiometric quantity, is required and this will give a room temperature pot life of less than an hour. The actual time depends on the ambient temperature and the size of the batch. With triethylenetetramine 12-13 pts phr are required. Although both materials are widely used in small castings and in laminates because of their high reactivity, they have the disadvantage of high volatility, pungency and being skin sensitizers. Properties such as heat distortion temperature (HDT) and volume resistivity are critically dependent on the amount of hardener used.

Similar properties are exhibited by *dimethylaminopropylamine* and *diethylaminopropylamine,* which are sometimes preferred because they are slightly less reactive and allow a pot life (for a 500 g batch) of about 140 minutes.

A number of modified amines have been marketed commercially. For example, reaction of the amine with a mono- or polyfunctional glycidyl material will give a larger molecule so that larger quantities are required for curing, thus helping to reduce errors in metering the hardener.

$$R\!-\!CH_2\!-\!\overset{O}{\overset{\diagup\!\!\diagdown}{CH\!-\!CH_2}} + H_2NR_1NH_2 \longrightarrow R\!-\!CH_2\!-\!\overset{OH}{\underset{|}{CH}}\!-\!CH_2\!-\!\overset{H}{\underset{|}{N}}\!-\!R_1\!-\!NH_2$$

These hardeners are extremely active. The pot life for a 500 g batch may be as little as 10 minutes.

The *glycidyl adducts* are skin irritants similar in behaviour in this respect to the parent amines. The skin sensitization effects in the primary aliphatic amine may be reduced by addition of groups at the nitrogen atom. The hydroxyethyl group and its alkyl and aryl derivatives are the most effective found so far.

$$H_2N\!-\!R\!-\!NH_2 + CH_2\!-\!CH_2 \longrightarrow H_2N\!-\!R\!-\!NH\!-\!CH_2\!-\!CH_2\!-\!OH$$
$$\underset{O}{}$$
$$HO\!-\!CH_2\!-\!CH_2\!-\!NH\!-\!R\!-\!NH\!-\!CH_2\!-\!CH_2\!-\!OH$$
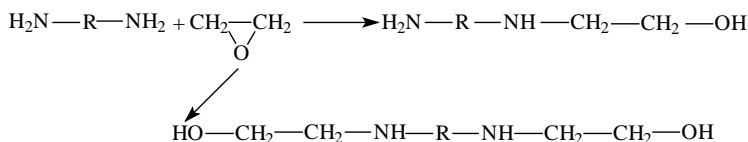
Both ethylene and propylene oxide have been used in the preparation of adducts from a variety of amines, including ethylene diamine and diethylene triamine. The latter amine provides adducts which appear free of skin sensitizing effects.

A hardener consisting of a blend of the two reaction products shown in the above equation is a low-viscosity liquid giving a 16-18 minute pot life for a 500 g batch at room temperature.
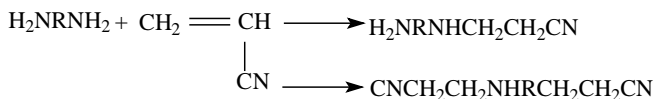
Modification of the amine with acrylonitrile results in hardeners with reduced reactivity.

$$H_2NRNH_2 + CH_2 =\!\!=\!\!= CH \longrightarrow H_2NRNHCH_2CH_2CN$$
$$\underset{CN}{\underset{|}{}} \longrightarrow CNCH_2CH_2NHRCH_2CH_2CN$$

The greater the degree of cyanoethylation the higher the viscosity of the adduct, the larger the pot life and the lower the peak exotherm. The products are skin sensitive.

It is thus seen that as a class the primarily aliphatic amines provide fast-curing hardeners for use at room temperatures. With certain exceptions they are skin sensitizers. The chemical resistance of the hardened resins varies according to the hardener used but in the case of the unmodified amines is quite good. The hardened resins have quite low heat distortion temperatures and except with diethylenetriamine seldom exceed 100°C. The number of variations in the properties obtainable may be increased by using blends of hardeners.

A number of aromatic amines also function as cross-linking agents. By incorporating the rigid benzene ring structure into the cross-linked network, products are obtained with significantly higher heat distortion temperatures than are obtainable with the aliphatic amines.

