

1

General Concepts about Epoxy Polymers

Jean-Pierre Pascault and Roberto J. J. Williams

1.1 Polymerization Chemistry of Epoxy Monomers

1.1.1 Typical Epoxy Monomers and Polymer Growth Mechanisms

The most popular epoxy monomers are those derived from the reaction of bis(4-hydroxy phenylene)-2,2 propane (called bisphenol A) and 1-chloroprene 2-oxide (called epichlorohydrin), in the presence of sodium hydroxide. The structure of the major product, bisphenol A diglycidyl ether (DGEBA or BADGE) and its condensed forms (Table 1.1a), is dependent upon the stoichiometry of the reactants. Typical monomers (“resins”) are marketed with n values lying in the range 0.03–10. At room temperature these monomers are crystalline solids for n values close to zero, liquids for n values up to $n = 0.5$, and amorphous solids (glass transition temperature, $T_g \sim 40\text{--}90^\circ\text{C}$) for higher n values.

Another major group of epoxy monomers derived from epichlorohydrin is that comprising monomers synthesized with an aromatic amine, such as methylene dianiline (TGMDA) (Table 1.1b).

Oxirane groups can be generated by peroxidation of carbon–carbon double bonds. Types of such oligomers are epoxidized oils or cycloaliphatic oxides (Table 1.1c).

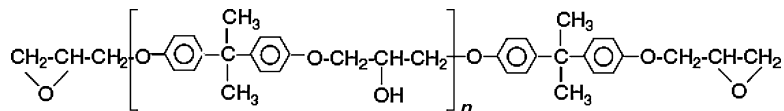
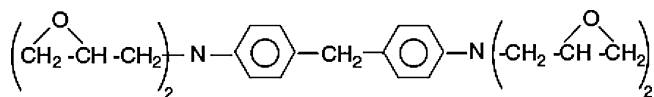
Epoxy monomers containing vinyl groups, like glycidyl (meth)acrylate or glycidyl oxystyrene (Table 1.1d), can be used for the synthesis of functional oligomers.

Linear or crosslinked epoxy polymers are obtained by reaction of the epoxy monomers with co-monomers (“hardeners”) and/or initiators. Epoxy polymers can be produced by step or chain polymerizations or, eventually, by a combination of both mechanisms.

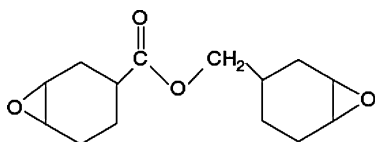
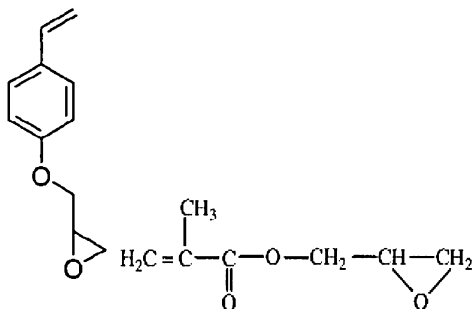
Step-growth polymerization proceeds via a step-by-step succession of elementary reactions between reactive sites. Each independent step causes the disappearance of two co-reacting sites and creates a new covalent bond between a pair of functional groups. The number of reactive sites per monomer (functionality) and the molar ratio between co-reactive sites are the main parameters that control the

Table 1.1 Formulas of the main epoxy monomers ("resins").

(a) Diglycidyl ether of bisphenol A, DGEBA (or BADGE)

(b) *N,N,N',N'*-tetraglycidyl-4,4'-methylene dianiline (TGMDA)

(c) 3,4-epoxycyclohexyl methyl 3',4'-epoxy cyclohexane carboxylate

(d) *p*-glycidyl oxystyrene (GOS) and glycidyl methacrylate (GMA)**GOS****GMA**

polymer structure. To obtain linear polymers, the reactants must be bifunctional; monofunctional reactants interrupt the polymer growth. A condition to obtain crosslinked polymers is that at least one of the monomers has a functionality higher than 2. The molar mass of the product grows gradually and the polydispersity tends to 2 for a linear polymer; for a crosslinked polymer the mass-average molar mass becomes infinite at a critical conversion (gelation).

