Green Polyester Polyol Synthesis Using Natural Oils for Polyurethane Coatings: Structural Reactor Design with Thin Film Catalysts

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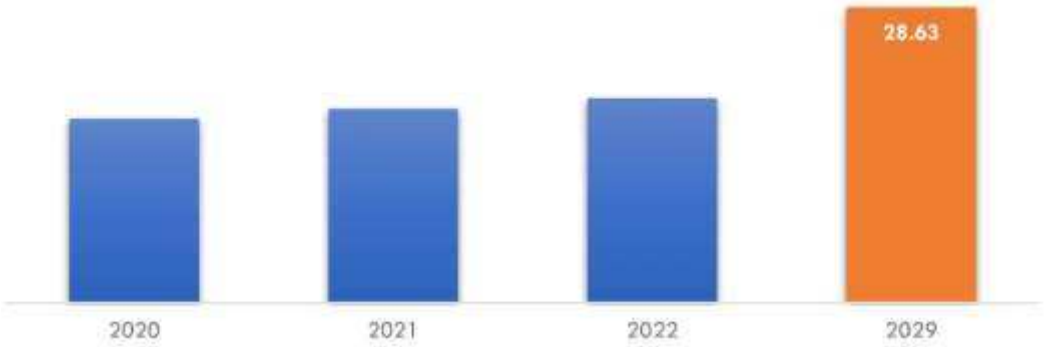
OUTLINE

- BACKGROUND INFORMATION
- INTRODUCTION
- LITERATURE REVIEW
- MOTIVATION
- PROCEDURE AND METHODS
- RESULTS
- FUTURE STUDIES

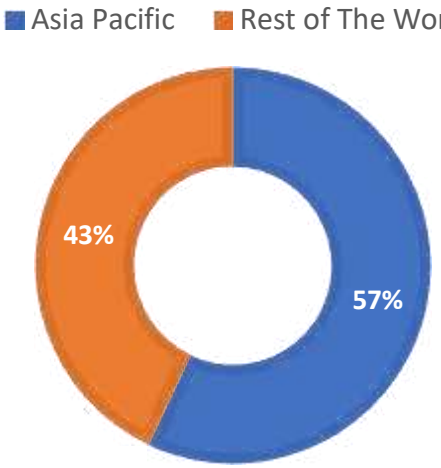
BACKGROUND INFORMATION

- The market segmentation is based on resin type; acrylic, vinyl, epoxy, amino and others.
- In the coating resins market, acrylic resin holds a dominant position.
- Polyester resins employed using it is extensive utilization in wood coatings, floor coverings, automotive and aerospace coatings.
- Volatile organic compounds (VOC) are emitted from synthetic polyester coating and it hampers air quality.
- Green coating product, with low concentration of VOC, is likely to be a leading trend in the future.

GLOBAL COATING RESINS MARKET, 2020-2029 ($ BILLION)



COATING RESINS MARKET BY REGION 2022



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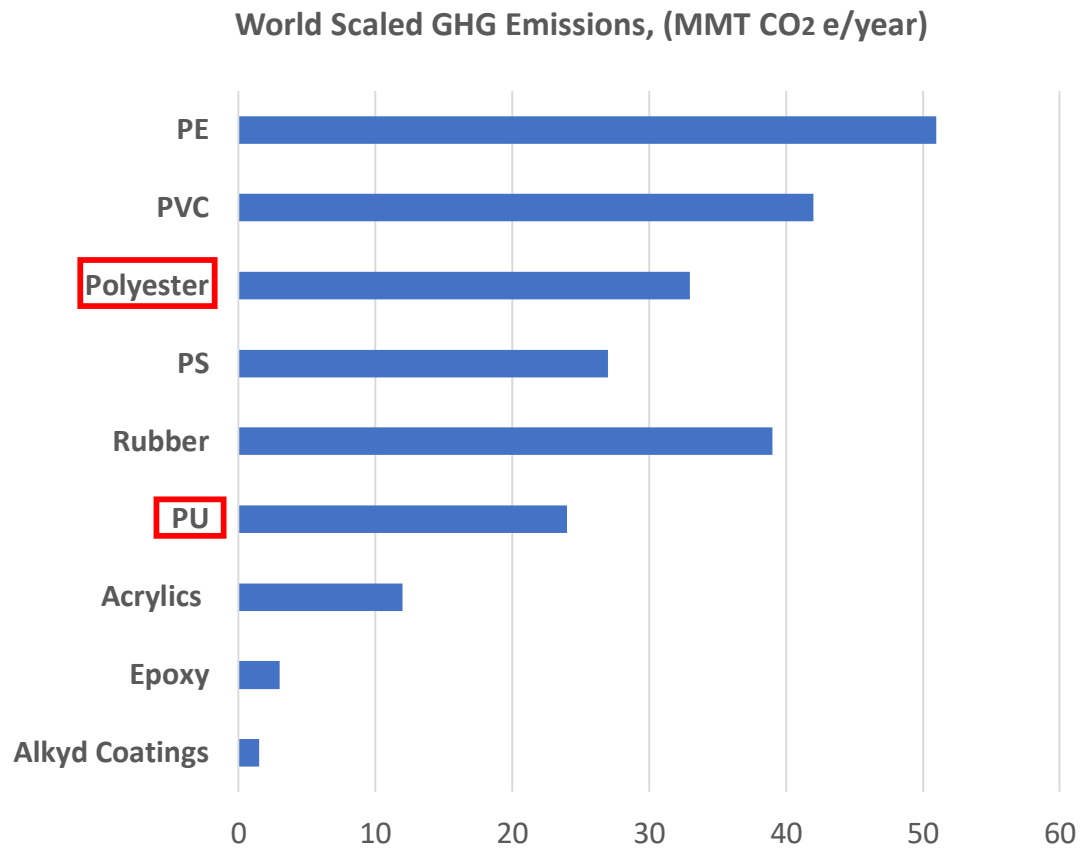
INTRODUCTION

- Polyol and isocyanate resins are basic components of polyurethane coatings.
- Polyester polyols offer advantages in terms of hydrolytic stability, high performance, viscosity and flexibility and provide improved adhesion, elasticity and UV resistance to the coatings.
- Traditionally, polyols are derived from petroleum, but this method is energy-intensive and costly.
- The depletion of global crude oil reserves, increasing prices and stricter environmental regulations are driving the demand for sustainable, cost-effective, eco-friendly, and renewable resources.
- 2022 Airbus sustainability report and THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION Directive; decreasing the VOC value in the coatings is the first major importance for the coating industry.



