

MECHANICAL AND THERMAL PROPERTIES OF ACRYLATED EPOXIDIZED PALM OIL AND EPOXY RESIN BLENDS

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Abstract

Epoxy resin is a popular thermoset resin and widely used in many high-performance applications. However, it is derived from petroleum-based products, which are non-renewable resources. In this study, epoxy resins were prepared by blending epoxy resin with acrylated epoxidized palm oil (AEPO) using a direct mixing process. The amount of AEPO was varied at 10, 20 and 30 wt.%. The interaction between AEPO, epoxy resin and hardener were examined by using scanning electron microscopy (SEM), flexural, impact test, dynamic mechanical analysis (DMA) and water absorption analysis. The results indicated that an increase of AEPO content increased the Izod impact strength and water absorption properties of the obtained epoxy resins up to 30 wt.%. However, the flexural strength and modulus as well as glass transition temperature are generally decreased with respect to increasing of AEPO content. This may be attributed due to weak interphase interaction between epoxy and AEPO that generally reduced crosslinking density of the resin. Based on overall mechanical properties, epoxy resin with the addition of 10 wt% is the optimum formulation for epoxy/AEPO resins due to its balanced properties. The resulting epoxy/AEPO resin is expected to find ways into applications such as adhesive, coating or matrices for polymer composites.

Keywords: Acrylated epoxidized palm oil, Epoxy, Mechanical properties, Thermal properties.

1. Introduction

Epoxy resin is one of the most common thermosetting resins, widely used in many industries such as automotive, aircraft, boat, construction, furniture, medical, coatings, adhesives, electronic and consumer products [1-3]. This is because epoxy resins have unique chemical and physical properties such as good mechanical properties, high stiffness, low shrinkage, excellent chemical and heat resistance [2], [4, 5]. Nevertheless, epoxy resins have disadvantages such as high brittleness and low impact strength. Besides, they are manufactured from petrochemical materials that are neither sustainable nor environmentally friendly. Recently, due to the threat of global warming, stringent environmental rules and regulations and declining crude oil reserves have created a groundswell of interest to develop products compatible with the environment from renewable resources. Therefore, attention has been directed to developing bio-based thermoset by direct synthesis or blending resin with natural resources as they are challenging to recycle due to their infusible and insoluble properties [6, 7].

The use of vegetable oils has attracted attention as renewable feedstock for the preparation of polymeric materials, since they have versatility, availability, renewability and biodegradability properties [8, 9]. However, vegetable oils are not reactive and do not interact strongly with polymer resins. For this reason, many researchers addressed the synthesis of functionalized vegetable oils epoxidation, acrylation, maleinization, amidation, glycerolysis reactions and hydroxylation in order to enhance the reactivity site of vegetable oil to facilitate more crosslinked structure [6, 10, 11]. In the literatures, the most common method for functionalizing vegetable oils is through epoxidation reactions [10-12]. Through this method, the carbon-carbon double bonds in fatty acids of vegetable oils are converted through the addition of an oxygen atom to produce an epoxy group, called an oxirane ring, which is more reactive towards free radical polymerization [13].

A few years ago, several researchers reported on the further modified epoxidized vegetable oil order to facilitate more cross-linked structures between the vegetable oil and the polymer matrix, which is through acrylation reactions. The presence of more functional group reactive sites promotes better crosslinking ability and thereby improves the curing times and temperature as well as strengthens the properties of the plant-based polymers [14, 15]. A few types of acrylated epoxidized vegetable oils have been reported as blending components in epoxy resins, i.e., soybeans [16], castor oil [14] and linseed oils [17]. Previous studies have shown that blending of epoxy resins with functionalized vegetable oil could enhance the toughness and overcome the brittleness or low impact strength properties of the epoxy resin [18, 19].

Acrylated epoxidized palm oil (AEPO) is a derivative product of palm oil, which can be obtained from the reaction of acrylic acid with epoxidized palm oil in the presence of a triethylamine (TEA) catalyst. The introduction of more functionalities such as acrylate and hydroxyl groups in AEPO enhance the crosslinking ability between the AEPO and polymer resin.

