

Mechanical properties and curing kinetics of biobased benzoxazine-epoxy copolymer for dental fiber post

Phattarin Mora

Srinakharinwirot University

Sarawut Rimdusit

Chulalongkorn University

Panagiotis Karagiannidis

University of Sunderland

Ukrit Srisorrachatr

Institute of Dentistry

Chanchira Jubsilp (✉ chanchira@g.swu.ac.th)

Srinakharinwirot University

Research Article

Keywords: Bioresource, Glass fiber post, Finite element analysis, Thermoset polymer

Posted Date: May 4th, 2023

DOI: <https://doi.org/10.21203/rs.3.rs-2852873/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Bioresources and Bioprocessing on September 16th, 2023. See the published version at <https://doi.org/10.1186/s40643-023-00684-x>.

Mechanical properties and curing kinetics of biobased benzoxazine-epoxy copolymer for dental fiber post

Phattarin Mora ¹, Sarawut Rimdusit ², Panagiotis Karagiannidis ³, Ukrit Srisorrachatr ⁴,
Chanchira Jubsilp ^{1,*}

¹ Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University, Nakhonnayok 26120, Thailand

² Research Unit in Polymeric Materials for Medical Practice Devices, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand.

³ School of Engineering, Faculty of Technology, University of Sunderland, Sunderland, SR6 0DD, United Kingdom.

⁴ Institute of Dentistry, Department of Medical Services, Nonthaburi 11000, Thailand

*Correspondence: chanchira@g.swu.ac.th; Tel.: +6626495000 ext 27104-6

Abstract

Biocopolymers based on vanillin/furfurylamine-biobenzoxazine (V-fa) and bioepoxy, epoxide castor oil (ECO), were prepared for fiber post application. The mechanical and thermal properties of the V-fa/ECO biocopolymers were assessed in regard to the influence of ECO contents. The addition of the ECO at amount of 20 % by weight into the poly(V-fa) preserved the stiffness, the glass transition temperature and thermal stability nearly to the poly(V-fa). Dynamic differential scanning calorimetry (DSC) was used to examine the curing kinetics of the V-fa/ECO system with different heating rates. In order to determine the activation energy (E_a), the experimental data were subjected to the isoconversional approaches, namely Flynn-Wall-Ozawa and Friedman. The V-fa/ECO monomer mixture showed averaged E_a values of 105 kJ/mol and 94 kJ/mol, corresponding to typical E_a of petroleum-based benzoxazine/epoxy.

The results derived using the curing reaction model and the experimental data were in good agreement, demonstrating the efficacy of the Flynn-Wall-Ozawa approach for determining the curing kinetics. The simulated mechanical response to external applied loads by finite element analysis of the tooth model restored with glass fiber-reinforced V-fa/ECO biocopolymer post showed a similar stress field with that restored with the commercial glass fiber post. Therefore, the biobased benzoxazine/epoxy copolymer overcomes many of the traditional shortcomings associated with petroleum-based epoxy resins used for dental fiber post, while demonstrating excellent mechanical and thermal properties.

Keywords: Bioresource; Glass fiber post; Finite element analysis; Thermoset polymer

1. Introduction

Fiber-reinforced polymer composites, polymer matrix reinforced with fibers such as glass, carbon, aramid, or natural fibers of plant origin, are commonly used in the construction, marine, automotive, and aerospace industries (Bhardwaj et al. 2021; Birniwa et al. 2023; Shadhin et al. 2021; Zhang et al. 2022; Zulkifli et al. 2016). In recent years, the evolution of fiber-reinforced polymer composite posts (non-metallic posts) or fiber posts as an alternative to metal and ceramic posts to reinforce tooth treated with endodontics has been investigated (Genovese et al. 2005; Mora et al. 2022; Pegoretti et al. 2002) due to the increasing demand for tooth-colored posts, the low biocompatibility and corrosion risk of cast metal posts, and the negative aesthetic impact. Among of fiber posts, conventional epoxies acted as a polymer matrix were the most widely used polymer bases. Various amines, anhydrides and acids are commonly used to cure epoxy resins based on diglycidyl ether components. Amines have some drawbacks such as high toxicity and short pot life (usable time), while anhydrides can be affected by the amount of moisture in the formulation (Hara 1990; Gotro 2022). Cross-linked

epoxy also has a problem, i.e., low thermal stability and moderate thermal expansion (Kurihara et al. 2012). In consequence, the recent studies are found the resins or polymers such as polybenzoxazine (a novel type of phenolic resin) and polyimide to substitute the conventional polymers for fiber posts (Elsubeihi et al. 2020; Mora et al. 2022). Additionally, the use of highly toxic hardeners for epoxies and the perception of hazardous industrial processes needs to be overcome. Copolymers of epoxy and polybenzoxazine have been reported, where polybenzoxazine acts as a curing agent for the epoxy and the addition of epoxy to the polybenzoxazine network has significantly higher glass transition temperature and flexural strength than polybenzoxazine, with only a minimal stiffness loss (Okhawilai et al. 2017; Rao et al. 2005; Rimdusit and Ishida 2000). In addition, curing kinetics of benzoxazine/epoxy system has also been studied by dynamic differential scanning calorimetry (Jubsilp et al. 2010; Shutov et al. 2022). It was found that there were two dominant curing processes which was similar to curing processes of the conventional epoxy without catalyst (Liu et al. 2009). The activation energy of polybenzoxazine/epoxy, i.e., 81 kJ/mol and 118 kJ/mol were found to be similar for epoxy curing under non-isothermal conditions, i.e., 69.7 and 88.7 kJ mol⁻¹ based on the Kissinger method, 68.2 and 86.9 kJ/mol based on the Flynn-Wall-Ozawa method (Wu et al. 2018). In addition, the no-difference curing kinetic model that was autocatalytic kinetic due to the autocatalytic effect of hydroxyl groups generated in the curing reaction of the benzoxazine/epoxy system and the epoxy have been observed (Jubsilp et al. 2010; Liu et al. 2009).

However, in recent years, with dwindling oil supplies and serious environmental concerns, bioepoxies and biobenzoxazines having similar properties to those of the petroleum bases had successfully developed from vegetable oils, lignocellulosic biomass (vanillin, eugenol, lignin), furans and tannins. Bioepoxies based on epoxidized vegetable oil such as epoxidized castor oil (ECO), epoxidized soybean oil (ESO), epoxidized linseed oil (ELO) have

been synthesized (Hu et al. 2019; Park et al. 2004). Castor oil (CO) is an inexpensive vegetable oil extracted from the seeds of the CO plant castor bean (*Ricinus communis*). The CO's long shelf life, relatively low toxicity, accessible availability, and unique functionality cause it superior to other vegetable oils (Sudha et al. 2017). For a novel renewable based benzoxazine, i.e., V-fa, it has been synthesized without solvents from vanillin produced from lignin and furfurylamine which is also an eco-friendly product derived from various agricultural by-products such as corncobs, sugar cane bagasse, wheat bran and oats. The formyl group in vanillin helps benzoxazines cure at low temperatures. The furan group containing poly(V-fa) has a high glass transition temperature, excellent thermal properties, and good adhesive properties (Sini et al. 2014). Hence the efforts for investigation of possibility of the biobenzoxazine/biepoxy system as a new material base was considered and appreciated. Hombunma et al. (2019) have developed the V-fa/ECO biocopolymers for shape memory materials under thermal stimulation. The V-fa/ECO biocopolymer with 40 wt% ECO showed good balance between thermo-mechanical properties and shape memory performances. While, under NIR light stimulation, the percent weight of ECO in the V-fa/ECO biocopolymer should be at least 50 since a high recovery ratio of 100 % within a 30 s of NIR irradiation was achieved (Amornkitbamrung et al. 2020). In addition, the V-fa/ECO with 50 wt% ECO reinforced with nanofiller such as graphene and MWCNT possess good shape fixity and good shape recovery under NIR actuation (Prasomsin et al. 2019; Srisaard et al. 2021). It is possible that the V-fa/ECO system could be tailor-made to meet the requirements for dental fiber posts.

Therefore, the aim of this work is to achieve biocopolymer based on bio-based benzoxazine (V-fa) and bio-based epoxy (epoxidized castor oil; ECO) suitable for polymer base dental fiber posts. The effects of ECO contents on curing behavior, mechanical property and thermal stability were investigated. The thermal curing kinetics of the biocopolymer were also studied by dynamic differential scanning calorimetry. Its kinetic parameters were

evaluated and predicted by the isoconversional methods, i.e., Flynn-Wall Ozawa and Friedman. In addition, the mechanical response to external applied loads of tooth models restored with a new glass fiber-reinforced V-fa/ECO biocopolymer post and with a commercial glass fiber post were simulated by finite element analysis, in hope of providing helpful guidance for dental fiber post application.

2. Materials and Methods

2.1 Materials

Bio-based vanillin/furfurylamine based benzoxazine monomer (V-fa) was prepared from vanillin and furfurylamine purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Paraformaldehyde was purchased from Merck Co., Ltd. (Darmstadt, Germany). Epoxidized castor oil (ECO) was provided by Aditya Birla Chemicals Thailand Ltd. (Rayong, Thailand). All chemicals were used as received. E-glass fiber plain fabrics with an areal density of 600 g/m² were purchased from Thai Poly Add Ltd. Partnership, Bangkok, Thailand.

2.2 V-fa monomer preparation

The V-fa monomer was prepared from vanillin, paraformaldehyde, and furfurylamine at mol ratios of 1:2:1 using solventless method (Ishida 1996). The three reactants were mixed in an aluminum pan at a temperature of 110°C for 1 h and a low viscosity yellow liquid monomer was obtained.