INTRODUCTION

- Soybean oil is the most abundant and low-cost vegetable oil.
- ESBO contains more than 99% triglycerides, and it has active sites which are three-membered oxirane groups in charge of ring-opening reactions.
- The aim of this study is to investigate the effect of different Al/Si-based catalyst dispersion-coated geometries, on polyester polyol.
- The mentioned catalysts will be coated with the dip coating method onto three distinct geometries.
- An investigation will be conducted to assess the impact of geometric alterations in the catalysts on the reaction and will compare with powder heterogeneous catalyst performance.

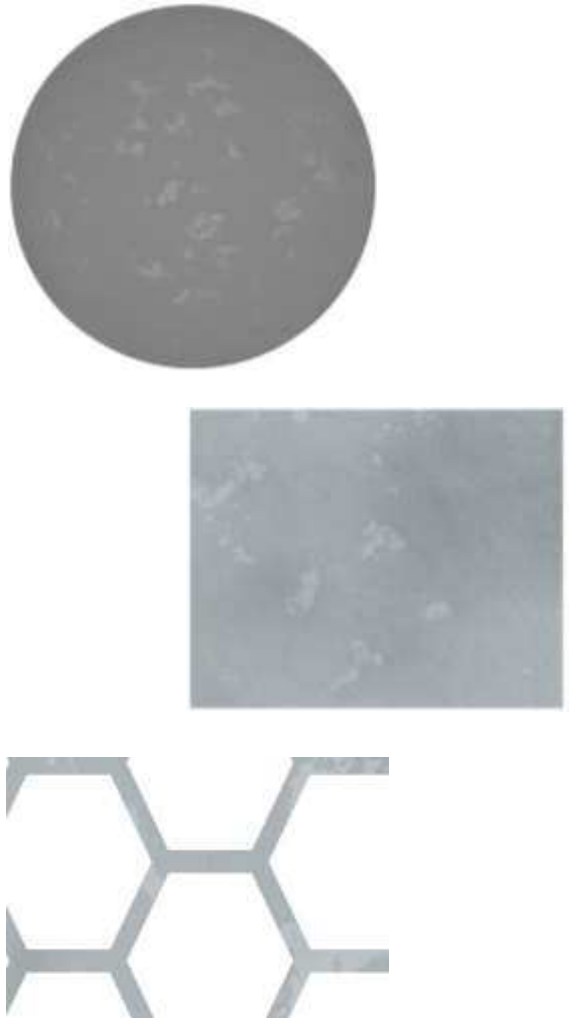


Figure 1. Thin Film Catalyst-Coated Ceramic Surface Representation in Different Geometries

LITERATURE REVIEW

In the Presence of Homogenous Catalysts

- Dai et al. (2009) performed a study on the production of different soy-based polyols.
- The ring opening of the epoxidized soybean oil (ESBO) was carried out using methanol, 1,2-Ethanedio, and 1,2-Propanediol in the presence of tetrafluoroboric acid.
- The molar ratio of epoxy groups to alcohol was 1:11 and the used catalyst amount was chosen as 1% of the total weight of ESBO.
- The reaction temperature was 95°C, the residence time was 3 hours.

