Polymer Process Engineering
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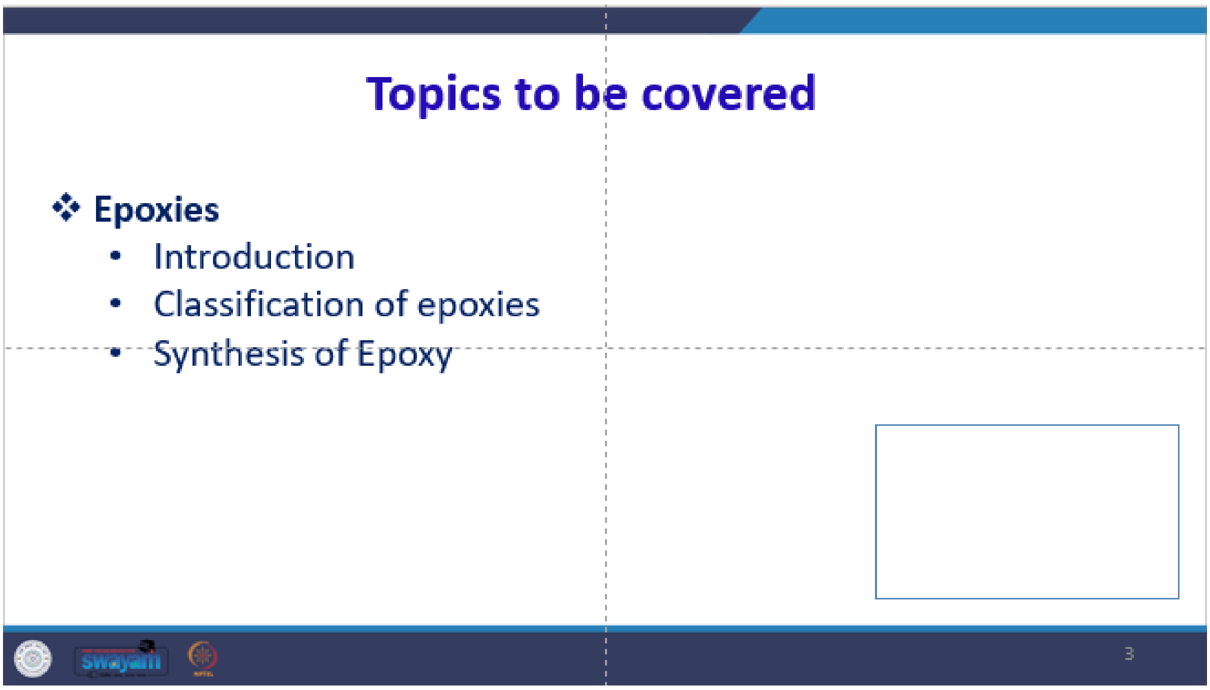
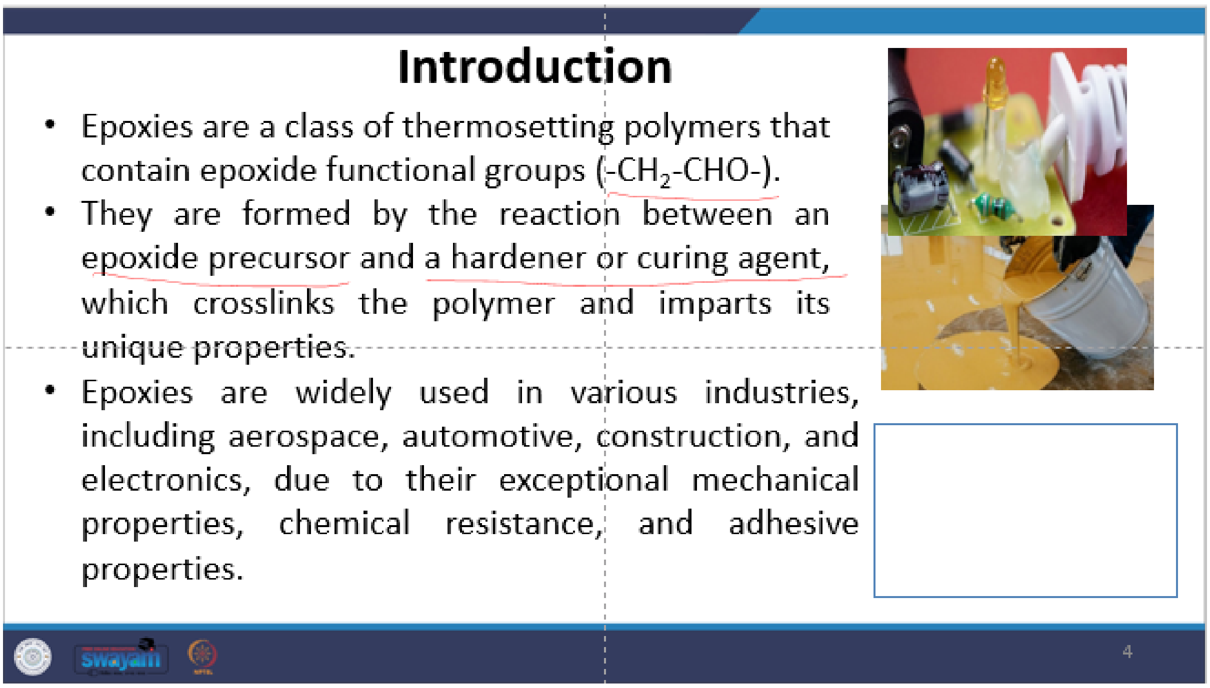
Lecture- 47
Polymers in Electronics: Epoxies

Hello friends, welcome to the another segment of polymers in electronics. Here we are going to discuss the epoxies under the edges of polymer process engineering. Now, we have already discussed about the polyurethanes in the previous lecture, in which we discussed about the introductory part of the polyurethane, then we discussed about the various modes of formation of these polyurethane. Then what should be the catalyst selection mechanism in the processing of polyurethane, then we classify them and then we discussed a lot of testing methods based on the ASTM standards, American Society for Testing Materials. Here we are going to discuss about the epoxies. The epoxies are playing a very vital role in the polymer synthesis, especially in the electronics application.


Topics to be covered

❖ Epoxies
  - Introduction
  - Classification of epoxies
  - Synthesis of Epoxy

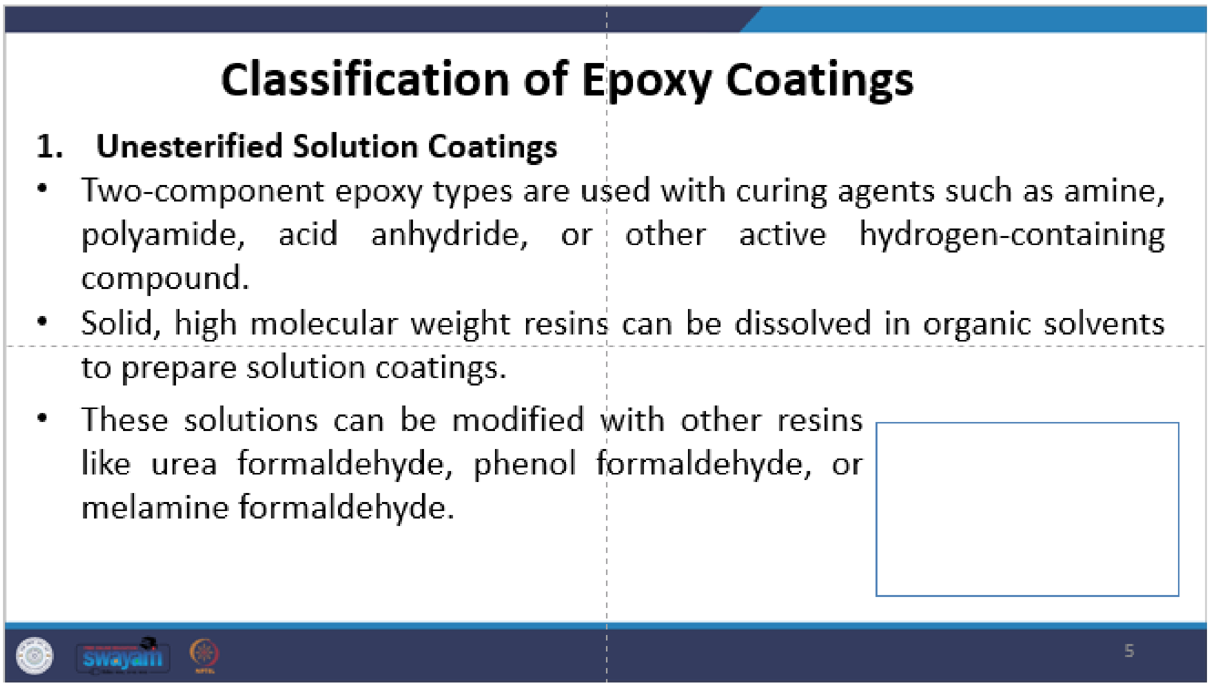
Then we cannot overlook the importance of epoxies and that is why this particular segment is divided into three broad segments. One is the introduction, then we will discuss about various classification streams of epoxies and then we will discuss that how we can synthesize those epoxies. Now, the epoxies, they are the class of thermosetting polymers that is the cross link polymers that contains the epoxide functional group, which is represented as CH2CHO and they are formed by the reaction between the epoxide precursor and a hardener or a curing agent, which cross links the polymer and imparts its unique properties. And these epoxies are widely used in the process in various industries like aerospace, automotive, construction, electronics and due to their exceptional mechanical properties or the chemical resistance and adhesive properties, they are very much popular.



Introduction

- Epoxies are a class of thermosetting polymers that contain epoxide functional groups (-CH_2-CHO-).
- They are formed by the reaction between an epoxide precursor and a hardener or curing agent, which crosslinks the polymer and imparts its unique properties.
- Epoxies are widely used in various industries, including aerospace, automotive, construction, and electronics, due to their exceptional mechanical properties, chemical resistance, and adhesive properties.

Now, there a broad spectrum of classification scheme of epoxy coating because epoxies are very much useful in coating application. So, first classification is unesterified solution coating. Now, the two components of epoxy, their types are used with the curing agents like amine, polyamide, acetonhydride and another active hydrogen-containing compound. Now, the solid high molecular weight resins, can be dissolved in an organic solvent to prepare the solution coating. Now, these solutions can be modified with other resins like urea formaldehyde, phenol formaldehyde or melamine formaldehyde.