2.3 V-fa/ECO biocopolymer preparation

The V-fa/ECO monomer mixtures were prepared by mixing the V-fa/ECO at a mass ratio of 80/20, 70/30, 60/40, 50/50, and 40/60. Each mixture was heated at 90°C in an aluminum pan and stirred until a homogeneous mixture was obtained. The mixtures were thermally cured in

an air-circulated oven with the curing steps: 150°C/1h, 160°C/1h, 170°C/2h, and 180°C/2h. The cured V-fa/ECO biocopolymers were characterized after cooling down to room temperature.

2.4 Characterization

Curing behavior of the samples was investigated by using differential scanning calorimeter model DSC1 Module from Mettler Toledo (Thailand) Ltd. (Bangkok, Thailand). A sample mass of 5–10 mg was sealed in a lidded aluminium pan and heated from 25 °C to 300 °C at heating rates of 5, 10, 15, and 20 °C/min under a nitrogen purge with a flow rate of 50 mL/min.

Molecular information of the samples was evaluated by fourier transform infrared spectra on a Perkin Elmer Spectrum GX FT-IR spectrometer equipped with an ATR accessory (Perkin Elmer Co., Ltd., Waltham, MA). All spectra were taken with 64 scans at a resolution of 4 cm^{-1} over a spectral range of 4000–650 cm^{-1} .

Dynamic viscoelastic analyzer (model DMA1, Mettler Toledo, Switzerland) was utilized to study dynamic mechanical properties of the samples under three-point bending mode. Distortion is measured at a frequency of 1 Hz with an amplitude of 30 μm . The sample was heated from 30 °C to 300 °C at a rate of 2 °C/min. The size of samples was 10 mm \times 50 mm \times 3 mm.

The degradation temperature of the samples was reported using a thermogravimetric analyzer (model TGA1 Module Mettler-Toledo, Thailand). Approximately 10 mg of sample was heated from 25 °C to 850 °C at a heating rate of 10 °C/min under nitrogen atmosphere with a flow rate of 50 mL/min.

3D model was created in the ANSYS Workbench 2022 R1 (Ansys, Inc. United States) Design Modeller. As shown in Figure 1, a model of a root canal treated tooth containing all structures (crown, composite resin, glass fiber (GF) reinforced V-fa/ECO biocopolymer post,

dentin, gutta-percha). A 3D mesh was then created using the structurally solid elements defined by the nodes. The numbers of generated elements and nodes for the tooth reconstructed with the post were 112376 and 208652, respectively.

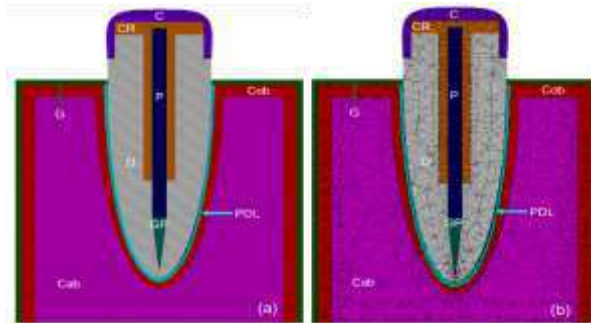


Figure 1. Schematic of tooth model restored with glass fiber post (GF-reinforced V-fa/ECO biocopolymer post); C - porcelain crown, CR - composite resin, P - post, GP - gutta-percha, D - dentin, Cob - cortical bone, PDL - periodontal ligament, Cab - cancellous bone.

3. Results and Discussion

3.1 Curing behavior of V-fa/ECO monomer mixtures

Figure 2 shows DSC thermogram plotted of the heat flow as a function of temperature for a heating rate of 10 °C/min to over 300 °C of V-fa, ECO, and V-fa/ECO monomer mixtures at various ECO contents. From the findings, the curing exothermic peak of the V-fa monomer is approximately 200 °C, while that of the ECO was not appeared. This behavior confirmed that the V-fa monomer can be cured by heat, whereas the ECO can be cured with the need of curing agent as like observed in the petroleum-based ones (Jubsilp et al. 2010; Shutov et al, 2022). Two low and high temperature curing exothermic peaks were obtained for the V-fa/ECO monomer mixtures. The low-temperature curing exothermic peak of the V-fa/ECO monomer mixture shifted slightly to higher temperatures with increasing ECO content, i.e., 204 °C, 205

°C, 207 °C, 208 °C, and 208 °C for 20, 30, 40, 50, and 60 wt% ECO, respectively, while an increase of the ECO showed no effect of the exothermic curing peak at the higher temperature of all V-fa/ECO monomer mixtures as the exothermic peak temperatures at the higher temperature were at about 249 °C. The existence of two exothermic curing peaks illustrated that different curing reaction pathways may occur simultaneously or sequentially. To distinctly confirm two different curing reaction pathways of the V-fa/ECO monomer mixtures, DSC thermogram of uncured V-fa/ECO (80/20) mixture and cured V-fa/ECO (80/20) at various curing conditions is depicted in Figure 3. The thermogram of partially cured V-fa/ECO (80/20) at 150°C for 1 h showed the two exothermic curing peaks and insignificant change in the exothermal peak temperatures, i.e., 200 °C at the lower temperature and 249 °C at the higher temperature. When the partially cured V-fa/ECO (80/20) were continually processed at 180 °C for 1 h. The exotherm curing peak at the lower temperature was almost disappeared, while the exothermic curing peak at higher temperatures was still appeared, implying that the effect of the curing peak at the lower temperature to the curing peak at the higher temperature could be neglected. Therefore, it is possible the curing peak at the lower temperature could be the oxazine ring opening of the benzoxazine. The higher temperature reaction may be the secondary hydroxyl which was formed during the benzoxazine ring opening reaction reacting with another epoxy ring (Ambrozic et al. 2020).

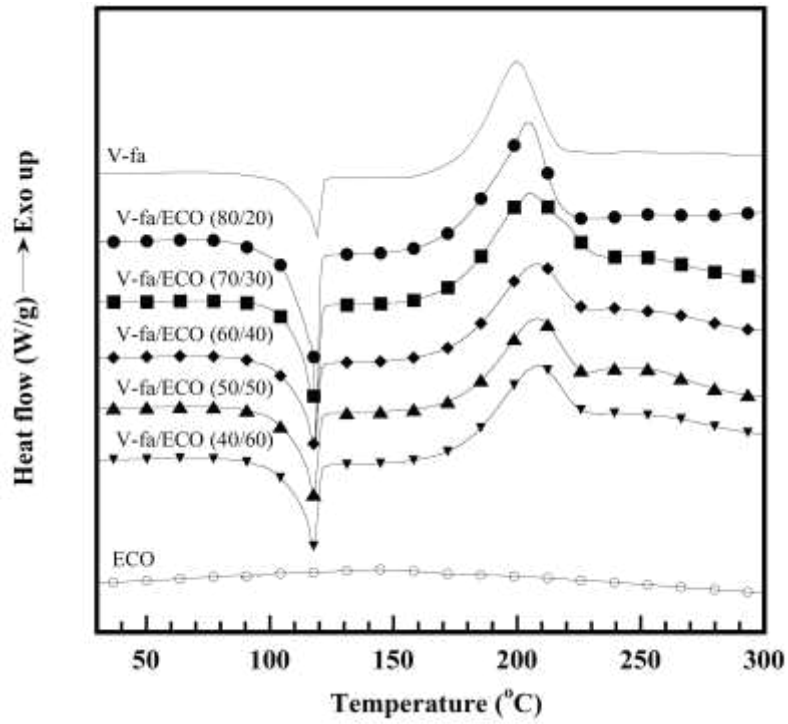


Figure 2. DSC thermogram of V-fa/ECO monomer mixtures at various ECO contents.

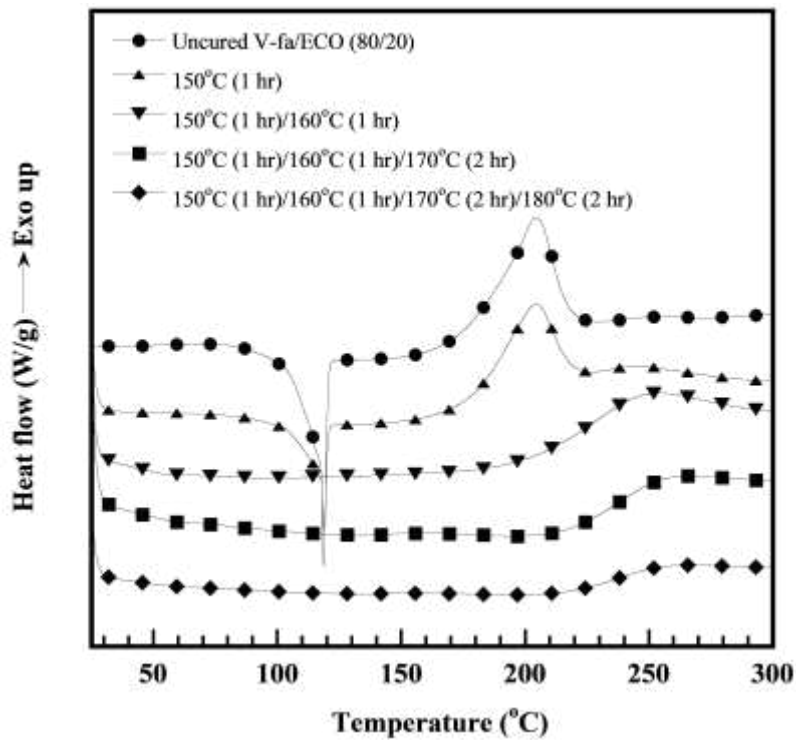


Figure 3. DSC thermogram of V-fa/ECO (80/20) monomer mixture at various curing conditions.

