Molecular Dynamic Simulation for replacing curing agent DETDA with generic bio-binder
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1. Introduction:

In 2020, the global epoxy market valued at USD 11.62 billion and has been predicted to grow at a 6.7% compound annual growth rate (CAGR) from 2021 to 2028. It is anticipated that the paints & coatings sector will significantly drive the market during the forecast period.[1] In North America and Western Europe, epoxy resins are highly in demand for residential constructions.

Epoxy resins and curing agents are the products obtained from chemical industries. Recently, there have been growing concerns of sustainability and toxicity due to use of products from petroleum and chemical industries. Studies have shown that long term exposure of humans to these products can cause conjunctivitis, asthma and rhinitis. These concerns have led to finding an alternative replacement for resins and curing agents. Amongst them are green epoxy resin or green epoxy hardeners. The composite market has already witnessed the introduction of green epoxy resins but with few drawbacks as below:

1) Resin manufacturing cost
2) Availability of the paired curing agent
3) Mechanical performance of the cured epoxy resin is compromised.

However, green epoxy hardeners are yet to be explored for partially or fully replacing the conventional industrial curing agents that are being used.

2. Project objective:

• The goal is to develop an economic, sustainable, and environment-friendly bio-binder from algae and realize a multifunctional additive to epoxy resin to completely replace conventional epoxy hardener and partially replace epoxy resin for curing and solidification.

• From algae, bio-binder can be acquired successfully that will replace conventional epoxy hardener and or reduce epoxy resin use in the epoxy resin system.

• The aim is to construct a molecular dynamic simulation to predict the physical property of the epoxy/bio-binder system. The working hypothesis is that a large number of atoms in the simulation system are allowed to interact with each other based on a well-defined molecular mechanics force field.

3. Modelling:

• The modelling of the resin and curing agent is done using Material's Studio software by BIOVIA.

• The mixing ratio provided by manufacturer for mixing the conventional resin and curing agent is 100:26.4 by weight.

• Considering 8 chains of Epon-862 the molecular weight would be 2496 amu, 4 chains of DETDA the molecular weight would be 712 amu and considering the making weight of resin to be 100 gms the closest mixing ratio achieved is 100:28.52 by weight. So, for modelling, to determine the number of chains required to achieve the mixing ratio is as shown in the table.

Epon-862 ($C_{19}H_{20}O_4$)		Curing Agent-W ($C_{11}H_{18}N_2$)	
Atom	Molecular Wt.(amu)	Atom	Molecular Wt.(amu)
Carbon(C)	19x12=228	Carbon(C)	11x12=132
Hydrogen(H)	20x1=20	Hydrogen(H)	18x1=18
Oxygen(O)	4x16=64	Nitrogen(N)	2x14=28
Total Mw. of 1 chain	312	**Total Mw. of 1 chain**	178

Table 1: Calculation of number of chains for quad-cell model

This molecular model with 8 chains of resin and 4 chains of curing agent is named as Quad-Cell as shown:
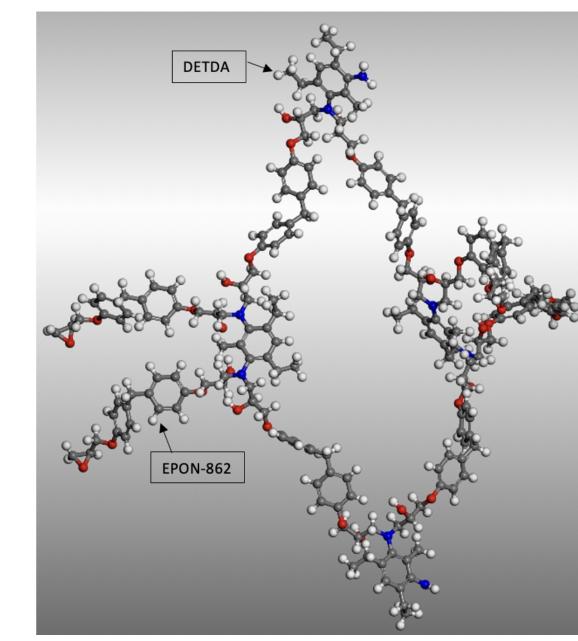

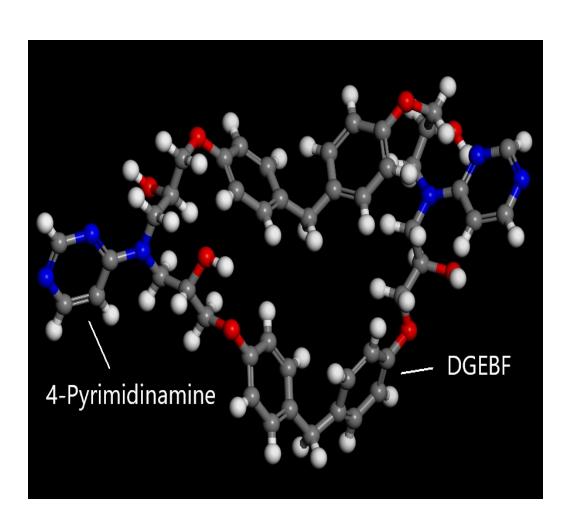Fig. 1: Quad-Cell Model with 8 chains of DGEBF and 4 chains of DETDA

The cross-linking is achieved through three principle reactions between a diepoxide and diamine as shown:

Fig. 2: Cross-linking mechanism [3]

The amine group (-NH_2) present in curing agent serve as a binding agent. Hence, the objective is replacing the curing agent-W partially/fully with generic bio-binder with possible amine (-NH_2) functional group. These different functional groups containing compounds are obtained from thermal liquefaction of algae. Few proposed models that are developed by replacing the curing agent-W are as shown in Fig. 2 and Fig. 3.

