# Environment Friendly UV-Curable Resins from Palm Stearin Alkyds

**Desmond Teck Chye Ang, Seng Neon Gan**

*Chemistry Department, University of Malaya, 50603 Kuala Lumpur, Malaysia*

**ABSTRACT:** Non-self-drying palm stearin alkyds were converted into UV-curable resins via fumarization and maleinization. The maleated alkyds (AlkM) and fumarized alkyds (AlkF) were characterized by ^{1}H-NMR and FTIR before they were formulated into UV-curable coatings, with methyl methacrylate as the active diluents, and benzophenone as UV photoinitiator. The film properties, which include the film hardness, adhesion, water and alkali resistance, and thermal stability, of the two series of alkyd coatings were compared. In both series, alkyds with high amount of $-CH=CH-$ could be cured with UV within short time to produce coatings with good film properties. Although both approaches, fumarization and maleinization, serve the same purpose to increase the level of unsaturation in the alkyd, it was found that coatings produced from the two series of alkyds have different UV curability and film properties. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

**Key words:** coatings; curing of polymers; radical polymerization; resins; polyesters

## INTRODUCTION

Development of environment friendly coatings has gained importance as a result of global recognition of the harmful effects of volatile organic compounds (VOC). Many products such as waterborne coatings, powder coatings, and radiation-curable coatings were developed to minimize the emission of VOC. Besides being environment friendly, some of these coatings are superior compared to the conventional ones.[1] UV-curable coatings are known to have rapid curing time, excellent film hardness, and high durability.[2] In addition, production of the coatings also involves lower operating costs, such as low energy consumption and cheaper maintenance.[3] These advantages lead to a promising future in radiation-curable coatings, as shown by a statistic that indicate growth in the market of the coating segments.[4] The statistic also revealed that albeit increasing productions and demands for radiation-curable coatings, the current consumption of such technology is still relatively low, indicating its potential in the future market.

Alkyds are tough resins derived from reaction of polyacids with polyols, in the presence of fatty acids as a major part of its composition.[5] It has been widely used as coatings in many fields owing to its excellent film forming ability, easily pigmented, and able to blend well with additives to form coatings with wide range of characteristics for various applications.[6] Besides, alkyd is very versatile as it can be easily modified with other materials, for example with rosins, styrene, phenolic resins, or silicones, to produce end products with desired characteristics.[7] Utilization of different types of polyol or polyacid in the formulation could significantly affect the properties of the alkyds. Some of the properties could also be altered by simply varying the amount of oil or fatty acids used in its formulation.

In this work, alkyds were synthesized from palm stearin and subsequently formulated into UV-curable coatings. Malaysia is currently one of the largest producers and exporters of palm oil, which covers 41.3% of world palm oil production, second to Indonesia, 44.5%.[8] Palm oil is usually separated into liquid (palm olein) and solid (palm stearin) fractions in order to cater for wider market range. The latter can be viewed as a co-product through the production of palm olein and has relatively limited demand, thus it is always traded at a cheaper price.[9] This makes palm stearin a cost-effective material to be used in many applications, especially in the field of research and developments of palm oil-based products.

Although palm stearin could serve as economical raw material in alkyd synthesis, it is reported to comprise limited amount of $-CH=CH-$ which could retard the UV curability of the unmodified alkyd produced from the oil. Long drying time of palm oil-based alkyd was reported by Issam and Cheun, where the alkyds require several days to dry.[10] Palm stearin composed of only 35% of

*Correspondence to:* D. Teck C. Ang (desmond8601@gmail.com).

unsaturated fatty acids,[11] while other oils commonly used in alkyd synthesis such as soybean oil or safflower oil have 85% and 90% of unsaturated fatty acids, respectively.[12] In order to compensate for the lack of —CH=CH— in palm stearin, the alkyds in this work were formulated with a portion of unsaturated diacids. Increased amount of —CH=CH— in the alkyd chain is expected to improve the UV curability and film properties of the alkyd coatings, thus making palm stearin a viable raw material in alkyd synthesis.