Chain-growth polymerization is characterized by the presence of initiation, propagation, chain transfer and termination steps. In the case of epoxies, the initiation step produces an ion (either an anion or a cation) that is called the active center of the polymerization. The ion may be generated by a chemical reaction or by an adequate source of irradiation. Once active centers are generated they produce primary chains by the consecutive addition of monomers through the

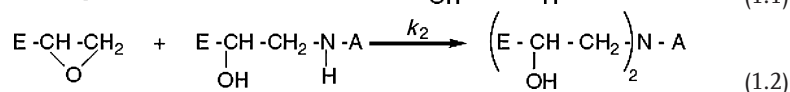
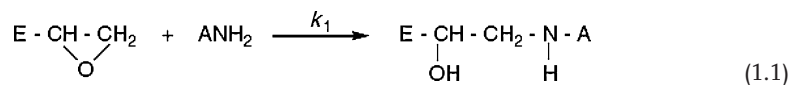
propagation step of the reaction. As active centers are always present at the end of primary chains, the propagation reaction continues until it becomes interrupted by a chain transfer step or a termination step. The main parameters controlling the polymer structure are the functionality of monomers, the molar ratio between initiator and monomers, the concentration of species that are involved in chain transfer steps, and temperature (thermal cycle) that affects the relative rates of different steps.

1.1.2

Step Growth Polymerization

Epoxy groups can react with amines, phenols, mercaptans, isocyanates or acids. Amines are the most commonly used curing agents/hardeners for epoxides and the case of step-growth polymerizations is mainly represented by epoxy-amine reactions.

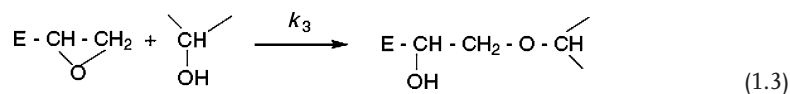
Epoxy groups react with primary and secondary amino hydrogens (NH):



Usually when the concentration of epoxy groups is equal to or lower than the concentration of NH groups, side reactions do not take place. The epoxy-amine reaction is therefore suitable for the synthesis of “model” networks. The reactivity of the amine increases with its nucleophilic character: aliphatic > cycloaliphatic > aromatic. Aliphatic amines are used for low-temperature curing systems (adhesives, coatings, etc.), and aromatic diamines for composite materials.

Hydroxy groups catalyze the reaction through the formation of a trimolecular complex, which facilitates the nucleophilic attack of the amino group. As secondary alcohols are continuously generated, epoxy-amine reactions are autocatalyzed [1].

When there is an excess of epoxy groups or when the secondary amino groups have a low reactivity, a third reaction can compete with the two previous ones:



The epoxy-hydroxy reaction (also called etherification) modifies the initial stoichiometric ratio based on epoxy to amino hydrogen groups.

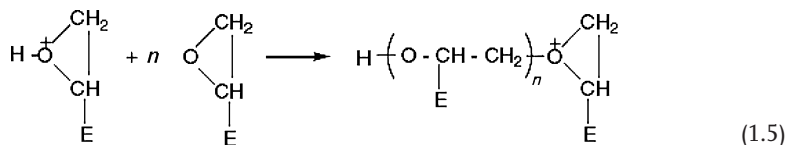
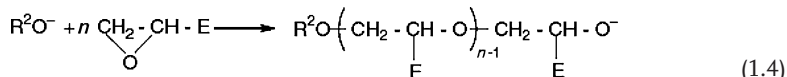
1.1.3

Chain Homopolymerization

Epoxy groups can react with both nucleophilic and electrophilic species. Thus both Lewis acids and bases are able to initiate the chain polymerization of epoxy

monomers [1]. Commonly used initiators (often named “catalytic” curing agents in the literature) include tertiary amines, imidazoles, or ammonium salts for anionic chain polymerization, and boron trifluoride complexes, complex aromatic salts of Lewis acids such as diaryl iodonium, triarylsulfonium, or arene diazonium for cationic chain polymerization.