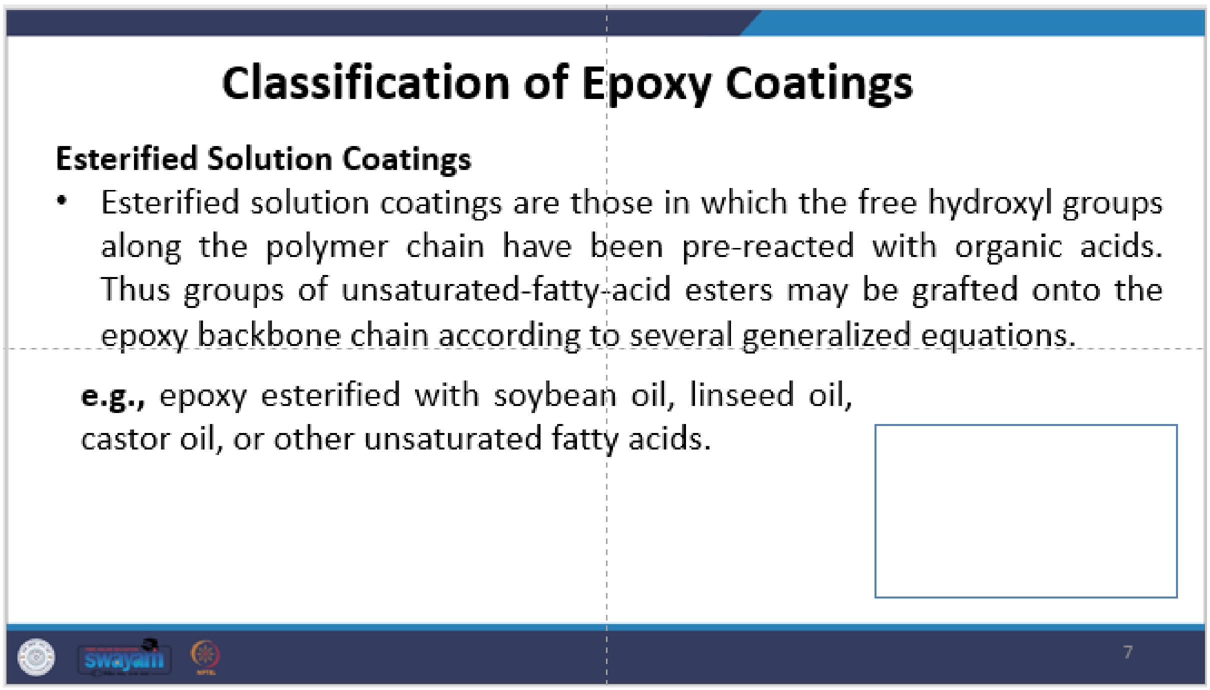
Classification of Epoxy Coatings

1. **Unesterified Solution Coatings**

- Two-component epoxy types are used with curing agents such as amine, polyamide, acid anhydride, or other active hydrogen-containing compound.
- Solid, high molecular weight resins can be dissolved in organic solvents to prepare solution coatings.
- These solutions can be modified with other resins like urea formaldehyde, phenol formaldehyde, or melamine formaldehyde.

These are the common polymers being used in variety of applications, one is the electrical switches and all those things. Now, solution coating, this can be cured at a room temperature or elevated temperature depending on the reactivity and amount of curing agent used. Now, heat curing, this requires removal of solvent by allowing an air-drying period or step by step cure. Sometimes entrapment of volatile or solvent is a serious problem in the solution coating. Now, incorporating the certain pigments because pigments and fillers, these are useful and these are very useful to impart the desired properties in the coating and therefore, the incorporation of the pigment and filler cannot be overlooked.

So, incorporating certain pigments and filler, this can help in releasing these solvents during the cure cycle. Another form is the esterified solution coating. Now, esterified solution coating are those in which the free hydroxyl groups along with the polymer chain, they have been pre-reacted with organic acids. This group of unsaturated fatty acid esters may be grafted on to the epoxy backbone chain as per the several generalized equations. One of the examples are epoxy esterified with soya bean oil, linseed oil, castor oil or other unsaturated fatty acids.



Classification of Epoxy Coatings

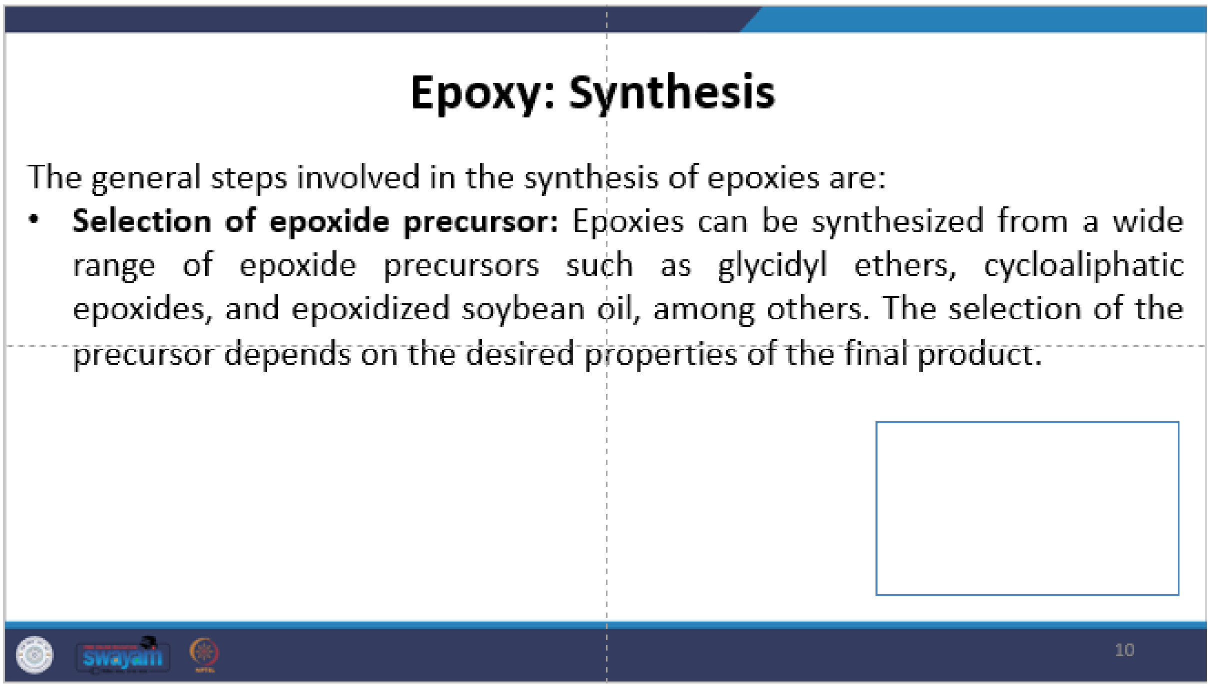
Esterified Solution Coatings

- Esterified solution coatings are those in which the free hydroxyl groups along the polymer chain have been pre-reacted with organic acids. Thus groups of unsaturated-fatty-acid esters may be grafted onto the epoxy backbone chain according to several generalized equations.

e.g., epoxy esterified with soybean oil, linseed oil, castor oil, or other unsaturated fatty acids.

Then metal naphthalates, they are dried used as an esterified epoxy formulation like in alkyd coating. Now, both air drying and baking type coating, these can be formulated with these kind of a dryers. Baking type enamels, this can cure at the room temperature and sometimes at higher temperature that is ranging from 60 to 180 degree Celsius in 20 to 60 minutes. So, if you lower the temperature, then obviously the time domain would be on the higher side. The addition of unsaturated chains in the resin results in more classical air oxidation curing mechanism and reducing the cost and achieving intermediate properties between non-esterified and alkyd resisters.

Then 100 percent solid coating, the 100 percent solid coating are two component non-ester type formulated without solvents or volatile ingredients and these coatings are called 100 percent solid because they do not contain any kind of solvent. So, they are perfectly solids and the resin used in these coating has a low enough viscosity to serve as both a vehicle and a reactive component. Now, let us talk about the epoxy synthesis. The general steps used very involved in the synthesis of epoxies are selection of epoxide precursor. This is very important.

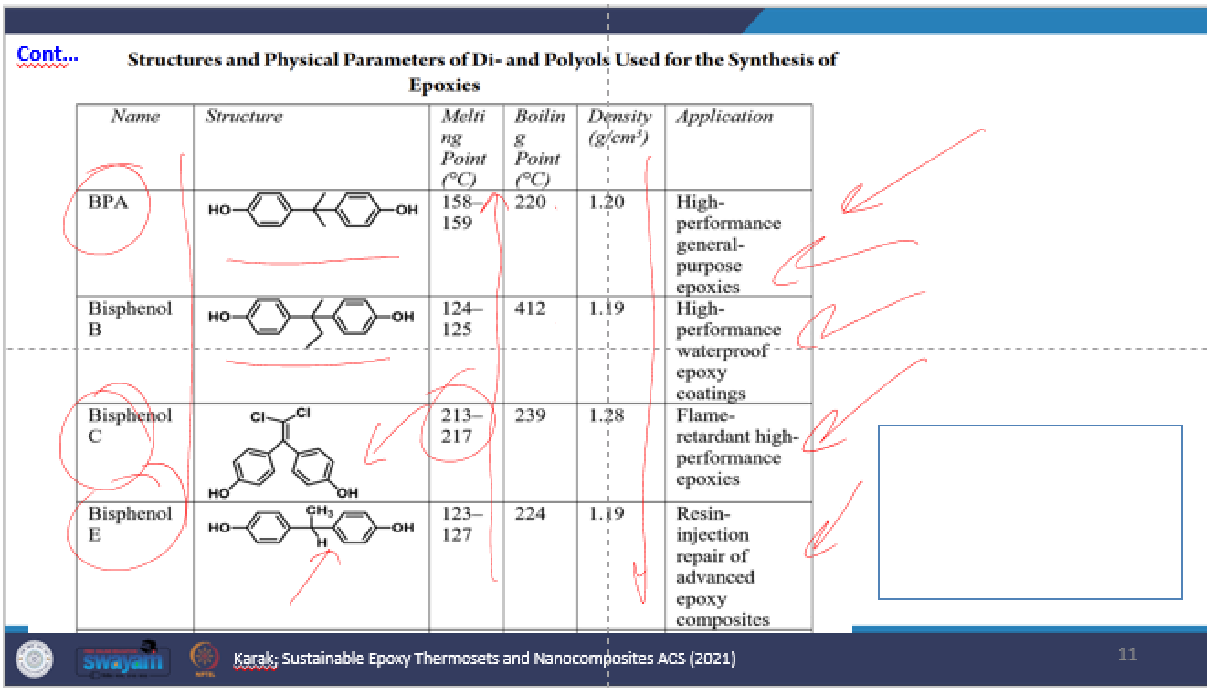


Epoxy: Synthesis

The general steps involved in the synthesis of epoxies are:

- **Selection of epoxide precursor:** Epoxies can be synthesized from a wide range of epoxide precursors such as glycidyl ethers, cycloaliphatic epoxides, and epoxidized soybean oil, among others. The selection of the precursor depends on the desired properties of the final product.

Now, the epoxies can be synthesized from a wide range of epoxide precursor like, glass idle ethers, cyclo aliphatic epoxides and epoxide soybean oil and among others. Now, their selection of the precursor depends on the desired properties of the final product. Now, here you see that the various structure and a physical parameter of dye and polyol used for the synthesis of epoxide. Like here, different type of names like bisphenol B, bisphenol A, bisphenol C, bisphenol E, all these are listed and here you see the different structures of these components. Apart from this, the melting point you can see that the melting point varies from 123 to say 217 to the higher and the boiling point right from 220, 412 to 224 and a density.



