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Characterisation and mechanical properties of unsaturated polyester/acrylated epoxidised palm oil polymer blend at different acrylated epoxidised palm oil processing method

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Abstract. Acrylated epoxidized palm oil (AEPO) prepared by the reaction of epoxidized palm oil (EPO) with acrylic acid, triethylamine initiator and hydroquinone inhibitor prepared at various temperature and reaction times. The unsaturated polyester (UPE) resin was blended thoroughly with 10 wt% of the modified palm oil at room temperature, and thermally cured at 100 °C and post-cured at 160°C. The prepared palm oil derivative was characterised by using Fourier Transform Infrared (FTIR) and the test proved the formation of acrylate functional group with characteristic absorbance at 1600-1600 cm⁻¹ that indicates C=C functional group of the acrylate. The polymer blend tensile strength of the palm oil acrylate processed at 110°C for 16 hours (M2) showed reduction from 25.56 MP to 13.26 MP (48%), reduction in tensile modulus from 1.47 GPa to 1.18 GPa (19.7%) and the highest impact strength among the four acrylates of polymer blend is 21.97 J/m from palm oil acrylate processed at 105°C for 16 hours (M3). However, polymer blend from M2 acrylate showed increased in elongation at break from 2.805 % to 3.493 % (24.5 %) compared to neat unsaturated polyester and it outweighed reduction in tensile and impact of the polymer blend.

1. Introduction

Polyester is the most versatile synthetic copolymer known nowadays [1]. Polyesters are widely used in industry as plasticizers, laminates, industrial constructions, insulations, molding compounds, tanks, boat building, truck roof and other field [2,3]. The vast applications of polyester are due to the low cost, ease excess and ease combination of polyester with reinforcement materials [2,4]. Among well known polyester is unsaturated polyester resin (UPE). The unsaturated (C=C) functional groups in the polyester chain acting as cross-linking site which can be chemically interacted with other reinforcement additive or crosslinking agent.

Petroleum derived from unsaturated polyester resin has been an interest in industry since last four decades due to its low cost, ease of handling and have good mechanical and thermal properties [5]. The continuous reliance on unsaturated polyester resin (UPE) rises the awareness on continuation of depleting petroleum reserved [4]. Synthetic unsaturated polyester resin (UPE) which synthesized from petroleum source is known with its excellent performance in many applications. One way to overcome the issue on petroleum resources without sacrificing polymer properties is by blending the synthetic polymer with plant oil [4]. Plant oils have become a significant material for both academic and industrial practitioners in intensive research as replacement to synthetic polymers in polymeric



materials. The rise of awareness in benefiting vegetable oil is due to its availability, inherent biodegradability and low price [6, 7]. Among research in vegetable oil / thermoset, blending includes epoxy with waste vegetable oil [8], UPE blends with epoxidized methyl linseedate [9], vinyl ester blends with acrylated epoxidized palm oil [10] and unsaturated polyester resin (UPE) blends with epoxidized palm oil [11]. One third of vegetable oil is covered by palm oil [12]. Malaysia is the second largest palm oil producer in the world as has covered 39% of world palm oil production and 44% of world exports [13]. Palm oil is categorized as non-drying oil due to lower unsaturation level in its fatty acid chain. It restricted the use of palm oil as main constituent in synthesizing polymer resin.

In order to produce new unsaturated polyester resin (UPE) resin using palm oil blend, the palm oil fatty acid chain needs to be modified to allow the chemical interaction within the synthetic unsaturated polyester resin. Acrylated epoxidized palm oil, styrene monomer and unsaturated polyester resin (UPE) share the same property with the presence of C=C functional group. The functional group is essential in cross-link the individual entities in the polymer to become one large continuous polymer chain. A continuous polymer chain allows propagation of energy along chain, thus expected to improve the mechanical and thermal properties of the blend polymer. Therefore, a specific method to synthesis acrylated epoxidized palm oil (AEPO) needed to be investigated so that maximum acrylate functional groups will be introduced in the palm oil. The additional rate of acrylic acid and reaction temperature must be controlled during preparation of epoxy acrylate adducts [15]. A study has been conducted on acrylation of epoxidized soy bean oil (AESO) at 110°C and was found that the lowest acid value in the prepared AESO was observed after 36 hours reaction [15]. Fakhari et al. studied on mechanical properties of unsaturated polyester resin/acrylated epoxidized palm oil (UPE/AEPO) blend and conducted acrylation of epoxidized palm oil at 80°C at 16 hours reaction [16]. Later, Salih et al. [17] conducted acrylation of epoxidized palm oil at 110°C at 16 hours reaction and characterized the UV cured acrylated epoxidized palm oil (AEPO) using FTIR and NMR analysis. Current limitation of the studies is continuation to the investigations on the effect of different acrylated epoxidized palm oil (AEPO) processing conditions on properties of acrylated epoxidized palm oil (AEPO) can be done to find the best synthesis methods to get the best and balance of unsaturated polyester resin/ acrylated epoxidized palm oil (UPE/AEPO) blending in term of mechanical and thermal behavior.

