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BIO-BASED EPOXY RESINS

*Synthesis, Chemistry, and Industrial Applications of Vegetable Oil
Epoxies*

MARIE SESHAT LANDRY

LANDRY INDUSTRIES INC. · MONCTON, NEW BRUNSWICK



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BIO-BASED EPOXY RESINS: SYNTHESIS, CHEMISTRY, AND INDUSTRIAL APPLICATIONS OF VEGETABLE OIL EPOXIES

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PREFACE

Why a plant oil – a substance we cook with – deserves a place beside bisphenol A at the heart of structural thermoset chemistry.

Epoxy resins are among the most versatile thermosets ever commercialized. They bond aircraft panels, protect steel pipelines, encapsulate microelectronics, and form the matrix of wind-turbine blades. For most of their history, the dominant building block has been the diglycidyl ether of bisphenol A (DGEBA), made from petroleum-derived bisphenol A and epichlorohydrin. Two pressures now push against that default: the desire to decouple materials from fossil carbon, and growing regulatory scrutiny of bisphenol A itself, which the European Union banned from food-contact materials in December 2024 [1].

Vegetable oils are an obvious place to look for alternatives. They are produced at agricultural scale, they are chemically well characterized, and their unsaturated fatty-acid chains can be converted into oxirane (epoxide) rings with chemistry first described more than a century ago [2]. Epoxidized soybean and linseed oils are already sold as commercial products whose data sheets lead with plasticization and stabilization of poly(vinyl chloride) [3, 4]. The scientific literature on turning them into structural resins is large and still growing [5–9].

The difficulty is that triglycerides are not DGEBA. Their epoxide groups sit in the middle of long, flexible aliphatic chains rather than at the ends of a rigid aromatic core. They react more slowly with amines, they plasticize the networks they form, and their functionality varies from one harvest to the next. Turning that chemistry into materials that can carry load, survive heat, and be manufactured at scale is the subject of this book.

How the book is organized

The nine chapters follow the life of a bio-epoxy from field to end-of-life. **Part I** covers the feedstocks and the epoxidation reactions that convert double bonds into oxiranes, including how to measure what was made. **Part II** describes chemical modifications that add reactivity or rigidity beyond the internal epoxide. **Part III** treats curing agents and the structure–property relationships of the resulting networks. **Part IV** turns to composites, nanocomposites, and dynamic covalent networks (vitrimers) that can be reprocessed. **Part V** addresses processing, applications, plant economics, life-cycle assessment, and regulation. Three appendices collect test methods, oil constants, and reaction schemes for curing agents.

Conventions

- **Abbreviations.** EVO = epoxidized vegetable oil; ESO, ELO, EHO = epoxidized soybean, linseed, and hemp oils; OOC = oxirane oxygen content (wt %); EEW = epoxide equivalent weight (g eq^{-1}); IV = iodine value (g I_2 per 100 g). A full glossary appears in the back matter.

- **Evidence.** Numerical values attributed to a source are reported as that source states them. Values marked *calculated* are derived in the text from stated equations. Tables of “typical” behaviour that are not tied to a citation are qualitative and are labelled as such.
- **Safety.** Peracids, hydrogen peroxide, epichlorohydrin, anhydrides, amines, and photoacid generators are hazardous. Safety boxes flag the main issues, but they are not a substitute for a formal hazard assessment.

The aim throughout is a reference that a materials scientist, polymer chemist, or chemical engineer can open at any chapter and use: chemistry first, then measurement, then the engineering consequences.

M. S. LANDRY

Moncton, New Brunswick · October 2026



FEEDSTOCKS, TRIGLYCERIDE CHEMISTRY, AND EPOXIDATION

*From the fatty-acid architecture of plant oils to the oxirane ring: how unsaturation is
turned into reactivity.*

CH. 1 · NATURAL OILS AS BIO-BASED POLYMER FEEDSTOCKS

CH. 2 · CHEMICAL EPOXIDATION ROUTES

NATURAL OILS AS BIO-BASED POLYMER FEEDSTOCKS

Every property of a vegetable-oil epoxy – its functionality, its viscosity, the glass transition of its cured network – is written first in the fatty-acid profile of the oil it came from.

IN THIS CHAPTER

- The triglyceride molecule and the fatty acids that matter for epoxidation.
- Composition data for soybean, rapeseed (canola), sunflower, hemp, linseed, castor, and tung oils, and the special case of tall oil.
- Waste and non-edible oils: what makes them harder to use and how they are cleaned up.
- The iodine value as a predictor of maximum epoxide yield, and why internal and conjugated double bonds behave differently.

1.1 STRUCTURE AND COMPOSITION OF TRIGLYCERIDES

A vegetable oil is overwhelmingly a mixture of triacylglycerols (triglycerides): glycerol esterified at all three hydroxyl groups with fatty acids. The glycerol core contributes about 41 g mol^{-1} of C_3H_5 to a molecule that typically weighs roughly $870\text{--}890 \text{ g mol}^{-1}$; almost all of the mass and nearly all of the chemistry reside in the three acyl chains. Minor components — free fatty acids, phospholipids, sterols, tocopherols, waxes, and pigments — are present at the per-cent level or below in crude oils and are largely removed by refining. They matter to the polymer chemist chiefly as impurities that consume reagents or poison catalysts (Section 1.2).

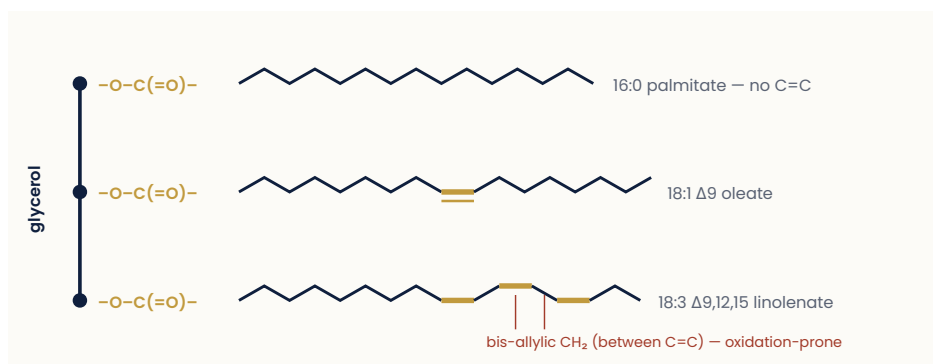


Figure 1.1 Schematic triglyceride carrying three different acyl chains. Double bonds (gold) are the sites that will become oxirane rings. In polyunsaturated chains they are separated by a single methylene group (bis-allylic position), which is unusually susceptible to autoxidation.

The fatty acids that matter

Fatty acids are described by the shorthand $C:D$, where C is the number of carbons and D the number of carbon–carbon double bonds, with positions given as Δ -numbers counted from the carboxyl carbon. In common oils the double bonds are almost always *cis* and, in polyunsaturated acids, methylene-interrupted. Table 1.1 lists the acids that dominate epoxy feedstocks.

Table 1.1 Fatty acids relevant to epoxidation. Structural descriptions are standard nomenclature.

Fatty acid	Shorthand	Double-bond positions	Relevance to epoxy chemistry
Palmitic	16:0	—	Saturated; contributes mass but no epoxide. Dilutes functionality.
Stearic	18:0	—	As palmitic; dangling chains act as internal plasticizer in the network.
Oleic	18:1	$\Delta 9$ <i>cis</i>	One internal epoxide per chain; mid-chain, sterically shielded.
Linoleic	18:2	$\Delta 9,12$ <i>cis</i>	Two epoxides three carbons apart; vicinal ring-opening can form cyclic ethers.
α -Linolenic	18:3	$\Delta 9,12,15$ <i>cis</i>	Three epoxides; the main reason linseed yields high-functionality resins.
γ -Linolenic	18:3	$\Delta 6,9,12$ <i>cis</i>	Minor component of hemp and borage oils.
Stearidonic	18:4	$\Delta 6,9,12,15$ <i>cis</i>	Minor component of hemp oil; four potential oxiranes.
Ricinoleic	18:1-OH	$\Delta 9$ <i>cis</i> , 12-hydroxy	Castor oil's signature; the hydroxyl gives a second reactive handle for urethane or ester chemistry.
α -Eleostearic	18:3 conj.	$\Delta 9c,11t,13t$	Conjugated triene of tung oil; behaves very differently toward electrophiles (Section 1.3).

Composition of the major oils

Oil composition varies with cultivar, climate, and processing, so specifications are expressed as ranges. The *Codex Alimentarius Standard for Named Vegetable Oils* gives authoritative ranges for edible oils [10]; for industrial oils such as linseed, castor, and tung, single-sample analyses from the research literature must serve [11]. Table 1.2 combines these sources with a multi-location study of hemp-seed oil [12].

Table 1.2 Fatty-acid composition (% of total fatty acids) and iodine value (IV, g I₂/100 g) of oils used as epoxy feedstocks. Ranges for soybean, low-erucic rapeseed and sunflower are Codex ranges [10]; hemp ranges are from samples grown in different agro-ecological zones [12]; linseed, castor and tung are single analyses with IV calculated from composition [11].

Oil	16:0	18:0	18:1	18:2	18:3	Other notable	IV
Soybean	8.0–13.5	2.0–5.4	17–30	48.0–59.0	4.5–11.0	—	124–139
Rapeseed, low-erucic (canola)	2.5–7.0	0.8–3.0	51.0–70.0	15.0–30.0	5.0–14.0	—	105–126
Sunflower (regular)	5.0–7.6	2.7–6.5	14.0–39.4	48.3–74.0	ND–0.3	—	118–141
Hemp seed	5.75–8.27	2.19–2.79	10.17–14.03	56.50–60.50	16.85–20.00	γ-18:3 0.63–1.65	154–165
Linseed	6.05	3.94	21.8	17.9	50.3	—	181 (calc.)
Castor	—	—	4.29	7.47	—	ricinoleic 88.2	87.9 (calc.)
Tung	3.32	2.47	6.82	9.04	—	α-eleostearic 78.4	226 (calc.)

ND = not detectable. Single-sample values are illustrative of the oil type, not specifications. Codex IVs refer to crude oils.

Three patterns stand out. First, soybean and sunflower are dominated by linoleic acid and therefore deliver roughly four to five double bonds per triglyceride — the workhorse “semi-drying” profile. Second, linseed oil is unusual among commodity oils in that roughly half of its chains are α-linolenic acid, giving close to six double bonds per molecule and the highest epoxide functionality of the common feedstocks. Third, hemp-seed oil sits between them: a linoleic-rich oil with an α-linolenic fraction of roughly a sixth to a fifth of the total, plus small amounts of γ-linolenic and stearidonic acids [12, 13]. Its iodine value of about 154–165 places it at the boundary between semi-drying and drying oils.

Castor oil is the exception to the rule that functionality equals unsaturation. With close to 90 % ricinoleic acid it carries only about three double bonds per molecule, but also between two and three secondary hydroxyl groups, which is why it is more often used as a polyol than as an epoxy precursor. Tung oil carries a conjugated triene on most of its chains; as Section 1.3 explains, conjugation changes both how it is analysed and how it reacts.

Tall oil: a fatty-acid stream, not a triglyceride

Crude tall oil is a by-product of kraft pulping of coniferous wood, recovered from the soap skimmed off black liquor and then fractionated. Unlike seed oils it consists mainly of *free* fatty acids (predominantly C18 unsaturated acids) mixed with rosin acids and unsaponifiable material, rather than triglycerides. For epoxy chemistry this has two consequences: the carboxylic acid groups must be esterified (for example to methyl or 2-ethylhexyl esters) before epoxidation, or they will open the oxirane rings as they form; and the rosin-acid fraction is itself a useful rigid, alicyclic co-monomer (Chapter 3). Tall-oil fatty acids are therefore best viewed as a feedstock for epoxidized *esters* and as a source of rigid rosin derivatives, not as a direct substitute for soybean oil.

1.2 WASTE FEEDSTOCKS AND CIRCULAR ECONOMY INTEGRATION

Edible oils raise an obvious objection: diverting food-grade oil into resins competes with nutrition and ties resin prices to food markets. Two families of alternatives reduce that tension — used cooking oils, and oils from plants that are not eaten.

Waste cooking oils (WCO)

Repeated frying exposes oil to water, oxygen, and temperatures near 180 °C. Three classes of reaction follow: hydrolysis, which liberates free fatty acids and partial glycerides; oxidation, which generates hydroperoxides that decompose into aldehydes, ketones, and polar oxidized triglycerides; and thermal polymerization, which forms dimeric and oligomeric triglycerides through both the double bonds and oxidized sites. Each class subtracts from epoxide yield. Oxidation and polymerization consume double bonds before the epoxidation reactor ever sees them. Free acids and water attack oxiranes as they form. Particulates and residual food solids foul catalysts and filters.

Nevertheless, WCO can be epoxidized with the same peroxyacetic-acid chemistry used for refined oils, and kinetic studies with homogeneous acid catalysts have been published [14]. The practical lesson from such work is that the attainable oxirane content is limited by the unsaturation that survives frying, so feedstock screening by iodine value is the first and cheapest quality gate.

Non-edible oils

Oils such as jatropha (*Jatropha curcas*), karanja or pongamia (*Pongamia pinnata*), mahua (*Madhuca* spp.), and cottonseed (largely a by-product of fibre production) have been studied as epoxidation feedstocks partly because they avoid direct food competition. Jatropha oil has been epoxidized with peroxyacetic and peroxyformic acids over acidic ion-exchange resins and its kinetics modelled in detail [15]; mahua and cottonseed oils have been epoxidized with aqueous hydrogen peroxide under acid catalysis [16, 17]. These oils frequently carry higher free-fatty-acid levels and characteristic minor toxicants (jatropha seed, for example, contains phorbol esters), so worker exposure and residue management belong in the process design from the start.

Pretreatment and quality control

Whatever the source, the aim of pretreatment is to deliver a dry, neutral, unoxidized triglyceride with as much of its original unsaturation intact as possible. A typical sequence is summarized in Table 1.3.

Table 1.3 Pretreatment steps for waste and non-edible oils before epoxidation, and what each protects against. Qualitative; specific targets should be set from in-house epoxidation trials.

Step	Removes / corrects	Why it matters for epoxidation	QC measurement
Settling, hot filtration	Food solids, carbonized particles, free water	Prevents catalyst fouling; removes nucleation sites for emulsions	Insolubles; visual clarity
Degumming (water or acid)	Phospholipids, metal soaps	Phospholipids stabilize emulsions; metals decompose H_2O_2	Phosphorus content
Neutralization or esterification	Free fatty acids	Carboxylic acids open oxiranes and buffer acid catalysts	Acid value (titration)
Adsorptive bleaching	Pigments, oxidation products, trace metals	Peroxides and transition metals catalyse non-selective H_2O_2 decomposition	Peroxide value; colour
Vacuum drying	Dissolved water	Water hydrolyses oxiranes to diols	Karl Fischer moisture
Characterization	—	Sets stoichiometry for oxidant and acid	Iodine value; fatty-acid profile by GC

CIRCULARITY, HONESTLY ACCOUNTED

“Waste” feedstocks are only circular if the collection, cleaning, and yield losses are counted. A WCO that has lost a third of its unsaturation needs more oil — and more pretreatment energy — per kilogram of epoxide. Chapter 9 returns to this point in the context of life-cycle assessment: the environmental advantage of a bio-epoxy has to be demonstrated, not assumed [18].

1.3 COMPARATIVE REACTIVITY AND IODINE VALUES**Iodine value as a measure of unsaturation**

The iodine value (IV) is the mass of iodine, in grams, that adds across the double bonds in 100 g of sample. In practice it is measured with Wijs reagent (iodine monochloride in acetic acid), with the excess back-titrated with thiosulfate [19]. Because one I_2 (253.8 g mol^{-1}) adds per $\text{C}=\text{C}$, the IV converts directly into moles of double bonds per 100 g:

$$n_{\text{C}=\text{C}} (\text{mol per } 100 \text{ g}) = \frac{\text{IV}}{2 \times 126.90} \quad (1.1)$$

By convention, oils with IV above about 150 are called *drying* (linseed, tung), those between about 125 and 150 *semi-drying* (soybean, sunflower), and those below about 125 *non-drying*. The classification predates polymer chemistry — it describes how quickly a film cures in air — but it maps neatly onto epoxide functionality.

Theoretical maximum oxirane oxygen

If every double bond is converted to an oxirane and no side reactions occur, each mole of C=C adds one mole of oxygen (16.00 g) to the molecule. The theoretical oxirane oxygen content of the epoxidized product, in weight per cent, is then

$$\text{OOC}_{\text{th}} = \frac{(\text{IV}_0 / 2A_{\text{I}}) \cdot A_{\text{O}}}{100 + (\text{IV}_0 / 2A_{\text{I}}) \cdot A_{\text{O}}} \times 100 \quad (1.2)$$

where IV_0 is the iodine value of the starting oil, $A_{\text{I}} = 126.90$ and $A_{\text{O}} = 16.00$ are the atomic masses of iodine and oxygen. This form of the relation is widely used in epoxidation studies [16].

The epoxide equivalent weight follows directly, because one oxirane contains one oxygen atom:

$$\text{EEW} (\text{g eq}^{-1}) = \frac{1600}{\text{OOC} (\%)} \quad (1.3)$$

Table 1.4 Theoretical (calculated) oxirane oxygen and epoxide equivalent weight from Eqs. 1.2–1.3, using mid-range iodine values from Table 1.2 (palm from Codex). Commercial benchmarks are shown for comparison.

Feedstock	IV used	OOC _{th} (%)	EEW _{th} (g/eq)	Benchmark
Palm	52.5	3.20	499	—
Castor	86	5.14	311	—
Rapeseed, low-erucic	115.5	6.79	236	—
Sunflower	129.5	7.55	212	—
Soybean	131.5	7.66	209	Commercial ESO: OOC > 6.8 % [3]
Hemp seed	159.5	9.14	175	—
Linseed	181	10.24	156	Commercial ELO: OOC 9.2 % [4]
Tung (calc. IV)	226	12.47	128	Not attainable: conjugated triene (see text)
DGEBA reference	—	—	185–192	EPON 828 data sheet [20]

WORKED EXAMPLE · HOW CLOSE IS COMMERCIAL ESO TO THE LIMIT?

A soybean oil with $\text{IV}_0 = 131.5$ contains $131.5 / 253.8 = 0.518$ mol C=C per 100 g. Full epoxidation adds $0.518 \times 16.00 = 8.29$ g O, so $\text{OOC}_{\text{th}} = 8.29 / 108.29 \times 100 = 7.66$ %. A commercial product specified at $\text{OOC} > 6.8$ % [3] therefore represents at least about 89 % of the theoretical oxirane content. The corresponding EEW, $1600 / 6.8 \approx 235$ g eq⁻¹, is about 25 % heavier per epoxide than DGEBA — a first, quantitative indication of why ESO networks are less densely crosslinked.