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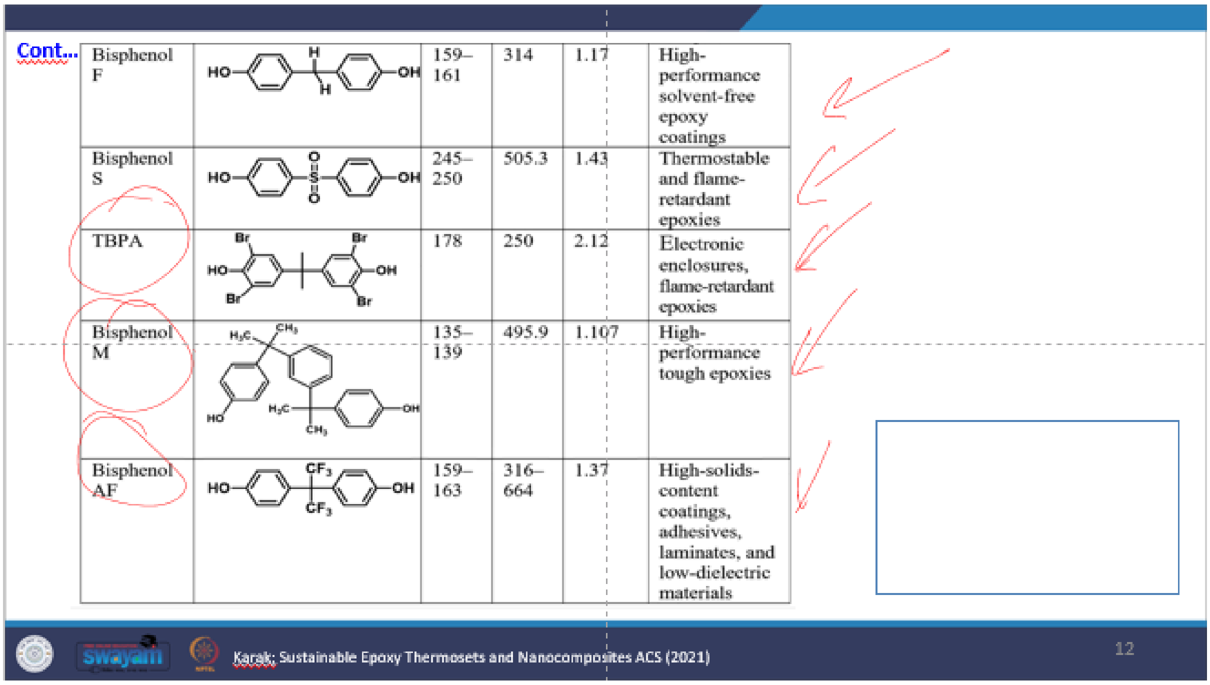
Structures and Physical Parameters of Di- and Polyols Used for the Synthesis of Epoxies

Name	*Structure*	*Melting Point (°C)*	*Boiling Point (°C)*	*Density (g/cm³)*	*Application*
BPA		158–159	220	1.20	High-performance general-purpose epoxies
Bisphenol B		124–125	412	1.19	High-performance waterproof epoxy coatings
Bisphenol C		213–217	239	1.28	Flame-retardant high-performance epoxies
Bisphenol E		123–127	224	1.19	Resin-injection repair of advanced epoxy composites

Karak; Sustainable Epoxy Thermosets and Nanocomposites ACS (2021)

But the crucial part is their application. So, the application like high performance general purpose epoxy, you can use the bisphenol A. Then high performance waterproof epoxy coating, then you can use the bisphenol B. And if you are looking for the flame retardant high performance epoxy, bisphenol C offers a better candidacy. Then resin injection repair if needed, then bisphenol E.



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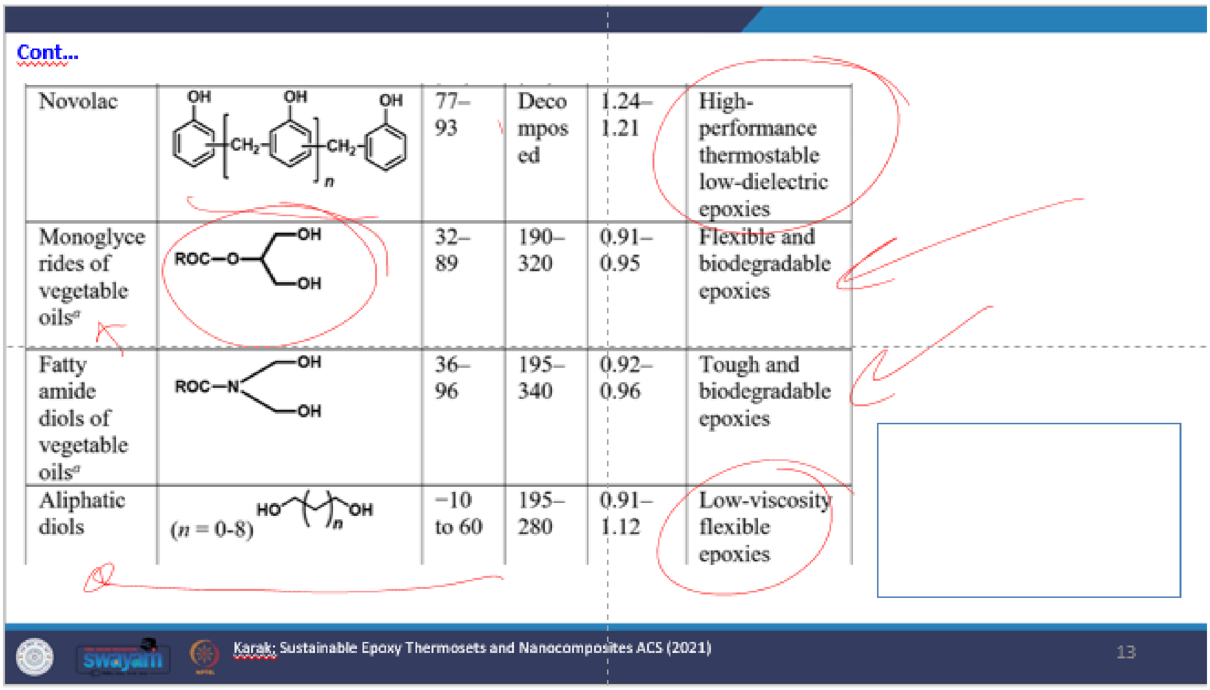
Bisphenol F		159–161	314	1.17	High-performance solvent-free epoxy coatings
Bisphenol S		245–250	505.3	1.43	Thermostable and flame-retardant epoxies
TBPA		178	250	2.12	Electronic enclosures, flame-retardant epoxies
Bisphenol M		135–139	495.9	1.107	High-performance tough epoxies
Bisphenol AF		159–163	316–664	1.37	High-solids-content coatings, adhesives, laminates, and low-dielectric materials

Karak; Sustainable Epoxy Thermosets and Nanocomposites ACS (2021)

Apart from this, other bisphenols are bisphenol F, bisphenol S, T bisphenol A, bisphenol M and bisphenol A. Now, here you see that they are having the wide range of uses like high performance solvent free epoxy coating to the thermo stable and flame retardant epoxies, then electronic enclosures, the flame retardant epoxies and high solid content coating adhesive laminates and low dielectric material. Now, you see by this way, there are wide range of their applications. Apart from this, there are certain more advanced epoxies like Novolac, you see the structure and this is having the high performance thermo stable low dielectric epoxy. Apart from this, monoglycerides of vegetable oils, you see that this is the typical structure of vegetable oils and they are flexible and biodegradable.



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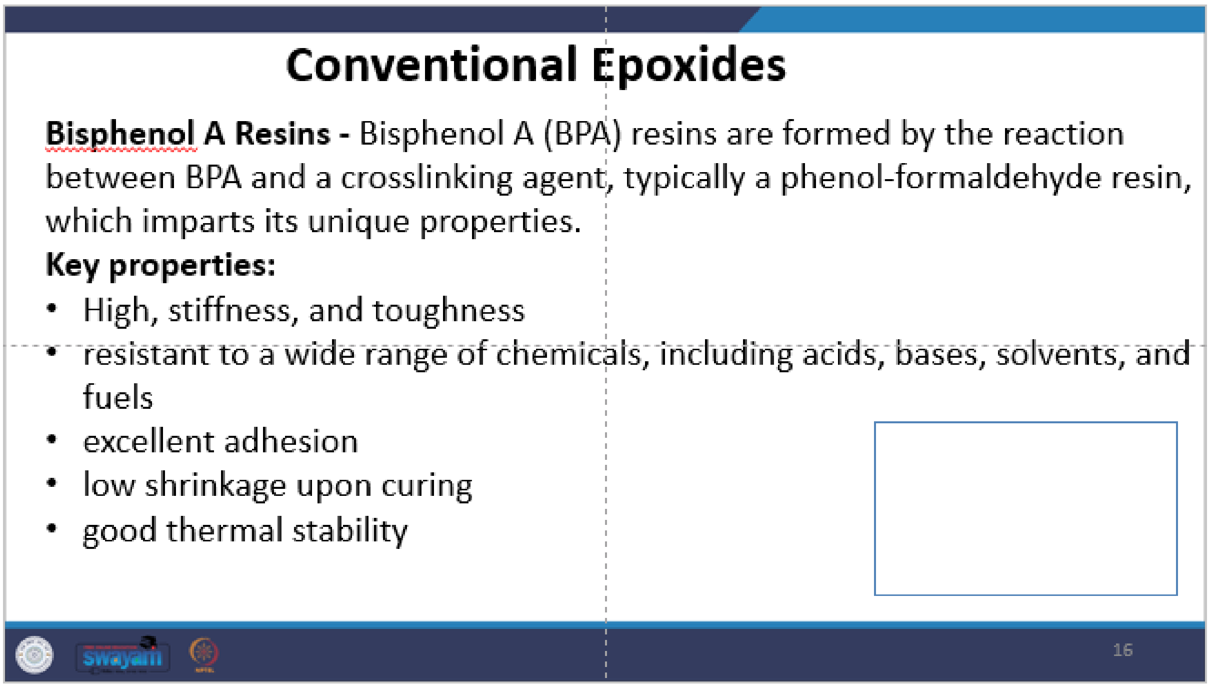
Novolac		77–93	Decomposed	1.24–1.21	High-performance thermostable low-dielectric epoxies
Monoglycerides of vegetable oils[a]		32–89	190–320	0.91–0.95	Flexible and biodegradable epoxies
Fatty amide diols of vegetable oils[a]		36–96	195–340	0.92–0.96	Tough and biodegradable epoxies
Aliphatic diols	(n = 0-8)	−10 to 60	195–280	0.91–1.12	Low-viscosity flexible epoxies

Karak; Sustainable Epoxy Thermosets and Nanocomposites ACS (2021)

So, if because of the environmental constraints and specific properties, if you are looking for the suitable thing, then they offer the better candidacy. Then if we are looking for the tough and biodegradable epoxies, then fatty amide oils of vegetable oils, they are offering a better candidacy. And if we are looking for the low viscosity flexible epoxy, then there are certain aliphatic diols. Apart from this, the hydrogenated bisphenol, they offers this see the difference in melting point and difference in the density. They are the weather resistance and the color stable epoxy.

Then if we look about the glycerol, they again very common I mean, if we are looking for the cost size aspect, then glycerol is having a prominent place. They are high performance biocompatible hyperbranched epoxies. Apart from this some of the more you can say more synthesized epoxies, if they are we are looking for the hyperbranched epoxies, then they offer the very good thing. Then sorbitol, they are the biodegradable hyperbranched epoxies. So, these are the some of the epoxies which we have enlisted apart from their molecular weight, apart from their density and all the applications.



Conventional Epoxides

Bisphenol A Resins - Bisphenol A (BPA) resins are formed by the reaction between BPA and a crosslinking agent, typically a phenol-formaldehyde resin, which imparts its unique properties.

