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TURKCOAT
CONGRESS

DEVELOPMENT OF BIOBASED EPOXY RESINS FOR COATING APPLICATIONS

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THE ASSOCIATION OF PAINT INDUSTRY

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OUTLINE

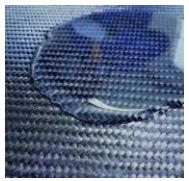
- Epoxy resins and their properties
- Bisphenol A free systems
- Development of Isosorbide based epoxy resins and its coating applications
- Development of Bisguaiacol F based epoxy resin and its coating applications
- Conclusion

What is epoxy resin?

- Epoxy is the cured end products of epoxy resins.
- Epoxy resins are reactive prepolymers and polymers which contain epoxide groups.
- Global Market: 3.2 mio MT/yıl, 80% Commodity applications, 20% Special applications (composites, adhesives etc.)
- Paint and coating, construction, composites, electric and electronics, adhesives etc.

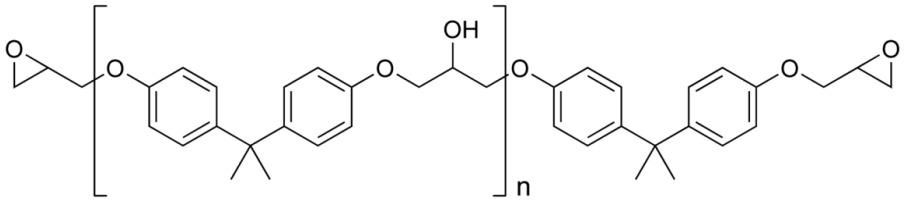




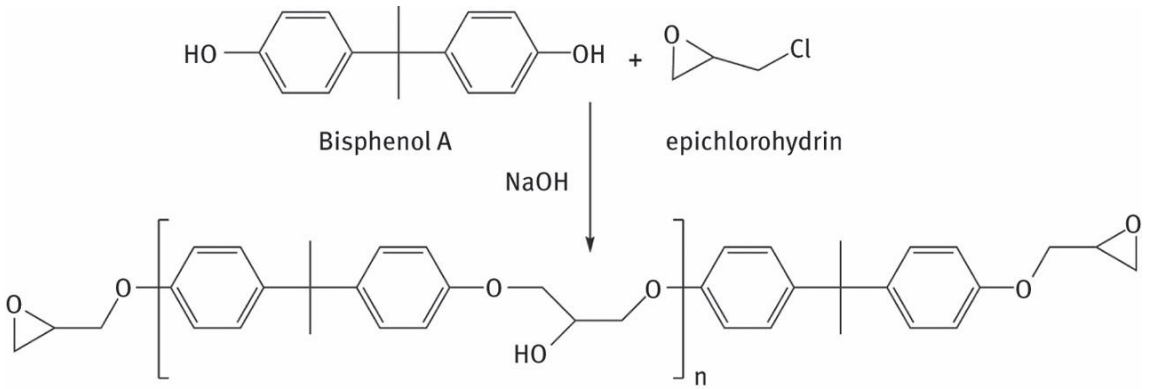


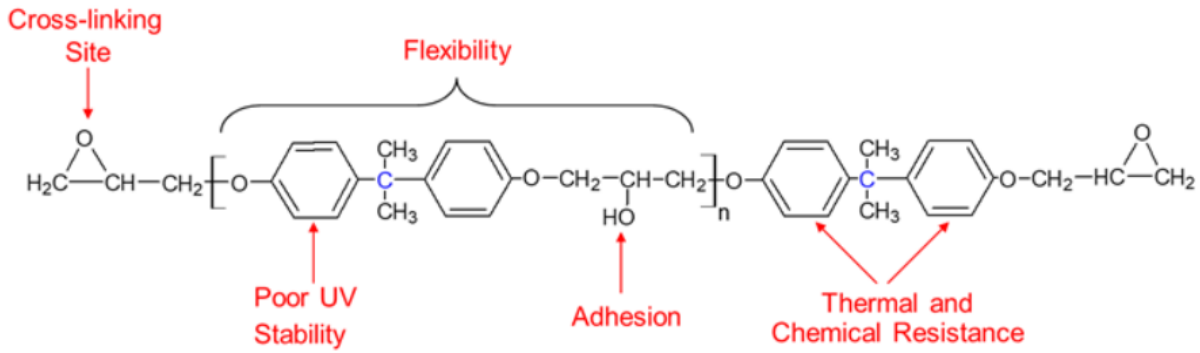

Key Properties of epoxy resins

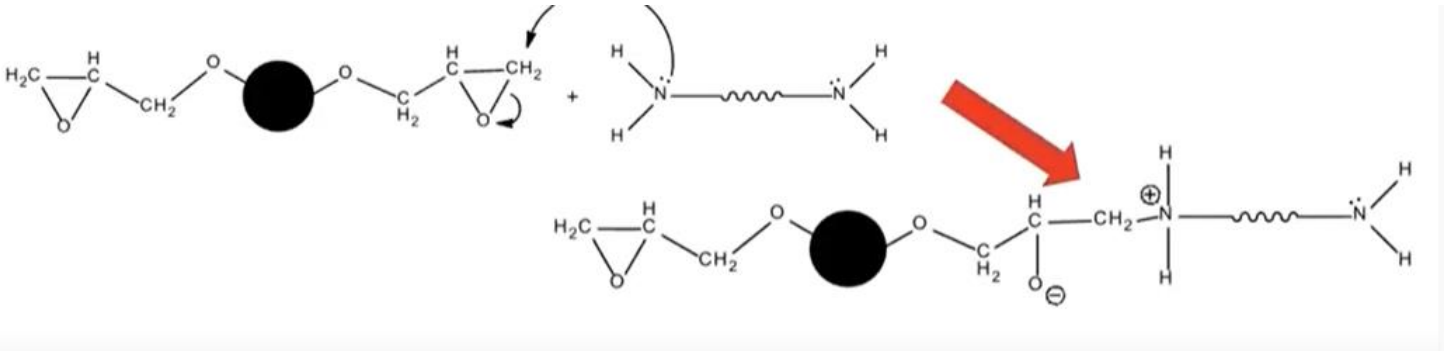
- The resin has good processability
- It can be formed under low pressure
- It is soluble in many solvents
- High corrosion resistance and electrical performance
- High strenght
- Maintain shape under prolonged stress
- Low Shrinkage
- Excellent adhesion to various substrates
- Effective electrical insulation
- Chemical and solvent resistance
- Low cost and low toxicity



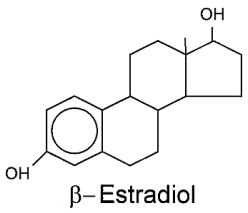
Synthesis mechanism of Bisphenol A Epoxy resin

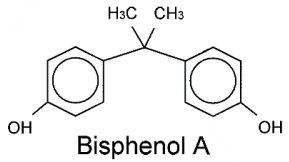


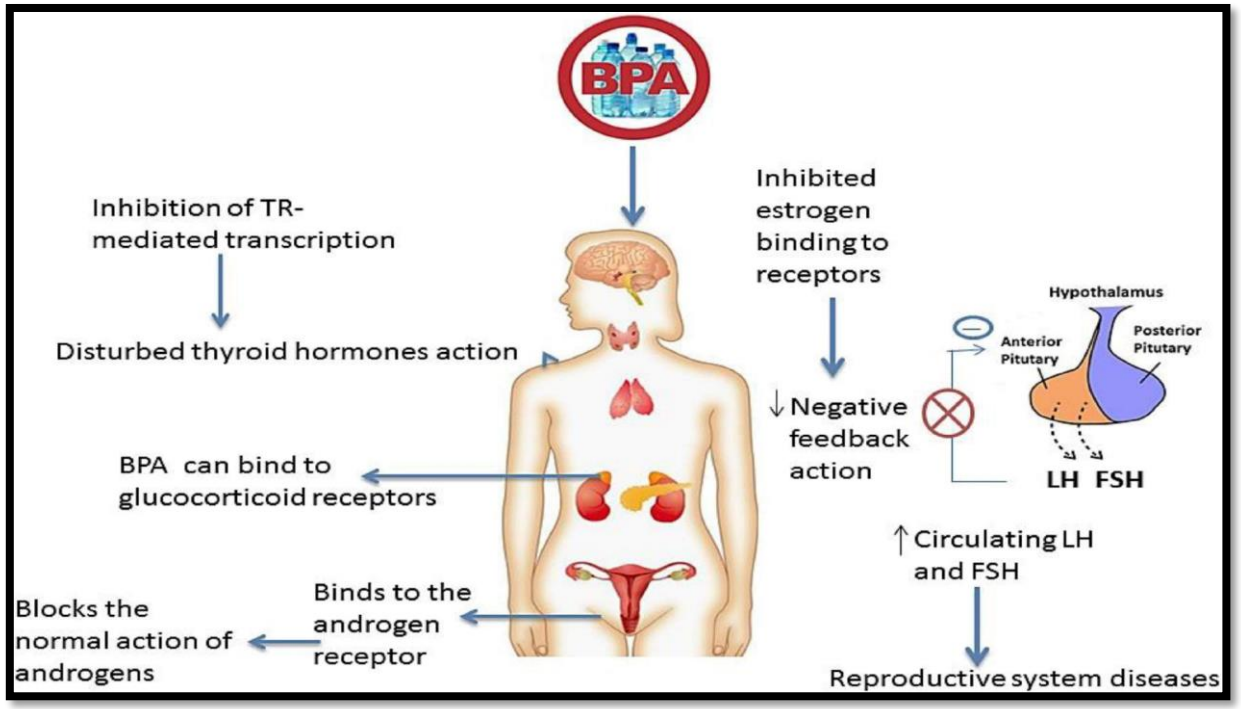


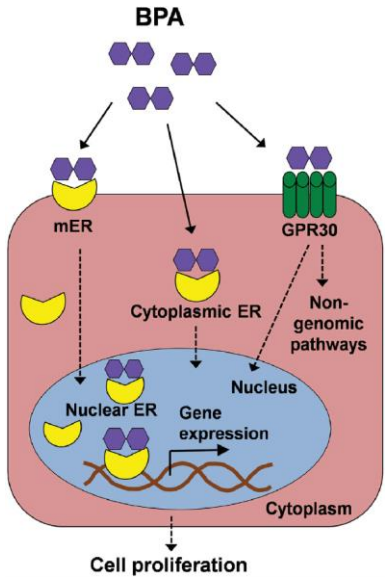


Why Bisphenol A Free?