This study aimed at developing and characterising bio-based polymer blend of unsaturated polyester resin with acrylated epoxidized palm oil. Acrylated epoxidized palm oil (AEPO) processing method was studied by varying the temperature, processing period and washing methods in order to determine optimum temperature and processing period for ideal use of energy in producing environment friendly polymer without sacrificing the mechanical properties of the material. This works is aimed to demonstrate that this synergistic balance can be achieved. Different process of producing acrylated epoxidized palm oil (AEPO) were conducted and being characterized using FTIR test. The synthesized acrylated epoxidized palm oil (AEPO) was blended in unsaturated polyester resin (UPE) at constant amount, 10 wt% and cured in an oven. The mechanical properties of the polymer were then conducted through standard test. The results provide a benchmark to identify the best processing condition of acrylated epoxidized palm oil (AEPO) in terms of temperature, reaction period and washing techniques to the novel, efficient and multifunctional unsaturated polyester resin/ acrylated epoxidized palm oil (UPE/AEPO) blend can be designed.

2. Materials and method

2.1. Materials

The unsaturated polyester resin (UPE) graded as Reversol P-9539 used as received from Impian Zente Sdn. Bhd. Epoxidised palm oil 031 (EPO 031) received from Budi Oil Sdn. Bhd. Acrylic acid, purchased from Merck, Germany. Triethylamine, supplied by Aldrich, UK. Hydroquinone, purchased

from Nacalai Tesque, Japan. Benzoyl peroxide, purchased from Merck, Germany. Diethyl ether, received from R&M Chemicals.

2.2. Preparation of acrylated epoxidized palm oil (AEPO)

Epoxidised palm oil (EPO) was measured and placed in a beaker with a magnetic stirrer. About 1% of triethyl amine and hydroquinone was then added to the beaker and was stirred for 1 hour with a speed of 350 rpm at 40°C. Under continuous stirring, acrylic acid with 1:9 ratio to EPO was added to the beaker dropwise and the temperature of the solution was gradually raised. The slow addition of acrylic acid is to control the reaction progress and to avoid homo-polymerization of the acrylic acid [15]. The mixture was stirred at different period depending on the batches. The resulting AEPO then was washed with diethyl ether, distilled water or by both solvents. The washed AEPO then was dried using rotary evaporator at 95°C until a constant weight of the flask was recorded.

Four batches of AEPO was prepared with each batch had different condition in processing the method. The first batch, M1 AEPO was synthesized at 80°C with 350 rpm stirring for 16 hours before it was washed with diethyl ether and distilled water. The second batch, M2 AEPO was synthesised at 110°C with 350 rpm stirring for 16 hours and washed with distilled water. The third batch, M3 AEPO was synthesised at 105°C with 350 rpm stirring for 16 hours and washed with diethyl ether and distilled water. The fourth batch, M4 AEPO was synthesised at 110°C with 350 rpm stirring for 36 hours and washed with distilled water.

2.3. Preparation of the UPE/AEPO blend

Total volume of 363 ml resin was measured. The initiator, benzoyl peroxide was measured by 1.5 phr and was added to the resin. The mixture was then manually stirred for 20 minutes. For the polymer blend, 10 wt% of the resin was replaced by the prepared AEPO. Four different AEPO were used which is M1 AEPO, M2 AEPO, M3 AEPO and M4 AEPO with densities of 0.98 g/ml, 0.802 g/ml, 1.028 g/ml and 0.836 g/ml, respectively. The AEPO then was blend with UPE and were manually stirred for 20 minutes. The polymer blend was further stirred for 20 minutes after added with benzoyl peroxide. The polymer blend was then poured in aluminium mould and cured at 100°C for 2 hours and post cured at 160°C for another 2 hours.

2.4. FTIR analysis

Fourier Transform Infra-red (FTIR) spectroscopy was used to determine the functional groups in EPO and AEPO and was investigated by FTIR Spectroscopy (Perkin Elmer Spectrum 100) using attenuated total refraction (ATR). The FTIR spectra were recorded in the wavenumber range 700 to 4000 cm⁻¹ with 50 – 100 % recorded transmission.

