

# Influence of Polybasic Acid Type on Physicochemical Properties of Pine Seed Oil Alkyd Resin

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**Abstract**— Pine seed oil was employed in the preparation of different medium length alkyd resin samples using alcoholysis and poly condensation process. The alkyds formation was monitored by determining the acid number of the reaction mixture at time intervals and the extents of the polyesterification reactions were evaluated. Both the Pine seed oil and its alkyd resins were characterized by Fourier Transform Infra red (FTIR) spectroscopy. Performance evaluation shows that properties of alkyd resin derived from Maliec anhydride are comparable with phthalic anhydride alkyd resins. However the Maliec alkyd resin shows better color, and lower poly condensation time. Better results were observed from the blending of phthalic and small portions of maliec anhydride.

**Keywords**— Alkyd resin, Pine seed oil, poly hydric alcohol, Alcoholysis, Polyesterification.

## I. INTRODUCTION

The recent shift towards green products has consequently triggered the demand for more oils needed to expand the present supplies in the oleochemical industry. However, the current popular oil seeds have not sufficiently catered for the local market ability to undergo chemical modifications and renewable nature. Vegetable oils have been used as modifiers of alkyd resin for the purpose of imparting certain properties, such as ability to provide air-dry coatings, film hardness, durability, cross linking and economical balance. (Shahla *et al.*, 2011).

Alkyd resins are the reaction products of polyhydric alcohols and polybasic acid, which are obviously polyesters. The reaction is essentially a polycondensation, modified with triglyceride oil. Apart from the nature of the triglyceride oil used in alkyd resin synthesis, the type of polybasic acid used can also influence the physicochemical and viscosity properties of alkyd resins (Ibanga and Edet, 2013).

## II. MATERIALS AND METHODS

### Materials

Pine seed oil were purchased from Technology Incubation Centre Kano, phthalic anhydride, maleic anhydride, glycerol, calcium carbonate, xylene, were of analytical grade and use without further purification. All other reagents and solvents used throughout this research work were of high purity.

### Physicochemical Properties

Physicochemical properties of Pine seed oil (e.g., acid value, saponification value, iodine value, density and viscosity) were determined using standard methods (AOCS, 1996), the results obtained are presented in table 1.

### Preparation of Alkyds

A known weight of Pine seed oils was heated to a temperature between 220<sup>0</sup>C and 240<sup>0</sup>C. Glycerol (10.0 g) and 0.3g calcium carbonate were added while maintaining the temperature at about 240<sup>0</sup>C. The completion of alcoholysis was confirmed by taking samples of the reaction mixture mixed with anhydrous methanol in a 1:1 volume ratio until a clear solution was obtained. Phthalic anhydride, Maliec anhydride and xylene were added while the reaction continued at about 240<sup>0</sup>C. The reaction was monitored by acid value determination at every one hour interval until a value of 10 or less was reached, then the reaction was quenched by immersing the reaction vessel in cold water. The drop in acid value with time for the different alkyd samples are shown in figure 1.

The alkyd samples were labeled as ALP1 47.7% (Pine oil and phthalic anhydride), ALP2 47.7% (pine oil and maliec anhydride), ALP3 47.7% (pine oil with Phthalic and Maliec). The recipe used is shown in Table 2. Xylene was used as the azeotropic solvents. Each alkyd was processed to an acid value equal or less than 10mgKOH/g.

### Physicochemical Characterization of the Alkyd Resins

The physicochemical properties of the alkyd resins prepared from the seed oils; such as viscosity, acid value, saponification value, and iodine values were determined using methods described by American Oil Chemists Society. (AOCS, 1996).

### FTIR Analysis

The FTIR spectra of the pine seed oil and the prepared alkyd resin samples were acquired using FTIR CARY 630 agilent at 4000-600cm<sup>-1</sup>. The key absorption peaks obtained are presented in table 2.