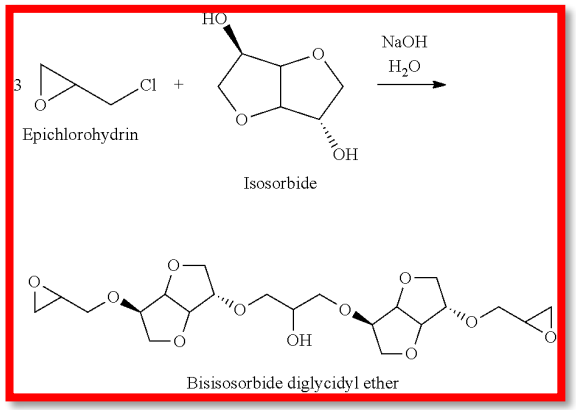


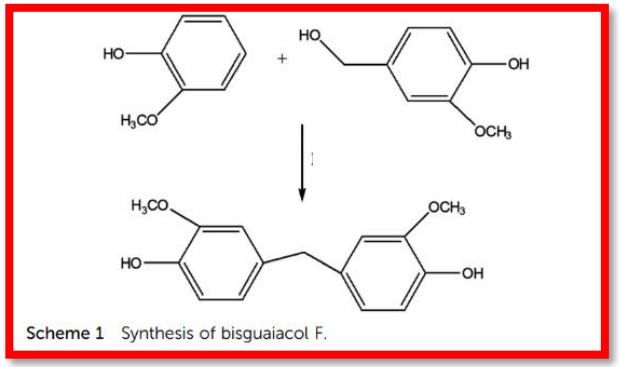


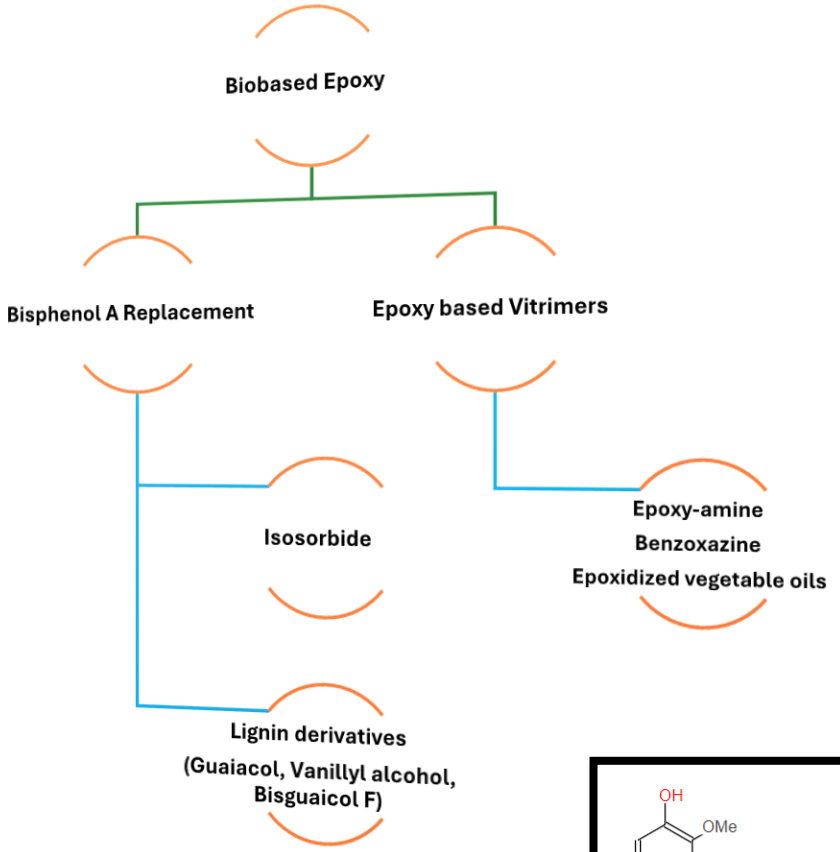
REACH-Restriction responsible German Authority

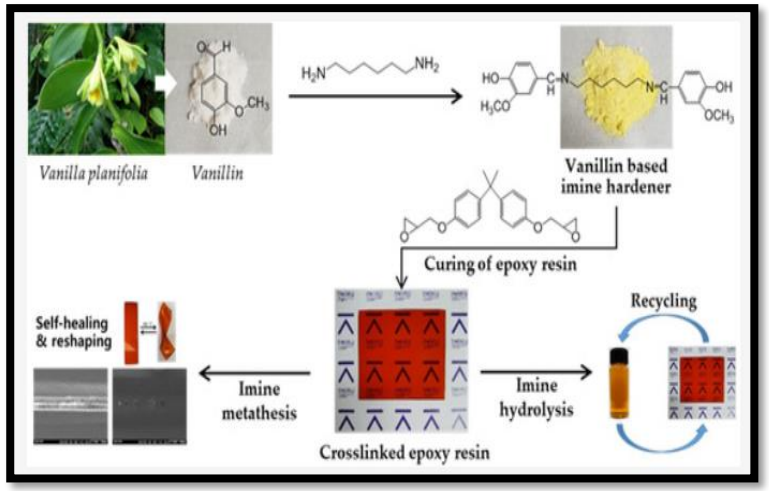
The six-month public consultation on the restriction proposal for "Bisphenol A and other bisphenols of similar environmental concern" concluded at the end of June 2023. Based on the information submitted, the competent German authorities have come to the conclusion that a revision of the dossier is necessary to an extent that exceeds the mandate of the currently ongoing review process by the scientific committees of the European Chemicals Agency (ECHA). The restriction proposal was therefore initially withdrawn in order to make this comprehensive revision possible. A re-submission of the revised proposal (including consultation) will be announced via ECHA's register of declarations of intent.

