

# GLOBAL EPOXY RESIN MARKET FORECAST & OPPORTUNITIES, 2030

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MARKET INTELLIGENCE. CONSULTING







# 4.3.1 Target End-Use Applications (Grade wise application details of Epoxy Resin)

There are many customised Epoxy Resin types commercially available from global manufacturers, compatible with a wide range of modifying resins, reactive and nonreactive diluents, curing agents, additives, rheology modifiers, and fillers.

**Application Include:** 

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**Paint & Coating:** Anti Fouling, Automotive, Marine, Packaging, Pavement Marking, Powder & Protective.

Electronics: Chip, Circuit Board, Encapsulation, Potting

**Composites**: Aerospace, Industrial, Recreational, Transportation & Wind.

Civil Engineer: Airports, Bridge & Roads, Flooring & Grouting, Manufacturing, Port

infrastructure, Railway station, Water (Waste & Portable).

# **Grade wise Application Include as below:**

	Epoxy Resin Applications				
	Types	EEW	Viscosity	Applications	
1	Bisphenol A- epichlorohydrin resin				
	a. Liquid Resin		<del>-</del>		
	i. Wide ranging Characteristic	95-450	5000-30000	Coating, Adhesive, Casting, flooring, Electrical Laminates, Mouldings, Glass cloth laminates, Structural laminates & Filament windings	
	ii. Chain Extension	120-200	2000-7000	Contain specific catalysts for conversion of these resins	
	iii. Lower viscosity resin			Contain reactive diluents, e.g. glycidyl ethers of iso- octanol or butane-I,4-diol	
	b. Solid Resins				
	i. (Solidification Pt is 60-180°C)	500-6000		Coatings, especially powder coatings( manufacture of Epoxy Resin esters for coatings with amino- or phenolic-resins) High chemical resistance for tube coating primers and stoving enamels Castings Prepregs	
	ii. Mixtures and solutions			Solvents include butoxy(ethoxy )ethanol, xylene, acetone, methyl	



				isobutyl ketone and combinations
2	Francis Namela			
	Derived from bisphenol A- epichlorohydrin resins			
	i. Phenol Liquid	170-190	30 000-90 000	Coatings, encapsulators, laminating, moulding, adhesives
	ii. Phenol Solid	190-220		Moulding Powder
		275-330		Adhesive, Coatings
	iii. Cresol Solid	200-240		Adhesive, Coatings, Mouldings
3	Polyhydric phenols			
	i. Bisphenol F: Diglycidyl ether of bisphenol F	158-175	5000-7000	Additive for BPA resins in coating and flooring
	ii. Others include: Tetraphenol ethane derivatives			Powder coating Polyglycidyl ether of tetraphenol ethane
4	Halogen-containing epoxides			Flame retardancy applications: general purpose laminating, moulding
5	Cyclo-aliphatic resins	131-143	350-450	Good UV light stability, electrical properties: general purpose casting resin, filament winding. Acid scavenger, plasticizer Union Carbide ERL-4221
6	Amines: Reaction products of epichlorohydrin with amines such as: DDM, Aniline, pamino-phenol & Triglycidyl pamino phenol			Solvent-free coatings, flooring Patch repairing, chemical - Resistant tank lining, Industrial flooring, adhesive, Laminating system, casting, Moulding etc.



# 4.3.2 Plant Process-description (Evaluation of major process commercially available for licensing:

**Production process of Liquid Bisphenol-A Epoxy Resin**: The one-step process proceeds via polycondensation of reacting epichlorohydrin (ECH) with bisphenol A (BPA), resulted with different chemical liquid substance known as bisphenol A diglycidyle ether (commonly known as BADGE or DGEBA). Bisphenol A-based resins are most widely commercialised resins (75-80%).