Propagation proceeds through an alkoxide (anionic polymerization) or an ozonium (cationic polymerization):



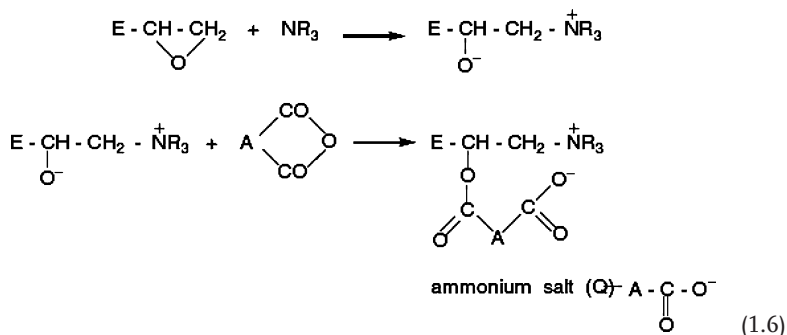
Chain transfer and complex termination steps arrest the chain propagation leading to relatively low values of the average degree of polymerization of primary chains (typically less than 10). The chain polymerization of epoxy monomers bearing two or more epoxy groups in the structure leads to networks [2].

1.1.4

Chain Copolymerization

While the epoxy–acid reaction follows a stepwise mechanism, the reaction of epoxides with cyclic anhydrides initiated by Lewis bases takes place through a chainwise copolymerization.

Initiation involves the reaction of the Lewis base with an epoxy group, giving rise to a zwitterion that contains a quaternary nitrogen atom (when the base used is a tertiary amine) and an alkoxide anion. The alkoxide reacts at a very fast rate with an anhydride group, leading to a species containing a carboxylate anion as the active center:



This ammonium salt can be considered as the initiator of the chainwise copolymerization:

1.2

Transformations During the Formation of an Epoxy Network

1.2.1

General Considerations

As discussed in the previous section, typical epoxy monomers used to generate a polymer network have two or more epoxy groups per molecule. For example, diglycidylether of bisphenol A (DGEBA) has two epoxy groups in its structure while *N,N,N',N'*-tetraglycidyl-4,4'-methylene dianiline (TGMDA) has four epoxy groups per molecule. The functionality of an epoxy monomer is defined by the number of “arms” (bonding sites) with which it participates in the formation of the polymer network. For example, DGEBA is bifunctional in the reaction with amine hydrogens but it is tetrafunctional in its homopolymerization or in the reaction with cyclic anhydrides (a bifunctional co-monomer). A necessary (although not sufficient) condition for the formation of an epoxy network is that at least one of the monomers involved in the reaction has functionality higher than two. Therefore, in the typical reaction of DGEBA with amines, the formation of a polymer network requires that the amine has a functionality higher than 2 (more than 2 amine hydrogens in the structure). Typically, aliphatic, cycloaliphatic or aromatic diamines (tetrafunctional co-monomers) are employed to generate a crosslinked polymer by reaction with DGEBA.

A polymer network may also be formed by combining two different reactions. For example, a linear polymer end-capped with epoxy groups may be formed by reacting an excess of DGEBA with a monoamine. Alternatively, a branched polymer may be generated by reaction of an appropriate DGEBA excess with a diamine. In a second step the homopolymerization of terminal epoxy groups by addition of a suitable initiator (for example, an imidazole), may be carried out to produce a polymer network.

Networks described so far are based on the formation of covalent bonds by a chemical reaction. Another type of polymer network may be produced by bonding linear or branched chains by secondary forces like Van der Waals interactions or H-bonds. The network produced in this way is a physical network and its most outstanding property is that it can be reversibly transformed from a solid (physical network) to a liquid (linear or branched polymer chains) by increasing the temperature or by using a suitable solvent. Examples of physical epoxy networks will be described in Chapter 6.

1.2.2

Gelation

Gelation is a critical transition that takes place during the formation of the polymer network and corresponds to the generation of a giant macromolecular structure that percolates the reaction medium. Macroscopically this transition is character-

ized by the change from a liquid to a solid (the sample viscosity tends to infinite). In the post-gel stage there is an increase in cross-link density with a corresponding increase in the elastic modulus of the solid. The fraction of polymer that is soluble in an appropriate solvent (sol fraction) decreases sharply in the post-gel stage. In the case of epoxy reactions, the characteristic time scale related to the local mobility of functional groups after gelation continues to be much shorter than the characteristic time scale to produce the chemical reaction. This means that, for most epoxy formulations, gelation does not influence the kinetics of the cross-linking reaction.

