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PHYSICOCHEMICAL CHARACTERIZATION AND PERFORMANCE EVALUATION OF UNMODIFIED AND MONTMORILLONITE (BENTONE) CLAY MODIFIED ALKYD RESIN FROM THEVETIA NERRIFOLIA SEED OILS

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Abstract
Thevetia Nerrifolia seed oil was extracted from its oil seed by soxhlet extraction using petroleum ether (40-60 ºC) as solvent. The oil was characterized and the oil yield, refractive index acid value, saponification value, iodine value, colour and relative density were found to be 47.77%, 1.464, 4.365 (mg/KOH), 125.62 (mg/KOH), 98.48 (wij), 4^+ and 0.926 respectively. Long oil alkyd resin was prepared by polycondensation of the Thevetia Nerrifolia seed oil monoglycerides produced by alcoholysis with phthalic anhydride. A portion of the alkyd resin prepared was modified with montmorillonite functionalized with alkyl ammonium hydroxide. The alkyd resins were characterized in terms of percentage non-volatile content, acid value, saponification value, iodine value, colour, drying schedule, chemical resistance and dry film hardness. These results compare favourably with alkyd resins from other known vegetable oils. The results also revealed that the incorporation of organo clay into alkyd resin structure has significantly improved physical and chemical film properties of the alkyd resin.

Keywords: Thevetia Nerrifolia seed oil, Montmorillonite clay, Alkyd resins.

Introduction
Alkyd resins are product of polycondensation reaction between a polybasic acid and polyhydric alcohol modified with a monobasic fatty acids or drying oil with suitable catalyst at controlled temperature [1]. The oils that are mostly employed for alkyd resin synthesis are linseed, soybean, castor and tall oils [2, 3]. These oils are largely imported to Nigeria for the formulation of coatings for metal cans used in packing of beverages, drugs, food etc. However, drying oils are available locally, which have remained untapped. These include rubber oil, soybean oil, walnut oil, *thevetia nerrifolia* seed oil, *jathropha curcas* seed oil tobacco oil etc [4].

Alkyd resins are by far the most important class of coating resins. It is estimated that alkyd resins contribute about 70% of the conventional binders used in surface coatings [5]. The popularity of alkyd resins as vehicle for coating is largely due to their unique properties such as film hardness, durability, gloss and gloss retention, resistance to abrasion etc. impacted on them through modification with drying oil [6].

One of the unique properties of alkyd resins which make them versatile binders in surface coating is their compatibility with other film formers like nitrocellulose resins [7]. Blending of alkyds with other resins yields new binder which combines the advantageous qualities of the alkyd and the blended resins. The wide spectrum of properties of alkyd resins is broadened by modification with a variety of materials like polyamide, urethanes, poly urea, nitrocellulose phenolic resin etc. this fact has vastly extended the use of alkyd resins to an extent that any new film-former developed is checked for compatibility with various types of alkyd resins [8]. Generally the alkyd contributes to coating flexibility, adhesion, durability and gloss, while the other resins confers faster drying rate, improved film hardness, rheology and resistance to chemicals.

Experimental
Thevetia Nerrifolia seeds were collected from Makurdi Local Government Area of Benue State. The seed were sun dried and then oven dried at 45ºC to constant weight and ground with porcelain mortar and piston to coarse particle size and stored in plastic containers for analysis. The oil was extracted using petroleum ether (40-60ºC) on a soxhlet

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extractor for four hours [9]. The refractive index, acid value, saponification value, iodine value colour and relative density were determined using the method described by A.O.A.C. [10].

The oil modified alkyd resin was prepared with *thevetia nerrifolia* seed oil, glycerol and phthalic anhydride using PbO as the catalyst. This was done according to the monoglyceride method involving alcoholysis and polycondensation [11].

The physico-chemical properties of the unmodified and modified resins were determined using ASTM standard methods ASTM D 1639-90 [12], ASTM D 1541-60 [13] and ASTM D 1962-67 [14].