Epon-862 ($C_{19}H_{20}O_4$)		4-Pyrimidinamine ($C_4H_5N_3$)	
Atom	Molecular Wt.(amu)	Atom	Molecular Wt.(amu)
Carbon(C)	19x12=228	Carbon(C)	4x12=48
Hydrogen(H)	1x20=20	Hydrogen(H)	5x1=5
Oxygen(O)	4x16=64	Nitrogen(N)	3x14=42
Total Mw. of 1 chain	312	**Total Mw. of 1 chain**	95

Table 2: Calculation of number of chains for proposed model replacing DETDA completely

The number of chains required for modelling were determined in the same way as that done for finding the number of chains for Epon-862 and curing agent-W to form a closed chain model.
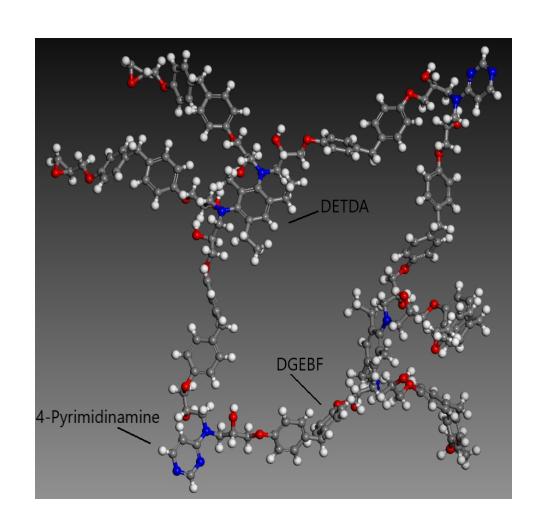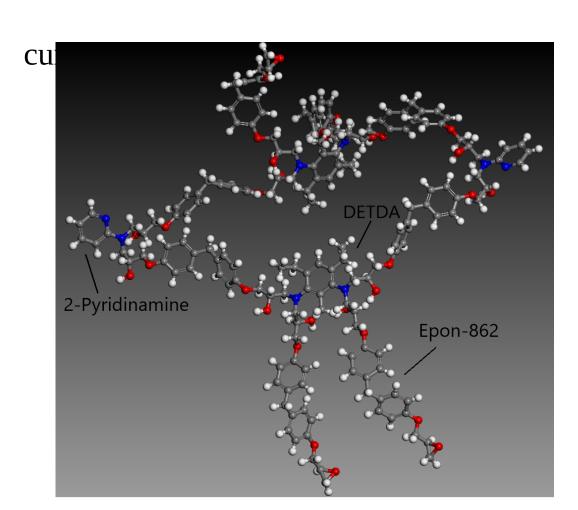

Fig. 2: Proposed bio-binder model

Similarly, for the proposed model having partial replacement of DETDA molecule, the number of chains to form a closed chain molecule is calculated as shown:

Epon-862 ($C_{19}H_{20}O_4$)		4-Pyrimidinamine ($C_4H_5N_3$)		Curing Agent-W ($C_{11}H_{18}N_2$)	
Atom	Molecular Wt. (amu)	Atom	Molecular Wt. (amu)	Atom	Molecular Wt. (amu)
Carbon(C)	19x12=228	Carbon(C)	4x12=48	Carbon(C)	11x12=132
Hydrogen(H)	1x20=20	Hydrogen(H)	5x1=5	Hydrogen(H)	18x1=18
Oxygen(O)	4x16=64	Nitrogen(N)	3x14=42	Nitrogen(N)	2x14=28
Total Mw. of 1 chain	312	**Total Mw. of 1 chain**	95	**Total Mw. of 1 chain**	178

Table 3: Calculation of number of chains for proposed model replacing DETDA partially

These are the possible compounds that may be present from those obtained by thermal liquefaction of algae. Once these compounds are confirmed, molecular dynamic simulation would be performed in the same way as they are performed on Epon-862 and cu
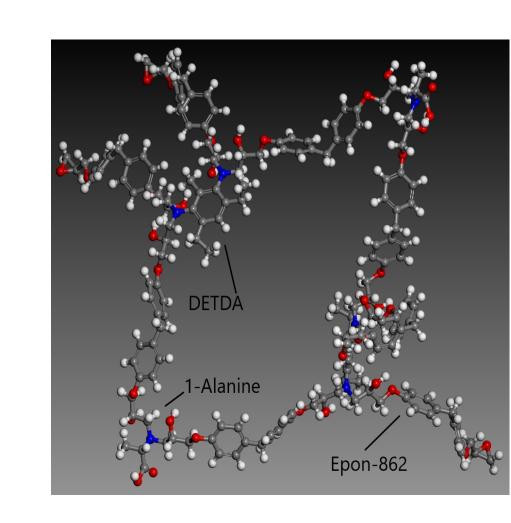

Fig. 3: Proposed bio-binder models

References:

1) https://www.grandviewresearch.com/industry-analysis/epoxy-resins-market

2) Zhao, X., Lu, S., Li, W., Zhang, S., Li, K., Nawaz, K., Wang, P., Yang, G., Ragauskas, A., Ozcan, S., & Webb, E. (2022). Epoxy as Filler or Matrix for Polymer Composites. In S. J. S. Chelladurai, R. Arthanari, & M. M.R.Meera (Eds.), Epoxy-Based Composites. IntechOpen. https://doi.org/10.5772/intechopen.102448

3) Wu, C., & Xu, W., (2006). Atomistic molecular modelling of crosslinked epoxy resin, *Polymer 47*, 6004-6009. https://doi.org/10.1016/j.polymer.2006.06.025