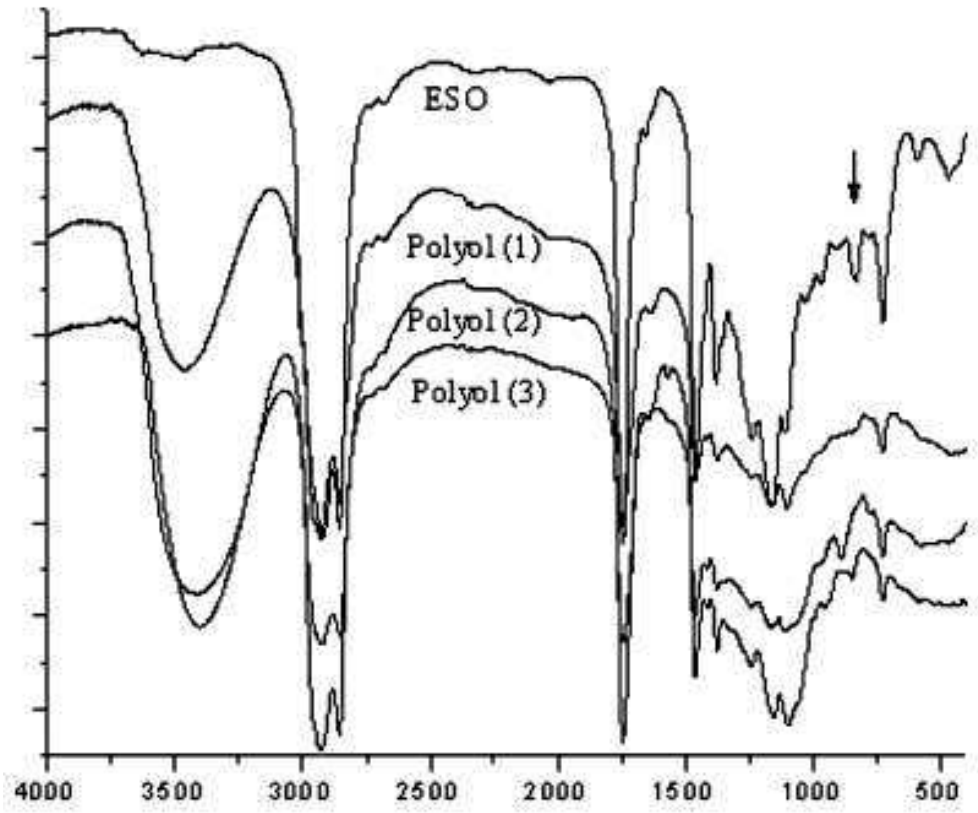


Figure 2. FTIR Spectra of ESO and Soy-Based Polyols [Dai et al., 2009]

LITERATURE REVIEW

In The Presence of Heterogenous Catalyst

- Lathi et al. carried out a study on lubricant base stock derived from epoxidized soybean oil in the presence of cationic ion exchange resins as a catalyst.
- Ring opening reaction of epoxidized soybean oil with different alcohols such as iso-amyl alcohol, n-butanol, and 2-ethyl hexanol using Amberlyst 15 which is a solid acid catalyst.
- The reaction temperature was in the range of 70-90 °C, and the residence time was in the range of 15-24 hours.
- The molar ratio of ESO/Alcohol was chosen as 1/2 and the catalyst concentration was 2% of the total mixture.

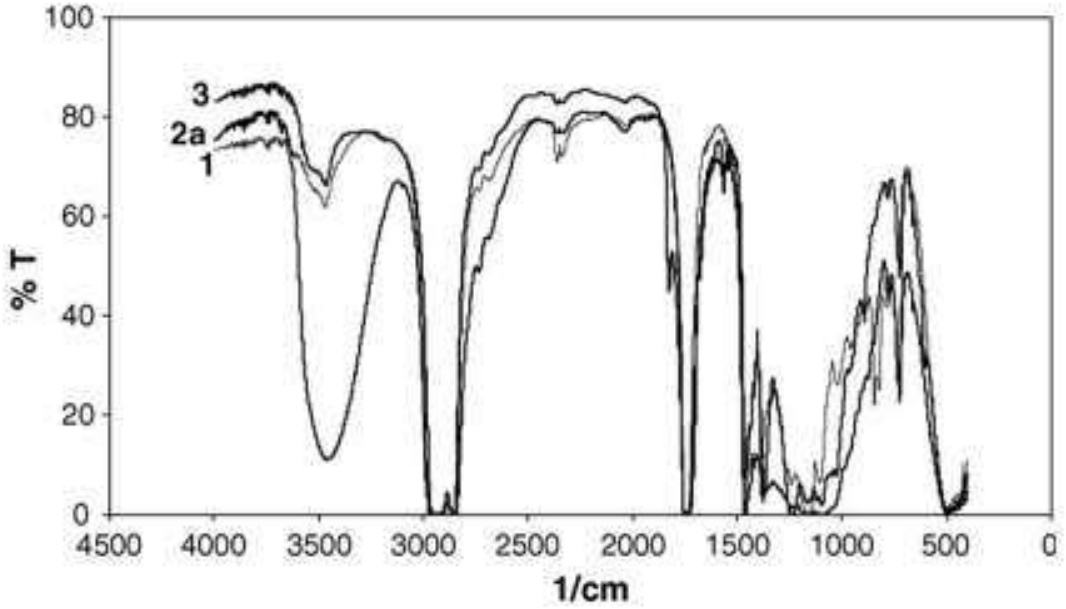


Figure 4. Comparison of the infrared spectra of the epoxidized vegetable oil (1), product of ring-opening reaction epoxidized vegetable oil with n butanol (2a), and product of esterification reaction of resulting hydroxyl group in the product 2a with acetic anhydride (Lathi et al. 2007)

MOTIVATION

- These reactions happen in vegetable oils oxirane ring-opening with proton donors like alcohol in the presence of an acid catalyst.
- Soybean oil has more than four double bonds per molecule, so it is a good alternative for producing vegetable oil-based polyol production.
- If alcohol participants possess highly branched groups, the positions of equilibrium are less favorable and the rates of esterification are slow.
- Esterification rate for alcohols; primary-R > secondary-R > tertiary-R