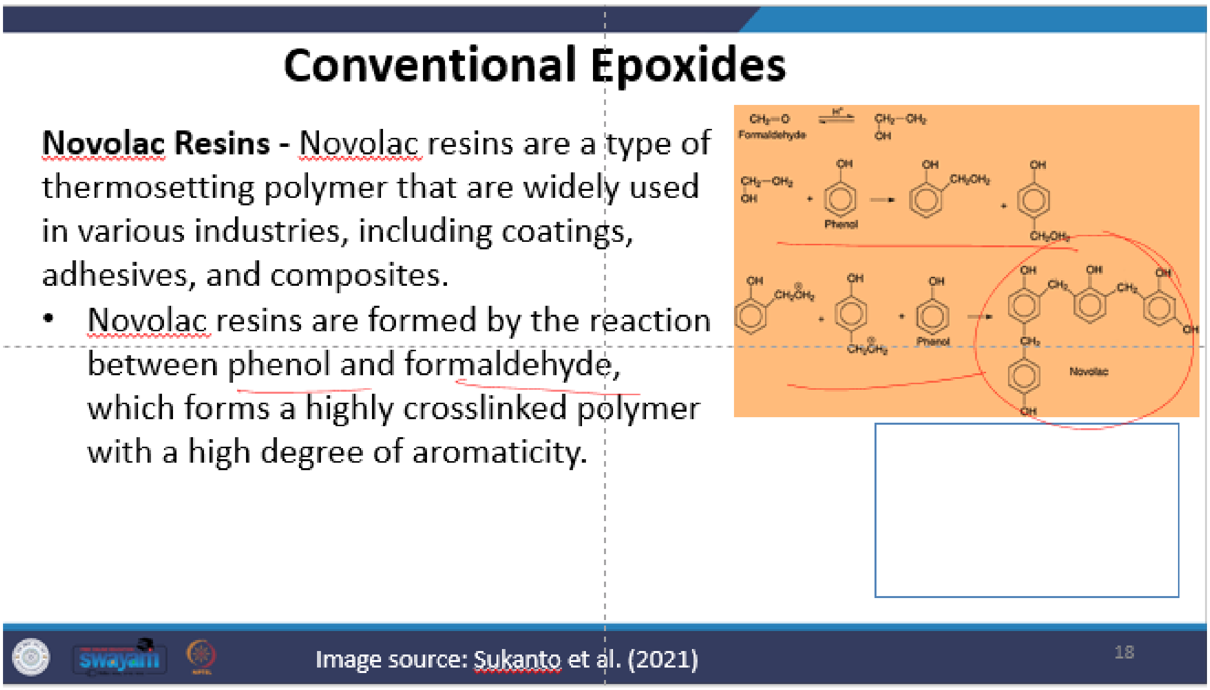
Key properties:

- High, stiffness, and toughness
- resistant to a wide range of chemicals, including acids, bases, solvents, and fuels
- excellent adhesion
- low shrinkage upon curing
- good thermal stability

Now, let us talk about some of the conventional epoxies in more detailed manner which we enlisted in the tabular form. One is the bisphenol A resin. The bisphenol A sometimes referred as a BPA. They are formed by the reaction between the BPA and the cross linking agent and typically a phenol formaldehyde resin which imparts its unique properties. There are several key properties associated with this BPA resin or bisphenol A resin.

They are high, stiff and toughness, resistance to a wide range of chemicals. This may include the acid, base, solvent, fuels, etcetera. They are having the excellent adjacent properties, having the low shrinkage once they cure and good thermal stability. Their uses are production of the composites, coating, adhesive and electrical insulation and they are also used in the production of epoxy resins which are similar in structure and properties to BPA resin, but they are formulated with a different curing agents. But there are certain environmental concerns are associated.

This has been a controversial compound due to its potential health effect on human and the environment and it has been shown to have the endocrine-disrupting effects and it has been linked to several health issues such as obesity, diabetes and cancer. So, as a result there has been growing interest in developing the alternative resin that do not contain BPA. Now, novolec resins, they are the type of thermosetting polymer that are widely used in various industries like coating, adhesive and composites. Now, these novolec resins they are formed by the reaction between the phenol and formaldehyde and which forms a highly cross-linked polymer with a high degree of aromaticity. Now, they the novolec resin, they have the several key properties like high thermal stability.



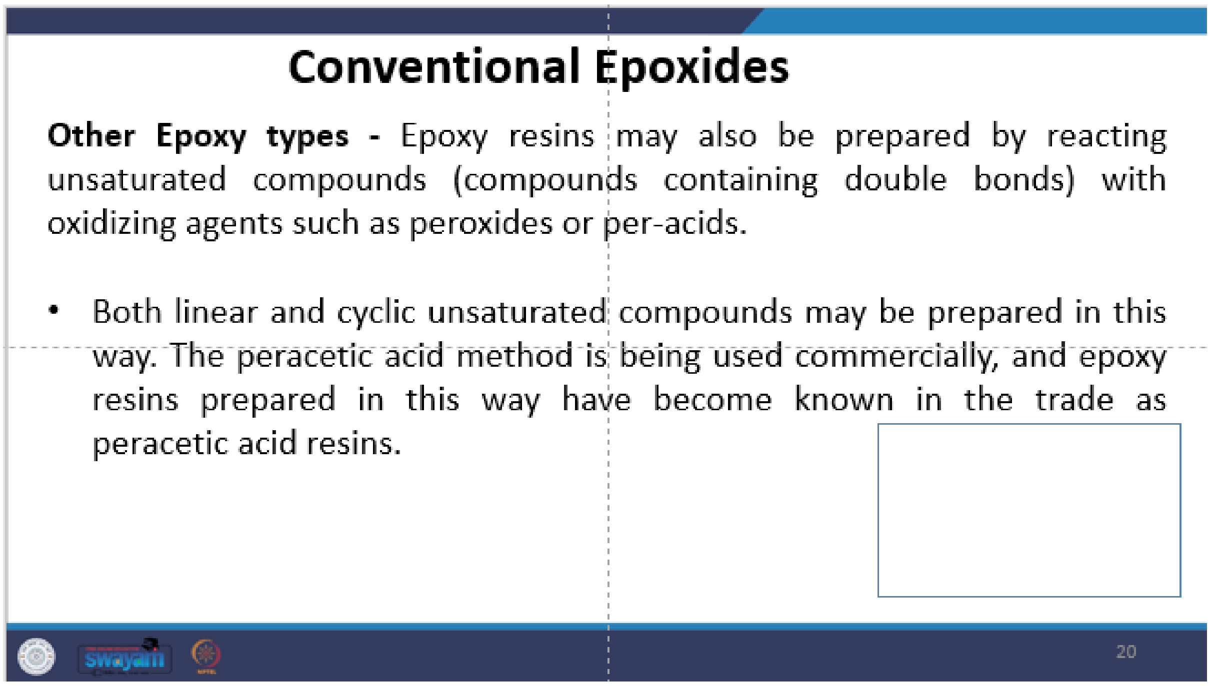
Conventional Epoxides

Novolac Resins - Novolac resins are a type of thermosetting polymer that are widely used in various industries, including coatings, adhesives, and composites.

- Novolac resins are formed by the reaction between phenol and formaldehyde, which forms a highly crosslinked polymer with a high degree of aromaticity.

Image source: Sukanto et al. (2021)

Now, these novolec resins, they have excellent thermal stability and they can withstand with high temperatures without degrading or melting. Now, this makes them ideal for use in high-temperature applications like coating, adhesive for aircraft and aerospace and also been used for when there is a wide range of delta t like if we use for in aerospace, they may have from minus 38 degrees Celsius to say 47 degree Celsius. So, lot of thermal thrust are involved, which is why they are being used in that particular application. Then flame retardancy, it has a good flame retardant properties, which make them suitable for use in applications where fire safety is in question. Then the electrical properties, the high dielectric strength, and the low dielectric constant make them ideal for use in electrical insulation application.



Conventional Epoxides

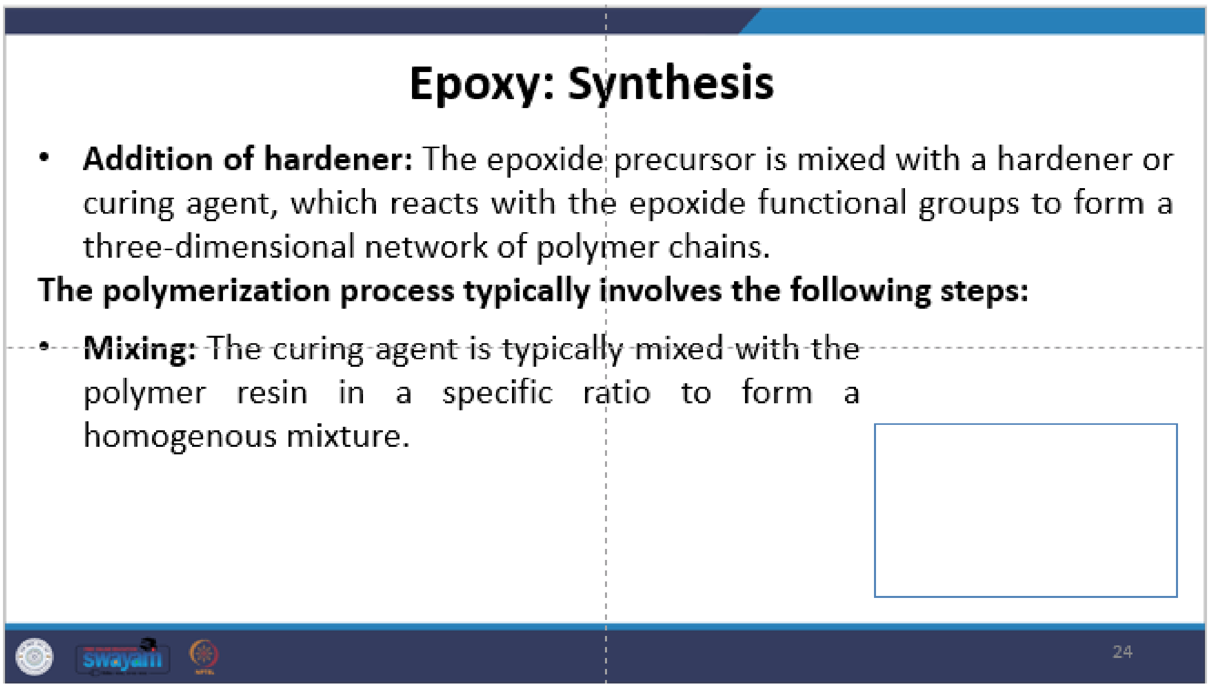
Other Epoxy types - Epoxy resins may also be prepared by reacting unsaturated compounds (compounds containing double bonds) with oxidizing agents such as peroxides or per-acids.

- Both linear and cyclic unsaturated compounds may be prepared in this way. The peracetic acid method is being used commercially, and epoxy resins prepared in this way have become known in the trade as peracetic acid resins.

Now, let us talk about the other epoxy types. The Epoxy resins, they may also be prepared by reacting unsaturated compounds like compounds containing double triple bonds and they have oxidizing agents such as peroxide or peracids. Now, the both linear and cyclic unsaturated compound may be prepared in this type of aspect and the peracetic acid method is being used commercially the epoxy resin prepared in this way have become known in the trade as peracetic acid resins. Whereas polyolefin resin, they have a distinct molecular structure compared to the bisphenol A series. Now, while both both containing epoxy rings, the position of the ring differs between these 2.

In epoxidized polyolefins, the epoxy resins, are present both along the chain and at the chain end. In the bisphenol A series, the epoxy ring is exclusively located at the end of the chain. Now, epoxy polyolefin resin can be cured with the common hardeners and catalysts used for bisphenol resin as well as the free radical initiators due to many double bond presences. Dicumyl peroxide and another peroxide catalyst they can also be used to cure these resins. Now, peracetic acid resins, have lower densities compared to bisphenol epoxy resin making them suitable for some airborne electronic applications.

Uncured peracetic acid resins, they are about 20 percent lighter in weight. So, in one aspect, they are very beneficial and these resins have better high-temperature performance resulting in a similar weight loss. They have comparable electrical properties, chemical properties, and solvent resistance to the bisphenol resin. Now, sometimes the addition of a hardener is very vital. So, the epoxide precursor is mixed with the hardener or curing agent, which reacts with the epoxide functional group to form a three-dimensional network of polymer chains and this makes them harden and harden.



