Progress Report as of January 25, 2022

I. Statement of the project objective(s):

Phase 1: Fabrication of soybean-based thermosetting epoxy materials, with aromatic networks (Synthesis, Characterizing, Fabrication of the biocomposites, and Evaluation of the mechanical properties)

II. Statement of quantifiable progress (QP) toward project objective(s) achieved:

QP1: Use of Deep Eutectic Solvent (DES) in soybean oil epoxidation

Referring to the previous interim progress report, we could able to understand that chemical epoxidation method yield epoxy product efficiently than enzymatic epoxidation. In enzymatic epoxidation, lipase enzyme suffers from peroxide sensitivity. On this basis, chemical epoxidation is preferable as the process is fast and economic. However, chemical method has environmental concern as harsh chemicals are a part of the process. Thus, it is very much essential to achieve epoxidation with greener approach. To overcome this, Deep Eutectic Solvent (DES) were used in the epoxidation process. In total, 28 DESs were screened and potential DESs were identified for soybean oil epoxidation.

1. Choline chloride (ChCl): Oxalic acid (1:1)
2. Acetylcholine chloride (AChCl): Oxalic acid (1:1)
3. ChCl: Urea (U) (1:2)
4. Betaine (Bet): Urea (1:2)
5. Choline Chloride: Butyric acid (1:3)
6. Acetylcholine Chloride: butyric acid (1:3)
7. Acetylcholine Chloride: valeric acid (1:4)
8. Acetylcholine Chloride: valeric acid (1:3)
9. Choline Chloride: Butyric acid (1:3)
10 Tetrabutylammonium Bromide (TBABr): Hexanoic acid (1:2)
11. (TBABr): Decanoic acid (1:2)
12. Menthol (Men): Thymol (Thy) (1:2)
13. Menthol (Men): Thymol (Thy) (2:1)
14. Borneol (Bor): Thymol (1:1))
15. Bor: Thy (1:2)
16. Men: Thy (1:1)
17. ChCl: Water (1:3)
18. ChCl: Water (1:4)
19. TBABr: Glycerol (1:4)
20. TBABr: Polypropylene glycol (PPG) (1:4)
21. Glutamic acid (Gly) : Glycerol (1:3) + 20% water
22. Arginine (Arg) : Glycerol (1:3) + 20% water
23. Arginine (Arg) : Glycerol (1:3)
24. Proline (Pro) : Glycerol (1:3)
25. Choline chloride (ChCl): Glycerol (1:3)
26. Glutamic acid (Gly) : Glycerol (1:6)
27. Arginine (Arg) : Glycerol (1:6)
28. Glutamic acid (Gly) : Glycerol (1:3)

Acetylcholine chloride (AChCl): Oxalic acid, Choline Chloride: Butyric acid and Acetylcholine Chloride: butyric acid based DES was found promising in catalyzing soybean oil epoxidation with a yield value of more than 80% (**Fig.1**). Subsequently, the process was optimized to achieve better results.

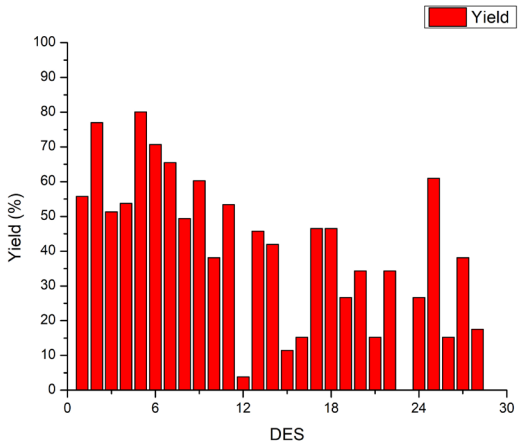

Fig.1: Yield % (Oxirane Content) vs.various DESs

QP2: DES mediated epoxidation on consistency of Epoxidized Soybean Oil (ESO)

A simple exercise was performed to understand the effect of DES mediated epoxidation on consistency of epoxidized soybean oil. The consistency of ESO was measure w.r.t. crude soybean oil in terms of relative mobility on a 45^{O} slanted smooth surface (**Fig.2**).

