

Development of Environmentally Friendly Palm Oil-Based Resins for Coating Applications

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Increasing environmental concerns have stimulated the efforts to utilize renewable natural resources. Many previous researchers have reported the synthesis of alkyds from plant oils for coatings, that are relatively inexpensive and have good properties. In particular, soybean, castor, linseed and tall oils were very successfully used because they have high level of unsaturation enabling their alkyds to air-dry. The conventional method of alkyd synthesis is carried out at high temperature via the condensation of the oil with glycerol and dicarboxylic acid in xylene, and the use of organic solvent has made the process environmentally unfriendly. Palm oil is a major crop in Malaysia and consequently it is attractive to look into its use as raw material for industrial applications. However, it is a non-drying oil, and its alkyds are not capable of forming coherent film by air oxidation, consequently, palm oil alone cannot be used for coatings. This paper would present a number of selected polymeric materials made from palm oil derivatives. The first approach is to produce a water-reducible alkyd without organic solvent during synthesis. The resin is cross-linked by using a water-based melamine resin. The second approach is to incorporate palm oil alkyd into conventional acrylate resin. Thirdly the unsaturation of the alkyd could be increased through incorporating unsaturated dicarboxylic acid. The final alkyd has low molecular weight distribution and yet it could air-dry and even become UV-curable. Mechanical and physical properties of the coatings that have been characterized include curing rate, film hardness, adhesion, and chemical resistance.

Keywords: Palm oil; coating; cure rate; characterizations; film performance

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A coating is the materials that applied to a surface to form a film on the surface. The most common coating is a paint. Coatings are applied all around us in our everyday life, for examples: on buildings, furniture and various metallic objects. The obvious advantage of coating is to beautify the appearance. The other function is even more important, that is to provide protection to the substrate particularly if it is metallic. Exposure of metallic parts to environmental air, moisture, and pollutants, inevitably could lead to corrosion and shorter service life [1]. Various types of surface coatings have been applied to provide protection to these substrates, and these include conventional solvent-based coating, powder coating, and UV-curable coating [2]. Increasing environmental concerns have stimulated the efforts to utilize renewable natural resources. Many previous researchers have reported the synthesis of alkyds from plant oils for paints and coatings, that have been commercialized [3]. Plant oils such as soybean, castor, linseed and tall oils have been very successfully used because they have very high level of unsaturation enabling their alkyds to air-dry. The conventional method of alkyd synthesis is carried out at high temperature via the condensation of the oil with glycerol and dicarboxylic acid in xylene. Traditionally, these alkyds have moderately high molecular weight

ranging from 40,000 to above 100,000, and have been produced in aromatic solvents at low solids content, and the use of organic solvent has made the process environmentally unfriendly.

Palm oil is a major crop in Malaysia and consequently it is attractive to look into its use as raw material for industrial applications. However, it is a non-drying oil because of its low content of unsaturation ($-C=C-$), as shown in Table 1, its total content of unsaturated fatty acids <75%, and thus its alkyds are not capable of forming good film by air oxidation, consequently, palm oil alone cannot be used directly as coating resins.

Environmentally friendly palm oil-based coating resins could be produced by the one or more of the following approaches: Replacing petroleum-based ingredients with palm oil derivatives, reducing or eliminating organic solvent and fastening curing at lower temperature. This paper would review three different palm oil-based coating resins based on the works carried out at the University of Malaya. These are (I) water-base baking enamel from palm stearin, (II) hybrid acrylate-alkyd resin from oleic acid, (III) UV-curable alkyd resin with incorporated maleic acid.

Table 1. Free fatty acids contents of some common plant oils.

