



Substituting the epoxy curing agent with a greener solution-towards sustainability

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Abstract

Traditionally, resins and hardeners are produced by chemical and petroleum industries. These industries make use of non-renewable energy resources like fossil fuels for manufacturing the resins and curing agents. In addition, most of the conventional curing agents used in epoxy resins are highly noxious in nature causing skin allergies and asthma. The green epoxy resin is capable of reducing these toxic effects but have few shortcomings including its cost and the mechanical performance of cured epoxy resin. On the other hand, there is a dearth of investigation in the evolution of green or sustainable curing agents known as bio-binders. This paper presents the prediction of mechanical properties by replacement of conventional curing agent with amine derivative synthesized from bio-degradable resource in a thermoset epoxy resin system. The properties are predicted by molecular dynamics simulations using Materials Studio Software.

Introduction

Epoxy resins are a class of reactive polymers and prepolymers that are generally used in industries for their exceptional adhesiveness, high mechanical properties and excellent chemical and thermal resistance. In recent times, epoxy resins have emerged as a cornerstone material in various industrial applications ranging from aerospace, automotive [1], electronics, coatings and paints to electrical insulators and composite materials. Typically, these resins require a curing agent or hardener to initiate the curing reaction that leads to a formation of dense three-dimensional structure. Traditionally, the hardeners used for curing and epoxy resins is the industrial products that uses non-renewable energy resources and is not bio-degradable raising sustainable and toxicity issues.

However, in the recent years, there has been a lot of interest in developing bio-degradable curing agents known as ‘bio-binders’ to tackle the sustainability concern. The

bio-binders are usually derived from natural and renewable resources like plants, natural oils and proteins which are easily bio-degradable. Bio-binders can be a sustainable and eco-friendly alternative to the conventional curing agents.

Research [1, 2] has found that it is possible to cure epoxy resins using bio-based curing agents. Amines are commonly used as curing agent because their nucleophilicity [3] makes them highly reactive at ambient temperatures. Polyamines from grapeseed oil, furanic amines from sugars and polysaccharides as well as cardanol [3] can be used as bio-curing agents.

The choice of biomaterial to be used for the bio-binder primarily depends upon its availability, cost and functional group that could react with the epoxy resin. The functional group is responsible for cross-linking with the epoxy resin that induces the curing process. Common functional groups found in the bio-degradable materials are carboxyl, hydroxyl, or amines. In addition to that, the cured epoxy using bio-binder should be able to fulfil the performance requirements like mechanical properties, thermal stability, and chemical resistance like those cured using traditional curing agent.

Researchers at North Carolina A&T State University developed several bio-binders through algae thermochemical liquefaction and found traces of various functional groups like amines [4]. One of them is 4-Pyrimidinamine with amine functional group. This paper presents the mechanical properties of an epoxy resin system with a bio-binder system

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obtained using molecular dynamics (MD) simulations. The mechanical properties are predicted using BIOVIA's Materials Studio [5] Software.

Modelling

The model developed in this study follows the procedure outlined in reference [6]. The usual mixing ratio provided by the manufacturer by weight for conventional resin and hardener is 100:26.4[7] for achieving the best curing. Accordingly, the number of molecular chains were determined having an effective density of 1.16 gm/cc. The closed ring structure formed had 8 chains of Di-glycidyl Ether of Bisphenol-F (DGEBF) and 2 chains each of Diethyl Toluene Diamine (DETDA) and 4-Pyrimidinamine as shown in the Fig. 1.

The lowest energy state of the model was achieved as given by Odegard et al. [8] using Geometry Optimization option in the software that made the model thermally stable. Using the Amorphous Cell Construction module, a cube of $35.2 \text{ \AA} \times 35.2 \text{ \AA} \times 35.2 \text{ \AA}$ was constructed having the DGEBF, DETDA and bio-binder molecules in the ratio 80:20:20 having 4300 total number of atoms. The constructed cell is as shown in the Fig. 2.

The Energy Minimization was done using the constant-volume and temperature (NVT) ensemble. The simulation was done using the condensed phase optimized ab-initio (COMPASSIII)[9] forcefield. The NVT was carried out for simulation time of 200 ps with the timestep of 1 fs at 298 K.

