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Alkyd Based Resin from Non-Drying Oil

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Abstract

Palm oil-based alkyd resins were synthesized by alcoholoysis and esterification reactions. Calcium oxide was used as a catalyst for the alcoholysis reaction between palm oil and glycerin. Esterification process was carried out by using phthalic anhydride and maleic anhydride. Physico-chemical properties of the resins such as density, viscosity, acid value, iodine value, saponification value, specific gravity, and moisture content were measured following ASTM and standard methods. The structural confirmation and hydrogen density of the prepared resins were determined by Fourier transform infrared and proton nuclear magnetic resonance spectroscopy, respectively. Molecular weight of the resins was determined by using gel permeation chromatography. The curing process involved heating at 140°C, without using any organic solvent in the presence of methyl ethyl ketone peroxide and cobalt-napthenate. ASTM methods were followed to measure the gloss, hardness and chemical resistivity of the resins. Temperature behaviors were observed by differential scanning calorimetry and thermogravimetric analysis. Produced resins were found thermally stable (up to 300°C). The variations of the properties were noticed due to the types of anhydrides in terms of molecular weight, thermal and chemical resistivity of the resins, although the other properties were found close to each other. Overall, the reported properties are found suitable for the materials to be used for surface coating applications.

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Keywords: Bioresin; Non-drying oil; Alkyd; Polycondensation; Thermal properties.

1. Introduction

Recently, invention of new materials from renewable resources has been given importance due to the concern of

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sustainability, scarcity of traditional raw materials and their high price. Polymers, a versatile-used material, are majorly being prepared from petroleum-based monomer. As the reserved feed stocks of petroleum are going to be depleted soon, the alternative of those materials should be ready to meet the spiraling demand of polymer. In addition, environmental legislation and restriction on the emission of volatile organic solvent in the preparation of organic solvent-based coatings is a limitation of the traditional practices. Annually-renewable and plant-based vegetable oils are now being extensively used for polymer preparation instead. They are available at low-cost, and found environmentally-friendly. Various kinds of vegetable oils like sunflower, castor, nahar seed and palm have been utilized to produce different kinds of polymeric resins [1-4]. The potential uses of these polymers include as adhesives, surface coatings, and insulators, binders for wood and matrix for composite preparation. The previous reports on vegetable oil-based polymers showed the required level of standard as like as traditional monomer-based one.

Triglyceride oil-based polymers were reviewed earlier, where various kinds of alkyd resins and their methods of preparation with property analysis were discussed [5]. They are extensively being utilized in the paint and coating industries, and as a precursor for domestic and industrial products. The fatty acid chain in the polymer contributes improved flexibility, adhesion and chemical resistivity. Previously, nahar seed oil was studied to produce three different types of polyesters by using phthalic and maleic anhydride [3]. The produced polymeric films were found highly chemical resistant, and can be used as non-polluting coating materials. In another work, water-borne coatings were prepared from rubber seed oil [6]. Different amount of maleic anhydride (MA) were used to treat the rubber seed oil for preparing non-polluting coatings and alkyd resins. It was found that addition of MA improved the acid and saponification value, whereas iodine value found to be decreased. The produced film showed high chemical resistivity to acid and brine solution. In another work, synthesis and characterization of alkyds were studied from jatropha and rapeseed oil to prepare varnish for electrical insulating purpose [7]. The level of standard was achieved by resins prepared from the oils. Palm oil was considered to prepare alkyd, polyester acrylate and water-reducible acrylic alkyd in different studies [8-10]. Reports on those stated positive effect of using palm oil as surface coating materials. Issam and co-workers reported in their work that without using drying agent, the curing process found difficulties, but using that the produced resins showed excellent adhesion onto aluminium surface as a substrate [10]. Ali and co-workers reported the preparation and characteristics of UV-curable acrylated polyester prepolymers, synthesized from palm oil for wood coating application, in their study. Different diluents were used to prepare different types of films for pendulum hardness, gloss and impact testing. Excellent adhesion property with gloss (at 60°) ranged from 58 to 74 were revealed from the discussion. In addition, prepolymer prepared from refined, bleached and deodorized showed better performance than that of crude palm oil-based one.