Fatty acid	Tall oil	Soya oil	Tung oil	Sunflower oil	Palm oil
Oleic acid $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	46%	24%	8%	42%	45%
Linoleic acid $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}-\text{CH}_2-\text{H}=\text{CH}(\text{CH}_2)_7\text{COOH}$	35%	53%	4%	47%	9%
Linolenic acid $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	12%	7%	3%	1%	-
Eleostearic acid $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	-	-	80%	-	-
Stearic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	3%	4%	1%	4%	5%
Palmitic acid $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	4%	12%	8%	6%	39%
TOTAL UNSATURATION FATTY ACID	93%	84%	95%	90%	54%

EXPERIMENTAL

Chemicals and Materials

Glycerol, oleic acid, and RBD palm stearin were kind gifts from Emery Oleochemical Malaysia Sendirian Berhad, and they were used as received. Followings are commercially available chemicals: phthalic anhydride (PA) (DC Chemical Korea), lithium hydroxide (HmbG Chemicals), benzophenone and methyl methacrylate (MMA) from Sigma Aldrich. Maleic acid (MA) was obtained from Merck. Pentaerythritol and trimellitic acid anhydride from Perstop AB, Sweden, tetrahydrofuran (THF) and other chemicals were from Thermo Fisher Scientific, and methylated melamine formaldehyde resin (Cymel 303) was from Cytec, USA. All Chemicals were used as received without further purification.

Methods of Preparations of Different Coating Resins

Synthesis of Water-Reducible Alkyd

A water-reducible alkyd (oil length 40%) was produced in two steps [4,5]. Alcoholysis between 90.0 g palm stearin and 30.0 g glycerin catalyzed by 0.5 g LiOH was first performed at 220°C for about 30 min to

form a mixture of monoglycerides. The second step was the polymerization through transesterification involving additional 60.0 g phthalic anhydride, 10 g pentaerythritol and 29 g trimellitic acid anhydride at 180-200°C. Progress of the reaction was monitored through checking the acid number of the reaction mixture by titrating aliquot of mixture, dissolved in 50 ml of xylene/ethanol (1:1), with standardized 0.1N ethanolic KOH. when the acid number fell below 60, the heating was turned off. The mixture was allowed to cool to 100° C before being diluted with a 1:1 mixture of n-butanol and butyl cellosolve to produce a final water-reducible alkyd of around 50% total resin content. This alkyd was label as WRA40.

Hybrid Acrylate-Alkyd resin

This hybrid resin is made in two stages [6,7]. An alkyd macromer is prepared from the reactions of 142 g glycerol, 140 g oleic acid and 218 g phthalic anhydride to produce an alkyd with oleic acid grafted as side chain. The alkyd macromer was a viscous liquid with an acid value and hydroxyl value of 16.5 and 133 mg KOH/g respectively. The structure can be verified by H-NMR as shown in Figure 1. The vinyl protons (b,c) of the oleic acid side chain can be seen at 5.3 ppm