BADGE Process: Bisphenol A or 2,2'bis(p-hydroxyphenyl) propane is produced from acetone and phenol with an acid catalyst such as 75% sulphuric acid or dry hydrogen chloride. The reaction conditions will depend on the design of the production unit. The purity of the product is high, >95% p,p'-isomer (para-para); the other isomers formed are o,p'(ortho-para) and o,o (ortho- ortho)'. For resin manufacture the p,p' isomer (para-para) content should be at least 98%. The light yellow colour of some Epoxy Resins may be due to trace impurities in the bisphenol A, such as iron, arsenic and highly coloured organic compounds. When a large excess of epichlorohydrin is reacted with bisphenol A with a stoichiometric amount of sodium hydroxide at about 65-70°C the resin produced contains about 50% diglycidyl ether of bisphenol A, DGEBA(BADGE) and the reaction may be represented formally as below:

**Two Step Process**: The two-step process is the reaction of bisphenol A (BPA) and epichlorohydrin (ECH) in presence of a catalyst (such as a quaternary ammonium salt), the first step by an addition reaction is to form a diphenol-propane chlorohydrin ether as



intermediate, and the second step is to be carried out in presence of Caustic, this closed loop reaction produces an Epoxy Resin.

# <u>Production process of solid bisphenol A Epoxy Resin</u>

**Higher molecular weight bisphenol A resins**: It is obvious that the bisphenol A/epichlorohydrin ratio is important for control of the average molecular weight of the resins produced with the repeat unit because the larger the value of n the smaller the epichlorohydrin / bisphenol A ratio required. The purity of the reactants is important and monofunctional reactants are chain terminators and hence their concentration has to be controlled. However, it is also necessary to optimize the reaction conditions to achieve the degree of polymerization required. For the production of oligomers with  $1 \le n \le 4$ , the so-called 'Taffy' process could be used but for much higher molecular weight polymers  $3 \le n \le 20$  the fusion or chain extension process (also called advancement process) is used.

**Taffy Process**: In taffy process,1-3 bisphenol A is reacted at 85–95°C in a controlled excess of epichlorohydrin (ECH) (to give polymer molecules along with glycidyl ether groups, at both ends) in the presence of Caustic and an inert solvent. This reaction is used to produce lower molecular weight (MW) epoxides. The low molecular weight epoxides are polydisperse mix of epoxides with "n" values lies between 0 and 1 and have an average molecular weight of 340-600.

**Detail Description of Taffy Process:** A mixture of bisphenol A and 10% aqueous sodium hydroxide solution is introduced in a reactor equipped with high-speed powerful agitator. The mixture is heated up to 45° C and ECH is added rapidly with agitation, giving off heat. The temperature is allowed to rise to 95° C, where it is maintained for approx. 80-85 min for the completion of reaction. Agitation is stopped, and mixture gets separate in two layers. The heavier aqueous layer is drawn off from bottom and the molten, taffy-like product is washed with hot water until the wash water gets neutral PH. The taffy-like product is dried at 135° C, gives solid resin with softening point of 70-75° C and an EEW value of 500. Alternatively, epichlorohydrin are removed by vacuum distillation at temperatures up to 180° C approx. The crude resin is then dissolved in a secondary solvent (Toluene) to facilitate water washing and salt removal. This secondary solvent is then recovered via vacuum distillation in order to obtain the resin product.



**Cons of Taffy Process**: In this process insoluble polymers are formed, which create handling and disposal problem.

**Advancement Process**: For manufacturing of higher molecular weight Epoxy Resins, liquid Epoxy Resin (LER) is reacted with calculated amount of bisphenol A, further catalyst solution is added to boost the reaction and the temperature is maintained at approx. 160 °C. This process is known as "Advancement process". The high molecular weight epoxides are manufactured by "Advancement" process using Benzyl trimethyl ammonium hydroxide as a catalyst.

# **Detail Description of Advancement Process**

Advancement process is widely practiced by coating producers to facilitate the handling of the high molecular weight, highly viscous Epoxy Resins used in many paint & coating formulations. The degree of polymerization is calculated by ratio of LER (formed from BADGE Process) to bisphenol A; an excess of the former provides epoxy terminal groups. The actual molecular weight obtained depends on purity of the starting materials, solvents & catalyst used. Reactive mono-functional groups are used as chain terminators to control MW and viscosity build. The below formula is used to calculate the amount of bisphenol A that is to be reacted with Epoxy Resin (LER) to obtain an advanced Epoxy Resin of predetermined EEW value. (EEW is Epoxy Equivalent Weight) is a measure of compounds which epoxy containing groups. The epoxy equivalent weight describes the mass in grams which one mole of epoxy groups contains.)

