Polymer Process Engineering
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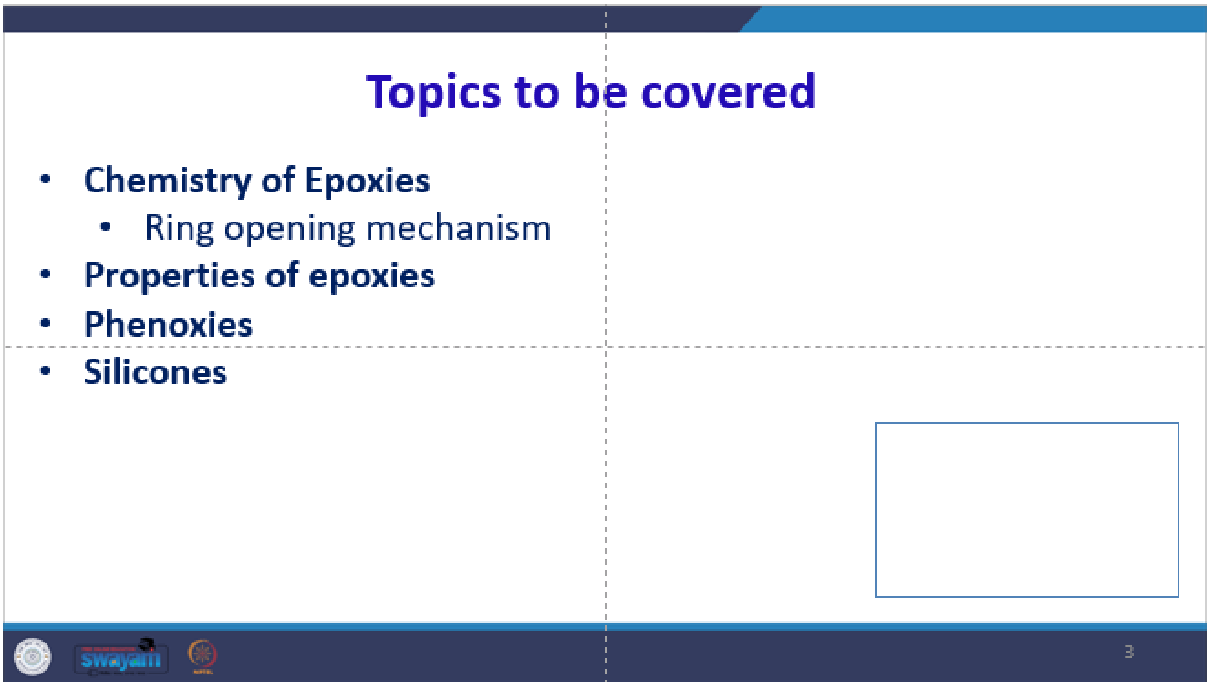
Lecture- 48
Epoxies, Phenoxies, and Silicones

Hello friends, welcome to the epoxies, phenoxies and silicon, under the edges of polymer process engineering. Now, before we go into detail, let us have a look at what we discussed in the previous. segment. The previous segment was devoted to the epoxies, where we discussed the introductory part of epoxies they use in the polymeric system. Then, we discussed the classification scheme of epoxies and then how we can synthesize the epoxies.



In this particular segment, we are going to discuss the chemistry aspect of epoxies, like ring opening mechanism, then we will discuss the properties of epoxies, then phenoxies will be discussed, and silicones. All these things are very important, especially when we deal the polymers in electronics applications. So, let us discuss the chemistry of epoxies. The chemistry of epoxies is based primarily on the high reactivity of the strained 3-membered epoxy, and they are called the auxiliary rings.

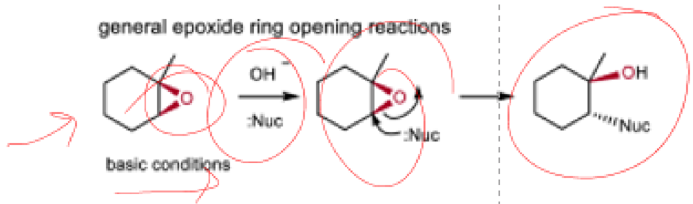
The Chemistry of Epoxies

- The chemistry of epoxies is based primarily on the high reactivity of the strained three-membered epoxy (also called oxirane) ring.
- With acidic or alkaline compounds or compounds containing active hydrogen atoms, the epoxy ring opens up and a polymerization reaction takes place, resulting in useful epoxy coatings, adhesives, encapsulants, and laminates.
- Besides the epoxy group, the pendant hydroxyl groups of an epoxy resin are also reactive, and further cross-linking or lengthening of the polymer chain can occur through these groups.

Now, with the acidic or alkaline compounds or compounds containing active hydrogen atoms, the epoxy ring opens up, and a polymerization reaction takes place. This results in the useful epoxy coating, adhesive encapsulants, and laminates. Besides the epoxy group, the pendant hydroxyl group of an epoxy resin they are also reactive, and for the crosslinking or the length of the polymer chain, can occur through these groups. So, if you need to widen the chain length or make more and more lengthening, then this kind of protocol can be used. Let us talk about the ring opening of epoxides with strong nucleophiles.

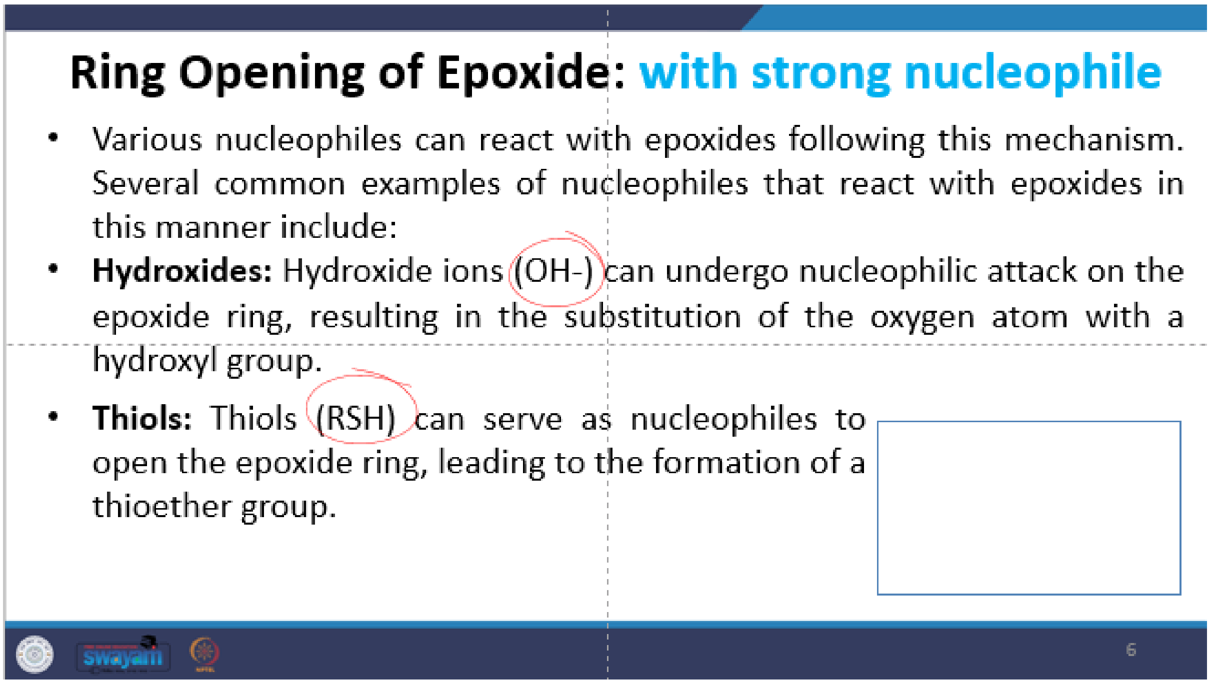
Ring Opening of Epoxide: with strong nucleophile

- Epoxides undergo ring-opening reactions through a **concerted mechanism** in which the oxygen atom of the epoxide serves as the leaving group. The resulting product contains an alkoxy group, requiring an aqueous or mild acidic work-up to obtain a neutral species.
- In the concerted mechanism, the nucleophilic attack and the departure of the leaving group occur simultaneously.



The epoxide undergoes the ring-opening reaction through a concerted mechanism in which the oxygen atom of the epoxide serves as a leaving group and the resulting product contains the alkoxy group. This requires an aqueous or mild acidic workup to obtain a neutral species. So, the concerted mechanism, the nucleophilic attack, and the departure of the leaving group occur simultaneously.

Here, you see that this is oxygen, and if we go for this base under the basic condition, the ring opening takes place. Now, various nucleophiles can react with the epoxides following the mechanism and several common examples of nucleophiles that react with the epoxides in this manner.



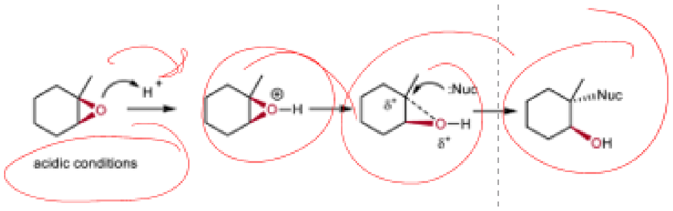
This includes the hydroxides, the hydroxide ion OH minus; this can undergo the nucleophilic attack on the epoxide ring and result in the substitution of oxygen atom with hydroxyl group. And thiols sometimes referred as RSH, can serve as a nucleophile to open the epoxide ring, leading to the formation of a thioether group. Then cyanides, cyanide ions referred to as CN minus, can act as a nucleophile and react with epoxides, leading to the formation of cyanohydrin products. Grignard regions, the Grignard regions such as alkyl or aryl magnesium halides, and referred as RNGX, can undergo the nucleophilic addition to epoxide, resulting in the formation of alcohols. Then lithium aluminum hydroxide referred as LiAlH4, this is a powerful reducing agent and that can react with epoxides leading to the formation of alcohols by reduction of oxygen atom.

Cont…

- **Cyanides:** Cyanide ions (CN-) can act as nucleophiles and react with epoxides, leading to the formation of a cyanohydrin product.
- **Grignard reagents:** Grignard reagents, such as alkyl or aryl magnesium halides (RMgX), can undergo nucleophilic addition to epoxides, resulting in the formation of alcohols.
- **$LiAlH_4$:** Lithium aluminum hydride ($LiAlH_4$) is a powerful reducing agent that can react with epoxides, leading to the formation of alcohols by reduction of the oxygen atom.

