



Synthesis, characterization and characteristics of waste-palmolein oil-based alkyd resins and their blend with epoxy resin

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The aim of this work is the valorization of waste palmolein oil. To attain the goal, the waste oil was purified and then converted to alkyd resin, by the two stage alcoholysis-polyesterification process. In the first stage the triglyceride was converted to monoglyceride by transesterification reaction with glycerol. The monoglyceride was then reacted with phthalic anhydride and/or maleic anhydride to synthesize the alkyd. The alkyd was then cured at 120°C in presence of epoxy to produce cured blend of alkyd and epoxy. It was then evaluated by assessing the adhesion, pencil hardness, gloss, thermal stability and chemical resistance, for possible coating applications. The values obtained for all these properties indicated positively for end use in coating applications.

Keywords: Waste palmolein oil, alcoholysis-polyesterification, polycondensation, alkyd resin.

Introduction

There has been a growing awareness and alarm on the finite and depleting nature of petroleum resources. It has become a cause of concern because the petroleum is the mother of all organic chemicals including polymers. So, there is a concerted search for an alternative source and the main target is biomass. Further, the linear route of production which is based on the tenet extract → use → discard is considered as the main reason for resource crunch, environmental degradation and generation of unmanageable amount of waste of diverse nature. Such realizations resulted in the propagation of the idea of circular economy in general and circular chemistry in particular^{1,2}. In the circular model, waste is considered as a highly useful resource. Waste as a resource cannot and must not be ignored if the aim is to achieve circularity of the resources and sustainability³.

Waste vegetable oil generated during cooking, constitute an important resource. It is reported that about 378 million L of waste cooking oil are produced per day in USA alone. Canada, European countries and UK are reported to produce 1,35000, 7,00000–10,00000 and 2,00000 tons of waste cooking oil per year respectively⁴. India consumes 22 mil-

lion tons of vegetable oil annually, producing about three to four million tons of waste cooking oil per year⁵. As the left-over oil after cooking has no food value, it is immensely important to find ways to produce value added products from it. The huge amount of waste cooking oil generated per year has already caught the attention of the industry. At present, the major use of waste cooking oil is in the energy sector for the production of bio-diesel^{6–9}. However, there is a great potential for the use of waste cooking oil in the paint and coating industry as well. This is because; the vegetable oils had been in use in the production of alkyds^{10–14}, for use in paint and coating formulations. Alkyds have several good attributes as coating materials such as strength, rapid drying, good adhesion, flexibility, gloss, good surface wetting, good penetration and good weathering behaviour¹⁵. The present work describes the use of waste palmolein oil as a feedstock for the synthesis of alkyds, their characterization and investigation on the characteristics for coating applications of its blend with epoxy resin.

Materials

Waste palmolein oil (WPO) was collected from the hotels near Gauhati University campus, Guwahati, Assam, India.

Analytical grade phthalic anhydride (Merck, Mumbai, India), maleic anhydride (SRL, Mumbai, India), litharge (PbO) (Qualigens, Mumbai, India) and glycerol (Fisher Scientific, Mumbai, India) were used as received. Commercial grade epoxy resin, epoxy hardener and cobalt-octoate were also used as received (Kumud Enterprise, Kharagpur, India). Silica gel (60–120 mesh) (Merck, Mumbai, India), petroleum ether (40–60°C) (Merck, Mumbai, India) and ethyl acetate (Merck, Mumbai, India) were the other chemicals used.

Methods

Purification of oil:

A silica gel (60–120 mesh) column was used to purify the waste oil. A mixture of 98% petroleum ether and 2% ethyl acetate was used as the eluting solvent. The eluent from the column was distilled under reduced pressure at 45°C to recover the pure oil.

Physicochemical properties of purified oil:

The standard procedures as per the American Society for Testing and Materials (ASTM), standards and American Association of Cereal Chemists' (AACC) international methods^{16–19} were followed to determine the physicochemical properties of the oil. The properties evaluated were acid value, % FFA, iodine value, specific gravity, refractive index, saponification value and peroxide value.