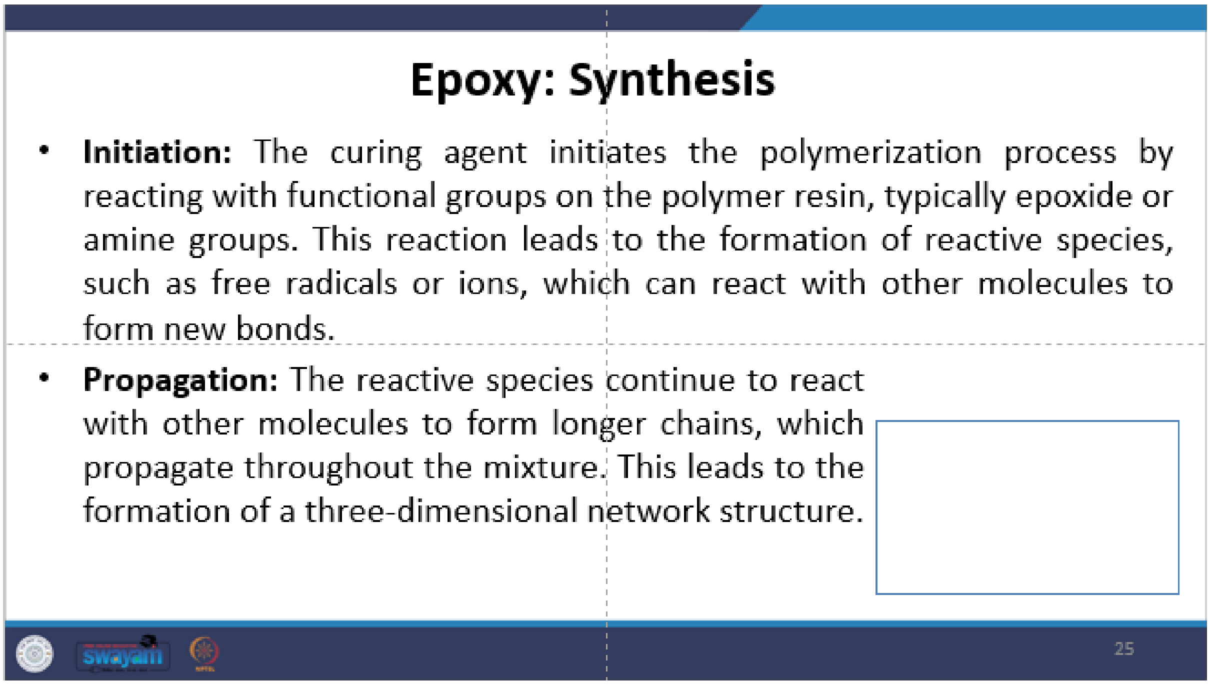
Epoxy: Synthesis

- **Addition of hardener:** The epoxide precursor is mixed with a hardener or curing agent, which reacts with the epoxide functional groups to form a three-dimensional network of polymer chains.

The polymerization process typically involves the following steps:

- **Mixing:** The curing agent is typically mixed with the polymer resin in a specific ratio to form a homogenous mixture.

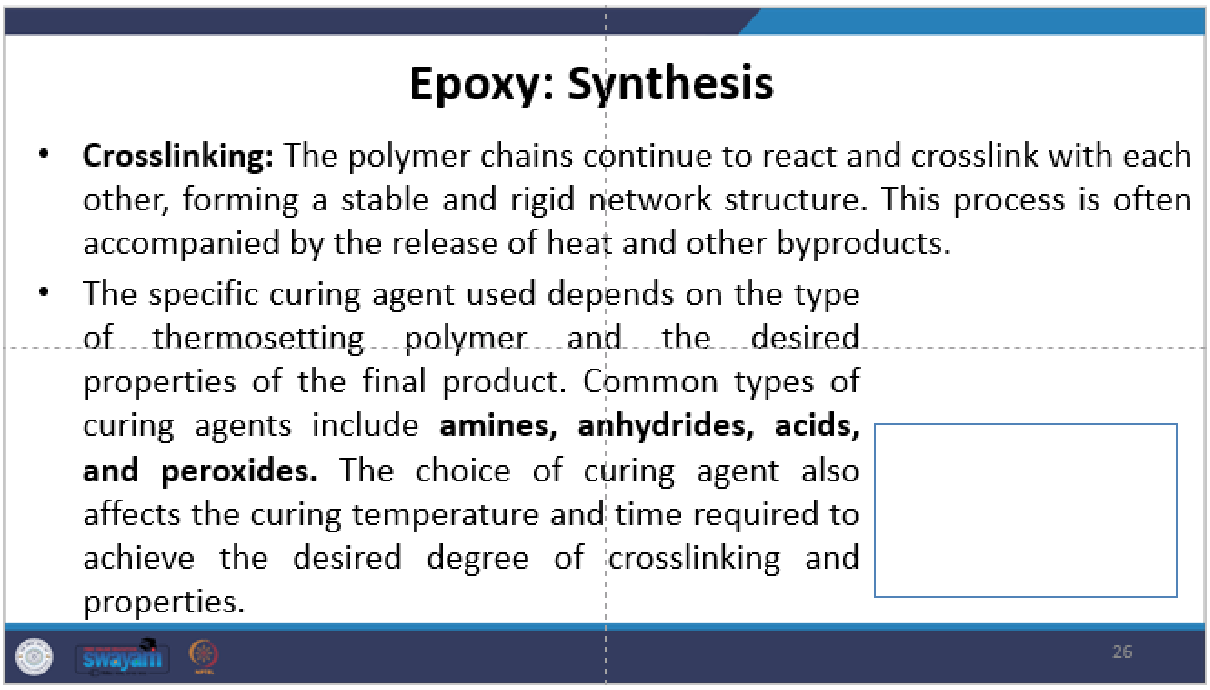
The polymerization process typically involves in different step. First step is the mixing. The curing agent is typically mixed with the polymer resin in the specified ratio to form a homogeneous mixture. So, this is again important thing and then initiation because we are performing the polymerization process.



Epoxy: Synthesis

- **Initiation:** The curing agent initiates the polymerization process by reacting with functional groups on the polymer resin, typically epoxide or amine groups. This reaction leads to the formation of reactive species, such as free radicals or ions, which can react with other molecules to form new bonds.
- **Propagation:** The reactive species continue to react with other molecules to form longer chains, which propagate throughout the mixture. This leads to the formation of a three-dimensional network structure.

So, initiation must must be there. So, the curing agent initiates the polymerization process by reacting with the functional group on the polymer resin, which is already present and typically epoxide or amine group. Now, this reaction leads to the formation of reactive species such as free radicals or iron which can react with other molecules to form a new bond or this can act as a source material for the propagation step. The next step is propagation. The reactive species continue to react with other molecules to form a longer chain, which propagates throughout the mixture. The only thing is required they must have either free radicals or iron in C2.



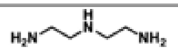
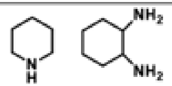
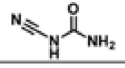
Epoxy: Synthesis

- **Crosslinking:** The polymer chains continue to react and crosslink with each other, forming a stable and rigid network structure. This process is often accompanied by the release of heat and other byproducts.
- The specific curing agent used depends on the type of thermosetting polymer and the desired properties of the final product. Common types of curing agents include **amines, anhydrides, acids, and peroxides.** The choice of curing agent also affects the curing temperature and time required to achieve the desired degree of crosslinking and properties.

So, this leads to the formation of a three-dimensional network structure. Then cross-linking. The polymer chains continue to react and cross-link with each other, forming a stable and rigid network structure. Now, this process is often accompanied by the release of heat and other byproducts. The specific curing agent used depends on the type of the thermosetting polymer and the desired properties of the final product.

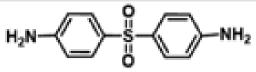
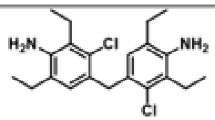
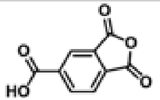
A common type of curing agent includes amine, anhydride, cysts and peroxide. The choice of curing agent also affects the curing temperature and time required to achieve the desired degree of cross linking and properties. Now, here we have enlisted some of the structure and application areas of hardener used in epoxy coating. Like if the basic thing in all our applications is the application arena. Now, if we require things that fast room temperature curing, then we have this one, then triethylene tetramine, then the fast room temperature curing, then thermo stable epoxy if we are looking for, then the suitable way is hexamethylenediamine.

Structures and Application Areas of Hardeners Used in Epoxy Curing

Name	*Structure*	*Application Areas*
Diethylenetriamine		Fast room-temperature curing
Triethylenetetraamine		Fast room-temperature curing
Hexamethylenediamine		Thermostable epoxies
Poly(oxypropylene)diamine		Tougher epoxies
N-amino ethyl piperazine		Room-temperature curing
Cycloaliphatic amines		Room-temperature curable, long pot life, high-performance epoxy
Dicyandiamide		Good viscoelastic properties
1-Ethyl-3-(3-dimethylaminopropyl)carbo diimide		Fast curable endodontic sealers

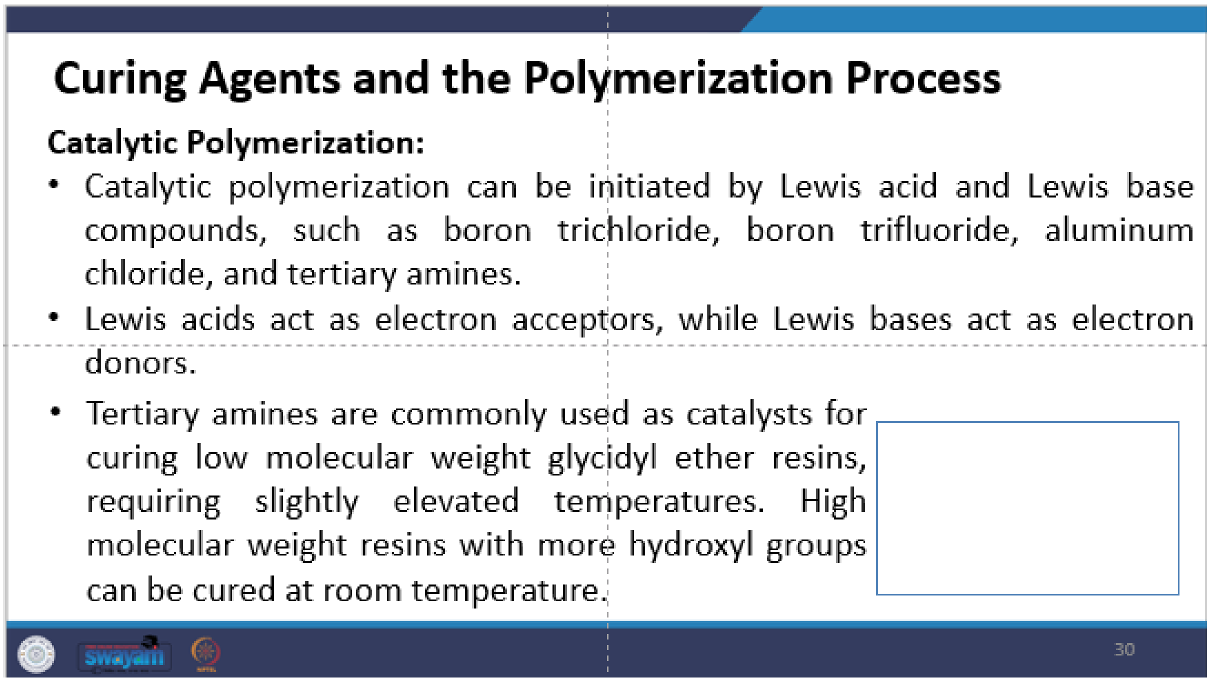
Karak; Sustainable Epoxy Thermosets and Nanocomposites ACS (2021)

Then if we the application requires tougher epoxies, then polyoxypropylene diamine one and if we require room temperature curing, then aminoethylpiperazine. So, by this way there are so many, so many hardeners they are used for this epoxy curing. Like diamino phenylsulfone and methylene. Like if we require good physical and dielectric properties, apart from this the tri-metallic anhydride, if the thermo stable high-performance epoxy thermo state applications are needed. Similarly, if we are looking for low-temperature curing, which may be tough and biocompatible epoxy thermosets, then the vegetable oil-based polyamidoamine this can be used.