In this study, palm oil is used to produce vegetable oil-based polymer resins. Palm oil is chosen due to its large availability in Malaysia. Expanding palm oil applications as a blending material in polymer resin is expected to increase profit returns in the agricultural sector while reducing the burden from petroleum-based products. Up to date, no studies have been conducted on the blending of epoxy resin

with acrylated epoxidized palm oil (AEPO) and cured with phenalkamine hardener. Thus, the present study focuses on investigating the effect of AEPO loading on the morphology, flexural, thermo-mechanical, morphological and water absorption properties of resulting epoxy/AEPO resins. The blending of AEPO with epoxy resin may produce new polymer resins with improved toughness properties, indirectly overcoming the major limitation of epoxy resin that have brittleness and low fracture toughness nature.

2. Experimental

2.1. Materials

Epoxidized palm oil (EPO) with an oxirane oxygen content (OOC) of 2.7 - 2.9 % and iodine value of 0.58 g per I₂/100g sample was procured from Budi Oil Sdn. Bhd. Liquid epoxy resin diglycidyl ether of bisphenol-A (DGEBA) epoxy resin with an epoxide equivalent weight of 182-192 gram/equivalent was supplied by Dow Chemical Company. The phenalkamines cardolite NX-2003D, with an active hydrogen equivalent (AHEW) index of 95 g equiv⁻¹, was obtained from Cardolite Corporation and used as hardener. Acrylic acid, diethyl ether, hydroquinone and triethylamine were purchased from Qrec Asia Sdn Bhd.

2.2. Synthesis of Acrylated Epoxidized Palm Oil (AEPO)

The synthesis of AEPO was carried out by following the procedure reported by Habib and Bajpai [20]. Epoxidized palm oil (1200 g) was reacted with acrylic acid (200 g) with the presence of triethylamine as a catalyst and hydroquinone as inhibitor for 14 hours at temperature of 80 °C. After synthesis, the mixture solution was cooled to room temperature and then dissolved in diethyl ether solution to remove unreacted acrylic acid. The mixture was washed multiple times with distilled water until the pH of the solution is equal to 7.0 and finally, the solution was kept in a vacuum oven for 4h with temperature set at 70 °C to remove excess solvent. The success of the acrylation reaction of epoxidized palm oil was confirmed by Fourier transform infrared spectroscopy (FTIR) testing.

2.3. Preparation of the Epoxy/AEPO resins

The sample was prepared by mixing epoxy resin directly with acrylated epoxidized palm oil (AEPO). The amount of AEPO was varied at 10, 20 and 30 wt.% [18]. The mixed solution was stirred using a mechanical stirrer on a hot plate at 55 °C for 1 hour. After that, phenalkamine hardener was added to the mixed solution and stirred continuously for another 5 minutes. The phenalkamine curing agent amount was based on the stoichiometric ratio. Finally, the samples were poured into an aluminum mould and cured at 25 °C for 3 h and post cured at 80 °C for 6h [21].

2.4. Testing and characterization

The surface morphology of resulting resins was determined by a Philip XL 40 Scanning Electron Microscopy (SEM) with acceleration voltage of 20 kV. The functional groups and structural characteristics of the epoxy/AEPO resins were studied using a Perkin Elmer spectrometer using KBr disks for 16 scans over wave number range of 4000-600 cm⁻¹. The flexural properties of epoxy/AEPO resins

were evaluated according to ASTM D790. The outer span and test speed were set at 80 mm and 7 mm/min, respectively. Five specimens were tested for each formulation. The notched Izod impact test was performed using Toyoseiki Izod Impact Tester according to ASTM D256. The dynamic mechanical analysis (DMA) test was conducted by using three bending point test with temperatures ranging from 30 to 200 °C with a heating rate of 5 °C/min, and with the frequency held at 1 Hz. The average crosslink density of the resulting resins can be calculated from rubbery modulus using the following Eq. (1) [22]:

$$\nu C = \frac{E'}{3RT} \quad (1)$$

where νC is the crosslink density of epoxy/AEPO network, E' is the storage modulus of the thermoset in the rubbery plateau region at $T_g + 30^\circ\text{C}$, R is the gas constant and T is the absolute temperature.

