Development of Epoxidized Palm Oil Based Coating Material from Used Cooking Oil and its Adhesion Performance

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Abstract**—** Used cooking oil that was thrown away as waste could possibly causing pollution. By utilizing the used cooking oil as additional component in formulating new epoxy coating, this could contribute in increasing sustainability of palm oil industry. In the same time, dependency on epoxy resin which has been used as main raw material in epoxy coating can be minimized because of it harmful effects towards human health. Used cooking oil experienced epoxidation process to add oxirane ring into the structure of fatty acid. Oxirane ring provide reactive site for crosslinking process in coating formulation. Formulated coating was then tested for their adhesion performance to determine the best coating's formulation which gives the best adhesion on the substrate. Result from X-Cut tape test showed that minimal adhesion performances were obtained from every coating formulation. This is in conjunction with spectrum analysis of used cooking oil before and after epoxidation where it showed that there is non-existence of oxirane ring in the epoxidized cooking oil. Adhesion performance results from Cross-Cut tape test have no distinctive trend that can be supported by fourier transform infrared spectroscopy (FTIR) analysis.

Keywords**—** epoxidized cooking oil, epoxy coating, epoxidation, adhesion performance

I. INTRODUCTION

A. *Epoxy coating*

Epoxy coating is a thermosetting polymer with unique characteristics that is used as durable paint and coating for floor and metals [1]. In the same time, epoxy coating also provide protection from corrosion and give finishing looks. Epoxy coating is a product of epoxy resin which is cross-linked with hardener. Pigments also added to increase the aesthetic value and extra layer of protection from corrosion. Table 1 show a common epoxy resin used to develop epoxy coating and theirs characteristics.

Table 1 Epoxy resins and their characteristics [1]

Types	**Viscosity**	**Flexibility**	**Chemical resistance**
Bisphenol A	Moderate-High	Moderate	Moderate
Bisphenol F	Moderate	Low-Moderate	Moderate
Phenoic Novolac	Moderate high	Low	High

Diglycidyl ether of bisphenol A (DGEBA) is a common epoxy resin used in formulating epoxy coating due to their high strength, excellent corrosion protection, and good adhesion to most surface [2]. Although using DGEBA in order to form epoxy coating yield satisfactory performance, DGEBA is carcinogenic and can cause tumour [3]. Besides that, DGEBA can affected men reproductive system [4]. Figure 1 shows structure of DGEBA.

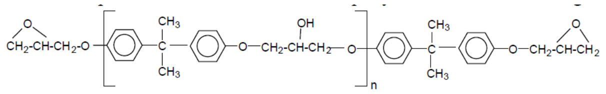


Figure 1 Structure of DGEBA [5]

DGEBA is widely used in producing composite and circuit boards, molding compounds for encapsulation and corrosion protection coating [6]. Cracking, alligatoring, lifting, edge failure and pinholding are among the coating failure that commonly occurs [1]. A strong and durable coating is require to overcome this problem and in the same time the surface preparation and ways of application of the paint to the substrate is among the contributing factors into this matter.

In order to reduce or eliminate the dependency on using DGEBA as the main based component of the formulation of epoxy coating, a substitution material need to be introduce for the development of safer epoxy coating towards human and environment. Material come from renewable source is the most suitable for formulation of new coating such as Annona squamosa oil [7], Mesua ferrea L. seed oil [8], and soybean oil [9], and palm oil [10].

B. *Cooking oil*

Palm oil is a type of edible vegetable oil that is produced from the palm fruit of oil palm tree. Palm oil mainly consist of triglycerides, vitamin E, carotenoids, phytosterols, phospholipids, free fatty acids, gums, and oxidation products [11], [12]. Palm oil is a versatile raw material because not only they are used in food industries but also utilize in oleo-chemical industries. In order to become acceptable for human consumption, palm oil undergoes refining process to produce palm olein where impurities such as undesirable odour, flavor, and color are remove but in the same time retaining the beneficial components. Palm olein are largely use as cooking oil because of it capability to withstand high temperature and in the same time have high antioxidant and limited amounts of unsaturated fatty acids [12]. Palm olein consists of oleic acid (39-45%) and linoleic acid (10-13%). Unsaturated fatty acids and saturated fatty acids also exist in approximately equal proportion in palm olein [13].