Determination of fatty acid composition of the oil:

The fatty acid composition of the oil, was determined in an indirect manner, first by converting the fatty acids of the oil into their methyl esters. A Perkin-Elmer Clarus 600 GC-MS equipped with an elite 5 MS (30.0 m×250 μm) capillary column was used for the analysis of the methyl esters. The oven temperature was maintained at 80°C for 5 min, then increased to 240°C at the rate of 10°C/min and finally kept at this temperature for 15 min. Temperatures of the injector, transfer and source were maintained at 220, 200 and 150°C respectively. Nitrogen was used as a carrier gas and total scan time was 35 min. MS was scanned from 20 to 400 Da. For identification of esters in fatty acid methyl esters of palmolein oil, library search was carried out using NITS, NBS and Wiley GC-MS library.

Spectroscopic analysis of the oil:

¹H NMR spectrum of the oil was recorded in a Bruker Advance III 300 MHz/54 mm NMR spectrometer. The solvent used was CDCl₃. FT-IR spectrum was recorded in KBr

plate. A Shimadzu FT-IR spectrophotometer in the range 450 to 4000 cm⁻¹ was used.

GPC of oil:

A Waters gel permeation chromatography unit equipped with styragel column (HR series 3, 4E) and a differential refractometer detector was used to determine the average molecular weight of the oil. HPLC grade tetrahydrofuran (THF) was the eluting solvent. The flow rate was 0.7 mL/min at room temperature.

Synthesis of alkyd resins

Alcoholysis-esterification process²⁰ was followed for the synthesis of alkyds. Three variants of alkyd resins from WPO were prepared, by varying the compositions of the constituents. The weight of the constituents are given in Table 1A and a schematic presentation of the synthetic process is presented in Fig. 1. The synthesis was carried out in a three necked round bottomed flask fitted with a mechanical stirrer, a thermometer and under a nitrogen atmosphere. A mixture of 33.88 g (0.04 mol) of palmolein oil, 7.36 g (0.08 mol) of glycerol and 0.05 weight percent (with respect to the oil) of PbO were heated at 225–230°C with continuous stirring at a constant speed of 450 rpm for 45–60 min until the formation of monoglyceride was complete. Methanol solubility test²¹ was used to confirm the completion of monoglyceride formation process. Aliquots of the reaction mixtures were withdrawn at different interval of time during the reaction and were tested with 3 volumes of methanol. A transparent clear liquid indicated the formation of monoglyceride. After conversion of oil to monoglyceride, the reaction mixture was cooled to 120°C and 0.12 mol of acid anhydride in the form of fine powder and 1.98 g excess of glycerol (27%) were added. The reaction temperature was then increased to 210°C. The reaction was continued at this temperature until an acid value in the range of 25–40 mg KOH/g was attained.

Curing of alkyd resins

The palmolein oil is not a drying oil. So, alkyds from it are generally cured by blending with another resin with better drying property. In the present case, alkyds were cured by blending with epoxy resin and epoxy hardener. 3 g of alkyd resin was mixed thoroughly with 2 g of epoxy resin for 5 min. Then 1 g of epoxy hardener (50 wt.% of epoxy resin) and 0.07 g of cobalt-octoate (~2 wt.% of alkyd resin) as accelerator were added to it. After 10 min of continuous mixing, it