$$BisA = EEWi - 1 - EEWf - 1 EEWi - 1 + PEW - 1$$



where Bis A is mass fraction of bisphenol A in the mixture at initial stage, EEWi is the EEW of the Epoxy Resin that is to be advanced (i stands for initial), EEWf is the EEW (f stand for Final) of the advanced Epoxy Resin, and PEW is the phenol equivalent weight of the bisphenol, its value is 115.1 g per equivalent for bisphenol A. In an advancement process, bisphenol A and a liquid BADGE resin (170–180 EEW) are heated to 155–199 °C in the presence of a catalyst and reacted (i.e., advanced) to form a high MW resin. This oligomerisation process is exothermic and proceeds rapidly to completion. The exotherm temperatures depends on the reaction mass and targeted EEW. In the cases of higher MW resins, exotherm temperature can reach >190-205 °C. Reaction catalysts facilitate the rapid preparation of medium to high MW linear resins, also control side reactions inherent with Epoxy Resin preparations, e.g., chain branching, by addition of the alcohol group generated in the chain-lengthening process to the epoxy group. Nuclear Magnetic Resonance (NMR) spectroscopy Method can be used to determine the extent of branching.

**Bisphenol F based Epoxy Resin**. Any multifunctional,  $f \ge 2$ , phenolic compound is a potential starting material for the manufacture of Epoxy Resins, these are 'formulated' to meet specific requirements. Also, some monofunctional phenols have been reacted with epichlorohydrin to produce monofunctional reactants for use as modifying diluent agents. The dihydric phenol which is produced by reaction of phenol with formaldehyde is called bisphenol F.

Resins can be manufactured from bisphenol F by similar methods to those used for bisphenol A and epichlorohydrin with a catalyst such as NaOH. These resins have lower viscosities than the equivalent DGEBA.



BISPHENOL-F AND BISPHENOL-A/F BLENDS: One can go with pure Bisphenol -F, Bisphenol A or Bisphenol A/F based Epoxy Resin. Bisphenol-F based resins are best known for low viscosity, chemical resistance and low crystallisation tendency in cold conditions. Bisphenol-F based pure and Bisphenol-A/F blend resins are recommended in varying viscosities for several applications like coatings, composites, floor coatings and construction applications.

# **Epoxy Novolac (Derived from bisphenol A-epichlorohydrin resins)**

$$CH_2$$
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 

The novolac resins, which are the reaction products from formaldehyde and excess phenol under acidic catalysis, when co-cured with high molecular weight solid bis-A Epoxy Resins result in coatings with excellent adhesion, film strength, flexibility and chemical resistance. They are especially useful in powder coatings applications for corrosion resistant pipe/reinforcing bars (rebars) and with brominated Epoxy Resins for FR3 electrical laminate production. The cure mechanism involves poly-addition to Epoxy Resin and is activated by acids such as p-toluene sulphonic acid.



# **Phenol Formaldehyde Epoxy Resin:**

# 1.1 Basic Chemistry:

# (a) Methylol monomer formation:

# (b)Liner Polymer

$$\begin{array}{c} \text{OH} \\ \text{HOH}_2\text{C} \\ \text{M} \end{array} \begin{array}{c} \text{OH} \\ \text{CH}_2\text{OH} \end{array} \\ \longrightarrow \left[ \begin{array}{c} \text{OH} \\ \text{-OH}_2\text{C} \\ \text{-CH}_2\text{OCH}_2 \end{array} \right]_{m/2}$$

# (c) Cross-linked tridimensional polymer

$$\stackrel{\mathsf{HOH_2C}}{\bigcirc} \stackrel{\mathsf{OH}}{\bigcirc}_{\mathsf{CH_2OH}} \longrightarrow \bigcirc \bigcirc \bigcirc \bigcirc$$

Phenolics are low-cost polymers with excellent physical & electrical properties and fast curing characteristics. Their poor colour characteristic can be partially overcome by adding pigment, dyes & fillers.

The main uses fall in these classes:

- Resin in solvent—coatings varnishes & laminated structure.
- Resins in water solutions adhesive bonding



Solid resin—all types of thermoset molded solid forms.