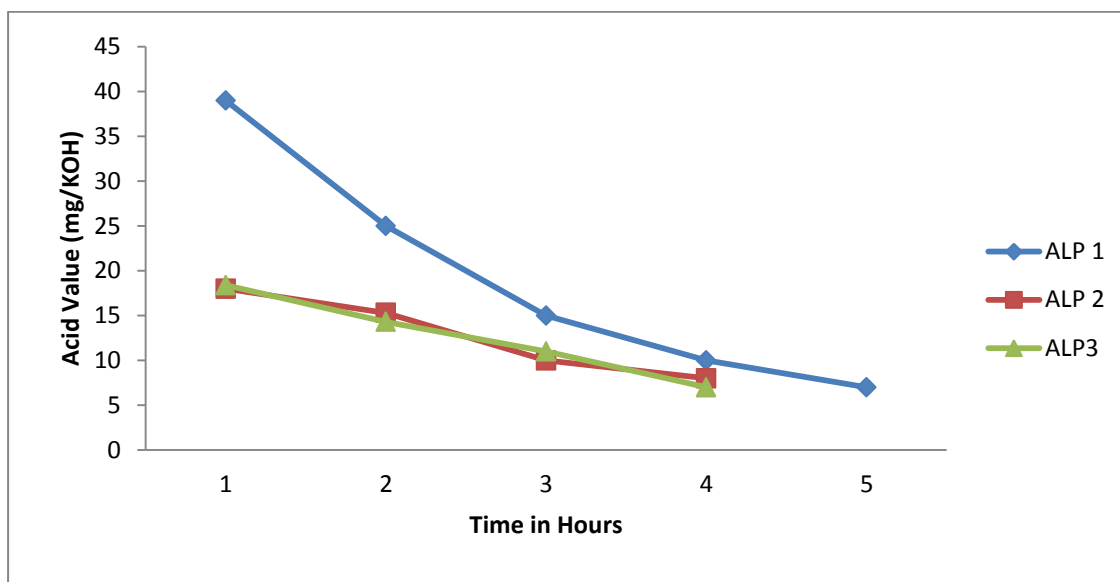


Figure 1. Graph of drop in acid value with time for pine alkyd resins

FTIR Spectra of the different alkyd resin samples with different polybasic type are shown in Figure 2,3,4, and 5.

#### Solvent Resistance Test

The dried panels were immersed in a beaker containing distilled water for 18 h. After 18 h, the panels were taken out, air-dried and inspected for any defects, like whitening, shrinkage, film softened, loss of gloss and lift off. Acid resistance test was carried out by preparing Aqueous solution of acid hydrochloric 0.1 M (HCl, in a beaker and warmed up to 80°C. The coated panels were immersed in the solution for 1h at 80°C, and then removed from the solution. The panel was then dried at room temperature for 24 h before checking for any deterioration. The water and Alkali resistance were determined using ASTM (D 1647-89, 2004). The resistances of the films to different solvent media (Ethyl methyl ketone, Acetone and toluene) were determined according to ASTM (D1647-59, 1996).Table 5 and 6.

#### Drying Time Test

In order to determine set-to-touch time, the coated films are lightly touched with the tip of a clean finger and immediately placed against a clean piece of clear glass .The film is considered dry-to-touch when film no longer sticks to finger and does not rub when the finger is lightly moved across the surface.

#### Flexibility Test

to evaluate the flexibility of the alkyd films, 2cm by 5cm size cardboard paper was used as the test panels. A brush was applied on one side of the panel and allowed to dry. The test was carried out by bending the film on paper to angle 180 in order to check any evidence of crack on the film.

#### Adhesion Measurement

Adhesion test was designed to assess the adherent strength of the film according to Shahla 2011. A criss-cross lattice pattern with six cuts in each direction was made after making the required cuts; the film was brushed lightly with a soft

brush to remove any detached chips of coatings. A piece, about 75 mm long, of pressure-sensitive tape was separated and placed over the grid and smoothed into place by finger. The tape is rubbed firmly with eraser to ensure sufficient contact with the film. The tape was removed after 90s in an angle close to 180°. The grid area was inspected by visual inspection for removal of any coating from the substrate. The adhesion is rated according to ASTM D3359-94.

### III. RESULT AND DISCUSSION

#### Physicochemical Properties of Oil

The Pine seed oil, used in this research work is of high purity, semidrying, with lower degree of unsaturation, as shown from the physicochemical properties presented in table 1.

Table 1: Physicochemical Properties of Pine seed oil.