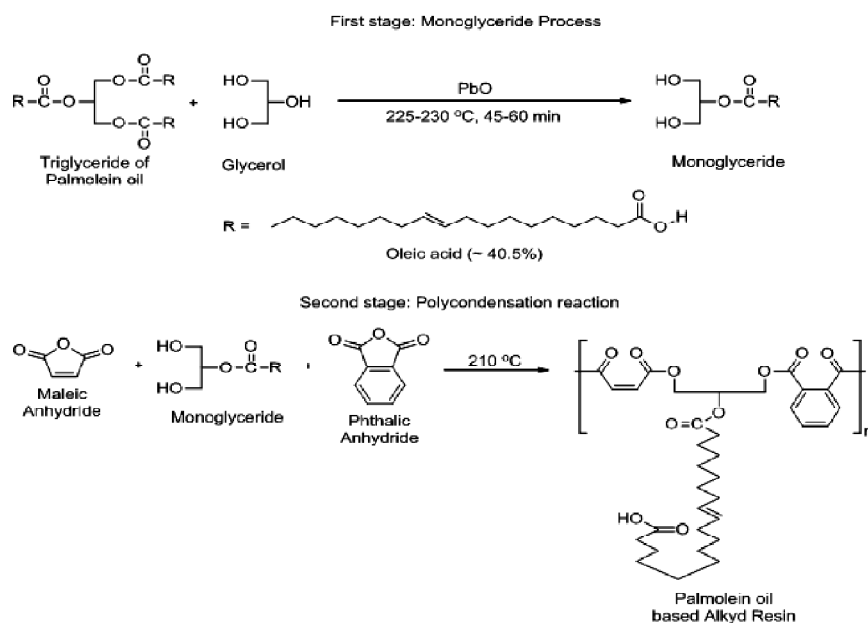


Fig. 1. The synthetic pathway palmolein oil alkyd resin.

was uniformly coated over Teflon coated pan. The pan was then heated in an oven at 60°C and gradually the temperature was raised to 130°C by slowly increasing the temperature at the rate of 10°C/h. The pan was taken out of the oven at different time intervals and checked for hardening of the film by pressing fingertip. The heating was stopped when the film hardened and time required for hardening is recorded.

Characterization and evaluation of pristine alkyd resin

¹H NMR spectra were recorded in a Bruker Advance III 300 MHz/54 mm NMR spectrometer. The solvent was CDCl₃. A Shimadzu FT-IR spectrophotometer was used to record the FTIR spectra. The spectra were recorded in the range 450 to 4000 cm⁻¹. Acid value, %FFA, iodine value, solubility, curing time, curing temperature etc. were evaluated on the prepared alkyd resins by following standard protocols. The gloss, adhesion and pencil hardness of the films of the alkyds were tested in accordance with the standard procedures. The behavior of the films in various solvents and reagents was tested. The thermal stability of the films was determined by thermogravimetric analysis in a Mettler Toledo TGA/DSC 1 Star thermogravimetric analyzer system.

Determination of volatile matters

Equal mass of each pristine resin samples were heated

in a hot air oven at 110°C and after a fixed interval of time, weight was recorded. Heating was continued until a constant weight was obtained.

Results and discussion

Physico-chemical properties of WPO:

The acid value, refractive index, specific gravity, free fatty acid, iodine value and saponification value of the WPO are presented in Table 1B.

Fatty acid composition of WPO:

Table 2 shows the fatty acid composition of WPO. The major constituents are oleic acid (C18:1) and palmitic acid (C16:0), other constituents are linoleic acid (C18:2), stearic acid (C18:0) and myristic acid (C14:0).

Spectroscopic analysis of oil

FT-IR analysis:

The FT-IR spectrum of WPO is presented in Fig. 2. The major absorption peaks and their assignments are given in Table 3A.

¹H NMR analysis:

¹H NMR spectrum of the WPO is shown in Fig. 5A. The major peaks and their assignments are presented in Table 3B.

Table 1

(A) Compositions of alkyd resins from WPO					
Alkyd code	Oil (g)	Composition	MA (g)	PA (g)	Glycerol (g)
WPOR ₁	33.88	100% PA	0	17.77	9.34
WPOR ₂	33.88	50% PA + 50% MA	5.883	8.89	9.34
WPOR ₃	33.96	75% MA + 25% PA	8.825	4.44	9.34
(B) Physicochemical properties of WPO					
Properties	Values				
Acid value (mg KOH/g)	0.34				
Refractive index (30°C)	1.462				
Specific gravity (30°C)	0.920				
Free fatty acid (mg/g)	3.676				
Iodine value (g I ₂ /100 g)	55.69				
Average molecular weight (g/mol)	847				
Saponification value (mg KOH/g)	207				