Meta-phenylenediamine, a crystalline solid with a melting point of about 60°C, gives cured resins with a heat distortion temperature of 150°C and very good chemical resistance. It has a pot life of six hours for a 200 g batch at room temperature whilst complete cures require cure times of four to six hours at 150°C. About 14 pts phr are used with the liquid epoxies. The main disadvantages are the need to heat the components in order to mix them, the irritating nature of the amine and persistent yellow staining that can occur on skin and clothing. The hardener finds use in the manufacture of chemical-resistant laminates.

Higher heat distortion temperatures are achieved using *4,4'-methylenedianiline* (diaminodiphenylmethane) and *diaminophenyl sulphone,* in conjunction with an accelerator, but this is at some expense to chemical resistance.

Many other amines are catalytic in their action. One of these, *piperidine,* has been in use since the early patents of Castan. 5-7 pts phr of piperidine are used to give a system with a pot life of about eight hours. A typical cure schedule is three hours at 100°C. Although it is a skin irritant it is still used for casting of larger masses than are possible with diethylenetriamine and diethylaminopropylamine.

Tertiary amines form a further important class of catalytic hardeners. For example, triethylamine has found use in adhesive formulations. Also of value are the aromatic substituted tertiary amines such as benzyldimethylamine and dimethyldiaminophenol. They have found uses in adhesive and coating applications. A long pot life may be achieved by the use of salts of the aromatic substituted amines.

Acid hardening systems
The use of acid hardening systems for epoxy resins was first described in Castan's early patent but use was restricted in many countries until the consummation of cross-licensing arrangements between resin suppliers in 1956. Compared with amine-cured systems, they are less skin sensitive and generally give lower exotherms on cure. Some systems provide cured resins with very high heat distortion temperatures and with generally good physical, electrical and chemical properties. The cured

resins do, however, show less resistance to alkalis than amine-cured systems. In practice acid anhydrides are preferred to acids, since the latter release more water on cure, leading to foaming of the product, and are also generally less soluble in the resin. Care must, however, be taken over storage since the anhydrides in general are somewhat hydroscopic.

The mechanism of anhydride hardening is complex but the first stage of reaction is believed to be the opening of the anhydride ring by an alcoholic hydroxyl group (or salt or a trace of water), e.g. Figure 6.
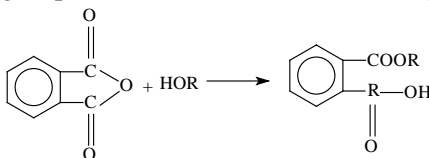
Figure 6

Hydroxyl groups attached to the epoxy resin would suffice for this purpose. Five further reactions may then occur.

(1) Reaction of the carboxylic group with the epoxy group.
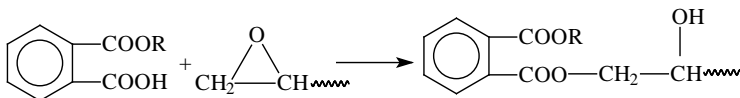
(2) Etherification of the epoxy group by hydroxyl groups.
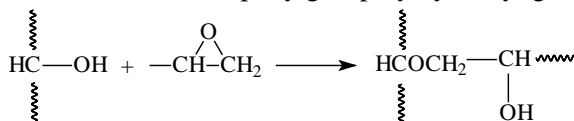
(3) Reaction of the monoester with hydroxyl group.
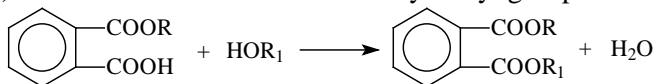
(4) Hydrolysis of the anhydride to acid by the water released in (3).

(5) Hydrolysis of the monoester with water to give acid and alcohol.

In practice it is found that reactions 1 and 2 are of greatest importance and ester and ether linkages occur in roughly equal amounts. The reaction is modified in commercial practice by the use of organic bases, tertiary amines, to catalyze the reaction.

The anhydrides are usually used at ratios of 0.85:1.1 moles anhydride carboxyl group per epoxy equivalent. Lower ratios down to 0.5:1

may, however, be used with some systems. The organic bases are used in amounts of 0.5-3%. These are usually tertiary amines such as α-methylbenzyldimethylamine and n-butylamine.

Three classes of anhydride may be recognized, room temperature solids, room temperature liquids and chlorinated anhydrides.