The water absorption test was conducted according to ASTM D570-81. The samples were immersed in distilled water at room temperature. The water uptake of the resulting resins was calculated using Eq. (2):

$$\text{Water absorption (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (2)$$

where W_w is the weight of the wet sample after immersion and W_d is the initial weight of the dry sample.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)

Figure 1 displays the SEM micrograph of the fracture surfaces of the virgin epoxy and epoxy/acrylated epoxidized palm oil (AEPO) resins at 10, 20 and 30 wt.%. As shown in Fig. 1 (a), the fracture surface of virgin epoxy resin was smooth and flat, showing some uniform cracks. This suggested that the epoxy resin had a brittle behaviour attributed to poor toughness, which implied that the crack propagated with minimal hindrance [23]. In contrast, the micrograph of epoxy resin with incorporation of AEPO in Fig. 1 (b), (c) and (d) displayed rougher fracture surface with the existence of uneven corrugation. This condition suggests that the stiffness properties of epoxy matrix reduced with the addition of AEPO due to the incorporation of a long flexible fatty acid chain of AEPO, which enhanced flexibility and decreased the rigidity of the resulting resins. Furthermore, the rougher surface of epoxy/AEPO resin indicated the improvement in fracture energy as more strength was needed to break the sample [24]. A similar trend was observed in several studies when vegetable oil was added to petrochemical based resin [23-25].

Figures 1(b), (c) and (d) show SEM images for epoxy/AEPO resins with 10 wt%, 20 wt.% and 30 wt.% of AEPO. The images proved that with increasing AEPO contents in epoxy resin, the rougher surfaces can be observed on the samples' fractured surfaces. This suggested the heterogeneous blending of vegetable oil and polymer resin due to different solubility of both materials [26].

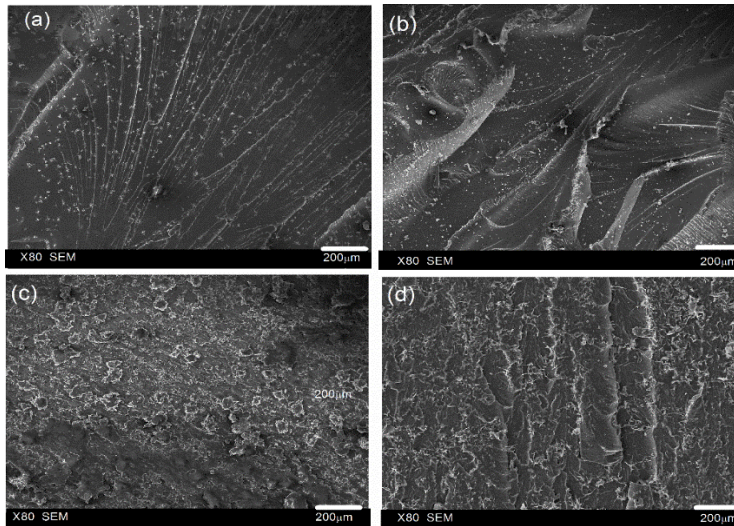


Fig. 1. SEM micrographs of flexural fracture surfaces at x80 magnification of a) Epoxy, b) Epoxy/AEPO 90/10, c) Epoxy/AEPO 80/20 and d) Epoxy/AEPO 70/30.

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis was used to examine the chemical interaction of the epoxy/acrylated epoxidized palm oil (AEPO) resins by identifying the presence of functional groups. Figure 2 shows the FTIR spectra of epoxy, uncured and cured epoxy/AEPO resins. The spectrum of AEPO showed broad -OH stretching vibrations at 3474 cm^{-1} . The strong C=O stretching vibration was visible at 1736 cm^{-1} . The peak at 1637 cm^{-1} was corresponding to the $\text{H}_2\text{C}=\text{CH}$ groups stretching vibration in acrylic acid. These results are similar to previous studies on acrylated epoxidation of vegetable oil reported by Fakhari et al. [27], Habib and Bajpai [20] and Wong et al. [28]. For uncured epoxy/AEPO resin spectrum, several important epoxy resin peaks were observed at $2853 - 2925$, 1036 and 915 cm^{-1} . The peak at $2853 - 2925\text{ cm}^{-1}$ indicated the CH stretching of CH_2 , CH aromatic, and aliphatic. The peak at 1036 cm^{-1} was assigned to the stretching of C-O-C ethers. The peak at 915 cm^{-1} was mainly associated with the stretching of C-O and C-O-C oxirane groups. These findings are consistent with the study reported by Nikolic et al. [29], Cholake et al. [30] and Balabanovich et al. [31]. Additionally, the functional groups of phenalkamine curing agent were observed at peaks $3304 - 3360\text{ cm}^{-1}$ and $1582 - 1605\text{ cm}^{-1}$ indicating existence of primary and secondary amine N-H stretching vibrations and C=C aromatic ring, respectively.