3.2 Molecular information of V-fa/ECO biocopolymers

To understand the chemical reactions for the curing process, FTIR spectra of the V-fa, ECO, V-fa/ECO monomer mixture, and V-fa/ECO biocopolymer are presented in Figure 4. The bands of the V-fa were observed as follows: 905 and 1229 cm^{-1} , and 1147 cm^{-1} attributed to C-O-C, and C-N-C of oxazine ring, 760 and 1583 cm^{-1} attributed to furan group, 1360 cm^{-1} attributed to tetra-substituted benzene ring, 1685 cm^{-1} attributed to carbonyl group (-CHO) (Hombunma et al. 2019; Sini et al. 2014). The bands of the ECO were 847, 913, and 1245 cm^{-1} attributed to oxirane ring, 1095 and 1742 cm^{-1} attributed to C=O stretching and C-O-C stretching of ethers (Sini et al. 2014). The broad band at 3500 cm^{-1} was also observed that was assigned to O-H stretching of hydroxyl groups (de Luca 2009). For the V-fa/ECO monomer mixture, all bands of the V-fa and the ECO were appeared. After curing process, the V-fa/ECO biocopolymer was obtained. A broad peak appeared at about 3200-3800 cm^{-1} and a band at 3400 cm^{-1} attributed to the hydroxyl group formed by the thermal ring-opening reaction of the oxazine ring. Meanwhile, the peak intensity of the oxazine ring disappeared, but new peaks appeared at 1090 and 1300 cm^{-1} attributed to the ether linkages formed by the reaction between the hydroxyl groups of poly(V-fa) and the epoxy groups of ECO, and by the epoxy homopolymerization. Based on the combination of DSC and FTIR analysis results, the chemical reactions for the curing process can be proposed for the V-fa/ECO biocopolymer as can be seen in Figure 5. The hydroxyl groups formed due to the oxazine ring opening are presented in Figure 5(a), while the ether linkage formation can be seen in Figure 5(b).

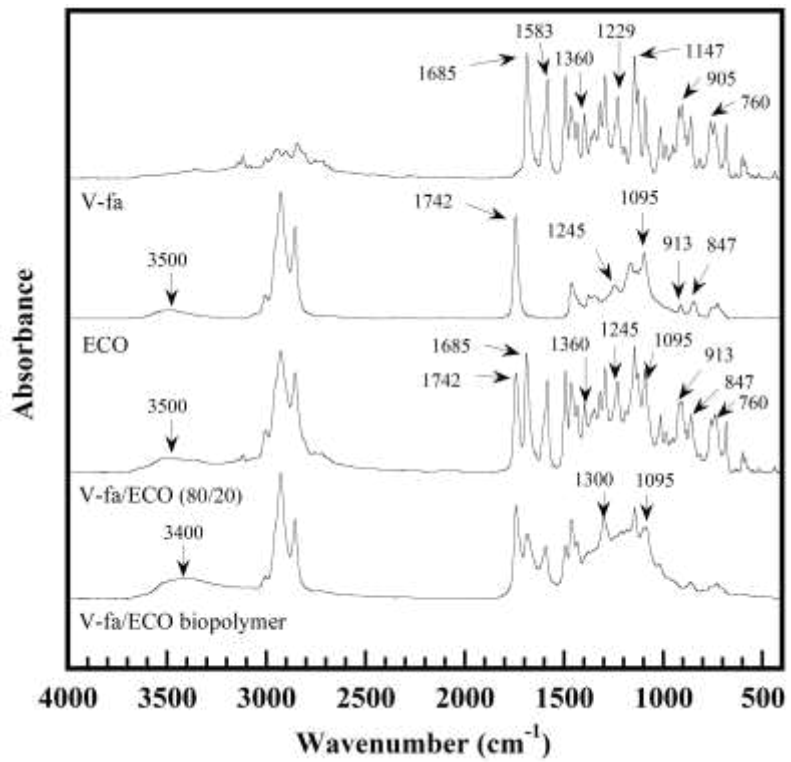


Figure 4. FT-IR spectra of (a) V-fa, (b) ECO, (c) V-fa/ECO monomer mixture, (d) V-fa/ECO biopolymer.

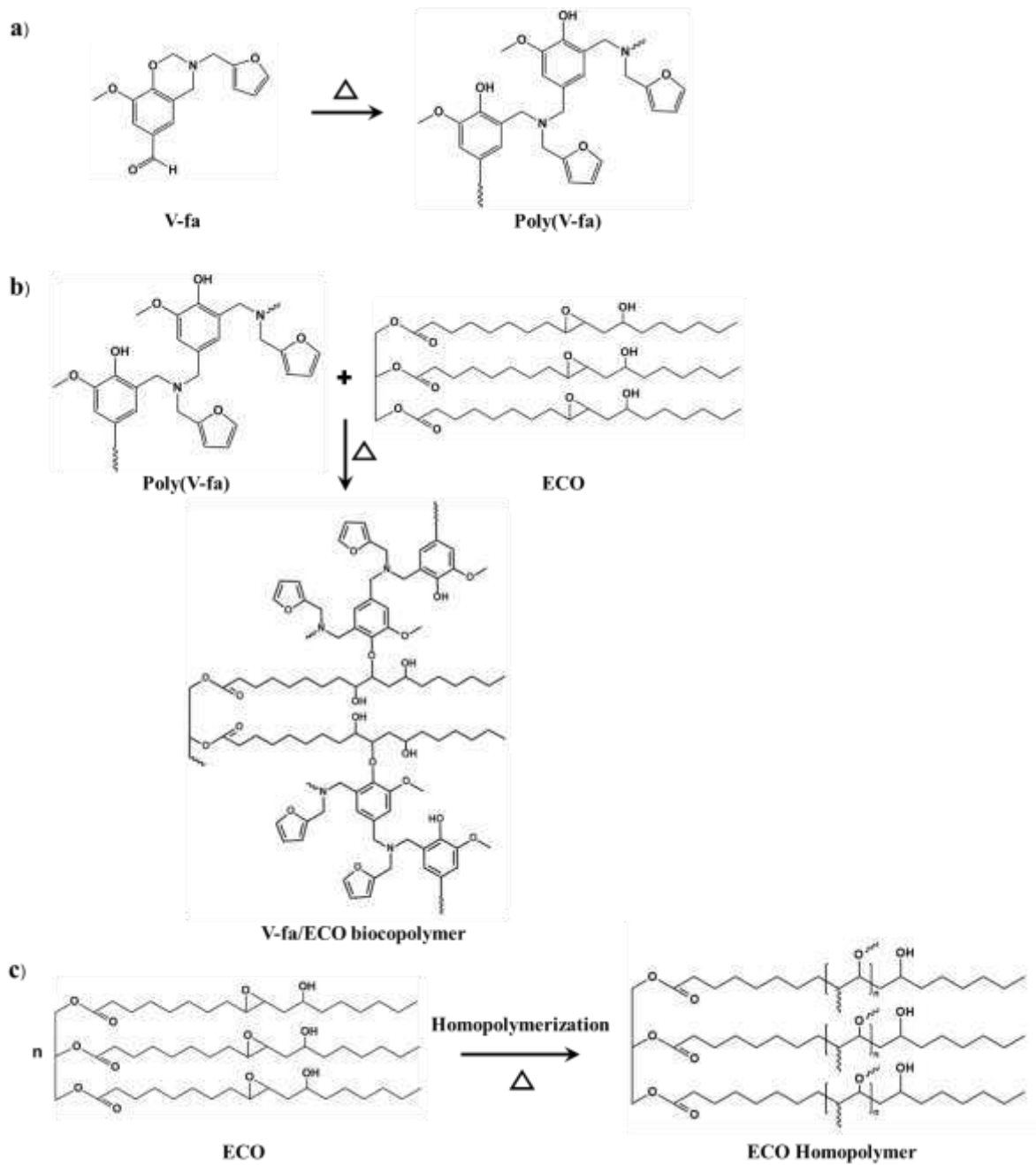


Figure 5. (a) proposed curing reaction of the V-fa monomer and (b) a plausible chemical reaction between the poly(V-fa) and the ECO (c) homopolymerization of ECO.

3.3 Dynamic mechanical analysis of V-fa/ECO biocopolymers

Dynamic viscoelastic properties, i.e., storage or elastic modulus and loss or viscous modulus of the V-fa/ECO biocopolymers are plotted in Figure 6. As shown in Figure 6(a), the storage modulus of the V-fa/ECO biocopolymers as a function of temperature were improved

by the addition of the V-fa, as similarly reported by Hombunma et al. (2019). It is possible that the poly(V-fa) contains benzene ring, providing lower molecular movement than the ECO which contains higher molecular mobility of long alkyl chain. These results indicated that the V-fa/ECO biocopolymers were innovative materials where stiffness and flexibility can be tailored by varying the V-fa and the ECO contents. In addition, the higher V-fa content in the V-fa/ECO biocopolymers can help improve the dimensional stability as its sharp dropping in storage modulus in the transition region at higher temperatures was obtained, therefore, as expected, the glass transition temperatures (T_g) of the V-fa/ECO biocopolymers were also enhanced with an increase of the V-fa content. In addition, it was observed that the obtained mechanical properties were like those of a conventional petroleum-derived epoxy resin (Saba et al. 2019; Zeng et al. 2015), petroleum-based polybenzoxazine (Jubsilp et al. 2013) and petroleum-based polybenzoxazine/epoxy (Rao et al. 2005; Rimdusit et al. 2005).

From Figure 6(b), two distinct T_g s, i.e., T_{g1} at the lower temperature and T_{g2} at the higher temperature were detected for the V-fa/ECO biocopolymers at 20-50 wt% ECO ($T_{g1} = 20\text{ }^\circ\text{C}$, $2\text{ }^\circ\text{C}$, $-2\text{ }^\circ\text{C}$, $-4\text{ }^\circ\text{C}$ and $T_{g2} = 158\text{ }^\circ\text{C}$, $130\text{ }^\circ\text{C}$, $107\text{ }^\circ\text{C}$, $98\text{ }^\circ\text{C}$, respectively), while single T_g for the V-fa/ECO biocopolymer at 60 wt% ECO was observed, i.e., $T_g = -18\text{ }^\circ\text{C}$. This characteristic indicated that the ECO domain in the V-fa/ECO biocopolymer significantly affected the T_{g1} value of the biocopolymer, while T_{g2} was the influence from the cross-linked V-fa/ECO domain (Hombunma et al. 2019). In addition, the increase of the T_{g1} of the V-fa/ECO (80/20) biocopolymer can be expected by reinforcement of glass fiber to reach the service temperature of the human tooth from food consumption, tooth restoration, and dental treatment.

