

# Bio-based epoxy thermosets of vanillin-derived epoxy monomer: effect of epoxy monomer functionality on thermal properties

Kimia Kiani<sup>1</sup>, Gholam Hossein Zohuri<sup>1\*</sup>, Mohsen Mogheiseh<sup>2,3</sup>

<sup>1</sup>Chemistry Department, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

<sup>2</sup>Machino Sanat Hyrcania, Incubation Center of Iranian Research Organization for Science and Technology (IROST), Golestan University, Golestan, Iran

<sup>3</sup>Shahid Fakhriyadeh Research Center, Golestan University, Golestan, Iran

Email\*: zohuri@um.ac.ir



## Introduction

Thermoset polymers are widely used in industrial applications because of their versatile properties and good durability which are provided by their highly cross-linked structure [1]. Many epoxy thermosets are prepared from the reaction of an epoxy monomer or pre-polymer (resin) with a co-monomer (hardener). Despite being classified as reprotoxic and banned for use in food contact applications, diglycidylether of bisphenol A (DGEBA) 75% of the epoxy resins produced worldwide are based on the (DGEBA) [2]. Vanillin obtained from lignin depolymerization is one of the only biomass-derived molecular phenol available at an industrial. It is also non-hazardous. Therefore, the use of this compound for renewable polymer synthesis recently attracted a lot of attention [3].

In this study, synthesis and characterization of new trifunctional bio-based epoxy reagent were reported. The curing agent were chosen from aliphatic amines to exhibit the influence of all sections of reagent's structures on thermal properties in the epoxy thermosets.



## Experimental

### Materials

Vanillin (99%), 1,3,6,8-tetraaminoctan (DDN, 97%), cyclopentanone ( $\geq 99\%$ ), hydrochloric acid (37%), epichlorohydrin (99%), triphenyl phosphine (TPP), sodium hydroxide (NaOH,  $\geq 97\%$ ), 1,4-dioxane ( $\geq 99.5\%$ ), chloroform ( $\geq 99\%$ ) were all purchased from Merck.

### Method

The epoxy monomers (GDVCP/GDVCPO) were synthesized by glycidylation of cyclopentanone, vanillin and hydrochloric acid mixture and glycidylation of oximated previous mixture, respectively. Then, a mixture of GDVCP/GDVCPO, TPP initiator and DDN hardener was mixed vigorously by stirrer bar in glass tube at 150 °C until the molten pre-polymer got dark. The viscous mixture was poured into a silicon mold (preheated before) and placed in an oven (vacuumed) for 12 h at 150 °C to synthesize of resultant epoxy thermosets (EDVCP-DDN/EDVCPO-DDN).



## Result and Discussion

The epoxy thermosets prepared in this study can be divided into two main groups. The first and second groups were created to investigate the influence of number and type of functionality of epoxy monomer on properties of the final products, respectively. Hence, all the curing processes were carried out at same condition to ensure about chain mobility during gelation and to obtain optimal cross-linking content. Therefore, effect of these parameters on thermal properties was investigated followed by evaluation the thermal stability of the final thermosets.

The progress of curing process was followed by evolution of the most significant bands in FT-IR spectroscopy and DSC thermogram to evaluate the real chemical transformation that is carried out. The results of FT-IR are shown in Fig. 1. The initial spectrum shows two absorption bands at range of 850 and 950  $\text{cm}^{-1}$  corresponding to the epoxy ring. These absorptions have disappeared (completely) in the spectrum of the cured material, whereas a new broad adsorption at 3400–3600  $\text{cm}^{-1}$  appeared due to the formation of the hydroxyl propyl moieties in the network structure of the resultant thermosets indicating the incorporation of reactants into the polymer networks. However, the absorption pattern of sample prepared by GDVCP showed higher intensity at 850–950  $\text{cm}^{-1}$  as compared to GDVCPO, which is corresponded to lower cross-linking density at this thermoset.