Repetition in using cooking oil for cooking especially frying is causing high possibility deterioration of cooking oil making it no longer usable. Hydrolysis, oxidation, and polymerization process occurred during frying. Free fatty acids (FFAs), aldehydes, ketones, acids, and other products were generated during frying [14], [15]. Increased in amount of these unwanted products in cooking oil also increase the rancidity of cooking oil thus affecting the taste of fried food [15]. Unwanted cooking oil eventually was thrown away as waste without proper treatment.

C. *Epoxidation*

Epoxidation process is a process where the unsaturation present in the palm olein is chemically modified into a value added product by addition of oxirane ring (Figure 2). It is desirable to achieve a high oxirane oxygen value and lower iodine value as these criteria is considered to be of better quality [16]. The epoxidation process involved of electrophilic addition mechanism as shown in Figure 3. Epoxidation reaction as shown in Figure 3 took place in similar way with unsaturated fatty acid structure. Oxirane ring formed at unsaturated bond (C=C) produce an epoxidized palm olein as shown in Figure 4.

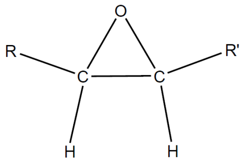


Figure 2 Structure of oxirane ring [10]

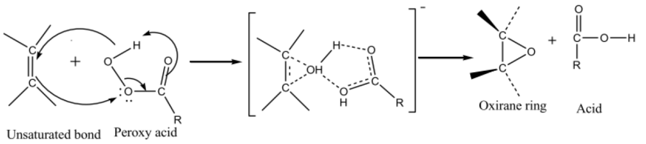


Figure 3 Epoxidation of unsaturated bond [17]

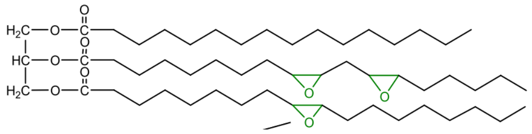


Figure 4 Structure of triglyceride after epoxidation with oxirane highlighted in green.

Annona squamosa oil [7], Mesua ferrea L. seed oil [8], and soybean oil [9], and palm oil [10] are among vegetable oil that undergoes epoxidation process performed by previous researchers.

Epoxidized cooking oil based epoxy coating was produced with formulation ratio of epoxidized cooking oil to epoxy resin is 10:90, 20:80, and 30:70. The produced coatings were then tested and rated based on their adhesion performance.

II. MATERIALS AND METHODOLOGY

A. *Materials and equipments*

Material: Formic acid (98-100% purity) and titanium (IV) oxide powder were bought from Merck. Cycloaliphatic amine adduct (Isophorone diamine with ≥ 99% purity) and diglycidyl ether of bisphenol A were purchased from Sigma-Aldrich. Used cooking oil obtained from domestic waste. Tape (follows ISO 2409:2003) used for adhesion testing was purchased from TQC Sheen. Hydrogen Peroxide (≥ 99% purity) was supplied by FKK laboratory. Riken sandpaper grade 80 and 180 were bought from hardware store in Seksyen 7 Shah Alam. Mild steel plate with dimension 60 x 60 x 3 mm was bought from hardware store in Seksyen 7 Shah Alam.

Equipment: Fourier Transform Infrared Spectrometer, TQC Sheen wet film thickness gauge (follow ASTM D4414, ASTM D1212 & ISO 2808), DPM-816 digital coating thickness tester, TQC Sheen Cross-Cut cutter, mixer, dip-coater machine, arcylic container, knife, steel ruler and grinding/polishing machine.