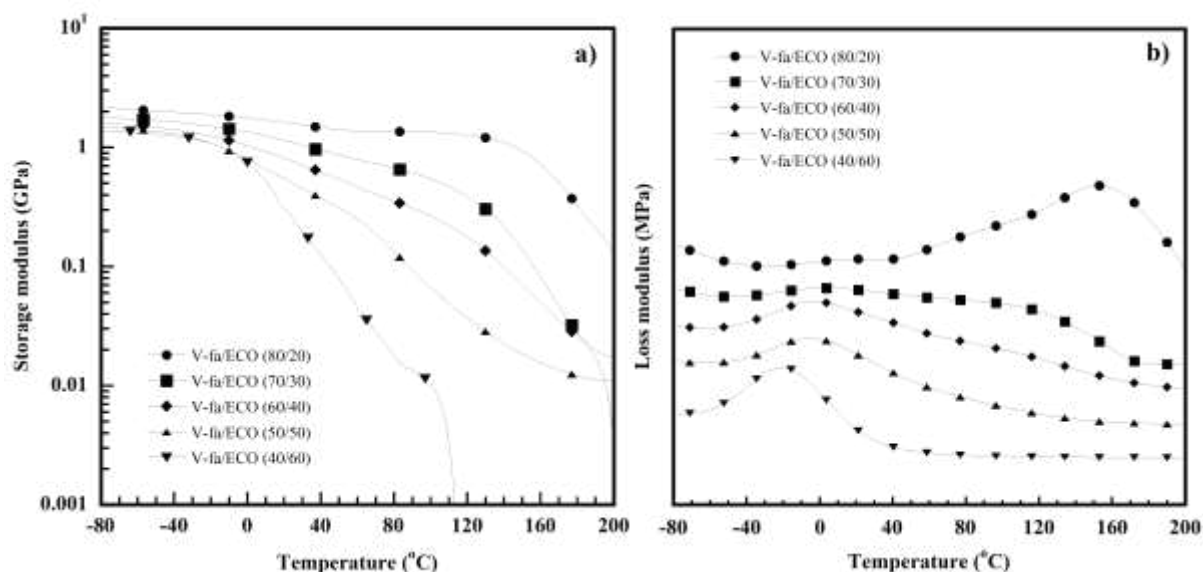


Figure 6. Thermomechanical property of V-fa/ECO biocopolymers at various ECO contents (a) storage modulus (b) loss modulus.

3.4 Thermal stability of V-fa/ECO biocopolymers

Thermal degradation is a type of polymer degradation in which detrimental chemical changes occur at elevated temperatures, changing their properties. Therefore, understanding the thermal degradation processes are important because of the proper use of polymers, their storage, and finally recycling. Thermal stability of the V-fa/ECO biocopolymers at various ECO contents was characterized by the degradation temperature at 5% weight loss (T_{d5}) as can be seen in Figure 7. It was found that the V-fa/ECO biocopolymers at 20, 30, 40, 50, and 60 wt% ECO showed the T_{d5} of 323 °C, 318 °C, 317 °C, 314 °C, and 313 °C, respectively, which tended to decrease with an increase ECO content due to lower T_{d5} , i.e., 310 °C of the ECO compared to the T_{d5} of the poly(V-fa), i.e., 343 °C. This indicated that the chemical structure of the ECO can be easily degraded compared to an aromatic ring bonded to an aldehyde group, hydroxyl phenolic, and a methoxy group of the poly(V-fa). However, the obtained result shows that the degradation temperature of the V-fa/ECO biocopolymers was significantly higher than the service temperature (~ 47 °C) of the human tooth for hot food and drink (Palmer et al.

1992). In addition, the T_{d5} of the poly(V-fa)/ECO biocopolymer was quietly similar to other polymers used for fiber posts such as epoxy (Nie et al. 2020) and bismaleimide (BMI) (Li et al. 2015). In addition, the char yield (CR) at 800 °C of V-fa/ECO biopolymer resulted mainly from the ECO constituent as a decrease the CR with an increase the ECO content of the V-fa/ECO biocopolymer was observed, i.e., from CR = 55 % for V-fa/ECO (80/20) to CR = 30 % for V-fa/ECO (40/60). This is because of higher CR of the poly(V-fa), i.e., 66 % than that of the ECO, i.e., 3.8 %. However, the CR of V-fa/ECO biocopolymer was rather high than epoxy and BMI polymers with the CR of 13-23.5 % at 700-800 °C (Li et al. 2015; Nie et al. 2020).

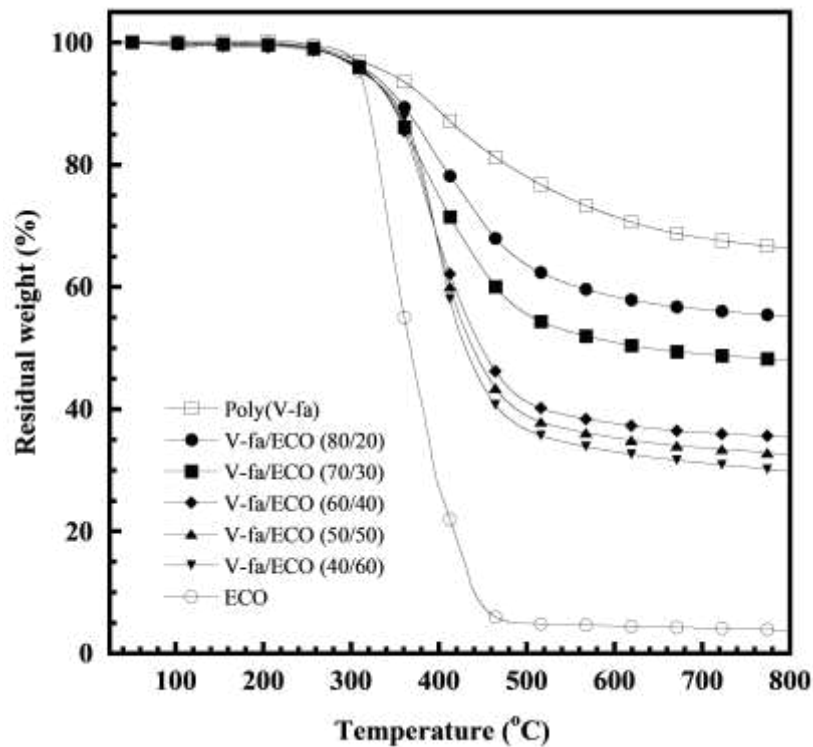


Figure 7. TGA thermogram of V-fa/ECO biocopolymers at various ECO contents.

3.5 Non-isothermal curing kinetic of V-fa/ECO system

Curing kinetic is an important aspect of polymer systems as it determines the time available for molding and storage. As with most chemical reaction systems, reaction rates are

temperature dependent. Studies of curing kinetic reaction are mainly carried out using non-isothermal and isothermal methods. Nonetheless, non-isothermal methods are widely accepted due to the advantage of not requiring prior knowledge of the reaction mechanism. As in recent years, using bio-based polymers to gradually replace polymers based on petroleum resources is sustainable alternatives for tailored applications such as dental posts. Therefore, non-isothermal curing kinetic of the bio-based benzoxazine/epoxy system should be investigated to compare with that of the petroleum-based benzoxazine/epoxy and the petroleum-based epoxy. In this work, the V-fa/ECO (80/20) monomer mixture was chosen to study curing kinetic because it showed balanced mechanical and thermal properties to be a matrix for glass fiber post.

DSC thermogram of heat flow as a function of temperature of the V-fa/ECO (80/20) monomer mixture at a heating rate of 5, 10, 15, and 20 °C/min is plotted in Figure 8 (a) which were used to evaluate the curing kinetic parameters, i.e., activation energy (E_a), pre-exponential factor (A) and order of reaction (n, m). As above mentioned in item 3.1, the curing reaction of the V-fa/ECO monomer mixtures consisted of two exothermic curing peaks. Therefore, each exothermic curing peak of the V-fa/ECO (80/20) monomer mixture heated by various heating rates was separated by peaks fitting and deconvolution using Pearson VII distribution, for example, the separated exothermic curing peak of the V-fa/ECO (80/20) monomer mixture with a heating rate of 10 °C/min were presented in Figure 8(b).

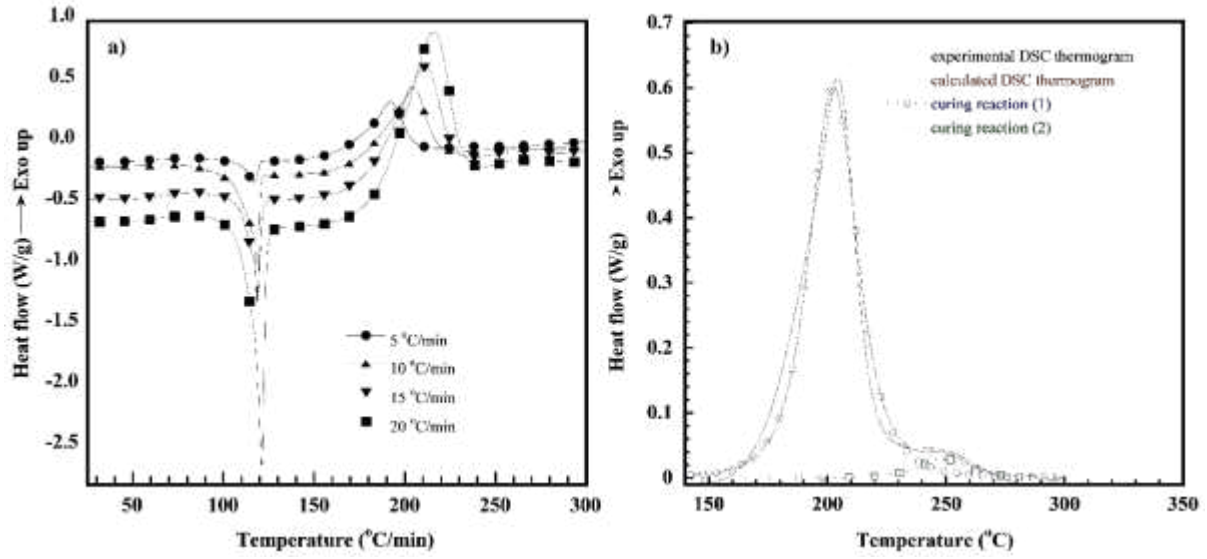


Figure 8. (a) DSC thermogram of V-fa/ECO (80/20) at various heating rates (β) (b) DSC thermogram of V-fa/ECO (80/20) recorded at 10 °C/min.

