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Self-Healable Bio-based Epoxy Resin from Epoxidized Palm Oil

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Epoxy resin is a thermoset with superior mechanical strength, thermal stability and dimensional stability, granted by the permanent crosslinking networks in the epoxy network. Despite its advantages, the rigid 3D epoxy resin precludes flow, resulting in the recycling and reprocessing of epoxy resin becomes impossible. The incorporation of covalent adaptable network (CAN) into the epoxy resin enable their network topology to be rearranged and permits recycling of epoxy resin. This project highlights the self-healing efficiency as well as mechanical and thermal properties of epoxy resin synthesized from various stoichiometric ratios (R) of curing agent (citric acid monohydrate) to epoxidized palm oil (EPO). EPO was cross-linked with citric acid monohydrate (CA) without the usage of a catalyst under specific curing condition to produce self-healable epoxy resin. Fourier – Transformed Infrared Spectroscopy (FTIR) analysis shows that the epoxide group in EPO successfully reacted with carboxylic groups in (CA) via ring-opening reaction to form **β** – hydroxyester networks. Thermogravimetric Analysis (TGA) analysis reveals the thermal stability of each formulation, indicating that R 0.5 possess the highest crystallinity and R 1.5 has the highest T_g (8.09 °C) among the others. Interestingly, R 1.0 which is the lowest in terms of thermal stability exhibited the best self-healing performance. To further improve the overall properties of the synthesized epoxy thermoset, reinforcement materials need to be added during the synthesis process.

1. Introduction

Epoxy Resin is a thermoset that possesses superior thermal and mechanical properties. These characteristics granted the epoxy resin to be matchless in demanding sectors (Fortman et al., 2018). The main drawback of these outstanding polymers is their inability to undergo any recycling and self-healing process, once the curing is completed. When exposed to a harmful environment, epoxy resin can be easily damaged and unable to be healed (Urdl et al., 2017). These properties result in an increase of burden to the environment of each disposal of epoxy resin. Recently, self-healing approach in epoxy resin attracted numerous researchers to generate outstanding product durability. Extrinsic self-healing, which consumes limited healing agents, do not allow multiple healing events at the same damage site (Urdl et al., 2017). The high number of microcapsules incorporated may lead to significant changes in bulk polymer properties (Urdl et al., 2017).

Montarnal et al. (2011) discovered that Covalent Adaptable Network (CAN) can be incorporated into the epoxy resin instead of using permanent cross-linking bonds. Under appropriate temperature, the invented polymer networks are able to transform from rubbery state to viscoelastic liquid in which the covalent bonds can reform and break, changing the topology of the network (Capelot et al., 2012). Dynamic exchange reaction between covalent bonds can be applied as one of the intrinsic self-healing strategies, which is able to overcome the limitation of the extrinsic self-healing approach (Krishnakumar et al., 2020).

Diglycidyl ether of bisphenol A (DGEBA), a common epoxy resin monomer, is synthesized from bisphenol A (BPA) and epichlorohydrin, which both are toxic to the human body (Qiu et al., 2019). To address the above dilemma, other authors develop a bio-based recyclable epoxy thermoset from fully bio-based and renewable feedstocks. Altuna et al. (2013) produced a green and self-healable epoxy thermoset by using epoxidized soybean oil and aqueous citric acid without any catalyst. The resulted epoxy resin exhibited good self-healing

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properties at 160 °C for 2 h, thanks to the presence of the β-hydroxyester network, one type of CANs. Di Mauro et al. (2020) reported a series of recyclable and repairable bio-based epoxy resin synthesized from twelve vegetable oils with imidazole as initiator. Products derived from vegetable oil with monounsaturated fatty acids exhibit greater facility of reprocessing, lower loss of cross-linking, mechanical performance and better solvent resistance compared to vegetable oils with tri-unsaturated fatty acids.

Malaysia is the world's second-largest producer of palm oil (PO) with a total production of crude palm oil (19.5 Mt), followed by Indonesia (44.0 Mt) in 2020 (CPOPC, 2020). Palm oil generates approximately 5 t of oil per ha which is 8 to 10 times higher than other vegetable oils such as rapeseed and soybean. Monounsaturated fatty acids in palm oil can be converted into the epoxy group via the epoxidation process, granting palm oil to be applied as building block for an epoxy resin.

