



Development and property evaluation of alkyd resins from watermelon (*Citrullus lanatus*) seed oil

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Watermelon Seed Oil (WSO) has been investigated for its suitability in the development of alkyds. Chemical method is used to extract the oil, and the WSO's physicochemical properties are determined. The alcoholysis-esterification method is used to prepare two grades of alkyds containing 30 percent WSO (alkyd I) and 60 percent WSO(alkyd II). The progress of the reaction is monitored by determining the volume of water of condensation and acid value as the reaction progresses. Film properties of the prepared alkyd are determined. The results of the physicochemical properties of the WSO reveal an iodine value of 119.38 gI₂/100g indicating that it is semi-drying oil and can serve as a modifier for alkyd resins production for the paint industry. Alkyd I has a higher acid value, a greater degree of polymerization and extent of the polymerization than alkyd II, according to the results. Alkyd II produce a harder film than that of alkyd I as observed from the scratch hardness test. Also, both alkyd show good flexibility properties and have good impact resistance on the coated panel. The present study, therefore, suggests that WSO can be considered as a modifier for alkyd resins production for the paint industry.

Keywords: Alcoholysis, Alkyd resin, *Citrullus lanatus*, Polymerization, Watermelon Seed Oil

Alkyd resins are used as binders for paints. The esterification of polyhydroxy alcohols with polybasic acids, modified with triglyceride oils produces alkyd resins polymers. They are the dominant resin or "binder" in most commercial "oil-based" coatings¹. Oil-modified alkyd resins are the alkyd resins developed in this way, and they make up about 70% of the typical binders used in surface coatings. They are the lowest material in cost if compared with other coating materials². From an ecological standpoint, their biological degradability makes them very fascinating binders. The type of oil chosen is determined by the drying conditions and the colour retention properties needed in the film, as the oil has a significant impact on the produced alkyds' properties. Therefore, an understanding of drying oil chemistry is required to design coating qualities that meet the needs of a certain application³. When oils are dispersed and exposed to air, they slowly absorb oxygen, generating dry, robust, transparent, and lasting films⁴. Due to the country's rapid economic development, the need for alkyd resin in Nigeria's surface coating industry has

skyrocketed. As a result of the growing world population, large amounts of oil are required for the manufacturing of alkyds. Therefore, additional research is needed to discover new sources of industrial oil as well as enhance current oil resources⁵. Natural oils are relatively cheap, readily available in large quantities, easy to process, and apply. Linseed, tall oil, soya oil, and other vegetable oils have been used to make alkyds; the high degree of unsaturation in these oils is a typical attribute. Exploration of low-cost sources of vegetable oils has become crucial in countries such as Nigeria, where existing vegetable oils are used for both edible and non-edible purposes, resulting in shortages and high material costs. Watermelon (*Citrullus lanatus*) is a *Cucurbit* family warm-season tree. Watermelon oil extracted from the seed of the watermelon plant is most valued for its large amount of oleic and linoleic fatty acids as well as other acids⁶. The main aim of this research is to use local raw material (watermelon seed oil) for the modification of alkyd resin as an alternative for high-cost oils like linseed oil.

Experimental Section

Materials

Phthalic anhydride (PA), Glycerol, Xylene, Methanol, Ethanol, Hexane, Toluene and Calcium oxide were purchased from Elisoye Nigeria limited and Wintech lab limited in Nigeria.

Sample collection and preparation

Watermelon pods were purchased from Obantoko market Odeda Local Government Ogun State, Nigeria. The seeds from the pod were washed thoroughly with distilled water; oven-dried at 50°C and allowed to cool. It was then grounded to a particle size of about 1mm using an electric blender.

Extraction of oil

The oil from ground seeds was extracted using a soxhlet extractor and n-hexane at 60°C. The ground sample was suspended above the flask containing the solvent and below the condenser in a cellulose thimble in an extraction chamber. The solvent evaporated as the flask was heated. The extraction process lasted for 2-3 h and the oil was collected.

Physiochemical properties of watermelon seed oil

The American Oil Chemistry Society's guidelines for assessing iodine value, saponification value, acid value, viscosity, peroxide value, and specific gravity were followed⁷.

Synthesis of Alkyd Resin using Watermelon Seed Oil (WSO)

Alkyd resin was made in two steps, as follows: Alcoholysis and Esterification/polycondensation⁸. The reaction was performed in three-neck round bottom flask with a mechanical stirrer, thermometer and a Dean and stark apparatus carrying a water-cooled condenser.