Property	Value
Iodine value (mg/g)	118.4100
Saponification value (mgKOH/g)	193.7000
Acid value (mgKOH/g)	2.0800
Peroxide value (meq/kg)	0.1200
Free Fatty Acid %	1.0400
Refractive Index	1.4716
Viscosity (MPa) 28°C	15.4100
Specific gravity	0.9314

#### FTIR Spectral Analysis

As seen from the spectra, there exist different absorption frequencies even though they are all polyesters. The functional groups present are similar to those obtained elsewhere (Issam, and Cheun, 2009). The FTIR spectra of the three samples were similar. Carbonyl group (C=O) were detected around 1721-1728 cm<sup>-1</sup>. Straight chain alkane (-CH-) were detected around 2870- 2957 cm<sup>-1</sup>.The C—O stretching due to ester were detected around 1112-1259 cm<sup>-1</sup>. Alkyd resin samples were successfully synthesize using pine seed oil. Apart from the nature of triglyceride oil used in alkyd resin synthesis, the type of polybasic acid type also plays a major role in the

physicochemical properties of the alkyd resin synthesizes via alcoholysis and polycondensation process, more so pine seed oil alkyd resins exhibited good performance characteristics. This is an indication that pine seed oil will play a great role in various industrial applications such as in the formulation of surface coatings.

Table 2. FTIR absorption frequencies of pine seed oil.

Band Number	Literature frequencies	Experimental frequencies	Remark
1	1100–1300	1112, 1132, 1160	C–O Stretching
2	1500–1400	1449, 1460	C= Stretching
3	3000–2850	2872, 2922, 2961	C–H Stretching, SP <sup>3</sup>

Table 3. Recipe used in the preparation of Pine Seed oil Alkyd resin.

INGREDIENTS	ALP1(g)	ALP2(g)	ALP3(g)
Pine seed oil	47.70	47.70	47.70
Phthalic hydride	24.10	0.00	23.68
Maleic anhydride	0.00	15.9	1.59
Glycerol	10.0	10.0	10.0
Calcium Carbonate	0.30	0.30	0.30
Xylene	0.03	0.03	0.03
Mole ratio	1:2	1.2	1:2

Key: ALP1 Alkyd resin sample derived from pine seed oil and phthalic anhydride,

ALP2 Alkyd resin sample derived from pine seed oil and maleic anhydride

ALP3 Alkyd resin sample derived from pine seed oil, phthalic and maleic anhydride

### Physicochemical Properties of Pine Alkyd Resins

The significant change in acid value as the reaction progresses may be attributed to the variations in acid value of the anhydrides used during the alkyd synthesis. ALP1 have acid values less than ALP2 which is higher than ALP3. Aydin *et al.* (2004) gave the acid value of maleic anhydride as 1144.2 mg KOH/g while phthalic anhydride has 757.5 mg KOH/g. Changes in the acid number with increasing reaction time for the different alkyd samples are plotted in Fig. 1.

The result of the saponification value of the alkyd sample agrees with that reported by Ibanga and Edet (2013), which shows the saponification values of phthalic alkyd resin of cotton seed oil lower than that of maleic resins, but there exist significant rise in saponification value from oil to resins. From the results obtained the iodine values of the resins drop drastically compared to their oils, this decrease in the degree of unsaturation can be attributed to high utilization of the double bonds present in the oil during resinification reaction. Phthalic anhydride has higher degree of unsaturation because of benzene ring in its structure, hence resins prepared with it generally dries slower while maleic anhydride with lower degree of unsaturation will dry faster. Moreso, Phthalic anhydride alkyd samples resists flow more than others. Maleic alkyd samples shows significant increase in viscosity.

Table 4. Physicochemical Properties of Pine Seed oil Alkyd Resin.

Alkyd sample	Colour	Acid value (mg/KOH/g)	Iodine value mg/g	Saponification value. (mg/KOH/g)	Viscosity mpa(27 C)	Refractive index	Relative density
ALP1	Light Brown	5.034	49.00	217.81	989.2	0.80	1.35802
ALP2	Golden yellow	9.87	53.06	225.43	989.9	0.78	1.35913
ALP3	Brown	8.72	51.00	220.54	999.3	0.78	1.40893

Table 5. Resistance of Alkyd resins to various solvent.

Alkyd resins	Water resistance	Alkali resistance 10% NaOH	Acid resistance		Solvents resistance		
			H <sub>2</sub> SO <sub>4</sub> 20%	HCl 10%	Acetone	Ethyl methyl ketone	Toluene
ALP1	Excellent	Fair	Excellent	Excellent	I	I	I
ALP2	Excellent	Poor	Excellent	good	I	I	I
ALP3	Excellent	Poor	Excellent	good	I	I	I

I= Insoluble,

### Film Characterization

The resistance of alkyd resin samples was evaluated in various solvent media and the results are presented in Table 5. All the alkyd samples show high resistance to water, acids and solvent but poor resistance to alkali. (Table 5). This is expected of polyesters because they are readily hydrolyzed by alkali. However the films were found to be highly resistant to distilled water, aqueous sodium chloride solution through out the immersion period. Among the resins, Phthalic anhydride showed poor resistance than the other two types of resins.