When the iodine value misleads: conjugated double bonds

The IV assumes that halogen adds quantitatively to every double bond. For conjugated systems that assumption fails. A careful study of tung-oil methyl esters found a Wijs iodine value of 156 against a value of 226 calculated from composition, and NMR evidence indicated that iodine monochloride cannot fully halogenate the conjugated triene of α -eleostearate [11]. The same electronic delocalization that frustrates the titration also changes reactivity toward peracids and favours competing Diels–Alder and radical chemistry. Tung oil is therefore a superb drying oil and a useful dienophile/diene partner, but a poor candidate for high-oxirane epoxidation, and its IV should never be used naïvely to set oxidant stoichiometry.

Internal versus terminal double bonds

Peracid epoxidation is an electrophilic addition: the reaction is faster at more electron-rich, more highly substituted alkenes. The 1,2-disubstituted *cis* double bonds in natural fatty acids are therefore reactive toward peracids — more so than the monosubstituted terminal alkenes found in, for example, 10-undecenoic acid derivatives. The situation reverses once the oxirane has formed. An internal epoxide is flanked on both sides by alkyl chains, so nucleophiles such as amines must approach a secondary carbon shielded by its neighbours. Terminal (glycidyl) epoxides present an unhindered primary carbon and react far faster with amines. This asymmetry — easy to make, slow to cure — runs through the rest of the book and motivates both the anhydride and cationic curing routes of Chapter 4 and the terminal-epoxide strategies of Chapter 3 [5, 21].

Two further structural effects follow from the methylene-interrupted pattern. First, in linoleate and linolenate chains, neighbouring oxiranes are separated by only one CH_2 ; when one ring opens, the resulting hydroxyl can attack its neighbour intramolecularly to form a five-membered tetrahydrofuran ring, consuming two epoxides without creating a crosslink. Second, the bis-allylic hydrogens of the unreacted oil are easily abstracted, so oils with high linolenic content oxidize during storage. Both effects argue for epoxidizing fresh, well-characterized oil promptly and for tracking oxirane content, not just iodine value, throughout processing (Chapter 2).

CHAPTER SUMMARY

- Triglyceride functionality is set by the fatty-acid profile; linseed and hemp oils offer the highest usable unsaturation among common feedstocks, soybean and sunflower an intermediate level.
- Codex ranges and literature analyses allow the theoretical oxirane oxygen to be calculated from the iodine value (Eq. 1.2); commercial ESO and ELO reach roughly 90 % of these limits.
- Waste and non-edible oils can be epoxidized, but oxidation, hydrolysis, and polymerization during use reduce yield; pretreatment and iodine-value screening are essential.
- Conjugated oils (tung) defeat the Wijs titration and peracid epoxidation alike; internal epoxides form easily but cure slowly with amines.

CHEMICAL EPOXIDATION ROUTES

Adding one oxygen atom to a double bond is easy. Adding it to millions of double bonds, quickly, safely, and without destroying the ring you just made, is the whole art of oil epoxidation.

IN THIS CHAPTER

- The Prilezhaev reaction and its industrial form: in situ performic or peracetic acid in a two-phase reactor.
- Side reactions that open the oxirane ring, and the catalyst and process choices that suppress them.
- Chemo-enzymatic epoxidation with immobilized lipase, and transition-metal catalysts that use hydrogen peroxide directly.
- How to prove what was made: oxirane titration, NMR, FTIR, and the bookkeeping of conversion and selectivity.

2.1 CONVENTIONAL PRILEZHAEV EPOXIDATION

In 1909 Nikolai Prileschajew reported that organic peroxy acids convert alkenes into oxiranes [2]. The reaction is a concerted electrophilic oxygen transfer — often drawn as the “butterfly” transition state, in which the peracid’s terminal oxygen is delivered to both alkene carbons at once while the carboxylic acid is released. Two consequences matter for oils. The reaction is *stereospecific*: the *cis* double bonds of natural fatty acids give *cis* epoxides. And it is *faster for electron-rich alkenes*, which is why the internal, disubstituted double bonds of triglycerides react readily (Chapter 1).

Pre-formed laboratory peracids such as *m*-chloroperoxybenzoic acid are too expensive and generate too much waste for bulk use. Industrial practice instead generates a short-chain peracid *in situ* from hydrogen peroxide and formic or acetic acid, in the presence of the oil.



(i) peracid formation — aqueous phase; acid-catalysed for R = CH₃, self-catalysed for R = H



(ii) oxygen transfer — oil phase or interface; carboxylic acid is regenerated and returns to step (i)

Formic acid is strong enough to catalyse its own perhydrolysis, so performic-acid systems usually run without an added mineral acid; performic acid is, however, less stable and more hazardous. Acetic acid forms peracetic acid only slowly without help, so peracetic systems use a strong-acid catalyst — sulfuric or phosphoric acid in solution, or a sulfonic-acid cation-exchange resin. Kinetic studies on soybean, jatropha, mahua, and cottonseed oils have mapped these systems in detail [15–17, 22].

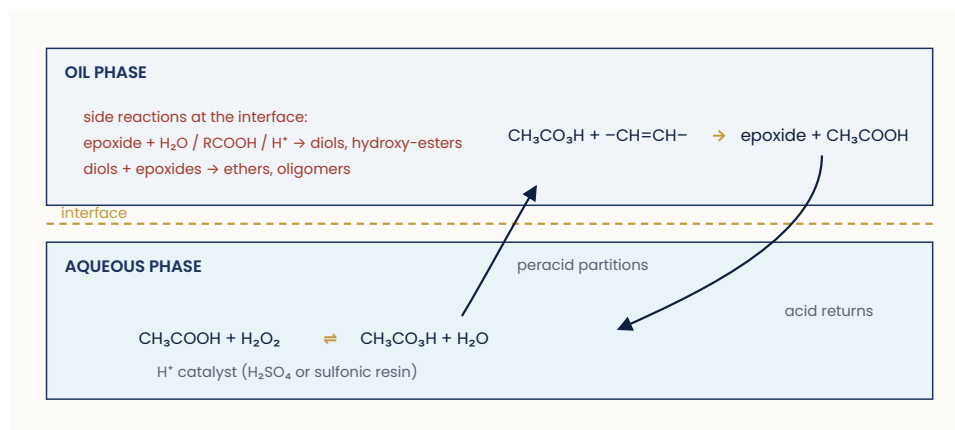


Figure 2.1 The in situ peracetic acid process as a two-phase cycle. Peracid forms in the aqueous phase, migrates to the oil, and delivers oxygen to the double bond; the carboxylic acid returns to be re-oxidized. Ring-opening side reactions are concentrated where acidic water meets epoxidized oil.

Kinetics in a liquid–liquid system

Because the oil and the aqueous oxidant are immiscible, the observed rate is a composite of peracid formation, mass transfer, and the epoxidation step itself. Under well-stirred conditions with peracid continuously regenerated, the consumption of double bonds is often treated as pseudo-first-order in unsaturation; at low agitation, interfacial transfer becomes limiting and rates depend on stirrer speed. Formation of peracetic acid is generally the slow chemical step, which is why catalyst loading has such a pronounced effect. A practical consequence is that rate data from one reactor geometry rarely transfer directly to another; kinetic models that resolve the two phases explicitly are needed for scale-up [15, 22].

Acid catalysts: homogeneous versus ion-exchange resins

Mineral acids are cheap and fast, but they also catalyse the ring-opening reactions that destroy product. Sulfonic-acid ion-exchange resins (the Amberlite/Amberlyst families and similar) offer three advantages: they are removed by filtration; they can be reused; and — the rationale most often given — their acid sites lie largely inside a polymer matrix that small molecules such as acetic acid and hydrogen peroxide can penetrate but bulky triglyceride epoxides cannot, so the acid catalyses peracid formation while being partly shielded from the product [15]. Resin catalysts are not immune to deactivation: swelling, fouling by oligomers, and leaching of acid sites all occur over repeated cycles and should be monitored.

Side reactions and selectivity

The oxirane ring is strained and, in acid, readily protonated. Once protonated it can be attacked by any nucleophile present:

- **Water** → vicinal diol (hydroxylation).
- **Formic or acetic acid** → hydroxy-formate or hydroxy-acetate esters.
- **Hydrogen peroxide or peracid** → hydroxy-hydroperoxides, which are both a yield loss and a safety concern.
- **Hydroxyl groups** already formed → ethers, including intramolecular tetrahydrofuran rings between neighbouring epoxides in polyunsaturated chains, and intermolecular oligomers that raise viscosity.

All of these are favoured by higher temperature, higher acid concentration, longer residence time, and more water. The kinetic picture that emerges from published studies is consistent: higher temperature accelerates epoxidation, but beyond an optimum the rate of ring-opening grows faster, so oxirane content passes through a maximum and then declines with time [16, 17, 22]. The operating window is therefore a compromise, and the endpoint must be chosen from oxirane measurements, not from double-bond conversion alone.

Three figures of merit are used to report an epoxidation:

$$X_{\text{C}=\text{C}} = \frac{\text{IV}_0 - \text{IV}}{\text{IV}_0} \quad (2.1)$$

$$\text{RCO} = \frac{\text{OOC}_{\text{exp}}}{\text{OOC}_{\text{th}}} \quad (2.2)$$

$$S = \frac{\text{RCO}}{X_{\text{C}=\text{C}}} \quad (2.3)$$

where $X_{\text{C}=\text{C}}$ is the fractional conversion of double bonds, RCO the relative conversion to oxirane (with OOC_{th} from Eq. 1.2), and S the selectivity — the fraction of consumed double bonds that survive as oxiranes. A product with high $X_{\text{C}=\text{C}}$ but low S has been over-reacted: its unsaturation is gone, but so are many of its epoxides.

Table 2.1 Process variables in in situ peracid epoxidation and their qualitative effects. Optimal values are feedstock- and reactor-specific.

Variable	Raising it tends to...	Main trade-off
Temperature	Increase epoxidation and peracid-formation rates	Faster ring-opening; greater risk of H ₂ O ₂ decomposition and runaway
H ₂ O ₂ : C=C ratio	Drive conversion toward completion	More water in the system; more oxidant to quench and treat
Carboxylic acid : C=C ratio	Increase peracid concentration and rate	More acidolysis of oxiranes; more acid to wash out
Mineral-acid loading	Speed peracetic acid formation	Strongly increases ring-opening; corrosion
Agitation intensity	Remove mass-transfer limitation	Emulsification makes phase separation slower
Inert solvent (e.g., toluene)	Dilute the oil phase; moderate viscosity and heat release	Solvent recovery cost and VOC handling
Reaction time	Increase conversion	Past the maximum, oxirane content falls

SAFETY · PEROXIDE AND PERACID SYSTEMS

- Epoxidation is strongly exothermic. Hydrogen peroxide should be *dosed* at a rate the cooling system can absorb, never charged all at once, so that unreacted oxidant does not accumulate.
- Performic and peracetic acids are unstable and can decompose violently, especially when heated, concentrated, or contaminated with metals. Avoid stainless or carbon steel surfaces that are not passivated, and exclude rust and metal fines.
- Oxygen evolved from peroxide decomposition can create flammable atmospheres over solvent-containing reactors; inerting and venting must be designed for it.
- Test the washed product for residual peroxide before any heated vacuum stripping or distillation.

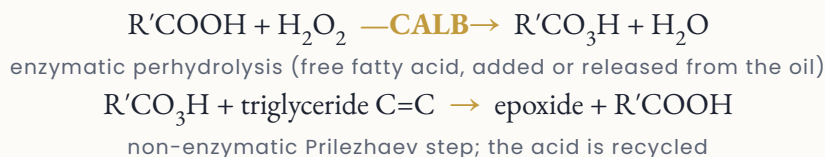
Work-up

At the endpoint the phases are separated; the organic phase is washed with water (and often a dilute bicarbonate or brine wash) until neutral, then dried and stripped under vacuum to remove water, residual carboxylic acid and any solvent. Ion-exchange catalyst is filtered off first. The finished product is characterized against a specification that typically includes oxirane oxygen, residual iodine value, acid value, colour and viscosity — the same parameters reported on commercial data sheets, where epoxidized soybean oil is specified at oxirane oxygen above 6.8 %, iodine value below 3 and acid value below 0.5 mg KOH g⁻¹ [3].

2.2 CHEMO-ENZYMATIC EPOXIDATION

Lipases do not epoxidize double bonds themselves, but some — most notably lipase B from *Candida antarctica* (CALB), typically used in immobilized form — catalyse *perhydrolysis*: the reaction of a carboxylic acid or ester with hydrogen peroxide to give a peroxy acid. Warwel and Rüschen Klaas showed in 1995 that when the sub-

strate is itself an unsaturated fatty acid, the peroxy fatty acid formed by the enzyme transfers its oxygen to a double bond, so that the fatty acid epoxidizes itself; they extended the approach to the complete and partial epoxidation of plant oils in 1999 [23, 24].



The attraction is mildness. No mineral acid is present, temperatures are modest, and so acid-catalysed ring opening is largely suppressed; high oxirane selectivity is the characteristic result. The process has been optimized specifically for soybean oil, with attention to the variables that control enzyme performance [25].

The limitations are equally characteristic:

- **Enzyme deactivation by hydrogen peroxide.** Peroxide oxidizes and denatures the protein, increasingly so at higher concentration and temperature. Slow, continuous dosing of H_2O_2 keeps its standing concentration low.
- **Cost and reuse.** Immobilized enzyme is expensive; economics depend on the number of batches it survives, which in turn depends on peroxide and temperature history.
- **Rate.** Reactions are generally slower than strong-acid peracid processes, which lengthens batch times.
- **Solvent.** Many reported systems use an organic solvent to keep viscosity and mass transfer manageable, adding recovery cost.

2.3 TRANSITION-METAL CATALYSIS AND HETEROGENEOUS ROUTES

Peracid processes use hydrogen peroxide only indirectly. Metal catalysts can activate H_2O_2 directly as metal–peroxo species, removing the carboxylic acid — and with it, a major source of ring-opening — from the system.

Tungsten

Peroxtungstates are among the most practical catalysts for H_2O_2 epoxidation. Venturello and D'Aloisio introduced quaternary ammonium tetrakis(diperoxtungsto)phosphates in 1988 as a new class of efficient catalysts for alkene epoxidation with hydrogen peroxide [26]. The lipophilic quaternary ammonium cation carries the active peroxo-anion into the organic phase, so these systems work as phase-transfer catalysts in biphasic oil/water mixtures — a natural fit for triglycerides.

Rhenium: methyltrioxorhenium

Methyltrioxorhenium (CH_3ReO_3 , MTO) was introduced as a catalyst for olefin oxidation by Herrmann and co-workers in 1991 [27]. With hydrogen peroxide it forms mono- and bis-peroxo complexes that epoxidize alkenes rapidly under mild conditions. Its Lewis acidity can promote ring opening, so nitrogen-base additives are commonly used to protect the epoxide. Rhenium's cost makes MTO more relevant to high-value specialty epoxides than to commodity ESO, but it is a useful benchmark for what a direct H_2O_2 catalyst can achieve.

Molybdenum and titanium

Molybdenum complexes are most effective with alkyl hydroperoxides rather than aqueous H_2O_2 , which limits their attraction for oils. Titanium silicalite (TS-1), highly selective with H_2O_2 for small alkenes, has micropores too narrow to admit a triglyceride; titanium sites grafted onto mesoporous silicas have therefore been the focus of heterogeneous research on fatty substrates. Leaching of the active metal and pore blockage by viscous products are the recurring obstacles for all heterogeneous oxidation catalysts in this application.

Why hydrogen peroxide

Hydrogen peroxide is the reference “green” oxidant because its only stoichiometric by-product is water. A simple calculated comparison of active-oxygen content shows why it also wins on mass efficiency (Table 2.2).

Table 2.2 Active-oxygen content of oxidants (calculated as 16.00 g O per mole of oxidant ÷ molar mass of the pure oxidant).

Oxidant	Molar mass (g/mol)	Active O (wt %)	Co-product
Hydrogen peroxide, H_2O_2	34.01	47.0	Water
<i>tert</i> -Butyl hydroperoxide	90.12	17.8	<i>tert</i> -Butanol
Peracetic acid	76.05	21.0	Acetic acid (recyclable)
<i>m</i> -Chloroperoxybenzoic acid	172.57	9.3	<i>m</i> -Chlorobenzoic acid

2.4 CHARACTERIZATION OF EPOXIDIZED VEGETABLE OILS

An epoxidized oil is a statistical mixture: triglycerides carrying different numbers of oxiranes, plus partially ring-opened species and oligomers. No single measurement describes it fully. A practical characterization package combines one quantitative titration with spectroscopic confirmation and a set of process-control indices.

Oxirane oxygen by titration

The workhorse method for epoxidized fatty materials is direct titration with hydrogen bromide in acetic acid: HBr opens the oxirane quantitatively to a bromohydrin, and the endpoint marks its consumption. AOCS Official Method Cd 9-57, *Oxirane Oxygen in Epoxidized Materials*, standardizes this approach for epoxidized fatty materials and epoxy compounds in general [28]. For epoxy resins, ASTM D1652 specifies manual and automatic titration of percent epoxide content over the range 0.1–26 % [29]. Variants that generate HBr in situ from perchloric acid and a quaternary ammonium bromide are widely used because they avoid handling HBr solutions.

Two reporting cautions apply. First, results may be expressed as oxirane oxygen, as “percent epoxide”, or as epoxide equivalent weight; the basis must always be stated, because the conversion factors differ. Second, any species that consumes HBr — basic residues, for example — biases the result, so samples must be neutral and dry.

WORKED EXAMPLE · FROM TITRATION TO EEW

Suppose 0.500 g of epoxidized oil consumes 14.2 mL of 0.1000 N HBr equivalent to reach the endpoint. Moles of oxirane = $0.0142 \text{ L} \times 0.1000 \text{ mol L}^{-1} = 1.42 \times 10^{-3} \text{ mol}$. EEW = $0.500 \text{ g} / 1.42 \times 10^{-3} \text{ eq} = 352 \text{ g eq}^{-1}$, and OOC = $1600 / 352 = 4.5 \%$. If the starting oil was soybean ($\text{OOC}_{\text{th}} \approx 7.7 \%$), the RCO is only about 59 % — a strong hint of incomplete reaction or ring opening, to be resolved by measuring the residual IV.

Nuclear magnetic resonance

^1H NMR gives the most direct molecular picture. The olefinic protons of the starting oil appear near 5.3–5.4 ppm and disappear on epoxidation; the methine protons on the oxirane ring appear as a new multiplet near 2.9–3.1 ppm. The glycerol backbone supplies a convenient internal standard: its four $\text{CH}_2\text{-O}$ protons (about 4.1–4.3 ppm) are unaffected by the reaction, so the ratio of epoxide to glycerol- CH_2 integrals gives the average number of oxiranes per triglyceride without an external reference. Signals from ring-opened products (CH-OH and CH-O-acyl protons near 3.4–3.9 ppm) quantify side reactions. In ^{13}C NMR, olefinic carbons near 127–132 ppm are replaced by oxirane carbons near 54–58 ppm. Exact shifts depend on solvent and on whether neighbouring epoxides are present, so assignments should be confirmed against a reference sample.

Infrared spectroscopy

FTIR is fast and suited to in-process monitoring. Epoxidation is tracked by the loss of the $=\text{C-H}$ stretch near 3010 cm^{-1} and the weak C=C stretch near 1650 cm^{-1} , and by the appearance of oxirane ring bands in the $820\text{--}845 \text{ cm}^{-1}$ region. Growth of a broad O-H band near $3400\text{--}3500 \text{ cm}^{-1}$ is the clearest sign of ring opening. The strong ester carbonyl near 1740 cm^{-1} is unchanged and serves as an internal reference for semi-quantitative band ratios.