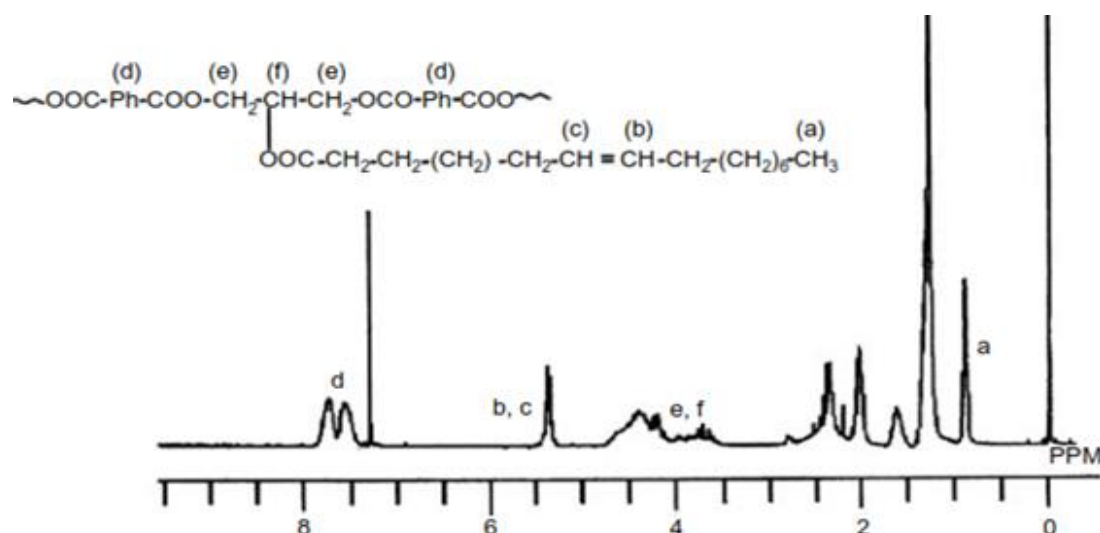


Figure 1: H-NMR spectrum of the alkyd macromer

In the second stage, the hybrid acrylate-alkyd resin was prepared by copolymerization of the alkyd monomer and methyl methacrylate (MMA), initiated by benzoyl peroxide dissolved in toluene and was carried out at 90°C for 8 h.

Synthesis of Alkyd Macromer with Incorporated Malic Acid

A series of three alkyd macromers was prepared by the reactions of palm stearin, PA and maleic acid (MA) and glycerol. Maintaining the amounts of palm stearin and glycerol; the ratio of PA:MA was varied from 100:0, 80:20 and 50:50. The three alkyds were labeled AlkMA0, AlkMA20 and AlkMA50 respectively. The solvent-free macromers were viscous liquids.

Characterization Methods

Rate of Cure by Drying Time Test

The rate of film formation during the drying of a coating is estimated by using ASTM D1640-83. The film is considered dry-to-touch when the film no longer sticks to finger and does not rub up when the finger is lightly moved across the surface. The second testing for curing is to determine the dry-hard time. With the end of thumb resting on the film and the forefinger supporting the test panel, a maximum downward pressure of the thumb on the film is exerted. The film is considered dry-to-hard when any mark left by the thumb is completely removed by the polishing operation.

Coating Film Adhesion

Film adhesion test was evaluated based on ASTM D3359. A crisscross lattice pattern with six cuts in

perpendicular direction were made. The crisscross area was cleaned lightly with a tissue paper. Adhesive tape was applied firmly over the cut pattern and pulled off rapidly at an angle of 180°. The grid area was inspected for any detached square of coating. The best adhesion performance is indicated by 5B (0% of area removed) while the worst performance is 0B (> 65% of area removed).

Pencil Hardness

The scratch hardness of a coating was estimated by pencil hardness test that was performed with a Gardner pencil scratch hardness kit according to ASTM D3365 with scale from 6B to 6H, where 6B is the softest and 6H the hardest in the following order: 6B<5B<4B<3B<2B<B<HB<F<H<2H<3H<4H<5H<6H. The sharpened pencil is rubbed with an abrasive paper at angle of 90° to obtain a flat, smooth and circular cross section. The pencil is moved over the surface using the pencil tester at an angle of 45° and a fixed pressure. The hardness was expressed in term of the designation of the hardest pencil that failed to scratch the film. For example, if torn mark was seen more than two times with 3H pencil and one time with 2H, the scratch-value was recorded as “2H”.

Water and Chemical Resistance

The tests were done on coated glass panels using methods adopted from ASTM D1647. Coated glass panels were immersed in distilled water for 18 h. Glass panels were inspected visually for any whitening formed upon removing the glass panels. Alkali resistance test was conducted by immersing another set of the coating in NaOH aqueous solution (0.1M). Acid and saltwater resistance test was done by immersing the coated glass panels in 0.1 M HCl and 5

wt% NaCl solution respectively, for 18 h. The panels were then removed and rinsed with distilled water, and inspected for any film defect.