Fig. 1 Closed chain molecule showing partial replacement of DETDA molecules

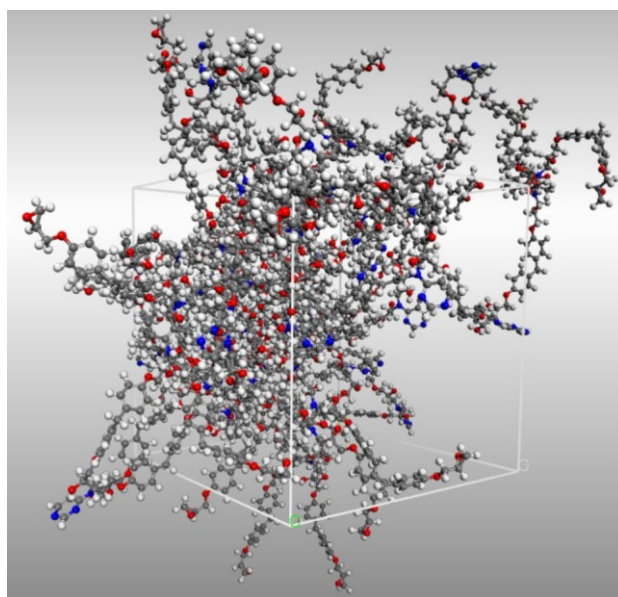
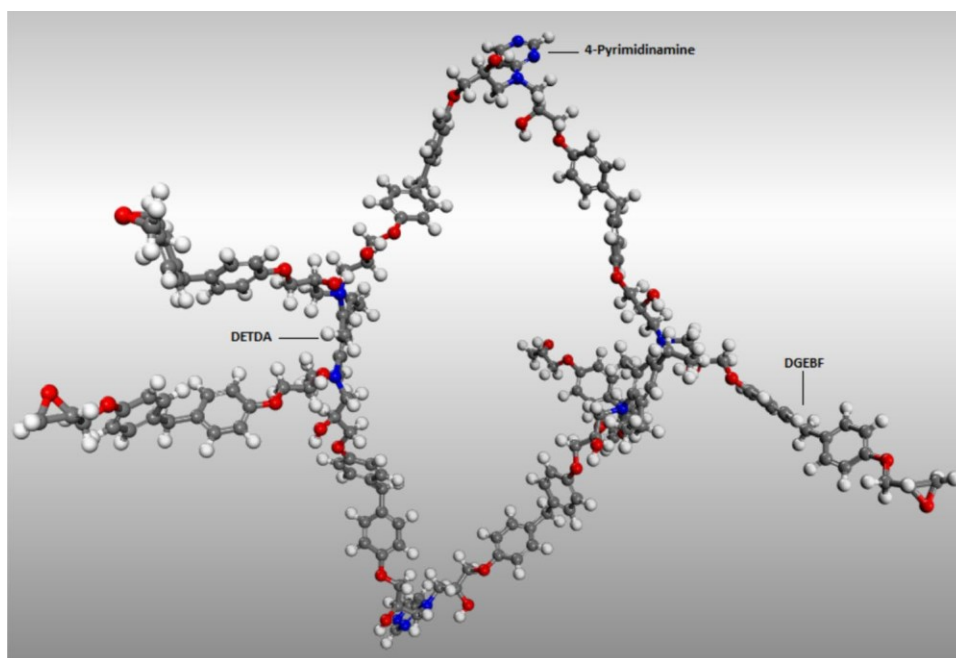


Fig. 2 Cell containing DGEBF, DETDA and bio-binder in the ratio 80:20:20

The model obtained at the end of each simulation process was used as the starting model for the next process.

Results and Discussions

The bio-binder was selected based on the results obtained from the thermal liquefaction of algae, which showed traces of 4-Pyrimidinamine. Since, it has amine functional group, it

Table 1 Reported elastic properties

Elastic property	Calculated value
Shear modulus (G)	1.85 GPa
Poisson's ratio (ν)	0.26
Bulk modulus (K)	3.25 GPa
Elastic modulus (E)	4.66 GPa

can replace partially/fully the conventional DETDA curing agent. The mechanical properties are predicted using the Constant strain method and the results were obtained in the form of 6×6 elastic stiffness matrix as shown:

$$C_{ij} = \begin{bmatrix} 6.3734 & 2.5875 & 3.0732 & -0.1249 & -0.0177 & 0.0834 \\ 2.5875 & 5.4455 & 2.9083 & -0.2735 & -0.2736 & -0.0977 \\ 3.0732 & 2.9083 & 5.3304 & -0.0231 & 0.1511 & -0.0642 \\ -0.1249 & -0.2735 & -0.0231 & 1.7496 & -0.1286 & 0.0282 \\ -0.0177 & -0.2736 & 0.1511 & -0.1286 & 1.3691 & -0.0133 \\ 0.0834 & -0.0977 & -0.0642 & 0.0282 & -0.0133 & 2.4227 \end{bmatrix}$$

According to the definition of isotropic materials, if the properties of materials are same in all directions then they are termed as isotropic materials. After close observation of the above matrix, it is found that the matrix is symmetric and the off-diagonal elements except C_{12} , C_{13} , C_{21} , C_{23} , C_{31} and C_{32} terms are nearly zero. So, from the matrix, it can be said that the material is nearly isotropic.