To the best of our knowledge, no works pertaining to the direct synthesis of self – healable bio-based epoxy resin from epoxidized palm oil (EPO) with citric acid monohydrate (CA). This study focuses on preparing a bio-based self-healable epoxy resin from EPO and CA without any catalyst. The effects of stoichiometric ratio (R) on thermal properties and self-healing performance were investigated in detail.

2. Experimental

2.1 Materials

EPO (1049 g/mol, 0.886 g/cm^3, oxirane oxygen content = 1.984 %) was purchased from Budi Oil Sdn Bhd and CA (210.14 g/mol. 99 % purity, $C_6H_8O_7 \cdot H_2O$) was supplied by Sigma Aldrich. All the materials were used directly without any pre-treatment.

2.2 Synthesis of epoxidized palm oil epoxy resin

80 wt% CA was mixed with 20 wt% distilled water. The mixture was then heated to 90 °C. After the curing agent was fully dissolved in distilled water, the aqueous solution was added into a beaker containing the proper weight of EPO at 90 °C. The solution was stirred continuously to generate an emulsion. The epoxy-acid reaction happened rapidly during the transformation of the emulsion into a homogeneous substance. The viscosity of the mixture increased and achieved gelation. After 10 mins of rapid mixing at 90 °C, the colour of the solution slightly changed to opalescent and the solution was poured into a container enclosed with non-stick film. The cast was located in a fan oven and the curing process was subjected for 6 h at 90 °C, followed by 12 h at 120 °C. Different stoichiometric ratios, R = carboxylic acid equivalents/epoxy equivalents were used and the formulation is shown in Table 1.

Table 1: Epoxy resin formulation table.

Sample Code	R	EPO (g)	CA (g)	H_2O (g)
R 1.5	1.5	10	2.003	0.501
R 1.2	1.2	10	1.603	0.401
R 1.0	1.0	10	1.335	0.338
R 0.8	0.8	10	1.068	0.267
R 0.5	0.5	10	0.668	0.167

2.3 Fourier – Transformed Infrared Spectroscopy (FTIR)

Main functional groups in the epoxy resin and EPO (10 mg) were identified by using a Shimadzu IR Tracer – 100 FTIR Spectrometer, in the 400 cm^{-1} to 4,000 cm^{-1} range, at a resolution of 4 cm^{-1} under attenuated total reflectance (ATR) mode.

2.4 Thermogravimetric Analysis (TGA)

Thermal degradation behaviour of the samples was investigated via a Perkin Elmer TGA 4000 thermo-gravimetric analyser. Under nitrogen atmosphere, samples (9 mg - 10 mg) were analysed at a heating rate of 10 °C /min from 40 °C to 700 °C.

2.5 Differential Scanning Calorimetry (DSC)

Glass transition temperature (T_g) of each formulation (10 mg) was determined using a Mettler-Toledo DSC 1 differential scanning calorimeter. Under 20 mL/min of nitrogen flow, the cured samples were heated from ambient temperature to 150 °C at a heating rate of 10 °C/min, upon reaching 150 °C, the temperature was held for 1 min before it was cooled at a rate of 20 °C/min to -50 °C. The sample underwent a second thermal cycle from -50 °C to 150 °C with a heating rate of 10 °C/min under the same nitrogen flow. The T_gs were determined based on the thermogram obtained from the second heating cycle.

2.6 Self-healing performance test

The test was conducted according to Altuna et al. (2013) with slight modification. The cured resins were cut into 2 mm x 5 mm x 40 mm samples, as shown in Figure 1. Two samples were placed in superimpose position and exposed to thermal treatment (140 °C for 1 h), while a compressive force was applied at the same moment to yield a 10 % deformation. The welding line between the two samples after thermal treatment was observed using an optical microscope.