B. *Methodology*

Figure 5 showed the overall steps taken in developing and testing the performance of coating based cooking oil. Cooking oil was epoxidized first and then followed by formulation of binder. In the same time test panel was prepared. Next, prepared test panel was coated. Once the coated test panel cured and completely dried, adhesion performance of the coating was tested. New formulation will be developed if unsatisfactory adhesion performance is obtained.

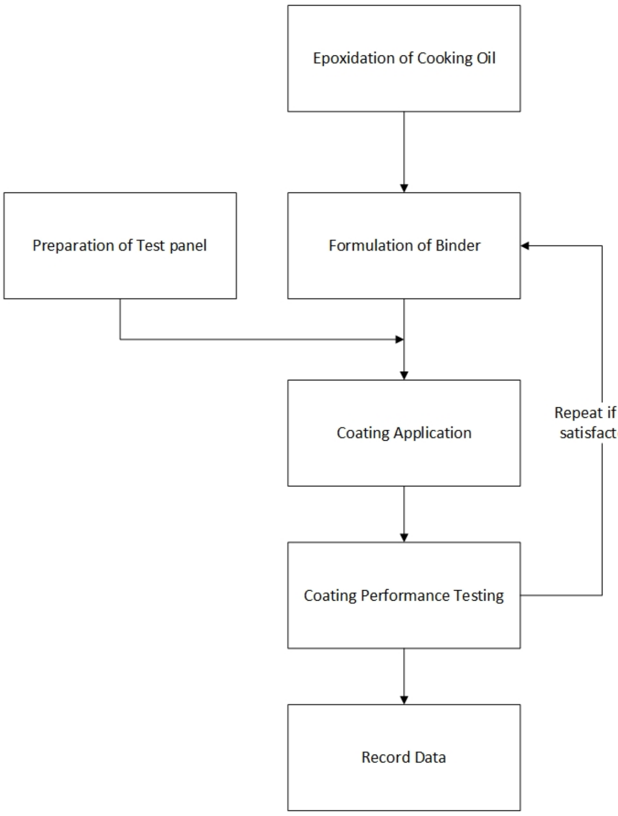


Figure 5 Overall steps in development of coating based cooking oil.

1) *Epoxidation of cooking oil*

. Used cooking oil undergoes epoxidation process in order to add oxirane ring into the structure of fatty acid chain in the palm oil. A molar ratio of used cooking oil:formic acid:hydrogen peroxide (1:5:4 mol/mol) was used in this epoxidation process with the mixture is heated and maintain at 45^{o}C [17]. The formic acid and hydrogen peroxide were mixed simultaneously in other container before added into the cooking oil.

During addition of formic acid and hydrogen peroxide into used cooking oil, the addition action is performs by slowly added drop wise of the mixture into the used cooking oil. This action performed in order to avoid an excessive development of oxygen in the mixture. While adding the formic acid and hydrogen peroxide mixture into cooking oil, in the same time the addition process was performed along with continuously mixing the solution by using mechanical mixer for 150 minutes.

A sample of unepoxidized cooking and epoxidized cooking oil (ECO) were taken for analysis by using Fourier Transform Infrared Spectroscopy (FTIR) technique. The spectrum of unepoxidized cooking oil and epoxidized cooking oil were then compared and analyse for presence of oxirane ring.

2) *Formulation of binder*

Blend of epoxidized cooking oil and epoxy resin were prepared with a weight ratio 0:100, 10:90, 20:80, and 30:70 (ECO:DGEBA) in different beakers. The mixture was mixed using mechanical stirrer at 400 rpm until no phase separation was observed.

Later on, titanium dioxide powder was added into all the binder mixture produced at weight ratio of 1:0.5 (Binder:TiO_2). The mixture was then mixed using mechanical mixer at mixer speed of 1010 revolution per minute (rpm) until homogenous phase obtained at approximately 1 hour.

Finally, cycloaliphatic amine adduct was added at a weight ratio of 1:0.25 (binder:amine). The mixture of binder and amine was then mixed using mechanical mixer at 400 rpm until no phase separation was observed.