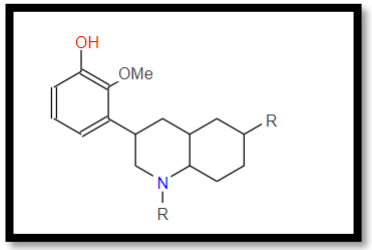
Bisphenol A Free Epoxy Resin Strategies

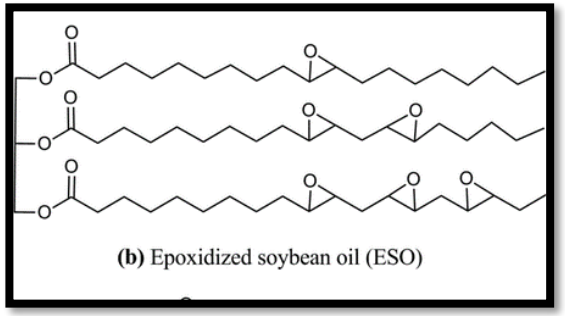






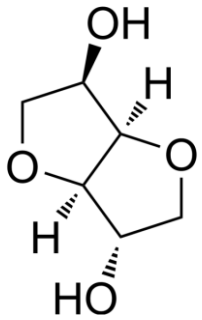


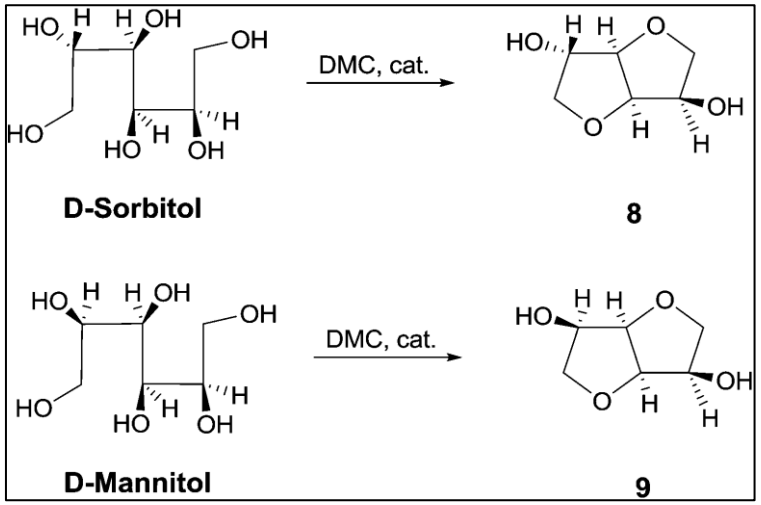


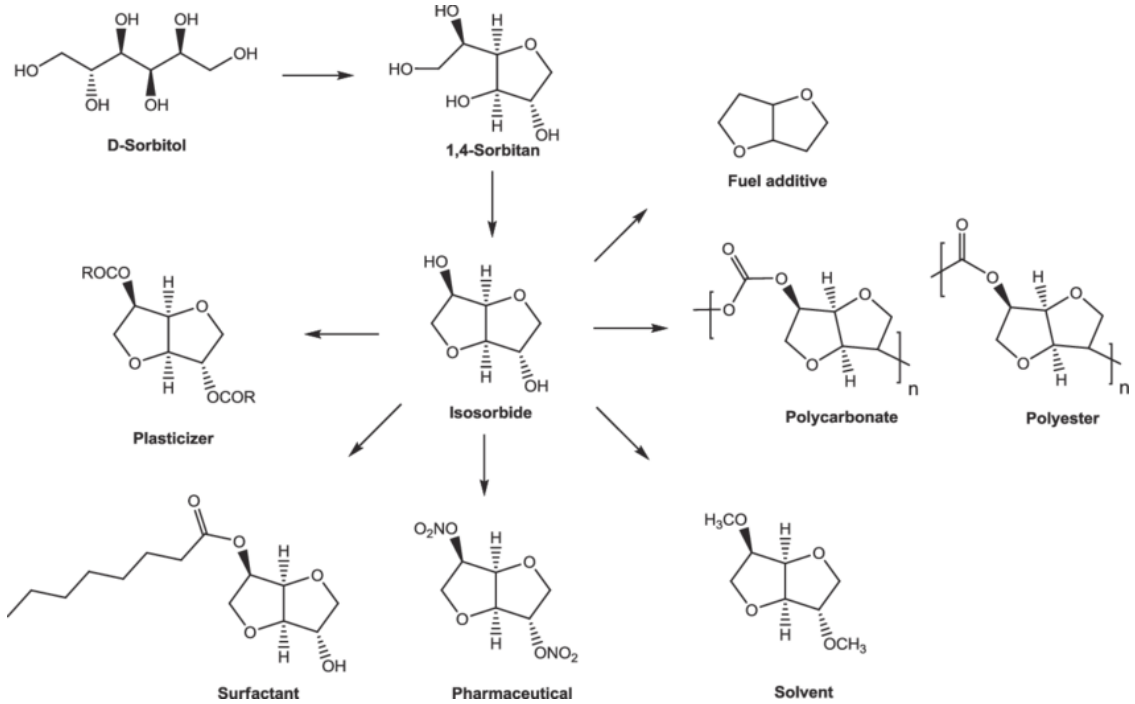


Janicki et al., European Polymer Journal, 2011
Periyasmy et al. NJC, 2016

Isosorbide and its Conventional Applications

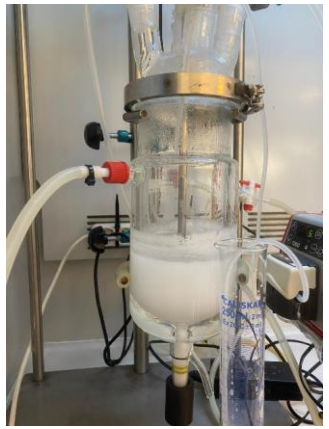


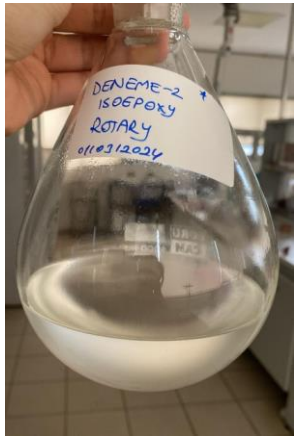




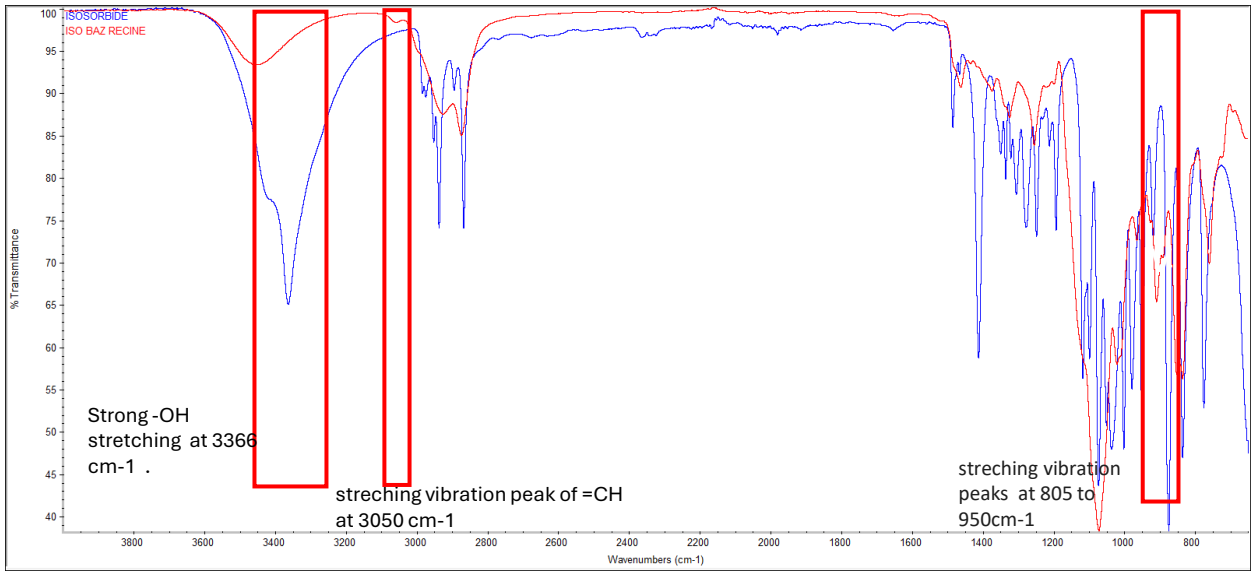
Janicki et al., European Polymer Journal, 2011
Periyasmy et al. NJC, 2016

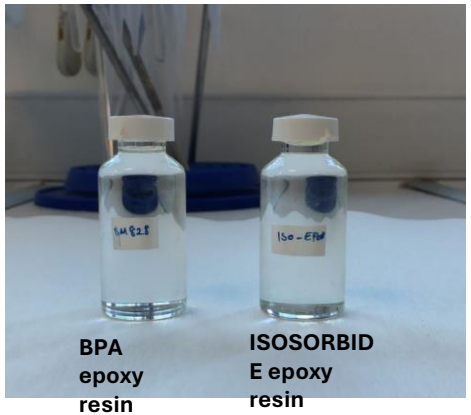
Synthesis of Isosorbide Based Epoxy Resin

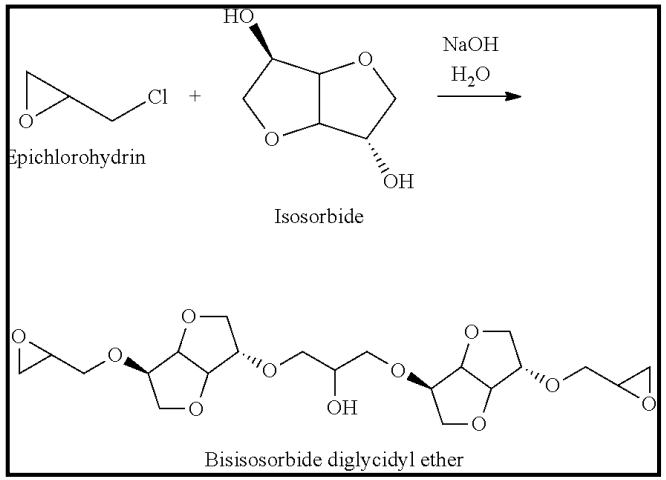




Optimized parameters
-ECH/BPA ratio
-NaOH/BPA ratio
-Reaction temperature and duration