The performance characteristics of the films were determined in terms of (1) *Hardness:* The uniformly coated panels were allowed to dry for 1 wk before testing. A relative measurement of hardness was achieved by rating the hardness of lead pencils.(2) *Adhesion:* Coated panels were allowed to mature for a week before undergoing the test. The cross-cut adhesion method was employed to perform the adhesion test [15]. The drying process was monitored in terms of the time of set-to- touch, surface-dry and dry-through.

The chemical resistance was determined at room temperature. The resistance of the films to different solvent media (water, brine, NaOH and H_2SO_4) was determined [16].

FTIR spectra of the bentone clay modified and unmodified alkyd resins were recorded to indicate the effect of modification on the alkyd resin.

Results And Discussion

The physicochemical properties of *thevetia nerrifolia* are shown in Table 1.0. From Table 1.0, the oil yield was found to be 47.47. The yield is appreciable and shows that it has potential in surface coating industry and in the manufacture of oleochemicals.

The saponification value of the oil was found to be 125.62. Saponification value indicates the average molecular weight of the oil,[17]. A high saponification value indicates that the oil contained higher proportions of low molecular weight fatty acids.

Acid value was found to be 4.365. Acid value of oil measures the extent to which the glycerides had been decomposed by lipase action. The decomposition is usually accelerated by heat and light. The acids that are usually formed include free fatty acids, acid phosphate and amino acids. Free fatty acids are formed at a faster rate than the other acids [18]. The iodine value of 98.48 indicated that the oil is non-drying, although the closeness of the value to the semi drying oils shows that there are high levels of poly unsaturated fatty acids [19].

The refractive index of 1.464, the relative density of 0.926 and the colour (Gardner) of 4^+ All conforms to the values given by literature for other vegetable oils. This is an indication that the oil extracted was of high degree of purity.

Table 1.0 Physicochemical Properties of Thevetia Nerrifolia

Property	**Value**
Oil yield (%)	47.47 ± 0.026
Refractive index	1.464 ± 0.001
Acid value (mg/KOH)	4.365 ± 0.017
Saponification value (mg/KOH)	125.62 ± 0.31
Iodine value (Wij's)	98.48 ± 0.02
Colour (Gardner)	4^+
Relative density	0.926 ± 0.003

The results of the physicochemical characterization of the unmodified and the bentone clay modified thevetia nerrifolia alkyd resins are presented in Table 2.0.

The acids value of 10.05 for unmodified and 10.5 for the modified indicate that the resins were cooked to the standard degree of polymerization for use in architectural coatings. This was however, very little change in the acid value of the modified alkyd resin.

The saponification values of the alkyds were observed to have increased considerably to 292.72 (mgKOH/g) and 325.66 (mgKOH/g) for unmodified and modified respectively as compared to *Thevetia Nerrifolia* seed oil. This was due to polymerization reaction [20].

The iodine values decreased considerably for both the unmodified and the modified alkyd resins. This could be attributed to dimerization and polymerization reactions at the reactive double bonds [20]. All the resins have a low percentage non-volatile content with high viscosities. Their usefulness will be limited particularly in the formulation of high solids-low P/B (high gloss) coatings [21].

Table 2.0 Physicochemical of Unmodified and Modified Alkyd Resins

Property	**Value**	
	Unmodified	**Modified**
Acid value (mgKOH/g)	10.05 ± 0.05	10.5 ± 0.01
Saponification value (mgKOH/g)	292.72 ± 0.03	325.66 ± 0.27
Iodine value (gI_2/100g)	42.56 ± 0.004	38.72 ± 0.03
% non-volatile (% wt)	48 ± 0.021	40 ± 0.02
Viscosity (Bubble second)	189 ± 0.31	178 ± 0.023
Colour	5	7^+

The FTIR spectra of unmodified and bentone clay modified alkyd resins are shown in Figure 1 and 2 respectively.