### Dryness Schedule

The result of drying schedule of the alkyd resin is presented in Table 6. From the result, it is evident that set-to-touch time as well as dry-through time of the alkyd samples depends on, nature of the polybasic acid used in the alkyd formulation. The drying schedule follows the order phthalic resins > phthalic/maleic > maleic resins. This results agrees with the findings of Zeno *et al.* (1999), which suggested that the higher the level of unsaturation, the faster the drying time.

Another factor that can contribute to these differences in drying time of the three alkyd paint samples could be the structure of the polybasic acid used in the alkyd resins preparation. Phthalic anhydride has a benzene ring in its structure, which contains conjugated bonds that can enhance auto-oxidation process. Maleic anhydride has a double bond in its aliphatic structure, which is less susceptible to auto-oxidation

Table 6. Dryness Schedule of Pine Seed oil Alkyd Resins.

Samples	Characteristics		
	Set to touch (min) indoor	Set to touch (min) outdoor	Dry through (hour)
ALP1	28	18	Overnight
ALP2	25	15	Overnight
ALP3	25	12	Overnight

Table 7. Adhesion, Flexibility Test of Alkyd Resin samples

Alkyd resin samples	Adhesion	Flexibility
ALP1	4B	Pass
ALP2	3B	Pass
ALP3	3B	Pass

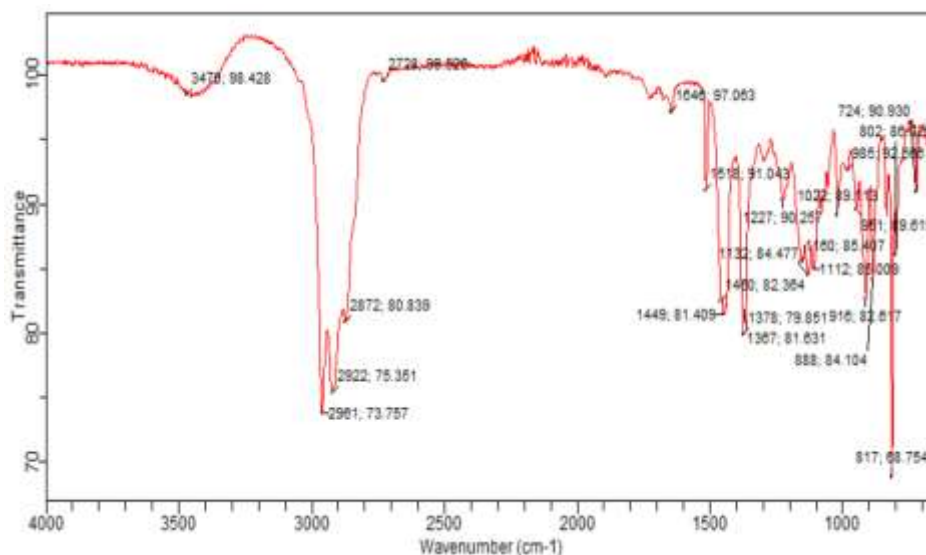


Figure 2. FTIR Spectra of pine seed oil

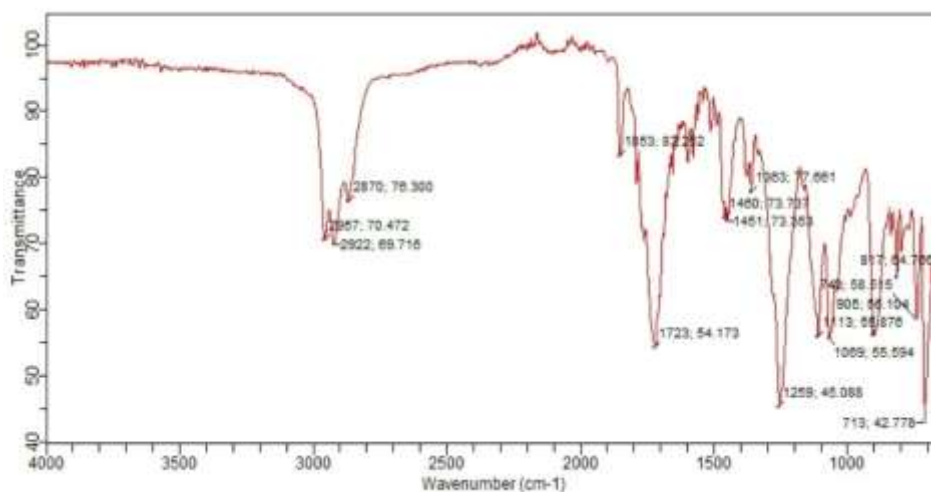


Figure 3. FTIR Spectra of ALP1

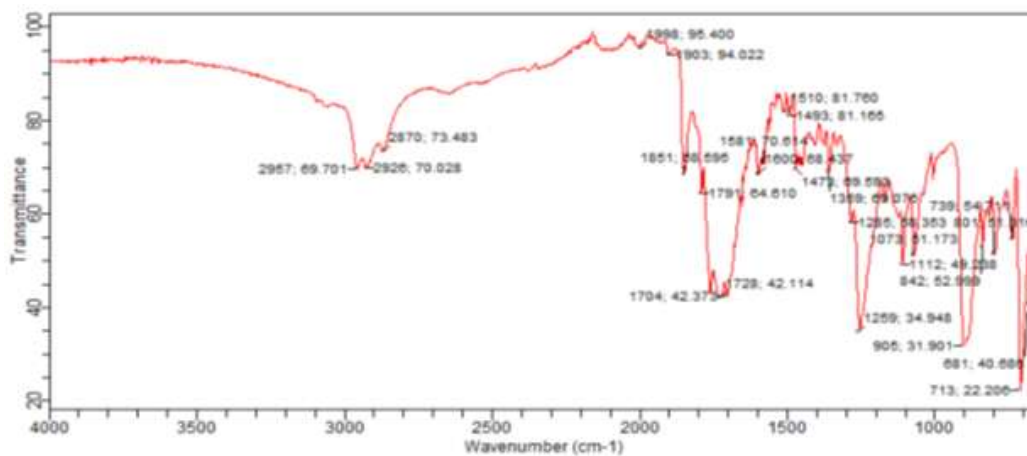


Figure 4. FTIR of ALP2

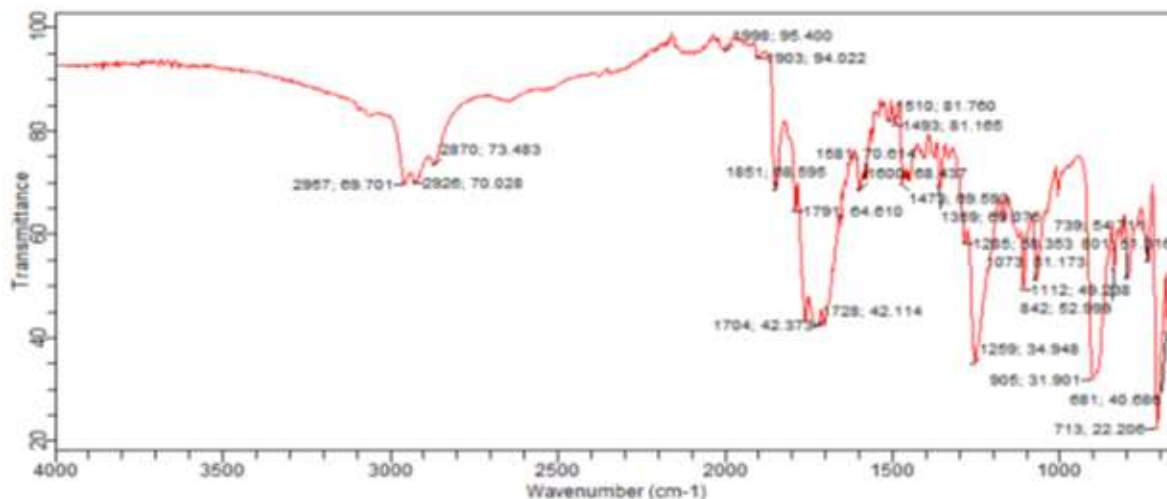


Figure 5. FTIR Spectra of ALP3

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