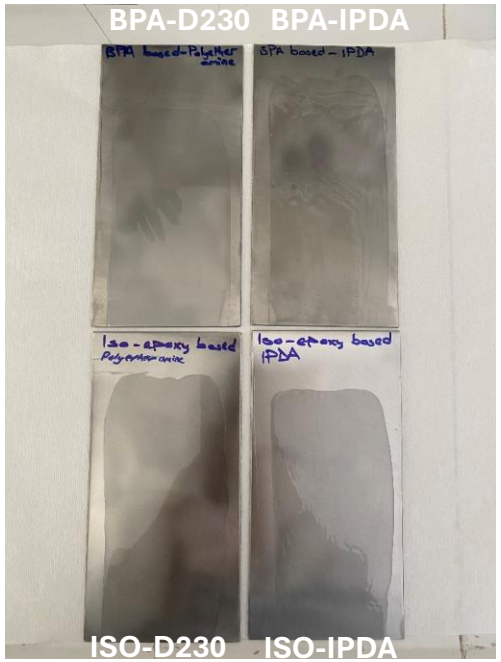




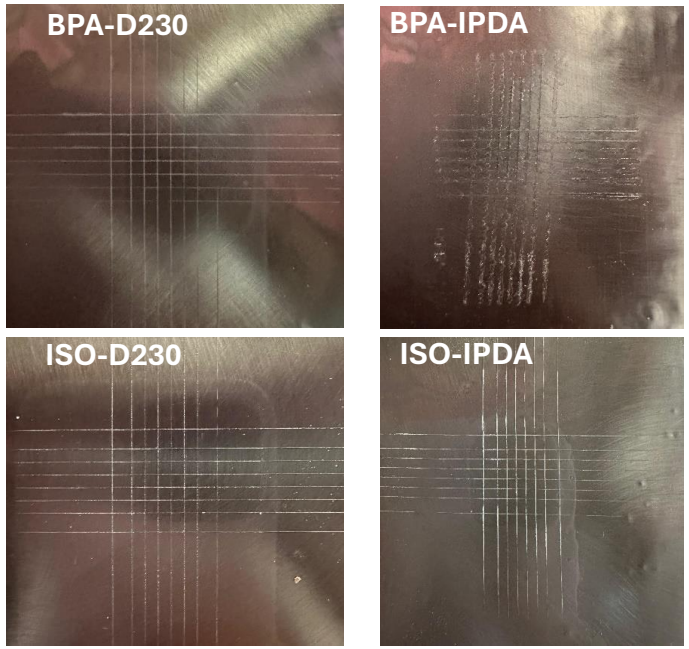
Epoxy resin type	Viscosity (mPa.s)	Density (g/ml)	EEW(g/eq)
BPA epoxy resin	11350	1,16	190
Isosorbide epoxy resin	9285	1,13	228

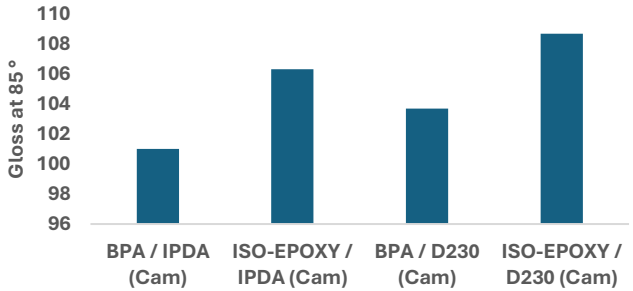
Coating Application of Isosorbide based epoxy resin