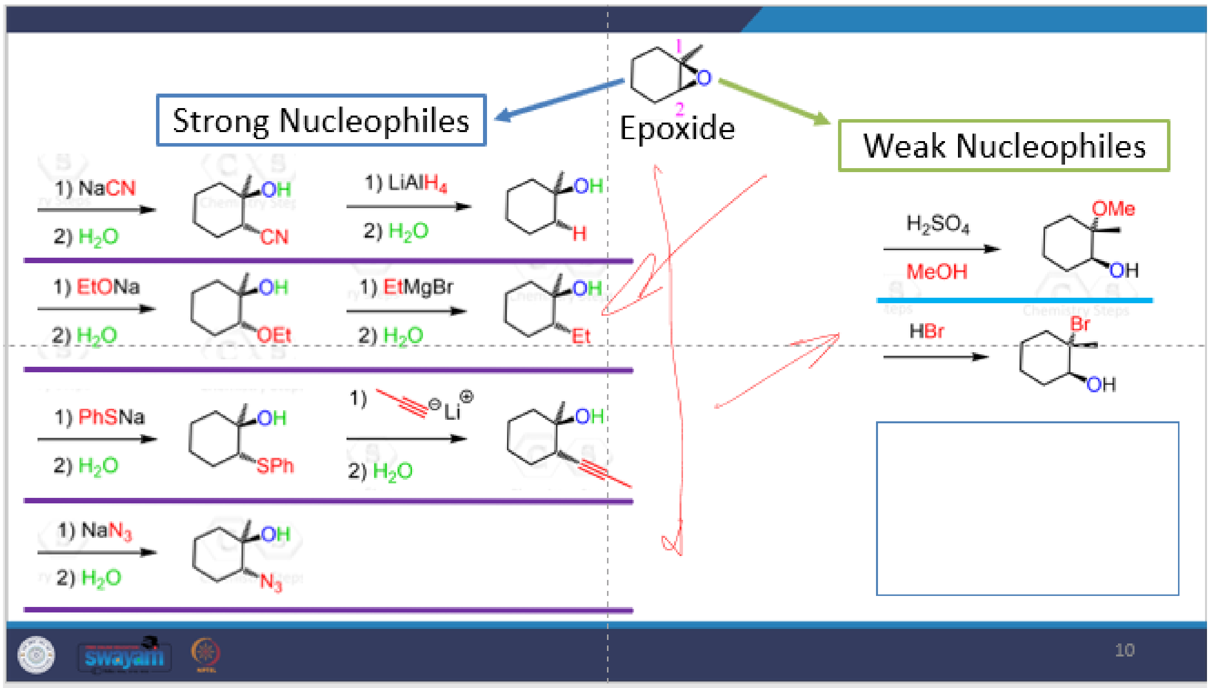
Ring Opening of Epoxide: with weak nucleophile

- When a weak nucleophile is used in acidic conditions, the nucleophilic attack occurs at the more substituted carbon which is consistent with the step-wise mechanism.
- In step-wise mechanism the nucleophilic attack happens only after the loss of the leaving group.

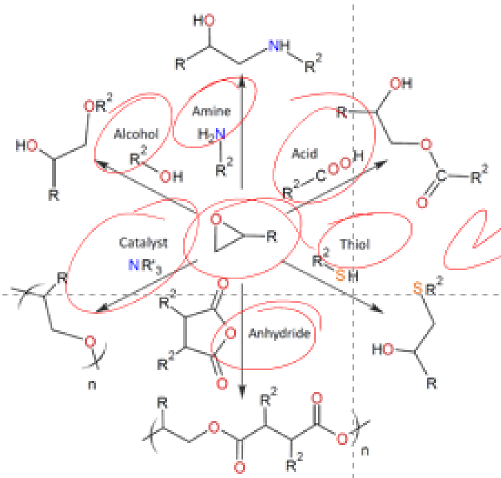


Now, let us talk about the ring opening of epoxide with weak nucleophiles. When a weak nucleophile is used in acidic conditions, the nucleophilic attack occurs at more substituted carbon, which is consistent with the stepwise mechanism. In the stepwise mechanism, the nucleophilic attack happens only after the loss of the leaving group. Now, here you see that we have maintained the acidic condition H plus, this is removing and then this form of this radical and got this one. Now, these are mainly of HX type of acid, which first protonates the epoxide thus making it more reactive since the oxygen is now a better leaving group.

After protonation, the halide attacks and opens the epoxide ring, forming an alcohol with an adjacent halide. Here you can see this particular thing. Now, here we have enlisted certain strong nucleophiles and weak nucleophiles like NaCnH2 to react with this one. So, these are some of the strong nucleophiles, and here are the weak nucleophiles. Now, this is the best example of ring-opening copolymerization and the cross-linking of epoxide with a different functional group like anhydride, we have used thiols, we have used amines, we have used alcohols with the help of catalysts and acids.



So, you can have a broad spectrum over here. Now, sometimes we are using the enzymes for the ring opening of epoxide. Now, the ring opening of epoxide can be catalyzed by various enzymes including epoxide, hydrolase like EHS and lipases. Now, epoxide hydrolysis, they are enzymes that specifically target the and hydrolyze the epoxide bonds and they promote the addition of water molecule across the epoxy group and resulting the formation of diols or vicinal hydroxyl groups. So, here you can see this enzymatic epoxide ring opening by epoxide hydrolysis or oxidoreduces then you can see over here.



Example: Ring-opening copolymerization and crosslinking of epoxides with different functional groups.

Image source: Polymerdatabase.com

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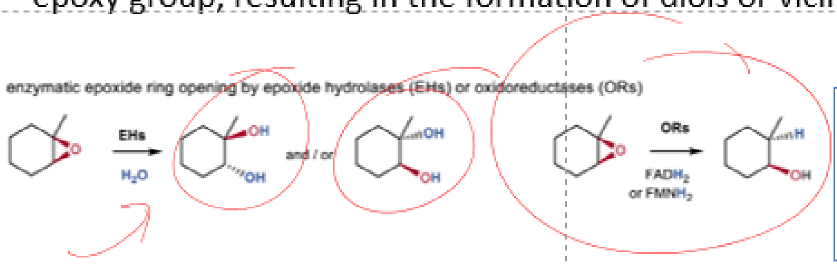
Now, the enzymatic ring opening of epoxide they offer several advantages compared to the traditional chemical method. Now, this includes the mild reaction conditions typically at ambient temperature and a neutral pH. They offer the high selectivity towards the specific epoxide substrates and avoidance of harsh chemical or hazardous regions. The enzymatic ring opening reactions they can be used for the synthesis of various valuable compounds. For example, it is implied that in the production of chiral building blocks, a pharmaceutical intermediate and the functionalized polymers.

Ring Opening of Epoxide: using Enzymes

- The ring-opening of epoxides can be catalyzed by various enzymes, including epoxide hydrolases (EHs) and lipases.
- Epoxide hydrolases are enzymes that specifically target and hydrolyze epoxide bonds. They promote the addition of a water molecule across the epoxy group, resulting in the formation of diols or vicinal hydroxyl groups.



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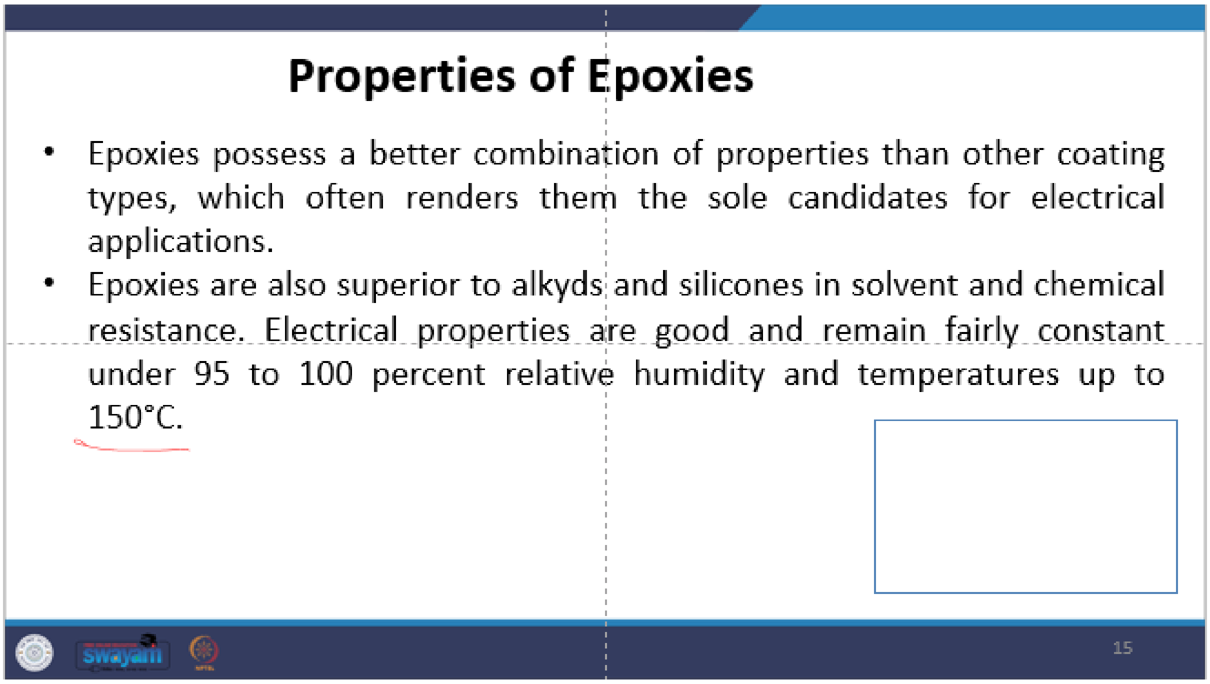
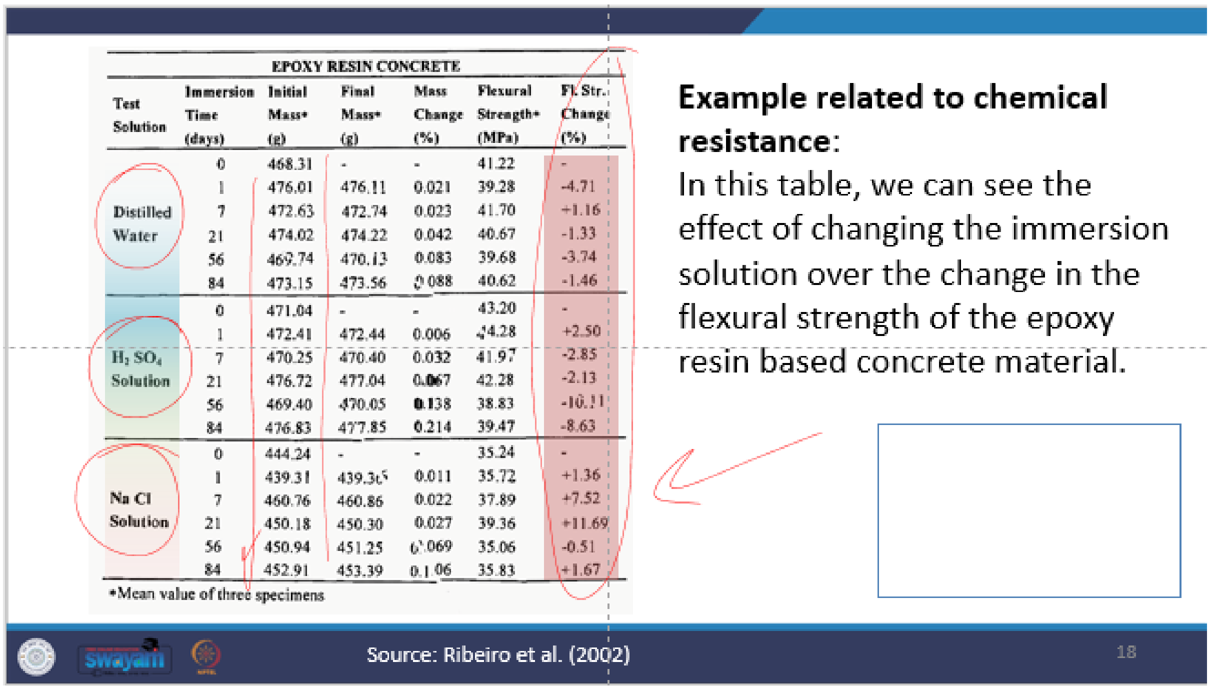
The use of enzyme allows the production of in geometrically pure products due to the inherent stereoselectivity of enzymatic reactions. Let us talk about the properties of epoxies. Now, epoxies possess a better combination of properties than other coating types, which often renders them the sole candidates for electrical application. Epoxies are also superior to alkytes and silicones in the solvent and are chemically resistant. The electrical properties are good and remain fairly constant under 95 to 100 percent relative humidity and the temperature up to say 150 degree Celsius.