Process-control indices

Table 2.3 Analytical toolbox for epoxidized vegetable oils. Commercial ESO/ELO specifications from supplier data sheets are given where available.

Measurement	What it tells you	Typical method	Commercial benchmark
Oxirane oxygen	Epoxide content (and EEW)	HBr titration (AOCS Cd 9-57; ASTM D1652)	ESO > 6.8 %; ELO 9.2 % [3, 4]
Residual iodine value	Unreacted double bonds	Wijs titration	ESO < 3.0; ELO < 4.0
Acid value	Residual carboxylic acid; hydrolysis	KOH titration	< 0.5 mg KOH/g
Hydroxyl value	Extent of ring opening	Acetylation / titration	—
Viscosity	Oligomerization; processability	Rotational viscometer, 25 °C	ESO 320–500 cP; ELO ~800 cP
Colour	Oxidation, impurities	APHA	ESO < 150; ELO < 225
Epoxide distribution	Oxiranes per molecule; side products	¹ H / ¹³ C NMR	—
Molecular-weight distribution	Oligomer fraction	Size-exclusion chromatography	—

Tracking viscosity alongside oxirane content is particularly informative: a rising viscosity at constant or falling OOC is the fingerprint of ether-forming oligomerization, which both consumes epoxides and complicates downstream processing (Chapter 8).

CHAPTER SUMMARY

- Industrial oil epoxidation is the Prilezhaev reaction run with in situ performic or peracetic acid in a two-phase system; its yield is limited by acid-catalysed ring opening rather than by oxygen transfer.
- Ion-exchange resins, controlled peroxide dosing, and stopping at the oxirane maximum are the main levers for selectivity; conversion, RCO, and selectivity (Eqs. 2.1–2.3) should all be reported.
- Lipase-mediated perhydrolysis gives very selective epoxidation under mild conditions but is limited by enzyme stability and cost; tungsten and rhenium catalysts use H₂O₂ directly.
- Oxirane titration, NMR with the glycerol backbone as internal standard, and FTIR together provide a defensible characterization.



SECONDARY FUNCTIONALIZATION AND CHEMICAL MODIFICATIONS

Beyond the internal oxirane: ring-opening derivatives, terminal epoxides, and rigid bio-based co-monomers.

CH. 3 · TAILORING REACTIVITY BEYOND INTERNAL OXIRANES

TAILORING REACTIVITY BEYOND INTERNAL OXIRANES

An epoxidized oil is not only a resin. It is a platform molecule — and the oxirane ring is the handle by which almost any other functionality can be attached.

IN THIS CHAPTER

- Ring-opening routes from epoxidized oils to polyols, acrylates, amines and acids.
- How to install terminal (glycidyl) epoxides on oil-derived molecules, and why they cure so differently.
- Rigid bio-based building blocks — lignin, rosin, itaconic acid, furans and cardanol — that raise crosslink density and glass transition.

Chapter 1 ended with an asymmetry: internal epoxides are easy to make but slow to react with nucleophiles, and they sit on long flexible chains that soften the networks they form. This chapter covers the two complementary responses. One is to *change the reactive group* — open the oxirane and install something more useful, or attach a terminal epoxide. The other is to *change the skeleton* — bring in rigid, often aromatic, bio-based co-monomers.

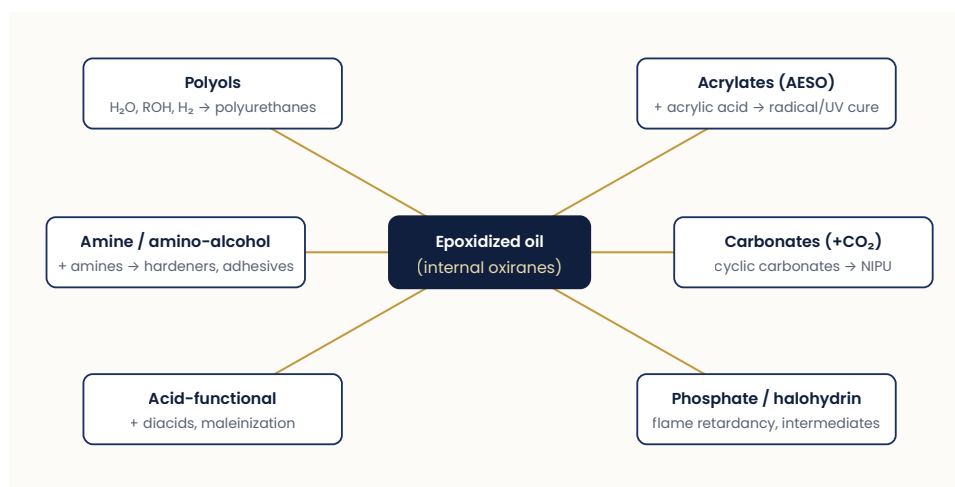


Figure 3.1 The epoxidized oil as a platform. Each spoke is a ring-opening or ring-expansion reaction that converts the internal oxirane into a different reactive group. NIPU = non-isocyanate polyurethane.

3.1 EPOXY RING-OPENING DERIVATIVES

Hydroxylation: polyols for polyurethane and hybrid networks

Opening the oxiranes with water, alcohols, hydrogen (hydrogenolysis), or acids converts an epoxidized oil into a polyol. These polyols are the largest non-epoxy use of epoxidized oils in polymer science, and their chemistry, structure–property relationships, and polyurethane applications have been reviewed comprehensively [30, 31]. Three points from that literature carry over to epoxy formulation:

- **Hydroxyl placement.** Ring opening places secondary hydroxyls in the middle of the chain, flanked by dangling chain ends. These are less reactive than primary hydroxyls and the dangling ends plasticize the network, exactly as with internal epoxides.
- **Functionality distribution.** Because the parent oil is a statistical mixture, the polyol is too; its average hydroxyl functionality is not the whole story, and the fraction of low-functionality molecules governs sol fraction and softness.
- **Partial opening.** Stopping ring opening part-way gives molecules that carry both hydroxyls and residual epoxides. These are useful in hybrid epoxy–urethane networks, and the hydroxyls also accelerate amine–epoxy reactions by hydrogen-bond activation of the oxirane (Chapter 4).

Acrylation: AESO and vinyl-ester-type prepolymers

Ring opening with acrylic acid converts each oxirane into a β -hydroxy acrylate ester. The product, acrylated epoxidized soybean oil (AESO), is no longer an epoxy at all but a multifunctional acrylate that cures by free-radical polymerization — thermally with peroxides or photochemically with radical photoinitiators. AESO and related maleinated and hydroxylated triglycerides were developed systematically as liquid-moulding resins and composite matrices, typically blended with a reactive diluent such as styrene to reduce viscosity and raise stiffness [32]. More recently, photocurable AESO has been printed into shape-memory biomedical scaffolds [33].

Acrylation chemistry needs care on three fronts: the acrylic acid and acrylated product must be protected from premature radical polymerization with inhibitors and dissolved oxygen; the ring-opening is usually catalysed (tertiary amines, phosphines, or metal salts are common), and over-heating favours oligomerization; and residual unreacted epoxide and free acrylic acid must be specified, because both affect cure and odour.

Amine- and carboxylic-acid-functionalized derivatives

Ring opening by amines gives β -amino alcohols, and if a diamine is used in excess, the product carries free amine groups and can serve as a bio-based hardener. Because internal oxiranes react slowly with amines, an alternative is to build the amine functionality on the double bond directly. Thiol–ene coupling of amine-bearing thiols to the unsaturation of the oil does exactly this, and has been used to prepare an amine-functional vegetable-oil hardener that, combined with an epoxidized oil, gives a resin in which both components derive from vegetable oil [34].

Carboxylic-acid functionality can be introduced by ring opening with diacids (leaving one acid group free), or by *maleinization* — the ene and Diels–Alder reactions of maleic anhydride with the oil’s unsaturation, which graft succinic anhydride groups onto the chains. Maleinized oils act as flexible anhydride hardeners. In a study on hemp oil, epoxidized hemp oil (EHO) was cured with blends of methyl nadic anhydride (MNA) and maleinized hemp

oil (MHO); MNA alone gave a stiff, brittle material with a curing time of about 170 min, while a 25 % MHO / 75 % MNA hardener blend gave a balanced material with about 180 % higher impact energy absorption and a much lower Young's modulus, and cut the curing time to about 78 min [35]. The result illustrates a general principle: oil-derived hardeners trade stiffness for toughness, and blending with a rigid co-hardener sets the balance.

Carbonation

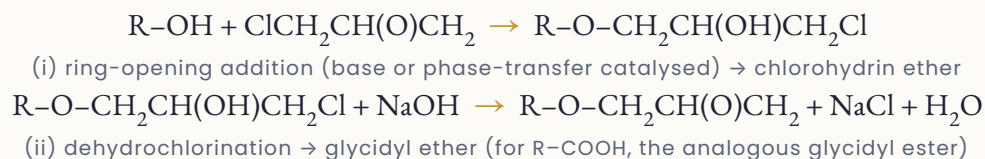
Oxiranes react with carbon dioxide over suitable catalysts to form five-membered cyclic carbonates. Carbonated oils react with amines to give hydroxyurethanes without isocyanates (non-isocyanate polyurethanes, NIPU). Although outside the epoxy family proper, this route shares the same epoxidized intermediates and is worth knowing as an alternative outlet for an epoxidation plant.

3.2 INTRODUCING TERMINAL EPOXY GROUPS

The single largest improvement in amine reactivity comes from moving the epoxide to the end of a chain. A glycidyl group ($-\text{CH}_2-\text{CH}(\text{O})\text{CH}_2$) presents a primary, unhindered carbon to the nucleophile — the same structural feature that makes DGEBA cure readily at room temperature with aliphatic amines.

Glycidylation with epichlorohydrin

The standard route attaches the glycidyl group to an oxygen nucleophile — a hydroxyl or a carboxylic acid — using epichlorohydrin (ECH):



Applied to fatty acids, the route gives glycidyl esters; applied to oil-derived polyols, it gives glycidyl ethers. Excess ECH suppresses chain extension (reaction of a newly formed glycidyl group with another hydroxyl), and residual hydrolysable chlorine is the key impurity to specify, because it affects electrical properties and long-term stability.

Epichlorohydrin itself need not be fossil-derived. Solvay's Epicerol® process produces ECH from glycerol, a by-product of biodiesel manufacture; the company reported a 60 % lower cradle-to-gate CO₂ balance and an eight-fold reduction in chlorinated by-products compared with the conventional propylene route [36]. These are company-reported figures and should be treated as such in any life-cycle study (Chapter 9). Since glycerol and fatty acids come from the same oil, an oil-derived glycidyl ester can, in principle, be entirely renewable.

SAFETY · EPICHLOROHYDRIN

Epichlorohydrin is toxic, a skin sensitizer and classified as a probable human carcinogen by several agencies. Glycidylation must be run in closed equipment with exposure monitoring, and residual ECH in products must be specified and controlled.

Routes without epichlorohydrin

Terminal epoxides can also be made by epoxidizing a terminal double bond. Esterifying fatty acids with allyl alcohol, or etherifying oil-derived polyols with allyl groups, gives terminal alkenes that a peracid or a metal/ H_2O_2 system can then epoxidize. Castor oil offers a natural source of terminal unsaturation through 10-undecenoic acid, obtained by pyrolysis of ricinoleic acid. The trade-off follows from Chapter 1: terminal alkenes are less electron-rich and therefore epoxidize more slowly with peracids, so more forcing conditions or more active catalysts are needed (Section 2.3).

Table 3.1 Internal versus terminal epoxides in oil-derived resins (qualitative comparison).

Property	Internal oxirane (EVO)	Terminal glycidyl group
Ease of formation	High — electron-rich internal C=C	Lower (peracid route) or requires ECH chemistry
Reactivity with amines	Low; sterically hindered secondary carbons	High; unhindered primary carbon
Preferred cure	Anhydrides, acids, cationic (Chapter 4)	Amines at ambient or moderate temperature
Network architecture	Crosslinks mid-chain; dangling chain ends	Crosslinks at chain ends; fewer dangling segments
Key impurities	Hydroxyls, oligomers from ring opening	Hydrolysable chlorine, residual ECH

3.3 BIO-BASED CROSSLINKING BOOSTERS

Even a perfectly terminal-functionalized fatty chain remains a long aliphatic spring. To approach the stiffness and glass transition of aromatic epoxies, bio-based formulations borrow rigidity from other renewable sources. Reviews of bio-based epoxy chemistry survey these building blocks in depth [5, 9]; the most relevant to oil-based systems are summarized below and in Table 3.2.

Raising functionality per molecule

One way to raise crosslink density without adding aromatics is to put more fatty chains on each molecule. Esterifying sucrose with soybean fatty acids and then epoxidizing yields epoxidized sucrose esters carrying many more oxiranes per molecule than a triglyceride; cured with anhydrides, these give high-bio-based-content thermosets [37]. The design lever is simple: more epoxides on a compact core means more elastically effective crosslinks per unit volume and fewer dangling chain ends per junction. The same logic underlies the use of other polyol cores.

Lignin

Lignin is the most abundant renewable aromatic polymer, and its phenolic and aliphatic hydroxyls can be glycidylated or used directly as co-reactants. Its value is aromatic rigidity and char formation; its difficulties are heterogeneity, high viscosity, poor solubility, and batch-to-batch variability tied to botanical source and isolation process. A recent review details how lignin structure and pretreatment govern the synthesis and properties of lignin-based epoxies [38]. Life-cycle studies have also cautioned that the chemicals used to extract and upgrade lignin can erode its environmental advantage [18].

Rosin

Rosin acids, available from pine resin and from tall oil, have a bulky hydrophenanthrene skeleton. Abietic-type acids isomerize to levopimaric acid, whose conjugated diene undergoes Diels–Alder addition with maleic anhydride or acrylic acid to give rigid polyfunctional adducts. Rosin-derived anhydrides have been prepared and evaluated specifically as replacements for petrochemical anhydride curing agents [39]; paired with epoxidized oils, they supply the rigidity the oil lacks.

Itaconic acid

Itaconic acid, produced by fermentation, is a small unsaturated diacid. Its glycidyl ester provides two epoxide groups plus a C=C bond that can take part in radical co-curing. An itaconic-acid-based epoxy cured with anhydride and comonomers has been reported as a bio-based alternative to conventional resins [40]; because of its low molecular weight and high epoxide density, it is also an effective reactive co-monomer for raising the crosslink density of EVO blends.

Furans

Furan rings derived from carbohydrates (via furfural and 5-hydroxymethylfurfural) offer a rigid, aromatic heterocycle without bisphenol A. Furan-based diglycidyl compounds have been synthesized and their thermosetting behaviour characterized, establishing them as candidates for high-performance bio-epoxies [41]. The furan ring also takes part in reversible Diels–Alder chemistry with maleimides — a route to thermally reversible crosslinks (Chapter 7).

Cardanol

Cardanol, distilled from cashew-nut-shell liquid (CNSL), is a phenol carrying a C15 unsaturated side chain at the *meta* position. It is a hybrid of the two worlds: an aromatic ring that can be glycidylated, and a fatty chain that confers flexibility and hydrophobicity. Its functionalization chemistry has been reviewed extensively [42]. Cardanol glycidyl ethers are sold commercially as low-viscosity reactive diluents (Chapter 8), and cardanol-derived phenalkamines are established curing agents (Chapter 4).

Table 3.2 Rigid and multifunctional bio-based building blocks for EVO formulations (qualitative).

Building block	Origin	What it adds	Main limitation	Ref.
Epoxidized sucrose esters	Sucrose + oil fatty acids	Many epoxides per molecule; crosslink density	Viscosity; synthesis cost	[37]
Lignin (glycidylated or native)	Pulping, biorefining	Aromatic rigidity; char yield	Heterogeneity; viscosity; extraction burden	[38]
Rosin anhydrides / acids	Pine resin, tall oil	Bulky alicyclic rigidity; hardener function	Colour; oxidation of residual unsaturation	[39]
Itaconic acid epoxy	Fermentation	High epoxide density; radical co-cure	Synthesis via ECH	[40]
Furan diglycidyl compounds	Carbohydrates	Aromatic-like rigidity without BPA	Cost; furan stability	[41]
Cardanol derivatives	Cashew-nut-shell liquid	Aromatic ring + flexible chain; low viscosity	Monofunctional diluents lower crosslink density	[42]

Blending: predicting the glass transition

Most practical formulations blend an EVO with one or more rigid partners. As a first estimate for miscible, fully cured blends, the Fox equation relates the glass transition of the blend to the weight fractions w_i and glass transitions $T_{g,i}$ (in kelvin) of the networks formed by each component alone:

$$\frac{1}{T_{g,\text{blend}}} \approx \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (3.1)$$

The equation is an approximation: real co-cured networks are not simple mixtures, and phase separation, incomplete cure of the slower component, and specific interactions all cause deviations. It is nevertheless useful for screening, and a large positive deviation from it is a sign of genuine co-network formation rather than mere mixing.

WORKED EXAMPLE · FOX ESTIMATE FOR AN EVO BLEND

Suppose an ESO-anhydride network has $T_g = 320$ K (47 °C) and a rigid bio-epoxy cured with the same anhydride has $T_g = 420$ K (147 °C). For a 60:40 (w/w) blend, $1/T_g = 0.60/320 + 0.40/420 = 0.001875 + 0.000952 = 0.002827$ K⁻¹, so $T_{g,\text{blend}} \approx 354$ K (81 °C). The input values here are illustrative, not measured; the exercise shows that replacing 40 % of the oil with a rigid partner can raise T_g by tens of degrees.

CHAPTER SUMMARY

- Ring opening converts epoxidized oils into polyols, acrylates (AESO), amine and acid-functional derivatives, and cyclic carbonates — a platform rather than a single resin.
- Glycidylation with epichlorohydrin (which can itself be glycerol-derived) or epoxidation of terminal alkenes installs reactive terminal epoxides that cure readily with amines.
- Rigidity is imported from sucrose cores, lignin, rosin, itaconic acid, furans and cardanol; the Fox equation offers a first estimate of blend T_g .



CURING CHEMISTRY AND NETWORK TOPOLOGY

Hardeners, catalysts, and light – and how they knit flexible triglycerides into load-bearing networks.

CH. 4 · CURING AGENTS AND MECHANISMS

CH. 5 · CROSSLINK DENSITY AND STRUCTURE-PROPERTY RELATIONSHIPS

CURING AGENTS AND MECHANISMS

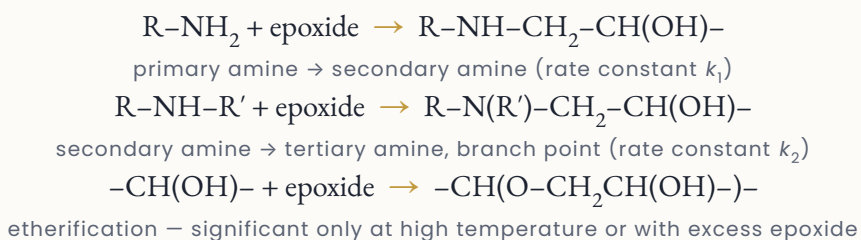
The hardener is half the network. For vegetable-oil epoxies it is often the more important half, because it must supply the reactivity and rigidity the oil cannot.