From Figure 8(b), the exothermic curing peaks of the V-fa/ECO (80/20) monomer mixture at lower temperature and at higher temperature were called curing reaction (1) and curing reaction (2), respectively, and the curing kinetic parameters of each curing reaction were then evaluated. With two curing reaction pathways of the V-fa/ECO (80/20) monomer mixture, it is possible that its curing reaction tends to complicate, resulting in the activation energy may often not unique. Therefore, the isoconversional methods, i.e., Flynn–Wall–Ozawa’s method (FWO) and Friedman’s method (FR) which completely evaluated the activation energy at different conversion levels regardless of the form of the kinetic equation was adopted in this work. The FWO is based on Eq. (1), while the FR is based in Eqs. (2) and (3) (Barros et al. 2020; Yousef et al. 2021).

$$\ln\beta = \ln\left(\frac{AE_a}{R}\right) - \ln g(\alpha) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \quad (1)$$

When $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$

$$\frac{d\alpha}{dt} = A(\alpha)f(\alpha)\exp\left(\frac{E_a}{RT}\right) \quad (2)$$

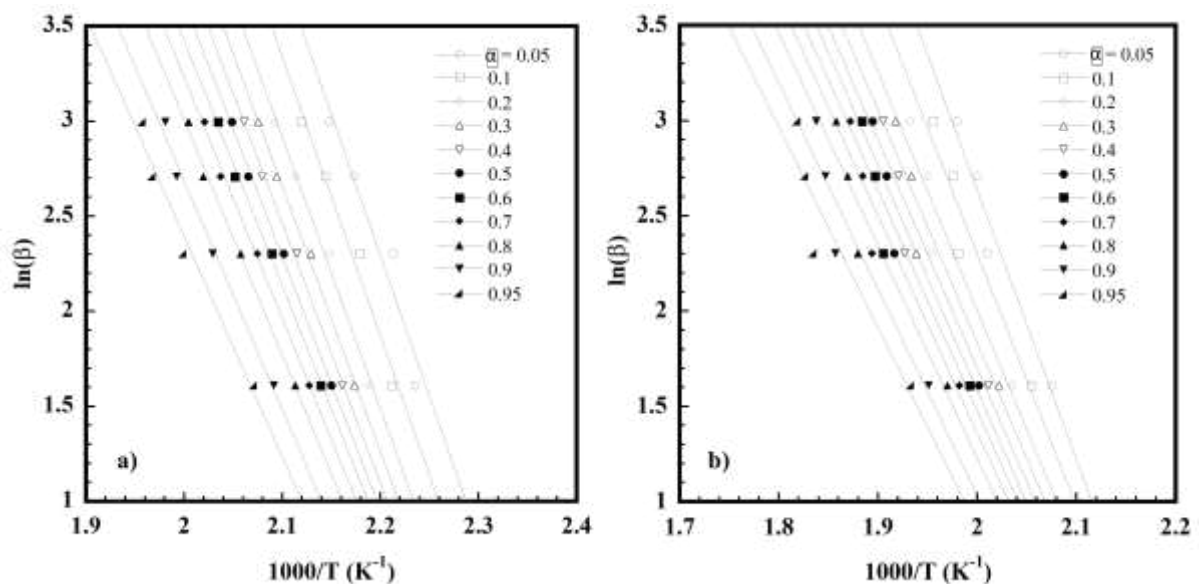
$$\ln \frac{d\alpha}{dt} = \ln \beta \frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (3)$$

where β is the heating rate, E_a is the activation energy at a given conversion (or apparent activation energy), R is the gas constant, T is the temperature at a certain conversion and $g(\alpha)$ is the integral conversion function.

Figure 9(a) plotted the $\ln\beta$ values as a function of $1/T$ at each constant curing conversion (α) according to the FWO for each curing reaction of the V-fa/ECO (80/20) monomer mixture. The straight line with the linear correlation coefficients where the slope allows the evaluation of the E_a as plotted in Figure 10(a). The E_a of each curing reaction tended to decrease with an increase in the curing conversion throughout the entire curing reaction were observed. For the curing reaction (1), the characteristic was an autocatalytic effect resulting from the hydroxyl groups generated from ring opening of the V-fa monomer by heat to promote the oxazine ring opening of the V-fa, leading to a decrease in the E_a as similarly observed for the guaiacol bio-based benzoxazine system (Ručigaj et al. 2016). In addition, it is also possible that viscosity of the V-fa/ECO (80/20) monomer mixture was reduced due to an increase of temperature during the process of the curing reaction, the elevated mobility of the chain segments of the monomer mixture and the growing effective collision of molecular reaction groups further also accelerated the diffusion rate and reduce the activation energy (Roudsari et al. 2014; Wu et al. 2018). For the curing reaction (2), this phenomenon is due to the fact that the generated hydroxyl group of the V-fa monomer partially protonates the oxygen atom of the epoxy group, causing a ring-opening reaction, resulting in a hydroxyl group (Jubsilp et al. 2006; Jubsilp et al. 2010; Shutov et al. 2022). The hydroxyl groups formed by oxirane ring opening have a self-

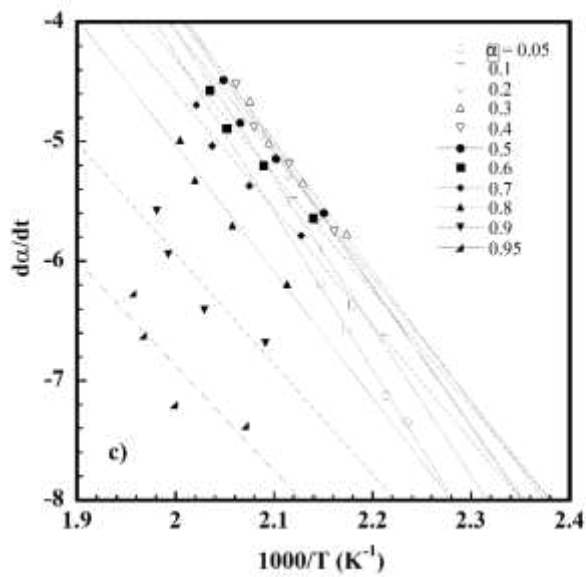
accelerating effect on the curing reaction (2) and lower activation energy values (Wu et al. 2018).

Figure 9(b) shows the relationship between $\ln[\beta(d\alpha/dt)]$ and $1/T$ at constant α for a set of heating rates (β) according to the FR. A family of straight line with slope of $-E_a/R$ was obtained. The E_a as a function of α are plotted in Figure 10(b). It can be seen a decrease of the E_a with conversion was like that observed in the FWO. As it was mentioned that the FWO method is potentially suited for use in curing systems where many reactions are occurring such that the activation energy varies with time and having not very different activation energies. Therefore, in this work, the average values of the activation energies of curing reaction (1) and curing reaction (2) of the V-fa/ECO (80/20) monomer mixture experimentally determined by the FWO were the appropriate kinetic used to determine the model. The average activation energy based on the FWO of the curing reaction (1) and the curing reaction (2) was 105 kJ/mol and 94 kJ/mol, respectively.

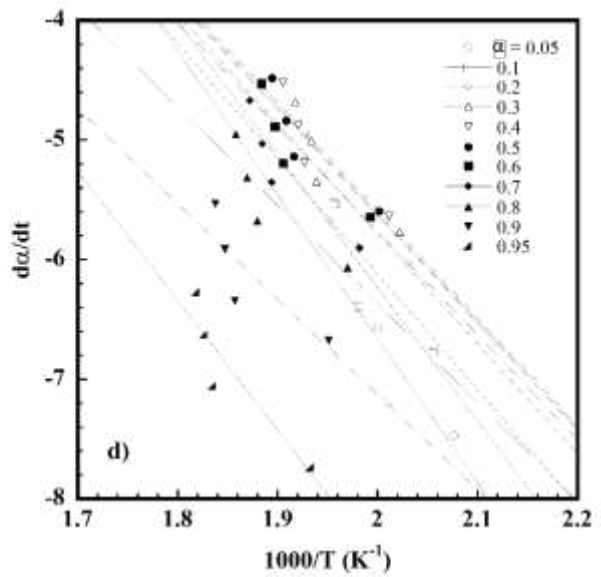


(a) curing reaction (1)

(b) curing reaction (2)



(c) curing reaction (1)



(d) curing reaction (2)

Figure 9. (a,b) FWO plots and (c,d) FR plots at various α of V-fa/ECO (80/20) monomer mixture for curing reaction (1) and curing reaction (2).