From FTIR spectra of cured epoxy/AEPO resin, the decrease of peak intensity at 1605 cm^{-1} indicated the consumption of C=C for $\text{HC}=\text{CH}_2$ AEPO acrylic groups from reactions with the phenalkamine curing agent. A broader absorption band at 3383 cm^{-1} for the cured epoxy/AEPO resin also proved the opening of epoxide ring and the formation of OH groups via acrylic reaction. Subsequently, the absorption band at 915 cm^{-1} disappeared in the FTIR spectra of the cured epoxy/AEPO resin, which further confirms the epoxy group of epoxy resin were fully ring-opened in the curing reaction. The decrease in peak intensity corresponding to the C=O ester of the AEPO peak at 1736 cm^{-1} and the gradual increase in intensity of the two

absorption bands at 1582 - 1605 cm^{-1} indicated the absorption of carbonyl by the amide group and NH by the secondary amide group, respectively. Figure 3 illustrates the mechanism of acrylation reaction of epoxidized palm oil (EPO). The esterification reaction of acrylic acid and EPO occurred in the presence of triethylamine (TEA) as a catalyst. During the acrylation reaction, the oxirane rings of AEPO were opened and the acrylate groups were grafted onto the AEPO triglyceride molecules.

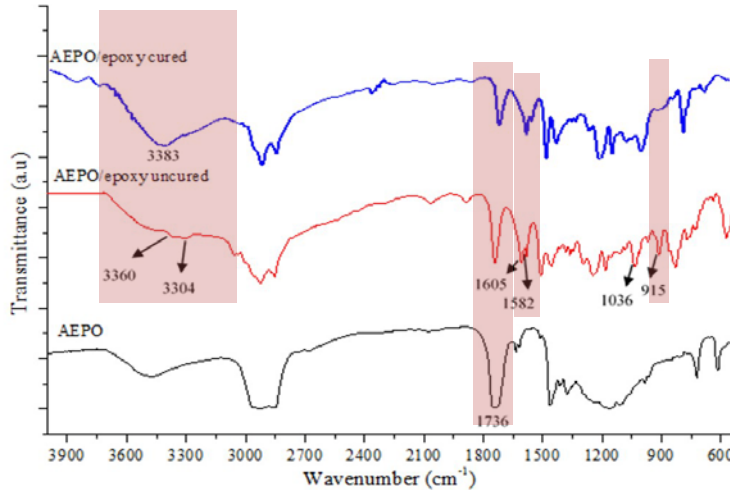


Fig. 2. FTIR spectrum of epoxy, AEPO, and epoxy/AEPO resins.

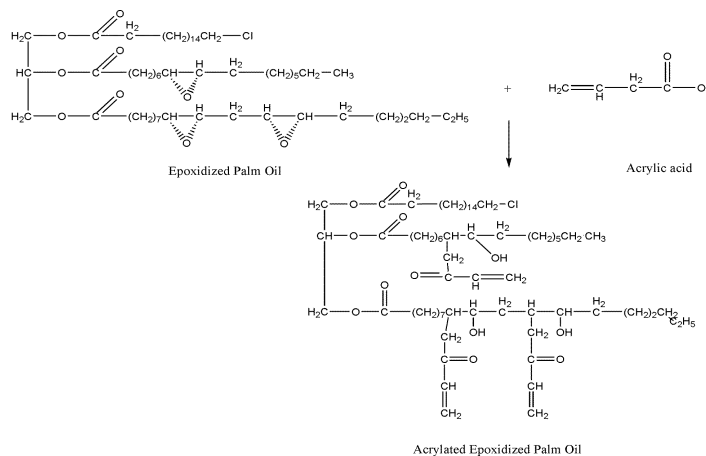


Fig. 3. The mechanism for the acrylated epoxidized triglyceride molecule.