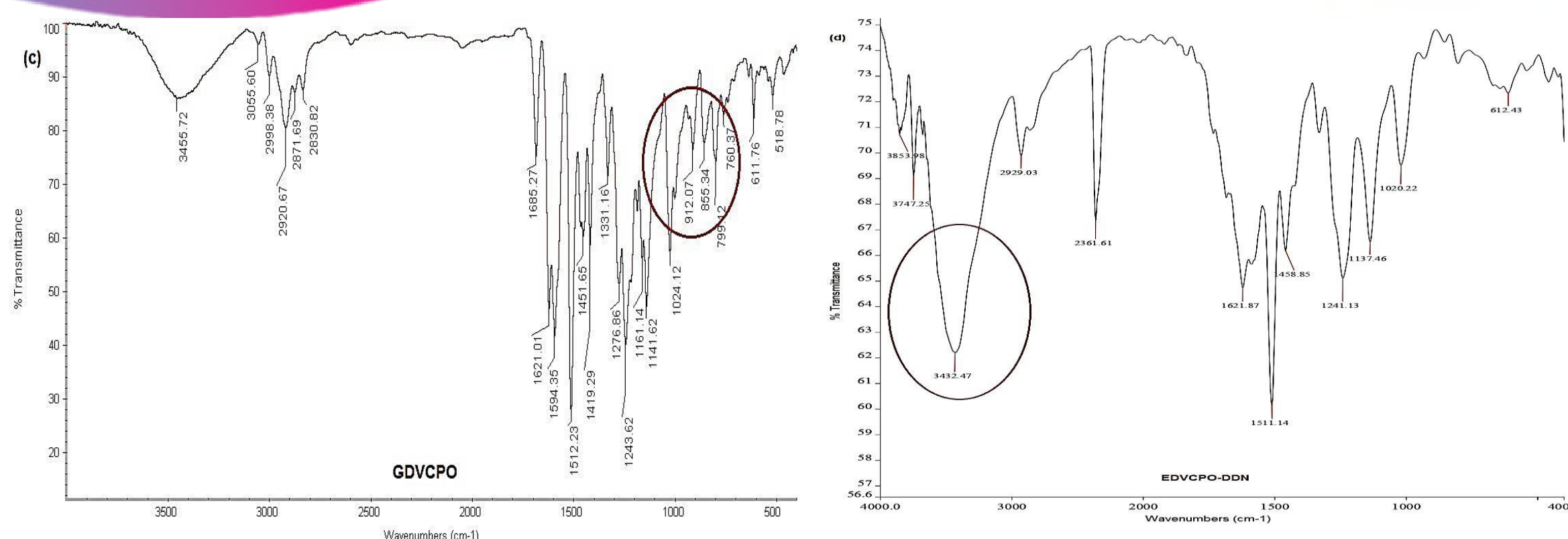
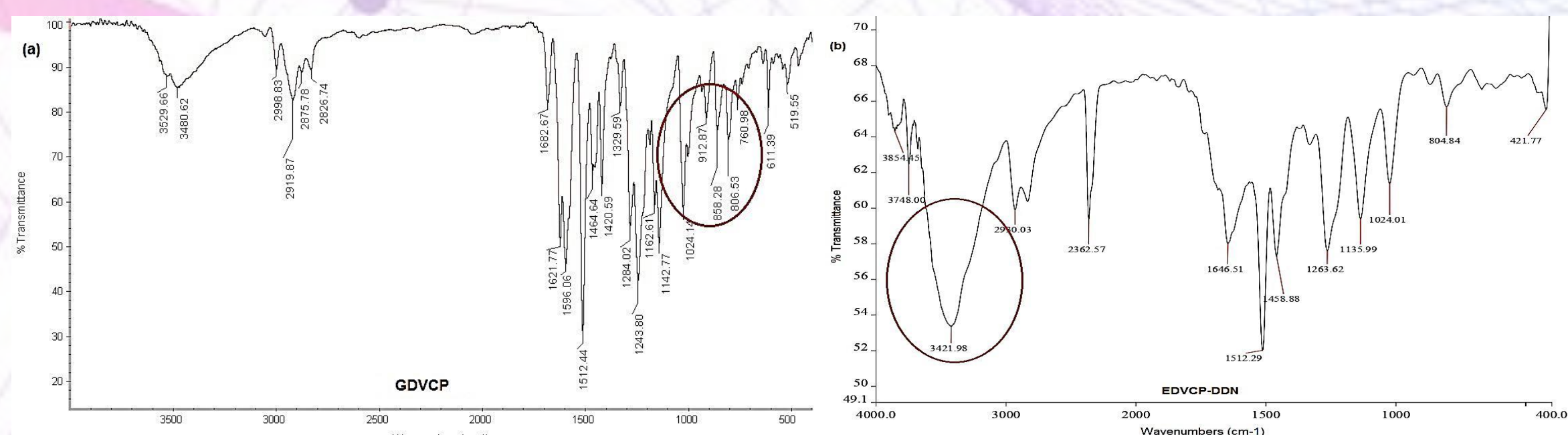


Fig. 1 FT-IR spectrum of (a) GDVCP epoxy monomer (b) EDVCP-DDN epoxy thermoset after curing process (c) GDVCP epoxy monomer (d) EDVCPO-DDN epoxy thermoset after curing process

As it can be seen in DSC thermogram (Fig. 2), the use of stoichiometric amount for mixing led most of the epoxy groups to fully cured. An optimal  $T_g$  of 140 °C is attained for an epoxy system with tri-functional group of epoxy monomer (EDVCPO-DDN). It seems with the raising of epoxy groups in epoxy system,  $T_g$  of the epoxy thermosets showed much higher value comparable to the other samples with di-functional epoxy groups (97 °C). It seems that, the glass transition temperature of the thermosets increased as the curing degree of reagents increased.