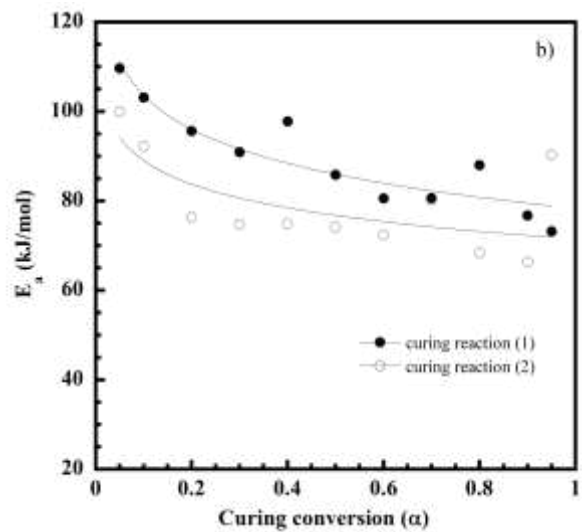
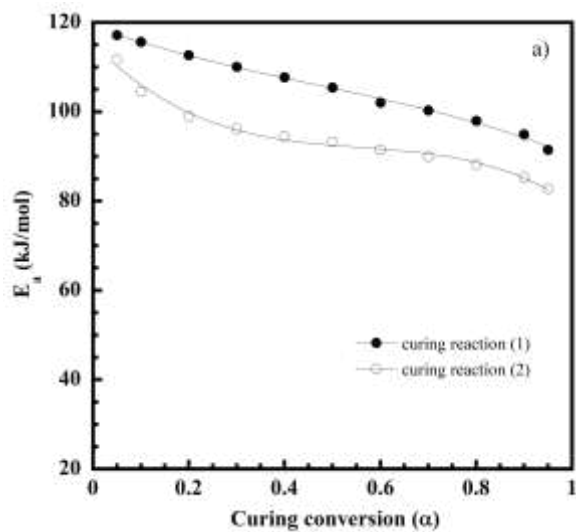


Figure 10. (a) E_a obtained from FWO (b) E_a obtained from FR of V-fa/ECO (80/20) monomer mixture: (●) curing reaction (1) and (■) curing reaction (2).

To confirm that the curing reaction (1) and curing reaction (2) is autocatalytic curing reaction, the curing reaction model of the V-fa/ECO (80/20) monomer mixture was investigated by the

FR. In case of the n th-order reaction, $f(\alpha) = (1-\alpha)^n$ is substituted in Eq. (3) and Eq. (4) is obtained. The slope corresponds to the reaction order (n).

$$\ln[Af(\alpha)] = \ln\left(\frac{d\alpha}{dt}\right) + \frac{E_a}{RT} = \ln A + n \ln(1 - \alpha) \quad (4)$$

Figure 11 shows the plot of $\ln[Af(\alpha)]$ which are summation of $\ln(da/dt)$ and E_a/RT and $\ln(1-\alpha)$ of the curing reactions (1) and the curing reaction (2) of the V-fa/ECO (80/20) monomer mixture at a heating rate of 5, 10, 15, and 20 °C/min. The E_a/RT value can be obtained using the average E_a from the FWO. The $\ln[Af(\alpha)]$ and $\ln(1-\alpha)$ are not linearly related and evidently show a maximum in the range of $\ln(1-\alpha)$ approximately around 0.51 to 0.22 which is equivalent to curing conversion (α) of about 0.2-0.4 (Barros et al. 2020), this suggests that both curing reactions are autocatalytic curing process.

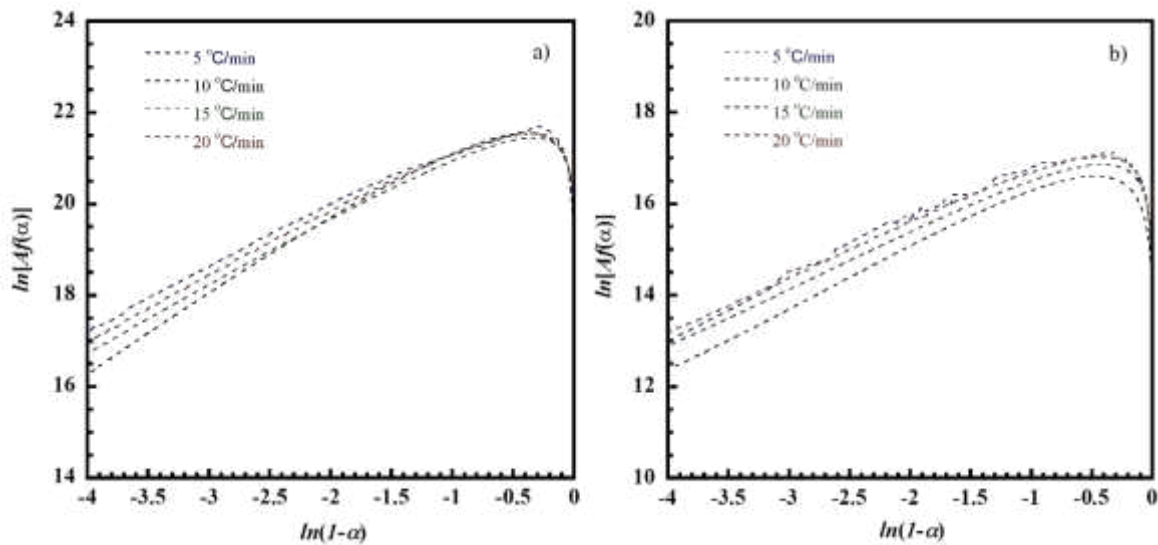


Figure 11. Plots of $\ln[Af(\alpha)]$ vs. $\ln(1-\alpha)$ of V-fa/ECO (80/20) monomer mixture at various heating rates and using average E_a from the FWO: (a) curing reaction (1) and (b) curing reaction (2).

For the autocatalytic curing reaction model considers reaction orders: m and n , as shown in Eq. (5) and by taking the logarithm of Eq. (6), a linear expression for the logarithm of curing rate can be obtained.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (1 - \alpha)^n \alpha^m \quad (5)$$

$$\ln\left(\beta \frac{d\alpha}{dt}\right) = \ln A - \left(\frac{E_a}{RT}\right) + n \ln(1 - \alpha) + m \ln(\alpha) \quad (6)$$

Eq. (6) can be solved by multiple linear regression. The A , m , and n values of two curing reaction can be obtained using the average E_a from the FWO. The degree of curing is in a range of 0.1-0.95. The results of the multiple linear regressions analysis for all heating rates of the V-fa/ECO (80/20) monomer mixture for the curing reaction (1) and the curing reaction (2) are listed in Tables 1 and 2, respectively.

Table 1. The kinetic parameters evaluated for the curing of the V-fa/ECO (80/20) (curing reaction (1)).

Heating rate (°C/min)	E_a (kJ/mol)	$\ln A$ (s ⁻¹)	Mean	n	Mean	m	Mean
5	105	22.68	22.80	1.54	1.50	1.08	0.80
10		23.04		1.57		0.79	
15		22.65		1.45		0.58	
20		22.81		1.44		0.72	

Table 2. The kinetic parameters evaluated for the curing of the V-fa/ECO (80/20) (curing reaction (2)).

Heating rate (°C/min)	E_a (kJ/mol)	$\ln A$ (s ⁻¹)	Mean	n	Mean	m	Mean
5	94	18.95	18.40	1.68	1.44	1.26	0.88
10		18.15		1.46		0.88	
15		18.14		1.34		0.68	
20		18.35		1.29		0.72	

Consequently, we obtain the mathematical models for autocatalytic kinetics of the V-fa/ECO (80/20) for curing reaction (1) and curing reaction (2) as,

$$\frac{d\alpha}{dt} = 1.13 \times 10^{10} A \exp\left(-\frac{12629}{T}\right) (1 - \alpha)^{1.5} \alpha^{0.8} \quad (7)$$

$$\frac{d\alpha}{dt} = 1.15 \times 10^8 A \exp\left(-\frac{11306}{T}\right) (1 - \alpha)^{1.44} \alpha^{0.88} \quad (8)$$

The experimental DSC peaks were compared with the calculated data from the models for the V-fa/ECO (80/20) monomer mixture, as shown in Figure 12. It is clear that the data calculated from the model are in good agreement with the experimental data. In addition, it was observed that bio-based benzoxazine/epoxy monomer system still showed two curing reactions similarly to that of the petroleum-based one (Shutov et al. 2022). The obtained activation energy of the V-fa/ECO (80/20) monomer mixture which is the biobased system was in the same range of the petroleum based benzoxazine/epoxy system such as bisphenol A/aniline based benzoxazine (BA-a) blended with bisphenol A/epichlorohydrin (epoxy).

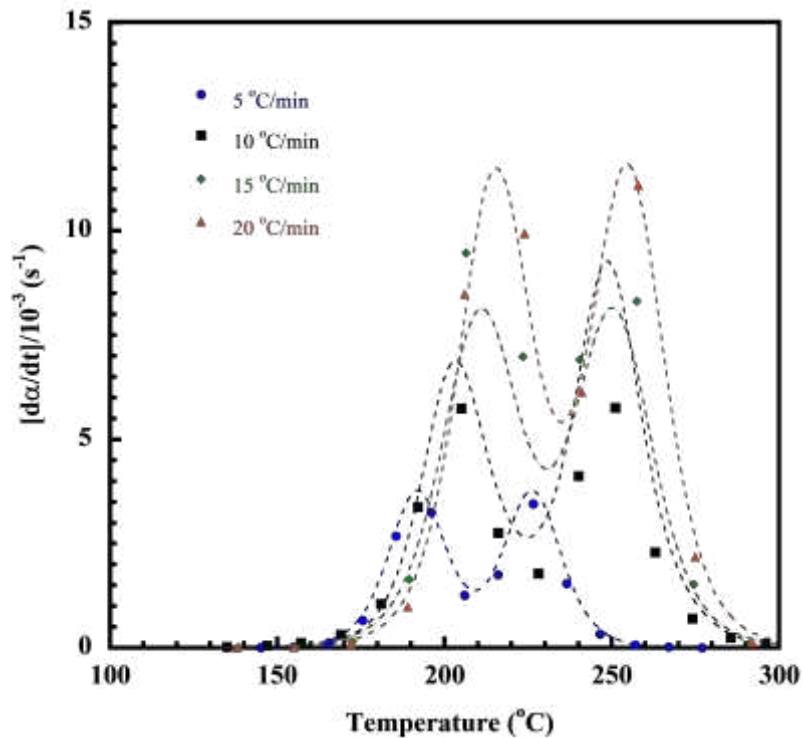


Figure 12. Comparison of the experimental (symbols) and calculated (solid lines) DSC peaks corresponding to the total curing process of V-fa/ECO (80/20) monomer mixture at different heating rates.