3.3. Flexural properties of epoxy/AEPO resins

The flexural strength of epoxy/epoxidized palm oil (AEPO) resin with various amount of AEPO are displayed in Table 1. A schematic representation of proposed network of cured epoxy/AEPO resin is shown in Figs. 4 and 5. From Fig. 4, it indicated an interaction that might take place between the amine group of phenalkamine hardener and the acrylated segments of the acrylic acid in step 1.

Subsequently, as the secondary amine is produced, they reacted with the epoxide group of epoxy resin that as illustrated in step 2 (Fig. 4). The complete mechanism interaction between epoxy, AEPO and phenalkamine hardener might occur through interaction between the hydroxyl group of epoxy/phenalkamine hardener with the oxirane group of AEPO as shown in Fig. 5. The flexural strength of all epoxy/AEPO resin was lower than that of the virgin epoxy resin. Flexural strength values decreased from 74.53 MPa for virgin epoxy resin to 47.52 MPa for epoxy resin with incorporation of 10 wt. % of AEPO. As shown in Table 1, the flexural strength of epoxy resins was reduced further with higher AEPO loading (20 and 30 wt.%). This can be explained due to the presence of unreacted saturated component in the structure of AEPO which lowered the reactivity of AEPO with epoxy resin and thereby reduced the crosslinked density of epoxy/AEPO resins [32]. The weak compatibility and interaction between epoxy and AEPO have caused a decrease in flexural strength of epoxy/AEPO resin due to the formation of nonuniform crosslinked structures. On the other hand, the presence of unreacted AEPO in the structure of cured epoxy/AEPO resins also results in a decrease in flexural strength. This is due to the possibility of self-polymerization of AEPO monomer which results in the formation of phase structure [33]. This observation was similar to the previous studies which indicated a reduction in mechanical strength as vegetable oil content increased [16, 34, 35].

A similar trend was observed in flexural modulus properties in which the flexural modulus decreased by 22.9 %, 32.5 % and 54.5 % with the addition of 10, 20, and 30 wt. % of AEPO, respectively, as stated in Table 1. This can be attributed to the plasticizing effect of AEPO, which significantly reduces the crosslink density of the epoxy system [36, 37]. The unreactive saturated component such as fatty acid pendant chains and long aliphatic fatty acid chains in AEPO structure also lowered the crosslink density, imparted matrix flexibility and reduced the flexural modulus of epoxy/AEPO resins [38, 39].

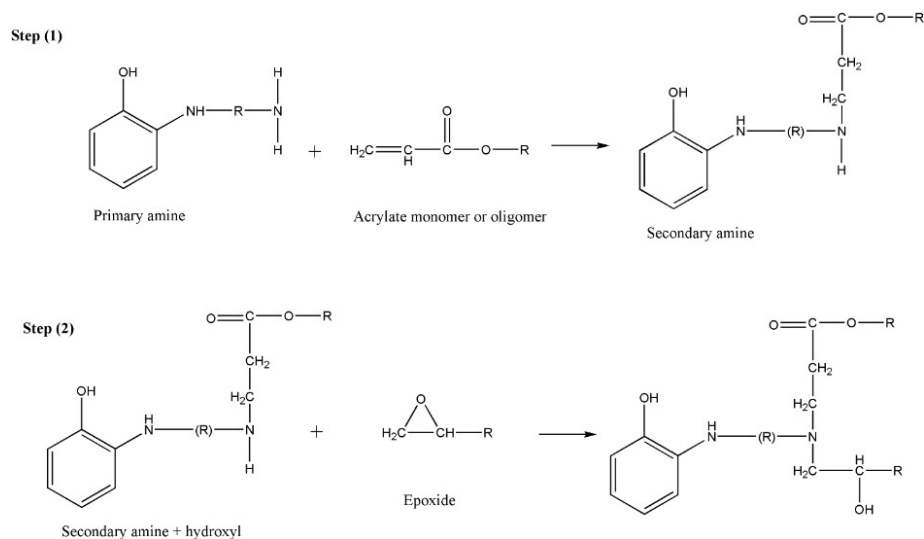


Fig. 4. The crosslinking reaction mechanism for epoxy resin with phenalkamine hardener.