IN THIS CHAPTER

- Amine curing: mechanism, stoichiometry, and why internal epoxides resist it.
- Anhydride curing: the alternating copolymerization initiated by tertiary amines and imidazoles.
- Bio-based hardeners: rosin anhydrides, natural acids, lignin derivatives, and cardanol phenalkamines.
- Cationic photopolymerization with onium salts, dual-cure systems, and the tools for measuring cure.

4.1 AMINE CURING SYSTEMS

Amines are the most widely used hardeners for conventional epoxies because they react at ambient or moderate temperature without a catalyst. The chemistry is a nucleophilic ring opening: each N–H hydrogen opens one oxirane, generating a secondary hydroxyl.



The hydroxyls generated by the reaction hydrogen-bond to oxirane oxygens and accelerate further ring opening, so amine-epoxy curing is *autocatalytic*. Phenols, alcohols and water accelerate it for the same reason; tertiary amines accelerate it by a different, base-catalysed path.

Classes of amine

- **Aliphatic polyamines** (ethylenediamine, diethylenetriamine, triethylenetetramine): fast, room-temperature cure; flexible networks; volatile and corrosive; prone to carbamation (“blush”) with atmospheric CO₂ and moisture.
- **Cycloaliphatic amines** (e.g., isophorone diamine): slower, give higher glass transitions and better colour stability.

- **Aromatic amines** (e.g., diaminodiphenyl sulfone, diaminodiphenylmethane): low basicity and reactivity, require elevated-temperature cure, and give the highest glass transitions and thermal stability; several carry significant toxicity concerns.

Stoichiometry

The amine hydrogen equivalent weight (AHEW) is the molar mass divided by the number of active N–H hydrogens. For stoichiometric balance, the parts of hardener per hundred parts of resin (phr) are

$$\text{phr}_{\text{amine}} = \frac{\text{AHEW} \times 100}{\text{EEW}} \quad (4.1)$$

WORKED EXAMPLE · AMINE LOADING FOR ESO VERSUS DGEBA

Isophorone diamine ($\text{C}_{10}\text{H}_{22}\text{N}_2$, 170.3 g mol^{-1} , four N–H) has $\text{AHEW} = 42.6 \text{ g eq}^{-1}$. For a DGEBA resin with $\text{EEW} 188 \text{ g eq}^{-1}$ (mid-range of a standard liquid resin [20]), $\text{phr} = 4260/188 = 22.7$. For an ESO with $\text{EEW} 235 \text{ g eq}^{-1}$ (OOC 6.8 %, Chapter 1), $\text{phr} = 4260/235 = 18.1$. The oil needs less hardener per unit mass because it carries fewer epoxides – one more reason its networks are less dense.

The internal-epoxide problem

For epoxidized oils, the textbook picture breaks down in a predictable way. The internal oxirane is a 1,2-disubstituted ring with alkyl chains on both carbons. An amine must approach a secondary carbon shielded on both sides, and the transition state is crowded. Rates are therefore far lower than for glycidyl ethers, and cure at ambient temperature is usually impractical. The difficulty compounds itself: as the network forms, the remaining epoxides become embedded in a matrix whose mobility falls, and vitrification can stop the reaction well short of full conversion. The literature consistently reports that EVO–amine systems require elevated temperatures, often show incomplete conversion, and give soft, low- T_g networks unless the oil is blended with a more reactive epoxy [5, 21]. Practical responses include:

- blending EVO with a glycidyl-functional resin (bio-based where possible), so that the amine builds a skeleton network that the EVO reinforces as a co-reactant;
- using accelerators (phenols, tertiary amines) and a staged cure with a final post-cure above the expected T_g ;
- converting the oil to a terminal-epoxide derivative (Chapter 3), or switching to anhydride or cationic chemistry, which are far less sensitive to the steric environment.

Following the cure

Differential scanning calorimetry (DSC) is the standard tool for cure kinetics. The fractional conversion α at any time is the heat released so far divided by the total reaction heat. Autocatalytic cure is commonly described by the Kamal–Sourour model [43]:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \quad (4.2)$$

where k_1 describes the non-catalysed and k_2 the autocatalysed path, each with Arrhenius temperature dependence, and m, n are empirical orders.

An apparent activation energy can be obtained without assuming a model from the shift of the exotherm peak temperature T_p with heating rate β , using the Kissinger relation [44]:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E_a} - \frac{E_a}{R T_p} \quad (4.3)$$

As the network builds, its glass transition rises with conversion. The DiBenedetto equation in the form popularized by Pascault and Williams relates the two [45]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha} \quad (4.4)$$

where T_{g0} and $T_{g\infty}$ are the glass transitions of the uncured mixture and the fully cured network, and λ is an adjustable parameter (often taken as the ratio of heat-capacity changes at the two transitions). When the rising T_g reaches the cure temperature, the system vitrifies and the reaction becomes diffusion-controlled; a post-cure above $T_{g\infty}$ is needed to reach full conversion.

4.2 ANHYDRIDE CURING

Cyclic anhydrides are the hardeners of choice for epoxidized oils. They react through the oxirane oxygen rather than by direct attack on a hindered carbon, they need elevated temperatures anyway, and they form ester-rich networks with low shrinkage, good electrical properties, and long pot life. Commonly used liquid anhydrides include methyltetrahydrophthalic anhydride (MTHPA), methylhexahydrophthalic anhydride (MHHPA), and methyl nadic anhydride (MNA); long-chain alkenyl succinic anhydrides are used where flexibility is wanted.

Mechanism

Uncatalysed epoxy–anhydride reactions are slow and initiated by hydroxyl groups. In practice a Lewis-base catalyst — a tertiary amine or an imidazole — is used, and the reaction becomes an anionic alternating copolymerization:

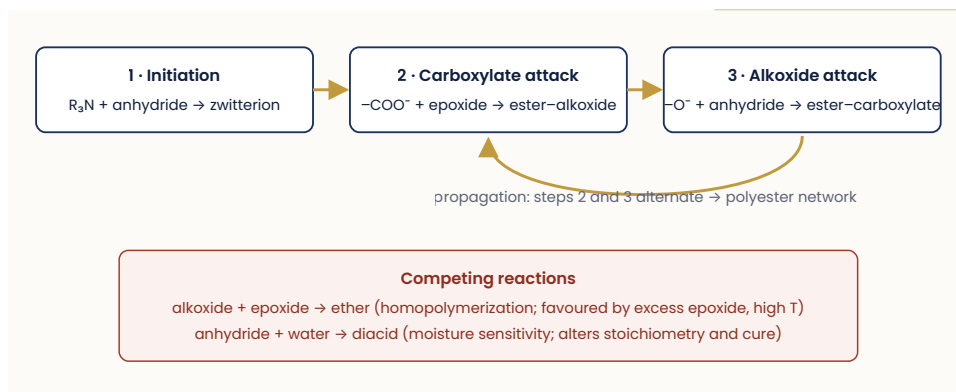


Figure 4.1 Base-catalysed epoxy-anhydride cure as an alternating anionic copolymerization. Each propagation cycle consumes one epoxide and one anhydride and forms two ester links. Etherification competes when epoxide is in excess.

Because etherification consumes epoxides without anhydride, the optimum anhydride-to-epoxide ratio (A/E) is frequently somewhat below 1 and should be established experimentally. The formulation equation is

$$\text{phr}_{\text{anhydride}} = \frac{\text{AEW} \times 100}{\text{EEW}} \times (\text{A/E}) \quad (4.5)$$

where AEW is the anhydride equivalent weight (molar mass divided by the number of anhydride groups).

WORKED EXAMPLE · MHHPA LOADING

MHHPA ($\text{C}_9\text{H}_{12}\text{O}_3$, 168.2 g mol^{-1} , one anhydride group) has AEW 168.2. At A/E = 0.9, an ESO with EEW 235 needs $168.2 \times 100/235 \times 0.9 = 64.4 \text{ phr}$; a DGEBA with EEW 188 needs 80.5 phr. Anhydride-cured EVOs therefore contain a large fraction of hardener by mass — which is why the bio-based content of the cured material depends heavily on whether the anhydride is itself renewable.

Catalysts

Tertiary amines (for example benzyldimethylamine and 2,4,6-tris(dimethylaminomethyl)phenol) and imidazoles (for example 1-methylimidazole and 2-ethyl-4-methylimidazole) are the common choices; their type and concentration strongly influence gel time, peak exotherm, and final properties. For epoxidized linseed oil, Boquillon and Fringant studied systematically how the choice of catalyst and of anhydride hardener shapes the resulting polymer networks [46]; Gerbase and co-workers characterized the dynamic mechanical and thermal behaviour of anhydride-cured epoxy resins based on soybean oil [47]. Both studies, and work on hemp oil [35], show the same pattern: higher-functionality oils (linseed, hemp) and more rigid anhydrides give stiffer networks with higher glass transitions, while flexible or oil-derived anhydrides raise toughness at the expense of stiffness.

SAFETY · ANHYDRIDES

Cyclic anhydrides are potent respiratory and skin sensitizers. Occupational exposure limits are low, and sensitized workers may react to very small exposures. Use closed handling, local exhaust ventilation and appropriate protective equipment; keep containers sealed, which also protects the anhydride from moisture.

4.3 BIO-BASED HARDENERS

An all-renewable epoxy needs a renewable hardener, and the curing agent often dominates both performance and bio-based carbon content (see the worked example above). The preparation and use of bio-based curing agents have been reviewed in depth [9, 48]; the families most relevant to oil-based epoxies are outlined here and in Table 4.1.

Rosin-derived acids and anhydrides

Diels–Alder adducts of rosin acids with maleic anhydride (maleopimaric acid and its anhydride derivatives) combine a rigid hydrophenanthrene ring system with anhydride or acid functionality. They have been prepared and evaluated specifically as replacements for petrochemical anhydride hardeners [39], and they pair naturally with EVOs: the oil supplies flexibility and epoxide groups, the rosin supplies rigidity.

Natural polycarboxylic acids

Carboxylic acids react with epoxides to form β -hydroxy esters, and polycarboxylic acids therefore crosslink EVOs directly. Citric acid is an attractive example: epoxidized soybean oil has been crosslinked with an aqueous citric acid solution without any added catalyst or solvent, giving networks that self-heal through transesterification of the β -hydroxy ester groups formed during cure [49]. Lignin-derived aromatic diacids are another route: divanillic acid and a butoxylated derivative cured with ESO under zinc catalysis gave networks with glass transitions (DMA $\tan \delta$ peak) of 20–62 °C depending on formulation, and the resulting materials were reprocessible vitrimers [50]. Chapter 7 develops the dynamic-network aspect of acid-cured EVOs.

Lignin-based polyphenols and polyacids

Lignin's phenolic hydroxyls can act as hardeners for epoxides (phenol–epoxy reactions require a basic catalyst and elevated temperature), and oxidative or chemical modification can convert lignin or its depolymerization products into polycarboxylic acids. Heterogeneity and limited solubility in oil-based resins remain the main barriers [38].

Phenalkamines from cashew-nut-shell liquid

Phenalkamines are Mannich bases made from cardanol, formaldehyde, and a polyamine. They combine a phenol (which accelerates the amine–epoxy reaction), amine hydrogens for cure, and cardanol's long hydrophobic chain. They are commercial curing agents valued for low-temperature and moisture-tolerant cure and for the water resistance they impart. The structure of the phenalkamine — in particular the amine used in the Mannich reaction — has been shown to govern the adhesive, viscoelastic, and thermal properties of the resulting epoxy networks [51]. Their bio-based fraction is partial, since the polyamine is usually petrochemical.

Table 4.1 Bio-based curing agents for vegetable-oil epoxies (qualitative overview).

Hardener family	Reactive group	Typical role with EVOs	Strengths	Watch-outs
Rosin anhydrides / acids	Anhydride, COOH	Rigid co-hardener	Raises T_g and modulus	Colour; viscosity; solid handling
Citric and other natural acids	COOH	Direct crosslinker	Catalyst-free cure possible; dynamic β -hydroxy esters	Water management; moderate T_g
Lignin-derived diacids (e.g., divanillic acid)	COOH	Aromatic crosslinker	Aromatic rigidity; vitrimer chemistry with Zn catalysts	Synthesis steps; solubility
Lignin polyphenols	Phenolic OH	Co-hardener, char former	Abundant; flame-retardant tendency	Heterogeneity; dispersion
Maleinized oils	Anhydride	Flexible hardener	Toughness; full oil origin	Lower stiffness and T_g
Phenalkamines (CNSL)	N-H + phenol	Amine hardener for blends	Low-temperature, damp-tolerant cure	Partly petrochemical; colour

4.4 CATIONIC AND UV-INDUCED CURING

Cationic ring-opening polymerization (CROP) is the curing mode least troubled by the internal-epoxide problem. A strong Brønsted acid protonates the oxirane oxygen; another epoxide attacks the activated ring, and the resulting oxonium ion propagates the chain. Because the attack is on an activated, partially carbocationic centre, steric hindrance matters less than in amine cure, and trisubstituted or 1,2-disubstituted epoxides polymerize readily.

Onium-salt photoinitiators

Crivello and Lam introduced diaryliodonium salts as photoinitiators for cationic polymerization in 1977 [52]; triarylsulfonium salts followed. On UV irradiation, these salts decompose to release a Brønsted superacid whose anion (for example SbF_6^- or PF_6^-) is weakly nucleophilic, so the propagating cation is not quickly terminated. Crivello and Narayan demonstrated in 1992 that epoxidized triglycerides are effective renewable monomers in photoinitiated cationic polymerization [53]. Key features of cationic photocure for EVOs:

- **No oxygen inhibition**, unlike radical acrylate cure — thin films cure to tack-free surfaces in air.
- **Dark cure**. The acid persists after irradiation, so polymerization continues in shadowed regions and after the lamp is switched off; a mild thermal bump accelerates it.
- **Sensitivity to bases and water**. Amines, basic fillers and moisture neutralize or transfer the active centre; formulations must be kept free of basic contaminants.
- **Chain transfer to hydroxyls**. Alcohols participate through an activated-monomer mechanism, incorporating themselves into the network; polyols are deliberately added as flexibilizers, but hydroxyls from ring opening during epoxidation also act this way.

Thermally latent cationic initiators — onium salts designed to release acid only above a threshold temperature — extend the same chemistry to one-component, heat-cured systems.

Dual-cure and hybrid networks

Two chemistries can be combined in one formulation to separate shaping from final property development:

- **Radical + cationic:** an acrylate (for example AESO) and an epoxide (for example ESO or ELO) cured simultaneously with radical and cationic photoinitiators gives an interpenetrating or hybrid network. The radical cure delivers rapid shape fixation; the cationic cure continues in the dark and reduces shrinkage stress.
- **UV + thermal:** a UV step gels the surface or the printed object, then a thermal post-cure (anhydride or latent cationic) completes the epoxide reaction in the bulk. This is the logic used for thick or filled parts and for 3D-printed objects (Chapter 8).

SAFETY · PHOTOINITIATORS AND UV

Hexafluoroantimonate salts carry antimony and fluoride hazards; many onium salts are irritants and some are sensitizers. UV sources require eye and skin shielding. Residual photo-acid in cured parts can be corrosive to adjacent metals — relevant for electronics encapsulation.

CHAPTER SUMMARY

- Amine cure is autocatalytic and stoichiometric (Eq. 4.1) but slow and incomplete with internal oxiranes; blending, accelerators, post-cure, or a change of chemistry are needed.
- Anhydride cure, catalysed by tertiary amines or imidazoles, is the most reliable route for EVOs; formulate with Eq. 4.5 and an experimentally optimized A/E ratio.
- Rosin anhydrides, natural acids (citric, divanillic), lignin derivatives, maleinized oils and phenalkamines offer partly or fully bio-based hardeners with distinct property trade-offs.
- Onium-salt cationic photocure is well suited to EVOs; dual-cure combines rapid shaping with full bulk conversion. Cure is followed by DSC (Kamal–Sourour, Kissinger) and T_g –conversion relations (DiBenedetto).

CROSSLINK DENSITY AND THERMAL/MECHANICAL STRUCTURE-PROPERTY RELATIONSHIPS

A triglyceride network is a set of rigid junctions joined by soft springs, with loose ends hanging off. Every measurable property follows from how many junctions there are, how far apart, and how much is left dangling.

IN THIS CHAPTER

- Why fatty-acid chains plasticize the networks they build, and how composition predicts it.
- Molecular weight between crosslinks, gel fraction, and how to estimate them.
- Reading DMA and TGA data for bio-based epoxies.
- Strategies for balancing stiffness, glass transition and toughness.

5.1 NETWORK ARCHITECTURE

Internal plasticization by fatty-acid chains

In a DGEBA network, nearly every atom lies on a path between two crosslinks. In a triglyceride network, a large fraction does not. Consider where the crosslinks sit. The ester-linked glycerol is a junction; each oxirane, once reacted, is another. The chain segment between the carboxyl carbon and the first epoxide (C2–C8 in an 18-carbon chain epoxidized at C9–C10) is elastically active. The segment *beyond* the last epoxide is a dangling end attached at one point only: nine carbons for an oleate (C10–C18 lies past the C9–C10 epoxide), six for linoleate (past C12–C13), and only three for linolenate (past C15–C16). Saturated palmitate and stearate chains are entirely dangling.

Dangling ends carry no load in the rubbery state, but they occupy volume, separate the junctions, and lower the glass transition in the same way a plasticizer does. This simple geometric argument explains two well-known trends: networks from linseed oil are stiffer and have higher T_g than those from soybean oil cured the same way, and oils rich in saturated acids give softer, weaker networks. It also explains why simply adding more hardener cannot make an EVO behave like DGEBA — the dangling mass is built into the monomer.

The elastically inactive fraction

A triglyceride that carries fewer than two epoxides cannot form two connections and cannot become an elastically effective part of the network. Its share can be estimated from the fatty-acid profile.

WORKED EXAMPLE · HOW MUCH OF AN OIL CANNOT CROSSLINK?

Assume (i) complete epoxidation, (ii) acyl chains distributed randomly over glycerol positions, and (iii) epoxides per chain equal to double bonds per chain. For soybean oil, take mid-range Codex values [10] rounded to sum to 1: saturated 0.155, oleic 0.235, linoleic 0.535, linolenic 0.075. A triglyceride has ≤ 1 epoxide only if all three chains are saturated ($0.155^3 = 0.0037$) or one is oleic and two saturated ($3 \times 0.235 \times 0.155^2 = 0.0169$). Total ≈ 2.1 % of molecules.

For hemp-seed oil, using mid-range values [12] rounded to saturated 0.10, oleic 0.12, linoleic 0.585, linolenic 0.195, the same calculation gives $0.001 + 0.0036 \approx 0.5$ %. Real oils are not randomly distributed — unsaturated acids are enriched at the glycerol 2-position — and real epoxidations are incomplete, so these are illustrative calculated values. They show that, at full conversion, the inactive fraction is small; in practice, sol fractions are dominated by incomplete reaction and ring-opening, not by intrinsically monofunctional molecules.