Crosslinking Reactions

The formation of coating film could be accomplished by crosslinking reactions leading to changes in chemical structures, molecular weights and glass transition temperatures. The changes in chemical structures could be studied by FTIR and NMR. Molecular weight distributions of the polymers were determined by GPC analysis, while the glass transition temperature is measured by DSC. Details of these techniques were described elsewhere [6,7].

RESULTS AND DISCUSSION

1. Water-reducible Baking Enamel

WRA40 has an acid number of 55, and M_n of around 1100 and M_w of around 1800 as determined by GPC. Clear baking enamel can be made by mixing 4 parts by weight of the WRA40 with 1-part Cymel 303 and diluted with water to suitable viscosity for coating application. About 10 g of the enamel was placed on a glass disk and dried in a vacuum oven at 40°C. After the removal of moisture, it remained as a sticky paste. A thin layer was spread onto the surface of NaCl cell and the FTIR spectrum was recorded. The NaCl cell was then heated to 140°C in the oven for 30 min to allow the enamel to set and the FTIR spectrum was recorded again.

Figure 2 shows the FTIR spectra of the enamel (a) before and (b) after curing at 140°C for 30 min. The broad band at 3430 cm^{-1} is due to hydroxyl group -OH of the alkyd. The peaks at around 1550-1580 cm^{-1} are due to the N-H deformation and C-H bending respectively of methoxymethyl structure from Cymel 303 melamine resin [4], and the peak at 1725 cm^{-1} is due to the carbonyl C=O of the -COOH and could be overlapping with ester groups as well. The peak at 1386 cm^{-1} is due to the C-H bending of the -N-CH₂-CH₃ structure. The peak at 2340 cm^{-1} in spectrum (b) is probably just related to the background CO₂ in the spectrometer.

Comparing the absorbance of these peaks in spectra (a) and (b), the -OH, N-H, and C-H have reduced by 15-20% during the curing of the enamel, while -C=O has remained almost the same (<2%). These observations were in agreement that the predominant crosslinking reactions involved the -OH and -COOH of alkyd with the methylol groups of Cymel 303 [3,4].

To evaluate the coating performance, the enamel was applied on mild steel panels and cured at 120, 140 and 160°C respectively. The dry-hard time was determined. Adhesion test and pencil hardness were determined after coatings were cooled down to room temperature and conditioned for 2 days (Table 2). As expected, the dry-hard time is shorter at higher curing temperature due to faster rate of crosslinking. The film adhesion was excellent, and the hardness was good. The film hardness was higher after curing at 160°C due to greater extent of crosslinking.