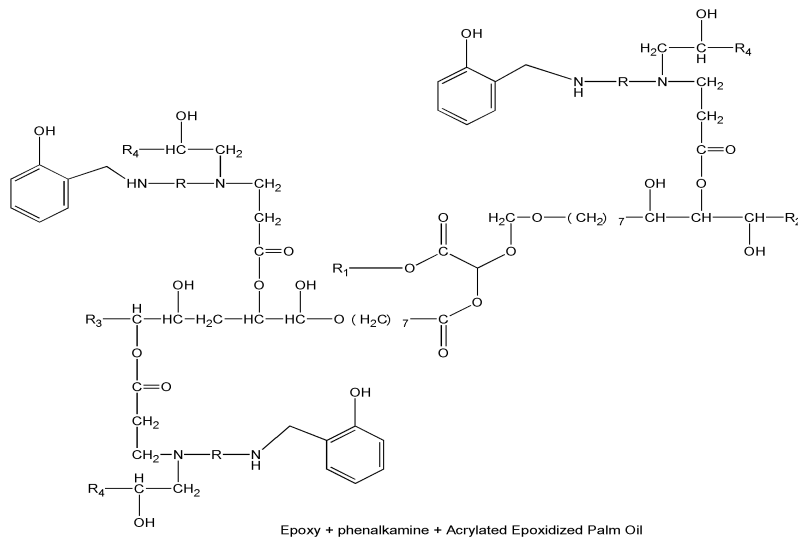


Fig. 5. The proposed complete reaction mechanism for epoxy/AEPO resin.

Table 1. Flexural properties of epoxy/AEPO resins.

Samples	Flexural strength (MPa)	Flexural modulus (GPa)
Epoxy	74.53	2.3
Epoxy/AEPO 90/10	47.52	1.6
Epoxy/AEPO 80/20	32.36	1.1
Epoxy/AEPO 70/30	24.68	0.79

3.4. Izod Impact strength of epoxy/AEPO resins

The Izod impact strength of epoxy systems with various amounts of acrylated epoxidized palm oil (AEPO) is displayed in Fig. 6. It was observed that the increase in AEPO content caused an increase in the Izod impact strength properties of epoxy/AEPO resins. For example, inclusion of 10 wt.% AEPO was observed to lead to an enhancement in Izod impact strength up to 16.3 % (37.1 J/m) as compared to the virgin epoxy resin (31.9 J/m). A similar trend was also observed for resins with greater amount of AEPO contents (20 wt.% and 30 wt.%). The improvement in Izod impact strength was found to be proportional to the AEPO content. At 30 wt.% of AEPO loading, the increment in Izod impact strength of AEPO/epoxy resins were up to 57.8 % (50.3 J/m). The incorporation of AEPO, which consist of long flexible fatty acid chains, increased the mobility of the resins that contribute to an improvement in the crack propagation resistance and increased energy requirements to break epoxy/AEPO resin samples. Therefore, the Izod impact strength of epoxy/AEPO resins was higher than that of virgin epoxy resin.

3.5. Dynamic mechanical analysis (DMA)

The viscoelastic behaviour of epoxy/acrylated epoxidized palm oil (AEPO) resins were studied by DMA. The storage modulus (E'), glass transition temperature (T_g) and crosslinking density of epoxy, epoxy/AEPO resins are summarized in Table 2. From Fig. 7, it can be seen that the storage modulus of epoxy/AEPO resins decreased with increasing AEPO content up to 30 wt%. The maximum loss in

modulus value for all samples was observed to occur at the glass transition region (T_g) between 65 to 85 °C. This might be caused by the decrease in crosslinking density as the free volume and mobility of molecular chain of epoxy resin increased with the introduction of AEPO. This result was expected as vegetable oils are intrinsically low modulus materials [32]. Thus, the addition of AEPO into epoxy resin reduced the stiffness of resulting epoxy/AEPO resins.

The parameters such as T_g , maximum $\tan \delta$ and crosslinking density of epoxy/AEPO resins are shown in Table 2. From the data, it is shown that the incorporation of AEPO shifted the peak position of the loss factor curves to lower temperature and decreased the glass transition temperature (T_g) of the epoxy/ resins. The T_g of all samples were dropped as the AEPO contents increased (20 and 30 wt %). This result suggested that the inclusion of larger number of dangling chains in the AEPO network into epoxy resin produced flexible structure and thereby reduced the crosslinked structure of epoxy resin [7, 40].