Cystamine		Biocompatibility curative
Diaminodiphenyl sulfone		Thermostable high-performance epoxy thermosets
Methylaniline		Good physical and dielectric properties
1.4-Diaminodiphenyl methane		Thermostable high-performance epoxy thermosets
4,4-Methylenebis(3-chloro-2,6-diethylaniline)		Good abrasion resistance
Trimellitic anhydride		Thermostable high-performance epoxy thermosets

Karak; Sustainable Epoxy Thermosets and Nanocomposites ACS (2021)

And if we are looking for thermo stable epoxy thermosets, then nadic methyl anhydride can be used, which has the structure like this. And if we the application involves biocompatible and biodegradable epoxy thermosets, then polyphenols such as tannic acid can be used. Now let us talk about the curing agent and polymerization process. First, let us take up the catalytic polymerization. The catalytic polymerization can be initiated by the Lewis acid and a Lewis base compound like boron trichloride, boron trifluoride, aluminium chloride and tertiary amines.



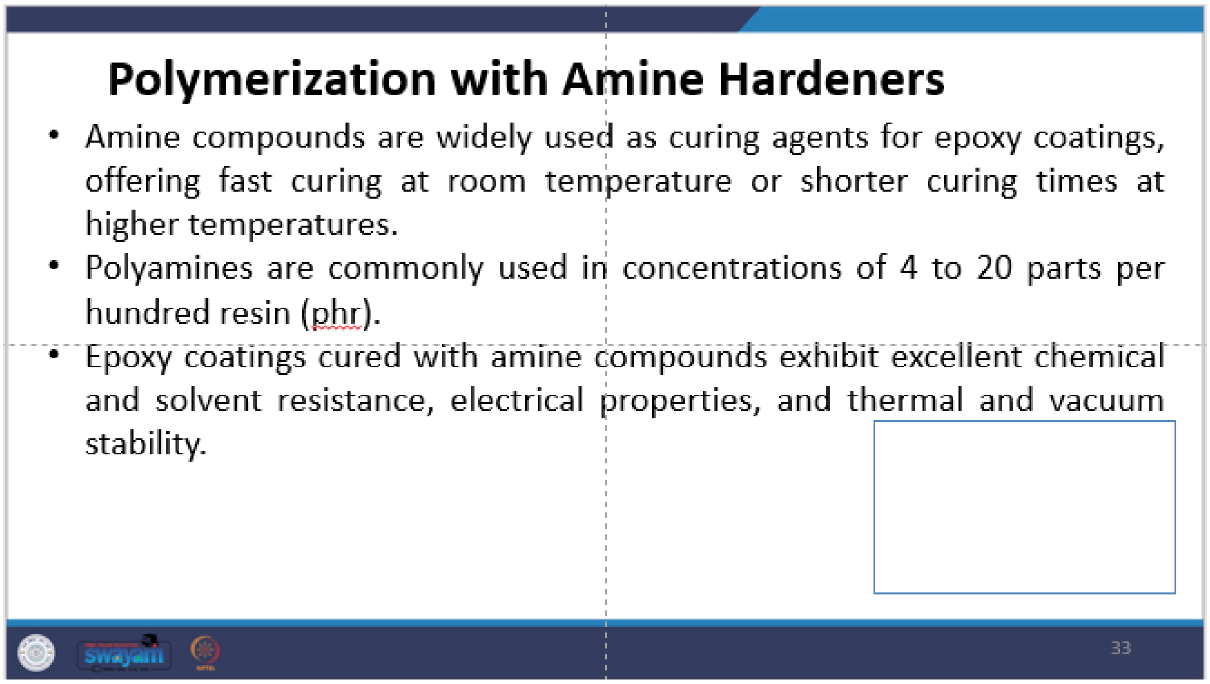
Curing Agents and the Polymerization Process

Catalytic Polymerization:

- Catalytic polymerization can be initiated by Lewis acid and Lewis base compounds, such as boron trichloride, boron trifluoride, aluminum chloride, and tertiary amines.
- Lewis acids act as electron acceptors, while Lewis bases act as electron donors.
- Tertiary amines are commonly used as catalysts for curing low molecular weight glycidyl ether resins, requiring slightly elevated temperatures. High molecular weight resins with more hydroxyl groups can be cured at room temperature.

Lewis acids they act as electron acceptors while Lewis bases they act as electron donors. Now tertiary amines they are commonly used as catalysts for curing low molecular weight, glycydal ether resin and this requires the slightly elevated temperature high molecular weight resin with more hydroxyl groups that can be cured at room temperature. Now tertiary amine catalysts they are used in quantities of say 5 to 15 parts per 100 resin, while Lewis acid or amine complexes they are used in amount of say 2 to 4 parts per 100 resin. Now handling free Lewis acid and bases can be challenging due to their corrosive irritating or toxic nature as well as their reactivity in a short pot life. Highly reactive catalysts like boron trifluoride they are typically sold and used as latent complexes or modified to reduce vapor pressure, and toxicities and extend pot lives.

Now the boron trifluoride can be employed as an amine complex such as aniline, boron trifluoride or trimethylene boron trifluoride which gradually dissociates at room temperature or more rapidly with the application of heat or other form of energy. Now, catalytic curing agent although effective have not been widely used in coating formulation compared to the polyamide and other additive hardeners. Now let us talk about polymerization with amine hardeners. Now amine compounds they are widely used as a curing agent for epoxy coating. They offer fast curing at room temperature or shorter curing time at higher temperatures.

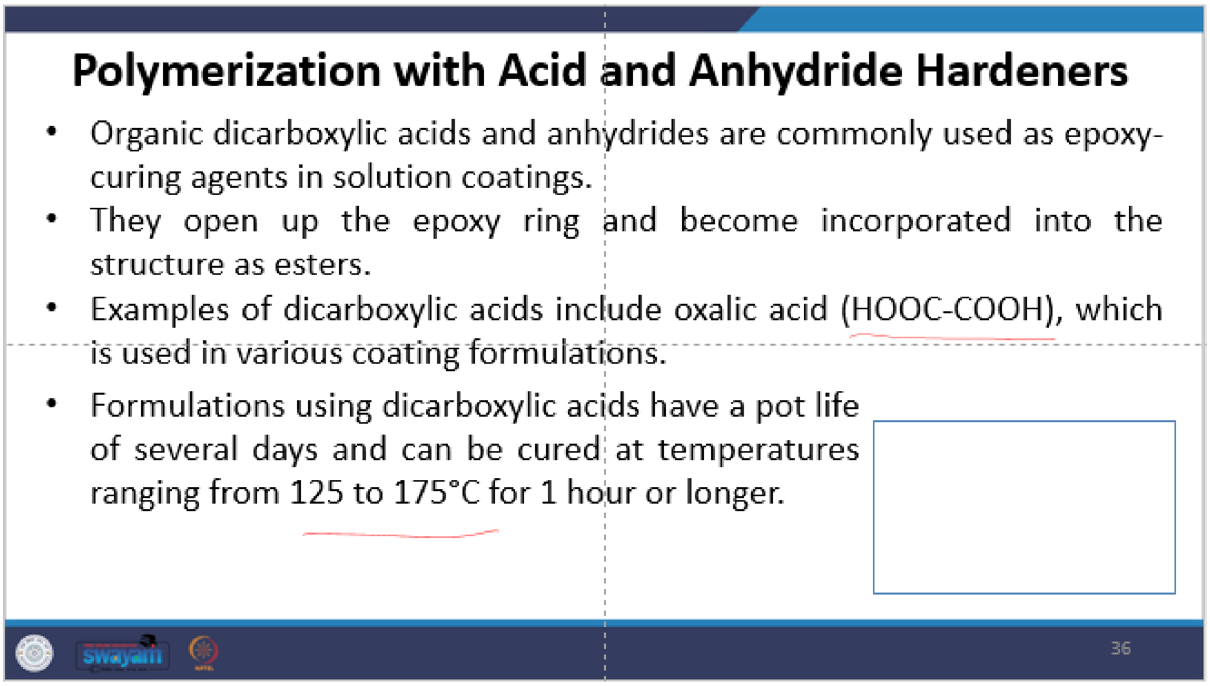


Polymerization with Amine Hardeners

- Amine compounds are widely used as curing agents for epoxy coatings, offering fast curing at room temperature or shorter curing times at higher temperatures.
- Polyamines are commonly used in concentrations of 4 to 20 parts per hundred resin (phr).
- Epoxy coatings cured with amine compounds exhibit excellent chemical and solvent resistance, electrical properties, and thermal and vacuum stability.

Now, polyamines they are commonly used in concentrations of 4 to 20 parts per 100 resin. Now epoxy coating cured with amine compound exhibits excellent chemical and solvent resistance, chemical properties and they possess thermal and vacuum stability. The post-curing or elevated temperature curing further enhances these properties and these are the various generic structure type of amine compounds used as a curing agent for epoxy coating. Now commercially available amine curing agents they are often modified to reduce vapor pressure, decrease skin irritation and control pot life. This modified amine this can be used as an eutectic mixture adduct with the lower molecular weight epoxy compound or complexes with boron trifluoride.

Now if we talk about the amine hardeners as we are discussing the primary and secondary aliphatic and aromatic amines, they are reactive with the epoxy resin at a concentration of 10 to 15 PHR. Ethylene di-amine is an example of an amine that participates in the epoxy cure mechanism, resulting in high molecular weight thermosetting epoxy coating. Modified amine compounds help in reduce skin irritation, noxious odor and corrosiveness, and they extend the pot life of epoxy formulation. Polymerization with acid and anhydride hardeners, organic dicarboxylic acid and anhydrides are commonly used as epoxy curing agents in solution coating, and they open up the epoxy ring and become incorporated into the structure as ester. An example of dicarboxylic acid includes oxalic acid H-C-O-H-C-O-O-H, which is used in various coating formulations.