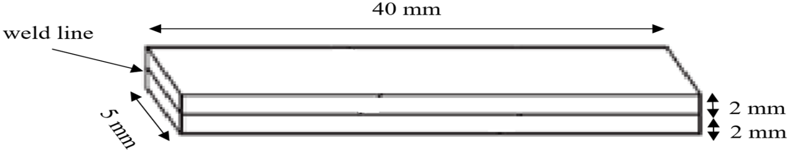

Figure 1: Dimensions and arrangement of samples used in the self-healing performance test.

3. Results and discussion

3.1 Cross-linking of EPO with CA

During the dissolution process of CA, it was dissociated to produce protons (Figure 2a). When CA is mixed with EPO, the generated proton catalyzes the epoxy-acid reaction by protonating the epoxide groups in EPO (Figure 2b) (Altuna et al., 2013). The protonated epoxide groups are able to be attacked by carboxylate anion (Figure 2c) or react with a water molecule (Figure 2d). Even though the formation of β-hydroxyester is preferred, the epoxide group does react with a water molecule (Sahoo et al., 2018). During the curing process, the sample undergoes crosslinking process between CA and EPO (Figure 2c). After the curing reaction, the sample are believed to exhibit a 3-dimensional rigid structure (Figure 2e).

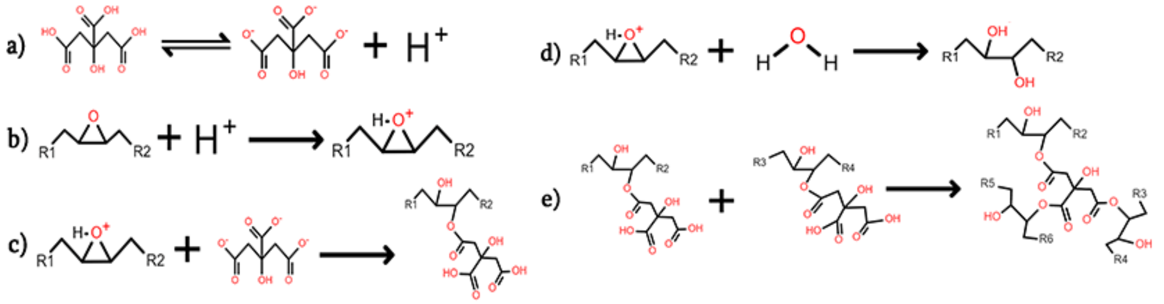

Figure 2: Reaction of EPO (a) dissociation of CA in aqueous solution, (b) protonation of the epoxide, (c) attack by CA's carboxylate anion, (d) attack by a water molecule and (e) curing process with CA.

3.2 Fourier-Transformed Infrared Spectroscopy

FTIR spectra of EPO and cured epoxy resin R 1.0 are shown in Figure 3. Epoxy group absorbance band (843 – 842 cm^{-1}) decreased while a new peak appeared at 1,155 cm^{-1}, corresponds to the absorbance of the vibration of C-O-C of β-hydroxyester bond when comparing R 1.0 with EPO (Pawar et al., 2016). This hints that the reactions between EPO and CA as shown in Figure 2 has occurred. The existence of the broad peak at 3,565 – 3,450 cm^{-1} in R 1.0 which corresponds to the free hydroxyl groups generated via the ring-opening reaction further strengthens this claim (Anusic et al., 2020).

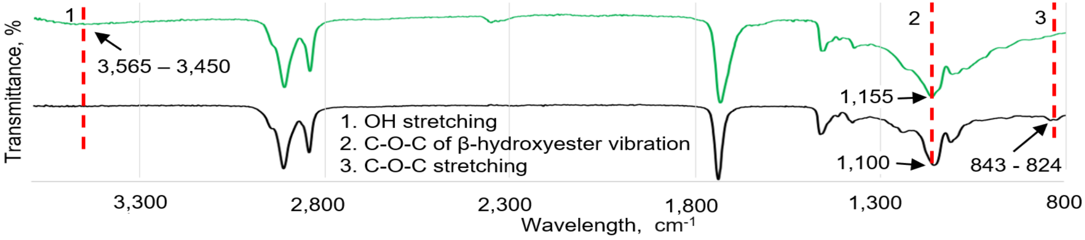

Figure 3: FTIR spectra of EPO and epoxy resin R 1.0.