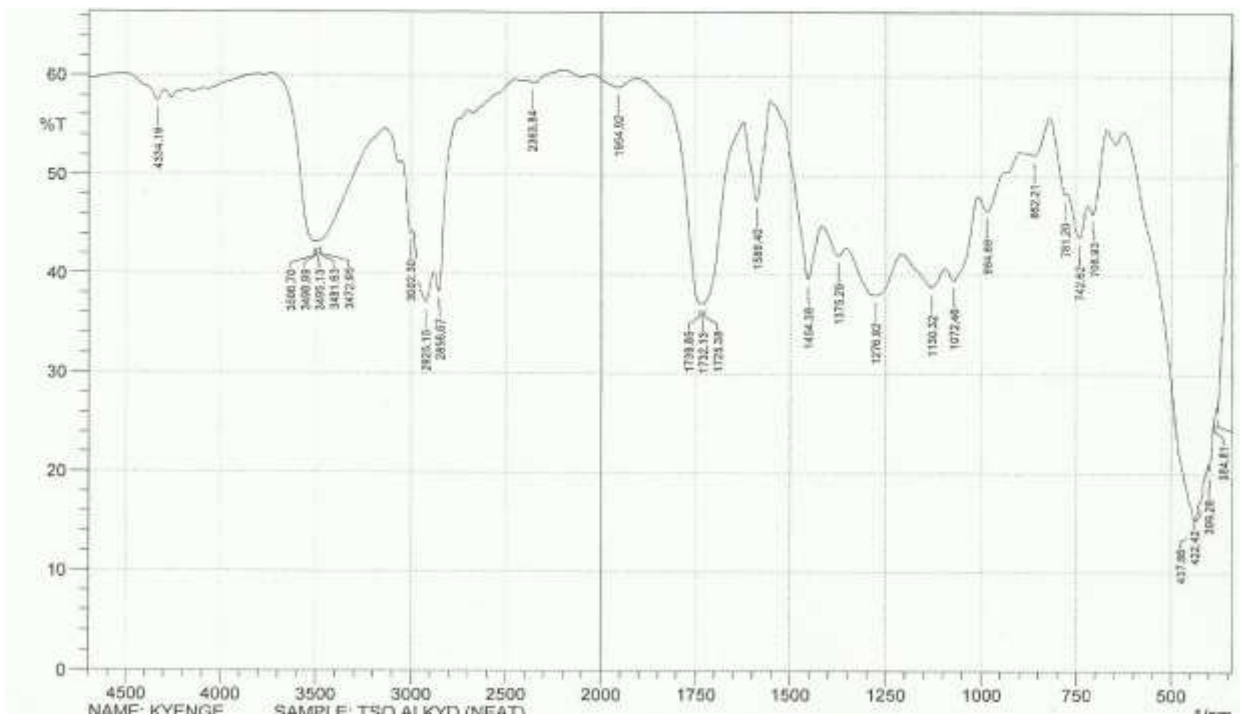

Figure 1 FTIR Spectrum of unmodified Alkyd from Thevetia Nerrifolia seed oil

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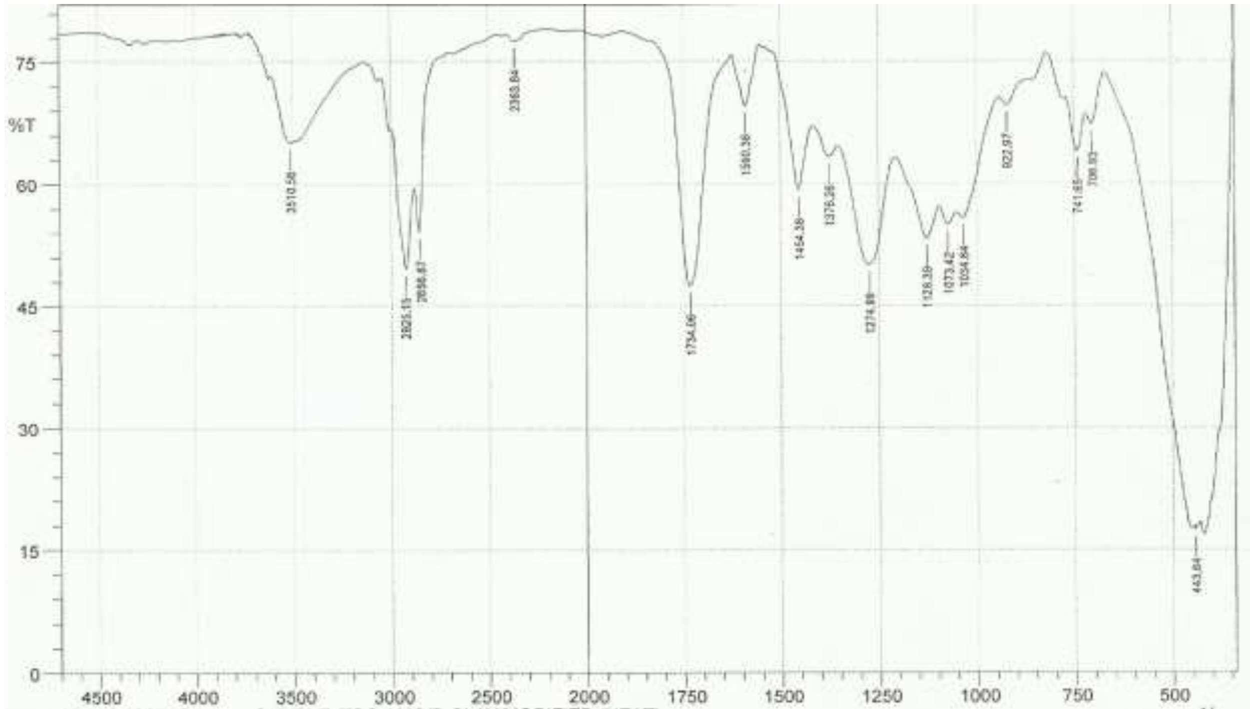