Among the most commonly used plant oils in the world, palm is one of them. The huge amount of oil is being utilized as cooking oil, and the commercial applications in non-food sectors are still rare. This oil can be utilized successfully for polymer preparation. Earlier, alkyd-type resins were prepared from palm oil, but a detailed report was not found in the previous document. Moreover, the limited unsaturation in the fatty acid chains of this oil found responsible for inferior curing properties compared to other drying oil based resins. Therefore, curing agent and dryer are needed in the curing process, additionally, in spite of using heat. In this study, different types of anhydrides of dibasic acid including aromatic and aliphatic category, were used to prepare different types of alkyds, and their properties were analyzed in detailed. The feasible route of synthesis and successful formulation of this bioresin can convert this valuable bioresource to a commercial, high temperature-sustained coating for metallic or wooden surfaces.

2. Experimental

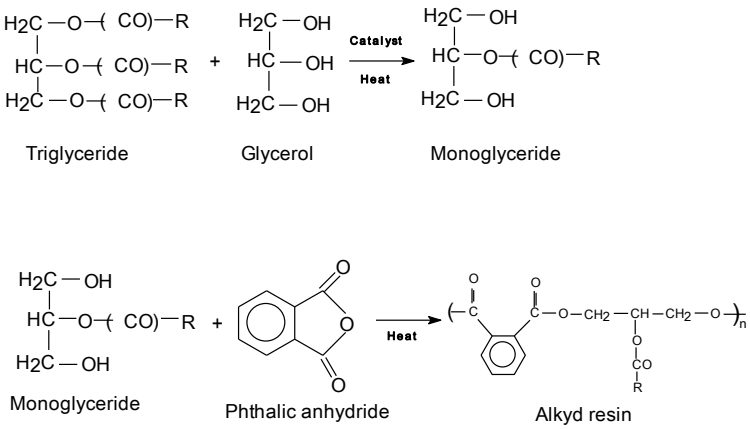
2.1. Materials

Palm oil was kindly supplied by Malaysian Palm Oil Board (MPOB). Phthalic anhydride (PA) and methyl ethyl ketone peroxide (MEKP) was purchased from Aladdin Industrial Corporation, Shanghai, China; glycerol and calcium oxide (CaO) were purchased from Aladdin Chemistry Co. Ltd., Shanghai, China. Cobalt-naphthanate was

purchased from Sigma Aldrich, USA. Maleic anhydride (MA) was purchased from Acros Organics, New Jersey, USA.

2.2. Methods

A four-necked glass vessel was used for the reactions. The vessel was placed on a magnetic heater with stirrer. An inert atmosphere was confirmed in the reaction chamber by a continuous flow of nitrogen gas. The details of the ingredients are listed in Table 1. In alcoholysis, oil, glycerol and catalyst (CaO) were taken in the reaction chamber, and heated for about 1.5 h at 230°C. The end point of the reaction was confirmed by the complete dissolution of the reaction products into methanol at a ratio of 1:3. After that, the reaction products were cooled to 120°C. In esterification process, PA and MA were used at the said ratio with the reaction products of the alcoholysis. The temperature was maintained at 230°C for nearly 2 h. The end point of the reaction was confirmed by measuring the acid value of the products. The reaction steps are illustrated in Scheme 1. After esterification, the reaction products were considered as liquid resin, and kept for further testing.



Scheme 1: Alcoholysis and esterification process

Table 1. Recipe of the preparation of resin

Resin type	Oil (g)	Glycerol (g)	CaO (g)	PA (g)	MA (g)
Resin-A	100	20	0.05	50	0
Resin-B	100	20	0.05	25	25
Resin-C	100	20	0.05	12.5	35.5

Resins are pre-polymer and usually transported in liquid state, and to be used in any application, curing is necessary. Curing process involves the formation or building of linkage or bridge among the polymer chains through the unsaturation or double bonds present in the backbone chain. Likewise normal polymerization, initiation of the curing is required and for that an initiator must start the process. In this process, MEKP (0.04 g) and cobalt nephthanate (0.02 g) were mixed with 1 g of resin and agitated manually and heated at 60°C for 10 min. After that the resins were poured onto Petridis and put in oven for drying or curing. The samples were checked frequently to trace the dryness or tackiness by using the finger tip. Only trace free samples were considered as cured polymeric film for further characterization. The time for curing was recorded as drying or curing time of the resins.