Phthalic anhydride (Figure 7 I) is an important example of the first class of hardener. It has a molecular weight of 148 and about 0.6-0.9 equivalent is used per epoxy group. For the lower molecular weight bis-phenol resins this works out at about 35-45 phr. The hardener is usually added at elevated temperature of about 120-140°C. It will precipitate out below 60°C but will again dissolve on reheating.

The resin is slow curing with phthalic anhydride and a typical cure schedule would be 4-8 hours at 150°C. Longer cures at lower temperatures tend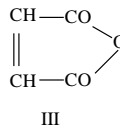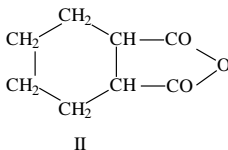 to improve the heat distortion temperatures and reduce the curing shrinkage. As with the amine hardeners the heat distortion temperature is very dependent on the amount of anhydride added and reaches a maximum at about 0.75 equivalent. Maximum heat distortion temperatures quoted in the literature are of the order of 110°C, a not particularly exceptional figure, and the hardener is used primarily for large castings where the low exotherm is particularly advantageous.

Hexahydrophthalic anhydride (Figure 7 II) (molecular weight 154) has a melting point of 35-36°C and is soluble in the epoxy resin at room temperature. When 0.5% of a catalyst such as benzyldimethylamine is used the curing times are of the same order as with phthalic anhydride. About 80 phr are required. In addition to the somewhat improved ease of working, the hardener gives slightly higher heat distortion temperatures (~120°C) than with phthalic anhydride. It is, however, more expensive. *Maleic anhydride* (Figure 7 III) is not usually used on its own because the cured resins are brittler, but it may be used in conjunction with pyromellitic dianhydride.
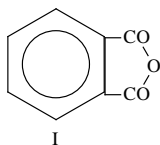
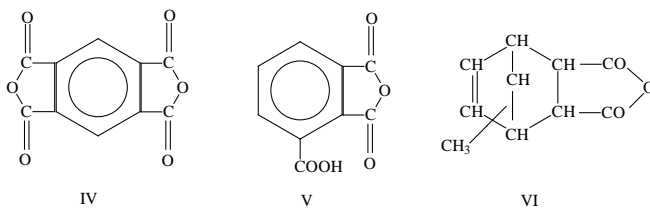Figure 7

In order to obtain cured products with higher heat distortion temperatures from bis-phenol epoxy resins, hardeners with higher functionality have been used, thus giving a higher degree of cross-linking. These include *pyromellitic dianhydride* IV, and *trimellitic anhydride* V.

Heat distortion temperatures of resins cured with pyromellitic dianhydride are often quoted at above 200°C. The high heat distortion is no doubt also associated with the rigid linkages formed between epoxy molecules because of the nature of the anhydride. The use of these two anhydrides has, however, been restricted because of difficulties in incorporating them into the resin.

The methylated maleic acid adduct of phthalic anhydride, known as *methyl nadic anhydride* VI, is somewhat more useful. Heat distortion temperatures as high as 202°C have been quoted whilst cured systems, with bis-phenol epoxides, have very good heat stability as measured by weight loss over a period of time at elevated temperatures. The other advantage of this hardener is that it is a liquid easily incorporated into the resin. About 80 phr are used but curing cycles are rather long. A typical schedule is 16 hours at 120°C and 1 hour at 180°C.

Other anhydrides that have been used include *dodecenylsuccinic anhydride,* which imparts flexibility into the casting, and *chlorendic anhydride,* where flame-resistant formulations are called for.

Miscellaneous hardener systems
In addition to the amine, acid and anhydride hardeners many other curing agents have been made available. These include a number of amides that contain amine groups. Among them are the polyamides already considered in the section on flexibilizers and which form the basis of some domestic adhesive systems. Amongst the advantages of the system is the fact that roughly similar quantities of hardener and resin are required and since this is not too critical adequate metering can be done visually without the need for quantitative measuring aids. Also used with epoxy resins for

adhesives is dicyanodiamide. Insoluble in common resins at room temperature, it is dissolved at elevated temperatures, forming the basis of a one-pack system.

Complexes of boron trifluoride and amines such as monoethylamine are of interest because of the very long pot lives possible. The disadvantages of these complexes are their hygroscopic nature and the corrosive effects of BF_3 liberated during cure.