Table 2. Fatty acid composition of WPO

Fatty acid	Chemical name	Common name	Formula	% (wt.%)
C14:0	1-Tetradecanoic acid	Myristic acid	C ₁₄ H ₂₈ O ₂	0.96
C16:0	Hexadecanoic	Palmitic acid	C ₁₆ H ₃₂ O ₂	40.04
C16:1	9Z-Hexadec-9-enoic acid	Palmitoleic acid	C ₁₆ H ₃₀ O ₂	0.16
C18:0	Octadecanoic	Stearic acid	C ₁₈ H ₃₆ O ₂	4.04
C18:1	<i>cis</i> -9-Octadecenoic	Oleic acid	C ₁₈ H ₃₄ O ₂	40.5
C18:2	<i>cis</i> -9, <i>cis</i> -12-Octadecadienoic	Linoleic acid	C ₁₈ H ₃₂ O ₂	13.92
C18:3	<i>cis</i> -10-Nonadecenoic acid	Linolenic acid	C ₁₈ H ₃₀ O ₂	0.13
C20:0	Eicosanoic acid	Arachidic acid	C ₂₀ H ₄₀ O ₂	0.25
Σ SFA ^a			45.29	
Σ MUFA ^b				40.66
Σ PUFA				14.05
S/P ^d				3.22

^aTotal saturated fatty acids. ^bTotal monounsaturated fatty acids. ^cTotal polyunsaturated fatty acids. ^dThe ratio of saturated to polyunsaturated fatty acids.

Table 3

(A) FT-IR absorption bands in WPO and their assignments		(B) Assignment of ¹ H NMR peaks of WPO	
Band (cm ⁻¹)	Assignment	Peak (δ ppm)	Assignment
3471.87	O-H stretching vibration	0.87–0.89	Protons of terminal methyl group
2924.09	Aliphatic C-H stretching vibration	1.60	Protons of internal -CH ₂ - groups
1743.65	C=O stretching vibration	2.01–2.05	Allylic protons of -CH ₂
1658.78	C=C stretching vibration	2.30–2.32	Alpha protons of ester groups
1454.33	C-H bending vibration	2.75–2.78	-CH ₂ of double allylic protons
1165.00	C-O-C stretching vibration	4.15–4.28	Protons of glyceride moiety
		5.32–5.35	Protons of the -CH=CH- moiety

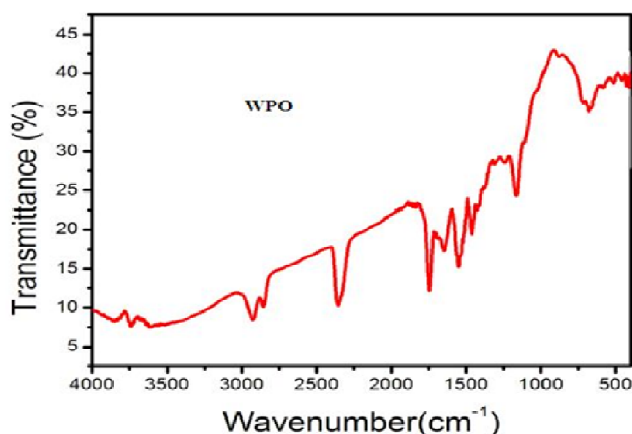


Fig. 2. FT-IR spectrum of waste palmolein oil.

Synthesis of alkyd resins

On reacting WPO with glycerol in the presence of catalyst litharge (PbO) at 230°C, a mixture of monoglyceride, diglyceride, triglyceride and glycerol is formed. This mixture is technically referred to as monoglyceride²². It when heated with phthalic and/or maleic anhydride at 210°C, it forms the polyester, the alkyd resin. The acid value was measured at different time interval to monitor the extent of polyesterification. The reaction was stopped as soon as the acid value was attained in the range of 25–40.