2.3. Characterization

The physico-chemical properties of oil such as acid value, iodine value, saponification value were measured

according to ASTM D1639, ASTM D5554 and ASTM D1962, respectively. The viscosity of the oil was measured by using BROOKFIELD (model- DV-IIIULTRA) programmable rheometer, USA. The measurement was taken at 20°C with the help of using spindle no. 18. The density of the oil was determined by a gas pycnometer (MICROMETRICS, model-ACCUPYC II 1340) using helium gas at 25±2°. The other properties like moisture content and specific gravity were measured using common laboratory methods. To examine the structural and functional group analysis, a Fourier transform of infrared spectrophotometer (Model- Thermo SCIENTIFIC, NICOLET AVATAR 370DTGS, USA) was used. The KBr method was employed for the analysis with scanning ranges from 400 to 4000 cm^{-1}. The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Nuclear Magnetic Resonance 500 MHz(Model: FT-NMR Avance III, Bruker, Switzerland)dissolving the samples in deuterated chloroform.

The physico-chemical and structural properties and proton density of the resins were measured following the aforementioned methods. To measure the non-volatile material content, three specimens were placed in the oven within 30 minutes after preparation of resin in previously weighted steel plate and heated for 2 h at 140°C. The non-volatile mater was calculated from the difference in initial and final weights of the plate. The mean value of the three results was reported as the percentage nonvolatile matter.

To measure the drying time, the aluminum plate of 50 x 50 x 0.1 mm^3 dimension was coated by immerging in resin at temperature 25± 2°C. The specimens were allowed to stand immersed in resin until free from bubbles and suspended for drying in dust free atmosphere. A piece of filter paper was used to check the tack free sample.

The gloss of the cured resins was measured by using a 60° gloss meter (Model-DR60A, China) and following ASTM D523 method. The pencil hardness of the cured resin was measured with the help of a pencil hardness tester (Model- B-3084) in scale of 6B to 6H of a standard set of pencils by dragging the pencil along the films, and following ASTM D3363 method. The gel permeation chromatography (GPC) machine (Model- Waters) was used to determine the molecular weight of the resins.

A thermogravimetricanalyzer, TA instrument (model- TA-Q500), and a differential scanning calorimeter, TA instrument (model- TA-Q1000), were used in nitrogen atmosphere (gas flow rate 40 ml/min) to evaluate the thermal properties of the cured films. A platinum and aluminum plate was used, respectively, for TGA and DSC analysis with sample weight nearly 5 mg. The ramp method was followed with a temperature range 30 to 600°C (heating rate 20°C/min) and 30 to 410°C (heating rate 10°C/min), respectively. To set the upper limit of the temperature for DSC analysis, TGA thermograms were used to find the degradation temperature of the cured resins.

For chemical resistance performance, near about 0.5 g of each type of cured film was immersed in various chemicals of different concentrations like hydrochloric acid (5%), sodium hydroxide (5%), sodium chloride (5%) and distilled water for 24 h at room temperature. For the test, a definite amount of material of each type was immersed in the aforementioned solutions and measured the weight loss after the time period. More the weight loss, less the resin is resistant to the respective chemical. A relative expression of the measurements such as excellent (not affected), fair (not affected but changes in color) and poor (less affected) were used to indicate the chemical resistivity of the film based on their weight losses.

3. Result and discussion

3.1. Oil properties analysis

The physico-chemical properties of the oil are listed in Table 2. The density and viscosity of the oil was found 0.8094 g/cm^3 and 86.4 mPa.s at 25°C, respectively. The specific gravity of the oil was found 0.8653, implying free from any heavy metals. The dryness of the oil was ensured by the low-value of moisture content, which was found around 0.27%. The oil was non-drying in nature with low iodine value of 46 g I_2/100 g of oil. The free fatty acid was measured by acid value found 0.65 mg KOH/ g of oil, whereas saponification value was found 209 mg KOH/g of sample. The fatty acid compositions of palm oil were found: 43.5% palmitic acid, 36.6% oleic acid, 9.1% linolic acid, 4.3% stearic acid, and 1% myristic acids.