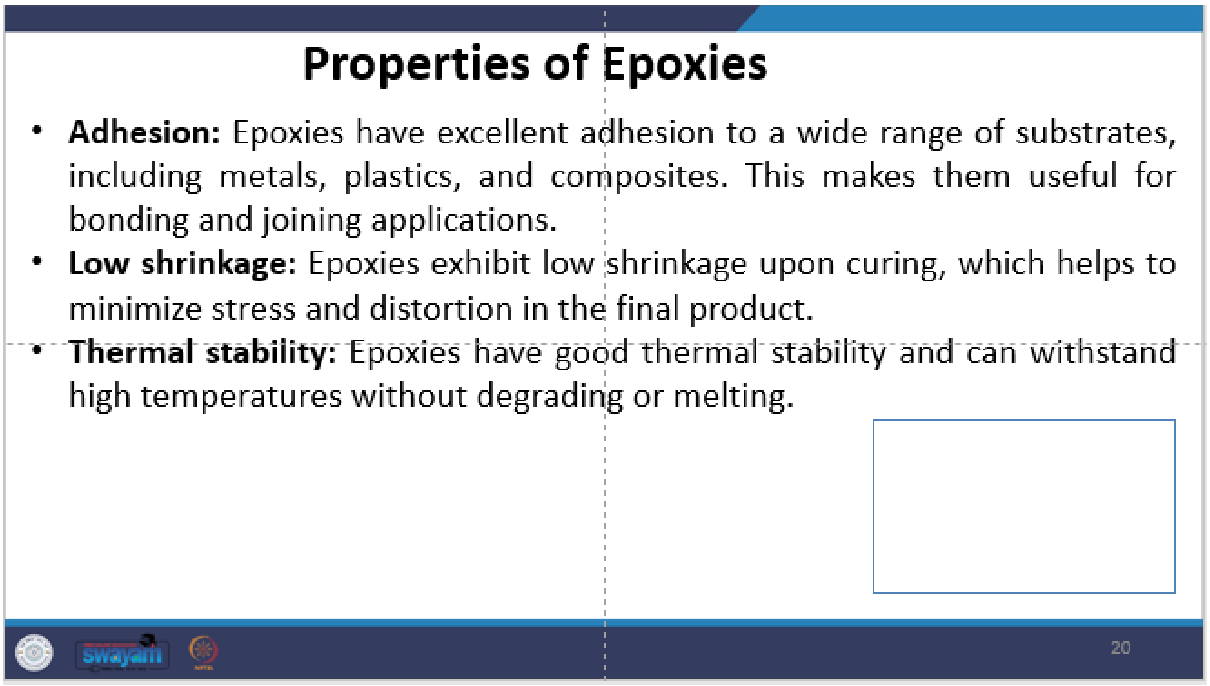
Therefore, three properties which single out epoxies from other coating types like one excellent addition to the wide variety of substrate under many environmental conditions, an excellent resistance to moisture, salt spray, organic solvent and chemicals and good electrical characteristics and stability of these parameters under various environmental conditions, notably moisture and temperature. Some of the key properties of epoxy includes also includes the high strength and epoxies are known for their exceptional mechanical properties including high strength stiffness and toughness and they can withstand high stresses and strains without breaking or deforming. Then the chemical resistance, epoxies are highly resistant with to a wide range of chemicals including acids, bases, solvent and fuels. Now this makes them ideal for use in harsh environment where exposure to chemical is in question. Now there are several examples this related to the chemical resistance.



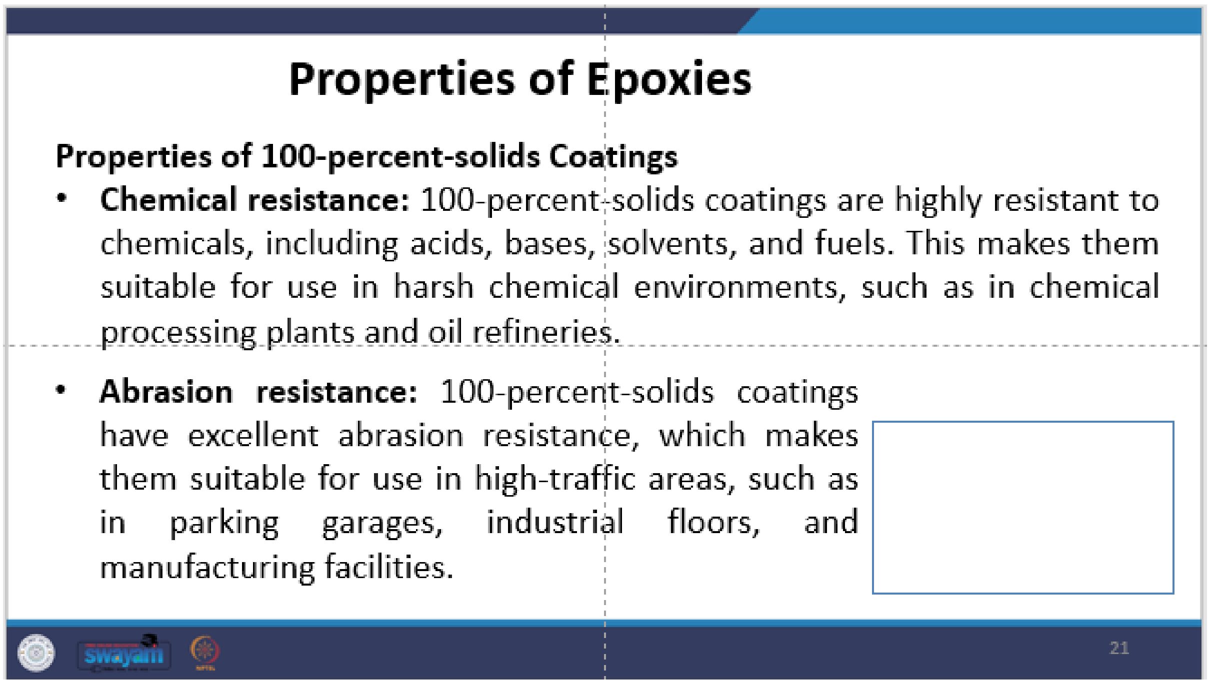
EPOXY RESIN CONCRETE						
Test Solution	Immersion Time (days)	Initial Mass* (g)	Final Mass* (g)	Mass Change (%)	Flexural Strength* (MPa)	Fl. Str. Change (%)
Distilled Water	0	468.31	-	-	41.22	-
	1	476.01	476.11	0.021	39.28	-4.71
	7	472.63	472.74	0.023	41.70	+1.16
	21	474.02	474.22	0.042	40.67	-1.33
	56	469.74	470.13	0.083	39.68	-3.74
	84	473.15	473.56	0.088	40.62	-1.46
H_2SO_4 Solution	0	471.04	-	-	43.20	-
	1	472.41	472.44	0.006	44.28	+2.50
	7	470.25	470.40	0.032	41.97	-2.85
	21	476.72	477.04	0.067	42.28	-2.13
	56	469.40	470.05	0.138	38.83	-10.11
	84	476.83	477.85	0.214	39.47	-8.63
Na Cl Solution	0	444.24	-	-	35.24	-
	1	439.31	439.3[illegible]	0.011	35.72	+1.36
	7	460.76	460.86	0.022	37.89	+7.52
	21	450.18	450.30	0.027	39.36	+11.69
	56	450.94	451.25	0.069	35.06	-0.51
	84	452.91	453.39	0.106	35.83	+1.67

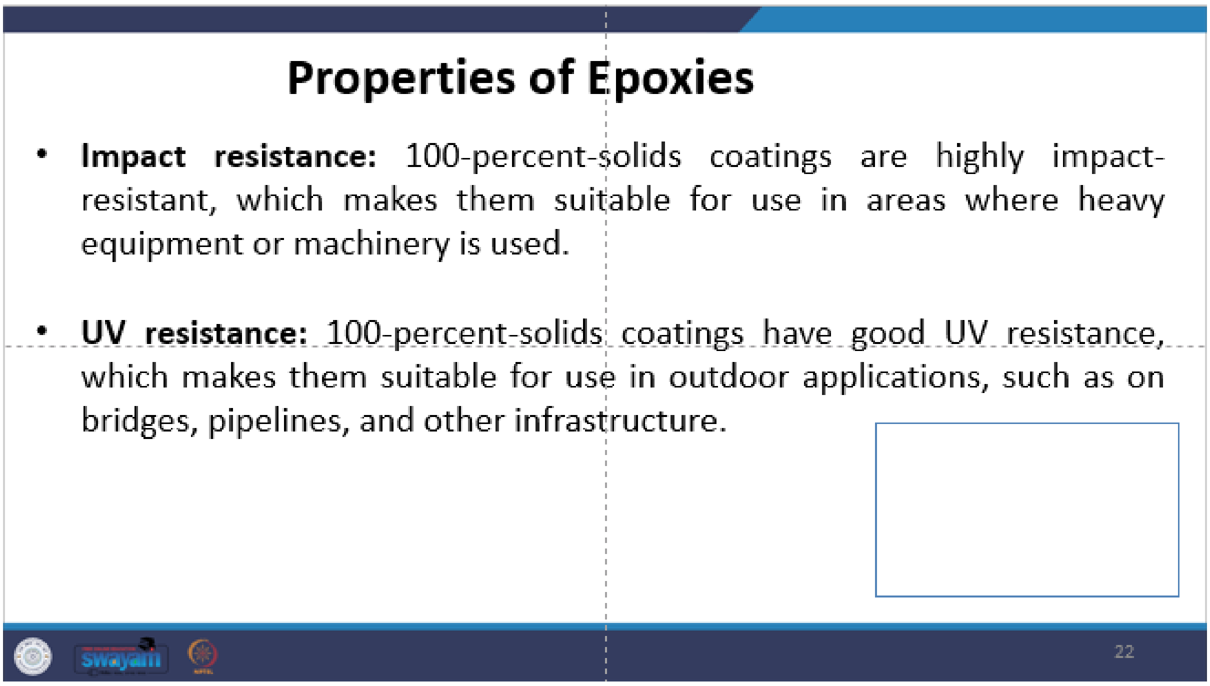
*Mean value of three specimens

So, in this particular table we can see the effect of changing the immersion solution over the change in the flexural strength of epoxy resin based concrete materials. Like we have prepared the stress solution of distilled water or H 2 SO 4 solution or NACL solution and with the varying immersion time with the initial mass which is enlisted and final mass and you can see the change in the flexural strength with respect to the percentage. Now if we compare the flexural strength of the concrete material for say 84 days in some of the scientists they have carried out this experiment and this 84 days of immersion in different testing solution it can be observed that the water and acid decrease the strength to 1.46 to say 8.63 percent respectively while salt immersion leads to improving the strength of the material.