2.5. Tensile test

The tensile strength, E-modulus, elongation at break and tensile toughness was tested using Universal Testing Machine (UTM) following the procedure of ASTM D-638. The machine (INSTRON 3367 Universal Testing) fitted with 5kN load cell operated at a cross-head speed of 1mm/min. The dimension of the dumbbell shape sample was 115 mm (length) x 25 mm (width) x 5 mm (thick) with a narrow section of 33 mm length and 6 mm width.

2.6. Impact test

The impact test was conducted according to ASTM256 at ambient temperature. The test was conducted using Impact pendulum tester (Zwick). The samples were prepared with dimension of 63.5 mm (length) x 12.7 mm (width) x 4 mm (thick) and notch depth at 0.75 mm. The sample was stand as a vertical cantilever beam and a single swing of 1kN pendulum impacted on the notch face.

3. Results and discussions

3.1. FTIR analysis

The FTIR spectroscopy of the four synthesized AEPO and neat EPO from wavenumber 2000 cm^{-1} to 700 cm^{-1} are shown as in figure 1 and table 1. A smaller range of spectrum wavenumber was highlighted because of the expected presence of spectrums representing functional groups in AEPO at the range of wavenumber. The characteristic of C-O-C (oxirane) functional group stretching was observed at the wavenumber between 840 cm^{-1} – 820 cm^{-1} . Meanwhile the presence of saturated fatty acid backbone was determined from C-H stretching band at C-H in-plane deformation band at 1377 cm^{-1} .

The FTIR spectrums clearly describe the functional groups in chemical structure of AEPO through new IR absorption band in the four AEPO spectrums. During acrylation process, ring opening of epoxy by nucleophile of acrylate will form hydroxyl (-OH) functional group. The fingerprint region for primary alcohol (-OH) is the two bands with strong intensity at range 1075 cm^{-1} to 1000 cm^{-1} and at range 1350 cm^{-1} to 1260 cm^{-1} . Referring to the FTIR spectrums, the M1, M2, M3 and M4 show a stretching at wavenumber 1294 cm^{-1} with 90%, 90%, 83% and 87% transmission (10%, 10%, 17% and 23% absorbance) respectively and strong stretching at 1030 cm^{-1} for M1 only. The spectrums indicate the ring opening of epoxy forming -OH group. The ring opening of epoxy allows introduction of acrylate in the opened epoxy bond. Acrylate functional group can be characterised from C=C stretching at range 1680 cm^{-1} to 1580 cm^{-1} . The presence of alkene functional group in M1, M2, M3 and M4 were supported by C=C stretching vibrations at 1618 cm^{-1} and 1635 cm^{-1} . All the four AEPOs show 95-96% transmission at C=C stretching vibrations. In addition, the four AEPOs show the out of plane C-H deformation through two bands at wavenumber between 980 cm^{-1} – 960 cm^{-1} . It is a useful identification of asymmetrically substituted double bond. M1 and M2 show 90% transmission (10% absorbance), M3 shows 84% transmission (26% absorbance) and M4 shows 91-92% transmission (8-9% absorbance). The high absorbance in M3 indicate the stronger vibration of the C-H deformation due to higher intensity of the out of plane C-H in the AEPO structure formed. The characteristic of acrylate functional group was also observed in the four AEPOs spectrum at wavenumber 1400 cm^{-1} -1420 cm^{-1} , showing -RCOO⁻ functional group with the strongest vibration observed in M2 AEPO spectrum. This characteristic indicates higher -RCOO⁻ proportions in M2 which is not removed after washing because the ion trapped in between UPE/AEPO structure. From the AEPO data, it can be concluded that all the four AEPO produced from four different methods had the stated major functional groups in AEPO. However, the recommended processing conditions will be M2 and M3 with temperature at range 105 to 110°C and processing time of 16 hours respectively due to higher absorption and stronger vibrations of the functional groups show in M2 and M3. Table 1 below simplified the major functional groups in EPO and AEPO.

Table 1: Assignment of FTIR spectrum of EPO and AEPO functional groups.