# General Resin characteristic can be controlled by:

- (a) Acid Solution catalyst with excess phenol—produces linear soluble thermoplastic.
- (b) Alkaline catalyst
  - One stage process: Correct ratio of phenol to formaldehyde is reacted with proper control of time and heat to yield a thermosetting or heat reactive powder which can be heated to an infusible, insoluble state via further cross linking.
  - Two stage process: Thermoplastic material from the acid catalysis process is mixed with hexamethylene tetramine, a white solid which breaks down to CH2O and NH3. The formaldehyde combines with the resin to form a thermosetting product with ammonium as catalyst.

Both one and two stage resins are used as commercial molding materials with the final cross-linked polymer having good resistance to all chemicals.

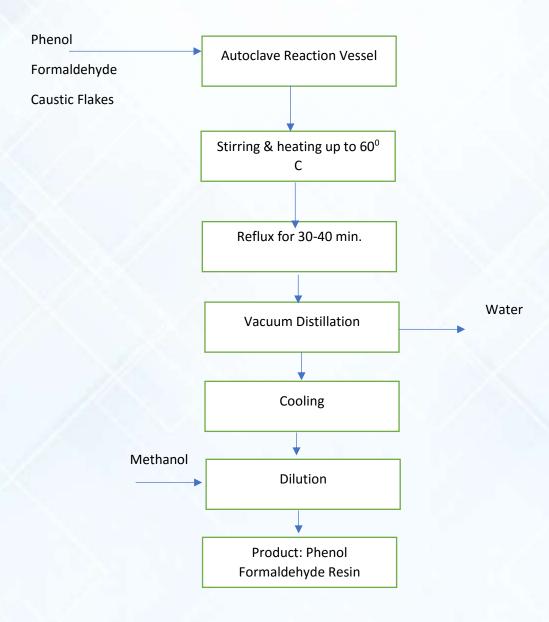
**Process Description:** Polymerization is an exothermic reaction which must be controlled by batch reaction as the material rapidly changes viscosity.

Phenol, formaldehyde and catalyst are mixed together in a jacketed autoclave and heated with steam. After reaction starts, the heat of reaction is removed by refluxing and water cooling. In the early stages of reaction, the heavier viscous resin separates as a bottom layer with an aqueous layer at the top. Dehydration is next completed in the kettle by a combination of heat and vacuum. The fused resin at 130-150° C is removed from the kettle, cooled and ground to a fine powder.

The heat reactive moulding powder prepared above can be mixed with fillers, colouring agents, lubricants and catalyst in a blender or ball mill. It is then heated further on a pair of differential heating rolls to prepare fast curing commercial phenolic moulding powder.



# **Process flow diagram**



# 4.3.3&4. Process Flow Diagram & Technology Licensor

# **Technology licensor**

- Tohto Kasei (Japan) (Now known as Nippon Steel & Simikin Chemical Co Ltd.), leader in resin producer, have its own epoxy licensing technology arrangements with numerous resin manufacturers in Asia. In India Grasim, Vilayat use this technology.
- Olin Systems: Olin Coorporation is the leading manufacturer & distributor of Epoxy Resin,



which offers highly advanced Epoxy & leading customer support worldwide. The company doesn't share their inhouse technology.

 Kukdo's System (Korean Technology): Kukdo's system is leading the global market through customized products and R&D. This companies all branches use their own technology.

Synthesis of Epoxy Resin: The Epoxy Resin has been synthesized by the bulk polymerization by the continuous process of polymerization. The material is available commercially at 98% purity & colourless mobile liquid. Many commercial liquid resin consist essentially of low molecular weight diglycidyl ether of Bis-phenol A (BADGE) together with small quantity of higher mol Wt polymer. During the reaction hydrochloric acid has release. HCl has reacted with caustic & salt has form. The molar ratio of the BPA to ECH is 1:2 i.e., 1 mole of BPA & 2 mole of ECH. It is responsible to produce higher mol. wt. resin but in actual practice this ratio is 2-3 times more i.e. up to 1:5 or 1:6 of BPA to ECH.

# Technology 1:

#### **Process Detail:**

#### **Pre-reaction Section**

Reaction starts with adding Excessive quantity of Epichlorohydrin (Fresh & recovered) with prescribed quantity of Bisphenol-A by using NaOH as catalyzer. As result of this reaction, Bisphenol-A chlorohydrin intermediate is formed.