Polymerization with Acid and Anhydride Hardeners

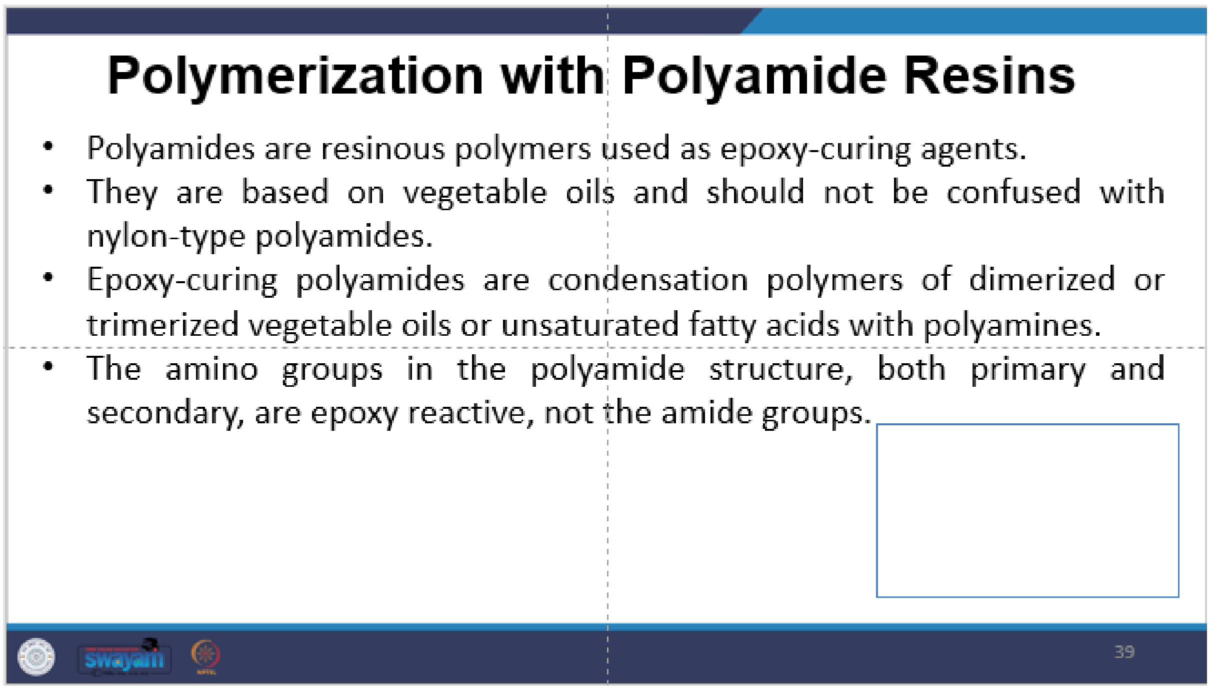
- Organic dicarboxylic acids and anhydrides are commonly used as epoxy-curing agents in solution coatings.
- They open up the epoxy ring and become incorporated into the structure as esters.
- Examples of dicarboxylic acids include oxalic acid (HOOC-COOH), which is used in various coating formulations.
- Formulations using dicarboxylic acids have a pot life of several days and can be cured at temperatures ranging from 125 to 175°C for 1 hour or longer.

The formulations using dicarboxylic acid have a pot life of several days and can be cured at temperatures ranging from 125 to 175 degrees Celsius for 1 hour or even longer. Another dicarboxylic acid in the series like H-O-C-C-O-H-C-O-H with N ranging from say, 1 to 8. They are less popular for solution coating due to their insolubility, difficulty in mixing with the resin and tendency to form the resin. So, all these are contributing effects. Now, anhydrides derived from the carboxylic acid are more commonly used and offer advantages over the amine amine-cured system.

An anhydride-cured system exhibit better thermal resistance and higher distortion temperature of 40 to 60 degree Celsius and improved electrical properties. Now, low dielectric constants such as 2.8 to 3 can be achieved with an anhydride curing agent. An anhydride curing agent, they are typically used in the concentration of say, 30 to 140 parts per 100 of resin, and they often require the accelerator or catalyst to promote faster reactions with epoxies and especially with the liquid type. The addition of a smaller amount of a tertiary amine catalyst, say in the 0.

25 PHR that is the parts per 100. This can result in a stable epoxy composition with low viscosity at room temperature and rapid curing at 120 degrees Celsius. Now let us talk about polymerization with polyamide resins. Now, the polyamide they are resinous polymers used as an epoxy curing agent, and they are based on vegetable oils and should not be confused with nylon type of polyamides. And epoxy curing polyamides are condensation polymers of dimerized or trimerized vegetable oil or unsaturated fatty acids with polyamines. So, the amino group in the polyamide structure with both primary and secondary are epoxy reactive and not the amide groups.

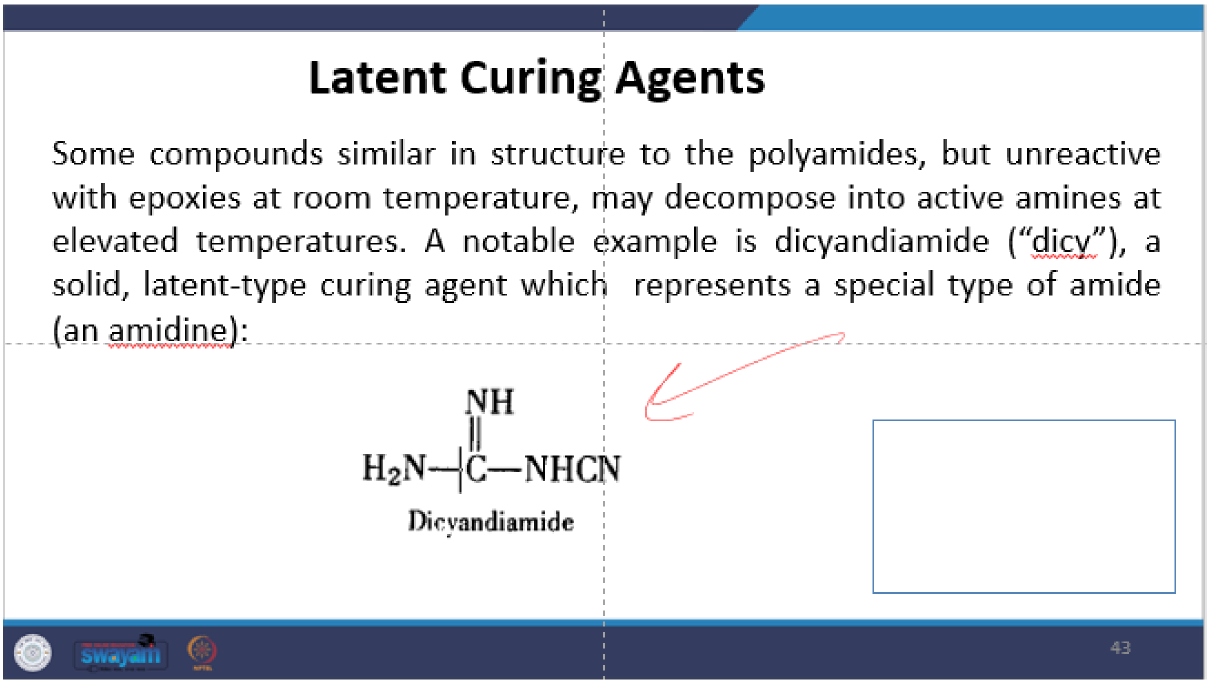
The hydrogen of the amide group is non-reactive due to its low acidity or reactivity. A typical structure of polyamide resin is based on dimerized linoleic acid or diethylene amine data. My example is dimer acid-based polyamide resin they derived from vegetable oil and polyamides. Now, trimer acid-based polyamide resin is derived from unsaturated fatty acids and polyamides. The polyamides based on the soybean oil and polyamines they are very much popular and they are also derived from the castor oil and polyamines.



Polymerization with Polyamide Resins

- Polyamides are resinous polymers used as epoxy-curing agents.
- They are based on vegetable oils and should not be confused with nylon-type polyamides.
- Epoxy-curing polyamides are condensation polymers of dimerized or trimerized vegetable oils or unsaturated fatty acids with polyamines.
- The amino groups in the polyamide structure, both primary and secondary, are epoxy reactive, not the amide groups.

And the specific structure and the properties of polyamide resin can vary depending upon the choice of vegetable oil, polyamine and reaction conditions. So, all the reaction parameters plays a very vital role respective of their soybean oil or castor oil or any kind of a vegetable oil which you are using. The presence of free secondary amine group here like this, this enables the cross linking of epoxy resin change. The reactive sites of cross linking they are located on the secondary amine groups and the R groups that can be either another linoleic dimer portion or a hydrogen atom.



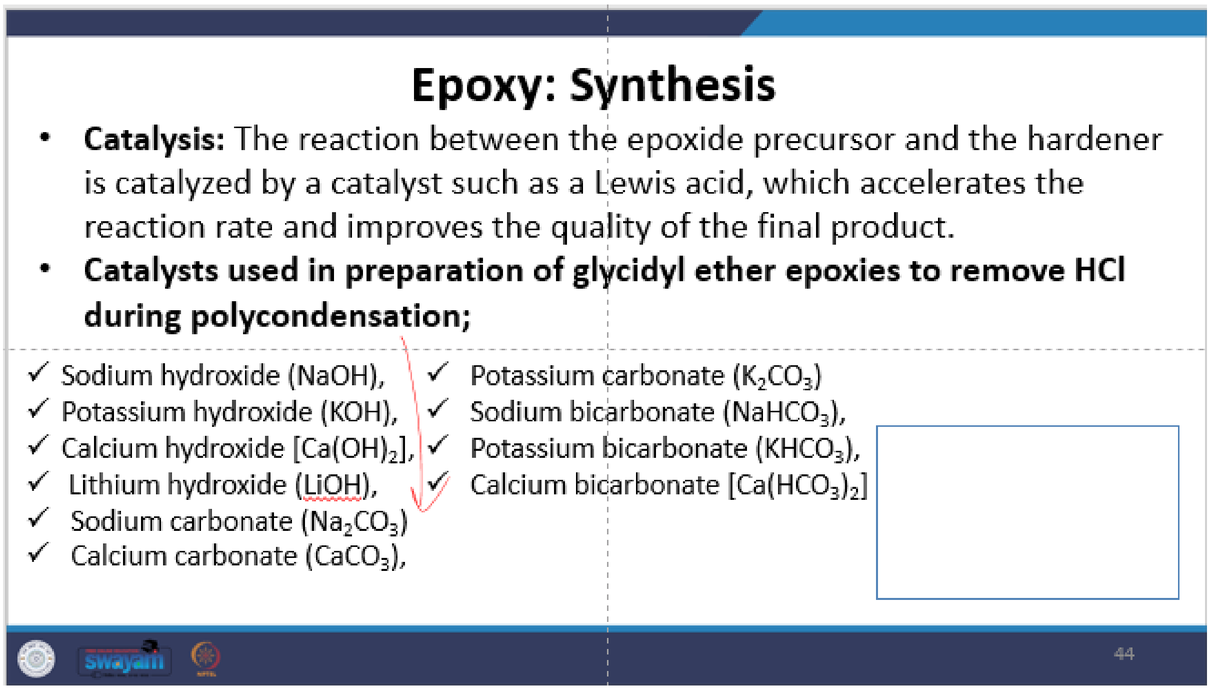
Latent Curing Agents

Some compounds similar in structure to the polyamides, but unreactive with epoxies at room temperature, may decompose into active amines at elevated temperatures. A notable example is dicyandiamide ("dicy"), a solid, latent-type curing agent which represents a special type of amide (an amidine):

$$H_2N-\overset{\overset{\displaystyle NH}{\|}}{C}-NHCN$$

Dicyandiamide

Now, let us talk about the latent curing agent. Now, some compound similar in structure to the polyamides, but unreactive with epoxies at room temperature may decompose into active latent type of curing agent which represents a special type of an amidine. Now, when we are talking about the synthesis, let us talk about the catalyst. The reaction between the epoxide precursor and the hardener is catalyzed by a catalyst like Lewis acid usually which accelerates the reaction rate and improves the quality of the final product. Now, catalyst used in the preparation of a glycidal ether epoxies to remove HCl during the poly condensation. So, there are various things can be used like sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium hydroxide, sodium carbonate, calcium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate and calcium bicarbonate.