Physical properties of pristine alkyd resins

Table 4A shows some of the physical properties of WPO

based alkyd resins. With the rise in amount of MA in the reactant composition, gel formation was observed. In such cases, the reaction was deliberately stopped at an early stage. The saponification value increased as the amount of phthalic anhydride decreased. Resins WPOR₃, having the highest content of MA, exhibit the maximum viscosity. The amount of volatile matter is low (3.17–4.37%) for all the resins and hence the resins may be suitable for non-polluting coating applications¹³.

Spectroscopic analysis of pristine alkyd resins

FT-IR analysis:

The FT-IR spectra of the alkyds from waste palmolein oils are presented in Fig. 3. The important absorption peaks and their assignments are shown in the Table 4B. Absorption due to ester group was observed at 1742–1743 cm⁻¹ and 1736–1739 cm⁻¹ for the oils and resins respectively. The change in values from oils to resins was indicative of change in structural environment around the ester carbonyl groups in resins due to reactions with phthalic and maleic anhydrides.

¹H NMR analysis:

¹H NMR spectra of the resins from WPO are shown in Fig. 5B. The major peaks and their assignments are presented in Table 5A. There is not much difference with the ¹H NMR spectrum of the oil, with only a few distinctive differences. The major difference is in the appearance of aromatic

Table 4

(A) Physicochemical properties of the synthesized alkyd resin					
Alkyd code	Acid value (mg KOH/g)	Free fatty acid (mg/g)	Saponification value (mg KOH/g)	Volatile matter (%)	Physical appearance
WPOR ₁	27.5	15.79	319.5	3.16	Dark brown transparent
WPOR ₂	33.57	13.70	326.8	3.70	Dark brown transparent
WPOR ₃	39.56	10.856	336.8	4.35	Dark brown transparent
(B) Absorption bands in resins and their assignments					
Absorption bands (cm ⁻¹)			Assignment		
WPOR ₁	WPOR ₂	WPOR ₃			
3437.15	3429.43	3452.58	O-H stretching vibration		
2924.09	2924.09	2924.09	Unsaturated C-H stretching vibration		
1736.78	1735.93	1739.79	C=O stretching vibration		
1639.49	1643.35	1627.92	C=C aromatic vibration		
1130.29 and 1276.88	1161.15 and 1280.73	1165.00 and 1280.73	C-O-C stretching vibration attached with aliphatic and aromatic moiety		
981.89	983.70	975.98	C-C stretching vibration		

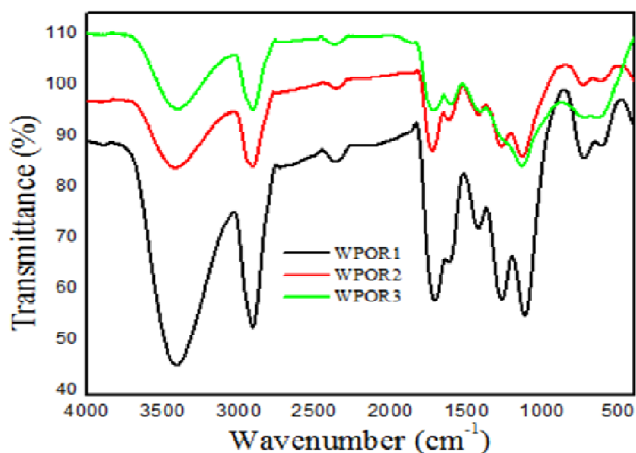


Fig. 3. FT-IR spectra of resins WPOR₁, WPOR₂ and WPOR₃.

protons in the spectra of resins from the phthalic anhydride. The second difference was observed in the signal due to methyl protons of glyceride moiety observed at δ 6.87–6.90 ppm. It may be due to the deshielding effect of benzene ring in phthalic anhydride²³.

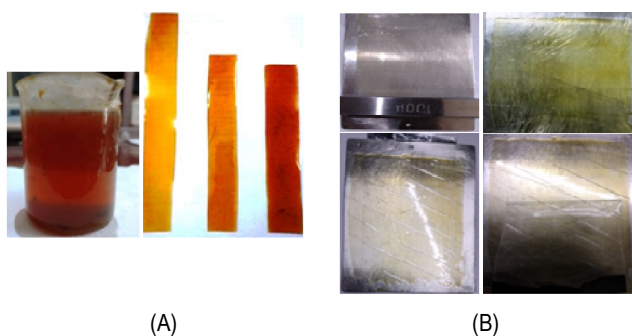


Fig. 4. Images showing (A) prepared and cured alkyd resin and (B) adhesion test.