Resins are made UV curable by introducing reactive functional group such as —CH=CH— into the system. There are several means to incorporate unsaturation into a polymer chain, such as through the reaction of acrylates with —OH groups of the polymer, or through esterification involving unsaturated monomers. Xu and Shi incorporated urethane acrylates into polyester chain endcapped with —OH groups.[13] Presence of high amount of unsaturation in the polyurethane (PU) renders it UV curable. Chen et al. synthesized PU with various level of unsaturation and showed that the amount of —CH=CH— in the resin affects the film properties and curability of the coatings.[14] Keimpe et al. also produced PU with high —CH=CH— functionality to improve its UV curability.[15]

Previous works done on modifications and conversions of palm stearin alkyds into coatings with good film properties proved that the solid fraction of palm oil could serve as a potential raw material in the coating industry.[16–18] This article reports the conversion of non-self-drying palm stearin alkyds into UV-curable resins via two approaches. The first approach is by incorporating fumaric acid into the alkyd chains, and the second approach is by incorporating maleic acid. As a result of the modifications, the alkyds are able to UV cure within short time and produce coatings with good film properties. Fumarized alkyds (AlkF) is able to produce coatings with better film hardness, and higher $T_g$. In the later part of the work, it was found that introduction of trimethylolpropane triacrylate (TMPTA) into the coatings managed to enhance some of the film properties.

## EXPERIMENTAL

### Materials

Refined, bleached, and deodorized (R.B.D.) palm stearin, and glycerol 99.5% were obtained from Emery Oleochemical Malaysia Sendirian Berhad (Selangor, Malaysia) and they were used as received. Methyl methacrylate (MMA) and TMPTA were obtained from Sigma Aldrich (St. Louis, Missouri), and they were treated with 1.5% w/v of NaOH aqueous solution and subsequently dried over activated
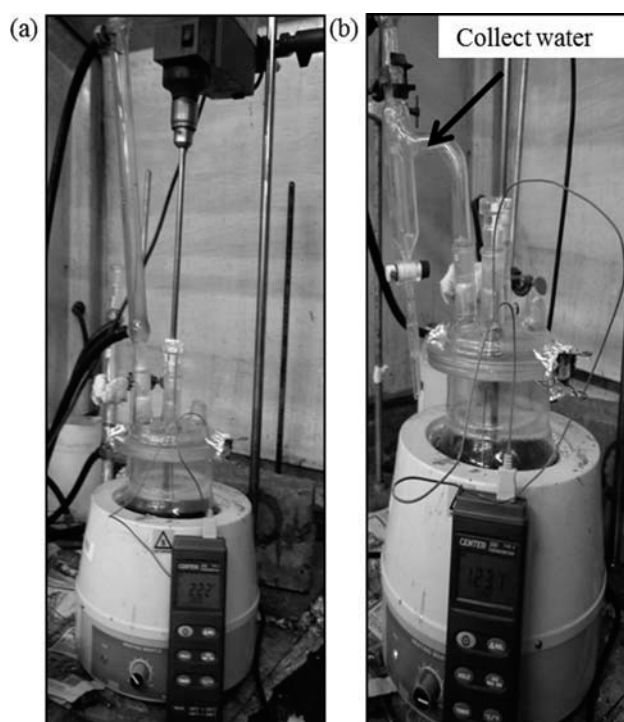


**Figure 1** Experimental setup for (a) alcoholysis process and (b) esterification process—additional customized glassware was attached to the reaction flask to collect water produced during the reaction.

molecular sieves prior to usage. All other chemicals were used without further treatment. Phthalic anhydride (PA) was obtained from D.C. Chemical Korea (Seoul, South Korea), fumaric acid (FA), maleic acid (MA), and benzophenone 99% were obtained from Sigma Aldrich (Steinheim, Germany), and $Ca(OH)_2$ was obtained from HmbG Chemicals (Hamburg, Germany).

### Syntheses of alkyds

Alkyds in this work were synthesized using the whole oil (palm stearin) as the source of fatty acids. The synthesis begins with alcoholysis process, where mixture of palm stearin, glycerol, and $Ca(OH)_2$ was gradually heated to 230°C and held constant for 2 h. The mixture was constantly stirred at 240 rpm using impeller fixed to a digital overhead stirrer throughout the synthesis. The completion of the alcoholysis process was confirmed by conducting solubility test (in alcohol) on the products. Upon completion of the first stage of the synthesis, temperature of the reaction mixture was reduced to < 150°C before adding mixture of diacids to begin the esterification process. Customized glassware was attached to the side of the reaction flask to trap water produced from the esterification. The reaction setup used during the synthesis is shown in Figure 1. The temperature of the reaction mixture was gradually increased to

### TABLE I
### Alkyd Compositions

| Alkyds | Amount (mol) | | | | |
|---|---|---|---|---|---|
| | Palm stearin | Glycerol | MA | FA | PA |
| AlkP | 1.09 | 1.81 | – | – | 1.73 |
| AlkM1 | 1.09 | 1.81 | 0.52 | – | 1.21 |
| AlkM2 | 1.09 | 1.81 | 0.69 | – | 1.04 |
| AlkF1 | 1.09 | 1.81 | – | 0.52 | 1.21 |
| AlkF2 | 1.09 | 1.81 | – | 0.69 | 1.04 |