COATING ON METAL SURFACES

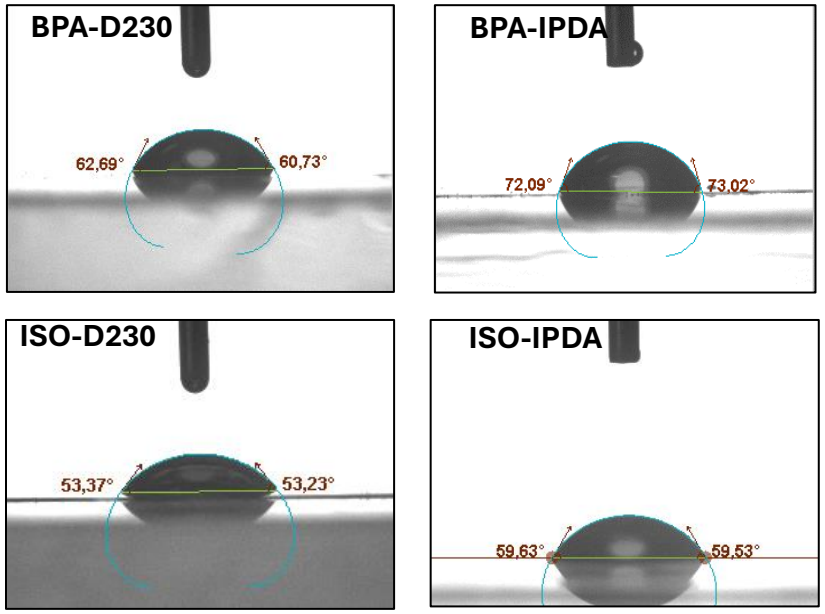


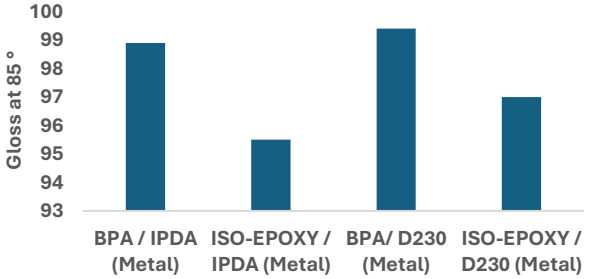
CROSS-CUT ADHESION RESULTS





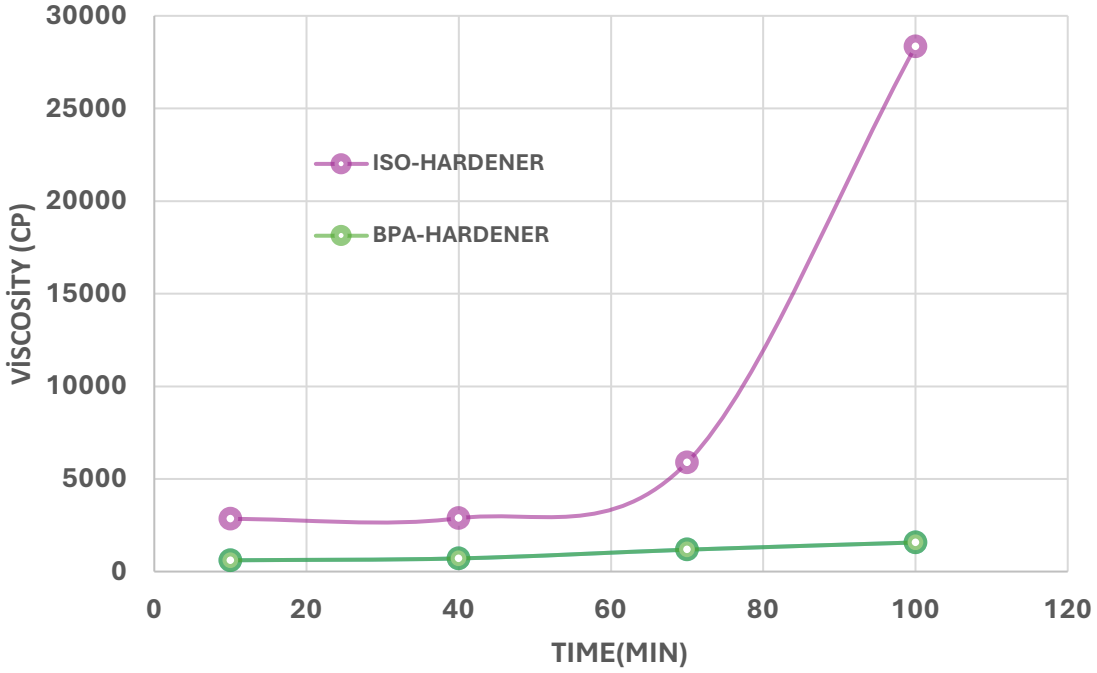
CONTACT ANGLE RESULTS



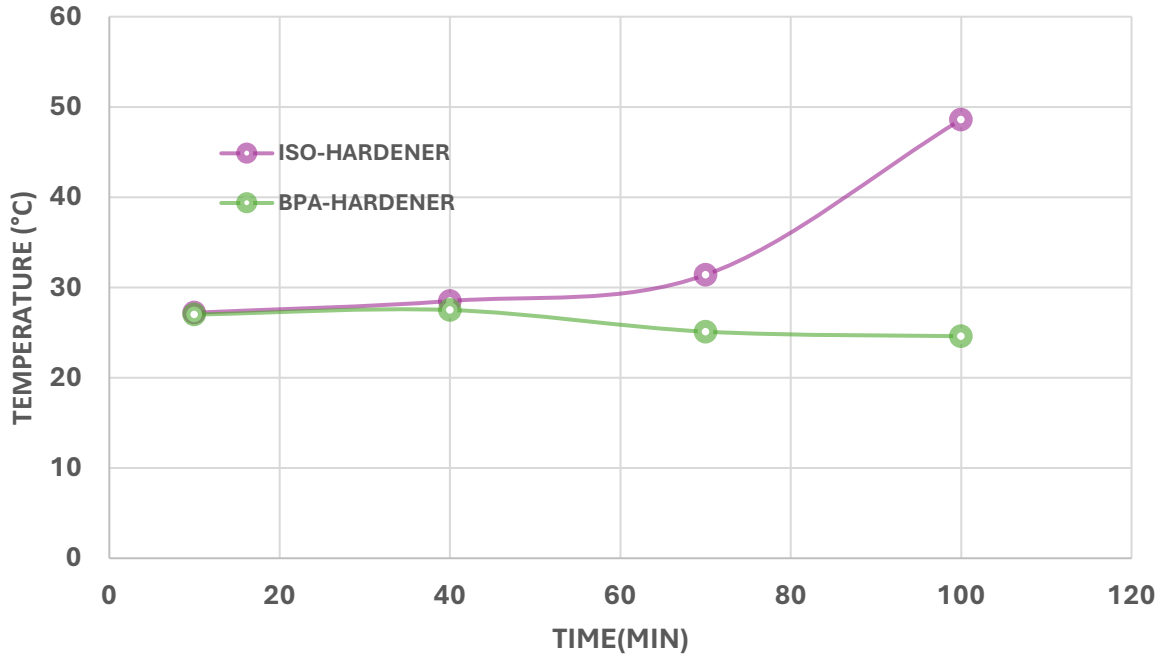


Curing Analysis of Isosorbide based epoxy resin

Viscosity development of BPA and Isosorbide based epoxy resins



Temperature development of BPA and Isosorbide based epoxy resins

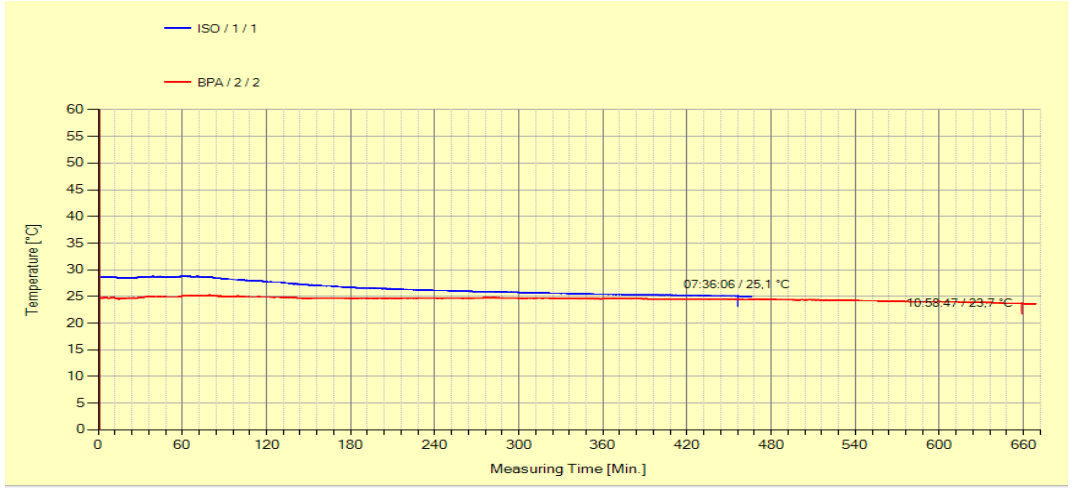


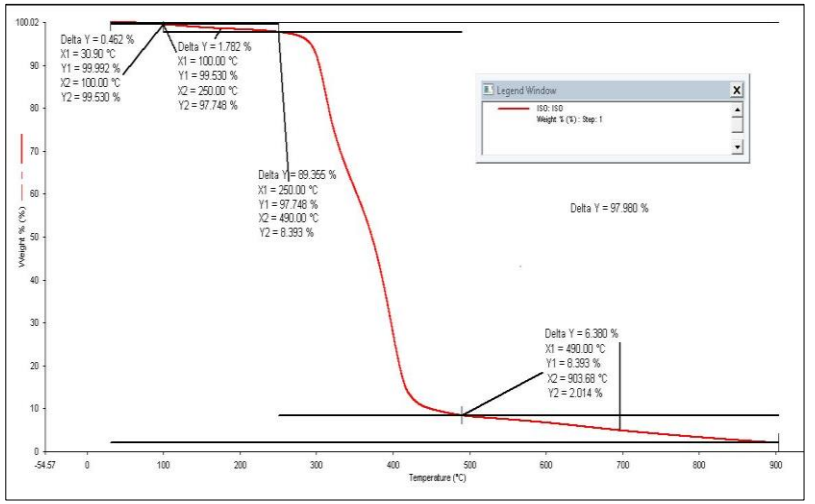
- Both epoxy resins were cured by amine mixture of polyetheramine and cyloaliphatic amine

Hardness, TGA and gel time properties of isosorbide based epoxy resin

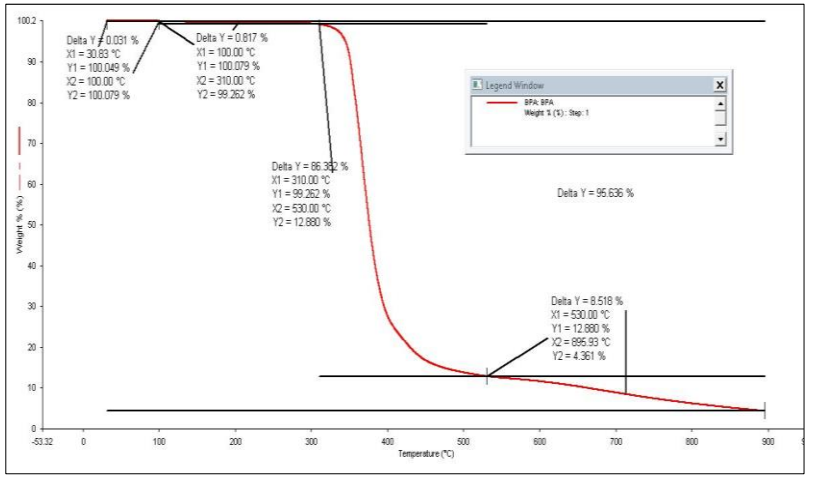
Shore D	
Isosorbide Based Modified Epoxy Resin	64
BPA Based Modified Epoxy Resin	75

Gel time results





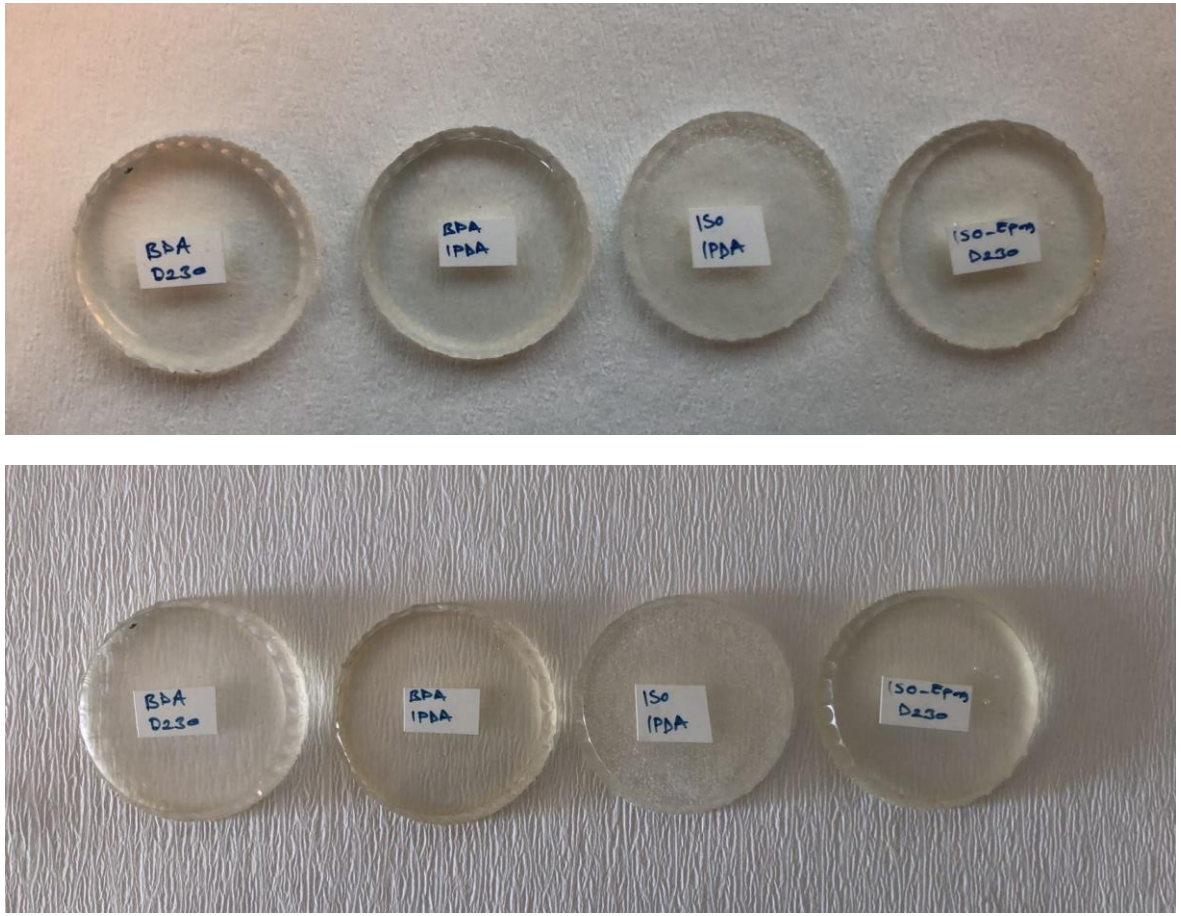
TGA Results (ISO)

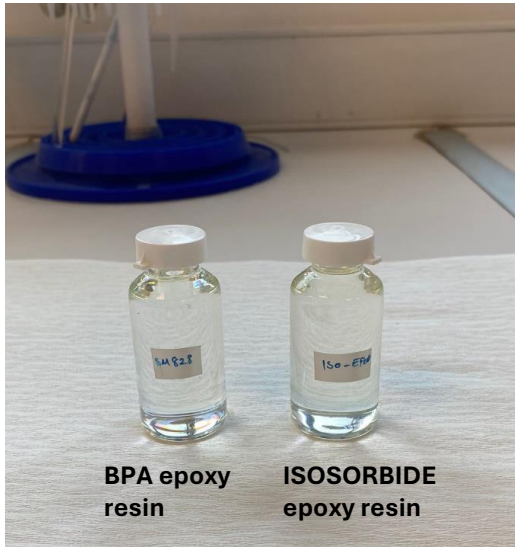


TGA Results (BPA)

- Epoxy resins were modifed by a reactive diluent 1,4-butandiol glycidyl ether. Both epoxy resins were cured by amine mixture of polyetheramine and cyloaliphatic amine.