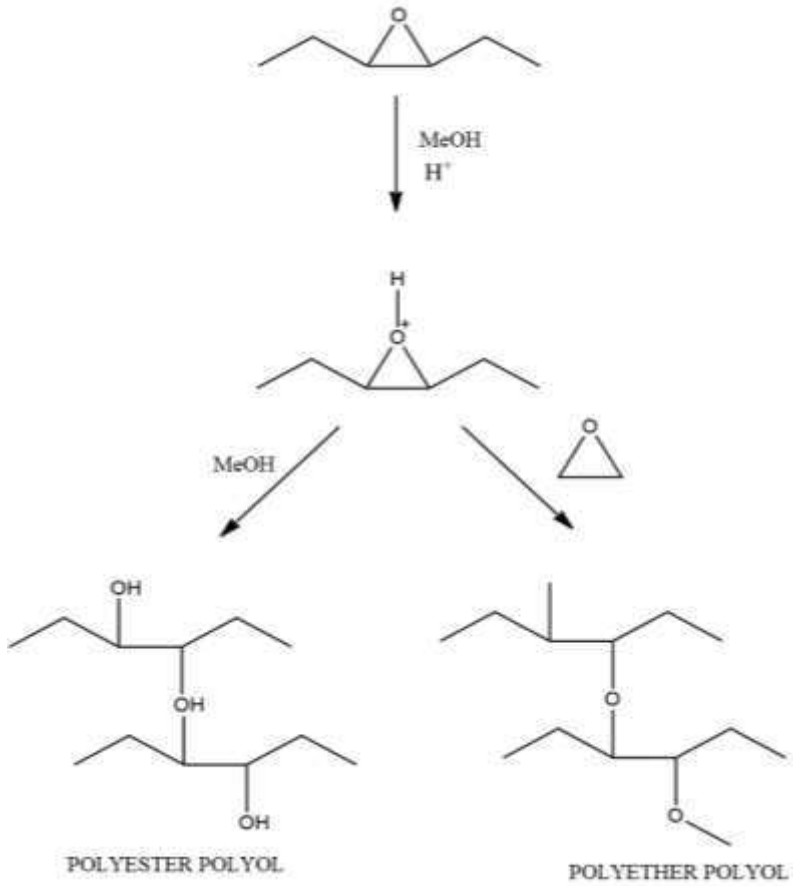


Figure 5. Simple Representation of Ring-Opening Reactions

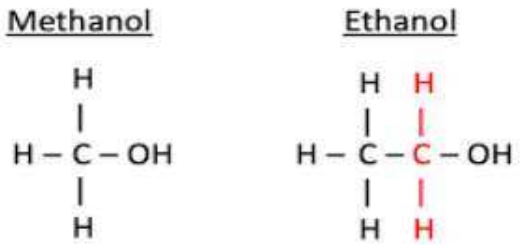


Figure 6. Methanol and Ethanol Chemical Structure

MOTIVATION

- The literature research shows that the heterogeneous catalysts can give as much as the same yields and lower reaction duration than the homogeneous ones.
- In light of all these reasons, the thin film catalyst type which is obtained by Katrena-K-AS50 commercial solid acid catalyst dispersion coated on different surfaces.

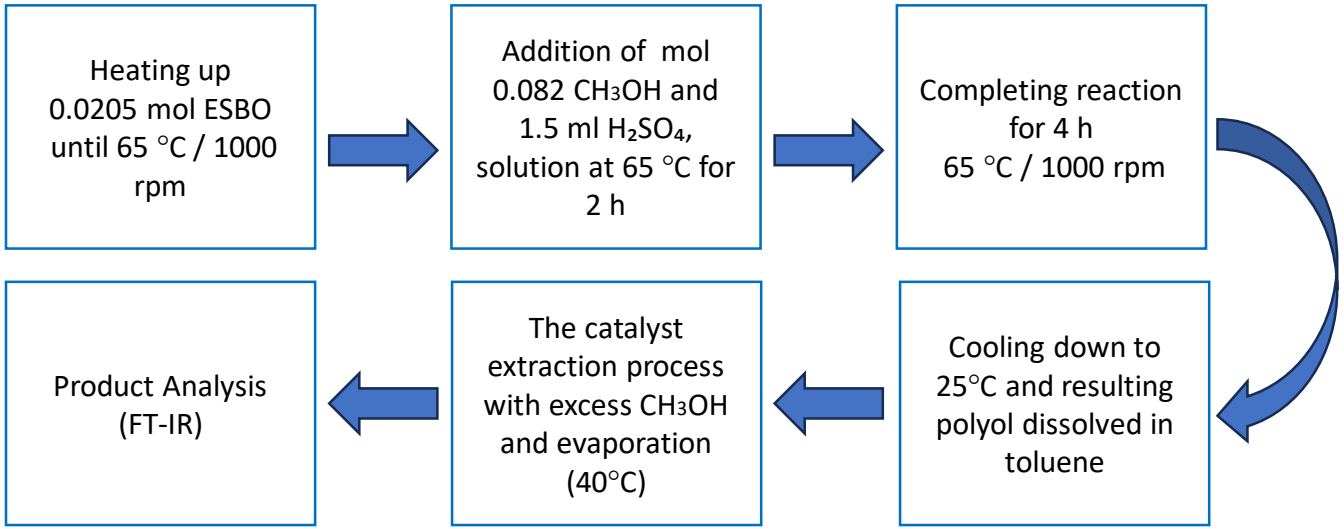
Headlight	Homogeneous Catalyst (H_2SO_4)	Heterogeneous Catalyst (K-AS50)	Thin Film Catalyst (K-AS50 dispersion)
Catalyst Phase	Same phase as reaction medium	Different from the reaction this is in the solid phase	Different from the reaction this is in the solid phase
Seperation & Recover	Difficult extraction and expensive recovering	Difficult separation for industrial applications	No need separation process for all applications
Reusability	Generally not reusable	Reusable	Reusable for many times
Diffusion	Not diffusion-controlled	May be diffusion-controlled	May be diffusion-controlled
Selectivity	High selectivity	High selectivity	High selectivity

PROCEDURE AND METHODS

Experimental Reaction Procedure in the Presence of Homogeneous Catalyst

- The ring-opening reaction was carried out.
- Catalyst: Commercial *homogeneous acid catalyst (H_2SO_4)*.
- ESBO and methanol was used as a reactant.