3) Preparation of test panel

Sand paper no. 80 was used to remove any layer of rust and pitting from the surface of test panel. Test panels were then lightly abraded using sandpaper no. 180 and wiped with acetone to remove metal dust that was produced from abrasion before coating application.

4) Coating application

Coating was applied using Motor-Driven Dip Coater Application as refer to ASTM D823-95. A custom made acrylic container was used in order to effectively coat the test panel and in the same time without using excessive amount of binder. The coating speed was kept constant for all test panels to maintain uniform thickness among all coating. Wet film thickness was measured using TQC Sheen wet film thickness gauge. Three readings were taken at each surface of test panel. Once desired wet film thickness was obtained, the coated test panels were left in laboratory under room temperature and standard condition to let the coating undergoes curing process at ambient temperature for 7 days [10].

5) Coating performance testing

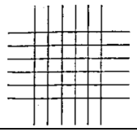
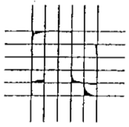
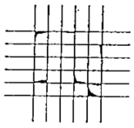
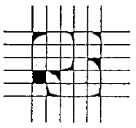
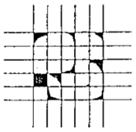
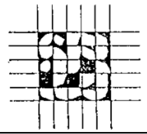
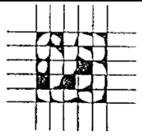
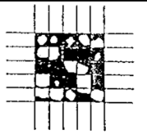
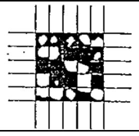
After the coated test panel cured for 7 days, dry film thickness of the coating was taken by using DPM-816 digital coating thickness tester and was recorded. The coated test panel was then undergoes adhesion performance test in order to determine the degree of adhesion performance. X-Cut and Cross-Cut Tape Test were used to rate adhesion performance by referring to ASTM D3359-09.

The adhesion performance was rated based on classification provided in ASTM D3359-09 in Table 2 and Table 3.

Table 2 X-Cut tape test adhesion classification

Classification	**Explanation**
5A	No peeling or removal
4A	Trace peeling or removal along incisions or at their intersection
3A	Jagged removal along incisions up to 1.6 mm (1/16 in.) on either side
2A	Jagged removal along most of incisions up to 3.2 mm (1/8 in.) on either side
1A	Removal from most of the area of the X under the tape
0A	Removal beyond the area of the X

Table 3 Cross-Cut tape test adhesion classification

Classification	**Percent Area Removed**	**Surface of Cross-Cut Area From Which Flaking Has Occurred for Six Parallel Cuts and Adhesion Range by Percent**
5B	0% None	
4B	Less than 5%	
3B	5 – 15%	 
2B	15 – 35%	 
1B	35 – 65%	 
0B	Greater than 65%	

III. RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FTIR) technique was performed to analyzed and identify the chemical bonds existed in the cooking oil before and after epoxidation process.

A. Epoxidation of cooking

Figure 6 showed the spectrum profile of cooking oil before undergoes epoxidation process. A stretch of C-H was observed between 2921.96 – 2852.85 cm^{-1}. The spectrum showed carbonyl stretch at 1743.80 cm^{-1} and methyl bending at 1464.28 cm^{-1}. Presence of nitrogenous compound showed at 1542 cm^{-1} and methylene group at 721.55 cm^{-1}. Bending of C-H was observed at 1377.59 cm^{-1}. Existence of C-O stretching and bending of O-H at 1159 cm^{-1} and 1116.95 cm^{-1} respectively.

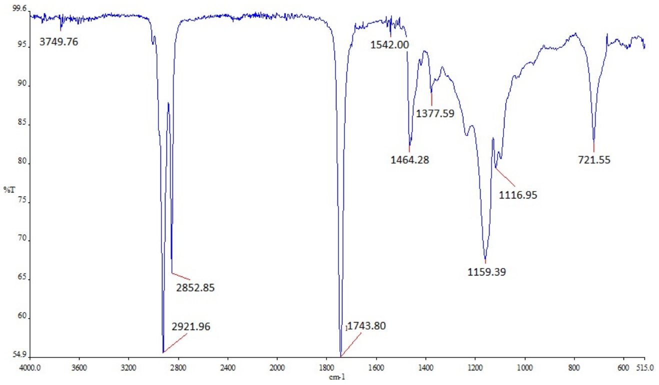


Figure 6 Spectral analysis of unepoxidized used cooking oil.