Very high cure rates may be achieved using mercaptans.

Comparison of hardening systems

The number of hardening agents used commercially is very large and the final choice will depend on the relative importance of economics, ease of handling, pot life, cure rates, dermatitic effects and the mechanical, chemical, thermal and electrical properties of the cured products. Since these will differ from application to application it is understandable that such a wide range of material is employed.

As a very general rule it may be said that the amines are fast curing and give good chemical resistance but most are skin sensitive. The organic anhydrides are less toxic and in some cases give cured resins with very high heat distortion temperatures. They do not cross-link the resins at room temperature.

In addition to the considerable difference of the properties of the cured resins with different hardeners it must also be stressed that the time and temperatures of cure will also have an important effect on properties. As a very general rule, with increasing aliphatic amines and their adducts the time of cure and temperature of cure (up to 120°C at least) will improve most properties.

Miscellaneous epoxy resins

In addition to the resins based on bis-phenol A there are now available a number of other resins containing epoxy groups. These can be treated in two main groups:

(1) Other glycidyl ether resins.
(2) Non-glycidyl ether resins.

Miscellaneous glycidyl ether resins

Glycidyl ether resins are formed by reaction of epichlorohydrin with poly-hydroxy compounds. In addition to the dominant use of bis-phenol A several other polyhydroxy compounds have been used. In

particular there has been increasing interest in the use of bis-phenol F. As made, this is a mixture of three isomers (Figure 8 (1a, b, c)). The resins are of a somewhat lower viscosity than the corresponding bis-phenol A materials. Hydrogenated bis-phenol A (known as bis-phenol H) (II) is also to show promise in resins with enhanced weathering characteristics. Other low molecular weight polyhydroxy compounds that have been used include glycerol (III) and the long chain bis-phenol from cashew nut shell oil (IV).
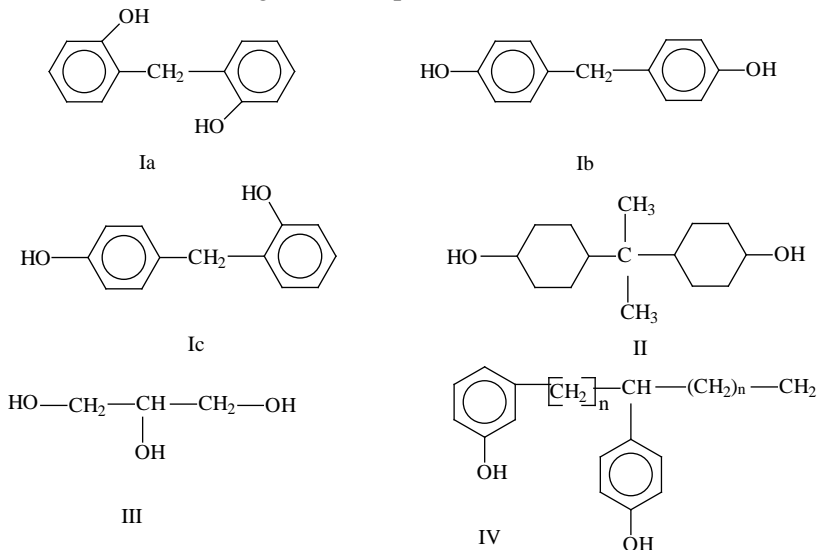
Figure 8

Novolak resins have also been epoxidized through their phenolic hydroxy groups. A wide variety of novolak resins may be used based on a range of different phenols, including cresols, ethylphenols, *t*-butylphenols, resorcinol, hydroquinone and catechol as well as phenol itself. The epoxide-novolak can also vary in its average molecular weight and in the number of phenolic hydroxy groups that have been reacted with epichlorohydrin. A typical epoxide-novolak resin would be as shown in Figure 9.