#### **Reaction Section**

Bisphenol-A chlorohydrin intermediate formed from the pre-reaction section is further changed to liquid Epoxy Resin by reaction with NaOH. Optimum process conditions are maintained in the reactor. Which minimizes hydrolysis of ECH and formation of by-product waste polymer and enables the production of high-quality Epoxy Resin of the required viscosity at high yields

Resin + 2 NaCl + 2 H<sub>2</sub>O

#### **ECH Detachment Section**

After the reaction process done, excessive quantities of unrelated ECH are separated from the product by increasing the temp and recovered through a vaporizer, same is returned to the ECH day tank for reuse. The crude epoxy is then sent to the next refining section. In order to protect the Epoxy Resin from thermal effect, vaporization of ECH is done under vacuum conditions, at the lowest possible temperature and in the shortest possible time.

#### Refining

In this section washing is done, toluene is added to dissolve resin in it. With continuous stirring & allowed salt solution to settle in the gravity settler, salt solution is separated from the resin manually by adding water. Again, DM water is added to wash the resin and remove the traces of salt from it.

#### **Filtration**

After refining, filtration is done to remove the impurities, suspended particles and rest of waste polymer by passing through the multilayer paper filter.



**Product Finishing Section:** Finally, Epoxy Resin is filtered to remove suspended filter cake via sparkler filter and is sent to the product tank through mixing tank.

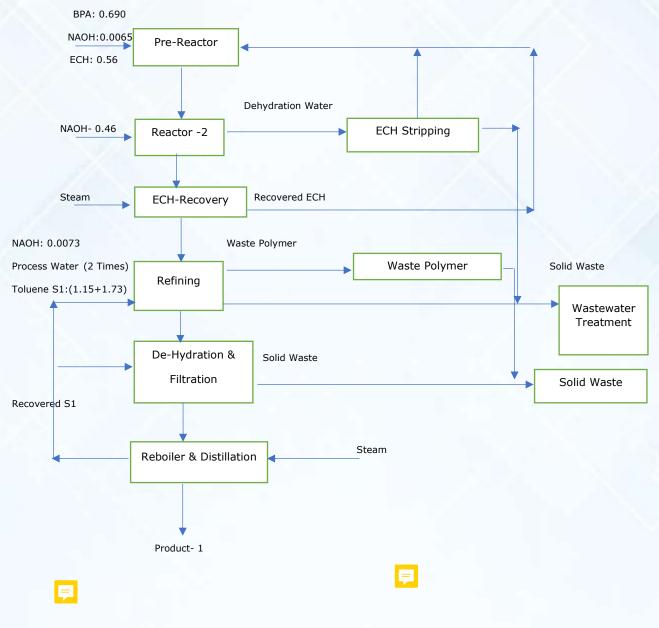
**De solvent:** In this section, dissolvent is done to remove the solvent, toluene from the resin by passing through falling film thin evaporator & Rotary film thin evaporator under vacuum.

**ECH Stripping:** ECH Evaporated during reaction contains ECH along with water,

water is stripped off in the distillation unit, recovered pure ECH is recycled for next batch.

**ECH Distillation:** ECH vapours from the ECH detachment section are recovered and distilled in this section to recover pure ECH which is recycled.

#### **Process Flow Diagram:**





# **Solid Epoxy Resin:**

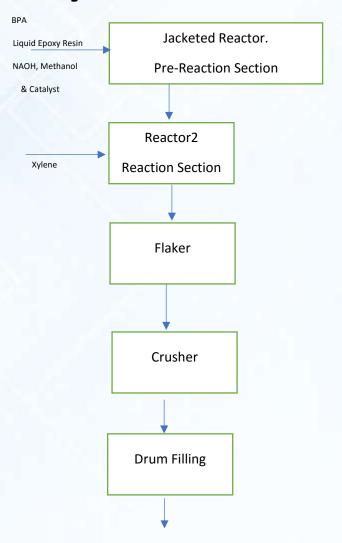
**Pre-Reaction Section:** In this section, Liquid Epoxy Resin, Bisphenol A & Catalyst is added in to the reactor (BPA & Catalyst is added in 2 Stages i.e. With progress of the reaction, 2<sup>nd</sup> lot of BPA & catalyst is added).

**Reaction Section:** Here reaction mixture from the pre reaction section is added with a solvent in control range of pressure (5-7 Bar) & temp (70-75°C) approximately.