220°C and held constant for the remaining of the synthesis. Acid number of the reaction mixture was measured periodically during the polyesterification using standard test method adopted from ASTM D1639. For the acid number test, a small amount of reaction mixture was withdrawn from the reaction flask and dissolved in neutral solvent (equal volume of isopropanol and toluene), followed by titration using standardized KOH. The reaction was allowed to continue until the acid number of the mixture is in the range of 21–24 mg KOH/g resin. On average, the total reaction time needed to cook the alkyds is in the range of 8–9 h. The alkyd compositions are shown in Table I and a plausible synthesis route of AlkF is shown in Figure 2. Unmodified palm stearin alkyd (AlkP) was formulated without unsaturated diacids to serve as control.

### Characterization of alkyds

The alkyds produced were characterized via FTIR and $^1$H-NMR. In FTIR analyses, alkyds were applied on KBr cell and scanned on Perkin Elmer FTIR (RX 1) from 400 to 4000 $cm^{-1}$ at a resolution of



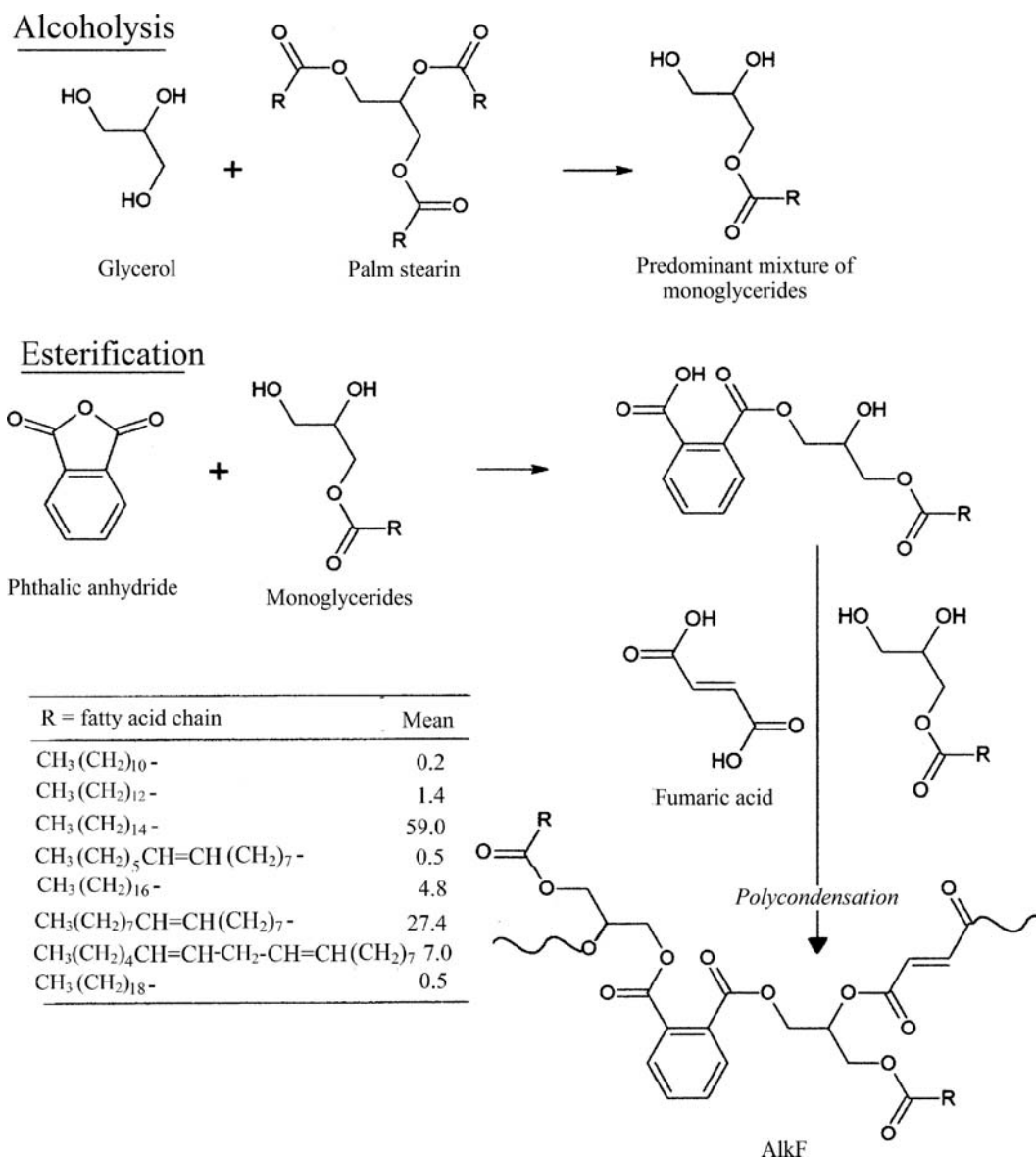| R = fatty acid chain | Mean |
|---|---|
| $CH_3(CH_2)_{10}-$ | 0.2 |
| $CH_3(CH_2)_{12}-$ | 1.4 |
| $CH_3(CH_2)_{14}-$ | 59.0 |
| $CH_3(CH_2)_5CH=CH(CH_2)_7-$ | 0.5 |
| $CH_3(CH_2)_{16}-$ | 4.8 |
| $CH_3(CH_2)_7CH=CH(CH_2)_7-$ | 27.4 |
| $CH_3(CH_2)_4CH=CH-CH_2-CH=CH(CH_2)_7$ | 7.0 |
| $CH_3(CH_2)_{18}-$ | 0.5 |