Figure 7 showed the spectrum profile of cooking oil after experienced epoxidation process. Based on the spectrum profile of ECO, there is no oxirane ring formed in the fatty acid structure. There is no formation of oxirane ring occur from the epoxidation process as the oxirane ring should produce a trough between 833 – 841 cm^{-1} [18], [19].

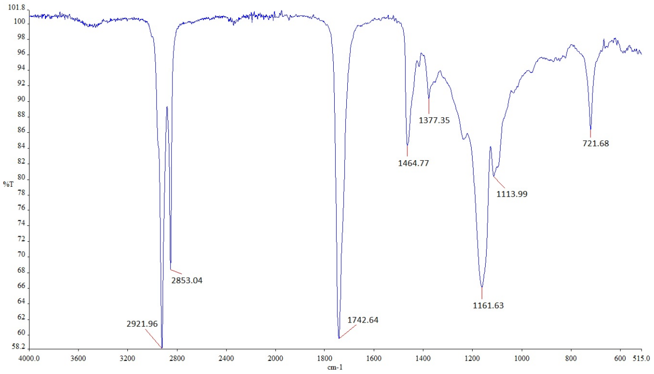


Figure 7 Spectral analysis of epoxidized used cooking oil.

Used cooking oil that was collected from domestic household might consist of very low amount of unsaturated fatty or none at all. Existence of unsaturated fatty acid in the cooking oil is crucial for epoxidation process because unsaturated fatty acid provide reactive site for epoxidation process to complete. The reactive site is ethylenic unsaturation (C=C). From spectral profile in Figure 6 also indicated that there is no presence of C=C bond. There is non-existence of oxirane ring because there is no addition reaction of oxygen into the double bond in the unsaturated fatty acid structure. Scala (2002) also supported that the double bond plays the main role in forming oxirane ring during epoxidation process. Non-existence of unsaturated fatty acid in cooking oil is due to decomposition process of unsaturated fatty acid during frying process [14], [15].

B. *Wet and dry film thickness of the coating*

Wet film thickness (WFT) of the coating from every formulation was taken using wet film thickness gauge right after applying the coating and before curing process. Figure 8 shows the recorded average wet film thickness of the coating for every formulation. Uniform wet film thickness of applied coating was obtained for every test panel. The error tolerance wet film thickness of every test panel is within acceptable limit thus unbiased result from adhesion performance testing can be obtained.

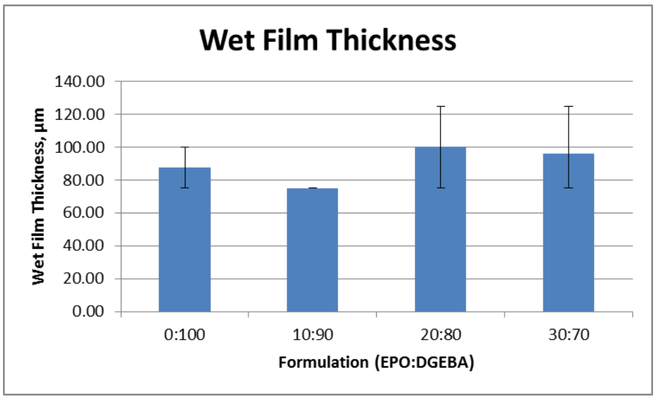


Figure 8 Wet film thickness of coating for different formulation.

Figure 9 shows dry film thickness (DFT) of the coating after cured for every formulation. Referring to the bar chart, a uniform thickness of coating was achieved for every test panel as the error bar within acceptable limit.