3.6 Feasibility of glass fiber (GF)-reinforced V-f/ECO biocopolymer for dental fiber post

The stress distribution from applying the occlusion at 45 degrees oblique load of 100 N by using finite element analysis (FEA) of tooth model restored with 65.4 vol% GF-reinforced V-f/ECO (80/20) biocopolymer post to compare with tooth model restored with commercial glass fiber post was investigated. The elastic properties of the isotropic materials and the glass fiber posts (orthotropic materials) used for the FEA are listed in Table 3 and Table 4, respectively.

Table 3. Elastic properties of the isotropic materials used for the FEA.

Material	Elastic Modulus (GPa)	Poisson's Coefficient
Porcelain (crown) (Genovese et al. 2005; Ko et al. 1992; Pegoretti et al. 2002)	120	0.28
Composite resin (Chatvanitkul and Lertchirakam 2010; Willems et al. 1992)	16.6	0.24
Gutta-percha (Genovese et al. 2005; Ko et al. 1992; Pegoretti et al. 2002)	0.00069	0.45
Dentin (Ko et al. 1992; Pegoretti et al. 2002)	18.6	0.31
Cortical bone (Ko et al. 1992; Pegoretti et al. 2002)	13.7	0.30
Periodontal ligament (Pegoretti et al. 2002)	0.0689	0.45
Cancellous bone (Pegoretti et al. 2002)	1.37	0.30

Table 4. Elastic properties for the orthotropic materials used for the FEA.

Elastic Constant	GF-reinforced V-fa/ECO biocopolymer post (65.4 vol%)	Commercial GF post (Coelho et al. 2009)
E_L (GPa)	21.47	37.00
$E_T = E_{T'}$ (GPa)	10.54	9.50
$G_{LT} = G_{LT'}$ (GPa)	7.50	3.10
$G_{TT'}$ (GPa)	4.22	3.50
$\nu_{LT} = \nu_{LT'}$	0.22	0.27
$\nu_{TL} = \nu_{T'L}$	0.11	0.34
$\nu_{TT'}$	0.25	0.27

Figure 13 shows von Mises stress (σ_v) contour maps of a tooth model restored with the GF-reinforced V-fa/ECO biocopolymer post and a commercially available glass fiber post. It was noticed that both tooth models exhibited the maximum σ_v in the cervical region in dentin. However, the tooth model restored with the GF-reinforced V-fa/ECO biocopolymer post showed the lower value of the maximum σ_v at the dental region, i.e., 28.267 MPa than that of the tooth model restored with commercial glass fiber post, i.e., 28.320 MPa. It is possible that the GF-reinforced V-fa/ECO biocopolymer post allowed to carry load fractions due to its quite similar elastic modulus to dentin with the elastic modulus approximately 18 - 20 GPa (Ko et al. 1992; Pegoretti et al. 2002). In addition, it was observed that the maximum σ_v at the post of the tooth model restored with the GF-reinforced V-fa/ECO biocopolymer post also showed lower than that of the commercial fiber glass post used to restore the tooth model. Therefore, this characteristic indicated that the chance of fracture of the root canal can be reduced by the utilization of the GF-reinforced V-fa/ECO biocopolymer as a glass fiber post.

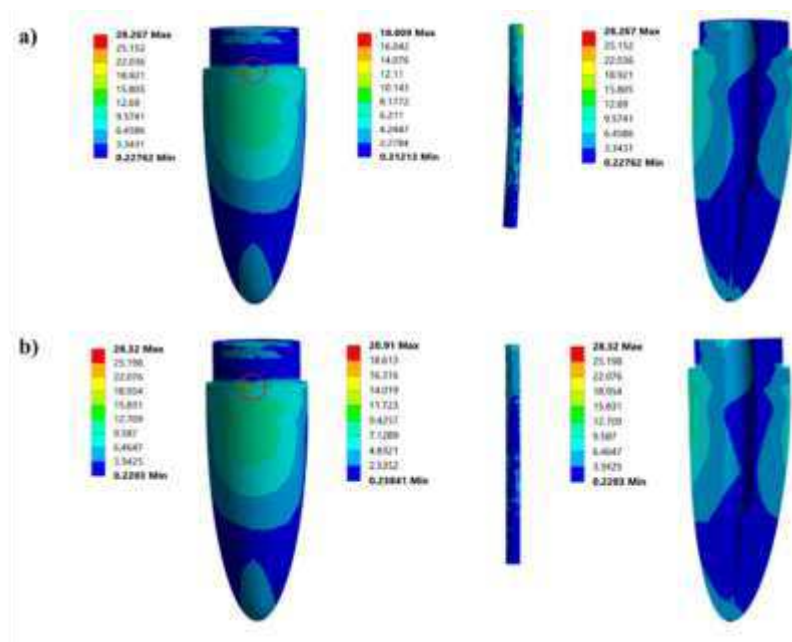


Figure 13. Contour map of the von Mises stress of tooth restored with glass fiber posts : (a) 65.4 vol% glass fiber-reinforced poly(V-fa)/ECO biocopolymer post, (b) commercial glass fiber post.

Conclusions

Benzoxazine-epoxy biocopolymer was successfully proved to act as a matrix for dental fiber post application. The obtained benzoxazine-epoxy biocopolymer showed good mechanical and thermal properties, i.e., storage modulus = 2.27 GPa, $T_g = 158\text{ }^\circ\text{C}$ and $T_{d5} = 323\text{ }^\circ\text{C}$. The curing reaction of V-fa/ECO monomer mixture indicated several reactions presenting overlapped peaks: the catalytic opening of oxazine ring and an epoxy group, the autocatalytic reaction of benzoxazine and etherification between benzoxazine and epoxide, and epoxy homopolymerization which are quite similar to reactions of petroleum-based benzoxazine-epoxy copolymer. Its curing kinetics were studied using the Flynn-Wall-Ozawa method and were derived assuming constant E_a . The kinetic equation of curing was obtained at $\frac{d\alpha}{dt} = 1.13 \times 10^{10} \exp\left(-\frac{105000}{RT}\right) (1 - \alpha)^{1.5} \alpha^{0.8}$ for curing reaction (1) and at $\frac{d\alpha}{dt} = 1.15 \times 10^8 \exp\left(-\frac{94000}{RT}\right) (1 - \alpha)^{1.44} \alpha^{0.88}$ for curing reaction (2). For glass fiber-reinforced V-fa/ECO biocopolymer acted as a dental fiber post, the proper proportion blending V-fa with ECO could be employed in dentistry as the matrix of fiber-reinforced dental root canal posts as the glass fiber-reinforced V-fa/ECO biocopolymer post has an elastic modulus that more closely approaches that of dentin while that for commercial glass fiber post was much higher.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data analyzed during this study are included in this article.

Competing interests

The authors declare that they have no competing interests.

Funding

The authors would like to express their sincere appreciations to The National Research Council of Thailand (NRCT) and Srinakharinwirot University (grant numbers N42A650377 and 588/2565), the NSRF via the Program Management Unit for Human Resources and Institutional Development, Research and Innovation (grant number B05F640094).

Authors' contributions

Conceptualization, C.J.; methodology, C.J. and P.M.; validation, C.J., S.R. and U.S.; formal analysis, C.J. and P.M.; data curation, C.J.; writing—original draft preparation, C.J. and P.M.; writing-review and editing, C.J., P.K. and S.R.; supervision, C.J.; funding acquisition, C.J. All authors have read and agreed to the published version of the manuscript.

Acknowledgments

Tanawichanun, K. Wongmak, N. and Bado, L. for creating of schematic of tooth models.

References

- Hara, O. 1990. Curing Agents for Epoxy Resin in: *Three Bond Technical News*, 32(20), 1-10
- Ambrozic, R., Rucigaj, A., Krajnc, M. 2020. A green approach toward epoxy-benzoxazine copolymers with shape-memory ability. *Express Polymer Letters*, **14**, 808-822.
- Amornkitbamrung, L., Srisaard, S., Jubsilp, C., Bielawski, C.W., Um, S.H., Rimdusit, S. 2020. Near-infrared light responsive shape memory polymers from bio-based benzoxazine/epoxy copolymers produced without using photothermal filler. *Polymer*, **209**, 122986.

- Barros, J.J.P., Silva, I.D.d.S., Jaques, N.G., Wellen, R.M.R. 2020. Approaches on the non-isothermal curing kinetics of epoxy/PCL blends. *Journal of Materials Research and Technology*, **9**(6), 13539-13554.
- Bhardwaj, N., Kumar, B., Agrawal, K., Verma, P. 2021. Current perspective on production and applications of microbial cellulases: a review. *Bioresources and Bioprocessing*, **8**(1), 95.
- Birniwa, A.H., Abdullahi, S.S., Ali, M., Mohammad, R.E., Jagaba, A.H., Amran, M., Avudaiappan, S., Maureira-Carsalade, N., Flores, E.I.S. 2023. Recent Trends in Treatment and Fabrication of Plant-Based Fiber-Reinforced Epoxy Composite: A Review. in: *Journal of Composites Science*, Vol. 7.
- Chatvanitkul, C., Lertchirakarn, V. 2010. Stress Distribution with Different Restorations in Teeth with Curved Roots: A Finite Element Analysis Study. *Journal of Endodontics*, **36**(1), 115-118.
- Coelho, C., Biffi, J., Silva, G., Abrahao, A., Campos, R., Soares, C. 2009. Finite element analysis of weakened roots restored with composite resin and posts. *Dental materials journal*, **28**, 671-8.
- de Luca, M.A., Martinelli, Márcia, Barbieri, Cláudia C.T. 2009. Hybrid films synthesised from epoxidised castor oil, γ -glycidoxypropyltrimethoxysilane and tetraethoxysilane. *Progress in Organic Coatings*, **65**(3), 375-380.
- Elsubeihi, E., Aljafarawi, T., Elsubeihi, H. 2020. State of the Art Contemporary Prefabricated Fiber-Reinforced Posts. *The Open Dentistry Journal*, **14**, 313-323.
- Genovese, K., Lamberti, L., Pappalettere, C. 2005. Finite element analysis of a new customized composite post system for endodontically treated teeth. *J Biomech*, **38**(12), 2375-89.
- Gotro, J. 2022. Epoxy Curing Agents – Anhydrides, Long Pot Life and Exceptional Properties, Vol. 2023.