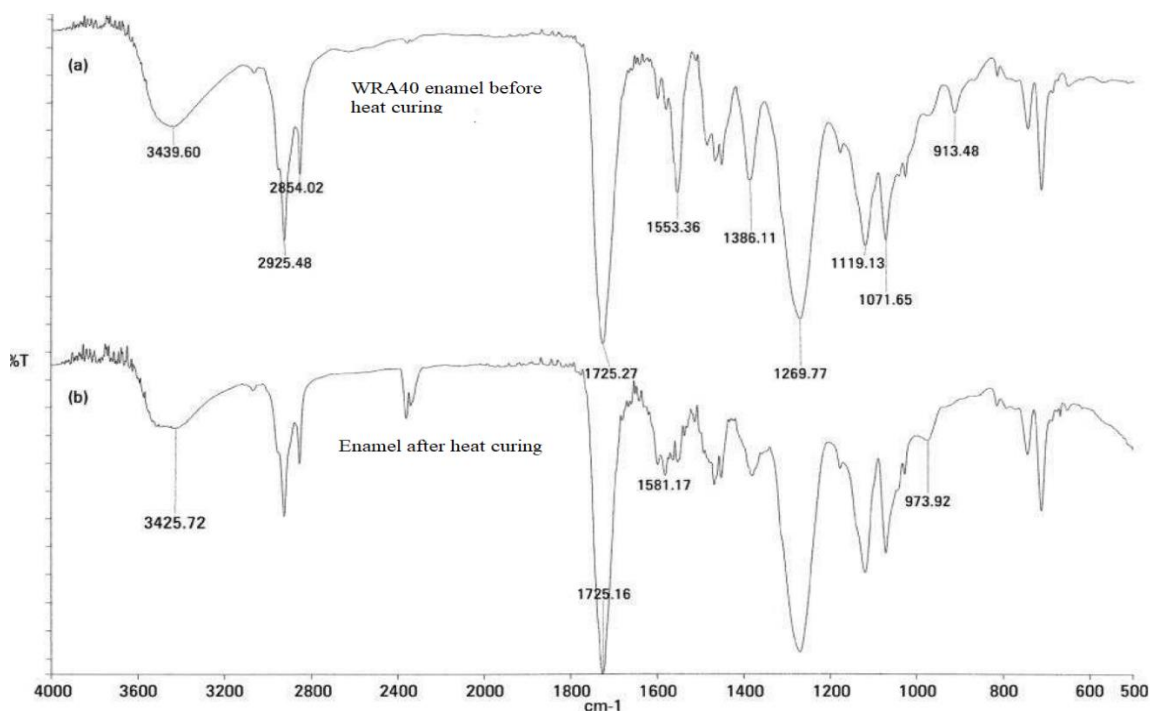


Figure 2. FTIR spectra of the enamel (a) before and (b) after curing

Table 2. Coating performance of WRA40 enamel

Curing temperature	120°C	140°C	160°C
Dry-hard time / min.	60	30	20
Adhesion	5B	5B	5B
Pencil hardness	2H	2H	3H

Table 3. Composition of hybrid acrylate-alkyd resin

Sample Code	Alkyd/g	MMA/g
AlkH1 (75% Alkyd : 25% MMA)	3	1
AlkH2 (50% Alkyd : 50% MMA)	2	2
AlkH3 (25% Alkyd : 75% MMA)	1	3

2. Hybrid Acrylate-alkyd Resin from Oleic Acid

For coating application, the hybrid acrylate-alkyd resins were copolymerized with MMA in 100 ml toluene at 90°C using 3.0 g benzoyl peroxide initiator as shown in Table 3. All the three hybrid resins were in the form of light yellowish viscous solution.

To check the drying time, a thin layer of the solution was coated on mild steel panel, and the dry-to-touch and dry-hard times were recorded. About 0.1 g of the dried film was scraped off and used for the glass transition temperature, T_g , determination by DSC. To carry out the water and chemical resistance tests, the hybrid resin solution was coated on glass panel and dried thoroughly for two days before carrying out the methods adopted from ASTM D1647, as described earlier. The results are summarized in Table 4.

The drying of these solution of hybrid resins is dependent on the evaporation rate of the solvent.

Thus, the dry-to-touch for the three resins were very similar. Likewise, their dry-hard times were only slightly different. The coatings of AlkH1 and AlkH2 showed excellent adhesion of 5B and pencil hardness of 3H, while AlkH3 showed adhesion of 4B (< 5% of the area is affected) and pencil hardness of 2H.

Thermal analysis by DSC showed that each hybrid resin has only one glass transition T_g , showing that the alkyd was highly miscible with PMMA.[6] Higher content of MMA in the hybrid resin has raised the T_g , and probably has made the film less flexible, consequently AlkH3 has lost some adhesion force and torn by 3H pencil, thus being rated as 2H.

Overall, the coatings of these hybrid resins shown good resistance to water and salt solution. They were slightly affected by dilute acid and alkali; upon drying the glass plates, the whitened appearance disappeared.