UV Stability of Isosorbide based epoxy resin

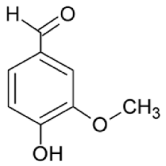


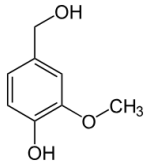


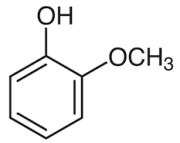
- Isosorbide base epoxy have higher yellowing resistance than BPA based epoxy resin.

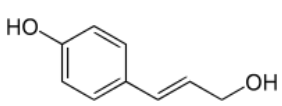
Appearance of epoxy samples after exposed to 50 °C, 0.82 w/m2 for 24 hours at QUV Chamber

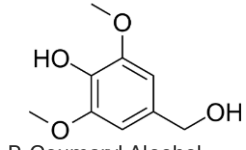
Lignin derivatives for epoxy resin production

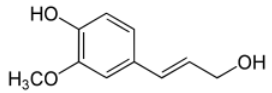

vanillin


vanillyl alcohol

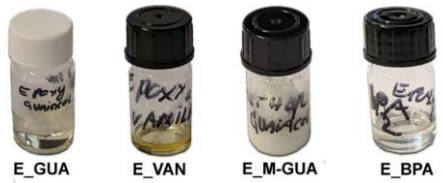

guaiacol

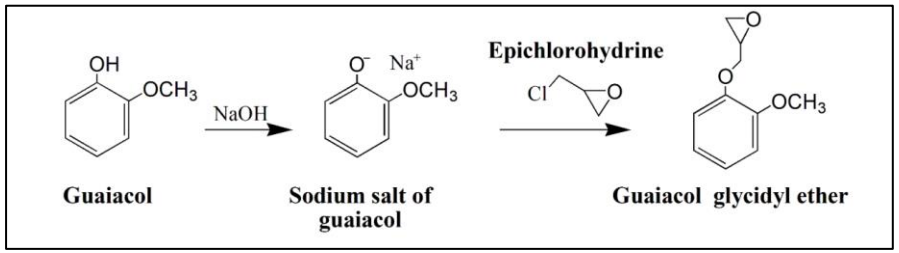

Syringyl Alcohol

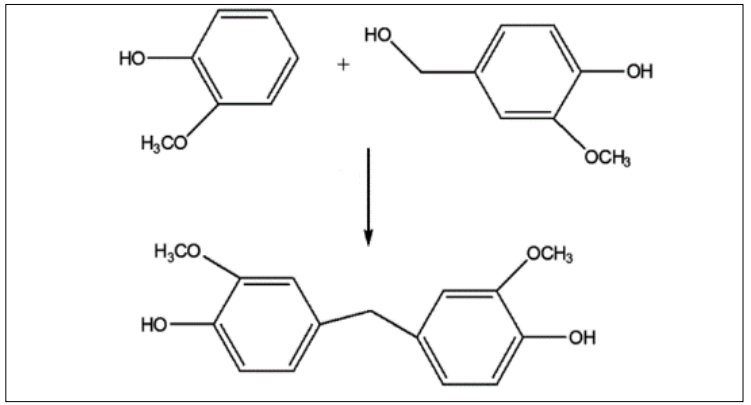

P-Coumaryl Alcohol


Coniferyl Alcohol

- *GF-based polymers have **similar thermal stability and mechanical strength** to BPA-based ones.*
- *BGF is also sufficiently different to BPA **not to cause endocrine disrupting effects.***

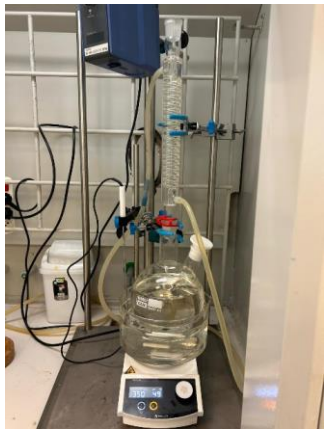


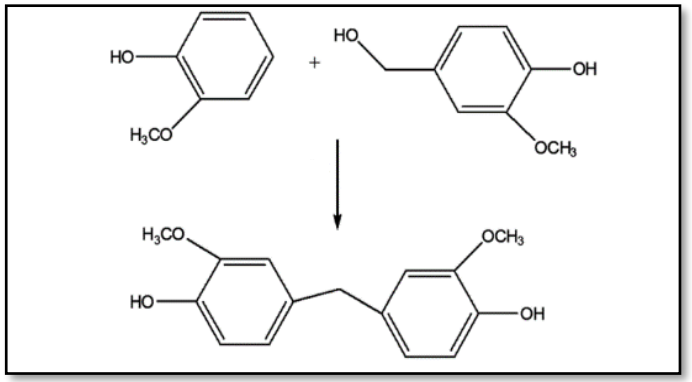




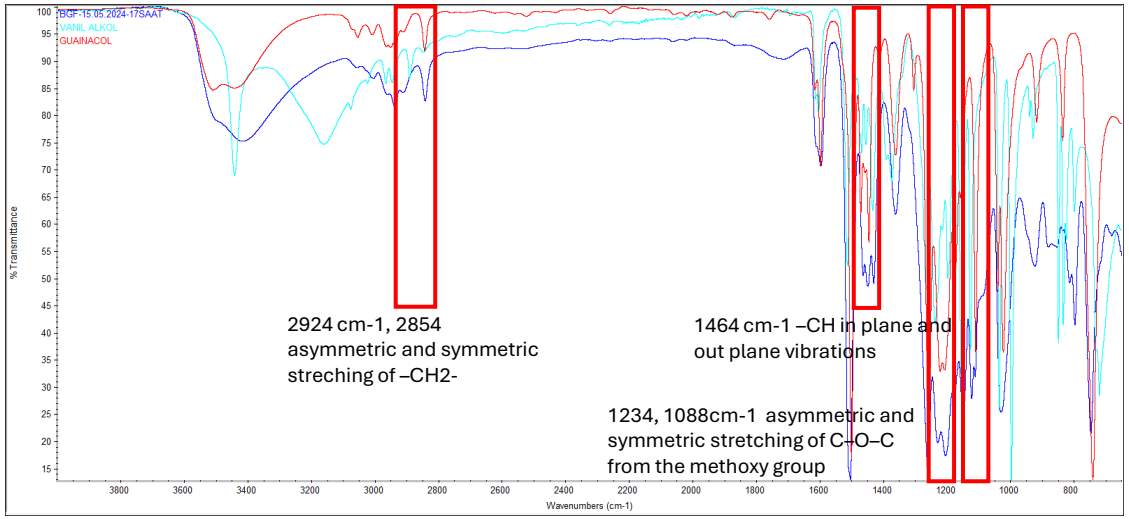
Velde et al., Bio-Based Epoxy Adhesives with Lignin-Based Aromatic Monophenols Replacing Bisphenol A Polymers, 2021