- Hombunma, P., Parnklang, T., Mora, P., Jubsilp, C., Rimdusit, S. 2019. Shape memory polymers from bio-based benzoxazine/epoxidized natural oil copolymers. *Smart Materials and Structures*, **29**(1).
- Hu, Y., Jia, P., Shang, Q., Zhang, M., Feng, G., Liu, C., Zhou, Y. 2019. Synthesis and Application of UV-curable Phosphorous-containing Acrylated Epoxidized Soybean Oil-based Resins. *Journal of Bioresources and Bioproducts*, **4**(3), 183-191.
- Ishida, H. 1996. Process for preparation of benzoxazine compounds in solventless systems, (Ed.) US Pat. 5, 516 (1996).
- Jubsilp, C., Damrongsakkul, S., Takeichi, T., Rimdusit, S. 2006. Curing kinetics of arylamine-based polyfunctional benzoxazine resins by dynamic differential scanning calorimetry. *Thermochimica Acta*, **447**(2), 131-140.
- Jubsilp, C., Panyawanitchakun, C., Rimdusit, S. 2013. Flammability and thermomechanical properties of dianhydride-modified polybenzoxazine composites reinforced with carbon fiber. *Polymer Composites*, **34**(12), 2067-2075.
- Jubsilp, C., Punson, K., Takeichi, T., Rimdusit, S. 2010. Curing kinetics of Benzoxazine–epoxy copolymer investigated by non-isothermal differential scanning calorimetry. *Polym. Degrad. Stab.*, **95**(6), 918-924.
- Ko, C.C., Chu, C.S., Chung, K.H., Lee, M.C. 1992. Effects of posts on dentin stress distribution in pulpless teeth. *J Prosthet Dent*, **68**(3), 421-7.
- Kurihara, S., Idei, H., Aoyagi, Y., Kuroe, M. 2012. Binder resin for friction material, binder resin composition for friction material, composite material for friction material containing the same, friction material and production method thereof, Google Patents.
- Li, S., Yan, H., Feng, S., Niu, S. 2015. Synthesis and characterization of a phosphorus-containing flame retardant with double bonds and its application in bismaleimide resins. *RSC Advances*, **5**(123), 101480-101486.

- Liu, F., Wang, Z., Liu, D., Li, J. 2009. Curing of diglycidyl ether of bisphenol-A epoxy resin using a poly(aryl ether ketone) bearing pendant carboxyl groups as macromolecular curing agent. *Polymer International*, **58**(8), 912-918.
- Mora, P., Nunwong, C., Sriromreun, P., Kaewsriprom, P., Srisorrachatr, U., Rimdusit, S., Jubsilp, C. 2022. High Performance Composites Based on Highly Filled Glass Fiber-Reinforced Polybenzoxazine for Post Application. *Polymers*, **14**(20), 4321.
- Nie, S., Jin, D., Xu, Y., Han, C., Dong, X., Yang, J.-n. 2020. Effect of a flower-like nickel phyllosilicate-containing iron on the thermal stability and flame retardancy of epoxy resin. *Journal of Materials Research and Technology*, **9**, 10189-10197.
- Okhawilai, M., Dueramae, I., Jubsilp, C., Rimdusit, S. 2017. Effects of high nano-SiO₂ contents on properties of epoxy-modified polybenzoxazine. *Polymer Composites*, **38**(10), 2261-2271.
- Palmer, D.C., Barco, M.T., Billy, E.J. 1992. Temperature extremes produced orally by hot and cold liquids. *Journal of Prosthetic Dentistry*, **67**, 325-7, 1992.
- Park, S.-J., Jin, F.-L., Lee, J.-R. 2004. Synthesis and Thermal Properties of Epoxidized Vegetable Oil. *Macromolecular Rapid Communications*, **25**(6), 724-727.
- Pegoretti, A., Fambri, L., Zappini, G., Bianchetti, M. 2002. Finite element analysis of a glass fibre reinforced composite endodontic post. *Biomaterials*, **23**(13), 2667-82.
- Prasomsin, W., Parnklang, T., Sapcharoenkun, C., Tiptipakorn, S., Rimdusit, S. 2019. Multiwalled Carbon Nanotube Reinforced Bio-Based Benzoxazine/Epoxy Composites with NIR-Laser Stimulated Shape Memory Effects. *Nanomaterials*, **9**, 881.
- Rao, B.S., Rajavardhana Reddy, K., Pathak, S.K., Pasala, A.R. 2005. Benzoxazine-epoxy copolymers: effect of molecular weight and crosslinking on thermal and viscoelastic properties. *Polymer International*, **54**(10), 1371-1376.

- Rimdusit, S., Ishida, H. 2000. Synergism and multiple mechanical relaxations observed in ternary systems based on benzoxazine, epoxy, and phenolic resins. *Journal of Polymer Science Part B: Polymer Physics*, **38**(13), 1687-1698.
- Rimdusit, S., Pirstpindvong, S., Tanthapanichakoon, W., Damrongsakkul, S. 2005. Toughening of polybenzoxazine by alloying with urethane prepolymer and flexible epoxy: A comparative study. *Polym. Eng. Sci.*, **45**(3), 288-296.
- Roudsari, G., Mohanty, A., Misra, M. 2014. Study of the Curing Kinetics of Epoxy Resins with Biobased Hardener and Epoxidized Soybean Oil. *ACS Sustainable Chemistry & Engineering*, **2**, 2111-2116.
- Ručigaj, A., Gradišar, Š., Krajnc, M. 2016. Kinetic investigation of a complex curing of the guaiacol bio-based benzoxazine system. **16**(3), 199-206.
- Saba, N., Jawaid, M., Alothman, O.Y., Almutairi, Z. 2019. Evaluation of dynamic properties of nano oil palm empty fruit bunch filler/epoxy composites. *Journal of Materials Research and Technology*, **8**(1), 1470-1475.
- Shadhin, M., Rahman, M., Jayaraman, R., Mann, D. 2021. Novel cattail fiber composites: converting waste biomass into reinforcement for composites. *Bioresources and Bioprocessing*, **8**(1), 101.
- Shutov, V.V., Bornosuz, N.V., Korotkov, R.F., Gorbunova, I.Y., Sirotin, I.S. 2022. Kinetics of benzoxazine and epoxy oligomer copolymerization. *Thermochimica Acta*, **714**, 179254.
- Sini, N.K., Bijwe, J., Varma, I.K. 2014. Renewable benzoxazine monomer from Vanillin: Synthesis, characterization, and studies on curing behavior. *Journal of Polymer Science Part A: Polymer Chemistry*, **52**(1), 7-11.
- Srisaard, S., Amornkitbamrung, L., Charoensuk, K., Sapcharoenkun, C., Jubsilp, C., Rimdusit, S. 2021. Effects of graphene nanoplatelets on bio-based shape memory polymers from

- benzoxazine/epoxy copolymers actuated by near-infrared light. *Journal of Intelligent Material Systems and Structures*, **33**(4), 547-557.
- Sudha, G.S., Kalita, H., Mohanty, S., Nayak, S.K. 2017. Biobased epoxy blends from epoxidized castor oil: Effect on mechanical, thermal, and morphological properties. *Macromolecular Research*, **25**(5), 420-430.
- Willems, G., Lambrechts, P., Braem, M., Celis, J.P., Vanherle, G. 1992. A classification of dental composites according to their morphological and mechanical characteristics. *Dental Materials*, **8**(5), 310-319.
- Wu, F., Zhou, X., Yu, X. 2018. Reaction mechanism, cure behavior and properties of a multifunctional epoxy resin, TGDDM, with latent curing agent dicyandiamide. *RSC Advances*, **8**(15), 8248-8258.
- Yousef, S., Eimontas, J., Striūgas, N., Subadra, S.P., Abdelnaby, M.A. 2021. Thermal degradation and pyrolysis kinetic behaviour of glass fibre-reinforced thermoplastic resin by TG-FTIR, Py-GC/MS, linear and nonlinear isoconversional models. *Journal of Materials Research and Technology*, **15**, 5360-5374.
- Zeng, C., Lu, S., Song, L., Xiao, X., Gao, J., Pan, L., He, Z., Yu, J. 2015. Enhanced Thermal Properties in a Hybrid Graphene–Alumina Filler for Epoxy Composites. *RSC Adv.*, **5**.
- Zhang, Y., Duan, C., Bokka, S.K., He, Z., Ni, Y. 2022. Molded fiber and pulp products as green and sustainable alternatives to plastics: A mini review. *Journal of Bioresources and Bioproducts*, **7**(1), 14-25.
- Zulkifli, N.N.b., Badri, K.b.H., Amin, K.A.M. 2016. Palm kernel oil-based polyester polyurethane composites incorporated with multi-walled carbon nanotubes for biomedical application. *Bioresources and Bioprocessing*, **3**(1), 25.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [graphicalabstract.jpg](#)