Table 4. Coating performance of the hybrid acrylate-alkyd resin

Test	Remark	AlkH1	AlkH2	AlkH3
Drying	Dry-to-touch /s	37	37	36
	Dry-hard /s	150	148	148
Mechanical testing	Adhesion	5B	5B	4B
	Pencil hardness	3H	3H	2H
	T_g / °C	75	89	96
Corrosion resistance	Water	no change	no change	no change
	NaCl (5%)	no change	no change	no change
	HCl (0.1 M)	a bit whitened	a bit whitened	a bit whitened
	NaOH (0.1 M)	whitened	a bit whitened	a bit whitened

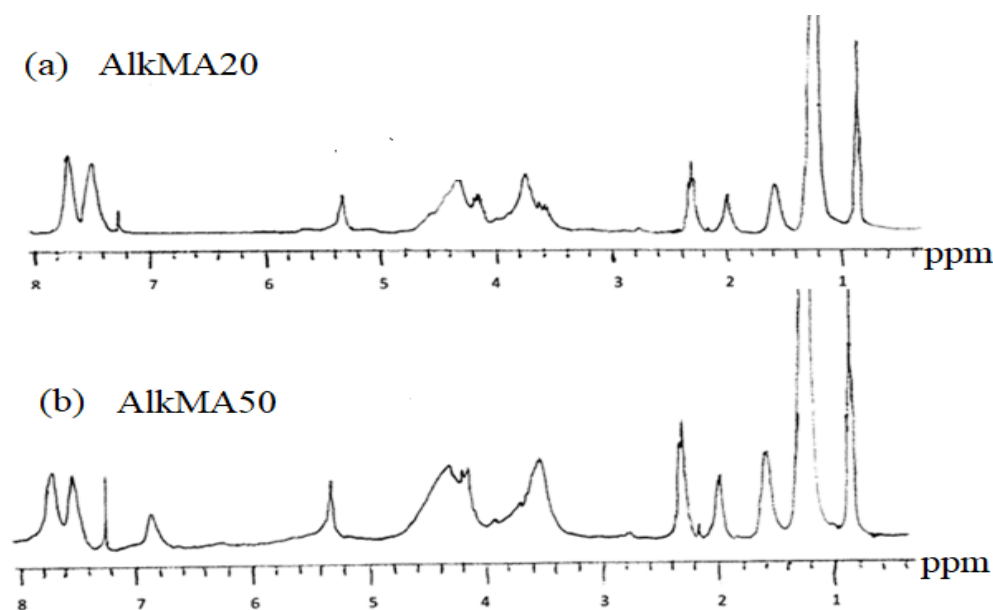


Figure 3. H-NMR spectra of the macromer (a) AlkMA20 and (b) AlkMA50

3. UV-curable Alkyd Resin with Incorporated Unsaturated MA

Figure 3 shows the H-NMR spectra of (a) AlkMA20 and (b) AlkMA50 macromers produced from the incorporation of malic acid ($\text{HOOCCH}=\text{CHCOOH}$) into the main chains of the alkyd. H-NMR spectra clearly showed the peak at 5.3 ppm due to $-\text{CH}=\text{CH}-$ of the incorporated maleic acid. These macromers could be made into UV-curable resins by mixing 60 parts alkyd to 40 parts MMA as diluents and 6 parts benzophenone as photo-initiator. UV-curing unit used in this work was “DYMAX UV Lamp” which bears a 400 W lamp that radiates UV light (λ 365 nm) at intensity of 225 mW/cm².

Film of 50 μm wet thickness was coated by a Sheen coater on a section of mild steel panel measuring 70 mm \times 200 mm. Rates of film formation during UV-irradiation was given by the times for dry-to-touch and dry-to-hard, by using the test method stated in ASTM D1640-83. The coating was allowed to condition for 2 days, before carrying out the Pencil Hardness and Adhesion Test. Water, salt, acid and alkali resistance (D1647-89) were conducted on the cured coatings on glass panels. Results were summarized in Table 5 below.

AlkMA0 was used as a control for comparison. It has no unsaturation, thus, even with addition of MMA and photo-initiator, it could not cure to a solid film under UV-irradiation for more than 10 min.