Figure 2: FTIR Spectrum of Bentone clay modified alkyd from Thevetia Nerrifolia seed oil

The FTIR Spectra of the unmodified alkyd resin shows the characteristic peaks at 1739.85 cm^{-1} corresponding to C=O stretch of ester group. A peak corresponding to –OH stretch of free carboxylic end group is shown at 3472.95 cm^{-1}. Also the peaks that occur at 742.62 cm^{-1} and 706.93 cm^{-1} is characteristic of compound with 1, 2- substituted benzene rings. The presence of fatty oil segments is indicated by the characteristic C-O-C stretch of fatty ester peaks at 1130.32 cm^{-1}[22].

The significant difference in absorption between the clay modified and the unmodified alkyd is the peak at 1034.84 cm^{-1} corresponding to Si-O absorption that is present only in the modified resin.

The results of the performance characteristics of the unmodified and modified alkyd resins is given in Table 3.0

Table 3.0 Performance Parameter of Unmodified and Bentone clay modified Alkyd Resin

Property	**Value**	
	Unmodified Alkyd	**Bentone (clay) modified Alkyd**
Adhesion (%)	73	96
Hardness	2H	5H
	DRYING SCHEDULE IN MINUTES	
Set-to- touch	42	36
Surface dry	120	75
Dry through	378	252

Long oil-alkyd resins have usually moderate adhesion. However, the adhesion of the clay modified alkyd resin was improved. Pencils graded from 5B to 5H were tested on coated mild steel panels. It was found that the hardness was also improved for bentone modified alkyd resin.[23]. The modified alkyd resin shows shorter drying times in terms of set-to-touch, surface dry and dry through. This could be due to the fact that the modified alkyd in more porous than the unmodified.

The results for the chemical resistance of unmodified and bentone clay modified alkyd resins is shown in Table 4.0

Solvent media	Unmodified Alkyd	Bentone clay modified Alkyd
Alkali (0.1 KOH	2	2
Acid (0.1 H_2SO_4)	1	1
Brine (5% w/w NaCl)	1	1
Distilled water	2	1

1= No effect, 2 = whitening of film, 3 = shrinkage of film, 4 = shortening of film

Films of these samples showed excellent resistance to acid and brine, the unmodified alkyd however, shows whitening of film in water. Both the unmodified and modified shows poor ristance to alkali. The poor alkali resistance of alkyds may be explained on the basis that they consist essentially of ester groups, which are known to be susceptible to hydrolysis by alkali

Conclusion

Alkyd resin prepared from *thevetia nerrifolia* seed oil shows comparable physicochemical properties as alkyd prepared from other well known oils in the synthesis of alkyd resins and hence can be used as a replacement for those oils. It is also evident that the incorporation of bentone clay into the alkyd resin improved the performance properties of the resin.

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