FTIR spectrum of each sample with different R is displayed in Figure 4. Faghihzadeh et al. (2016) mentioned that peak intensity indicates the concentration of the respective functional groups. In Figure 4a, the arise of OH groups intensity (3,565 cm^{-1} – 3,300 cm^{-1}) is due to the formation of β-hydroxyester networks as well as the unreacted CA in R 1.2 and R 1.5 (Altuna et al., 2013). In Figures 4b and 4c, R 0.5 displays the greatest intensity of carbonyl group (1,740 cm^{-1}) and the most representative absorbance band for β-hydroxyester bond (1,174 cm^{-1}), with other samples (Anusic et al., 2020). These findings may be attributed to the amount of β-hydroxyester bonds formed in R 0.5 is the highest. In Figure 4d, the disappearance of epoxy group absorbance peak (843 cm^{-1} - 834 cm^{-1}) in all samples is responsible for the consumption of epoxy groups during the ring-opening reaction.

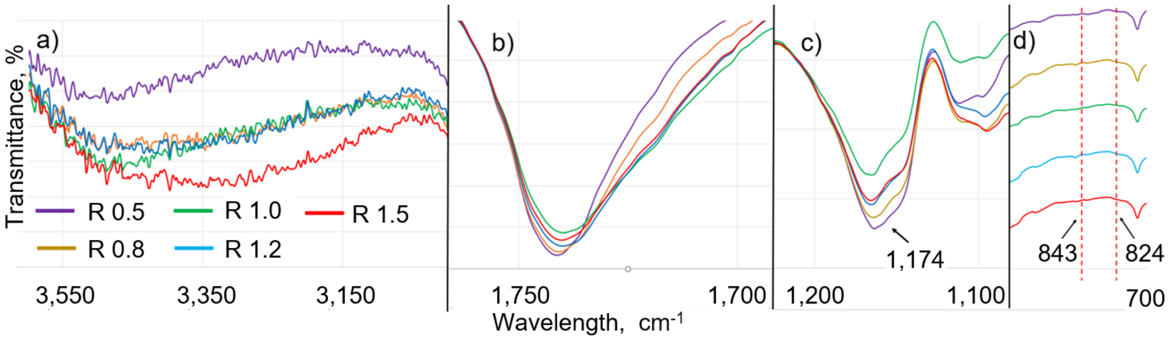

Figure 4: Major peaks in the FTIR spectra of epoxy resin synthesized at different R (a) 3,565 cm^{-1}- 3,300 cm^{-1}, (b) 1,740 cm^{-1}, (c) 1,174 cm^{-1} and (d) 843 cm^{-1} – 824 cm^{-1}.

3.3 Thermogravimetric analysis

Figure 5 depicts the mass loss curves and the derivative mass loss curve of the five epoxy resins. From Figure 5a, under an inert atmosphere, the epoxy resins were thermally stable up to 150 °C. The first decomposition stage (1st Phase) occurred between 150 °C to 340 °C, was owned by the crosslinked section of the EPO (Sahoo et al., 2018). At the 2nd Phase, onset degradation temperature commenced at around 340 °C, followed by a single degradation to 430 °C, which is contributed by the chain scission in the oil-based ester groups (Sahoo et al., 2018). The 3rd Phase that occurred beyond 430 °C is responsible for the ether and ester groups degradation in the β-hydroxyester network (Sahoo et al., 2018). The whole degradation process completed at around 500 °C. Figure 5b shows that, at the 1st Phase, R 1.0 exhibited the most obvious peak, following by R 1.5 and R 1.2. This could be related to the melting of the unreacted CA in the resin epoxy as these formulations contain excess CA (Schilling et al., 2008). The sudden rise of a peak in sample R 1.0 may be a result of the loss of moisture content (Tajau et al., 2017). In the 2nd Phase, R 1.2 displays the sharpest peak, indicating that its ester bond content was the highest. This finding proved that R 1.2 contained more unreacted oil-based content and this is in line with the FTIR spectrum presented in Figure 4b (Pawar et al., 2016).