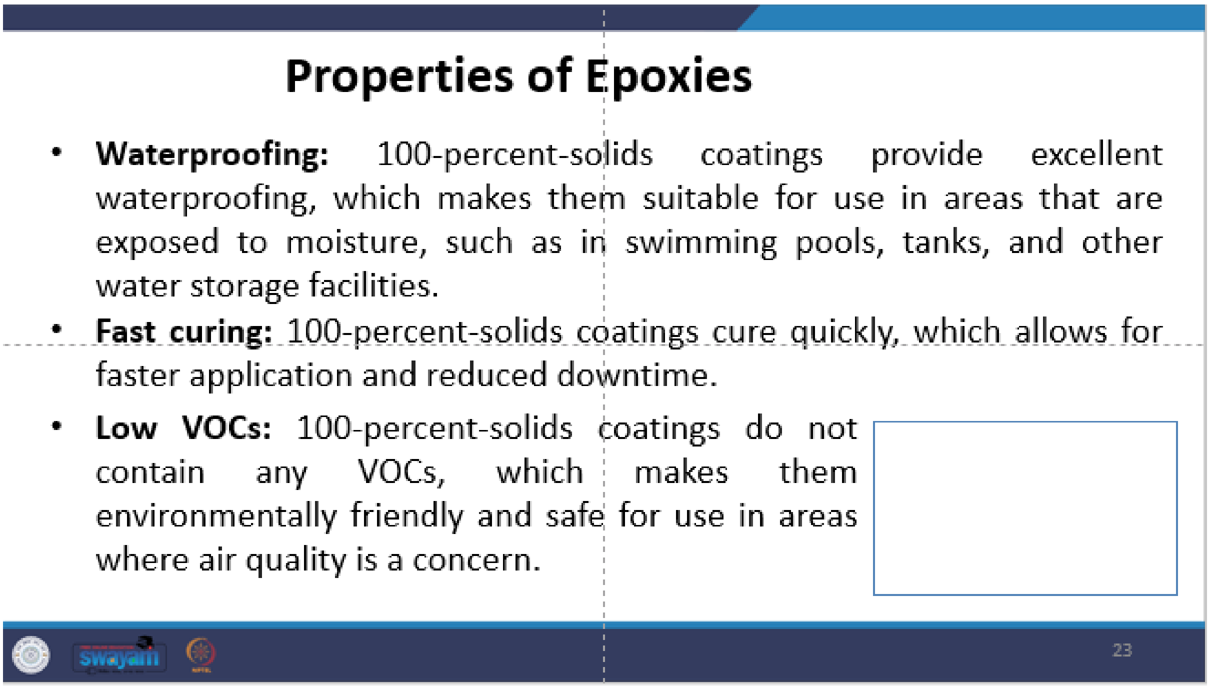


Now adhesion, adhesion the epoxies they have the excellent adhesion to a wide range of substrate including metals, plastics and components and this make them useful for bonding and joining application. Low shrinkages, the epoxies exhibit low shrinkage upon curing which helps to minimize stress and distortion in the final product. Thermal stability, epoxies they have the good thermal stability and can withstand at high temperatures without degrading or melting. Now sometimes we talk about the properties of 100 percent solid coating, the chemical resistance a 100 percent solid coating they are highly resistant to chemicals this including acid, bases, solvent and fuels and this makes them suitable for the use in harsh chemical environment like chemical processing plants or oil refineries. Then abrasion resistance, abrasion is very good properties to be look into.





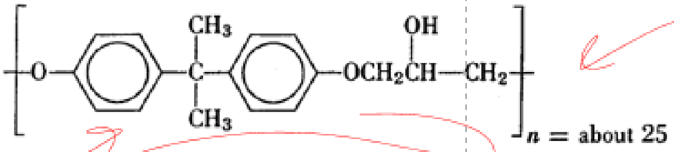
So, abrasion resistance 100 percent solid coating they have excellent abrasion resistance which makes them suitable for use in high traffic areas such as in parking garage, industrial floors, manufacturing facilities, digging operations all these things. The impact resistance, the 100 percent solid coating they are widely impact resistant which makes them suitable for use in area where heavy equipment or machinery is used. The UV resistance 100 percent solid coating have the good UV resistance which makes them suitable for the use in outdoor application like as on bridges, pipelines and other type of infrastructural projects. Then waterproofing 100 percent solid coating provides the excellent waterproofing which makes them suitable for use in areas that are exposed to moisture like in swimming pools, tanks and other water storage facilities. Fast curing 100 percent solid coating cure quickly with which allows for faster application and reduced downtime.



Low VOCs volatile organic contents the 100 percent solid coating do not contain any VOCs which makes them environmentally friendly because VOCs creates a lot of environmental problem especially when any human being inhales then it creates a lot of problem. So, they do not contain any VOCs that is why they are safe for the use in area where the air quality is in question or concerned. Phenoxes the phenoxes they are also known as phenyl ether resins and they are the type of the thermosetting resins which are similar in a structure to epoxies. They are prepared from dihydric phenols and epichlorohydrin presence of caustic. Now the commercially available coating utilizes bisphenol A as the dihydric phenol and their structure may be represented like this.

PHENOXIES

- Phenoxies, also known as phenyl ether resins, are a type of thermosetting resin that are similar in structure to epoxies. They are prepared from dihydric phenols and epichlorohydrin in the presence of caustic.
- Commercially available coatings utilize bisphenol A as the dihydric phenol, and their structure may be represented as

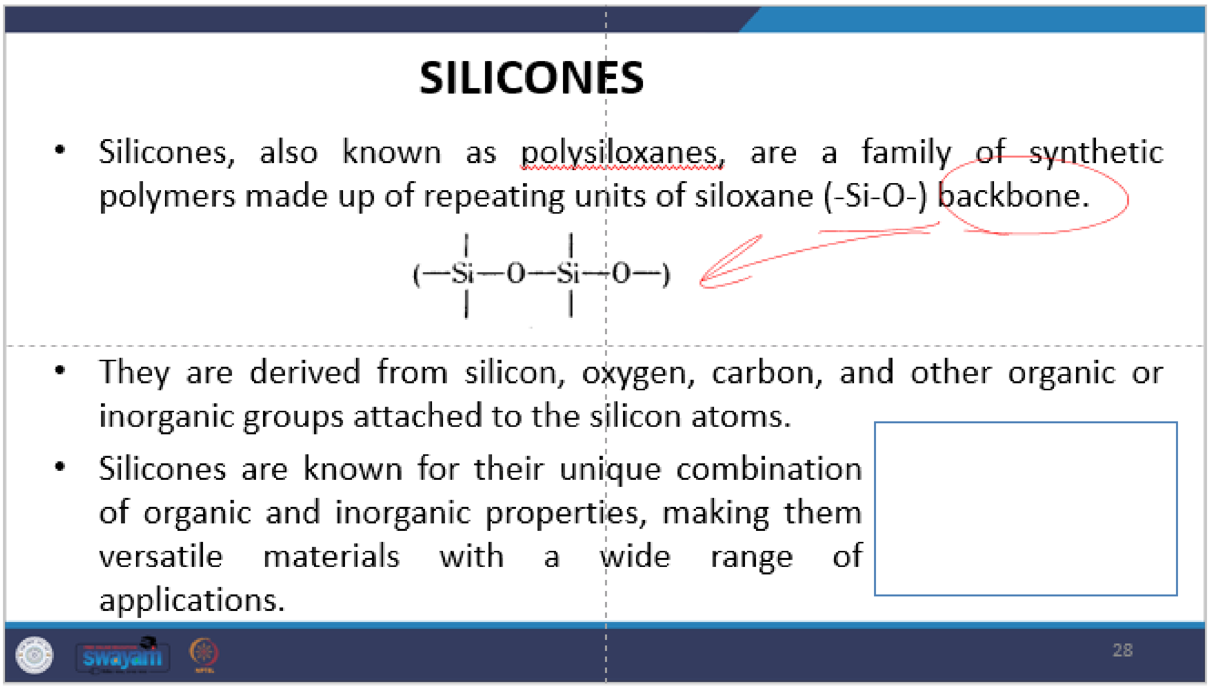


Typical phenoxy resin structure

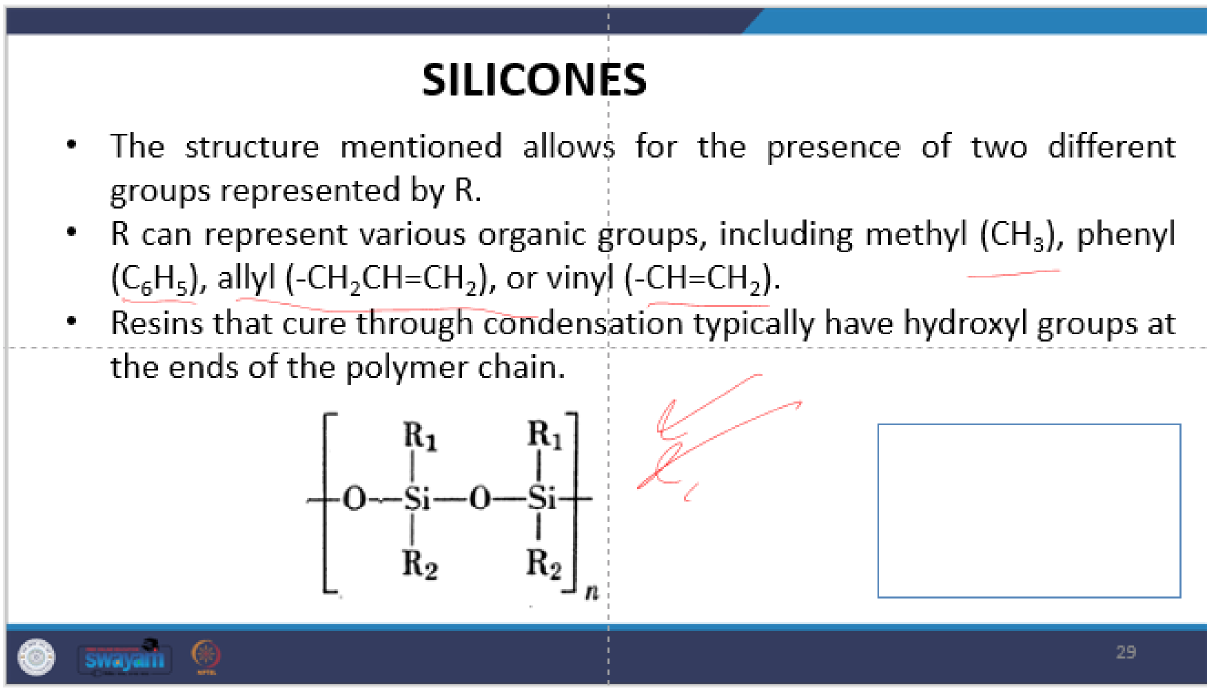
Source: Licari and Hughes (1991), Handbook of polymer coatings

Now you see this is the typical phenoxy resin structure. Now resins for the coating they have the linear thermoplastic polymers with the molecular weight of 80000 to 2 lakhs. The coatings are applied from the solution forming film 0.4 to over 2 mils thick upon the solvent evaporation and different formulations are available with varying drying times depending on the organic solvents which are being used. Coatings with methyl ethyl ketone solvent dry very fast because of low boiling point of methyl ethyl ketone solvent.