Figure 7. Representative Model for Reactor Set-Up



Reaction Parameters and Characterization:

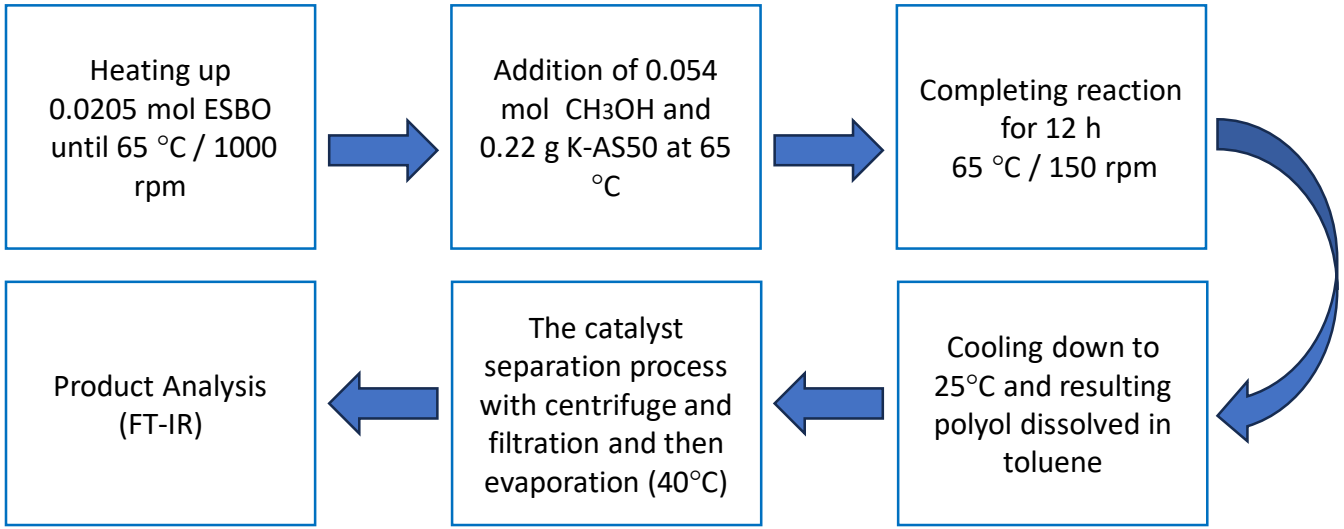
- **Reactor**: 200 ml glass reactor with a heater and stirrer
- **Reactant mole ratio**: ESBO:Methanol= 1:4
- **Temperature**: 65 °C
- **Catalyst amount**: 10 wt% of reactants
- **Characterization**: FT-IR

PROCEDURE AND METHODS

Experimental Reaction Procedure in the Presence of Heterogeneous Catalyst

- The ring-opening reaction was carried out.
- Catalyst: Commercial *heterogeneous acid catalyst (Katrena, K-AS50).*
- ESBO and methanol was used as a reactant.

Figure 8. Representative Model for Reactor Set-Up



Reaction Parameters and Characterization:

- **Reactor**: 200 ml glass reactor with a heater and stirrer
- **Reactant mole ratio**: ESBO:Methanol = 1:11
- **Temperature**: 65 °C
- **Catalyst amount**: 0.5 wt% of ESBO
- **Characterization**: FT-IR

PROCEDURE AND METHODS

Catalyst Coating (Dip-Coating) Method

- There are different methods to coat a surface with the catalyst suspension like as; frame coating, spin coating or spray coating.
- In this method, cover both sides of the surface effortlessly and in one move.
- The main factor that affects the film thickness is withdrawal speed.
- The substrate to be coated was submerged in the initial solution and then pulled out at a consistent withdrawal speed (160 mm/min) during the process.
- The process was carried out under 23°C with the ceramic plate having the dimensions of 15mm x 20mm x 2mm .

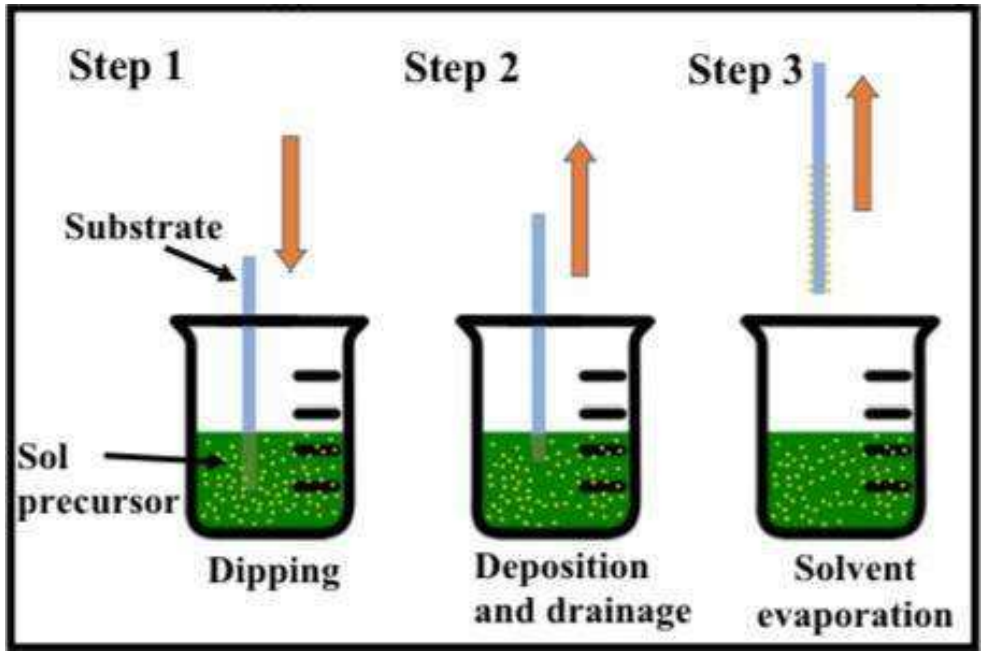


Figure 9. Sequential Stages of the Dip-Coating Method

PROCEDURE AND METHODS

Catalyst Dispersion Preparing Parameters

- The dispersion include; Excess water, K-AS50 acid catalyst, surfactant
- The catalyst dispersion was prepared under 25 °C, 500 rpm for 4h.
- The prepared catalyst solution was coated on ceramic surfaces that have high mesoporous using the dip-coating method.