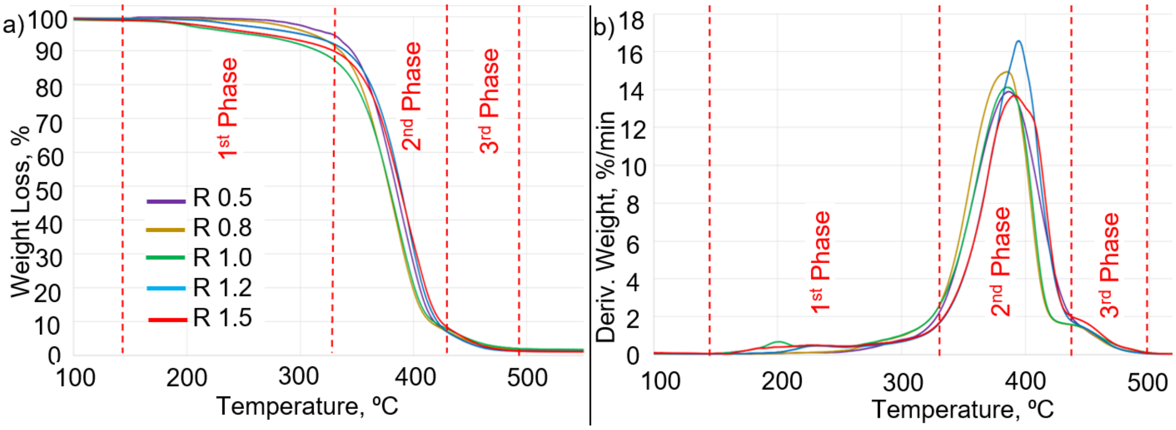

Figure 5: TGA thermograms of the epoxy resins from 100 °C to 550 °C: (a) mass loss curve and (b) derivative mass loss curve.

3.4 Differential Scanning Calorimetry

From Figure 6a, all formulation shows an obvious crystallization exothermic peak during the cooling stage. It is noteworthy that the enthalpy of crystallization, ΔHc, decreased with the increase of CA loadings in the samples. R 0.5 displays the highest crystallinity relative to other samples (Li et al., 2018). From Figure 6b, melting enthalpy of R 0.5 is the highest as compared to other formulations and it is also apparent that the lower the CA loadings, the greater the crystallinity of the epoxy resin, resulting in greater enthalpy of crystallization and melting.
From Table 2, R 0.5 exhibits the lowest T_g (1.41 °C) comparing to other samples. The arise of T_g is granted by the increase of excess CA in the samples. This trend may be caused by the higher crosslinking density of the end products due to the higher chance of CA reacted with the epoxy group in EPO (Sahoo et al., 2018). In this study, EPO-epoxy resins present a significantly lower T_g compared to DGEBA-epoxy resin (44 °C) reported by Sahoo et al., (2018), attributed to the lower crosslinking density and higher flexibility in EPO-epoxy resin. This is because of the presence of steric hindrance of the internal epoxide group and triglyceride aliphatic chain in EPO towards the curing reaction (Pawar et al., 2016).

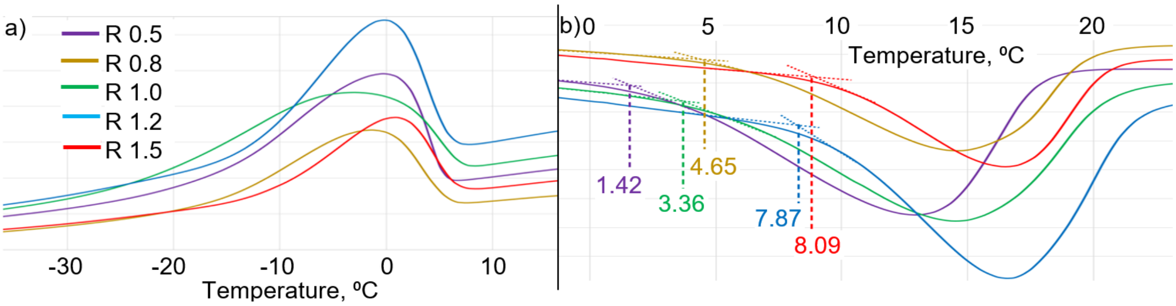

Figure 6: DSC analysis of each formulation on (a) cooling thermograms and (b) 2^{nd} heating thermograms.