**Solidification Section:** Here Epoxy Resin (i.e. formed in reaction section) is passed through the flaker (with required utilities (chilled water & steam)) & further pass through the crusher to collect the final solid product.

For the suppression of catalytic reaction, a few amount of Methanol is added in reactor.

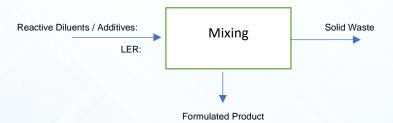
# **Process Flow Diagram:**





#### **Formulated Resins:**

**Mixing**: Different grade Liquid Epoxy Resin is mixed with various types of additives or Reactive Diluents to meet customer specific applications or other special Resin.



**Example**: amine cured epoxy coating is an epoxy coating where an anime-based hardener was used in the curation process.

## Technology-2:

## **Process Detail:**

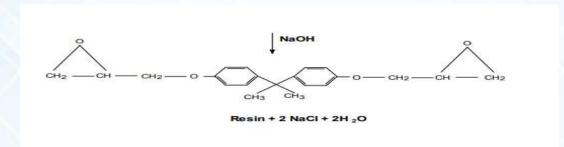
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#### **Reaction Section**

Bisphenol-A chlorohydrin intermediate formed from the pre-reaction section is further changed to liquid Epoxy Resin by reaction with NaOH. Optimum process conditions are maintained in the reactor. Which minimizes hydrolysis of ECH and formation of by-product waste polymer and enables the production of high-quality Epoxy Resin of the required viscosity at high yield



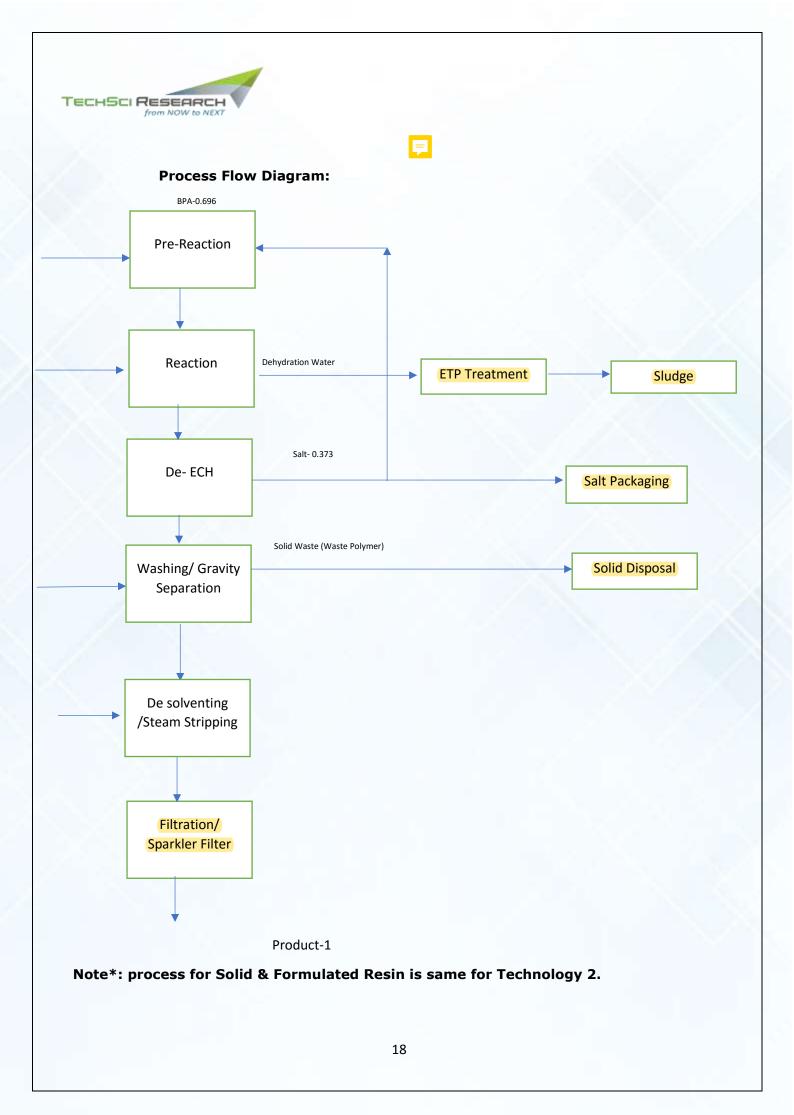
**ECH Stripping & Recovery:** ECH Evaporated during reaction contains ECH and water, water is stripped off in the distilled unit, pure ECH is recycled for next batch