Curing of alkyd resins

Table 5B shows curing time and temperature of WPO based alkyd resins. From the data, it can be concluded that with the increase of maleic anhydride content in resin, the degree of unsaturation increased, which decreased the curing time. WPOR₃ (75% MA) show the lowest curing time (3 h at 90°C) whereas the WPOR₁ (0% MA) has the highest curing time. This is because, the presence of unsaturation facilitated crosslinking²⁴.

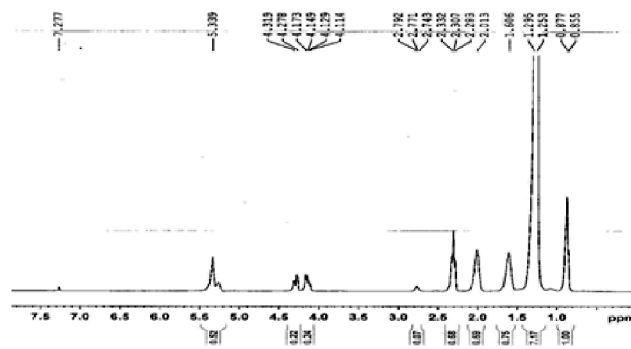


Fig. 5A. ¹H NMR spectrum of waste palmolein oil.

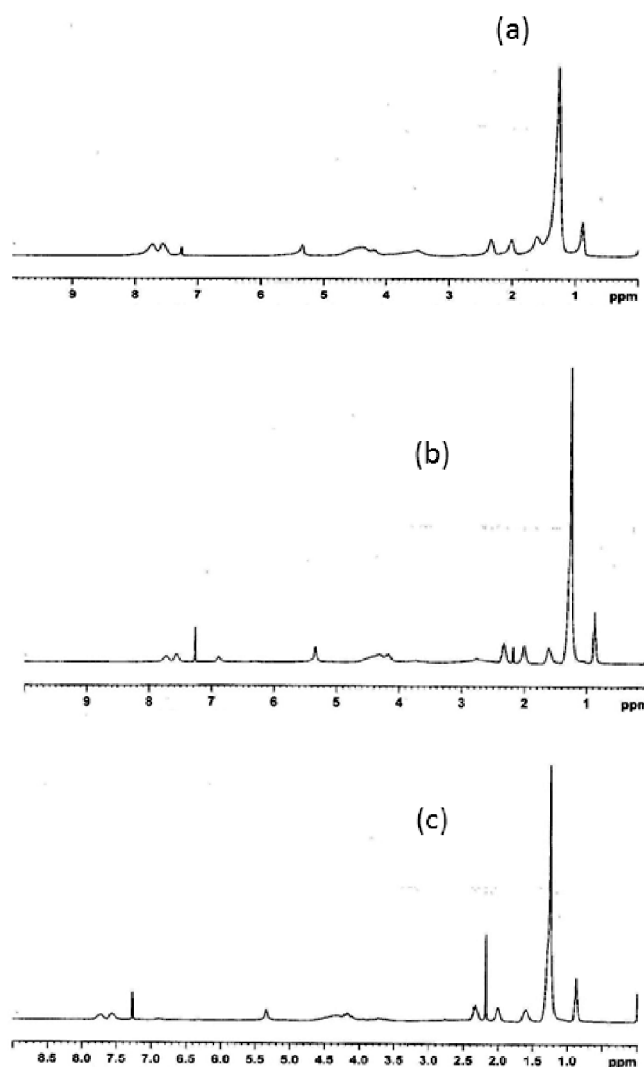


Fig. 5B. ¹H NMR spectra of resins from waste palmolein oil: (a) WPOR₁, (b) WPOR₂ and (c) WPOR₃.