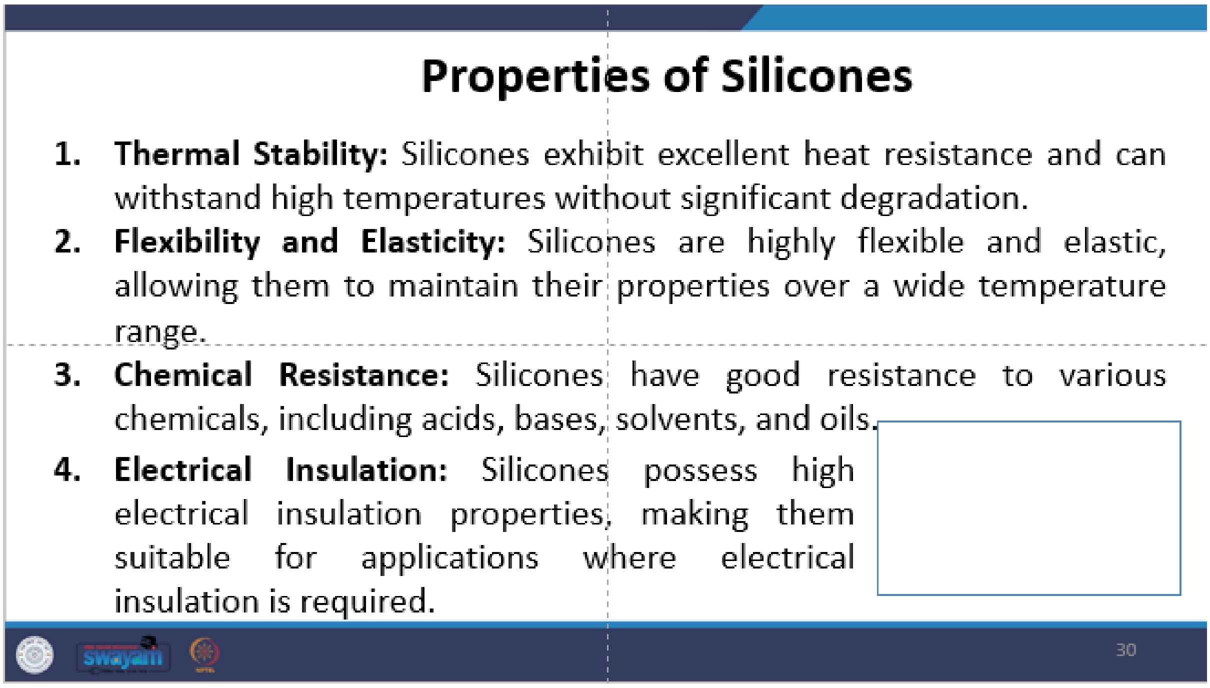
Now while those these cellulose acetates they are slower and intermediate drying times can be achieved by using blends of these two solvents. Phenoxy coatings they have the limited uses in electrical or electronic application and they are commonly used as coating for can lining and as a primer for epoxy vinyl or acrylic top coats. The electrical and physical properties of phenoxy coatings are favorable under ambient conditions. Now these properties deteriorate rapidly when exposed to the temperature above 80 degree Celsius. So, 80-degree Celsius temperature is the limiting temperature sometimes.



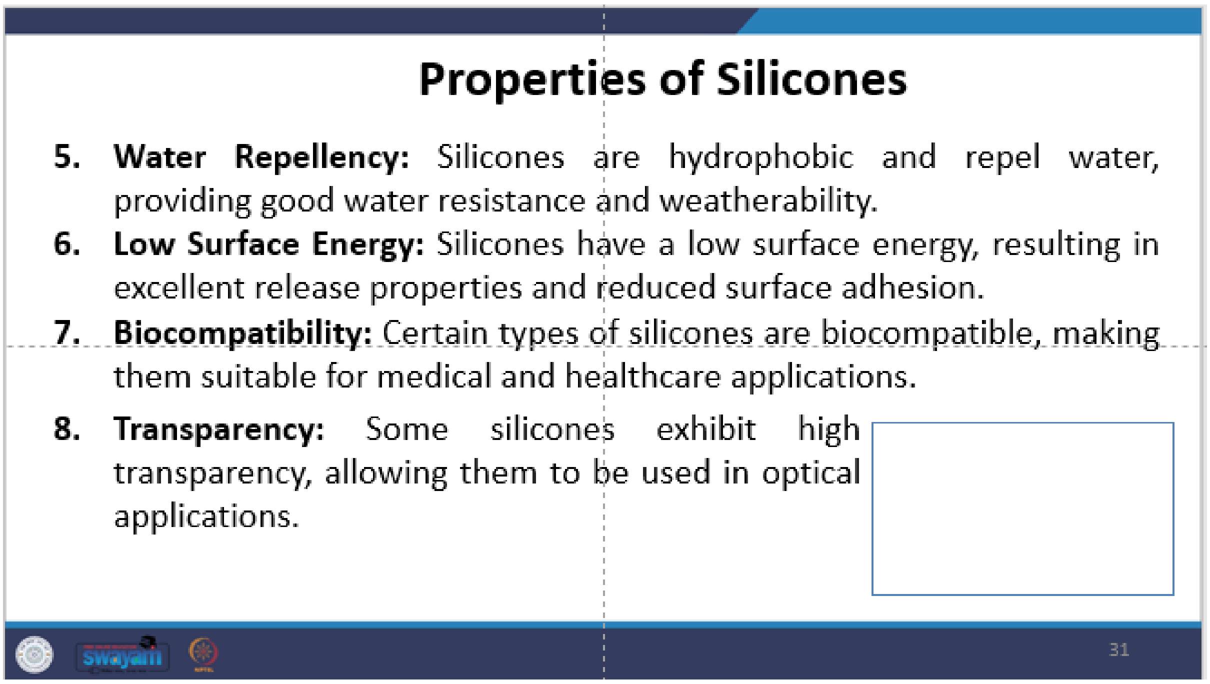
Now phenoxy coating face challenges related to the complete solvent release leading to the quick formation of a surface film and entrapment of solvent within the coating. Let us talk about the silicones. Silicones they are also known as polysiloxanes and they are the family of synthetic polymers made up of repeating units of siloxane SIO backbone like this SIO, SIO. And they are derived from silicon, oxygen, carbon and other organic or inorganic group attached to the silicon atom. And silicones are known for their unique combination of organic and inorganic properties making them versatile material with a wide range of applications.



The structure which we mentioned this allows for the presence of two different groups represented by R. Now this R can be represented various organic group including methyl, phenyl, C2H6, allyl, C2H2, CH2, CH2, double bond CH2, adobenyl, CH, double bond CH2 and reasons that cure through condensation typically have the hydroxyl group at the end of the polymer chain. Now let us talk about the various properties attached to the silicones. One important property is the thermal stability. Now the silicon exhibits excellent heat resistance and can withstand with the high temperature without significant degradation.

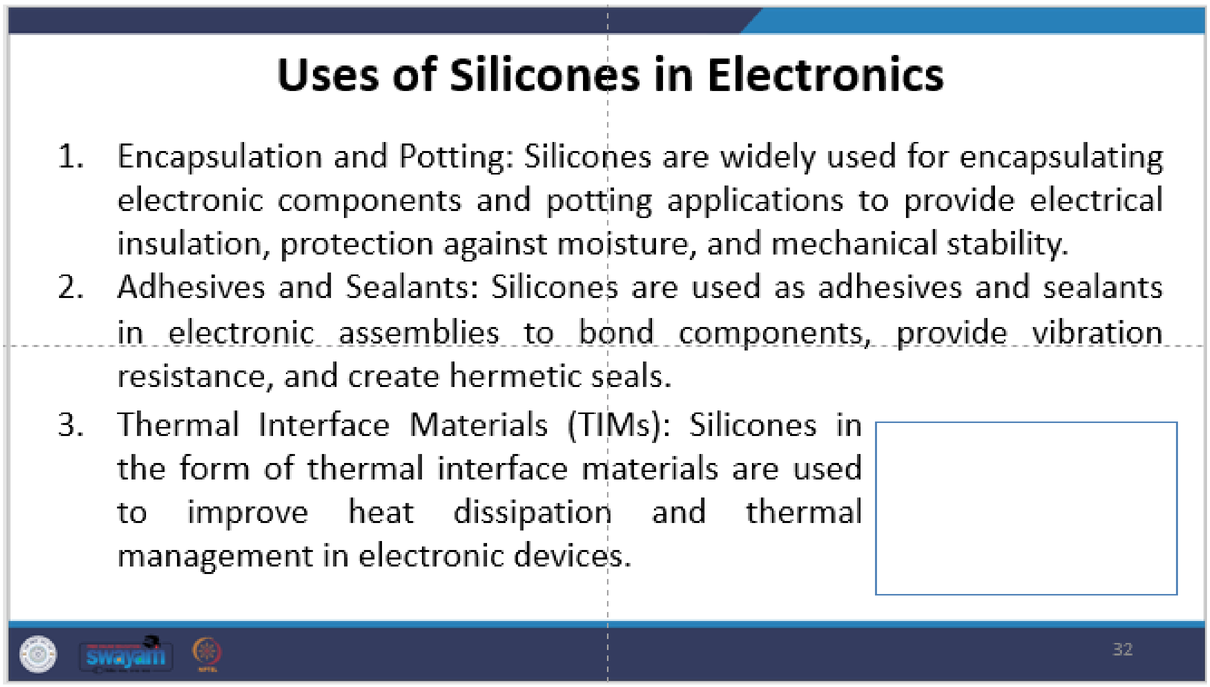


Another property in question is the flexibility in elasticity. The silicones are highly flexible and elastic in nature and that allows them to make maintain their properties over a wide temperature range. Then the chemical resistance, the silicones have a good resistance to various chemicals this including acid, bases, solvent, oils. So, they create a barrier in such a way. Then electrical insulation, silicon they possess high electrical insulation properties making them suitable for application where electrical insulation is required.