For isotropic materials, the elastic properties are determined with the help of Lamé's constant [6] and are represented by λ and μ . The Lamé's constant calculated from the above matrix are:

$$\lambda = 2.02 \text{ GPa}$$

$$\mu = 1.85 \text{ GPa}$$

From these, the elastic properties were calculated as referred in [6, 10] and are given in the following Table 1:

With the help of MD Simulations, the elastic modulus predicted is in accordance with the reported values [11–13] for the conventional epoxy resin and hardener. This shows that the bio-binder 4-Pyrimidinamine could be a good alternative for the replacement of conventional curing agents.

Conclusion

The use of bio-degradable curing agents in epoxy resins shows a prominent step towards more environment friendly and sustainable materials. There are still various challenges to overcome, such as cost and availability but the environmental impacts are very significant. The simulation of MD model shows that partial replacement of conventional curing agent DETDA can be done with bio-binder

4-Pyrimidinamine. The bio-binder was selected from the traces of Amines found in the algae thermal liquefaction. The elastic modulus calculated from the Lamé's Constant is 4.66 GPa and is in well accordance with the previous reported values. The research showed promising outcomes without the loss of mechanical properties in comparison to the conventional epoxy resin and hardener.

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Data Availability If needed, all the required data would be provided on request.

Declarations

Competing interests Not Applicable.

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References

1. *Polymers* 2023, 15(2), 385; DOI: <https://doi.org/10.3390/polym15020385>
2. A.Q. Dayo, J. Wang, A.R. Wang, D. Lv, A. Zegaoui, M. Der-radji, W.B. Liu, Mechanical and thermal properties of a room temperature curing epoxy resin and related hemp fibers reinforced composites using a novel in-situ generated curing agent. *Mater. Chem. Phys.* **203**, 293–301 (2018). <https://doi.org/10.1016/j.matchemphys.2017.10.004>
3. Baroncini, E. A., Kumar Yadav, S., Palmese, G. R., & Stanzione III, J. F. (2016). Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *Journal of Applied Polymer Science*, 133(45). DOI: <https://doi.org/10.1002/app.44103>
4. Zhang, L., Wang, L., & Kelkar, A.D., "NSF Annual Project Report Award#2000318(09/01/2020–08/31/2021)".
5. Materials Studio User Manual, BIOVIA Support, San Diego, CA.

6. Makh, N. S., Zhang, L., & Kelkar, A. D. (2023). Replacement of Epoxy Curing Agent with Bio-Binder 1,4-Diaminobutane-A Green Solution. *SAMPE Conference Proceedings, Seattle, WA, April 17–20, 2023*. DOI: <https://doi.org/10.33599/nasampe/s.23.0175>
7. Resolution Performance Products, Product bulletin EPIKOTE™ Resin 862/EPIKURE™ Curing Agent W System.
8. G.M. Odegard, T.S. Gates, L.M. Nicholson, K.E. Wise, Equivalent-continuum modeling of nano-structured materials. *Compos. Sci. Technol.* **62**, 1869–1880 (2002)
9. R.L.C. Akkermans, N.A. Spenley, S.H. Robertson, compass iii: automated fitting workflows and extension to ionic liquids. *Mol. Simul.* (2020). <https://doi.org/10.1080/08927022.2020.1808215>
10. Y. Mo, H. Zhang, J. Xu, Molecular dynamic simulation of the mechanical properties of PI/SiO₂ nanocomposite based on materials studio. *J. Chem. Pharm. Res.* **6**(6), 1534–1539 (2014)
11. V. Varshney, S.S. Patnaik, A.K. Roy, B.L. Farmer, A Molecular Dynamics Study of Epoxy-Based Networks: Cross-Linking Procedure and Prediction of Molecular and Material Properties. *Macromolecules* **41**, 6837–6842 (2008)
12. S.V. Kallivokas, A.P. Sgouros, D.N. Theodorou, Molecular dynamics simulations of EPON-862/DETDA epoxy networks: structure, topology, elastic constants, and local dynamics. *Soft Matter* **15**(4), 721–733 (2019)
13. Komuves, F., Kelkar, A.D., Mohan, R., & Kelkar V. A. (2010, April 12–15). *Prediction of Mechanical Properties of Epon-862 (DGEBF)-W (DETDA) using MD Simulations*, 51st AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference, Orlando, Florida.

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