Table 5

(A) ¹ H NMR peaks of the resins and their assignments			Assignment		
WPOR ₁	WPOR ₂	WPOR ₃			
0.85–0.87	0.85–0.87	0.85–0.87	Protons of terminal methyl group		
1.25	1.25	1.25	Protons of all the internal -CH ₂ - groups present in the fatty acid chain		
1.60	1.60	1.60	Protons of -CH ₂ - group attached next to the above terminal methyl group		
3.63–4.46	3.63–4.46	3.63–4.46	Methylene protons of glycerol moiety		
5.34	5.34	5.34	Protons of unsaturated		
6.87–6.90	6.87–6.90	6.87–6.90	Protons for -CH- of glyceride moiety		
7.56–7.72	7.56–7.72	7.56–7.72	Aromatic protons		
(B) Curing time and temperature of alkyd resins		(C) The pencil hardness, adhesion and gloss properties of cured resins			
Alkyd code	Curing time (h)	Alkyd code	WPOR ₁	WPOR ₂	WPOR ₃
WPOR ₁	4.5 h at 130°C	Pencil hardness	H	HB	2B
WPOR ₂	3.5 h at 110°C	Adhesion (%)	100	100	100
WPOR ₃	3 h at 90°C	Gloss (60°)	88	81	78

Physical properties of the cured alkyd resins

The properties of the films from cured alkyd resins from WPO are given in Table 5C. The pencil hardness value is highest for resin WPOR₁ with 100% PA. The presence of rigid aromatic moiety from phthalic anhydride accounts for the higher pencil hardness^{24,25}. The adhesion characteristics of all the resins are very good due to the presence of polar ester bonds²⁶. The gloss property of the resins was also found to be good. These results indicate that the resins have the potential for surface coating application²⁷.

Chemical resistance

The performances of the cured resins from WPO under different chemical conditions are given in Table 6. For this, equal mass of each cured film was dipped in the reagents and after a fixed time period, weight change was measured. More the weight loss less is the resistance of the resin to the respective reagent and vice versa.

It was found that resins are highly resistant to dilute HCl, aqueous NaCl solution, aqueous C₁₉H₄₂BrN (CTAB) solution, dilute C₁₆H₃₄ (hexadecane), hot water and distilled water. Resins WPOR₁ (100% PA) is fairly resistant to alkali. It may be due to the resistance of aromatic ester groups towards hydrolysis¹². But the resins with maleic anhydride show poor resistance to alkali. This poor alkali resistance of the resins may be traced to hydrolysable aliphatic ester groups²⁶.

Thermal analysis

The thermo gravimetric analysis (TGA) of the cured resins was done in an inert atmosphere (N₂ atmosphere) to measure the thermal stability of the cured alkyd resins. The TGA curves of the cured resins are given in Fig. 6. All the resins showed one-step degradation pattern. The residual weights observed at the end of thermal degradation are also comparable. The temperature for the major weight loss for WPOR₁, WPOR₂ and WPOR₃ were observed at 385°C, 388°C and 394°C respectively.

Table 6. Chemical resistance of cured resins

Alkyd code	10% HCl	0.5 N NaOH	10% NaCl	Distilled water	Hot water (80°C)	10% Hexadecane	10% CTAB
WPOR ₁	Excellent	Fair	Excellent	Excellent	Excellent	Excellent	Excellent
WPOR ₂	Excellent	Poor	Excellent	Excellent	Excellent	Excellent	Excellent
WPOR ₃	Excellent	Poor	Excellent	Excellent	Excellent	Excellent	Excellent