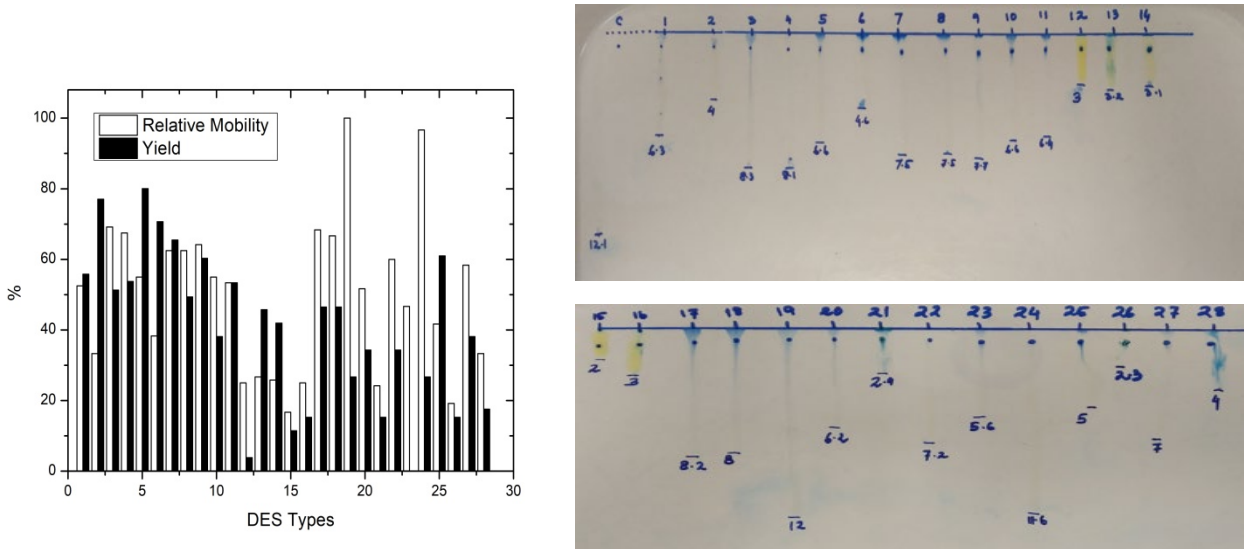

Fig.2: Effect of epoxidation on consistency of ESO
(C: Crude soybean oil; 1-28 is various DES mediated ESO)

On average, there is a doubling in the consistence of the product up on epoxidation. Thymol based DES showed significant increase in consistency through oxirane yield was limited less than 30%.

QP3: Optimization of soybean oil epoxidation process with Deep Eutectic Solvent

In this optimization exercise, previously screened best five DESs (Acetylcholine chloride (AChCl): Oxalic acid, Choline Chloride: Butyric acid and Acetylcholine Chloride: butyric acid) were choose and reaction condition was optimized (**Fig.3**). Five types of DES, DES loading, reaction temperature and

formic acid concentration were varied in various ranges and optimum reaction condition was achieved on the basis of maximum oxirane yield (**Fig.3**).

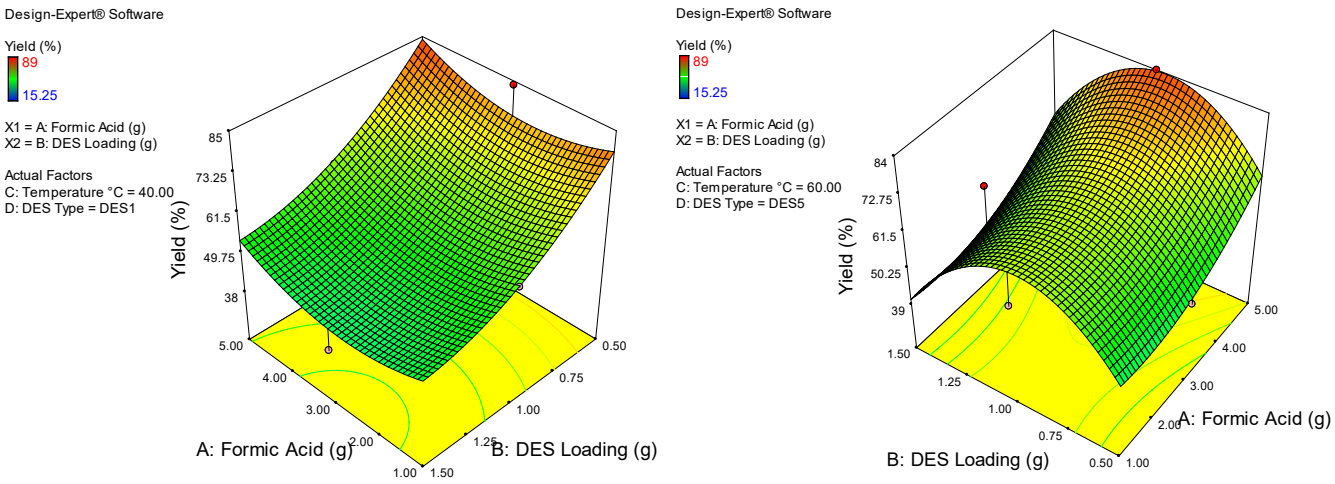

Fig.3: DES Mediated Reaction Optimization (Selected images for representation only)

A numerical optimization was carried out to achieve the optimum condition as, formic acid 1.00g; DES1: 0.50g for 86.20% oxirane yield. The goals for the numerical optimization were as in Table 1.

Table 1: Numerical Optimization Constraints

Factors	Goals	Lower Limit	Upper Limit	Importance
Formic Acid (g)	Minimize	1	5	3
DES Loading (g)	In range	0.5	1.5	1
Temperature °C	In range	40	60	1
DES Type	In range	1	5	3
Yield (%)	Maximize	38.12	89	5

QP4: Incorporation of aromatic network in the ESO

Incorporation of aromatic network was attempted as mention in reaction 1 of **Fig.4**.

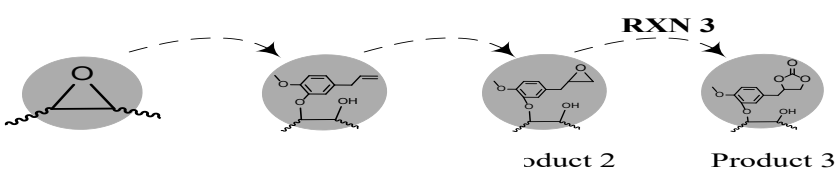

Fig.4: Synthesis of soybean-based thermosetting epoxy materials

The aromatic product is synthesized and characterization of the aromatic epoxidized product and epoxidized soy bean oil is under progress.

III. Activities planned between now and the next reporting period:

- Characterization of aromatic epoxidized product using FTIR and DSC
- Amine curing study of ESO

IV. Problems and/or obstacles that may impact the completion date, cost or scope of the project:
We are facing issue with speed of chemicals supply. Probably due to pandemic supply chain is affected and we hope to receive all required material on time to progress better with time. We are also facing challenges in recruiting skilled manpower to accelerate the progress.