In Figure 1, the FTIR spectrum of palm oil is illustrated. The major peaks in against of their functional groups

were identified through this observation. Peaks were detected at around 720 and 1150 cm^{-1} are probably due to the methylene rocking vibration and C-O-C stretching vibration of ester, respectively. The C-H bending vibration and C=O stretching vibration of triglyceride esters were confirmed by the peak at 1455 and 1750 cm^{-1}, respectively. The C=C stretching vibration for the unsaturated fatty acids can be depicted by the peak at 1650 cm^{-1}. The -CH stretching vibration for aliphatic compound was detected by the peaks rise at around 2855 and 2950 cm^{-1}. The -OH stretching vibrations were established by the small peaks in the region of 3200 to 3600 cm^{-1}.

Table 2: Properties of palm oil and various types of resin

Properties	Oil	Resin-A	Resin-B	Resin-C
Density (g/cm^3)	0.8094	0.9145	0.9234	0.9502
Viscosity (mPa.s) (Spindle-18, rpm-5 at 25°C)	86.4	92.1	97.2	95.6
Acid value (mg KOH/g)	0.65	1.35	2.38	4.27
Iodine value (g I_2/ 100 g)	46.33	1.24	1.75	2.03
Saponification value (mg KOH/g)	209.21	233.32	245.43	258.33
Specific gravity	0.8653	0.8967	0.8901	0.8921
Colour	Light yellow	Light brown	Light brown	Light brown
Moisture content (%)	0.27%	0.10	0.11	0.15
Non-volatile material content (%)	-	97.2	98.2	96.2
Yield (wt%)	-	67	75	62
Drying time	-	11 hr 32 min	10 hr 11 min	9 hr 23 min
Number average molecular weight (Mn)	764	768	788	869
Weight average molecular weight (Mw)	1865	2283	2374	2803
Polydispersity index (PDI)	2.46	2.97	3.01	3.23
Gloss (60°)	-	65	77	62
Pencil hardness	-	2B	2B	2B

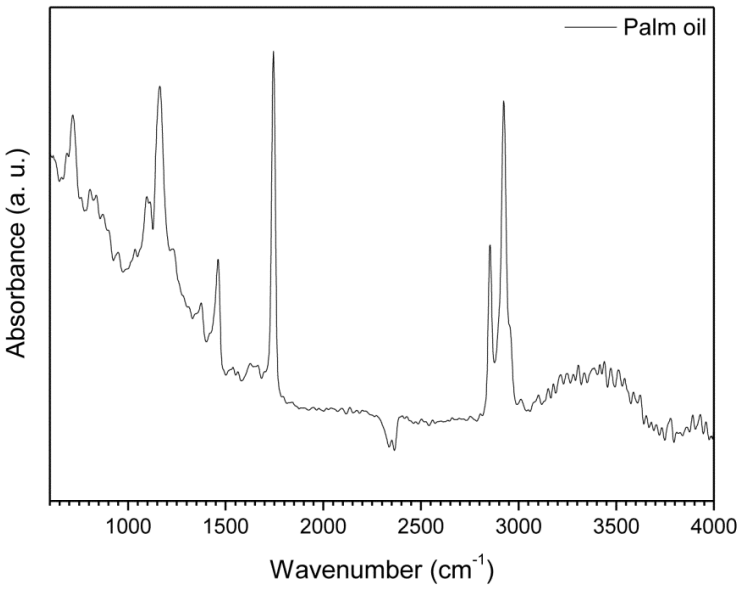


Fig. 1. FTIR spectra of palm oil

Figure 2 demonstrates the ^1H NMR spectrum of palm oil. From the figure, the peaks at δ = 0.85–0.90 ppm for the

proton of terminal methyl group. The protons of all the internal -CH_2 groups present in the fatty acids were confirmed by the peaks at δ = 1.60 ppm. Peak at δ = 2.0 and that at δ = 2.75 ppm for allylic and double allylic proton, accordingly. The α-proton of ester group found at δ = 2.30 ppm. The -CH_2- protons of glycerol found at δ = 4.1–4.3 ppm and the protons for -CH of glycerol and unsaturated carbons appeared at δ = 5.33–5.35 ppm.