This molecule has a functionality of four. Commercial epoxide-novolak resins have functionalities between 2.5 and 6.
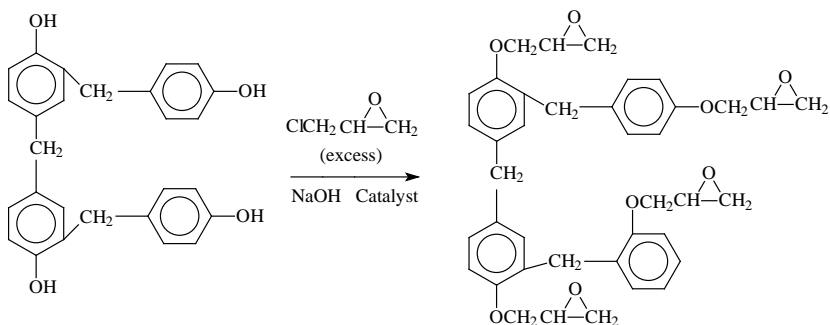
Figure 9

When cured with room temperature curing system these resins have similar thermal stability to ordinary bis-phenol A type epoxides. However, when they are cured with high-temperature hardeners such as methyl "nadic" anhydride both thermal degradation stability and heat deflection temperatures are considerably improved. Chemical resistance is also markedly improved. Perhaps the most serious limitation of these materials is their high viscosity.

Their main applications have been in heat-resistant structural laminates, "electrical" laminates resistant to solder baths, chemical-resistant filament-wound pipe and high-temperature adhesives.

Low-viscosity diglycidyl ether resins of undisclosed composition have been marketed in the United States and in Britain. The materials are stated to be totally difunctional, i.e. free from monofunctional reactive diluents. The cured resins have properties very similar to those of the standard diglycidyl ether resins.

To produce resins of high heat distortion temperature it is important to have a high density of cross-linking and to have inflexible segments between the crosslinks. This approach has been used with reasonable success using certain anhydride hardeners such as pyromellitic dianhydride and with the cyclic aliphatic resins. Attempts have also been made to use glycidyl ether resins of higher functionality such as the tetrafunctional structure.

$$CH_2\overset{O}{\frown}CH-CH_2-O \quad\quad O-CH_2-\overset{O}{\frown}{CH}-CH_2$$

(benzene rings with central CH—CH linkage and lower glycidyl ether groups)

$$CH_2\overset{O}{\frown}CH-CH_2-O \quad\quad O-CH_2-\overset{O}{\frown}CH-CH_2$$
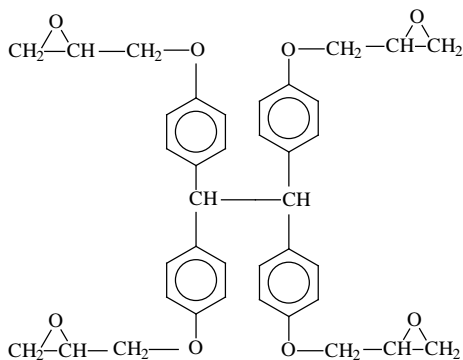
Because of the higher viscosity of such resins their use has been restricted to applications where they may be used in solution.

As a result of the demand for flame-resistant resins, halogenated materials have been marketed. A typical example is the diglycidyl ether of tetrachlorobis-phenol A.

The resin is a semisolid and must be used either in solution form or as blends.

$$CH_2\overset{O}{\frown}CH-CH_2-O-\underset{Cl}{\overset{Cl}{\bigcirc}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Cl}{\overset{Cl}{\bigcirc}}-O-CH_2-\overset{O}{\frown}CH-CH_2$$
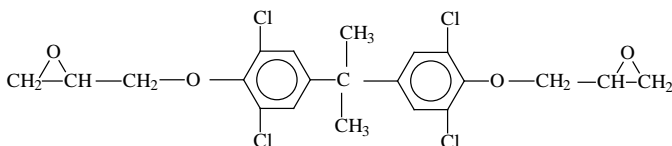
In practice the bromo analogue has been more widely used. This arises from a combination of two reasons. In the first instance the tetrabromo resin contains 48% halogen whilst the tetrachloro resin contains 30% halogen.

Secondly, whereas 26-30% chlorine is required to make the resin effectively fire retardant, only 13-15% of bromine is required. It is therefore possible to achieve a greater flexibility in formulation with the bromine resins, which may be blended with other resins and yet remain effectively fire retardant.