Figure 10. K-AS50 Al/Si Based Solid Catalyst Powder (< 8µ)

Figure 11. Thin Film Catalyst Coated Ceramic Plate

Catalyst Weight in Dry Film Theoretical Calculation

$D_{df} = (M\%/100/D_m\text{-}(100\text{-}M\%)/D_w) = 2.39$

$C_w\% = (D_{df}*3*0.0001*100*T) = 0.31\%$

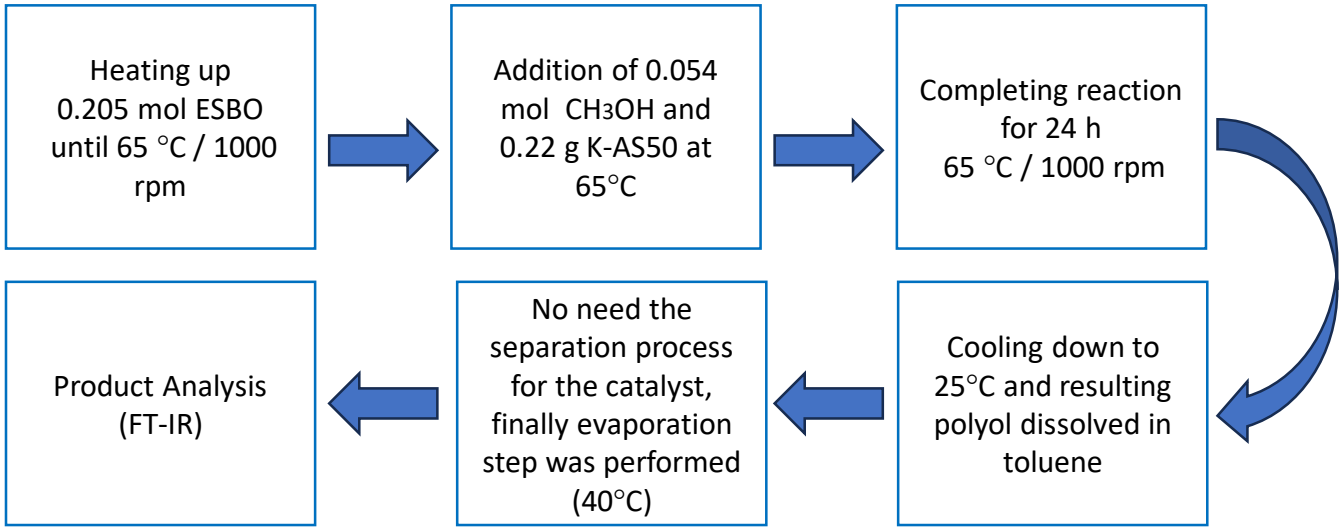
Catalyst Bulk Density (D_c)	Surface Area (A)	Coating Thickness (T)	Mixture Density (D_m)	Water Density (D_w)	%Mixture in Weight (%M)	Dry Fim Density (D_{df})	Catalyst Weight in 30 µ Dry Film (C_w)
2.8 g/cm^3	3 cm^2	30 µ	1.27 g/cm^3	1 g/cm^3	15	**2.39**	**%0.31**

PROCEDURE AND METHODS

Experimental Reaction Procedure In the Presence of Thin Film Catalyst

- The ring-opening reaction was carried out
- Catayst: *Thin film acid catalyst (Katrena, K-AS50 Dispersion)*.
- ESBO and methanol was used as a reactant.

Figure 12. Representative Model for Reactor Set-Up



Reaction Parameters and Characterization:

- **Reactor**: 200 ml glass reactor with a heater and stirrer
- **Reactant mole ratio**: ESBO:MeOH (CH_3OH) = 1:11
- **Temperature**: 65 °C
- **Catalyst amount**: 0.3 wt% of ESBO
- **Characterization**: FT-IR