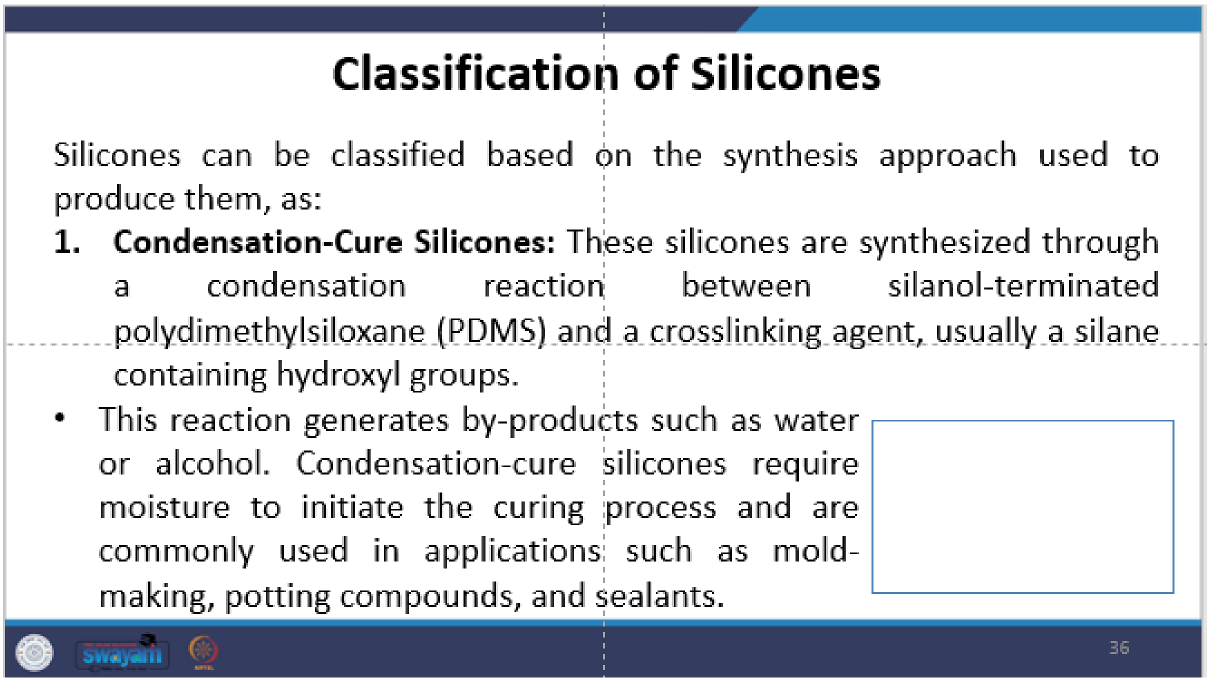
Then water repellency, the silicones they are hydrophobic in nature and repel water. This provide the good water resistance and weatherability. So, the shelf life can be enhanced. Then lower surface energy, silicon has a low surface energy resulting in excellent release property and reduced surface adhesion. Biocompatibility, the certain type of silicones they are biocompatible in nature and making them suitable for the medical and healthcare application.

The transparency, some silicon exhibits high transparency allowing them to use in the optical application. So, you see that a wide spectrum of uses are there. Then let us talk about the use of silicones in the electronics. The encapsulation and potting, the silicones are widely used in encapsulating electronic components and potting applications to provide the electrical insulation, protection against the moisture and mechanical stability. The adhesive and sealant, the silicones are used as adhesive and sealant in electronic assemblies to bond components, provide vibration resistance and create hermetic seals.

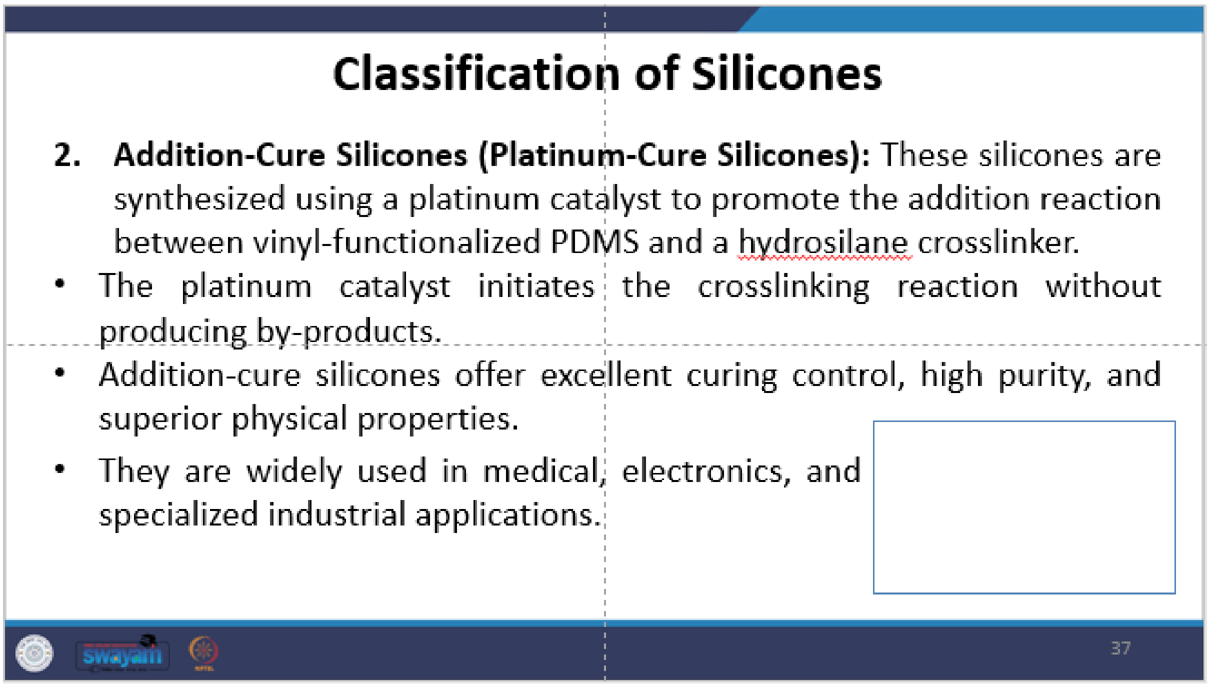


Thermal interface materials, TIMs, and silicon in the form of thermal interface material are used to improve heat dissipation and thermal management in electronic devices. Gaskets and O-rings, silicones are utilized as gasket and O-rings to provide effective sealing and protection against environmental factors in electronic systems. Conformal coating, the silicon-based conformal coatings are applied in the printed circuit board to protect against moisture, dust and chemicals while maintaining the electrical insulation properties. Then membrane and diaphragm, the silicon find application in the membrane and diaphragm for sensors, switches, and actuators due to their flexibility, durability and compatibility with various fluids. Some typical applications they are including insulation for heating cables, insulation for wire, hookup, aircraft, and ignition, then circuit board coating and welded module conformal coatings also referred to as dip or freeze coating, then semiconductor junction coating, then electronic component protective coating, water repellency, then impregnation varnishes for coil, stators, rotors, generators, transformers, varnishes for flexible mica sheets, mica tape, glass cloths, leavings, then the clear or pigmented corrosion protective coatings, ablative coatings, insulating coating for power supplies, connectors, relays, magnetic amplifiers, gel coating for integrated circuits.

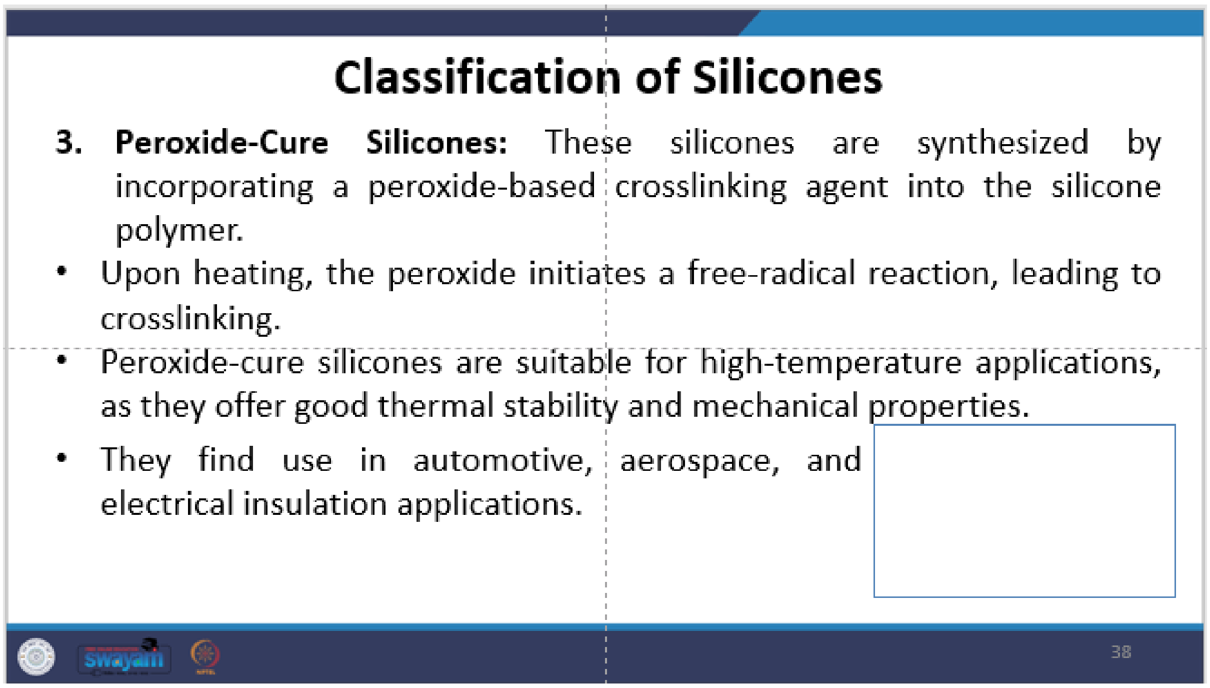
Now, the unique property of silicones make them more valuable material in the electronic industries enabling to protection, insulation, reliable functioning of electronic components and devices. Now, when silicones they are widely used, then it is a prime responsibility to get it classified. So, there are various classification scheme of silicones and these can be classified based on the synthesis approach used to produce them like condensation-cured silicones. These silicones are synthesized through a condensation reaction between the cinalol-terminated polydimethylsiloxane PDMS and cross-linking agent usuryicilane containing hydroxyl group. Now, this reaction generates byproducts such as water or alcohol and condensation-cured silicon require moisture to initiate the curing process and are commonly used in application such as mold-making, potting compounds, and sealants.