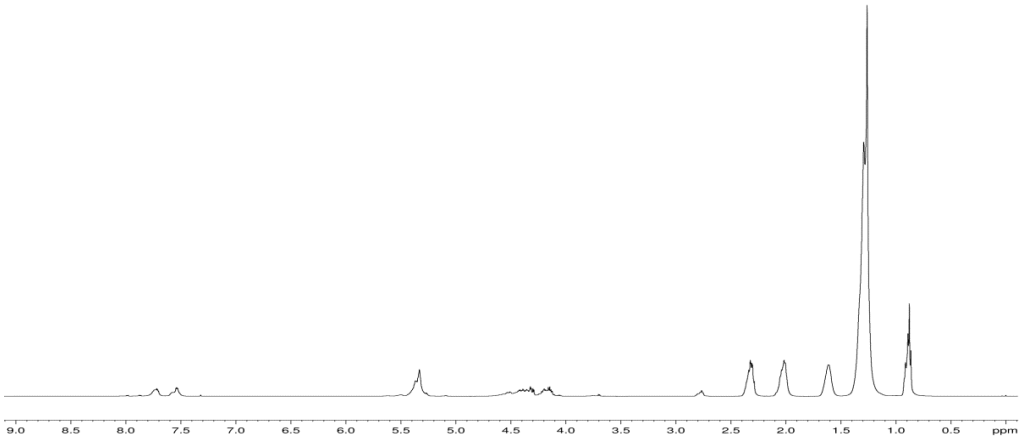


Fig. 2.^{1}H NMR spectra of palm oil

3.2. Resin properties analyses

Various physico-chemical properties such as yield, drying time, non-volatile material content, acid value, iodine value, density and viscosity of the resins were measured and listed in Table 2. The colours of the resins were light brown, whereas the that of oil was light yellow. The density of the resins was found in the range of 0.9145 to 0.9502 g/cm^3, which is higher than the oil's density. The same trend of result was observed for viscosity measurement of the resins. The viscosity of the resin A, B and C was found 92.1, 97.2 and 99.6 mPa.S at 25°C. The density and viscosity found improved due to addition of PA and MA in the polymeric chain of the alkyds. In addition, the crosslinking in the polymers are important determinate for the viscosity, which was found best in resin C compared to the others, although for the ease of application, a relatively lower viscous coating materials are suggested [10]. The acid value of the resin A, B and C was found 1.35, 2.38 and 4.27 mg KOH/g of sample, which is found lower than that of oil indicating the acidity present on them. The unsaturation of the resins found to be decreased much from the oil, measured by the iodine value of the resins, indicating the utilization of the double bonds present in the oil during the resinification reaction. The saponification values of the resins are found to be decreased with PA content decreased and the ranges were about 233 to 258 mg KOH/g of sample. However, the specific gravity of the resins found a little change compared to that of oil. Very low moisture was detected for the case of resins, around 0.1 to 0.15%. The non-volatile material content found to be as high as 96.2 to 98.2%, indicating solid portion of the resins and non-polluting category [6]. The yield% found moderate, ranged from 62 to 75%. Resin A showed 11 h 32 min, whereas resin B and resin C, respectively, showed 10 h 11 min and 9 hr 23 min. The higher drying times of the resins were because of non-drying nature of palm oil, which contain almost 51% of saturated fatty acid chains.

The functional groups and structures of the resins were determined by FTIR analysis as shown in Figure 3. From the figure, it is probable that the absorbance peak at around 750 cm^{-1} was due to aromatic -CH bending vibration, whereas the peak at 980 cm^{-1} seemingly because of C-C stretching vibration. C-O-C stretching vibrations can be depicted by the peaks at around 1120 and 1250 cm^{-1}, respectively, for aliphatic and aromatic compound. For all the three types of resins, the peaks at around 1740 cm^{-1} for the carbonyl group (C=O) stretching vibration, confirmed the

changes around the peak obtained for the same for the case of oil, at around 1750 cm^{-1}. Next to that, the asymmetric and symmetric vibration for $-CH_2$ can be ensured by the peak at around 2850 cm^{-1}, while that at 2920 cm^{-1} helped to anticipate the starching vibration for –CH moiety.