Molecular weight between crosslinks

The molecular weight between crosslinks, M_c , and its counterpart, the crosslink density $\nu_e = \rho/M_c$ (mol m^{-3}), are the central parameters of network structure. From the theory of rubber elasticity, the storage modulus in the rubbery plateau above T_g is approximately

$$E'_{\text{rubbery}} \approx 3 \nu_e R T = \frac{3 \rho R T}{M_c} \quad (5.1)$$

where ρ is the density, R the gas constant and T the absolute temperature at which E' is read (commonly $T_g + 30$ – 50 K).

Eq. 5.1 is exact only for ideal networks of long, flexible chains. For the short-chain, highly crosslinked networks typical of thermosets, Hill has examined the corrections and the conditions under which the simple relation remains useful [54]; Nielsen's classic review collects empirical relations between crosslinking, modulus, and glass transition [55]. For comparisons among EVO formulations, Eq. 5.1 is best used as a *relative* measure: the ranking it gives is usually reliable even when absolute values are not.

WORKED EXAMPLE · CROSSLINK DENSITY FROM DMA

A cured EVO network of density 1100 kg m^{-3} shows $E' = 12 \text{ MPa}$ at 373 K in the rubbery plateau. Then $\nu_e = E'/(3RT) = 12 \times 10^6 / (3 \times 8.314 \times 373) = 1290 \text{ mol m}^{-3}$, and $M_c = \rho/\nu_e = 1100/1290 = 0.85 \text{ kg mol}^{-1}$ (850 g mol^{-1}). The input values are illustrative. Doubling the plateau modulus would halve M_c .

Gel fraction

Gel fraction measures the insoluble, network-bound portion of a cured sample. A weighed specimen (m_0) is extracted in a good solvent for the monomers — often by Soxhlet extraction — then dried to constant mass (m_d):

$$\text{Gel fraction (\%)} = \frac{m_d}{m_0} \times 100 \quad (5.2)$$

For EVO thermosets, gel fraction is a sensitive indicator of cure completeness and of the elastically inactive fraction discussed above. The extract can be analysed (by NMR or chromatography) to identify what failed to react — unreacted oil, free hardener, or low-functionality species. Equilibrium swelling of the gel in the same solvent provides a second, independent estimate of crosslink density via the Flory–Rehner treatment, provided the polymer–solvent interaction parameter is known.

5.2 THERMOMECHANICAL PERFORMANCE

Dynamic mechanical analysis

DMA applies a small oscillating strain over a temperature ramp and records the storage modulus E' (elastic response), the loss modulus E'' (dissipation), and their ratio $\tan \delta = E''/E'$. Figure 5.1 shows the typical shape for a thermoset.

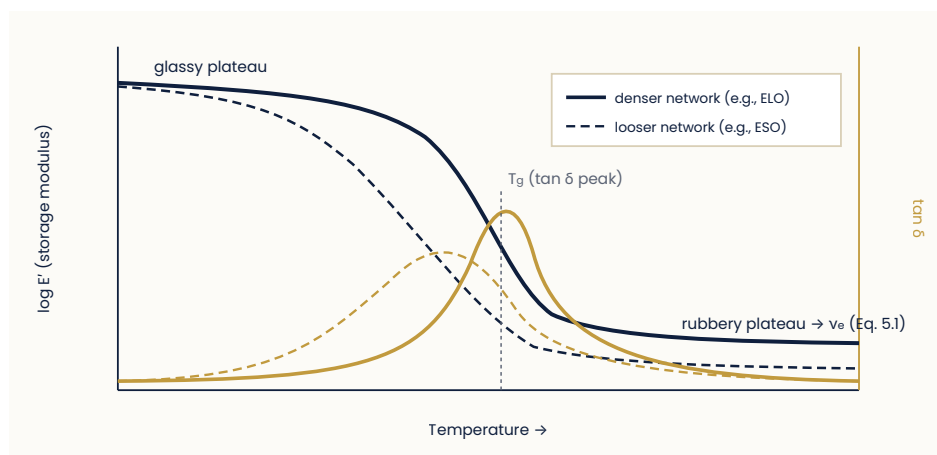


Figure 5.1 Schematic DMA response of two EVO thermosets (illustrative, not measured data). The denser network shows a higher rubbery plateau, a higher $\tan \delta$ peak temperature, and a narrower, lower $\tan \delta$ peak. Broad $\tan \delta$ peaks are characteristic of the heterogeneous networks formed from statistically mixed oil molecules.

Three features of a DMA trace are worth reading deliberately:

- **Which T_g ?** The onset of the drop in E' , the peak of E'' and the peak of $\tan \delta$ give successively higher values. Reports must state which is used; the $\tan \delta$ peak is most common in the bio-epoxy literature.
- **Peak breadth.** A broad $\tan \delta$ peak signals a wide distribution of local environments — expected for EVO networks, where each molecule carries a different number of epoxides. Very broad or double peaks can indicate phase separation in blends.
- **Rubbery plateau.** Its height gives crosslink density (Eq. 5.1); a plateau that continues to fall with temperature suggests incomplete cure or, in dynamic networks, bond exchange (Chapter 7).

Published data illustrate the ranges involved. Gerbase and co-workers characterized the dynamic mechanical and thermal behaviour of soybean-oil-based epoxies cured with anhydrides [47]; Boquillon and Fringant reported how catalyst and anhydride choice change linseed-oil networks [46]. For ESO crosslinked with lignin-derived divanillic

acids, $\tan \delta$ peak temperatures ranged from 20 to 62 °C, Young's moduli from about 3 to 286 MPa depending on formulation, and the 5 % mass-loss temperature exceeded 300 °C for all films [50]. Those numbers capture the central challenge: EVO networks readily reach useful thermal stability, but their glass transitions and moduli sit far below those of aromatic structural epoxies unless rigid co-monomers or hardeners are added.

Thermogravimetric analysis

TGA records mass loss as a function of temperature under inert gas or air. For EVO thermosets, degradation typically proceeds in overlapping stages: loss of volatiles and unreacted species at lower temperature; scission of the ester and β -hydroxy-ester linkages, which are the weakest links in anhydride- and acid-cured networks; and decomposition of the aliphatic fatty chains at higher temperature. Char yield in nitrogen is generally low for purely aliphatic networks and rises with aromatic content (lignin, rosin, furan, cardanol), which is one reason these co-monomers also improve fire performance.

Degradation kinetics are extracted from runs at several heating rates. The Kissinger method (Eq. 4.3, applied to the peak of the derivative mass-loss curve) gives a single apparent activation energy [44]; isoconversional methods give its variation with extent of degradation, which is more informative for multi-step processes. Thermal stability indices such as $T_{5\%}$ and $T_{\max}$ should always be reported with heating rate and atmosphere.

Balancing flexibility and rigidity

The structure–property picture suggests a toolkit, summarized in Table 5.1. The overarching rule is that each lever that raises stiffness and T_g also tends to lower toughness and elongation; the formulator chooses the balance for the application.

Table 5.1 Formulation levers for EVO thermosets and their typical directional effects (qualitative).

Lever	Stiffness / T_g	Toughness / elongation	Notes
Higher-IV oil (linseed, hemp vs soybean)	↑	↓	More epoxides, shorter dangling ends
Rigid hardener (cycloaliphatic or rosin anhydride)	↑	↓	Hardener often dominates network rigidity
Flexible hardener (maleinized oil, long-chain acid)	↓	↑	Cf. EHO/MHO results [35]
Rigid bio-epoxy co-monomer	↑	↓ (moderate)	Estimate with Fox equation (Eq. 3.1)
Stoichiometry near optimum; full post-cure	↑	→	Minimizes sol fraction and dangling hardener
Rigid fibres or nanofillers	↑ (modulus)	↑ or ↓	Depends on interface (Chapter 6)
EVO as minor phase in a rigid epoxy	↓ (slight)	↑	Phase-separated soft domains act as tougheners [21]

The last row reverses the usual perspective. Instead of reinforcing a soft oil network, a small fraction of epoxidized oil can be added to a rigid epoxy, where it may phase-separate during cure into soft domains that blunt cracks — the same principle used with reactive liquid rubbers. Reviews of EVO blends with conventional epoxies discuss this toughening route and its limits [21]. For fully bio-based structural materials, the more promising path is the reverse: an EVO-rich matrix stiffened by rigid bio-based hardeners and fibres.

CHAPTER SUMMARY

- Dangling fatty-chain ends act as built-in plasticizers; their length falls from oleate to linolenate, which is why higher-IV oils give stiffer networks.
- At full conversion, the intrinsically non-crosslinkable fraction is small (calculated $\approx 2\%$ for soybean, $\approx 0.5\%$ for hemp); sol fractions in practice reflect incomplete cure and side reactions.
- Rubbery-plateau modulus gives crosslink density (Eq. 5.1); report which DMA T_g definition is used; broad $\tan \delta$ peaks reflect network heterogeneity.
- EVO networks reach good thermal stability but low T_g and modulus unless rigid hardeners, co-monomers, or reinforcements are used.



ADVANCED FORMULATIONS, COMPOSITES, AND FUNCTIONAL MATERIALS

Reinforcement at every scale, and networks designed to be reprocessed, healed, and recovered.

CH. 6 · NANOCOMPOSITES AND HYBRID MATERIALS
CH. 7 · RECYCLABILITY, DEGRADABILITY, AND VITRIMERS

NANOCOMPOSITES AND HYBRID MATERIALS

Reinforcement is where a soft bio-based matrix earns its structural credentials. The difficulty is never the filler's intrinsic strength — it is getting load across the interface.

IN THIS CHAPTER

- Graphene, graphene oxide, carbon nanotubes and carbon nanosheets in EVO matrices — and how to disperse them.
- Natural and mineral fibre composites: hemp, flax, jute and basalt.
- Nanocellulose and nanoclays for stiffness and barrier properties.
- Micromechanical models (Halpin–Tsai, Kelly–Tyson, tortuosity) for first-pass design.

6.1 CARBON-BASED NANOMATERIALS IN BIO-EPOXIES

Carbon nanomaterials offer three things a vegetable-oil epoxy lacks: very high stiffness per unit mass, electrical and thermal conductivity, and — for platelets — barrier properties. They are effective at low loadings, often well below 5 wt %, provided they are individually dispersed and well bonded to the matrix.

The family

- **Graphene and few-layer graphene:** highest intrinsic stiffness and conductivity; chemically inert surfaces that bond poorly to polymers unless functionalized.
- **Graphene oxide (GO):** graphene sheets decorated with epoxide, hydroxyl and carboxyl groups. Easily exfoliated and chemically reactive, but electrically insulating until reduced (rGO). Its acidic surface groups are catalytically active: GO and a GO/ZnO composite have been shown to catalyse the ring opening of epoxidized soybean fatty-acid methyl esters [56] — a reminder that a “filler” may also change cure chemistry and pot life.
- **Carbon nanotubes (CNTs):** one-dimensional, high aspect ratio, conductive; prone to bundling and entanglement that raise viscosity sharply.
- **Carbon nanosheets from biomass:** two-dimensional carbons produced by carbonizing and activating plant material. A notable example is the interconnected carbon nanosheets derived from hemp bast fibre and reported for high-rate supercapacitor electrodes [57]. Their use as reinforcements in epoxy matrices is far less studied than graphene's; for a hemp-based resin, a hemp-derived carbon filler is an intriguing route to a single-crop composite, but its mechanical benefit in EVO matrices remains a research question rather than an established result.

The dispersion problem in triglyceride networks

Epoxidized oils are viscous and of low polarity. Pristine graphene and CNTs re-aggregate in them through van der Waals forces; GO, being polar, is incompatible with the hydrophobic chains. Poor dispersion produces agglomerates that act as defects, so properties can *fall* with loading. Strategies fall into four groups (Table 6.1).

Table 6.1 Strategies for dispersing carbon nanomaterials in EVO matrices (qualitative).

Strategy	Examples	Advantage	Risk
Covalent grafting of matrix-compatible groups	Amine- or silane-functionalized GO; grafting fatty chains via oxirane ring opening	Strong interface; filler co-cures with matrix	Damages sp ² network; lowers conductivity
Non-covalent adsorption	π -stacking aromatics (pyrene derivatives), surfactants, cardanol derivatives	Preserves filler properties	Weaker interface; free surfactant plasticizes
Solvent-assisted mixing	Disperse in a solvent, mix with resin, strip solvent	Good exfoliation	Residual solvent; re-aggregation during stripping
High-shear processing	Three-roll milling, ultrasonication, high-speed mixing	Solvent-free; scalable (milling)	Heat build-up; CNT shortening; incomplete exfoliation

Because GO's oxygen groups react with epoxides and anhydrides, GO can become covalently bound during cure — beneficial for load transfer, but it shifts stoichiometry and, as noted above, may accelerate ring opening. Formulations should be re-optimized after adding reactive fillers, and DSC should be repeated rather than assumed unchanged.

Estimating reinforcement: the Halpin–Tsai equations

For discontinuous fibres and platelets, the Halpin–Tsai equations give a convenient first estimate of composite modulus [58]:

$$\frac{E_c}{E_m} = \frac{1 + \zeta \eta \phi}{1 - \eta \phi}, \quad \eta = \frac{E_f/E_m - 1}{E_f/E_m + \zeta} \quad (6.1)$$

where E_c , E_m , E_f are the composite, matrix and filler moduli, ϕ the filler volume fraction, and ζ a shape factor (for aligned fibres or platelets loaded along their length, $\zeta \approx 2 \times$ aspect ratio).

WORKED EXAMPLE · WHAT CAN 1 VOL % OF PLATELETS DO?

Take an EVO matrix with $E_m = 1$ GPa, a platelet filler with an effective in-matrix modulus $E_f = 100$ GPa (well below graphene's intrinsic value, to reflect imperfect transfer), aspect ratio 100 ($\zeta = 200$), and $\phi = 0.01$. Then $\eta = (100 - 1)/(100 + 200) = 0.33$ and $E_c/E_m = (1 + 200 \times 0.33 \times 0.01)/(1 - 0.0033) \approx 1.67$. The model predicts a two-thirds increase in modulus from one volume per cent — if the platelets are aligned and individually dispersed. Random orientation, agglomeration and a weak interface each erode this sharply; inputs are illustrative.

Functional properties

Electrical conductivity in carbon-filled composites rises abruptly once filler particles form a connected network at the percolation threshold, which is lower for high-aspect-ratio fillers. Conductive EVO composites are of interest for antistatic coatings, electromagnetic shielding and sensors. Thermal conductivity gains are typically more modest, because heat transport is limited by phonon scattering at filler–matrix interfaces.

6.2 BIO-MINERAL AND CELLULOSIC REINFORCEMENTS

Natural-fibre composites: hemp, flax and jute

Bast fibres — hemp, flax, jute — are bundles of cellulose-rich cells with good specific stiffness, low density, and low embodied energy compared with glass. Combined with an EVO matrix, they produce composites with high overall bio-based content. AESO-based resins were developed as matrices for natural-fibre composites in early systematic work [32], and hemp-fibre composites with epoxidized soybean oil matrices continue to be reported [59].

The recurring engineering issues are:

- **Interface.** Fibres are hydrophilic; oil matrices are not. Alkali treatment (mercerization) removes surface waxes, hemicellulose and pectin and roughens the surface; silanes and acetylation lower polarity. Hydroxyl-bearing species formed by partial ring opening of the EVO can also improve wetting by hydrogen bonding.
- **Moisture.** Absorbed water plasticizes fibres, swells them and can react with anhydride hardeners. Fibres must be dried immediately before impregnation, and moisture uptake in service must be designed for.
- **Variability.** Fibre properties vary with variety, retting and processing; statistical design allowables are needed.
- **Thermal limit.** Natural fibres degrade at elevated temperatures, which constrains cure and post-cure schedules.

Load transfer in short fibres: the critical length

A discontinuous fibre carries its full strength only if it is long enough for shear stress at the interface to build tension to the fibre's breaking stress. The critical fibre length follows from the Kelly–Tyson analysis [60]:

$$l_c = \frac{\sigma_f d}{2 \tau} \quad (6.2)$$

where σ_f is the fibre tensile strength, d its diameter, and τ the interfacial shear strength.

WORKED EXAMPLE · WHY THE INTERFACE MATTERS

For an elementary fibre with $\sigma_f = 600$ MPa and $d = 20$ μm , an interfacial shear strength $\tau = 5$ MPa gives $l_c = (600 \times 20)/(2 \times 5) = 1200$ $\mu\text{m} = 1.2$ mm. Doubling τ to 10 MPa through surface treatment halves l_c to 0.6 mm, so a larger fraction of each chopped fibre carries full load. Inputs are illustrative.

Basalt fibres

Basalt fibres are drawn from melted volcanic rock, with no need for the boron and fluorine additives of some glass formulations. They are inorganic rather than bio-based, but they pair with EVO matrices to make composites with natural, low-processing raw materials on both sides of the interface. Basalt offers good stiffness, chemical resistance and temperature tolerance, and it can be hybridized with natural fibres — for example basalt skins over a hemp or flax core — to combine durability with low density. Sizing chemistry compatible with epoxidized oils is the key development need.

Nanocellulose

Cellulose nanocrystals (CNC, rod-like, highly crystalline) and cellulose nanofibrils (CNF, long, flexible, entangled) are the nanoscale building blocks of plant fibres. They offer high stiffness, low density and a fully bio-based origin. Their surfaces are densely hydroxylated, which helps them network strongly through hydrogen bonds (useful for stiffness and barrier) but makes them incompatible with hydrophobic EVO matrices. Effective incorporation therefore usually involves surface modification (acetylation, silylation, esterification with fatty acids, or grafting of epoxy-reactive groups) or solvent exchange from water into a carrier compatible with the resin. As with GO, surface hydroxyls react with anhydrides and epoxides, so nanocellulose participates in the cure.

Nanoclays and barrier performance

Layered silicates such as montmorillonite, once organically modified and exfoliated, act as impermeable platelets that force diffusing molecules along a tortuous path. The classic Nielsen tortuosity model gives the relative permeability of a composite with aligned platelets of aspect ratio α at volume fraction ϕ :

$$\frac{P_c}{P_m} = \frac{1 - \phi}{1 + (\alpha/2) \phi} \quad (6.3)$$

With $\alpha = 200$ and $\phi = 0.03$ (calculated), $P_c/P_m = 0.97/4 \approx 0.24$ — a four-fold reduction in permeability from three volume per cent of perfectly aligned, exfoliated platelets. Real values are smaller because of imperfect alignment and exfoliation, but the model explains why platelet fillers are the tool of choice for barrier coatings.

Table 6.2 Reinforcements for EVO matrices compared (qualitative).