**Figure 2** Plausible synthesis route of AlkF.

4 cm$^{-1}$. $^1$H-NMR analyses were conducted on JEOL JNM-GSX 270 NMR and the samples were dissolved in deuterated chloroform with tetramethylsilane (TMS) to lock the signal at 0 ppm. Viscosity test were conducted on alkyd solutions (35% w/w of alkyd in toluene) using Ubbelohlde viscometer, with glycerol as the standard. The viscosity measured is the viscosity of alkyd solution as alkyd by itself is too viscous to be measured using Ubbelohlde viscometer.

## Preparation of coatings

Coating mixtures were prepared by mixing 6 parts alkyd : 4 parts MMA, and 9 parts per hundred parts resins (pphpr) of benzophenone was added as UV photoinitiator. MMA was introduced as the active diluent in the coating. The coating mixture was stirred at ambient temperature until it is homogenous, and the preparations were done in dim light to avoid pre-curing of the mixture. A bar coater with fixed gap 25 μm was used to coat the mixture on treated iron panel. Immediately after it was coated on the panels, the coatings were irradiated under UV light for a total of 240 s. The coatings were stored in dark compound for 24 h before evaluating their film properties. The UV-curing unit used in this work is "DYMAX UV Curing Light Source Flood Lamp System" which bears a 400 W lamp that radiates UV light (λ 365 nm) at intensity of 225 mW/cm$^2$. The curing took place at room condition.

## Determination of film properties

The film hardness of the coating was measured relative to the hardness of pencil lead (ASTM D3363). Sheen pencil hardness kit was used for this test, and the hardest pencil that failed to scratch the coating was recorded. Adhesion of the coatings was measured via crosshatch adhesion tape test method from ASTM D3359. Glass transition temperatures ($T_g$) of the cured coatings were measured using Mettler Toledo 822e while thermogravimetric analysis (TGA) thermograms were obtained using thermogravimetric analyzer (TGA 6, Perkin Elmer). Differential scanning calorimetry (DSC) scans were conducted from −60 to 60°C at a heating rate of 20 °C/min under N$_2$ atmosphere, and the $T_g$ was obtained upon heating. TGA scan were conducted from 50 to 875°C at heating rate of 15 °C/min under N$_2$ atmosphere.

In water and alkali resistant test, coating mixtures were applied and cured on glass panels. Water resistance test was conducted in two sets, with the first set of coated glass panels immersed in water for 18 h. After the immersion, the coatings were removed and the presence of any film whitening was recorded. Coatings which exhibit film whitening were left to dry at room condition, at the time needed for the whitening to disappear during the

drying was recorded as well. The second set of water resistance test was carried out to study the weight increase of the coatings during immersion in water which lasted for 66 h. The weights of the coatings were measured at the 18th, 42nd, and 66th h of immersion. Before measuring the weights of the coatings after each immersion, they were gently wiped dry to remove the water on the surface. The % weight increase of the coating from its initial weight before the immersion was recorded. Alkali resistant test was conducted by soaking the cured coatings in NaOH aqueous solution (30 g/L), and the duration of immersion in alkali solution needed for film defects to be apparent was recorded. The film defects include film whitening, blistering, and removal. The test methods were adopted from ASTM D1647.

## Enhancing film properties of alkyd coatings

Another set of alkyd coatings composed of (6 parts alkyd : 3 parts MMA : 1 part TMPTA, and 9 pphpr benzophenone) was prepared and UV cured in similar manner as the other coatings which composed of 6 parts alkyd : 4 parts MMA. Film hardness, DSC, and TGA thermograms of the two sets of coatings with different compositions were compared.