The gel conversion for a particular system may be predicted by combining a variety of kinetic and statistical methods [1]. In general, the gel conversion decreases when increasing the functionality of the monomers. For example, for an ideal stepwise polymerization of an f -functional monomer with a g -functional co-monomer, mixed in stoichiometric amounts, the gel conversion is given by:

$$x_{\text{gel}} = [(f - 1)(g - 1)]^{-1/2} \quad (1.9)$$

where the term ideal refers to: (i) equal reactivity of functional groups of the same type, (ii) absence of substitution effects (functional groups remaining in a partially reacted monomer keep their initial reactivity), (iii) absence of intramolecular cycles in finite species. For the particular case of reacting DGEBA ($f = 2$) with a diamine ($g = 4$), the ideal gel conversion is $x_{\text{gel}} = 3^{-1/2} = 0.577$. If secondary amine hydrogens are less reactive than primary amine hydrogens, the gel conversion increases due to the fact that linear structures are formed first in preference to branched structures. For the limiting case, where the secondary amines react only when the primary amines are exhausted, the predicted gel conversion increases to $x_{\text{gel}} = 0.618$. Experimental values of x_{gel} in the range of 0.58 to 0.60 are typical for stoichiometric formulations of DGEBA with diamines.

For chainwise polymerizations the gel conversion depends in a complex way on the relative rates of the different steps and on the amount of initiator added to the formulation. Increasing the amount of initiator leads to shorter primary chains and a corresponding increase in the gel conversion.

During processing of the epoxy formulation gelation must be avoided prior to the shaping of the final part (for example, during mold filling of an injected part or prior to the consolidation step in autoclave processing). This is usually accomplished by the use of an appropriate thermal cycle. A better control is achieved if the system can be formulated such that the cross-linking reaction takes place at a significant rate above a particular temperature threshold. The use of latent initiators may be used for this purpose in chainwise polymerizations. Alternatively, the cross-linking may be produced by combining different reactions in different temperature ranges. For example, epoxy-amine formulations prepared with a convenient epoxy excess may be reacted to complete amine conversion at low temperatures to obtain an ungelled prepolymer. The reaction of the epoxy excess at high temperatures after the shaping operation produces the final cross-linked material.

1.2.3

Vitrification

During polymerization of an epoxy formulation vitrification may occur if the glass transition temperature of the system, T_g , equals and becomes higher than the reaction temperature, T . The condition $T_g \geq T$, can be achieved for both isothermal or non-isothermal processing and before or after gelation (gelation and vitrification are independent transitions). When the system gets into the glassy state the polymerization kinetics is severely retarded. The effect becomes more significant with an increase in the difference ($T_g - T$) and the reaction may be considered arrested for practical purposes when this difference lies in the range of 20–30°C (depending on the particular system and on the way in which T_g is defined). Unreacted epoxy formulations may be safely stored in the glassy state provided that ($T_g - T$) is high enough to avoid any significant advance in the polymerization reaction. The same procedure may be adopted for partially reacted formulations. However, in this case the sample must be submitted to this condition before gelation in order to produce the final shaping when re-heating above T_g .

The glass transition temperature of the reacting system increases with conversion because of the increase in the molar mass during the pre-gel stage and the increase in cross-link density during the post-gel stage. Several expressions relating T_g with conversion (x) have been proposed in the literature. A popular one is the following [6]:

$$(T_g - T_{g0}) / (T_{g\infty} - T_{g0}) = \lambda x / [1 - (1 - \lambda)x] \quad (1.10)$$

where T_{g0} is the glass transition temperature of the initial formulation, $T_{g\infty}$ is the glass transition temperature of the cross-linked polymer reacted to full conversion, and $\lambda = \Delta c_{p\infty} / \Delta c_{p0}$, is the ratio of changes in the specific heat through the glass transition for the fully cured and the initial samples.

Equation 1.10 may be used to predict the evolution of the glass transition temperature with conversion for a particular formulation, provided that a DSC (differential scanning calorimetry) characterization of the initial and fully reacted samples is available.