Table 5. Coating performance of the UV-curable resin from alkyd

Test	Remark	AlkMA0	AlkMA20	AlkMA80
Drying	Dry-to-touch /s	Non-drying	65	50
	Dry-hard /s	Non-drying	48	45
Mechanical testing	Adhesion	-	5B	5B
	Pencil hardness	-	3H	4H
Corrosion resistance	Water	-	no change	no change
	NaCl (5%)	-	no change	no change
	HCl (0.1 M)	-	no change	no change
	NaOH (0.1 M)	-	a bit whitened	no change

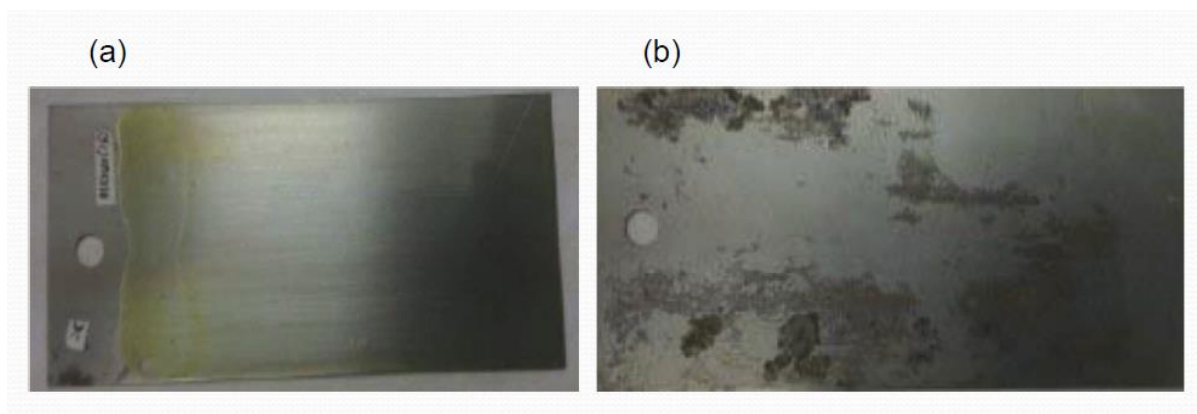


Figure 4. (a) AlkMA20 resin coated on the front of panel; (b) the uncoated bottom of the same panel showed sign of rusting after 6 months on the bench.

Under UV-irradiation, AlkMA80 cured faster than AlkMA20 due to the higher amount of unsaturation, and presumably formed more crosslinks at a faster rate, hence its pencil hardness was also higher. Both of them showed excellent adhesion of 5B. Both coatings showed good resistance to water, salt solution and dilute acid. Only AlkMA20 was slightly affected by dilute alkali; however, upon drying the glass plates, the whitened appearance has disappeared.

Figure 4 shows photos of two sides of a steel panel after being coated on top-side (a) with UV-curable resin made from AlkMA20 and cured, and was left exposed to the laboratory atmosphere for about six months. The bottom-side (b) that was not protected by the coating has shown signs of serious rusting.

CONCLUSION

Palm oil, being a non-drying oil, could not be made into coating resin by itself as it lacks the ability to auto-oxidize. This paper reviews three different types of coating resins that could be produced from palm oil derivatives through different drying mechanisms.

The water-based baking enamels could be cross-linked through reactions with melamine resins. Its advantage is without the use of organic solvent. The acrylate-alkyd hybrid resins have high glass transition temperatures ($> 75^{\circ}\text{C}$) and they are soluble in hydrocarbon solvent, and they could achieve fast drying as the solvent evaporates off. On the other hand, solventless UV-curable resins could be cured at room temperature upon irradiation with UV-light for less than a minute. The novelty of these works lies in the development of new products from palm oil, which is an environmentally friendly and sustainable raw material, and also lower cost as compared to petrochemical-based resins.

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