The crosslink density of epoxy/AEPO resins is calculated based on Eq. (1) [22] and stated in Table 2. In this study, the crosslink density was found to decrease with increasing AEPO content. These findings are again consistent with the decrement in flexural strength properties as discussed earlier.

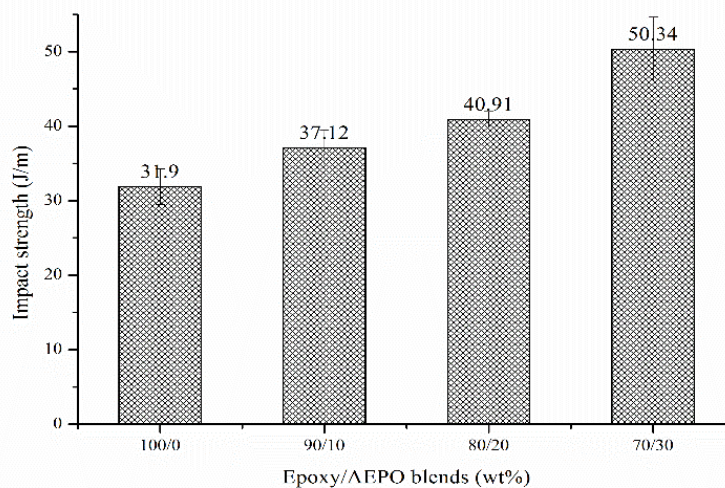


Fig. 6. Izod impact strength of epoxy/AEPO resins.

Table 2. T_g , maximum $\tan \delta$, and crosslinking density results of epoxy/AEPO resins.

Formulation (epoxy/AEPO)	T_g (°C)	$\tan \delta_{max}$	Crosslinking density ($\times 10^5 \text{ mol/m}^3$)
Epoxy	85.5	0.72	0.21
Epoxy/AEPO 90/10	74.2	0.65	0.13
Epoxy/AEPO 80/20	70.1	0.65	0.12
Epoxy/AEPO 70/30	65.6	0.59	0.09

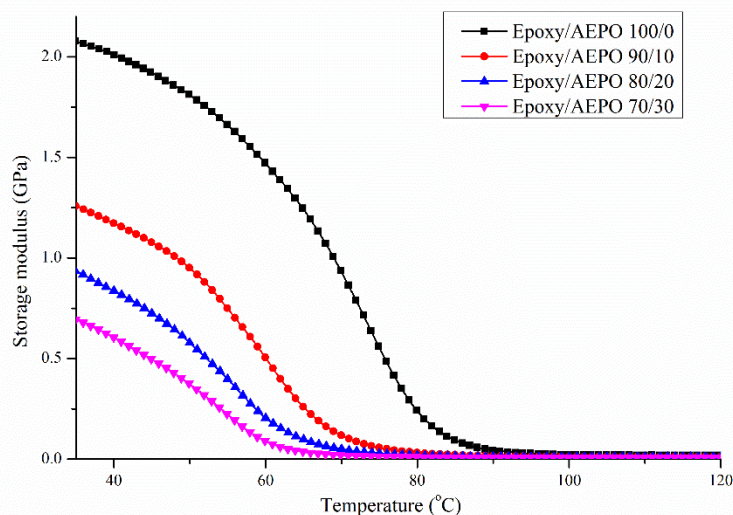


Fig. 7. Temperature dependence of the storage modulus of epoxy/AEPO resins.

3.6. Water absorption

Figure 8 shows the plot of water absorption of epoxy and epoxy/acrylated epoxidized palm oil (AEPO) resins. From the graph, it can be observed that all samples exhibited fastest water absorption for the first 400 h and then began to slow in absorption with increasing time of immersion. The water absorption of virgin epoxy resin was 0.58 % at the maximum hours of immersion (2808 h). This phenomenon can be explained by considering the presence of micro-voids or gaps that caused capability of water molecules to penetrate through the epoxy network [41]. In addition, the epoxy matrices consist of hydrophilic functional group such as hydroxyl in epoxy resin which will form hydrogen bonds with water molecules [42].