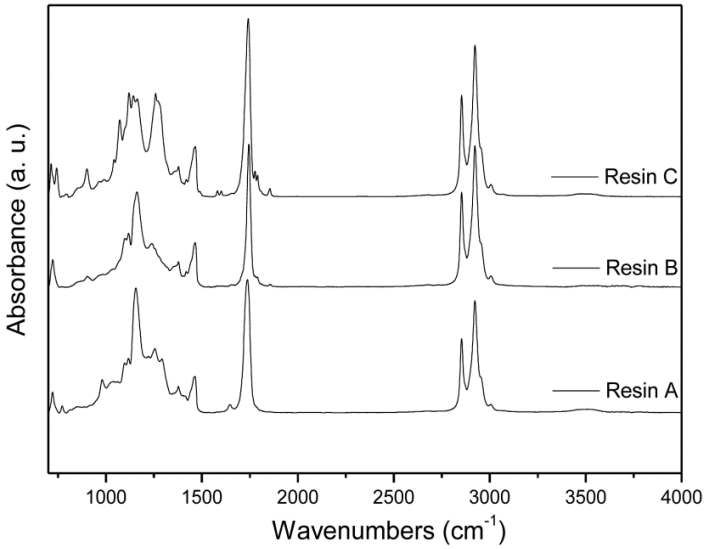


Fig. 3. FTIR spectra of different resins

The information for proton density of different moieties can be depicted in the Figure 4, 5 and 6 by ^1H NMR spectra of the resins A, B and C, respectively. The proton for terminal methyl groups of fatty acids was confirmed by the peak at around ∂ 0.87. Peaks next to that at the range of 1.25 to 1.30 are due to protons of all $-CH_2$ present in the chain. Peaks appeared at 4.2 to 4.4 probably due to the methylene protons of glycerol molecule and that at 5.25 to 5.4 are due to the unsaturated carbon. The peak appeared at 6.25 to 6.85 ppm for the -CH present in glycerol molecule. This is may be due to the presence of anhydride groups from the MA and PA, which results in deshielding effect. The proton for the aromatic ring can be depicted by the peak at ∂ 6.8–7.5.