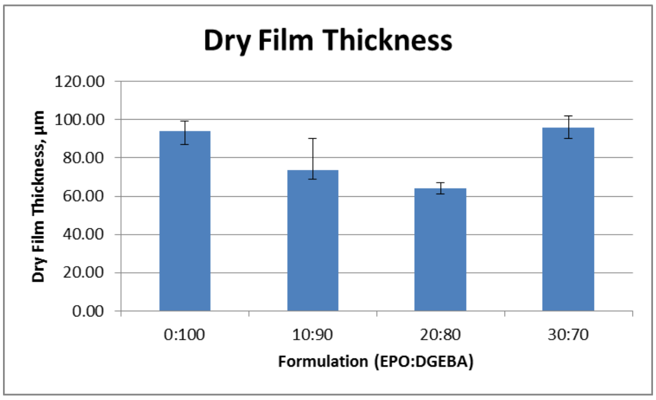


Figure 9 Dry film thickness of coating for different formulation.

Theoretically dry film thickness of the coating should be thinner than wet film thickness. This is because during curing and drying process, evaporation occurred where water content in the coating was evaporated. The water was removed and leaving behind dissolved solid on the surface of substrate. This can be seen by referring to formulation 30:70 (ECO:DGEBA) where in Figure 8, the coating wet film thickness can be as high as 120 µm. The possibility obtaining WFT of 120 µm was shown by maximum error bar in the Figure 8. The DFT of the same formulation in Figure 9 shows that the highest value of DFT can be achieve only up to 100 µm.

C. *Adhesion performance*

Adhesion performance of the coating for every formulation tested by using x-cut and cross-cut tape test method are presented in Figure 10. Results from x-cut tape test showed that coating with formulation 10:90 and 30:70 produced the best adhesion classification which is 4A while formulation 0:100 and 20:80 yield classification 2A and 3A respectively. There is no distinctive trend can be observed in result obtained from X-Cut tape test.

Test result obtained from the cross-cut tape test shows that there is only minimal adhesion performance obtained among all the formulation. All the formulation that was tested by Cross-Cut tape test was classified as 1B. Although adhesion for formulation 30:70 (Cross-Cut tape test) in Figure 10 was classified as 2B, the error bar showed that the adhesion performance for this formulation has possibility to obtain lower classification. These data agree with result of FTIR of epoxidized cooking oil in Figure 7 that there is non-existence of epoxy ring in the epoxidized cooking oil.

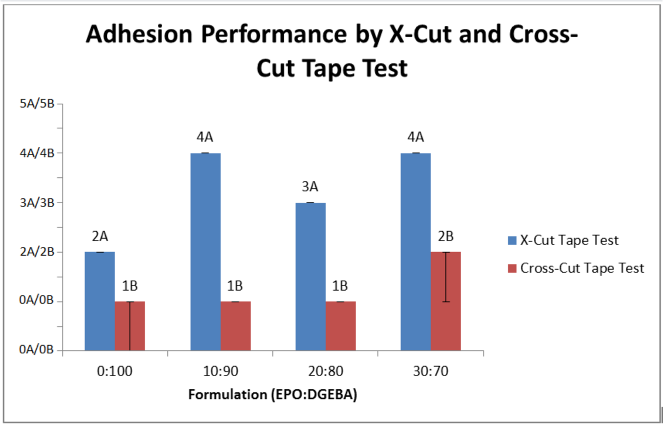


Figure 10 Adhesion performance of coating with different formulation tested via X-Cut and Cross-Cut test tape.

IV. CONCLUSION

New cooking oil based epoxy coating was developed with a ratio of epoxidized cooking oil to epoxy resin is 10:90, 20:80, and

30:70. Adhesion performance of the developed coatings was tested. Comparison between unepoxidized cooking oil and epoxidized cooking oil FTIR analysis shows that non-existence of oxirane ring in epoxidized cooking oil. Minimal adhesion performance is obtained from Cross-Cut tape test for all formulation. This correlated with absence of oxirane ring (833 – 841 cm^{-1}) from the epoxidized cooking oil observed in spectrum profile. Cooking oil does not contain unsaturated fatty acid that is needed for epoxidation process.

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