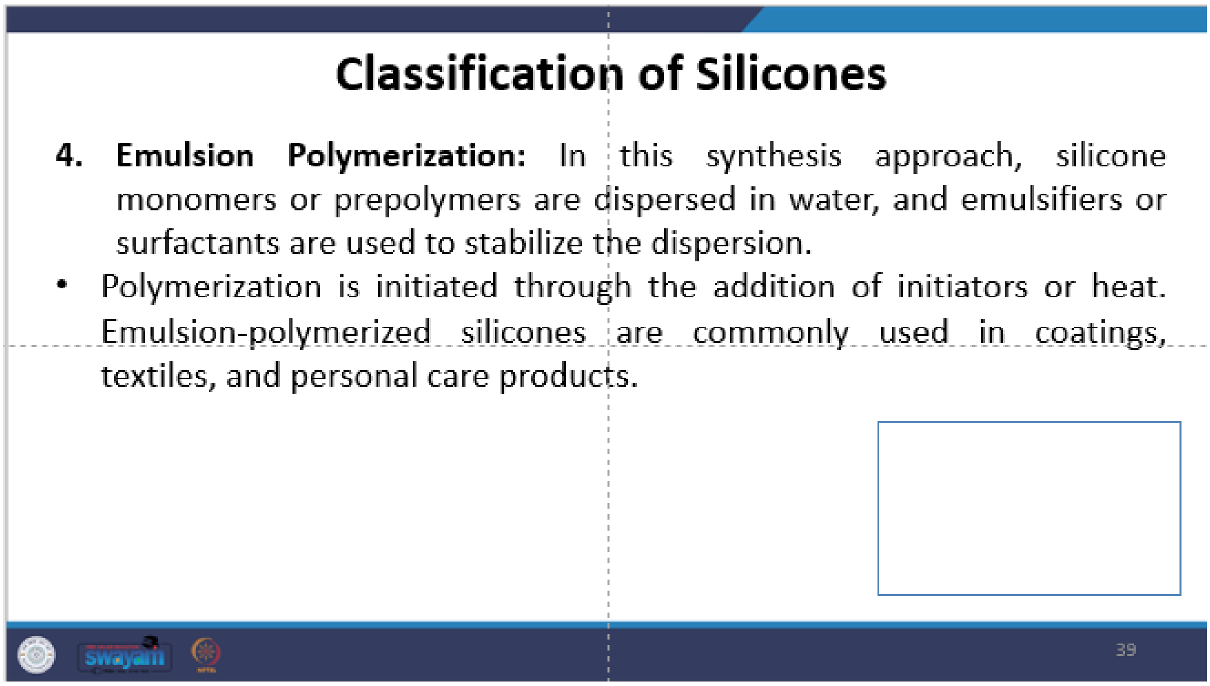
Then addition cured silicones that is sometimes referred as platinum-cured silicon. These silicones are synthesized using a platinum catalyst to promote the addition reaction between the vinyl-functionalized PDMS and hydroxylene crosslinker. The platinum-catalyzed initiates the cross-linking reaction without producing byproduct and additional cured silicon offer excellent curing control, high purity, and superior physical properties, and they are widely used in medical electronics and specialized industrial application. Another class is the peroxide-cured silicones. Now, these silicones are synthesized by incorporating a peroxide-based cross-linking agent into the silicon polymer.



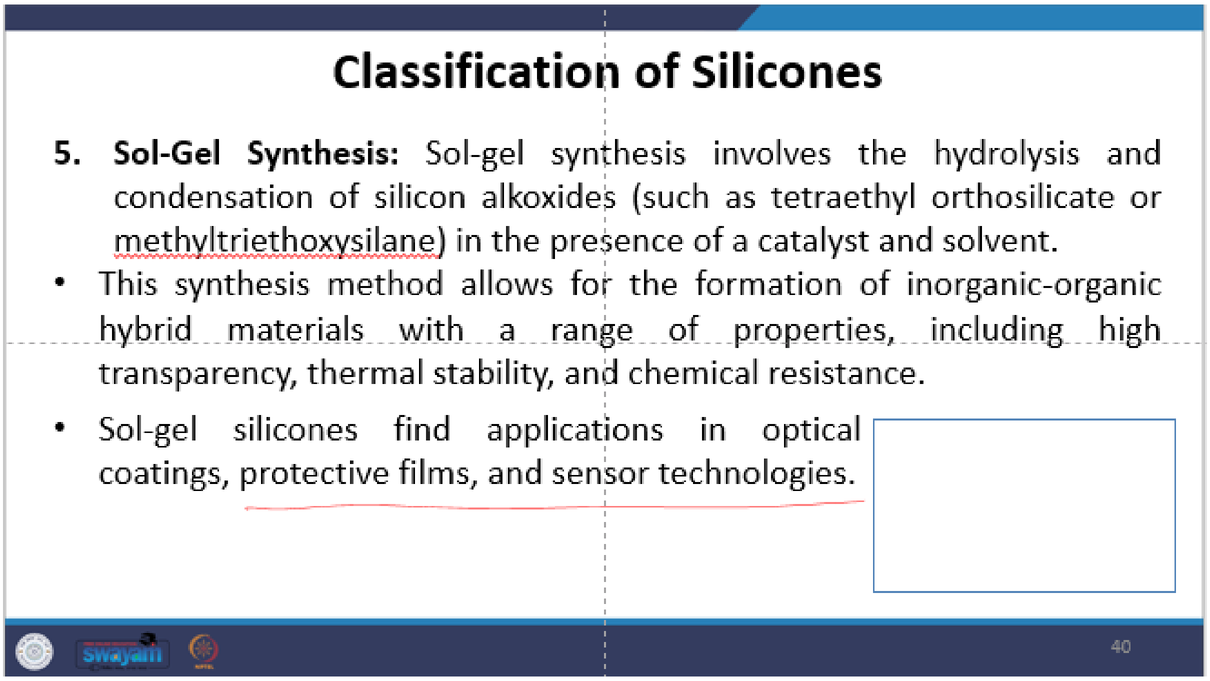
So, upon heating the peroxide initiator, a free radical reaction leads to the cross and peroxide-cured silicones are suitable for high-temperature applications as they offer good thermal stability and mechanical properties. They find use in automotive aerospace and electrical insulation applications. Another class is the emulsion polymerization. In this, the synthesis approach adopts silicon monomer or prepolymer dispersed in water and an emulsifier or surfactant are used to stabilize their dispersion. and polymerization is initiated through the addition of initiator or heat, and emulsion polymerized silicones are commonly used in coating, textile and personal care products. Another type of classification is based on sol-gel synthesis.



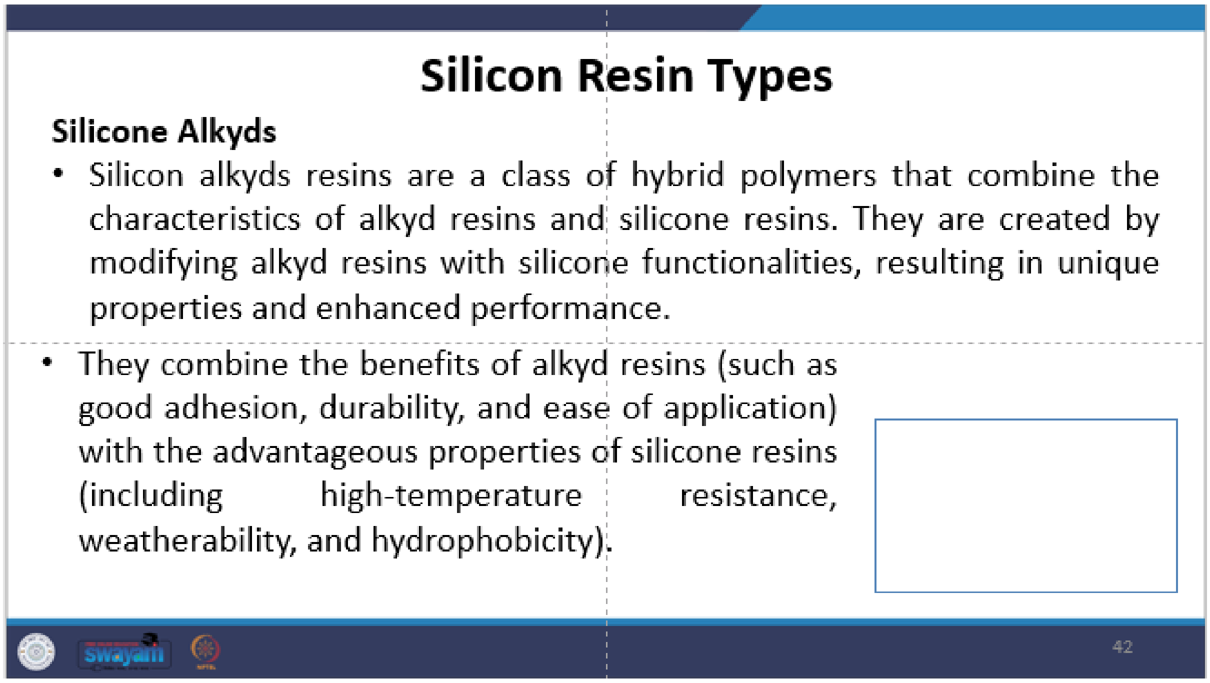
The sol-gel synthesis involves the hydrolysis and condensation of silicon alkoxides such as tetraethyl ortho silicate or methyl tri ethoxy silane in the presence of a catalyst and solvent. The synthesis method allows the formation of inorganic-organic hybrid materials with a range of properties, including high transparency, thermal stability, and chemical resistance.



Now, sol-gel silicones have applications in optical coating, protective film, and sensor technologies. It is important to note that this classification represents different approaches to silicon synthesis, and each category may have variation and specific formulation depending on the desired properties and application. Now, let us talk about the different types of silicon resin.



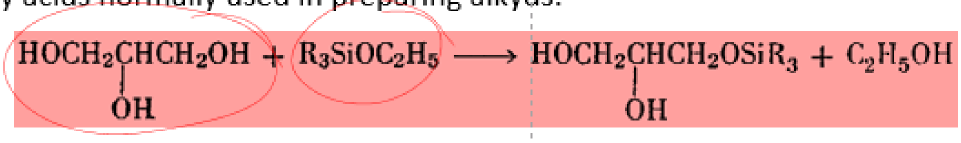
One is the silicon alkydes. Silicon alkyde resins they are the class of hybrid polymers that combine the characteristics of alkyd resin and silicon resin and they are created by modifying alkyd resin with silicon functionalities resulting in unique properties and enhanced performance. They combine the benefits of alkyd resin such as good aeration, durability and ease of application with the advantage's properties of silicon resin, this including high temperature resistance, weather ability, hydrophobicity. Now, they are usually prepared by reacting glycerol with the silicon ester or selenol instead of the fatty acid normally used in preparing alkyds. Now, other silicon, the esters and hydroxyl terminated silicones, this may be used to give the structure like this. Now, thalic anhydride is then condensed with this product and yield a high molecular weight, high cross-linked silicon alkyd of which a typical structure can be represented like this.



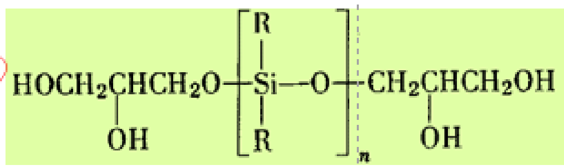
Now, they offer improved thermal stability, UV resistance, chemical resistance, and weather resistance compared to the conventional alkyd resin. Now, the specific properties of silicon alkyd resin can be tailored by adjusting the type and amount of silicon modification in the alkyd backbone. Let us talk about the structure. Now, silicon alkyd resins, they have the complex structure consisting of alkyd resin backbone with incorporated silicon functionalities. The alkyd proportion typically this includes the long chain fatty acids, polyols and acid catalyst which undergo the esterification reaction to form the alkyd resin.