## RESULTS AND DISCUSSION

### Characterization of alkyds

FTIR spectra of AlkP, AlkF1, and AlkF2 are shown in Figure 3 and no significant difference is observed from the spectra except for the increasing intensity of the peaks at 1650 cm$^{-1}$ that corresponds to the stretching of —C=C—. In Figure 4, peak at 6.8 ppm is only apparent in the $^1$H-NMR spectra of AlkM2 and AlkF2, but absent in the spectrum of the control alkyd, suggesting that the vinyl protons of the incorporated diacids, —OOC—CH=CH—COO— resonated at 6.8 ppm. Peak at 5.3 ppm originated from the resonance of vinyl protons from the fatty acid chains, —CH=CH—. Normalized FTIR peak absorbance, $A_{1650}/A_{1440}$ is shown in Table II, along with the amount of —OOC—CH=CH—COO— in the alkyds calculated from the $^1$H-NMR spectra. The results in Table II show that the amount of —OOC—CH=CH—COO— in AlkM2 > AlkM1 and AlkF2 > AlkF1 is consistent with the amount of unsaturated diacids introduced during the syntheses (Table I).

### UV curing of alkyd coatings

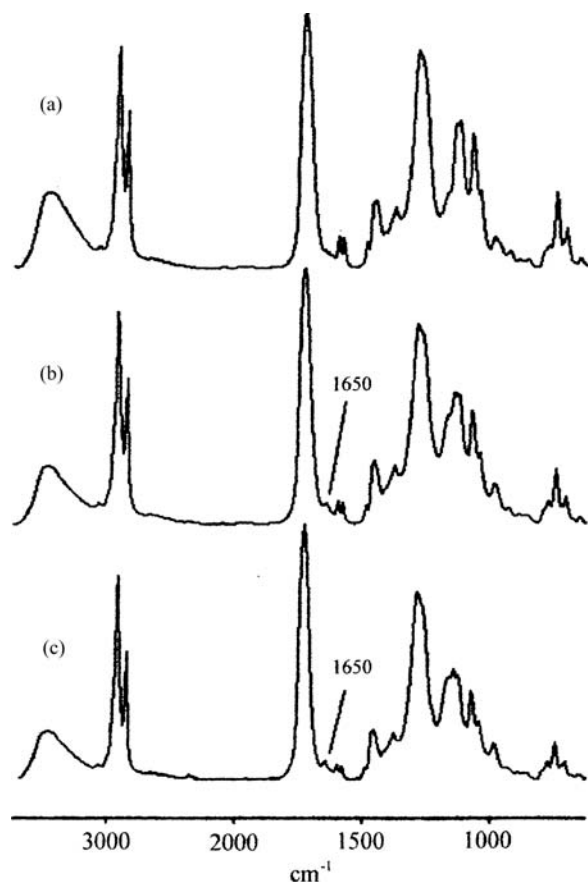The UV curability of AlkF2 coating is shown in Figure 5 where the FTIR peak absorbance at 1660 cm$^{-1}$

**Figure 3** FTIR spectra of (a) AlkP, (b) AlkF1, and (c) AlkF2.



**Figure 4** Expanded $^1$H-NMR spectra of (a) AlkP, (b) AlkF2, and (c) AlkM2, with inset of a plausible structure of fumarized alkyd.