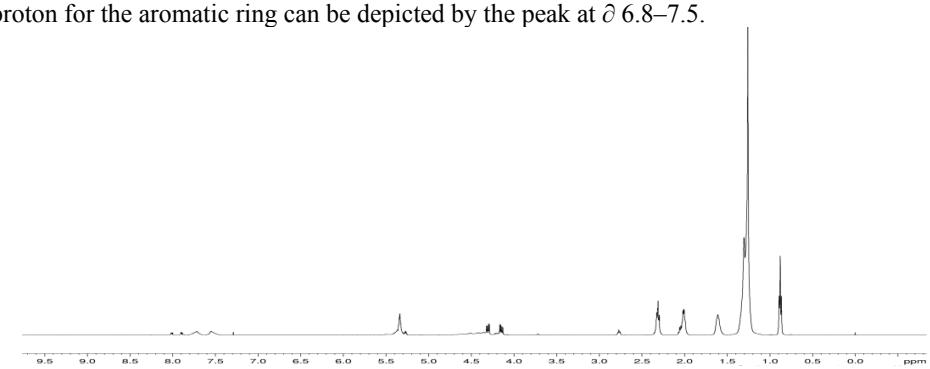


Fig. 4. ^1H NMR spectra of Resin A

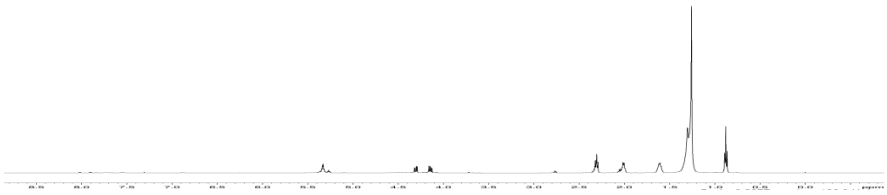


Fig. 5. ^{1}H NMR spectra of Resin B

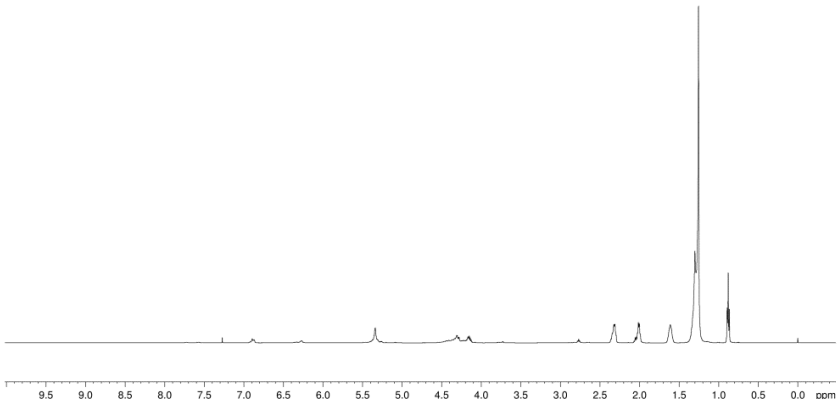


Fig. 6. ^{1}H NMR spectra of Resin C

An acceptable gloss at 60° was shown by the resins of values 75, 87 and 72. The drying time found high for all the three resins. The number average molecular weight (Mn) of the resins were found 768 (resin A), 788 (resin B) and 869 (resin C), while the weight average molecular weight (Ww) found for the resins, respectively, 2283, 2374 and 2803. The increase of molecular weight probably due to higher crosslinking density with higher amount of MA present in the resins. Thus the polydispersity index also found increasing as an order of resin C> resin B> resin A (Table 2). Finally, the hardness found similar for all the resins. Although the film hardness depends on the crosslinking density of the surface of the film, which may be highest in the resin C, but presence of stable and rigid aromatic moiety in the backbone chain of the PA-based film (resin A) also showed the similar [11-12]. Resin B showed the same behaviour due to presence of both aromatic and aliphatic anhydride in their backbone chain.

The thermal stability and degradation profiles of various cured films are presented in Figure 7. From the thermogravimetric analyses, it was found that nearly 1 to 2 wt% of moisture was removed during heating above 100°C for all the films. The removal of moisture and weight loss for that was confirmed by the isothermal heating of the polymers at 110°C for 2 h, which indicates a same amount of weight loss without any change in chemical structure as observed by FT-IR spectroscopy. It was found that all the types of films shown a higher thermal stability and the initiation of the degradation started near about at 306°C. It was found that resin C shows the highest thermal stability than the others. The onset degradation temperatures were found to be 306, 312 and 315°C for the case of Resin A, Resin B and Resin C, respectively. The order of thermal stability is as follows: Resin C > Resin B > Resin A. The higher thermal stability is may be due to increase in cross linking density because of higher percentages of MA. The residues after 600°C for all the samples were found in the range of 5-7 wt%. The thermal stability of these resins was found high enough to be used for any type of high-temperature-sustained surface coating application.

The DSC thermograms of the films are illustrated in Figure 8. From the graph, a general idea can be depicted about the melting temperature of the cured resins. The thermosetting resins showed a broad region close to the melting point. The melting temperature found maximum, 335°C, for the case of resin C, whereas the other two, resin B and resin A, showed 313 and 306°C, respectively. For resin B, a broad peak ranging from 313 to 340°C was found

due to the reflection of the equally presence of both the aliphatic and aromatic anhydride in the backbone chain of the polymer. The higher crosslinking density due to the presence of MA and higher thermal stability of aromatic ring because of PA, are probably the reasons behind the thermal behavior showed by resin B.