RESULTS

Ring-Opening Reaction FT-IR Results In the Presence of a Homogeneous Catalyst

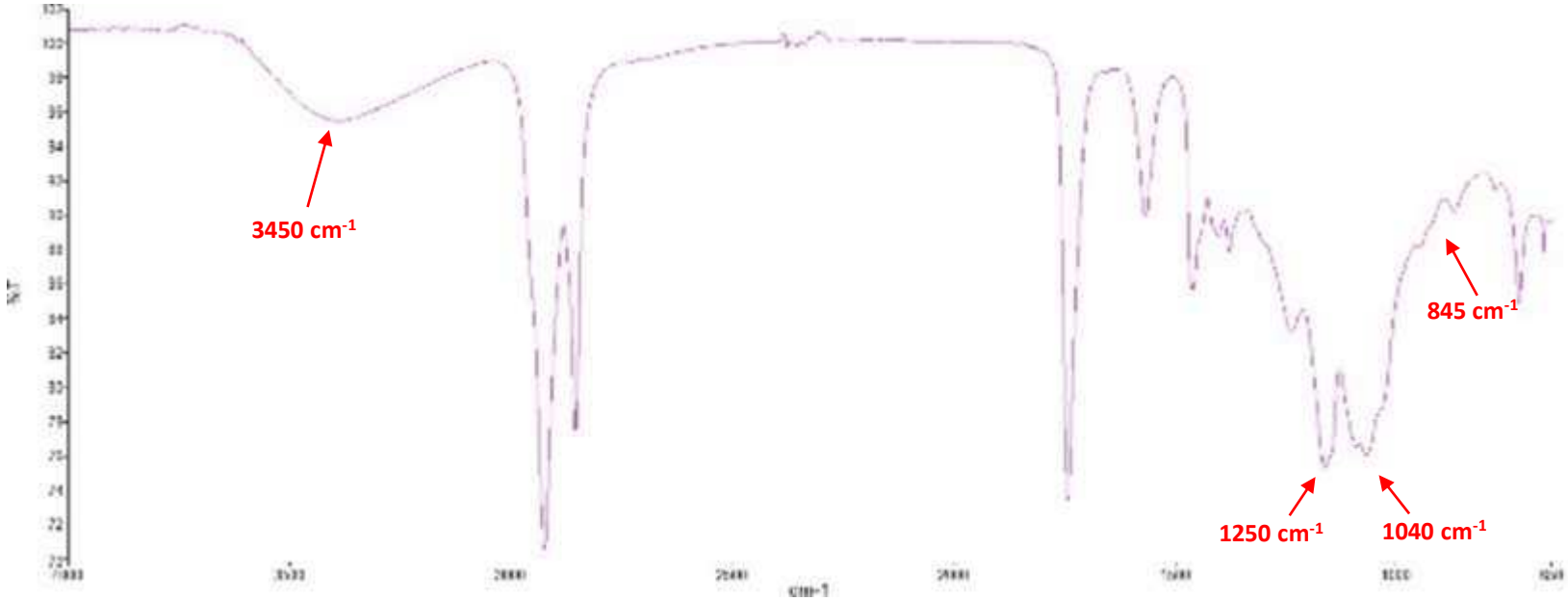


Figure 13. FT-IR Analysis after the end of the Reaction

- The reaction was performed using H_2SO_4 as a catalyst and MeOH as a nucleophile and the FT-IR results are given in Figure-13.
- The results of this study were obtained after 10 tries with a 10% error.
- The disapperance of the epoxy group 845 cm^{-1} and the appearence of the hydroxyl group at 3450 cm^{-1} in FT-IR spectra of polyol.
- The peaks at from 1040 cm^{-1} and 1250 cm^{-1} indicated that polyether and polyester groups are formed.

RESULTS

Ring-Opening Reaction FT-IR Results In the Presence of a Heterogeneous Catalyst

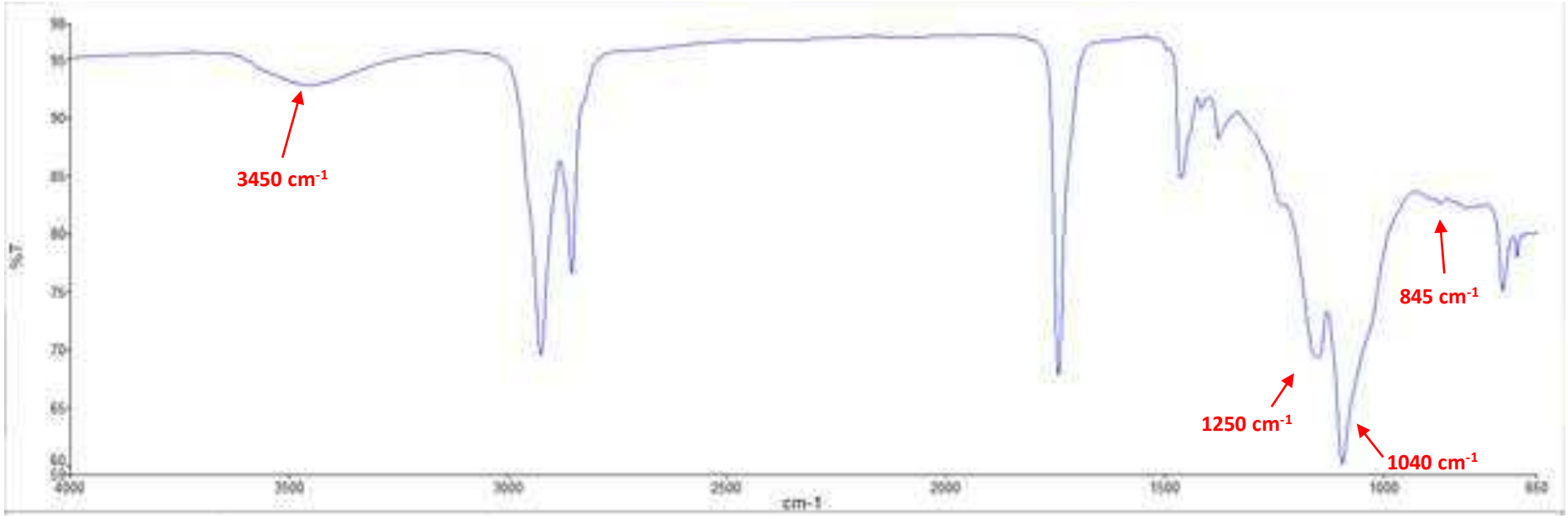


Figure 14. FT-IR Analysis after the end of the Reaction

- The reaction was performed using K-AS50 as a catalyst and MeOH as a nucleophile and the FT-IR results are given in Figure-14.
- The results of this study were obtained after 10 tries with a 10% error.
- The disappearance of the epoxy group 845 cm^{-1} and the appearance of the hydroxyl group at 3450 cm^{-1} in FT-IR spectra of polyol.
- The peaks at from 1040 cm^{-1} and 1250 cm^{-1} indicated that polyether and polyester groups are formed.