Mention may also be made of fixed diethers, some of which are unsaturated. These materials may be cured by a variety of mechanisms. An example is the allyl glycilyl mixed ether of bis-phenol A.

$$CH_2\overset{O}{\frown}CH-CH_2-O-\bigcirc-\underset{CH_3}{\overset{CH_3}{C}}-\bigcirc-O-CH_2-CH=CH_2$$
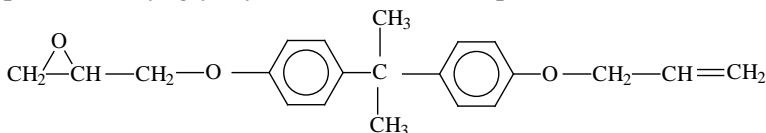
Non-glycidyl ether epoxides

Although the first and still most important epoxy resins are of the glycidyl ether type, other epoxy resins have been commercially marketed in recent years. These materials are generally prepared by epoxidizing unsaturated compounds using hydrogen peroxide or peracetic acid.

$$\text{C—C} \longrightarrow \overset{O}{\text{C—C}}$$
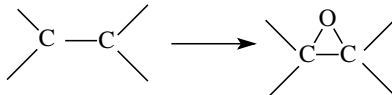
Such materials may be considered in two classes :

(1) Those which contain a ring structure as well as an epoxy group in the molecule – the cyclic aliphatic resins.

(2) Those which have an essentially linear structure on to which are attached epoxy groups – the acyclic aliphatic epoxy resins.

Cyclic aliphatic resins

Cyclic aliphatic epoxy resins were first introduced in the United States. Compared with standard diglycidyl ether resins, the liquid cyclic aliphatic resins are paler in colour and have a much lower viscosity. Whereas in general the cyclic aliphatic resins react more slowly with amines, there is less difference with acid anhydrides.

Because of the compact structure of the cycloaliphatic resins the intensity of cross-linking occurring after cure is greater than with the standard diglycidyl ethers. The lack of flexibility of the molecules also leads to more rigid segments between the cross-links.

As a consequence the resins are rather brittle. The high degree of cross-linking does, however, lead to higher heat distortion temperatures than obtained with the normal diglycidyl ether resins.

Heat aging resistance does not appear to be as good as with the bis-phenol A epoxide but outdoor weathering is said to be superior.

The cycloaliphatic resins have applications in the tension insulators, rocket motor cases and transformer encapsulation.

Because of their low viscosity the liquid cyclic aliphatic resins find use in injection moulding and extrusion techniques, as used for glass-reinforced laminates. They are also very useful diluents for the standard glycidyl ether resins.

Acyclic aliphatic resins

These materials differ from the previous class of resin in that the basic structure of these molecules consists of long chains whereas the

cyclic aliphatics contain ring structures. Three subgroups may be distinguished, epoxidized diene polymers, epoxidized oils, and polyglycol diepoxides.

Typical of the epoxidized diene polymers are products produced by treatment of polybutadiene with peracetic acid. The structure of a molecular segment indicates the chemical groupings that may be present.

$$—(CH_2—CH—CH—CH_2)—(CH_2—CH{-}CH—CH_2)—$$

with OH and O (C—O—CH$_3$) groups on the first segment (I), and an epoxide O bridge on the second segment (II).

I   II

$$—(CH_2—CH{=}CH—CH_2)—(CH_2—CH)—(CH_2—CH)—$$

with CH=CH$_2$ pendant group (IV) and CH—CH$_2$ epoxidized group (V).

III   IV   V

Residue (I) is a hydroxy-acetate segment produced as a side reaction during the epoxidizing process, (II) is an epoxy group in the main chain, (III) is an unreacted segment, (IV) is an unreacted pendant vinyl group present through a 1:2 addition mechanism whilst (V) is an epoxidized derivative of the vinyl group.

The epoxidized polybutadiene resins available to date are more viscous than the diglycidyl ethers except where volatile diluents are employed. They are less reactive with amines but have a similar reactivity with acid anhydride hardeners. Cured resins have heat distortion temperatures substantially higher than the conventional amine-cured diglycidyl ether resins. A casting made from an epoxidized polybutadiene hardened with maleic anhydride and cured for two hours at 50°C plus three hours at 155°C plus 24 hours at 200°C gave a heat distortion temperature of 250°C.

Epoxidized drying oils have been available for several years as stabilizers for poly(vinyl chloride). They may be considered to have the skeletal structure shown in Figure 10.

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