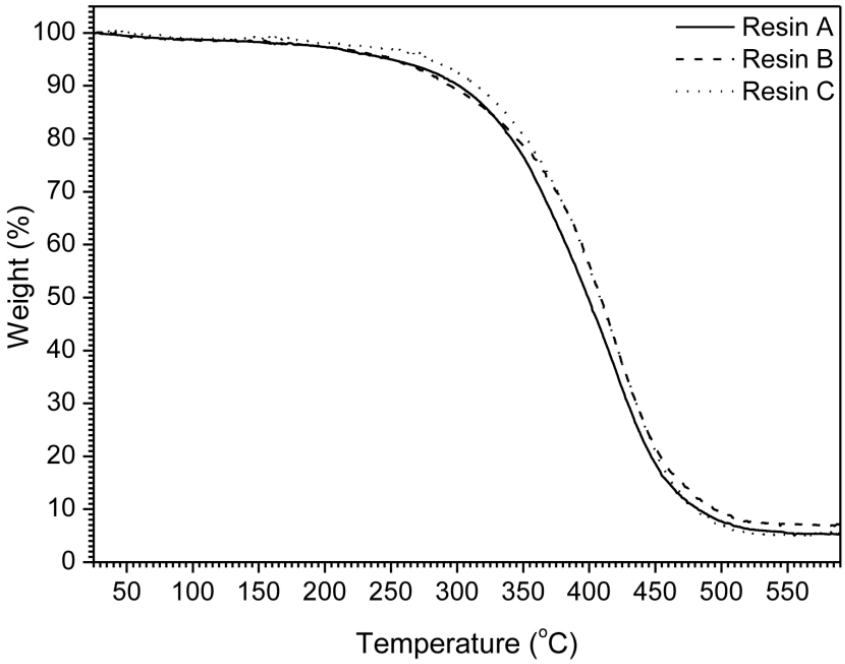


Fig. 7. Weight vs. temperature curves of different resins

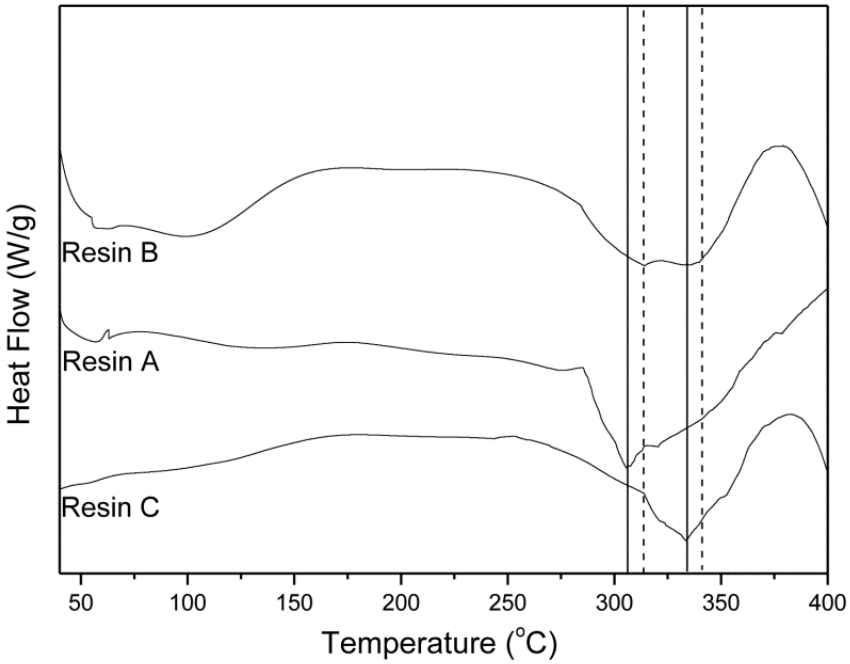


Fig. 8.DSC thermograms of various resins.

The chemical resistance performances of various cured films are presented in Table 3. It was observed that all kinds of films were unaffected and highly resistant to distilled water, aqueous sodium chloride solution during the immersion period. Among the resins, resin A showed superior resistivity than the other two types of resins. For example, resins based on PA showed excellent resistivity to NaOH solution and fairly resistivity to HCL solution, and this may be due to the presence of aromatic functional group, whereas MA-based resins were found fair and poor resistant to the alkali and acid solution, respectively. The poor resistivity to alkali is probably due to hydrolysable ester group present in the resin B and C [13].

Table 3. Chemical resistivity of various types of resins

Solution	Resin-A	Resin-B	Resin-C
Distilled water	Excellent	Excellent	Excellent
5%HCl (aq.)	Excellent	Fair	Fair
5%NaOH (aq.)	Fair	Poor	poor
5%NaCl (aq.)	Excellent	Excellent	Excellent

4. Conclusion

Three different types of alkyds were prepared fruitfully with adequate yield percentages from palm oil by following alcoholysis and esterification reaction, and using different rations of phthalic and maleic anhydrides. The structural confirmations of these resins were determined by FTIR and ^{1}H NMR technique. The properties of these bio-based resins were found influenced significantly by the variations of the rations of the anhydrides. Overall, high gloss, good hardness, sufficient molecular weight and PDI with excellent resistivity to water, acid and alkali were noticed by the property evaluation of these resins. In addition, high temperature sustainability was also observed, which suggests these materials to be applicable for surface coating and binders for composites.

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