RESULTS

Ring-Opening Reaction FT-IR Results In the Presence of a Catalyst Dispersion

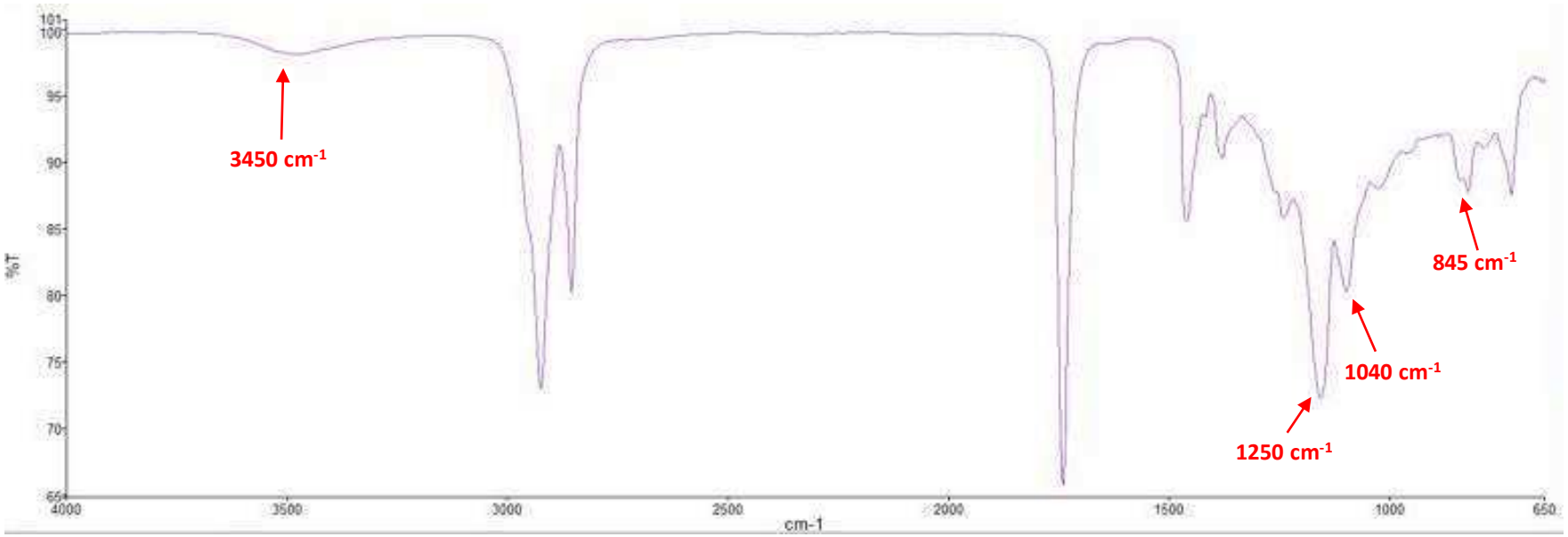


Figure 15. FT-IR Analysis after the end of the Reaction

- The reaction was performed using thin film as a catalyst and MeOH as a nucleophile and the FT-IR results are given in Figure-15.
- The results of this study were obtained after 10 tries with a 10% error.
- The disapperance of the epoxy group 845 cm^{-1} and the appearence of the hydroxyl group at 3450 cm^{-1} in FT-IR spectra of polyol.
- The peaks at from 1040 cm^{-1} and 1250 cm^{-1} indicated that polyether and polyester groups are formed.

RESULTS

Ring-Opening Reaction FT-IR Results Comprasion

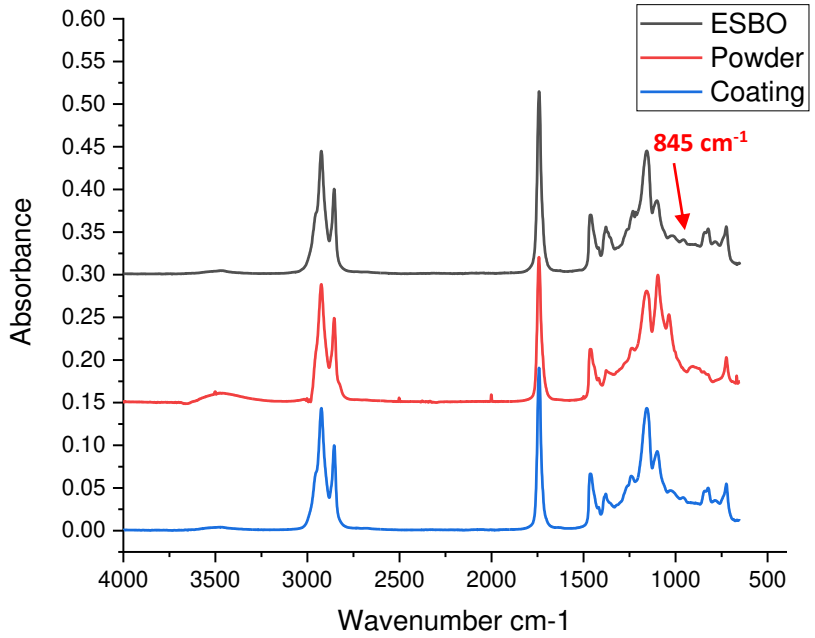


Figure 16. FT-IR Analysis Comprasion

Table 2. Reaction Epopxy Conversion Results depend on Area Under the Curve FT-IR Peaks

Catalyst Type and Load	Epoxy Conversion
K-AS50 Heterogeneous	≈ 60%
K-AS50 Thin Film	≈ 15%

- By comparing the dispersion rate of epoxy peaks, the area under the peaks was calculated.
- When the results are proportioned to the epoxy peak area in ESBO, approximate epoxy conversion values are obtained.

FUTURE STUDIES

- Catalyst weight optimization in thin film with loading optimization of dispersion.
- By increasing the surface area of the coated catalyst will prevent mass transfer limitations (surface pretreatment, different surface types, different additives for catalyst suspension and different geometries).
- Different catalyst coating methods will tried (spray coating, spin coating).
- As a nucleophilic reactant n-butanol can be tried to reduce the reaction to a single phase like a cosolvent.
- Reaction parameters and selectivity will be studied also in the presence of a basic catalyst with thin film technology.
- Different characterization methods will tried (XRD, H-NMR, GPC).
- For industrial applications, when these studies make upscaling, reaction mechanism data will be investigated and modeled.

Figure 17. Industrial Scale Reactor Design Representation

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