has significantly reduced after the coating was irradiated under UV light for 60 s. It was found that under similar experimental condition, AlkF1 and AlkF2 coatings required longer UV irradiation (60 s) to achieve tack-free state as compared to AlkM1 and AlkM2 coatings (45 s). A coating is considered tack-free when the film produced is no longer tacky to touch. The slight difference in the tack-free time of the coatings may be attributed to different extent of crosslinking that took place during the alkyd syntheses. Despite of the same amount of unsaturated diacid introduced during the syntheses of AlkM and AlkF, the latter were found to have higher amount
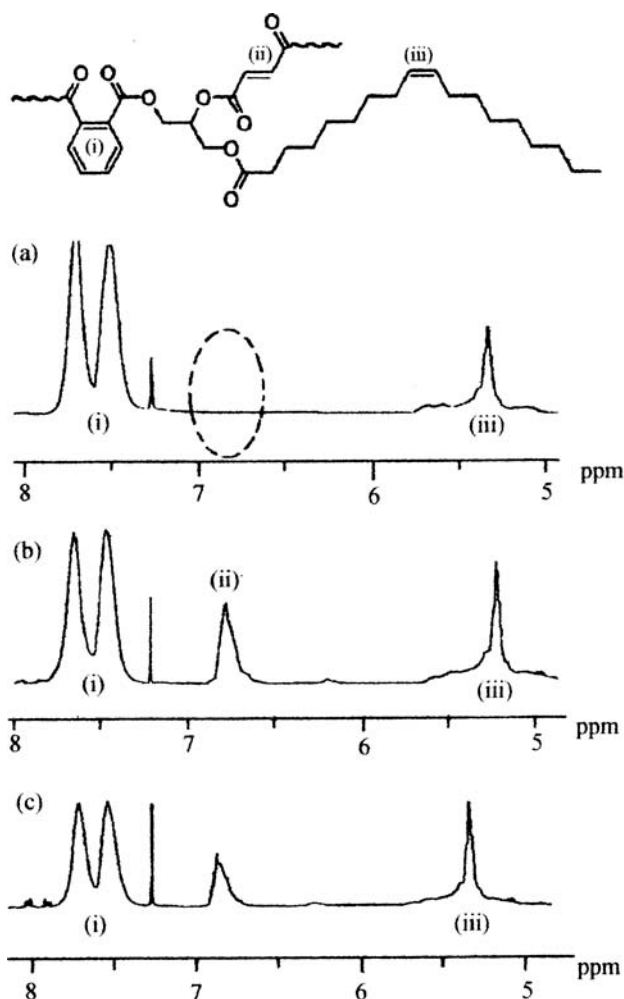
of —OOC—CH=CH—COO— (Table II). There are possibly more —OOC—CH=CH—COO— in AlkM that has undergone crosslinking during the synthesis. Viscosities of the alkyd solutions (35% w/w in toluene) in Table II also suggest that the maleated alkyds did experience greater extent of crosslinking during the syntheses as compared to the fumarized alkyds. Note that all the alkyds in this work have similar percentage of conversion, 92%. A system

**TABLE II**
**Characterization of Alkyds via FTIR, $^1$H-NMR, Viscosity Test, and Acid Number Test**

| Alkyds | FTIR $A_{1650}/A_{1440}$ | HNMR/ ($\times 10^{-4}$ mol/g alkyd) | | Viscosity of alkyd solution (35% w/w in toluene) (mPa s) | Acid number/ (mg KOH g$^{-1}$) |
|---|---|---|---|---|---|
| | | Amount of —OOC—CH=CH—COO— formulated | Amount of —OOC—CH=CH—COO— calculated from spectra | | |
| AlkP | – | – | – | 6.6 | 21.6 |
| AlkM1 | 0.39 | 7.3 | 3.5 | 12.8 | 24.0 |
| AlkM2 | 0.44 | 9.8 | 4.2 | 20.3 | 23.7 |
| AlkF1 | 0.45 | 7.3 | 4.2 | 10.8 | 24.0 |
| AlkF2 | 0.47 | 9.8 | 6.1 | 10.9 | 24.1 |

Figure 5 FTIR spectra of AlkF2 coatings at (a) 0 s and (b) 60 s of UV irradiation.

## TABLE III
### Physicochemical Properties of Alkyd Coatings Composed of 3 Parts Alkyd: 2 Parts MMA

| Alkyd coatings | Pencil hardness | $T_g$ (°C) | Adhesion | Water resistance[a] | Alkali resistance[b] |
|---|---|---|---|---|---|
| AlkP | 5B | −0.5 | 5B | X | 0.3 |
| AlkM1 | 3B | 1.8 | 5B | O | 13.0 |
| AlkM2 | H | 9.9 | 5B | O | 15.6 |
| AlkF1 | B | 3.4 | 5B | O | 9.1 |
| AlkF2 | 2H | 17.2 | 5B | O | 11.8 |

[a] Coating conditions after 18 h immersed in water (O = not visibly affected, X = presence of whitening but disappear after 2 h of drying at room condition).
[b] Duration of immersion (min) in aqueous NaOH (30 g/L) before apparent film defect.

—OOC—CH=CH—COO—/g resin produced coatings with pencil hardness 3B, while AlkF1 with 4.2 × 10$^{-4}$ mol of —OOC—CH=CH—COO—/g resin is able to produce film with pencil hardness 1B. $T_g$ of the coatings in Table III are consistent with the pencil hardness test results. These are not surprising as alkyds with higher amount of unsaturation could produce coatings with greater crosslink density upon curing, and consequently improve the film hardness, and elevate the $T_g$.

As for the adhesion test, all the coatings excelled with adhesion grade 5B to iron substrate. AlkM and AlkF coatings showed excellent water resistance as none of the coatings were affected from the 18-h immersion in water. The opposite was observed during the alkali resistance test, where all of the coatings showed defects within the first hour of immersion in NaOH solution (30 g/L), and it is attributed to the presence of abundant ester linkages in the coatings which are susceptible toward alkali hydrolysis. However, increasing the amount of unsaturation managed to increase the resistance slightly where a longer immersion is required for film defects to be apparent.