	Functional group	Wavenumber (cm^{-1})	
		EPO	AEPO
A	C-O-C	826	810 – 840
B	C-H (in C=C)	-	980-960
C	-CH-	1377	1377
D	C=C (trans)	-	1618
E	C=C (trans)	-	1635
F	-OH	-	1294 and 1030
G	-RCOO ⁻	-	1400-1420

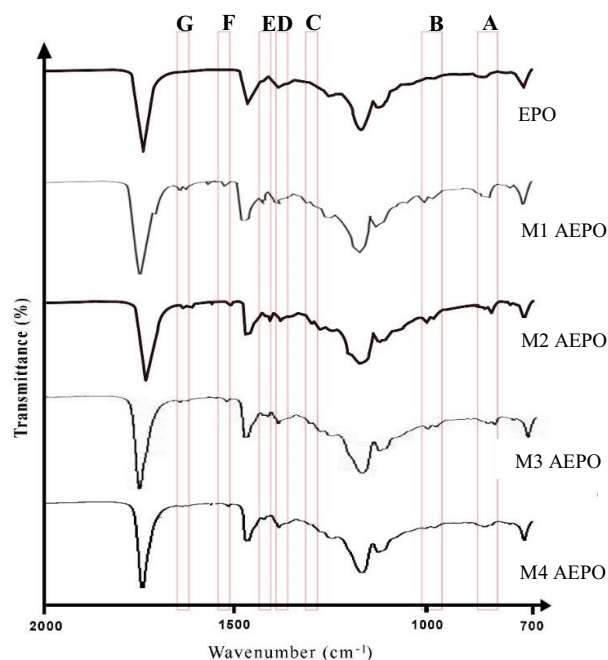


Figure 1: FTIR spectrum of neat UPE, M1 AEPO, M2 AEPO, M3 AEPO and M4 AEPO.

3.2. Mechanical properties

The change in tensile, Young's modulus, strain at break and impact for neat UPE UPE/AEPO blend were varied at M1, M2, M3 and M4 methods (figure 2). From the graph, it is apparent that the addition of 10 wt% AEPO in UPE reduced the tensile strength and tensile modulus of the UPE. The tensile strength of UPE in M2 was reduced from 25.56 MPa to 13.26 MPa (48 %). It is the highest reduction of UPE tensile property. This effect is attributed to the higher molecular weight of M2, no strength and low stiffness effect of AEPO. Therefore, it is expected that higher proportion of AEPO obtained through M2.

Meanwhile the blending of M2 shows the smallest reduction in tensile modulus property, from 1.47 GPa to 1.18 GPa (19.7%). Acrylation reaction is an exothermic reaction [15]. Thus, increase in temperature will favour the formation of acrylates. Therefore, from this experiment, synthesis of AEPO by M4 and M2 (110°C) has introduced more acrylate functional groups at epoxy functional groups in EPO compared to reaction at 80°C (M1) and 105°C (M3). The replacement of UPE by bio-resins reduced fragility of the components, due to the long chain of fatty acid chain [18]. Besides, the lower crosslinking between synthetic polymer and bio-resins also contributed to the observed result [19]. Therefore, in this study, it can be concluded that the lower crosslinking between synthetic polymer and bio-resins also contributed to the observed result [20]. However, the decrease in tensile modulus of M2 is the lowest among the other AEPOs. This suggest to the balance of C=C in M2 to crosslinking with UPE and the crosslink of UPE with styrene compare to the other methods. A similar result was achieved in a work of UPE/AEPO blend and UPE/AESO blend [16, 21].

The elongation at break of neat UPE and UPE blends were as shown in figure 3. From the graph, there was an increase in elongation at break of UPE/M2 AEPO and UPE/M3 AEPO compared to neat UPE. Method 2 showed the highest increment of elongation at break from 2.805 % to 3.493 % (24.5 %). The result suggested that blending of UPE with AEPO had sacrifice the tensile strength but had increased ductility of the UPE. The increased in elongation at break property was due to partly successful cross-linking between stiff UPE and ductile AEPO. This cause the polymer chain to become flexible when elongated. The M2 and M3 processing method with temperature 105°C and 110°C and process time of 16 hours had produced AEPO that readily form flexible UPE.

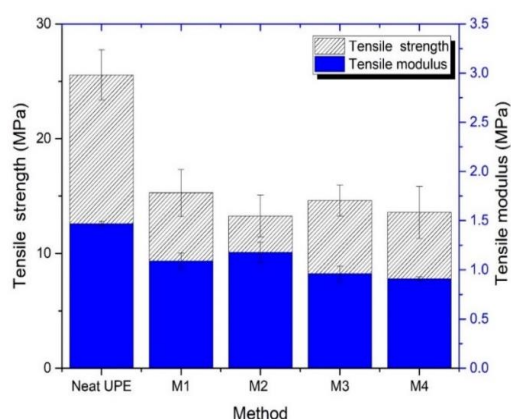


Figure 2: Tensile strength and tensile modulus of neat UPE, M1, M2, M3, and M4 AEPOs with UPE blend.