**Refining**: In this section, toluene is added to dissolve resin in it and salt solution is separated from the resin manually by adding water. There are 3 layers are formed, the resin and toluene stay in the upper layer (called Organic layer) &NaCl water in the lower layer & centre one is unreacted BPA, it is called Emulsion layer. Again, DM water is added to wash the resin and remove the traces of salt from it.

**De-solvent:** After filtration section, Epoxy Resin is sent to reboiler & vacuum distillation column for Toluene recovery.

Product Finishing Section: Epoxy Resin is finally filtered to remove traces of impurities







# 4.3.6 Utilities Overview (Cooling Water System, DM Water Plant, Compressed Air System, power, steam & effluent processing details):

# For 100 KT Plant (per annum)

Fresh water requirement will be 923 KLD. 710 KLD treated water after UF/RO system will be reused/recycled back in process. Water will be sourced from the near water supply system.

Typical Common Utility to be use				
1	Electricity			
2	Gas			
3	Fuel Oil			
4	Steam			
5	Cooling tower Water			
6	Process Water			
7	7 Recycled process water			
8	Recycled cooling tower water			
9	Softened Water			
10	10 Demineralized water			
11	Instrumentation Air			
12	2 Inert Gas			
13	Nitrogen, purchased			
14	14 Refrigeration			

# **Power Requirement**

Nearest State Electricity Board will supply power through grid in that area. The peak demand of power would be approx. 5500 kVA. DG sets will be installed as a backup arrangement.

S No.	Stack Attached to	No. of working hrs	Type of Fuel used
	D. T. A	0.4	Coal / Biomass or
1	Boiler-1	24	Natural Gas
2	Thermic Fluid Heater	24	Natural Gas
3	Boiler-2	24	Coal / Biomass or Natural Gas
4	DG Set-1	As per requirement	Diesel
5	DG Set-2	As per requirement	Diesel



# 4.3.7 Waste generation, Management, and disposal:

Wastewater generation will be 700 KLD. From that, 615 KLD will be recycled and 85 KLD will be discharged to CETP after achieving desired norms. Unit will provide 750 KLD capacity of ETP followed by RO & UF. High TDS (Total Dissolved Solids) stream will be treated in MEE/MVR (Multi Effect Evaporator/ Mechanical Vapor Recompressor)

Hazardous wastes like resin sludge with polymers, resin-soaked cotton waste / gloves & chemical contaminated saw dust, office garbage, filter material, waste glycerine, spent solvent, spent oil, activated carbon, ETP (Effluent Treatment Plant) sludge, and waste barrel will be generated during the production. MEE/MVR salts (i.e., NaCl Salt) need to be send to authorized vendors & to managed as per the Hazardous Wastes (Management, Transport and Transboundary) Rules 2016 as amended till date.

S No	Type of Waste	Source	Method of collection	Treatment/Disposal
1	ETP Sludge + Evaporation residue	Process	Bag	Collection, storage and Disposal at Approved TSDF Site
2	Resin-Soaked Cotton Waste/ Gloves, Chemical, Contaminated Saw dust, Office Garbage	Process	Bag	Incineration
3	Filter Material	Process	Bag	Incineration
4	Waste Glycerine	Maintenance	Drum	Incineration
5	Spent Solvent	Process	Drum	Via ETP
6	Spent Oil	Maintenance	Drum	Via Register Recycler
7	Activated Carbon	Process	Bag	Via Register Recycler
8	ETP Sludge	ETP	Bag	Via TSDF
9	Discarded Container	Process	Drum	Via Authorised Vendor
10	Process Residue	Process	Drum	Via CHWIF
11	Salt (NaCl)	Process	Bag	Sell to Authorised Vendor

**TSDF:** Treatment, Storage, & Disposal Facility.

**CHWIF:** Common Hazardous waste Incineration facility.

**CETP:** Common Effluent Treatment Plant