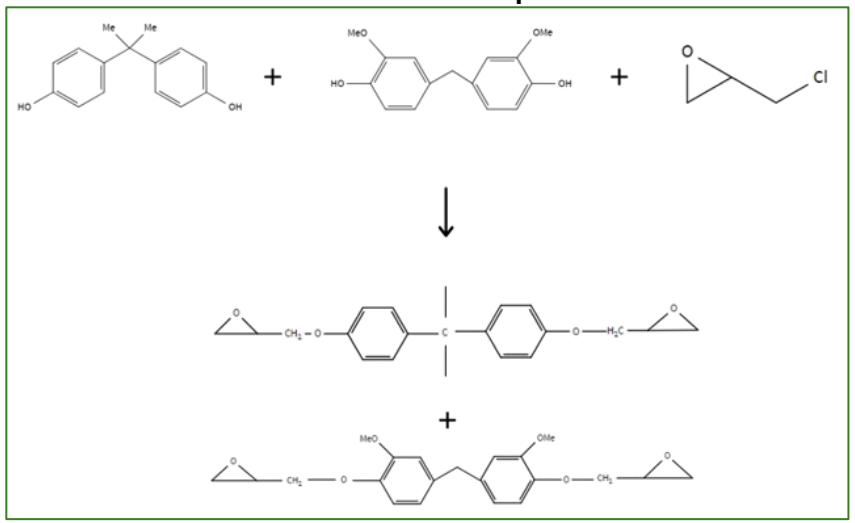
Synthesis of Bisguaiacol F Epoxy Resin





Synthesis mechanism of Bisguaiacol F





BGF-BPA Epoxy Resin Synthesis Mechanism

Appearance of BGF

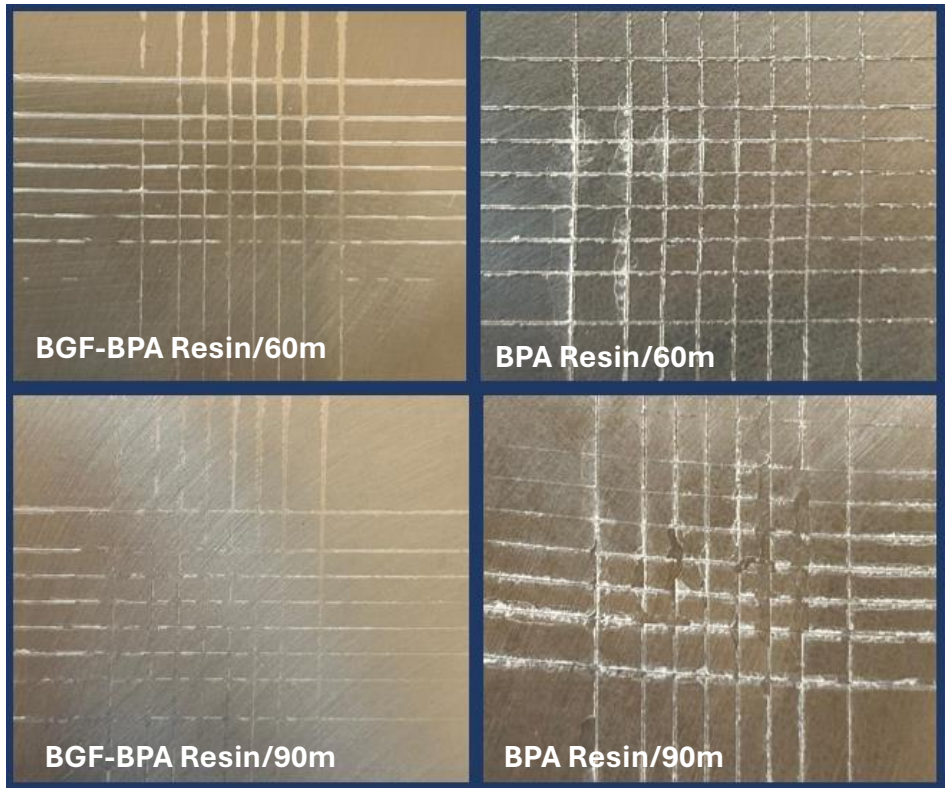
Appearance of BGF/BPA epoxy resin

BGF-BPA Resin	20:80	40:60	50:50	60:40	80:20
EEW (g/eq)	195	205	210	225	250
Appearance	Near Transparent	Light Yellow	Yellow	Dark Yellow	Brownish
Viscosity	25000	58000	93000	105000	120000

Physicochemical properties of BGF-BPA epoxy resin

Coating Application of Bisguaiacol F Epoxy Resin

Cross-Cut Test



Hardness Test

Shore A			
BGF-BPA Reçine+D230	93	91	96
BGF-BPA Reçine+IPDA	97	97	97
BPA-D230	98	94	95
BPA-IPDA	97	95	98

Shore D			
BGF-BPA Reçine+D230	56	59	60
BGF-BPA Reçine+IPDA	63	63	64
BPA-D230	56	60	61
BPA-IPDA	63	56	57

Glossmeter Test

BGF-BPA Reçine / IPDA					Ortalama Değerler
AÇILAR	20°	80,9	84,6	87	84,2
	60°	99	100	102	100,3
	85°	96,6	96,8	96,4	96,6

BPA / IPDA					Ortalama Değerler
AÇILAR	20°	87.2	83	78.9	83,0
	60°	118	117	118	117,7
	85°	99,3	99,2	98,2	98,9

BGF-BPA Reçine / D230					Ortalama Değerler
AÇILAR	20°	109	109	109	109,0
	60°	111	111	110	110,7
	85°	100	100	100	100,0

BPA / D230					Ortalama Değerler
AÇILAR	20°	107	110	107	108,0
	60°	116	115	115	115,3
	85°	99,4	99,4	99,5	99,4

Conclusion

- Isosorbide based epoxy resin was synthesized succesfully with acceptable EEW, viscosity and appearance. A lignin derivative, Bisguaiacol F was synthesized in the laboratory. %50-50 Bisguaiacol F/Bisphenol A epoxy resin was synthesized succesfully using this product.

- Coating tests showed that both isosorbide and lignin based based epoxy resin have acceptable gloss, adhession and surface properties compared to BPA based resin.

- According to curing tests, isosorbide based epoxy resin has shorter pot life and shows more exotherm than BPA based epoxy resin.

- QUV tests showed that isosorbide based epoxy resin has better yellowing resistance than BPA based epoxy resin in cured samples.

Futurework

- Mechanical properties of Isosorbide based epoxy resin will be tested for further applications.

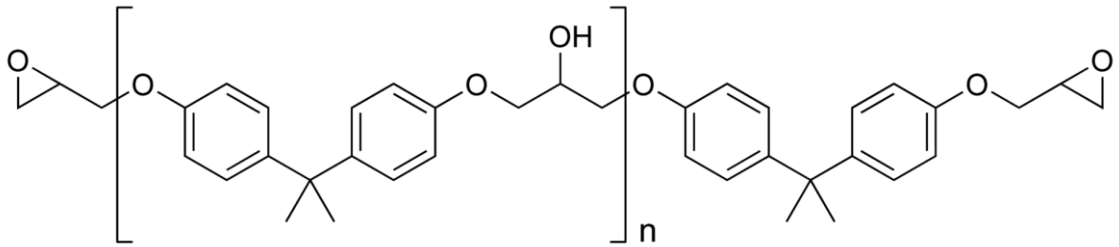
- Mechanical and thermal properties of Bisguaiacol F based epoxy resin will be tested for further applications.

THANK YOU ☺

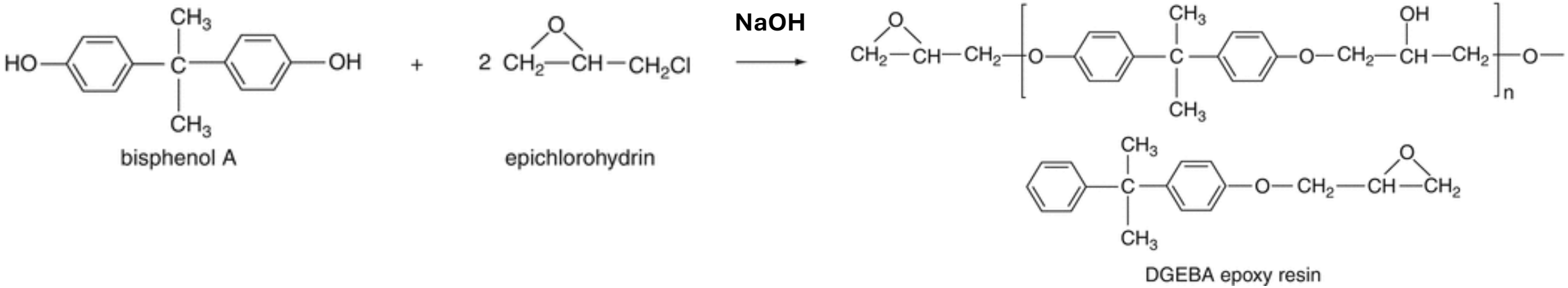
QUESTIONS?