Reinforcement	Scale	Primary benefit	Main challenge	Bio-based?
Graphene / rGO	Nano, 2D	Stiffness, conductivity, barrier	Dispersion; interface	No (unless biomass-derived)
Graphene oxide	Nano, 2D	Reactive interface; barrier	Polarity mismatch; alters cure	No
Carbon nanotubes	Nano, 1D	Conductivity at low loading	Viscosity; bundling	No
Biomass carbon nanosheets	Nano, 2D	Conductive, renewable carbon	Little composite data in EVOs	Yes (carbonized)
Hemp, flax, jute fibres	Micro / macro	Specific stiffness; bio-content	Moisture; variability; interface	Yes
Basalt fibres	Micro / macro	Durability; temperature tolerance	Sizing compatibility	Natural mineral
Nanocellulose (CNC/ CNF)	Nano	Stiffness; barrier; bio-content	Hydrophilicity; drying	Yes
Organoclays	Nano, 2D	Gas and moisture barrier	Exfoliation; modifier stability	Natural mineral

CHAPTER SUMMARY

- Carbon nanomaterials can stiffen and functionalize EVO matrices at low loadings, but only with deliberate dispersion and interface engineering; reactive fillers such as GO can alter cure chemistry.
- Hemp-derived carbon nanosheets are an attractive but largely unexplored filler for hemp-oil-based resins.
- Natural-fibre composites require dried, surface-treated fibres; the Kelly–Tyson critical length (Eq. 6.2) shows why interfacial strength governs short-fibre performance.
- Nanocellulose and organoclays add stiffness and barrier; Halpin–Tsai (Eq. 6.1) and tortuosity (Eq. 6.3) models provide first-pass estimates.

RECYCLABILITY, DEGRADABILITY, AND VITRIMERS

Thermosets were defined by the fact that they could not be melted. Bio-based epoxies built on ester bonds give us a chance to keep their strength and lose that defining flaw.

IN THIS CHAPTER

- Vitrimers: permanent networks that flow by associative bond exchange, and why acid- and anhydride-cured EVOs are natural candidates.
- Measuring and interpreting stress relaxation; the topology-freezing temperature.
- Reprocessing, welding and self-healing — and their practical limits.
- Hydrolytic and enzymatic degradation of ester networks, and solvolysis for composite recycling.

7.1 DYNAMIC COVALENT NETWORKS (VITRIMERS)

The vitrimer concept

In 2011 Montarnal, Capelot, Tournilhac and Leibler described epoxy networks that remained insoluble and permanently crosslinked at all temperatures, yet could be reshaped and repaired when hot — behaviour they likened to silica glass [61]. The networks were made from epoxides and carboxylic acids or anhydrides, which produce β -hydroxy esters, together with a transesterification catalyst (zinc salts were prominent). At elevated temperature, hydroxyl groups exchange with ester groups: one ester bond breaks only as another forms. The number of crosslinks — and so the network's integrity — is conserved, but the topology can rearrange, and the material flows.

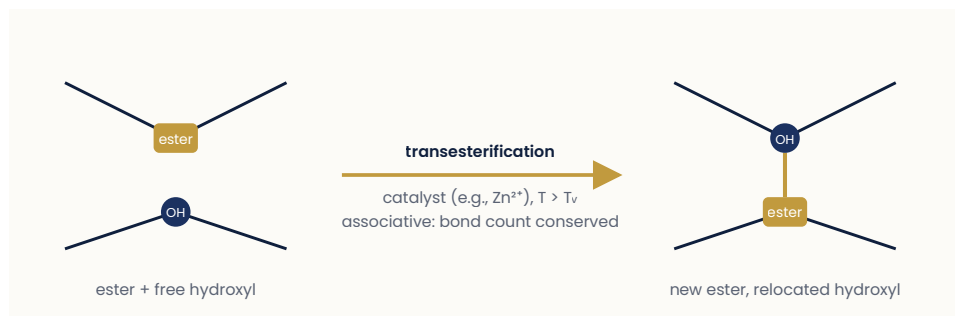


Figure 7.1 Associative exchange in an ester vitrimer. A hydroxyl attacks an ester, and a new ester forms as the old one is released. The total number of crosslinks is unchanged, so the network never dissolves, but its topology can rearrange — allowing stress relaxation, reshaping and healing.

This associative mechanism distinguishes vitrimers from *dissociative* dynamic networks (such as furan–maleimide Diels–Alder adducts), in which bonds break first and re-form later, so crosslink density drops on heating and the material can depolymerize to a liquid. Reviews have since mapped the many exchange chemistries that give vitrimer behaviour — transesterification, transamination of vinylogous urethanes, imine metathesis, disulfide and boronic-ester exchange among them [62].

Why epoxidized oils are natural vitrimer precursors

Chapter 4 showed that acids and anhydrides are the preferred hardeners for EVOs. Both create exactly the β -hydroxy ester motif that transesterification vitrimers require, and the triglyceride itself contributes three more ester groups per molecule. Two published systems illustrate the range:

- **Catalyst-free citric acid networks.** Epoxidized soybean oil crosslinked with aqueous citric acid, with no added catalyst or solvent, gave networks whose thermally activated self-healing — assessed by stress relaxation and lap-shear testing — was attributed to transesterification of the β -hydroxy esters formed during polymerization [49].
- **Lignin-derived diacids with zinc catalysis.** ESO cured at 180 °C with divanillic acid or a butoxylated derivative, using zinc acetylacetonate hydrate (5 mol % relative to COOH), relaxed stress at 170–200 °C with activation energies of 111.8 ± 18.7 and 118.6 ± 22.7 kJ mol⁻¹ for the two stoichiometric formulations. Films were reprocessed by hot pressing at 230 °C and 5 MPa for 1 h through five cycles, retaining roughly 40–50 % of their original tensile strength and modulus; at 100 °C, a scratch in one formulation narrowed from about 53 μ m to about 7 μ m within an hour [50].

The second example also shows the limits honestly: repeated reprocessing at high temperature degraded the network, and properties fell with each cycle. Reprocessability is real, but it is not the same as indefinite recyclability.

Stress relaxation and the topology-freezing temperature

The signature measurement for a vitrimer is stress relaxation: a constant strain is applied above T_g and the decay of stress is recorded. For a single exchange process, relaxation is often approximated by a Maxwell model,

$$\frac{G(t)}{G_0} = \exp(-t / \tau^*) \quad (7.1)$$

and the characteristic relaxation time τ^* (commonly taken where $G/G_0 = 1/e$) follows Arrhenius behaviour because the rate-limiting step is a chemical exchange reaction:

$$\tau^*(T) = \tau_0 \exp(E_a / R T) \quad (7.2)$$

The viscosity of a vitrimer therefore falls gradually and predictably with temperature, like that of silica, rather than abruptly as in thermoplastics. By convention, the topology-freezing temperature T_v is the temperature at which the viscosity reaches 10^{12} Pa s — the conventional liquid–solid transition. With the Maxwell relation $\eta = G \tau^*$, it can be estimated from relaxation data. Catalyst type and loading shift T_v , as Capelot and co-workers demonstrated [63].

WORKED EXAMPLE · ESTIMATING T_v

A vitrimer has a rubbery shear modulus $G = 4$ MPa ($\approx E'/3$ for $E' = 12$ MPa). At T_v , $\eta = 10^{12}$ Pa s, so $\tau^*(T_v) = 10^{12}/(4 \times 10^6) = 2.5 \times 10^5$ s. Suppose relaxation measurements give $\tau^* = 1000$ s at 473 K and $E_a = 112$ kJ mol⁻¹ (similar in magnitude to the activation energies above). From Eq. 7.2, $\ln(2.5 \times 10^5/1000) = (E_a/R)(1/T_v - 1/473)$, so $1/T_v = 1/473 + 5.52 \times 8.314/112\,000 = 2.524 \times 10^{-3}$ K⁻¹, giving $T_v \approx 396$ K (123 °C). Inputs are illustrative; the calculation shows how a modest activation energy places T_v uncomfortably close to service temperatures.

Reprocessing, healing and their trade-offs

Above T_v , vitrimers can be compression-moulded from ground scrap, thermoformed, welded to themselves or to other parts, and healed by heat and pressure. For bio-based epoxies, three trade-offs dominate:

- **Creep versus processability.** Fast exchange (low E_a , active catalyst) eases reprocessing but allows creep under sustained load. EVO networks, whose T_g is often modest, are especially exposed: if T_g and T_v both sit near service temperature, dimensional stability suffers.
- **Catalyst choice.** Zinc salts are preferred to organotin compounds on toxicity grounds; catalyst-free systems rely on internal catalysis by hydroxyls or tertiary amines, typically with slower exchange.
- **Thermal budget.** Reprocessing temperatures overlap with the onset of ester pyrolysis and oxidation of residual unsaturation; each cycle can cost properties, as the five-cycle study above illustrates [50].

7.2 CHEMICAL DEGRADABILITY AND CIRCULAR END-OF-LIFE**Hydrolysis of ester backbones**

Anhydride- and acid-cured EVO networks are polyesters, and every ester is, in principle, a cleavable link. Hydrolysis is slow under neutral conditions and accelerated by acid or, especially, base. How fast a crosslinked network degrades depends less on the ester itself than on access to it:

- **Water uptake.** Hydrophobic fatty chains limit swelling and slow hydrolysis; hydroxyl-rich formulations absorb more water.
- **Mobility.** Degradation is faster above T_g , where water and catalyst diffuse more readily.
- **Crosslink density.** Tighter networks resist penetration and require more bonds to be cut before fragments become soluble.

Enzymatic degradation

Lipases, esterases and cutinases hydrolyse ester bonds, and triglyceride-derived esters are their natural substrates. In bulk crosslinked networks, however, enzymes act only at the surface, so degradation is surface-erosive and slow. Claims of “biodegradability” for EVO thermosets must therefore be supported by standardized testing under defined conditions; bio-based origin alone does not establish biodegradation, and many bio-based thermosets are not biodegradable on any practical timescale.

Solvolysis for matrix–fibre separation

For composites, the most valuable end-of-life outcome is often recovering the fibres intact. Solvolysis — dissolving the matrix by chemical cleavage in a hot solvent — is particularly well suited to ester-rich networks:

Table 7.1 Solvolysis routes for ester-based EVO thermosets and composites (qualitative).

Route	Typical medium	Bonds cleaved	Recovered products	Considerations
Alkaline hydrolysis	Aqueous or alcoholic NaOH/KOH	Esters (saponification)	Fibres; carboxylate salts and polyols	Can damage natural fibres; neutralization waste
Acid hydrolysis	Aqueous mineral or organic acids	Esters; some ethers	Fibres; acids and polyols	Corrosion; slower for hydrophobic networks
Alcoholysis / glycolysis	Ethylene glycol, alcohols + transesterification catalyst	Esters (exchange with solvent)	Fibres; hydroxy-terminated oligomers	Recovered polyols can be re-used in new resins; same chemistry as vitrimer exchange
Aminolysis	Amines, amino-alcohols	Esters → amides	Fibres; amide-functional oligomers	Products can act as hardeners

Because vitrimer exchange and alcoholysis are the same reaction, an ester vitrimer can be dissolved by flooding it with a small-molecule alcohol in the presence of its own catalyst: the network is cut into soluble fragments without harsh reagents. This is perhaps the most practical circular route for fibre-reinforced EVO composites — recover the fibres, and recover the matrix as a polyol for the next generation of resin.

AN END-OF-LIFE HIERARCHY FOR BIO-EPOXIES

- **Repair** — heal damage in place (vitrimer or self-healing networks).
- **Reshape and reprocess** — remould scrap or end-of-life parts above T_v .
- **Recover** — solvolyse the matrix; reclaim fibres and polyol fragments.
- **Return** — biodegradation or composting, only where demonstrated by standard tests.
- **Recover energy** — incineration with energy recovery as the last resort.

CHAPTER SUMMARY

- Vitrimer networks are permanently crosslinked networks that flow through associative exchange; acid- and anhydride-cured EVOs, rich in β -hydroxy esters, are natural candidates.
- Published ESO vitrimers show transesterification activation energies around 110–120 kJ mol⁻¹ and multi-cycle reprocessability with property losses.
- Stress relaxation (Eqs. 7.1–7.2) gives τ^* , E_a and an estimate of T_v ; creep resistance and thermal budget are the main design constraints.
- Ester networks are chemically recyclable: alcoholysis and hydrolysis recover fibres and oligomeric polyols; biodegradability must be demonstrated, not assumed.



INDUSTRIAL PROCESSING, APPLICATIONS, AND TECHNO- ECONOMICS

From the reactor to the market: processing windows, end uses, plant economics, life-cycle impact, and regulation.

CH. 8 · COMMERCIAL PROCESSING AND END-USE APPLICATIONS
CH. 9 · TECHNO-ECONOMIC ANALYSIS AND LIFE CYCLE ASSESSMENT

COMMERCIAL PROCESSING AND END-USE APPLICATIONS

A resin becomes a product only when it can be mixed, poured, infused, sprayed or printed within the time and temperature a factory allows – and still meet the specification at the end.

IN THIS CHAPTER

- Coatings, adhesives and sealants: where EVOs fit today and where they need help.
- Liquid composite moulding (RTM, VARTM): viscosity, permeability and fill time.
- Reactive diluents from cardanol and terpenes.
- Electronics encapsulation and vat-photopolymerization 3D printing.

8.1 COATINGS, ADHESIVES, AND SEALANTS

Where EVOs are used today

The best-established use of epoxidized oils is not as a thermoset at all. Commercial ESO and ELO data sheets list their primary uses as plasticizing and heat/light-stabilizing PVC compounds and emulsions, acid scavenging in chlorinated materials and lubricants, and serving as a chemical intermediate for polyols and polyesters [3, 4]. In this role the oxirane rings act as acid scavengers that trap hydrogen chloride released as PVC ages. This existing supply chain matters for thermoset developers: ESO is available at scale, with established specifications and quality control.

Solvent-free and high-solids coatings

Coatings are the most natural thermoset outlet for EVOs. Their flexibility, adhesion to metal, low viscosity and low volatility suit solvent-free formulations, and their slow amine cure is less of a handicap in baked or UV-cured systems:

- **Anhydride-cured baking enamels** exploit the reliable anhydride chemistry of Chapter 4; EVO can be the sole epoxy or a flexibilizing co-resin.
- **UV-cationic coatings** use the onium-salt chemistry demonstrated for epoxidized triglycerides [53]: fast, oxygen-insensitive cure of thin films on metal, wood or paper.
- **Hybrid coatings** add rigid bio-epoxies (Chapter 3) to raise hardness and solvent resistance.

Waterborne bio-epoxy dispersions

Waterborne epoxies replace solvents with water by dispersing the resin as fine droplets, either with added non-ionic surfactants or by building emulsifying segments (such as polyether chains) into the resin, often via phase-inversion emulsification. The hardener — typically a water-compatible amine adduct — resides largely in the aqueous phase, and film formation requires coalescence of the droplets before cure locks them in place. For EVOs, the challenges are the slow amine reactivity of internal oxiranes, which slows film development at ambient temperature, and the need to protect the oxiranes from hydrolysis during storage, which requires near-neutral pH and controlled temperature. Glycidyl-functional oil derivatives (Chapter 3) are more practical than plain EVOs in two-component waterborne systems.

Adhesives

Two adhesive classes are of interest:

- **Structural adhesives**, which need high modulus, high T_g and toughness. Here EVO serves mostly as a toughening co-resin or as a partner to rigid bio-based epoxies, cured with phenalkamines or cycloaliphatic amines for room-temperature systems, or anhydrides for heat-cured ones. Phenalkamine structure is known to influence adhesive and viscoelastic properties [51].
- **Pressure-sensitive adhesives (PSAs)**, which need the opposite: a T_g well below use temperature and only light crosslinking, so that the material flows into surface roughness under light pressure yet resists shear. The low crosslink density and flexible chains that limit EVOs as structural resins are advantages here, making lightly crosslinked EVO networks a logical route to bio-based PSAs.

Sealants

Sealants combine flexibility, adhesion and durability rather than stiffness. EVO plasticizers are already used in PVC-based sealants and plastisols; as reactive components, they can reduce migration and exudation compared with non-reactive plasticizers because the oil becomes bound into the network.

8.2 COMPOSITE MANUFACTURING TECHNIQUES

Liquid composite moulding

Resin transfer moulding (RTM) injects resin under pressure into a closed mould containing a dry fibre preform; vacuum-assisted resin transfer moulding (VARTM, also called vacuum infusion) draws resin through a preform under a flexible bag using atmospheric pressure alone. Both require low resin viscosity throughout filling, a pot life longer than the fill time, and a cure that can be completed in the tool or in a subsequent post-cure.

Here epoxidized oils have an under-appreciated advantage. The viscosity of commercial ESO at 25 °C is 320–500 cP and that of ELO about 800 cP [3, 4], whereas a standard liquid DGEBA resin is 110–150 P (11–15 Pa s) [20] — roughly twenty to forty-five times more viscous. Anhydride hardeners are themselves low in viscosity, and anhydride–EVO mixtures with latent catalysts combine low viscosity with long pot life, which suits infusion well. The penalty comes later, in cure temperature and final properties, which is why EVO-rich infusion resins usually include a rigid bio-epoxy or rigid anhydride.

Fill time and permeability

Flow through a fibre preform follows Darcy's law. For one-dimensional infusion at constant pressure difference ΔP , the time to fill a length L is

$$t_{\text{fill}} = \frac{\phi \mu L^2}{2 K \Delta P} \quad (8.1)$$

where ϕ is the preform porosity, μ the resin viscosity, and K the preform permeability.

WORKED EXAMPLE · INFUSING A 1 M PANEL

With $\phi = 0.5$, $\mu = 0.4 \text{ Pa s}$, $L = 1 \text{ m}$, $K = 1 \times 10^{-10} \text{ m}^2$ and $\Delta P = 0.1 \text{ MPa}$ (vacuum infusion): $t_{\text{fill}} = (0.5 \times 0.4 \times 1)/(2 \times 10^{-10} \times 10^5) = 10\,000 \text{ s} \approx 2.8 \text{ h}$. Because t_{fill} scales with μ , a resin ten times more viscous would need over a day – or a warmer resin, a more permeable preform, or shorter flow paths. Inputs are illustrative.

Natural-fibre preforms bring additional constraints: they compact differently from glass, often have lower permeability, absorb resin into the fibre lumen, and must be dried immediately before infusion to prevent moisture from reacting with anhydride hardeners (Chapter 6).

Viscosity management with bio-based reactive diluents

When rigid co-resins or fillers raise viscosity, reactive diluents restore processability. Unlike solvents, they react into the network:

- **Cardanol glycidyl ethers.** Commercial cardanol-based monofunctional epoxy diluents are recommended at about 2–20 % of total resin weight to lower viscosity, enable solvent-free formulations, and add water resistance, flexibility and thermal-shock resistance [64]. Being monofunctional, they reduce crosslink density, so loading must be balanced against T_g .
- **Terpene oxides.** Limonene, from citrus peel, can be epoxidized to limonene oxide (one epoxide) or limonene dioxide (two: a trisubstituted ring epoxide and a 1,1-disubstituted exocyclic one). Both are low-viscosity, and the difunctional dioxide can act as a crosslinking diluent; the two epoxides differ in reactivity, which complicates cure design.
- **Glycidyl esters of short fatty acids** and other oil-derived glycidyl compounds (Chapter 3) offer terminal epoxides with low viscosity and good amine reactivity.

8.3 ELECTRICAL ENCAPSULATION AND 3D PRINTING

Electronics packaging

Encapsulants and potting compounds protect circuits from moisture, contamination, vibration and heat. Their requirements are demanding and specific:

Table 8.1 Encapsulant requirements and how EVO chemistry bears on them (design considerations; qualitative).