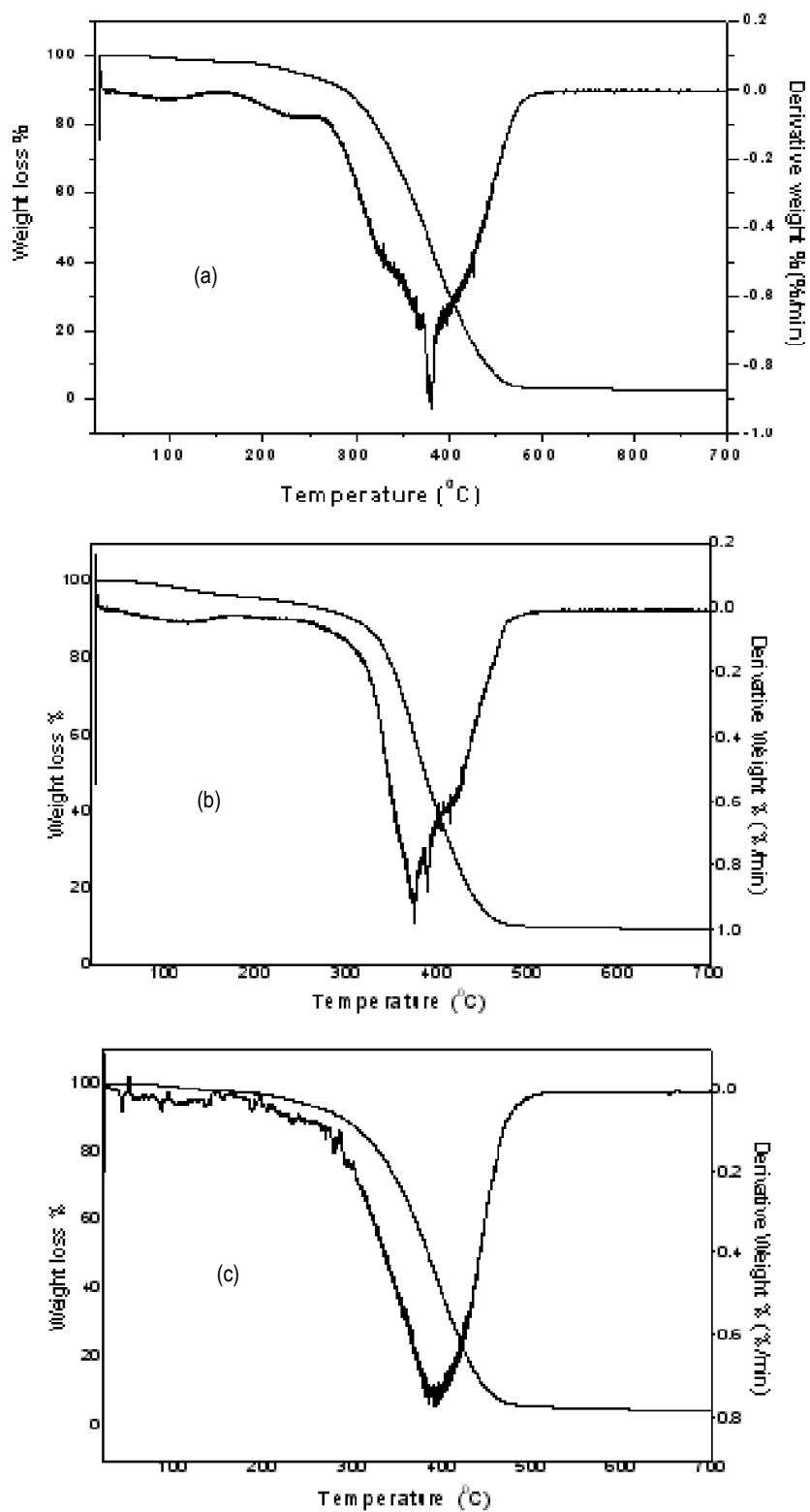


Fig. 6. TGA/DTG for resins from waste palmolein oil: (a) WPOR₁, (b) WPOR₂ and (c) WPOR₃.

Conclusions

Alkyd resins from waste palmolein oil and mixtures of maleic and phthalic anhydride in different ratios were synthesized and evaluated. The cured blend of alkyd with epoxy resins have desired properties for application as coating material. Thus, the results indicated that the waste palmolein oil can be valorized by converting to alkyd resin which on blending with epoxy resin exhibited properties suitable for coating applications.

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