1.2.4

Reaction-Induced Phase Separation

Many epoxy formulations include a particular modifier, such as a rubber, a thermoplastic, a liquid crystal, a foaming agent, and so on, that is miscible before reaction but becomes phase separated in the course of polymerization (reaction-induced phase separation) [7]. The origin of phase separation is the increase in the average molar mass of the reacting system during the pre-gel stage and the increase in crosslink density during the post-gel stage. An increase in molar mass produces a decrease in the contribution of the entropy of mixing while, after gelation, the presence of a cross-linked network generates an elastic contribution that limits the amount of modifier in the swollen network.

Reaction-induced phase separation is employed to produce different morphologies in the final products that are appropriate to increase toughness (e.g., rubber-modified epoxies), to generate an optical response induced by an electric field (polymer-dispersed liquid crystals), or to produce a porous material (foam) after elimination of the phase-separated modifier. By varying the initial concentration of modifier and the reaction temperature (or the thermal cycle) a variety of morphologies may be developed in the final material. Conditions are usually selected to produce appropriate morphologies for the desired application but balancing a possible deleterious effect on other mechanical or thermal properties. A typical example of this balance is the case of rubber-modified epoxies. Rubber addition increases toughness but decreases the elastic modulus and the glass transition temperature of the final product (through the fraction of rubber remaining dissolved in the epoxy matrix). The amount of rubber is selected to obtain a convenient balance of thermal and mechanical properties.

Block copolymers are used as modifiers of epoxy formulations to obtain nanostructured materials with specific properties (Chapter 5). In this case it may be that both blocks are initially miscible and the less-miscible block becomes phase separated in the course of polymerization or that one of the blocks is immiscible in the initial formulation. Nanostructures generated during reaction or present in the initial system can be fixed in the final product, provided that the miscible block does not phase separate or undergoes only a partial phase separation after gelation.

1.2.5

Transformation Diagrams

The three independent events (phase separation, gelation and vitrification) taking place during the isothermal polymerization of a modified epoxy formulation may be determined by employing appropriate techniques. A set of cloud-point times (t_{cp}), gelation times (t_{gel}) and vitrification times (t_{vit}) may be obtained for different polymerization temperatures and plotted in a temperature versus time transformation (TTT) diagram [8]. Figure 1.1 shows such a plot for the transitions observed for a formulation consisting of stoichiometric amounts of DGEBA and ethylenediamine (EDA), modified by 17.6% in volume of castor oil (CO), a bio-based modifier [9]. At about 37°C gelation and vitrification take place simultaneously. At lower temperatures ungelled glasses are obtained.

The time scale of the TTT diagram may be transformed into a conversion scale by employing isothermal conversion vs. time curves (or the expression of the polymerization kinetics). In this way, the TTT diagram may be transformed into a conversion versus temperature transformation (CTT) diagram [10]. Figure 1.2 shows a CTT diagram for the same system as Figure 1.1. It is observed that the experimental gel conversion values are very close to the theoretical prediction for an ideal system ($x_{gel} = 0.577$). Moreover, the cloud-point conversion increases with temperature, meaning that castor oil becomes more miscible on increasing the temperature (upper critical solution temperature, UCST). This behavior may be

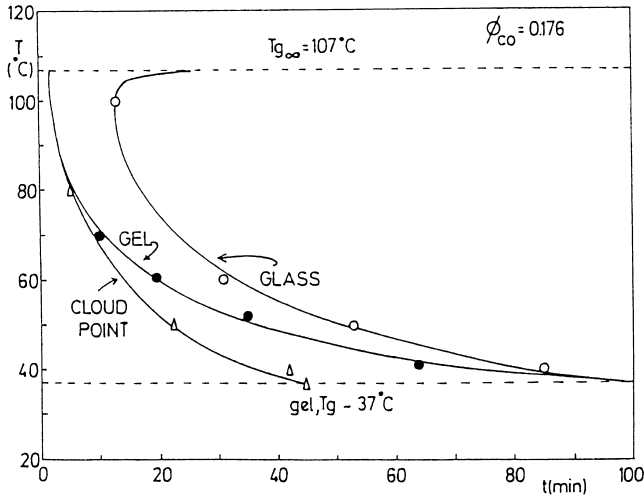


Figure 1.1 TTT diagram for a DGEBA-EDA formulation modified with 17.6% in volume of castor oil (CO) (Reprinted with permission from [9]; copyright 1993 Wiley).