Requirement	Why it matters	EVO-specific considerations
Low dielectric constant and loss	Signal integrity; heat from dielectric loss	Long aliphatic chains are low-polarity; ester and hydroxyl groups add polarity; residual moisture raises loss
Low ionic contamination	Corrosion and leakage currents	Glycidylated derivatives carry hydrolysable chlorine; photo-acid residues are corrosive; acid catalysts must be removed
Low moisture uptake	Delamination, “popcorning”, dielectric drift	Hydrophobic chains help; ring-opened hydroxyls hurt
Matched thermal expansion	Stress on die and solder joints	Low- T_g networks expand more above T_g ; mineral fillers are needed
T_g above operating temperature	Dimensional and dielectric stability	Requires rigid co-monomers or anhydrides; vitrimer creep must be considered
Flame retardancy	Safety standards	Aliphatic networks give low char; aromatic bio-co-monomers or additives needed

Anhydride cure, already the standard for many electrical-grade conventional epoxies, transfers well to EVOs. The opportunity is a low-polarity, hydrophobic bio-based matrix; the risk is that ester and hydroxyl content and modest T_g offset that advantage. Any claim of low-dielectric performance must be backed by dielectric spectroscopy across the operating frequency and humidity range.

Vat-photopolymerization 3D printing (SLA and DLP)

Stereolithography (SLA) cures a resin vat point-by-point with a laser; digital light processing (DLP) cures whole layers at once with a projected image. Both need resins with low viscosity (for recoating each layer), fast and spatially confined photocure, and adequate green strength. Three chemistries are used:

- **Radical acrylates.** AESO cures quickly by radical photopolymerization and has been printed into shape-memory (“4D”) biomedical scaffolds [33]. Viscosity and oxygen inhibition at surfaces are managed with reactive diluents and photoinitiator choice.
- **Cationic epoxides.** Onium-salt photoinitiators cure EVOs without oxygen inhibition and with lower shrinkage, but more slowly, and the continued dark cure can blur feature edges.
- **Hybrid acrylate–epoxy.** Radical cure fixes the geometry layer by layer; cationic or thermal post-cure develops the epoxy network and final properties (Chapter 4).

The depth to which each layer cures is described by the working-curve relation widely used in stereolithography:

$$C_d = D_p \ln \frac{E}{E_c} \quad (8.2)$$

where C_d is cure depth, D_p the light penetration depth of the resin, E the exposure dose and E_c the critical dose for gelation.

As a calculated example, a resin with $D_p = 0.15$ mm and $E_c = 10$ mJ cm⁻² exposed at 40 mJ cm⁻² cures to $0.15 \times \ln 4 \approx 0.21$ mm — enough for a 0.1 mm layer with good interlayer overlap. Absorbers that reduce D_p sharpen resolution at the cost of longer exposures.

Table 8.2 End uses for vegetable-oil epoxies: chemistry match and principal hurdle (qualitative synthesis of Chapters 4–8).

Application	Best-fit chemistry	EVO advantage	Principal hurdle
PVC plasticizer / stabilizer	Unreacted EVO	Established commodity use	— (mature)
Baked and UV coatings	Anhydride; cationic UV	Low viscosity, flexibility, adhesion	Hardness, chemical resistance
Waterborne coatings	Glycidyl derivatives + amine adducts	Bio-content, low VOC	Ambient reactivity; dispersion stability
Pressure-sensitive adhesives	Lightly crosslinked acid/anhydride	Low T_g is desirable	Balancing tack and shear
Structural adhesives	Blends with rigid bio-epoxies	Toughening	Modulus and T_g
Natural-fibre composites (RTM/VARTM)	Anhydride + rigid co-resin	Very low viscosity; high bio-content	Cure temperature; moisture; T_g
Electronics encapsulation	Anhydride, filled	Hydrophobic, low-polarity chains	Ionic purity, T_g , flame retardancy
3D printing (SLA/DLP)	AESO radical; hybrid	Photoreactive, tunable	Mechanical properties, resolution

CHAPTER SUMMARY

- ESO and ELO are established commodities as PVC plasticizers and stabilizers; thermoset uses build on that supply chain.
- EVOs are far less viscous than liquid DGEBA, which favours coatings and infusion; cure temperature and network rigidity are the trade-offs.
- Darcy's law (Eq. 8.1) links viscosity to infusion time; cardanol and terpene-oxide diluents manage viscosity at a cost in crosslink density.
- Electronics and 3D printing are promising but demanding outlets; claims must be backed by dielectric, purity and resolution data.

TECHNO-ECONOMIC ANALYSIS (TEA) AND LIFE CYCLE ASSESSMENT (LCA)

“Bio-based” is a description of origin. Whether a resin is affordable, and whether it is better for the planet, are separate questions – and both must be answered with numbers.

IN THIS CHAPTER

- The anatomy of an industrial epoxidation plant, and how to estimate its capital and operating costs.
- Feedstock supply and price risk for agricultural versus petrochemical raw materials.
- Life-cycle assessment of bio-epoxies: functional units, allocation, biogenic carbon, and hotspots.
- Regulation: REACH, bisphenol A restrictions, bio-based content standards, and Canadian requirements.

9.1 INDUSTRIAL SCALE-UP AND PROCESS ECONOMICS

Anatomy of an epoxidation plant

Translating the chemistry of Chapter 2 to production gives a process with six main sections (Figure 9.1). The reactor section is the heart of the plant and its most safety-critical part: semi-batch stirred tanks (or, increasingly, continuous reactors) with controlled hydrogen-peroxide dosing, high heat-removal capacity, and peroxide-decomposition safeguards.

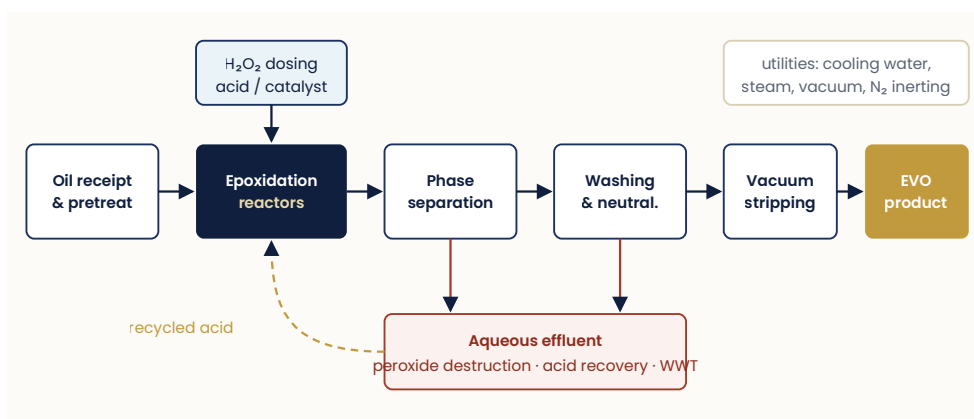


Figure 9.1 Block flow diagram of an in situ peracid epoxidation plant. Safety systems (temperature-interlocked peroxide dosing, emergency quench, venting) are concentrated around the reactor; the aqueous effluent carries residual peroxide and carboxylic acid that must be destroyed or recovered.

Mass balance

A first-pass mass balance sets raw-material demand and is the foundation of any cost model.

WORKED EXAMPLE · RAW MATERIALS PER TONNE OF ESO

For ESO at OOC = 6.8 %, the oxygen added per 100 g of oil is x where $x/(100 + x) = 0.068$, so $x = 7.30$ g. One tonne of ESO therefore contains 0.932 t of oil and 68 kg (4.25 kmol) of oxirane oxygen. The stoichiometric hydrogen peroxide is $4.25 \text{ kmol} \times 34.01 \text{ kg kmol}^{-1} = 145 \text{ kg}$ (100 % basis). With a 1.5 : 1 molar excess to compensate for decomposition and incomplete selectivity, demand rises to about 217 kg of 100 % H_2O_2 , or 434 kg of a 50 % solution. The excess ratio is an assumption to be replaced by plant data; the rest follows from Eqs. 1.2–1.3.

Capital expenditure (CapEx)

Early-stage capital estimates usually scale from a known plant or from purchased-equipment costs:

- **Capacity scaling.** The cost of a plant of capacity S_2 is estimated from a reference plant (C_1, S_1) as $C_2 = C_1 (S_2/S_1)^n$, with the exponent n conventionally about 0.6 (the “six-tenths rule”). The economies of scale this implies are a central reason epoxidation is concentrated in large plants.
- **Factored estimates.** Total installed cost is estimated as purchased-equipment cost multiplied by an installation factor (the Lang factor approach), with factors for fluid-processing plants higher than for solids plants because of piping, instrumentation and civil work.
- **Safety and environmental systems** — peroxide-rated materials of construction, cooling redundancy, emergency relief, effluent treatment — are a larger share of capital for oxidation plants than for many other chemical processes and should be costed explicitly, not left to a generic factor.

Operating expenditure (OpEx)

For commodity epoxidized oils, raw materials dominate operating cost, and the oil itself dominates raw materials. A transparent cost model is easily built and updated as prices change (Table 9.1); we deliberately give its structure rather than prices, which are volatile and location-specific.

Table 9.1 Structure of a unit-cost model for an epoxidized oil (per tonne of product). Quantities in the first rows follow from the worked mass balance; all prices are user inputs.

Cost element	Quantity basis (per t EVO)	Driver
Vegetable oil	$\approx 0.93 \text{ t}$ (ESO at 6.8 % OOC)	Commodity oil price; pretreatment losses
Hydrogen peroxide	$145 \text{ kg} \times \text{excess ratio}$ (100 % basis)	H_2O_2 price; decomposition losses
Carboxylic acid (net)	Make-up after recovery	Recovery efficiency
Catalyst	Mineral acid consumed, or resin/enzyme amortized per batch	Catalyst life (number of cycles)
Utilities	Cooling, steam, vacuum, electricity	Batch time; stripping duty
Effluent treatment	Aqueous phase volume and COD	Washing strategy; acid recovery
Labour, maintenance, overheads	Fixed per year $\div$ annual output	Plant scale and utilization
Capital charge	Annualized CapEx $\div$ annual output	Discount rate, plant life

Supply-chain security and price volatility

Agricultural and petrochemical feedstocks carry different risks. Vegetable-oil prices respond to weather and harvests, to biofuel mandates that compete for the same oils, and to trade policy; they are also correlated with energy prices through fertilizer, transport and biodiesel demand. Petrochemical feedstocks follow crude oil and natural gas but are less exposed to harvest risk. Three strategies reduce exposure for a bio-epoxy business: feedstock flexibility (a process qualified on several oils, using the iodine value to adjust stoichiometry); integration with waste or by-product streams (used cooking oil, tall oil, non-edible oils; Chapter 1); and long-term supply contracts or regional crop development. Specialty oils such as hemp-seed oil offer high functionality but currently have small, less liquid markets, which favours them for high-value applications rather than commodity resins.

9.2 ENVIRONMENTAL IMPACT AND SUSTAINABILITY METRICS

The LCA framework

Life-cycle assessment under ISO 14040 and 14044 proceeds through goal and scope definition, inventory analysis, impact assessment and interpretation. A cradle-to-gate study of a resin covers everything from raw-material extraction or cultivation to the factory gate. A useful demonstration for bio-epoxies is the cradle-to-gate comparison of epoxies derived from bark extractives, lignin and triglycerides using ReCiPe midpoint and endpoint methods: the triglyceride-based epoxy performed best of the three and the lignin-based epoxy worst, owing to the chemicals used in lignin extraction and upgrading; electricity use in synthesis and manufacturing was the main hotspot; all three made significant contributions to toxicity-related categories; and the authors concluded that bio-sourced epoxies should not be assumed environmentally friendly without full assessment [18].

Choices that decide the answer

- **Functional unit.** Comparing “1 kg of resin” favours whichever resin is cheapest to make per kilogram, regardless of performance. If a bio-resin is less stiff, a stiffness-equivalent part needs more of it. A functional unit tied to performance — for example, a panel of given bending stiffness, or a square metre of coating providing a defined service life — is more defensible.
- **Allocation.** Oilseed crushing yields oil and meal. Whether burdens are split by mass, by economic value, or avoided by system expansion can change the oil’s footprint substantially; studies must state and test their choice.
- **Biogenic carbon.** Carbon taken up by the crop is stored in the resin. Some methods credit this uptake at cradle-to-gate; others account for it only with end-of-life release. Mixing conventions across studies invalidates comparisons.
- **Co-reactants.** Hydrogen peroxide production is energy-intensive, and the hardener can be a large fraction of the cured mass (see below). A bio-based epoxy cured with a fossil anhydride may carry much of the fossil footprint it was meant to avoid.
- **Agricultural impacts.** Land use, fertilizer-derived nitrous oxide, eutrophication and pesticide ecotoxicity can offset carbon advantages; they must appear in the impact assessment, not only climate change.

WORKED EXAMPLE · BIO-BASED CARBON IN AN ANHYDRIDE-CURED ESO

Take 100 g ESO cured with 64.4 g MHHPA (A/E 0.9; Chapter 4). Using triolein ($C_{57}H_{104}O_6$, 77.3 % C) as a proxy, ESO at 6.8 % OOC is about 72.1 % carbon, all biogenic; 72.1 g. MHHPA ($C_9H_{12}O_3$) is 64.3 % carbon, all fossil; 41.4 g. Bio-based carbon = $72.1/(72.1 + 41.4) = 63.5$ % of total carbon, although the hardener is only 39 % of the mass. Replacing MHHPA with a rosin-derived or oil-derived anhydride is therefore the single largest lever on the bio-based content of the cured material. (Calculated values; catalyst neglected.)

Comparing EVO with DGEBA

Cradle-to-gate comparisons of EVO-based and DGEBA-based resins are sensitive to all the choices above, and published results are not directly comparable unless they share functional unit, allocation and biogenic-carbon convention. A robust internal comparison should therefore: (i) model both systems in the same database and method; (ii) include the hardener and catalyst; (iii) use a performance-based functional unit; (iv) report climate change alongside land use, eutrophication and toxicity; and (v) test sensitivity to allocation and to the source of epichlorohydrin, which may itself be glycerol-derived [36].

9.3 REGULATORY LANDSCAPE AND STANDARDIZATION

REACH in the European Union

Under Regulation (EC) No 1907/2006 (REACH), substances manufactured in or imported into the EU at one tonne or more per year per manufacturer or importer must be registered with a dossier of hazard and exposure information [65]. Epoxidized oils, being variable mixtures derived from biological material, are typically handled as

substances of unknown or variable composition (UVCB), which makes accurate substance identity — fatty-acid profile, oxirane content and impurity ranges — part of the regulatory, not just the commercial, specification. Polymers are generally exempt from registration, but their monomers and reactants are not.

Bisphenol A restrictions

The regulatory pressure on BPA is a principal market driver for alternatives. In December 2024 the European Commission adopted Regulation (EU) 2024/3190, banning BPA in food-contact materials such as can coatings, reusable plastic drinking bottles and kitchenware, with an 18-month phase-out period and exceptions where no safe alternatives are available; the ban also covers other hazardous bisphenols and derivatives classified under the CLP Regulation [1]. Because epoxy can linings have historically relied on BPA-based resins, this creates a direct opening for BPA-free epoxies — but any replacement must itself satisfy food-contact migration and safety requirements, which bio-based origin alone does not guarantee.

Verifying bio-based content

Bio-based claims are verified by measuring radiocarbon, since carbon from recent biomass contains ^{14}C and fossil carbon does not:

- **ASTM D6866** determines biobased carbon content in solid, liquid and gaseous samples by radiocarbon analysis. Method B uses accelerator mass spectrometry with isotope-ratio mass spectrometry; Method C uses liquid scintillation counting on sample carbon converted to benzene. Results are expressed as fraction of modern carbon relative to the NIST oxalic-acid standard SRM 4990C. Method B's instrumental error is about 0.1–0.5 % (1 RSD), but inter-laboratory uncertainty can reach ± 3 % absolute [66].
- **EN 16785-1** combines radiocarbon analysis with elemental analysis to determine the *bio-based content* of a product — counting biogenic hydrogen, oxygen and nitrogen as well as carbon — for products in any physical form that contain carbon [67].

The two metrics differ: in the worked example above, bio-based *carbon* is 63.5 %, while bio-based *content* by EN 16785-1 would also count biogenic H and O and would not count the oxygen supplied by hydrogen peroxide. Claims should name the standard and the metric.

Canada

For a Canadian producer, two frameworks are central. Under the Canadian Environmental Protection Act, 1999, substances not listed on the Domestic Substances List require notification under the New Substances Notification Regulations before manufacture or import above prescribed quantities; new bio-based monomers and hardeners must be checked against this requirement early. Workplace hazard communication follows WHMIS 2015, Canada's implementation of the Globally Harmonized System, which requires compliant safety data sheets and labels for hazardous products — including peroxides, anhydrides, amines and epichlorohydrin.

Safety data and responsible claims

Every formulation component needs a current safety data sheet, and cured products should be assessed for residual monomers (epichlorohydrin, anhydride, amine) where they contact food, skin or drinking water. Marketing claims require the same discipline as technical ones: “bio-based” must be quantified by a named standard, “biodegradable” demonstrated by a standard test under stated conditions (Chapter 7), and “lower carbon” supported by an LCA with disclosed boundaries.

CHAPTER SUMMARY

- An epoxidation plant is a peroxide-oxidation process whose cost is dominated by oil; a transparent mass balance (≈ 0.93 t oil and 145 kg H_2O_2 stoichiometric per tonne ESO) anchors any cost model.
- Agricultural feedstocks carry harvest and policy risk; feedstock flexibility and waste-stream integration mitigate it.
- LCA results depend on functional unit, allocation, biogenic-carbon convention and hardener choice; triglyceride-based epoxies compared favourably with other bio-epoxies in one cradle-to-gate study, but “bio-based” never guarantees “lower impact”.
- REACH, the EU BPA ban, ASTM D6866 and EN 16785-1, and Canada’s CEPA and WHMIS frameworks define the regulatory path to market.

STANDARD TEST METHODS FOR BIO-BASED EPOXIES AND INTERMEDIATES

A working index of the methods used across this book, grouped by what they measure. Designations are given for orientation; always obtain and follow the current edition from the issuing body.

Standards cited in the text as references — ASTM D1652, AOCS Cd 9-57, AOCS Cd 1-25, ASTM D6866 and EN 16785-1 — were checked against the issuing bodies' records when this book was prepared [19, 28, 29, 66, 67]. Other designations below are widely used in polymer and composites testing and are listed to help the reader find the appropriate procedure; their scope and current revision should be confirmed before use. Where an ISO equivalent exists, laboratories outside North America often prefer it.

A.1 FEEDSTOCK OILS

Table A.1 Methods for characterizing feedstock oils.

Property	Method(s)	Principle / notes
Iodine value	AOCS Cd 1-25 (Wijs); ISO 3961; EN 14111	ICI addition to C=C; back-titration with thiosulfate. Underestimates conjugated unsaturation (tung oil) [11].
Fatty-acid profile	GC of fatty-acid methyl esters (FAME)	Transesterify, separate by gas chromatography; report area % with response factors.
Acid value / free fatty acids	Titration with ethanolic KOH (AOCS and ISO methods)	Free carboxylic acids open oxiranes; key pretreatment QC.
Peroxide value	Iodometric titration (AOCS and ISO methods)	Hydroperoxides from oxidation; catalyse H ₂ O ₂ decomposition.
Moisture	Karl Fischer titration	Water hydrolyses oxiranes; specify before epoxidation.
Phosphorus	ICP-OES or colorimetric	Indicator of residual phospholipids after degumming.