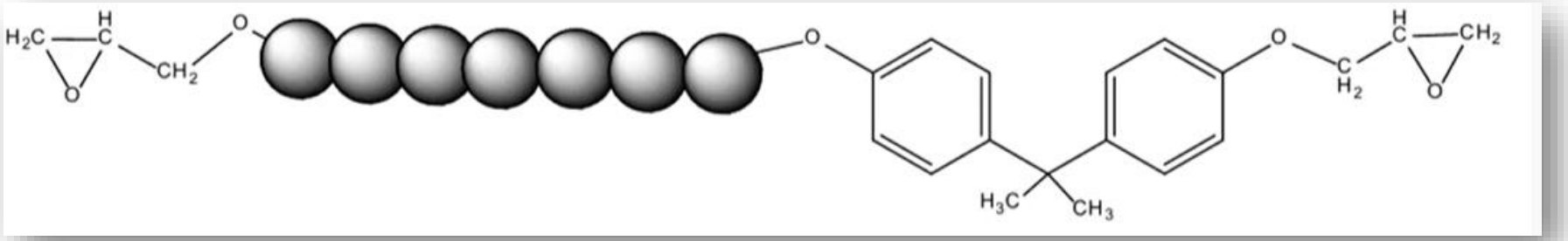
Key Properties of epoxy resins

- The resin has good processability
- It can be formed under low pressure
- It is soluble in many solvents
- High corrosion resistance and electrical performance
- High strenght
- Maintain shape under prolonged stress
- Low Shrinkage
- Excellent adhesion to various substrates
- Effective electrical insulation
- Chemical and solvent resistance
- Low cost and low toxicity

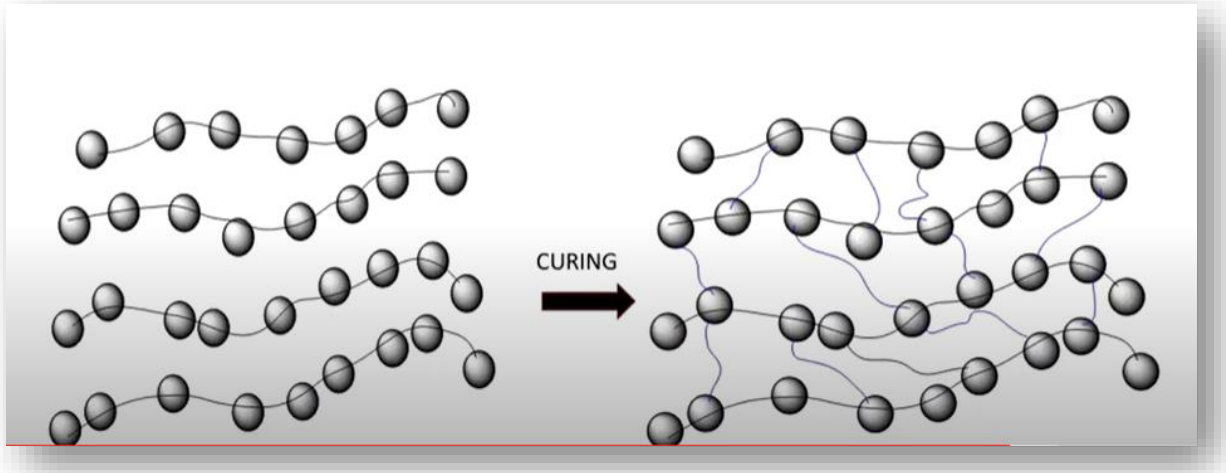


Synthesis mechanism of Bisphenol A Epoxy resin



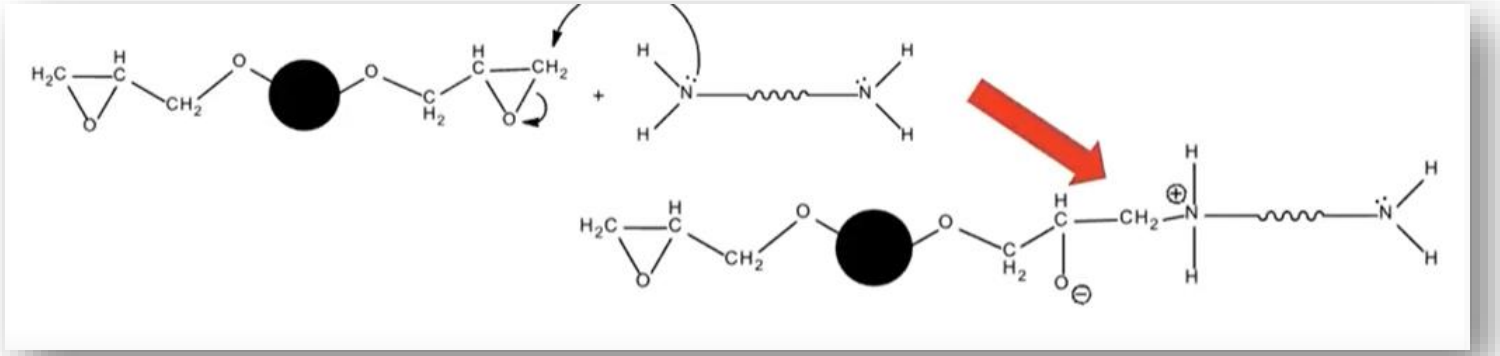


Epoksi Reçinenin Kürlenmesi



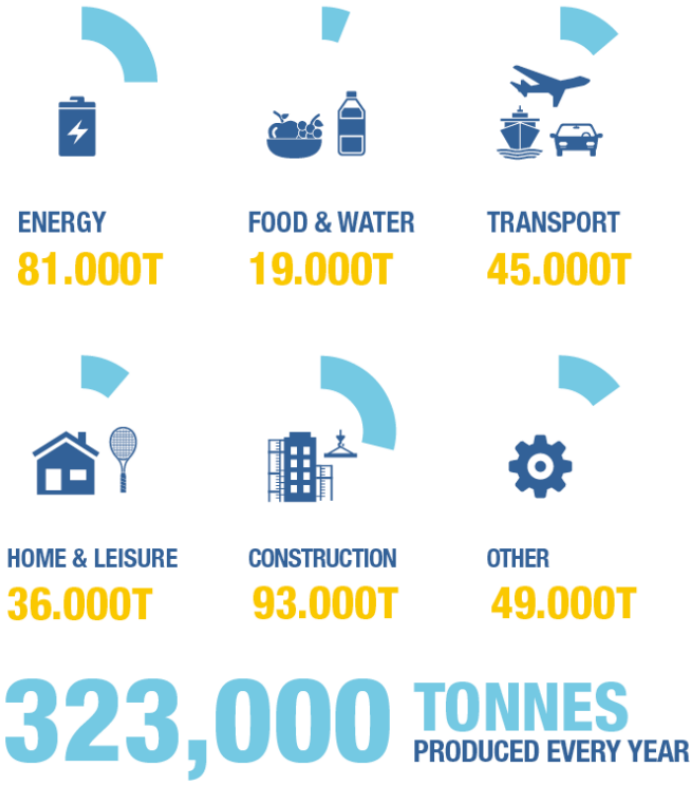
Curing agents

Aliphatic amines
Aromatic amines
Polyamides
Amidoamines

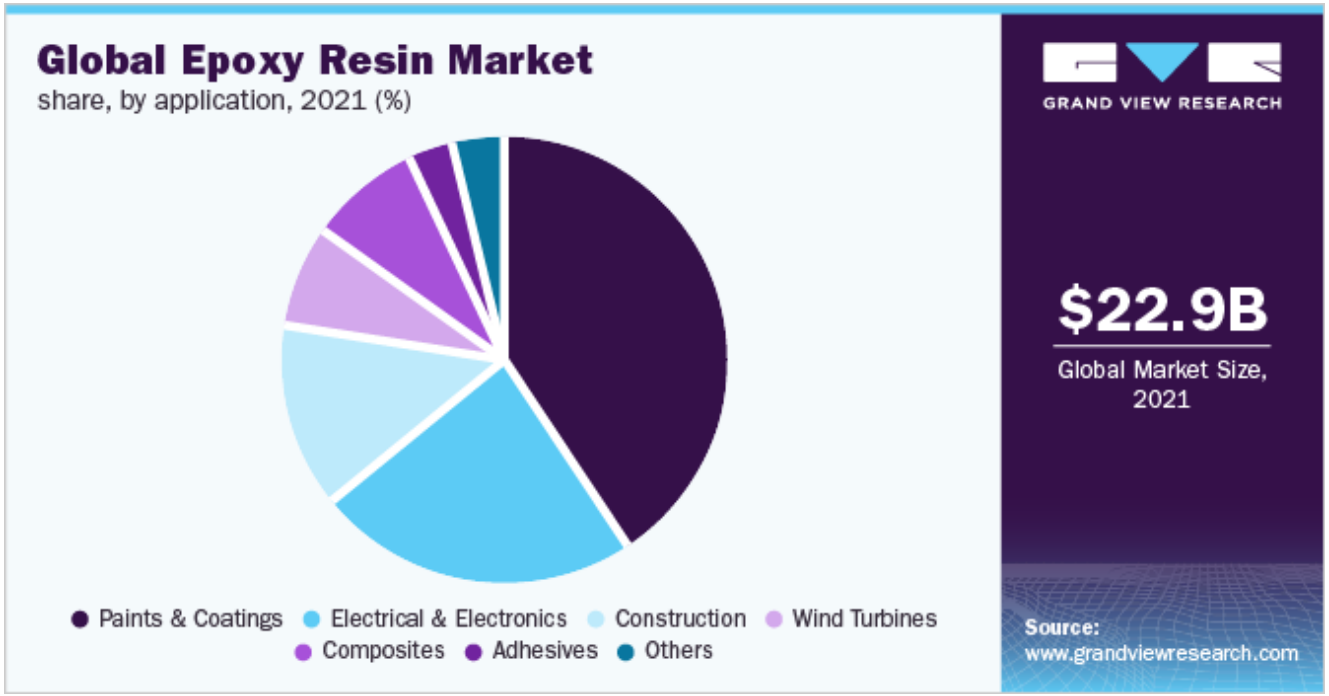


Epoksi Reçine Global Pazar

EUROPE



GLOBAL



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