Figure 6 shows the change in the weight % of cured coatings in a separate water resistance test.

with higher amount of crosslinks have higher molecular weight polymers, and possibly highly branched structure that are responsible for the increase in the viscosity.[19] Presumably due to the higher amount of crosslinks present in AlkM prior to UV curing, it is able to achieve tack-free state slightly faster than AlkF coatings.

### Film properties of UV-cured coatings

The two series of alkyds produced coatings with different properties as shown in Table III. The cured AlkF coatings have better film hardness and this is attributed to the higher amount of unsaturation incorporated into the alkyd. For example, AlkM1 which composed of 3.5 × 10$^{-4}$ mol of
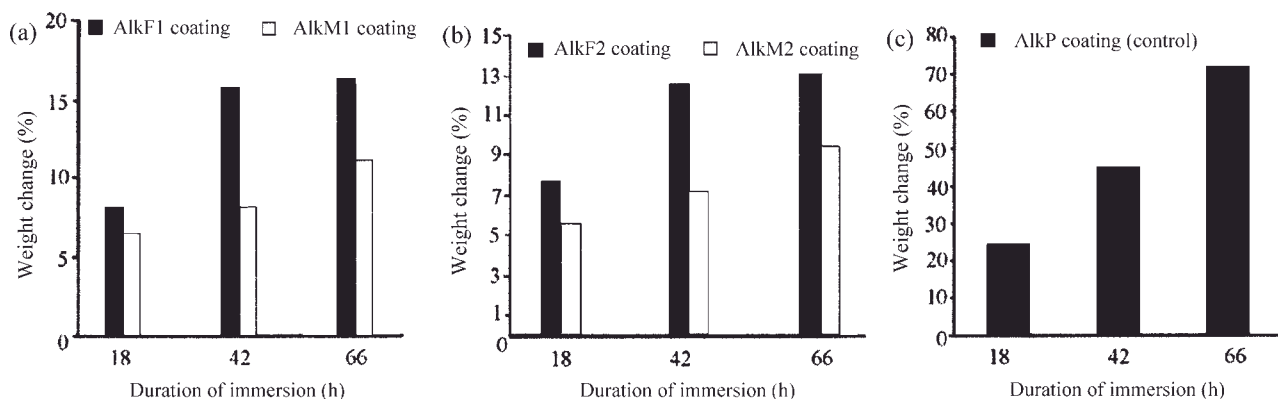


Figure 6 Percentage weight changes of cured coatings during water immersion test (a) AlkF1 and AlkM1 coatings, (b) AlkF2 and AlkM2 coatings, and (c) AlkP coatings.

Contrary to the results from pencil hardness test, and $T_g$ of the films, AlkF coatings experienced higher % weight increase than AlkM coatings after they were immersed in water for 66 h. Presumably, the presence of unreacted acids in AlkF coating could have led to the increase in water uptake as they can form hydrogen bonding with water. Despite the differences between the two series of coatings, incorporation of unsaturated diacids proved to increase their water resistance, from 71.8% increase in the unmodified alkyd coating (AlkP), to < 15% in coatings from the fumarized or maleated alkyds.

Coatings composed of 6 parts alkyd : 3 parts MMA : 1 part TMPTA were found to have better film properties. The pencil hardness test results in Figure 7(a) showed that the film hardness of the
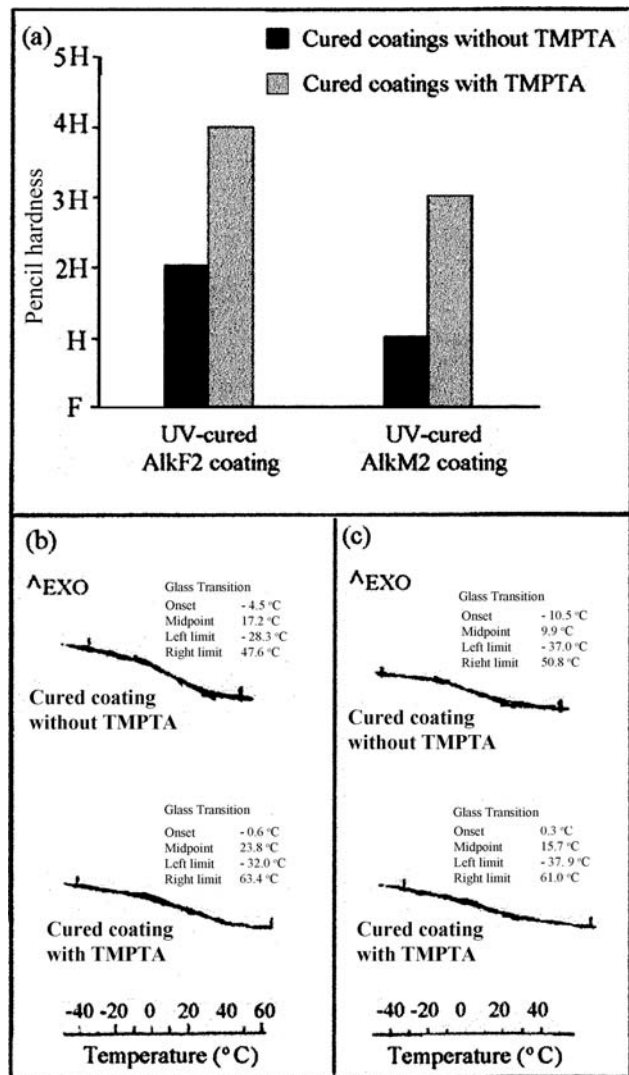