A.2 EPOXIDIZED OILS AND EPOXY RESINS

Table A.2 Methods for epoxidized intermediates.

Property	Method(s)	Principle / notes
Oxirane oxygen	AOCS Cd 9-57	Direct titration with HBr in acetic acid; for epoxidized fatty materials and epoxy compounds in general [28].
Epoxy content (percent epoxide)	ASTM D1652	Manual or automatic titration; 0.1–26 % epoxide [29]. State the basis (oxirane O, epoxide, or EEW).
Residual unsaturation	Iodine value (as A.1)	Tracks double-bond conversion (Eq. 2.1).
Hydroxyl value	Acetylation or phthalation, then titration	Measures ring opening during epoxidation.
Epoxide distribution, side products	^1H and ^{13}C NMR	Glycerol CH_2 (4.1–4.3 ppm) as internal standard; oxirane CH near 2.9–3.1 ppm.
Functional-group screening	FTIR (ATR)	Oxirane bands 820–845 cm^{-1} ; O–H growth signals ring opening.
Viscosity	Rotational viscometry at controlled temperature	Oligomerization indicator; processing parameter.
Molecular-weight distribution	Size-exclusion chromatography	Quantifies dimers and oligomers.
Hydrolysable chlorine	Saponification and argentometric titration	For glycidylated (ECH-derived) products.

A.3 CURE AND CURED NETWORKS

Table A.3 Methods for cure monitoring and cured-network properties (designations for orientation).

Property	Typical designations	Used in
Cure exotherm, T_g by DSC	ASTM D3418; ISO 11357	Cure kinetics (Eqs. 4.2–4.4)
Dynamic mechanical properties	ASTM D4065; ASTM D7028 (T_g of polymer–matrix composites)	T_g , crosslink density (Eq. 5.1)
Thermogravimetry	ASTM E1131; ISO 11358	Thermal stability, char yield
Gel fraction / swelling	Solvent extraction (procedures often adapted from ASTM D2765, written for crosslinked ethylene plastics)	Eq. 5.2
Tensile properties	ASTM D638; ISO 527	Modulus, strength, elongation
Flexural properties	ASTM D790; ISO 178	Stiffness of resins and composites
Impact	ASTM D256; ISO 180 (Izod)	Toughness screening
Fracture toughness	ASTM D5045	K_{Ic} , G_{Ic}
Hardness	ASTM D2240 (Shore)	Coatings and cast resins
Stress relaxation (vitrimers)	Rheometer or DMA, step strain	Eqs. 7.1–7.2

A.4 BIO-BASED CONTENT AND SUSTAINABILITY

Table A.4 Methods for sustainability claims.

Claim	Method	Output
Biobased carbon content	ASTM D6866 (Methods B, C)	Fraction of modern carbon; biobased carbon % of total organic carbon [66]
Bio-based content (all elements)	EN 16785-1	Radiocarbon + elemental analysis [67]
Life-cycle impacts	ISO 14040 / 14044	Impact-category results with stated functional unit and boundaries
Biodegradation	Standardized respirometric tests for the relevant environment	Must be demonstrated; not implied by bio-based origin

APPENDIX B

PHYSICAL AND CHEMICAL CONSTANTS OF COMMON PLANT OILS

Reference data for formulation and stoichiometry. Composition and iodine values are taken from the sources indicated; all derived quantities are calculated here from those data.

B.1 FATTY ACIDS

Table B.1 Formulae and molar masses of the principal fatty acids (calculated from IUPAC atomic masses C 12.011, H 1.008, O 15.999).

Fatty acid	Shorthand	Formula	Molar mass (g/mol)	C=C	Other functionality
Palmitic	16:0	C ₁₆ H ₃₂ O ₂	256.43	0	—
Stearic	18:0	C ₁₈ H ₃₆ O ₂	284.48	0	—
Oleic	18:1 Δ9c	C ₁₈ H ₃₄ O ₂	282.47	1	—
Linoleic	18:2 Δ9c,12c	C ₁₈ H ₃₂ O ₂	280.45	2	Methylene-interrupted
α-Linolenic	18:3 Δ9c,12c,15c	C ₁₈ H ₃₀ O ₂	278.44	3	Methylene-interrupted
γ-Linolenic	18:3 Δ6c,9c,12c	C ₁₈ H ₃₀ O ₂	278.44	3	Methylene-interrupted
Ricinoleic	18:1 Δ9c, 12-OH	C ₁₈ H ₃₄ O ₃	298.47	1	Secondary hydroxyl
α-Eleostearic	18:3 Δ9c,11t,13t	C ₁₈ H ₃₀ O ₂	278.44	3	Conjugated triene

B.2 OILS: COMPOSITION-DERIVED CONSTANTS

Average triglyceride molar mass is calculated as $M_{TG} = 3M_{FA,avg} + 92.09 - 3 \times 18.02$, where $M_{FA,avg}$ is the composition-weighted mean fatty-acid molar mass (normalized to 100 %). Double bonds per triglyceride and the calculated iodine value $IV_{calc} = 3 n_{C=C,avg} \times 253.81/M_{TG} \times 100$ follow. γ-Linolenic acid in hemp is grouped with α-linolenic (both 18:3).

Table B.2 Calculated constants for common oils, from the composition sources indicated. For linseed, castor and tung, our calculated IVs agree with the values reported by the composition source (181, 87.9, 226) [11], which serves as a check on the method.

Oil (composition source)	$M_{FA,avg}$	M_{TG} (g/mol)	C=C per TG	IV_{calc}	IV reported	OO_{th} (%)
Soybean (Codex mid-range) [10]	278.3	873	4.65	135	124–139	7.66*
Rapeseed, low-erucic (Codex mid-range)	280.4	879	4.05	117	105–126	6.79*
Sunflower, regular (Codex mid-range)	279.7	877	4.53	131	118–141	7.55*
Hemp seed (mid-range) [12]	278.7	874	5.65	164	154–165	9.14*
Linseed [11]	278.6	874	6.26	182	181 (calc.)	10.24
Castor	296.4	927	3.22	88	87.9 (calc.)	5.14*
Tung	278.3	873	7.80	227	226 (calc.); 156 Wijs	n.a.†

* OO_{th} from Eq. 1.2 using the mid-range reported IV (Table 1.4). † Conjugated triene; peracid epoxidation does not approach the theoretical value.

B.3 COMMERCIAL EPOXIDIZED OILS AND A DGEBA REFERENCE

Table B.3 Typical properties from supplier technical data sheets, with EEW calculated from Eq. 1.3.

Property	ESO (Vikoflex® 7170) [3]	ELO (Vikoflex® 7190) [4]	Liquid DGEBA (EPON™ 828) [20]
Oxirane oxygen	> 6.8 %	9.2 %	—
Epoxide equivalent weight (g/eq)	< 235 (calc.)	174 (calc.)	185–192
Iodine value	< 3.0	< 4.0	—
Acid value (mg KOH/g)	< 0.5	< 0.5	—
Viscosity at 25 °C	320–500 cP	800 cP	110–150 P
Colour (APHA)	< 150	< 225	—
Specific gravity / density	0.99	1.03	1.16 g/mL

B.4 USEFUL CONVERSIONS

Table B.4 Conversion relations used in this book.

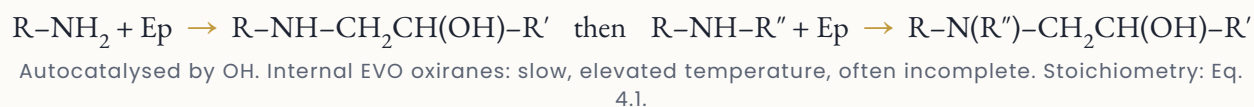
From	To	Relation
Iodine value	mol C=C per 100 g	$IV / 253.81$
Iodine value	Theoretical OOC (%)	Eq. 1.2
Oxirane oxygen (%)	EEW (g/eq)	$1600 / OOC$
EEW	Epoxide groups per molecule	M_n / EEW
AHEW, EEW	Amine phr	$AHEW \times 100 / EEW$ (Eq. 4.1)
AEW, EEW, A/E	Anhydride phr	$AEW \times 100 / EEW \times A/E$ (Eq. 4.5)
Rubbery E'	Crosslink density	$\nu_e = E' / (3RT)$ (Eq. 5.1)
1 P (poise)	Pa s	0.1 Pa s (1 cP = 1 mPa s)

COMPREHENSIVE REACTION SCHEMES FOR BIO-BASED CURING AGENTS

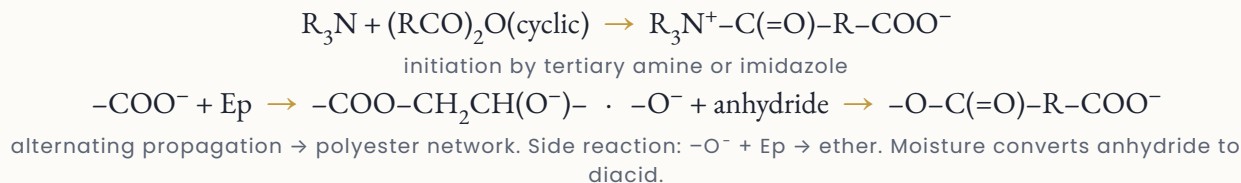
A compact atlas of the reactions that build, modify and recycle vegetable-oil epoxy networks, with the conditions and pitfalls that matter in practice. “Ep” denotes an oxirane ring; R groups are fatty-chain or hardener residues.

C.1 NETWORK-FORMING REACTIONS

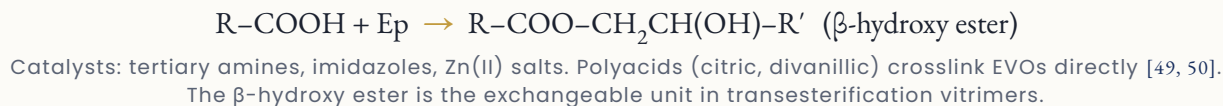
C.1.1 Amine-epoxy (Chapter 4.1)



C.1.2 Anhydride-epoxy, base-catalysed (Chapter 4.2)



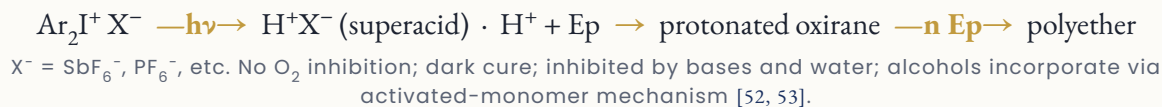
C.1.3 Carboxylic acid-epoxy (Chapters 4.3, 7.1)



C.1.4 Phenol-epoxy

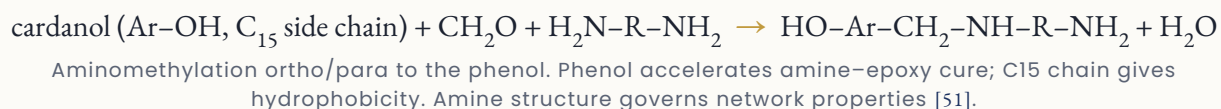


C.1.5 Cationic ring-opening polymerization (Chapter 4.4)

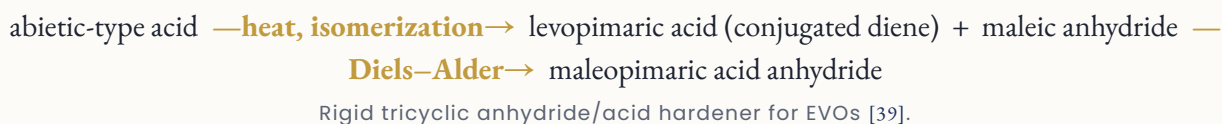


C.2 SYNTHESIS OF BIO-BASED HARDENERS

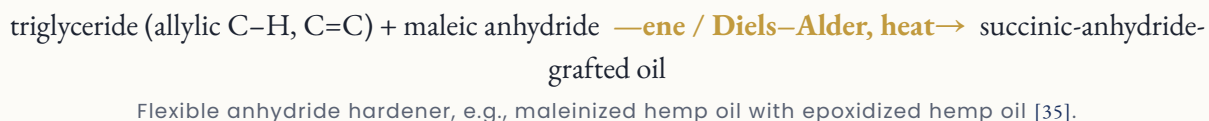
C.2.1 Phenalkamine (Mannich reaction)



C.2.2 Rosin-maleic anhydride adduct (maleopimaric anhydride)



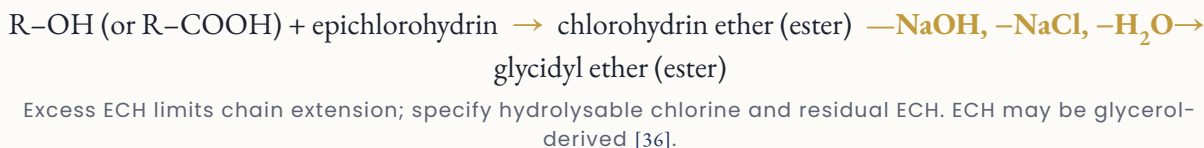
C.2.3 Maleinized oil



C.2.4 Amine-functional oil by thiol-ene coupling

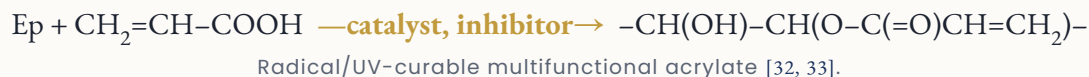


C.2.5 Glycidylation (terminal epoxides; Chapter 3.2)

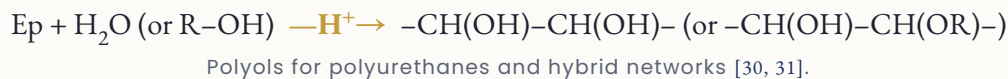


C.3 MODIFICATION AND EXCHANGE REACTIONS

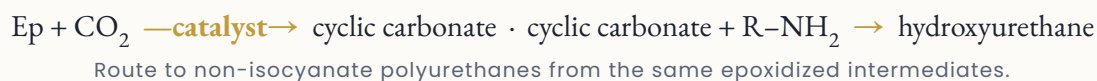
C.3.1 Acrylation of EVO (AESO)



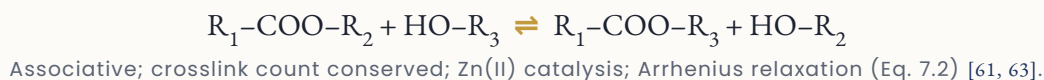
C.3.2 Hydroxylation (polyols)



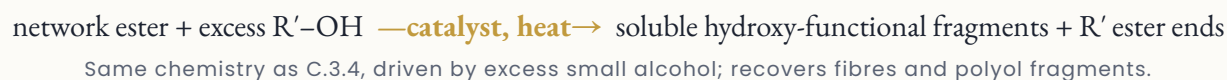
C.3.3 Carbonation



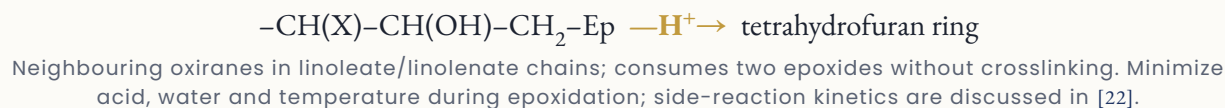
C.3.4 Transesterification exchange (vitrimers; Chapter 7)



C.3.5 Alcoholysis for recycling



C.3.6 Intramolecular cyclization (side reaction)



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GLOSSARY OF ABBREVIATIONS AND TERMS

A/E

Anhydride-to-epoxide molar ratio.

AESO

Acrylated epoxidized soybean oil.

AEW

Anhydride equivalent weight (g eq^{-1}).

AHEW

Amine hydrogen equivalent weight (g eq^{-1}).

Associative exchange

Bond exchange in which a new bond forms as an old one breaks, conserving crosslink count (vitrimers).

Bis-allylic

A CH_2 group lying between two $\text{C}=\text{C}$ bonds; easily oxidized.

CALB

Candida antarctica lipase B.

CNC / CNF

Cellulose nanocrystals / cellulose nanofibrils.

CNSL

Cashew-nut-shell liquid, source of cardanol.

CNT

Carbon nanotube.

CROP

Cationic ring-opening polymerization.

DGEBA

Diglycidyl ether of bisphenol A.

DLP / SLA

Digital light processing / stereolithography (vat photopolymerization).

DMA

Dynamic mechanical analysis.

DSC

Differential scanning calorimetry.

ECH

Epichlorohydrin.

EEW

Epoxide equivalent weight (g eq^{-1}) = $1600/\text{OOC}$.

EHO / MHO

Epoxidized / maleinized hemp oil.

ELO

Epoxidized linseed oil.

ESO

Epoxidized soybean oil.

EVO

Epoxidized vegetable oil.

FAME

Fatty-acid methyl ester.

GO / rGO

Graphene oxide / reduced graphene oxide.

IV

Iodine value (g I_2 per 100 g).

LCA

Life-cycle assessment (ISO 14040/14044).

M_c

Molecular weight between crosslinks.

MHHPA / MTHPA / MNA

Methylhexahydrophthalic / methyltetrahydrophthalic / methyl nadic anhydride.

MTO

Methyltrioxorhenium, CH_3ReO_3 .

NIPU

Non-isocyanate polyurethane.

OOC

Oxirane oxygen content (wt %).

phr

Parts per hundred parts of resin, by mass.

PSA

Pressure-sensitive adhesive.

RCO

Relative conversion to oxirane, $\text{OOC}_{\text{exp}}/\text{OOC}_{\text{th}}$.

REACH

EU Regulation (EC) No 1907/2006 on chemicals.

RTM / VARTM

Resin transfer moulding / vacuum-assisted RTM (infusion).

TEA

Techno-economic analysis.

TGA

Thermogravimetric analysis.

T_g

Glass transition temperature.

T_v

Topology-freezing temperature of a vitrimer ($\eta = 10^{12}$ Pa s).

UVCB

Substance of unknown or variable composition, complex reaction products or biological materials.

WCO

Waste cooking oil.

WHMIS

Workplace Hazardous Materials Information System (Canada).

ABOUT THE AUTHOR

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BIO-BASED EPOXY RESINS

Epoxy resins hold the modern world together — and for most of their history they have been built on petroleum and bisphenol A. This technical reference shows how the triglycerides of soybean, linseed, hemp, castor and other plant oils can be converted into epoxy thermosets, and what it takes to make those materials perform.

- Feedstock chemistry, iodine values and theoretical oxirane yields
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- Terminal epoxides, acrylates, polyols and rigid bio-based co-monomers
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- Network structure, DMA, TGA and formulation trade-offs
- Nanocomposites, natural-fibre composites and vitrimers
- Processing, applications, techno-economics, LCA and regulation

With worked examples throughout and a reference list verified against bibliographic databases, it is written for materials scientists, polymer chemists and chemical engineers working toward renewable thermosets.