As the amount of AEPO increases, the water absorption of resin increases for all samples. The epoxy/AEPO resin at 30 wt.% AEPO loading depicted highest water absorption up to 1.33 % compared to that of 10 wt.% AEPO loading composites (0.97 %). This could be due to the presence of hydroxyl groups in the AEPO backbone chain which causes a hydrophilic behaviour of AEPO. These hydroxyl groups are able to bond hydrogen with water molecules [43]. Therefore, as AEPO content increased, the water uptake also would increase. These results are consistent with the findings of the reduction of flexural strength of epoxy/AEPO resins as discussed previously. In addition, the reduction in the number of crosslink density in the cured epoxy/AEPO resin based on dynamic mechanical analysis (DMA) results would also be the reason for the increased water absorption of epoxy/AEPO resin. This is because the low crosslink density would increase the ability of water molecules to penetrate into the free volume of resin network structure [44]. Therefore, the water absorption of epoxy/AEPO resin increased with reduction in crosslinking density. After immersion hour of 1500, it can be observed that the water absorption penetration rate decreased gradually with increasing time of immersion for all samples. This condition could be due to the water saturation that penetrates into the micro void of the epoxy/AEPO resins.

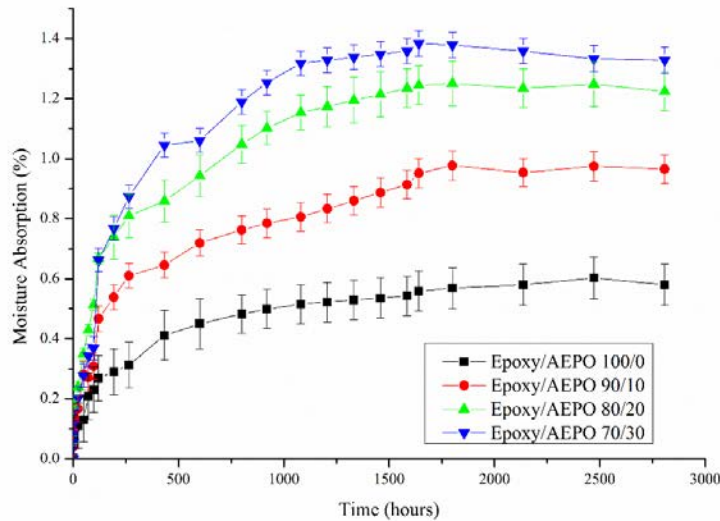


Fig. 8. Water absorption of epoxy and epoxy/AEPO resins.

4. Conclusion

This work shows that thermoset resins from epoxy and acrylated epoxidized palm oil (AEPO) cured with phenalkamine hardener have been successfully prepared. The results revealed the partial replacement of epoxy resin with AEPO produced resins with acceptable properties. The findings showed epoxy resin with the presence of AEPO showed remarkable improvement in Izod impact strength indicating a toughening effect. The scanning electron microscopy (SEM) images proved rougher fractured surface of the epoxy / AEPO resins, proving the plasticizing effect of the resins. Nevertheless, due to the presence of unreactive saturated components such as fatty acid pendant chains in the epoxy network system, which decreased the crosslinking density of the epoxy/AEPO resins, the flexural strength and modulus as well as the glass transition temperature (T_g) of epoxy / AEPO resins were reduced with the introduction of AEPO. Based on overall mechanical properties (stiffness, strength and toughness), epoxy resin with addition of 10 wt% AEPO loading was determined as the optimum formulation. Nevertheless, to enhance the mechanical properties of the epoxy/AEPO resin, the use of filler can be explored in future studies.

Nomenclatures

E' Storage modulus
 T_g Glass transition temperature

Greek Symbols

δ delta

Abbreviations

AEPO Acrylated Epoxidized Palm Oil
 AHEW Active Hydrogen Equivalent

ASTM	American Society for Testing and Materials
DMA	Dynamic Mechanical Analysis
EPO	Epoxidized Palm Oil
FTIR	Fourier Transform Infrared Spectroscopy
OOO	Oxirane Oxygen Content
SEM	Scanning Electron Microscopy

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