**Figure 8** (a) TGA thermograms of AlkF2 coating at two different coating compositions and (b) TGA thermograms of AlkM2 coating at two different coating compositions.

coatings has increased as a result of introducing TMPTA into the system. The trifunctional monomer served as crosslinker, where it participated in crosslinking reaction during the curing process to channel greater branching and extensive network of crosslinks. As expected, the $T_g$ of the coatings with 10% w/w of TMPTA has also improved [Fig. 7(b,c)], consistent with the pencil hardness test results. As shown in Figure 8, improvement was also observed in the thermal stability of the coatings, owing to the occurrence of 3-D crosslinking by TMPTA that has led to more crosslinked structures.

## CONCLUSION

UV-curable alkyds were synthesized using palm stearin as the source of fatty acids. The modified palm stearin alkyds are able to produce coatings with short UV-curing time, and good film properties, such as, pencil hardness 2H, good water resistance, and excellent adhesion (5B) to iron substrate. Two series of modified alkyds, AlkF and AlkM were synthesized using FA and MA respectively. Although similar experimental conditions were applied during the syntheses, AlkM was found to have lower amount of unsaturation than AlkF, attributed to



**Figure 7** (a) Pencil hardness test results, (b) DSC thermograms of AlkF2 coatings, and (c) DSC thermograms of AlkM2 coatings; without TMPTA at composition (6 parts alkyd : 4 parts MMA), and with TMPTA at composition (6 parts alkyd : 3 parts MMA : 1 part TMPTA).
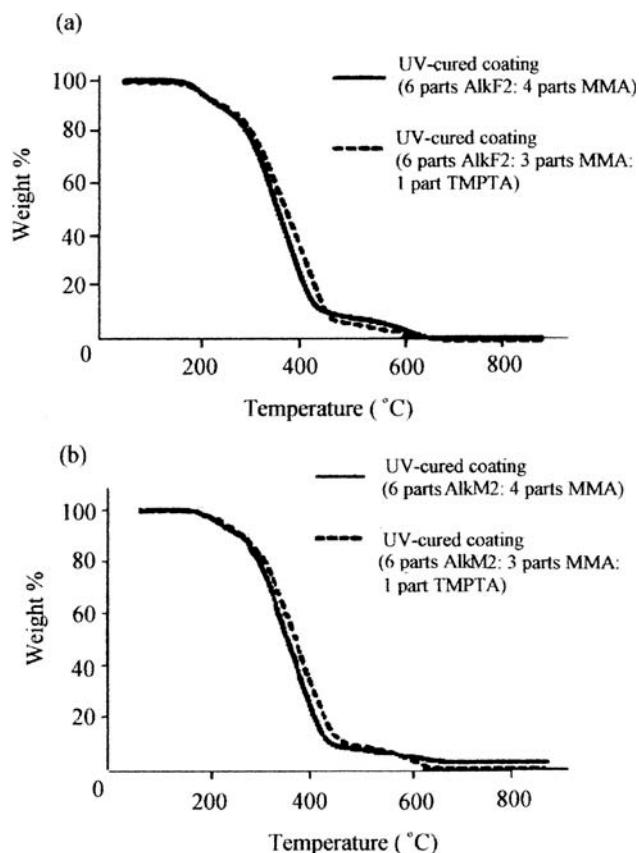
crosslinking reaction that took place during the synthesis. From the results in this work, fumarization is the better approach in introducing unsaturation into the alkyds as it allows better control of the reaction during the synthesis, and produced alkyds with relatively higher level of unsaturation. Consequently, AlkF coatings have better film hardness and higher $T_g$. Introduction of TMPTA as crosslinker managed to enhance some of the film properties of the cured coatings.

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