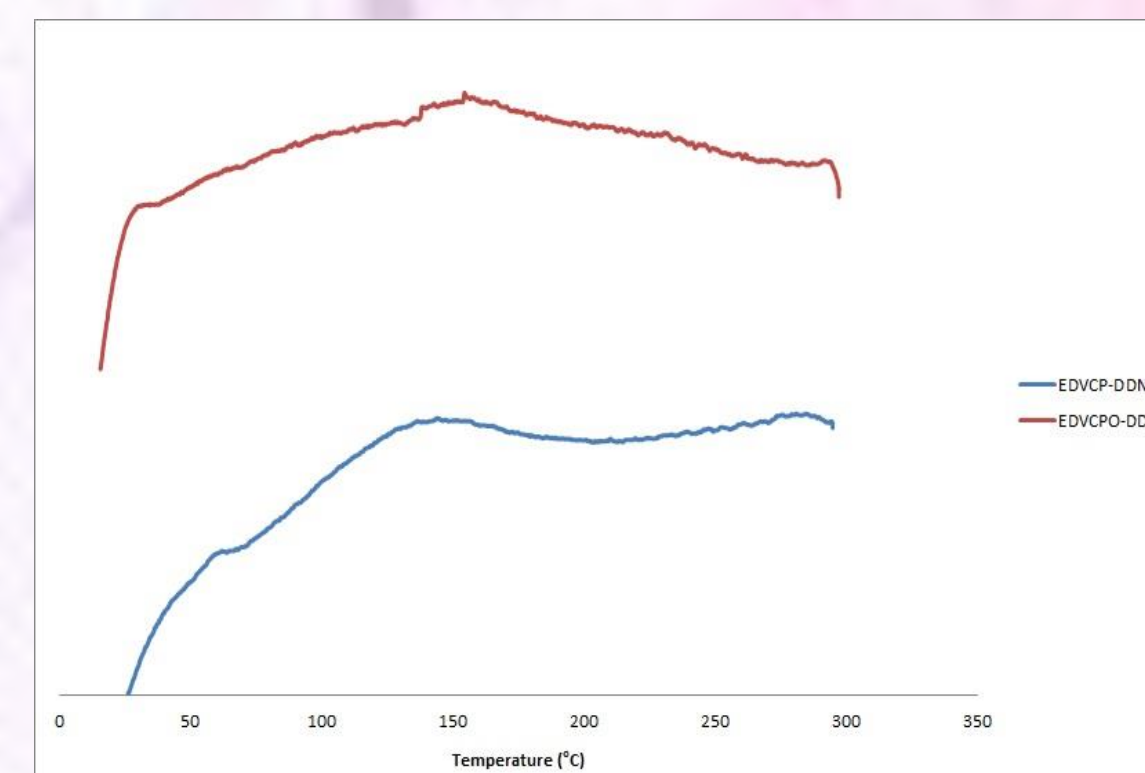


Fig. 2 DSC thermograms of thermosets obtained using DDN hardener and different epoxy monomers



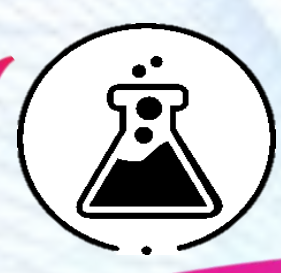
## Conclusion

A new bio-based tri-functional epoxy resin was prepared with glycidylation of tri-hydroxyl precursor which itself was synthesized with oximation of two-functional material derived from vanillin. The parameters such as type and number of functionality were found to develop the thermal properties and stability of the materials to the higher value. For instance, the epoxy networks containing tri-functional epoxy groups displayed enhanced thermal stability and thermal properties (such as  $T_g$ ) comparable to the other samples with di-functional epoxy groups, which is attributed to the rigid structure formed inside the network.



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## References

- [1] M. Mogheiseh, R. Karimian, and M. Khoshsefat, Chem. Pap., 2020, 74, 3347.
- [2] M. Fache, C. Mont r mal, B. Boutevin and S. Caillol, Eur. Polym. J., 2015, 73, 344.
- [3] L. Hollande, I. Do Marcolino, P. Balaguer, S. Domenek, R.A. Gross and F. Allais, Front. Chem., 2019, 7, 159.