SILICONES

They are prepared by reacting glycerol with a silicone ester or a silanol instead of the fatty acids normally used in preparing alkyds:



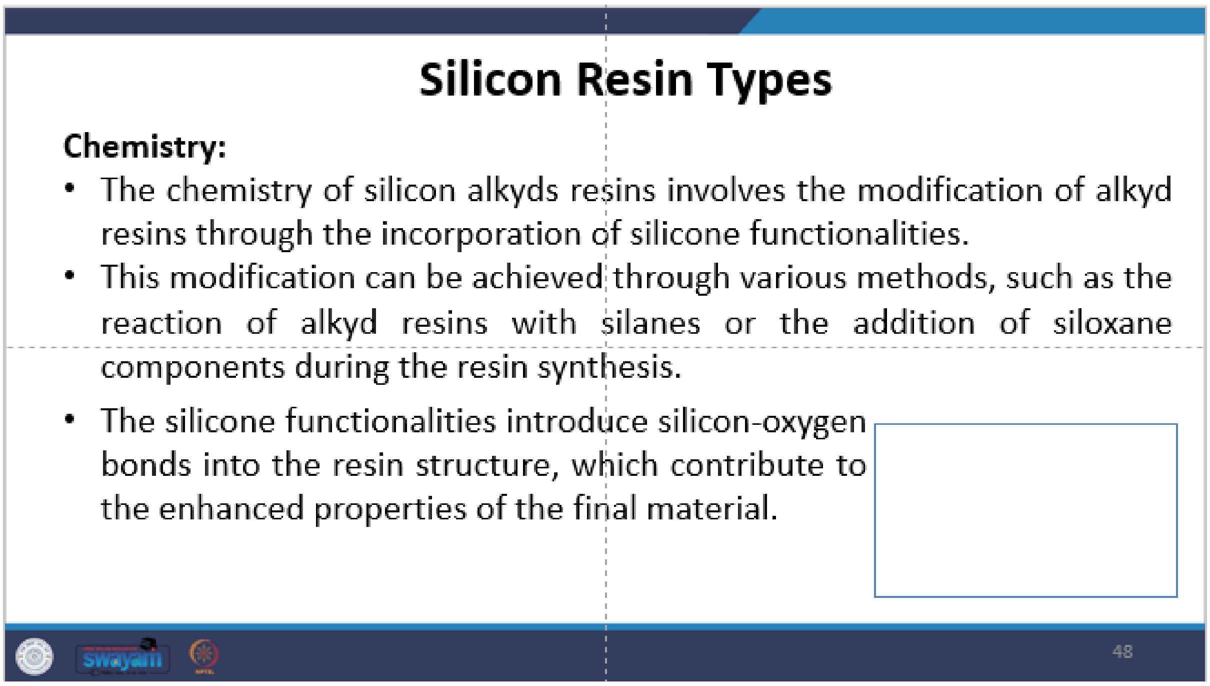
Other silicone diesters and hydroxyl-terminated silicones may be used to give Structures;



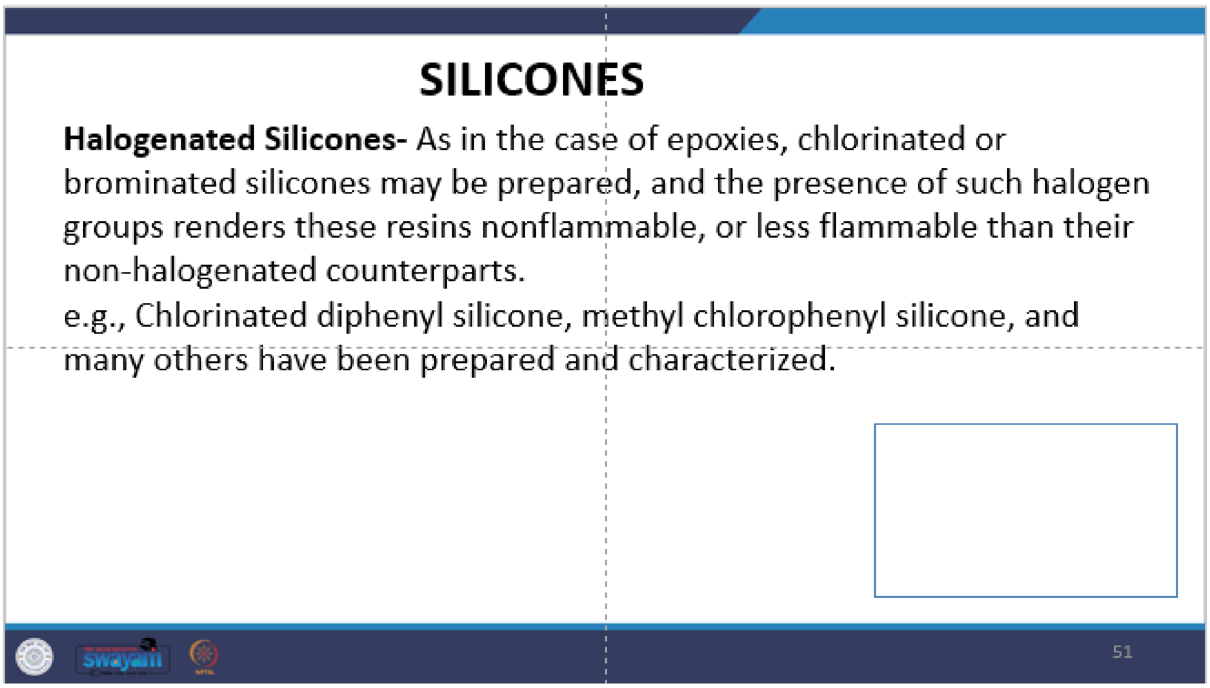
Silicon Resin Types

- They offer improved thermal stability, UV resistance, chemical resistance, and weather resistance compared to conventional alkyd resins.
- The specific properties of silicon alkyds resins can be tailored by adjusting the type and amount of silicone modifications in the alkyd backbone.

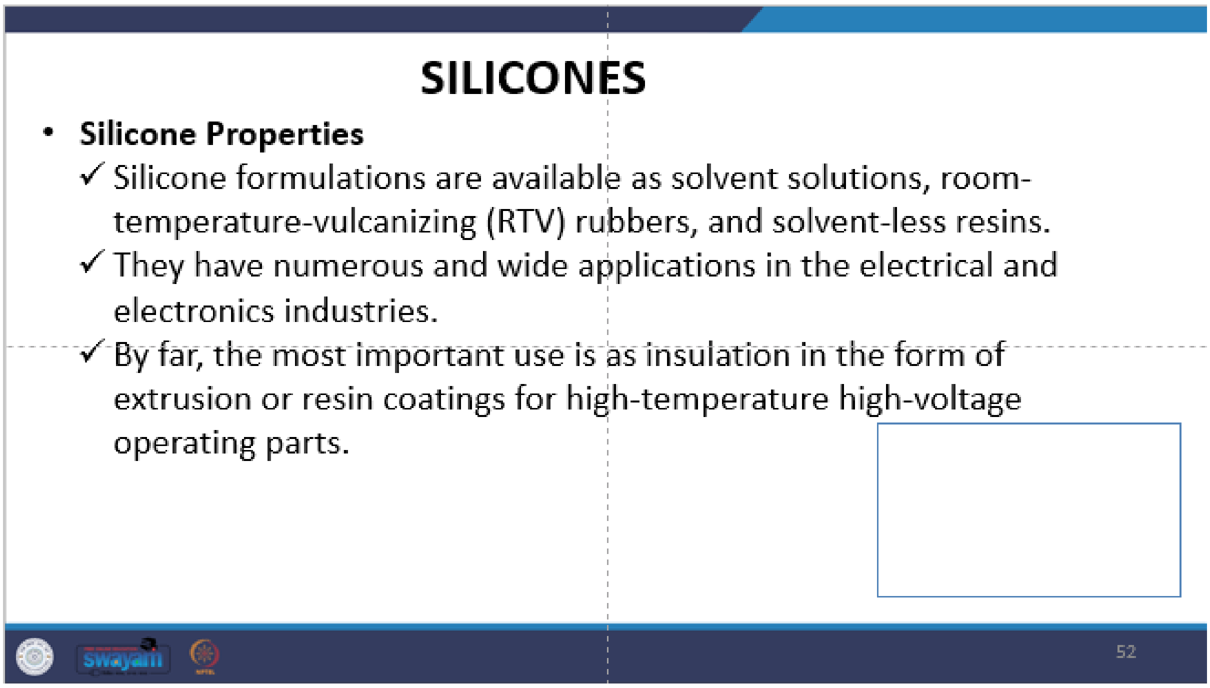
Now, silicon functionality such as silane or siloxane groups, are introduced into the alkyd structure through the modification process. Let us talk about the uses. Now, silicon alkyd resin find application in various industries, including coating, adhesive, sealant, and protective finishes. They are particularly suitable for demanding environments where high-temperature resistance, weather resistance, chemical resistance, and durabilities are required. Common applications this include the coating industrial coating, marine coating, high-temperature coating, and architectural finishing.



Well, let us talk about the chemistry. The chemistry of the silicon alkyd resin involves the modification of alkyd resin through the incorporation of silicon functionalities. This can be achieved through various methods like the reaction of alkyd resin with silanes or the addition of siloxane compound during the resin synthesis and this functionality introduces silicon-oxygen bond into the resin structure which contribute to the enhanced properties of the final material. It is apparent that numerous modifications of this basic chemistry, are possible, giving rise to a multitude of proprietary silicon alkyd coating and silicon alkyd provides coating with greater flexibility, hardness and thermal stability than alkyd. But naturally, then they would not possess the high thermal and oxidative resistance of the unmodified silicones and must therefore be considered intermediate in nature. Nevertheless, these intermediate properties are considered very important in achieving a compromise between the thermal stability and ease of handling of for many applications and silicon alkyd coating are widely employed as a moisture barrier and corrosion protective coating for electronic component like resistors, transistors and integrated circuits.



Let us talk about the halogenated silicones. Now, as in the case of epoxies, the chlorinated or brominated silicones may be prepared and the presence of such halogen group renders these resins non-flammable or less flammable than their non-halogenated counterparts like chlorinated diphenyl silicon, methyl chlorophenyl silicon and many others have been prepared and characterized.



The silicon formulations under the ages of silicon properties, are available as a solvent solution, room temperature, vulcanizing, RTV reversal, and solvent-less resins, and they have numerous and wide applications in electrical and electronics industries.

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)

By far, the most important use is insulation in the form of extrusion or resin coating for high-temperature, high-voltage operating parts. So dear friends, in this particular segment, we discussed the various applications of epoxies, we discussed the silicones, how they are synthesized, what are the different classification schemes which is important, what are the different uses, how the industrial applications can be incorporated with the help of these silicones and for your convenience we have listed various references which you can utilize for further studies. Thank you very much.