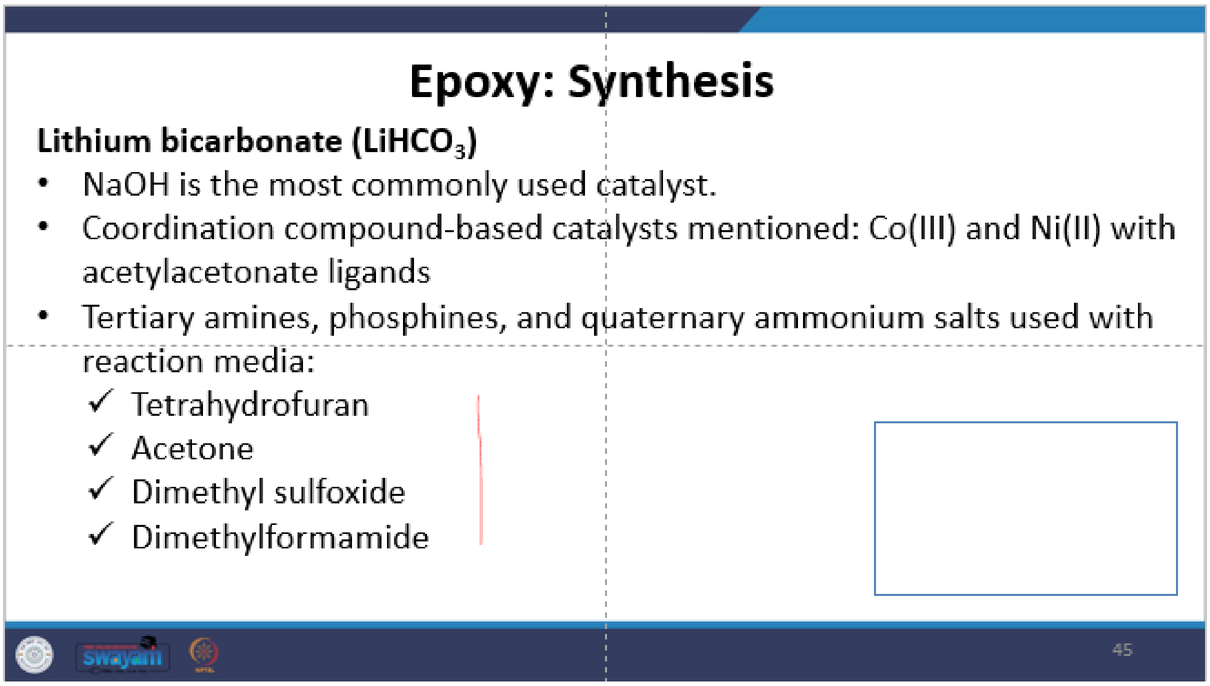


Epoxy: Synthesis

- **Catalysis:** The reaction between the epoxide precursor and the hardener is catalyzed by a catalyst such as a Lewis acid, which accelerates the reaction rate and improves the quality of the final product.
- **Catalysts used in preparation of glycidyl ether epoxies to remove HCl during polycondensation;**

✓ Sodium hydroxide (NaOH),
✓ Potassium hydroxide (KOH),
✓ Calcium hydroxide [$Ca(OH)_2$],
✓ Lithium hydroxide (LiOH),
✓ Sodium carbonate (Na_2CO_3)
✓ Calcium carbonate ($CaCO_3$),
✓ Potassium carbonate (K_2CO_3)
✓ Sodium bicarbonate ($NaHCO_3$),
✓ Potassium bicarbonate ($KHCO_3$),
✓ Calcium bicarbonate [$Ca(HCO_3)_2$]

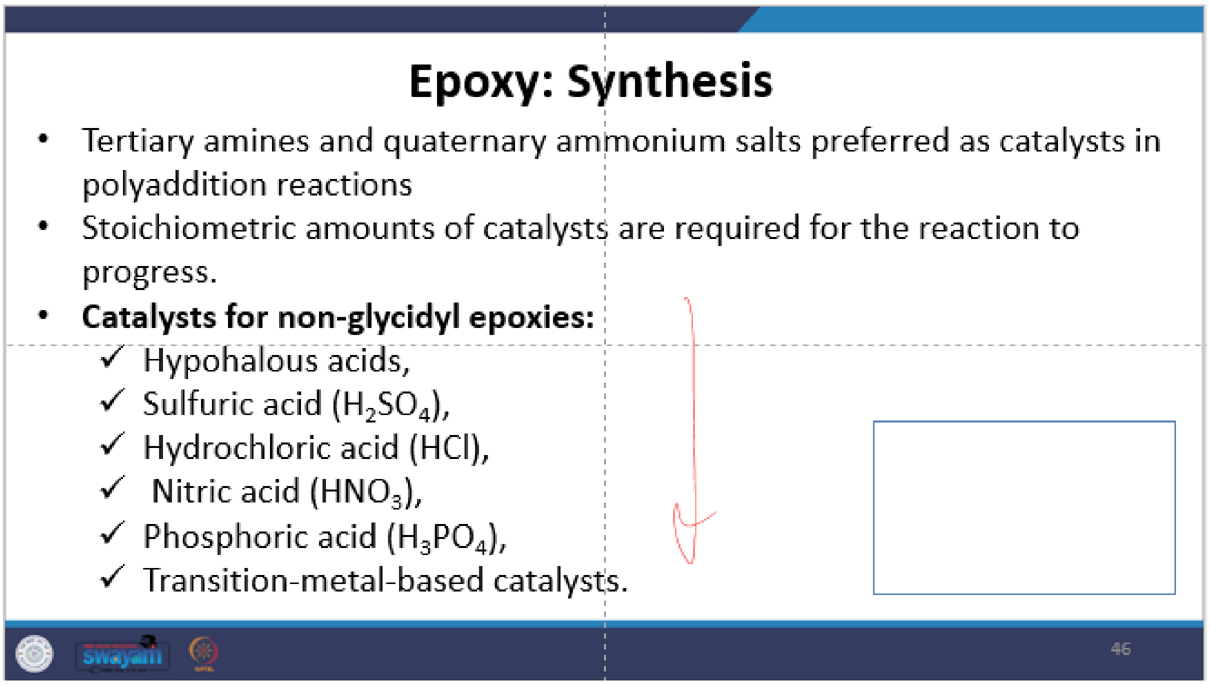
So, these can be used for the same. Lithium bicarbonate is one of the most popular and this is most commonly used catalysts. The coordination compound-based catalyst usually mentions cobalt or nickel with the acetylation is a ligand. Now, tertiary amines that phosphines and quaternary amine ammonium salts are used with the reaction media like tetrahydrofuran, acetone, dimethyl sulfoxide and dimethyl formamide. Tertiary amines and quaternary ammonium salts are preferred as catalysts in poly addition reactions. And the stoichiometric amount of catalyst they are required for the reaction to progress and the catalyst for the non-glycidal epoxies.



Epoxy: Synthesis

Lithium bicarbonate ($LiHCO_3$)

- NaOH is the most commonly used catalyst.
- Coordination compound-based catalysts mentioned: Co(III) and Ni(II) with acetylacetonate ligands
- Tertiary amines, phosphines, and quaternary ammonium salts used with reaction media:
  - ✓ Tetrahydrofuran
  - ✓ Acetone
  - ✓ Dimethyl sulfoxide
  - ✓ Dimethylformamide

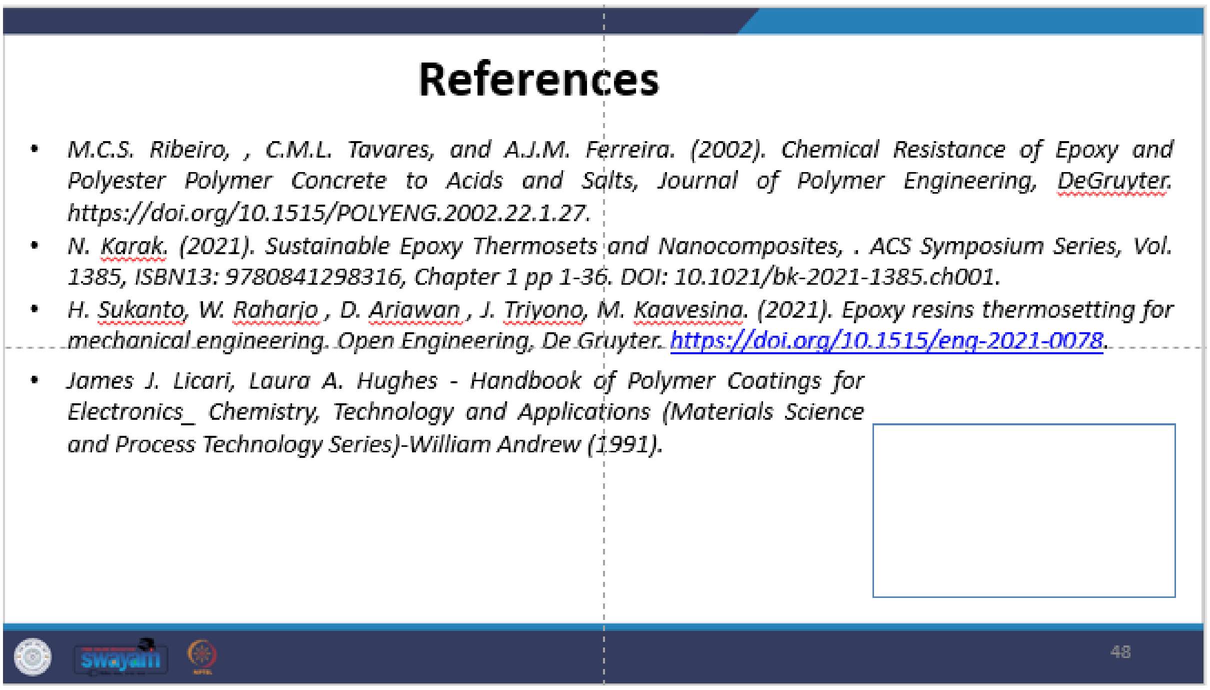


Epoxy: Synthesis

- Tertiary amines and quaternary ammonium salts preferred as catalysts in polyaddition reactions
- Stoichiometric amounts of catalysts are required for the reaction to progress.
- **Catalysts for non-glycidyl epoxies:**
  - ✓ Hypohalous acids,
  - ✓ Sulfuric acid (H_2SO_4),
  - ✓ Hydrochloric acid (HCl),
  - ✓ Nitric acid (HNO_3),
  - ✓ Phosphoric acid (H_3PO_4),
  - ✓ Transition-metal-based catalysts.

This can be used as the hypoalloy acid, sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid and transition base, transition metal-based catalyst. Now, catalysts that are used in pre-carboxylic acid based epoxidation reactions of vegetable oil or olefinic double bonds. Now, enzymes can also serve as a catalyst in these reactions. Let us talk about the post-curing. After the initial reaction is complete, the epoxies may undergo a post-curing process to improve their mechanical properties, thermal stabilities, and chemical resistance.

Now, this is achieved by subjecting to epoxies at elevated temperatures for a certain period of time. So, dear friends, in this particular segment, we discussed all aspects of epoxies, which are again an integral part of electronics applications, especially in polymers. We discussed the classification, we discussed different mechanism, we discussed different processes like initiation, propagation and all those things.



References

- *M.C.S. Ribeiro, , C.M.L. Tavares, and A.J.M. Ferreira. (2002). Chemical Resistance of Epoxy and Polyester Polymer Concrete to Acids and Salts, Journal of Polymer Engineering, DeGruyter. https://doi.org/10.1515/POLYENG.2002.22.1.27.*
- *N. Karak. (2021). Sustainable Epoxy Thermosets and Nanocomposites, . ACS Symposium Series, Vol. 1385, ISBN13: 9780841298316, Chapter 1 pp 1-36. DOI: 10.1021/bk-2021-1385.ch001.*
- *H. Sukanto, W. Raharjo , D. Ariawan , J. Triyono, M. Kaavesina. (2021). Epoxy resins thermosetting for mechanical engineering. Open Engineering, De Gruyter. https://doi.org/10.1515/eng-2021-0078.*
- *James J. Licari, Laura A. Hughes - Handbook of Polymer Coatings for Electronics_ Chemistry, Technology and Applications (Materials Science and Process Technology Series)-William Andrew (1991).*

And for your convenience, we have listed a couple of references which you can utilize if required. Thank you very much.