Table 2: Summarized DSC analysis of each sample.

Sample Code	T_g (°C)	ΔH_c (J/kg)	T_m (°C)	ΔH_m (J/kg)
R 0.5	1.42	31820	12.80	36240
R 0.8	4.65	25620	14.35	28780
R 1.0	3.36	28490	14.29	34120
R 1.2	7.87	23620	16.24	30980
R 1.5	8.09	19910	16.34	26960

ΔH_c = enthalpy change during crystallization, T_m = peak temperature of melting endothermic peak, ΔH_m = enthalpy change during the melting process.

3.5 Self-healing performance test

As presented in Figure 7, after heated at 140 °C for 1 h, the weld line of R 0.5, R 0.8 and R 1.0 disappeared, indicating a satisfactory intrinsic self-healing performance compared to the other two formulations namely, R 1.2 and R 1.5. The intrinsic self-healing ability was owned by the presence of CAN in the epoxy resin. Overall, R 1.0 displays the best self-healing ability, in line with the report by Capelot et al. (2012) which stated that equal stoichiometry of one acid to one epoxy ring is more beneficial to transesterification reactions. Another interesting point is, EPO-epoxy resin was able to undergo self-healing at a lower temperature as compared to ESO-epoxy resin, which underwent successful self-healing at 160 °C for 1 h (Altuna et al., 2013).

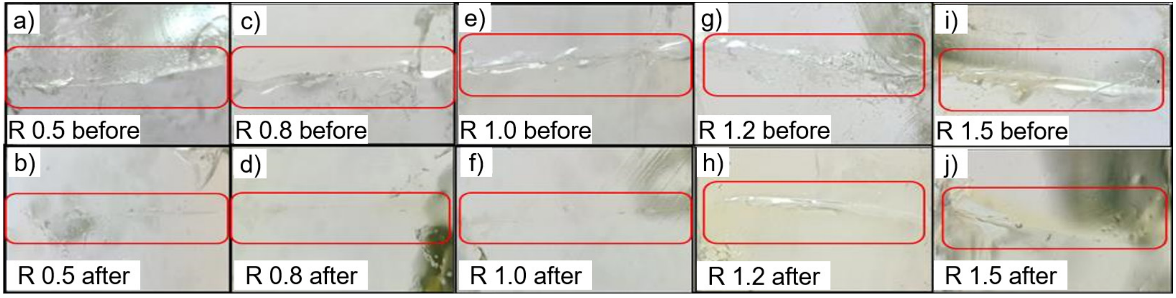

Figure 7: Top view of the epoxy resin before: (a) R 0.5, (c) R 0.8, (e) R 1.0, (g) R 1.2, (i) R 1.5 and, after (b) R 0.5, (d) R 0.8, (f) R 1.0, (h) R 1.2 and (j) R 1.5 the self-healing test.

4. Conclusions

A bio-epoxy thermoset with successful self-healing performance was synthesized via the reaction between EPO and CA. FTIR indicated that the epoxide group in EPO reacted with the carboxylic group in CA to form β-hydroxyester bonds in all formulations. R 0.5 displayed the highest thermal stability and crystallinity. R 1.5 has the highest T_g (8.09 °C), contributed by the higher crosslinking density. R 1.0 displays the best self-healing effect and implies equal stoichiometric ratios have an outstanding advantage in connection with self-healing performance. As T_g and self-healing ability have a greater impact in epoxy resin application, R 1.0 is the epoxy resin with desirable properties. In future work, the bio-based epoxy resin can be enhanced with nano-reinforcement for the sake of better thermal properties and self-healing performance.

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