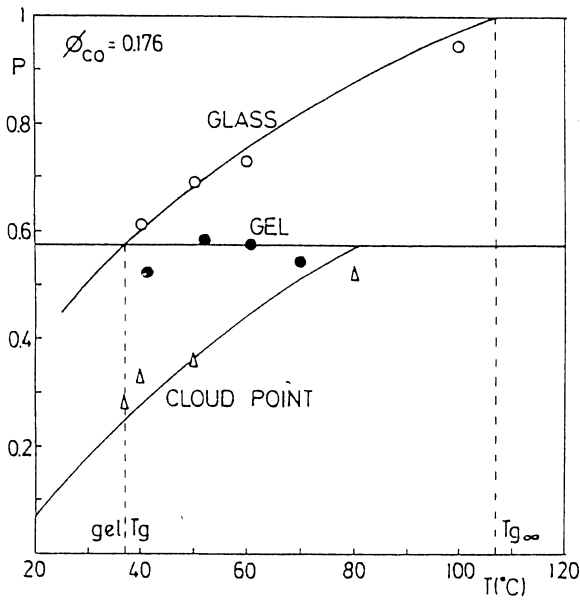


Figure 1.2 CTT diagram for a DGEBA-EDA formulation modified with 17.6% in volume of castor oil (CO) (Reprinted with permission from [9]; copyright 1993 Wiley).

used to control the extent of phase separation and the average size of phase separated domains.

1.3

General Properties of Epoxy Networks

Cross-linked epoxies exhibit outstanding properties that have placed them as the standard option for a variety of applications such as adhesives, coatings, composites for structural applications, and so on. [1]. Some of the reasons for this are:

- 1) No emission of volatile products in the polymerization reaction.
- 2) Flexibility in the election of monomers and co-monomers enabling one to obtain a variety of products from low- T_g rubbers to high- T_g materials.
- 3) Possibility to use and combine different polymerization chemistries appropriate for the particular processing needs.
- 4) Very low contraction during polymerization (for some formulations contraction may be entirely eliminated).
- 5) Very high adhesion to a variety of surfaces due to the polar groups present in the structure.
- 6) Possibility of introducing different modifiers to generate optical properties (as in dispersions of droplets of liquid crystals in an epoxy matrix), or to increase toughness (rubber- or thermoplastic-modified epoxies), and so on.

Although in many applications the same typical formulations and processing techniques are still in use since their implementation, in the last decade a revival of the field was produced by a combination of several independent factors. Innovations in the industrial sector led to new materials such as thermoplastic epoxy polymers (Chapter 2) and epoxyacrylates for high performance coatings (Chapter 3). Both economic and ecological arguments led to a great interest in the development of epoxy formulations from renewable resources (Chapter 4). Developments in the nanosciences and nanotechnologies pervaded the whole materials field, including the epoxies. Nanostructured epoxies produced by modification with block copolymers led to a set of new properties (Chapter 5). Formulations that can undergo a self-nanostructuring process can be used to generate reversible networks (physical gels, Chapter 6). Improvements in the optical response of polymer-dispersed liquid crystals may be achieved by adding block copolymers to a liquid crystal/epoxy blend (Chapter 7). Epoxies modified with polyhedral oligomeric silsesquioxanes (POSS) and other organic-inorganic hybrid materials can be used to generate new properties for specific applications (Chapter 8). Clay-modified epoxies can be used to increase mechanical and barrier properties as well as fire resistance (Chapter 9). Modification by carbon nanotubes (CNT) can lead to outstanding mechanical, thermal and electric properties (Chapter 10). Innovations in

formulation and processing techniques have led to better adhesives (Chapter 11), nanostructured coatings (Chapter 12), epoxy composites (Chapters 13 and 14), thermoplastic curable epoxies (Chapter 15), structural foams (Chapter 16), and self-healing epoxies (Chapter 17).

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