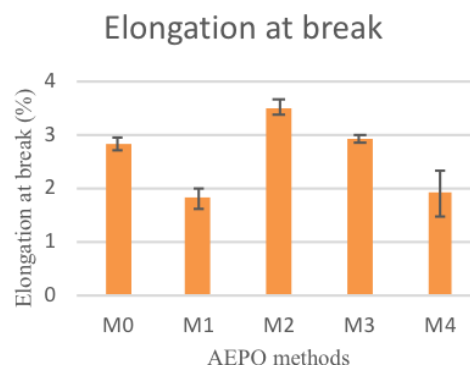


Figure 3: Elongation at break of neat UPE, M1, M2, M3 and M4 AEPOs with UPE blend.

The Izod impact strength of neat UPE and UPE blend at 10 wt% AEPO was shown in Figure 4. As can be seen in the figure, the impact strength of the polymer was decreased in the presence of 10 wt% AEPO in UPE polymer. The highest impact strength among the UPE/AEPO blends is M3 (21.97 J/m), while the lowest is M4 (13.80 J/m). Meanwhile, M1 and M2 (17 J/m) blends showed moderate impact strength. The reduced impact strength in all polymer blends are due to greater cross-linking density in the polymer chain and result to brittle polymers [19]. The cross-linking is between C=C in AEPO with C=C in styrene and UPE to form C-C single bond reduced free C=C in the polymer chain. C-C single bond is weaker than C=C double bond. Thus, the decreased density of C=C in the polymer chain reduced the strength of polymer chain to overcome the supplied impact. Due to high density of C=C in UPE/M1 AEPO and UPE/M2 AEPO blends, 20 minutes polymer blend is not enough to allow all the available C=C to cross-link with UPE. Moderate impact strength of M1 and M2 AEPO show the balance between formation of cross-linking between the polymer blends and the energy absorbed by the remaining C=C that does not involved in the cross-linking.

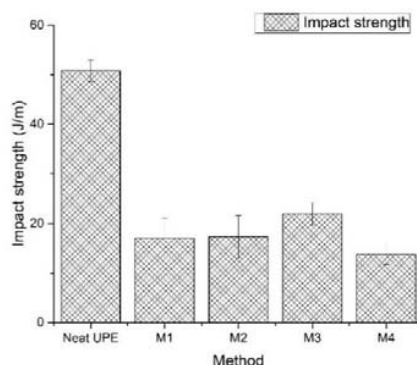


Figure 4: Izod impact strength of neat UPE, M1, M2, M3 and M4 AEPO/UPE blend

4. Conclusion

This work shows that it is possible to blend AEPO in UPE and cure the sample to form thermoset polymer. In this study AEPO was synthesised using four different conditions includes different temperature of 80°C, 100°C and 105°C and different processing period which is 16 hours and 36 hours. The prepared AEPO from the respective methods were labelled as M1, M2, M3, M4 and neat UPE. All the methods showed that AEPO were successfully synthesised as all the samples show

functional group absorption of C=C, -OH and -HOC=O in FTIR test. The blending of constant 10 wt% AEPO in UPE had decreased the tensile modulus, and tensile strength. The polymer blend tensile strength of the palm oil acrylate processed at 110°C for 16 hours (M2) showed reduction from 25.56 MP to 13.26 MP (48%), reduction in tensile modulus from 1.47 GPa to 1.18 GPa (19.7%) and the highest impact strength among the four acrylates of polymer blend is 21.97 J/m from palm oil acrylate processed at 105°C for 16 hours (M3). The phenomena were expected due to introduction of stiffer AEPO in the UPE system and failure of acrylates to cross-linking with UPE. Besides, decrease in impact strength is due to decrease of strong C=C in the polymer chain. The presence of AEPO in the polymer chain sacrifice tensile and impact strength but improved elongation at break of UPE blend due to long and flexible chain of AEPO. Polymer blend from M2 acrylate showed increased in elongation at break from 2.805 % to 3.493 % (24.5 %) compared to neat unsaturated polyester. In conclusion, AEPO produced from Method 2 shows balanced mechanical properties when blend with UPE. Therefore, longer processing time is not an essential factor in producing AEPO as the best condition in preparing AEPO can be concluded at 110°C and processed in 16 hours. As the addition of bio-resin in synthetic UPE had reduced UPE mechanical performance, it is suggested that reinforce material is needed to regain and improved the mechanical properties of the polymer blend.

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