Alcoholysis

Alcoholysis was carried out at a temperature of 250 – 260°C inside a reactor in which a known weight WSO was reacted with glycerol. To speed up the reaction, a CaO catalyst was included. The tolerance of the mixture to methanol was used to monitor the development of the ester interchange. After the alcoholysis process, the reactor was cooled to around 180°C.

Esterification/polycondensation

PA was added to the monoglyceride in the reactor and was heated to 220 – 240°C for esterification. The water of condensation was removed by azeotropic distillation using xylene (cooking solvent). The

increase in viscosity of the alkyd resin and the calculation of acid value were used to keep track of the progress of the esterification/condensation reaction. The acid value was calculated every 30 min until the required acid value was achieved. The reaction was terminated, cooled and diluted with xylene (Table 1).

Film properties of watermelon oil alkyds

Determination of Drying Time

The resin was thinned with xylene to a brushable consistency. The thinned resin was applied by brush on a 15× 15cm steel panel. The coated panel was kept in a vertical position and allowed to air dry. The time required for the film to feel dry to touch (surface drying) and non-sticky (hard drying) were recorded.

Determination of scratch hardness

The resin was thinned with xylene to a brushable consistency. The thinned resin was applied by brush onto 15 × 15cm steel panel. The coating was allowed to air dry for 48h. Pencils with hardness varying from HB (softest) to 6H (hardest) were purchased from a book shop. By rubbing perpendicularly on abrasive paper, the lead (graphite-clay) in the various pencils was squared off. Every pencil was held at 450° to the panel and pushed forward at a pressure just below that needed to break the lead. Hardness was reported as the grade of pencil that did not cause any marring of the surface of the coated panel.

Determination of Flexibility

The resin was thinned with xylene to a brushable consistency. The thinned resin was applied by brush to a 15 × 15 cm steel panel. The coating was allowed to air dry for 48 h. The panel was bent around a cone 1/8" thick with the coated side away from the mandrel. Any crack in the coating on the bend is reported as a failure. The bent edge was viewed with a magnifying glass to see airline cracks.

Determination of impact resistance

The resin was thinned with xylene to a brushable consistency. The thinned resin was applied by brush

Table 1 — Alkyd samples preparation recipe

Ingredients (g)	Alkyd Resin	
	I (30%)	II (60%)
Oil content (WMO).	60.00	120.00
Glycerol	55.19	31.85
Phthalic anhydride	84.81	48.15

15 × 15 cm tin panel. The coating was allowed to air dry for 48 h and a 1 kg weight was dropped from a height of 25 inches down a guide tube onto a hemispherical indenter that rested on the coated panel. The coated panel was observed for cracks using magnifying glasses. Any crack on the coated panel is reported as a failure.

Determination of water, acid, alkali and solvent resistance

The resin was thinned with xylene to a brushable consistency. The thinned resin was applied by brush onto a 15×15 cm steel panel. The coating was allowed to air dry for 48 h. The coated panels were then exposed to different solvents for the same period; 15mins. The coated steel panels were observed for softening of film, shrinkage of film and complete removal of the film using ASTM D 1308-67⁹.

Results and Discussion

Properties of the WSO

Table 2 shows the properties of WSO. The oil yield is 51.1% by the seed's weight which is much higher than most seed oils like soyabean oil (19.54%)¹⁰. This indicates that the Watermelon seed contains a high amount of oil that can be employed for different applications. It has higher acidity (acid value 2.5) than linseed oil (1.0)¹¹ but is lower than soybean oil (3.31)¹². The saponification value of WSO is in the same range as soybean oil (181-187) indicating that it is can be useful in the formation of soap, hair shampoo, etc. The level of unsaturation of vegetable oil, as indicated by its iodine content, is perhaps the most important property for its use in surface coatings. The iodine value of 119.38 mgKOH/g for WSO similar to that of soybean oil (119-128 mgKOH/g)¹³, was recorded. Consequently, WSO may be graded as semi-drying oil with similar properties to soybean oil which has been used in the production of alkyd resin. This means that when a thin layer of

WSO is heated, the autoxidation process causes it to dry into a hard film.

Water of Condensation

Figure 1 shows the water evolved as polymerization progressed. It was revealed that there was a gradual increase in the water of condensation for alkyd samples I and II until a constant value was reached indicating the condensation reaction.

Acid value

Figure 2 depicts the acid value steadily declining at the start of the reaction. The separate reactivity of primary and secondary hydroxyl groups of glycerol has been used to describe this pattern of a shift in acid value during the poly-condensation reaction. Since the reaction of a primary hydroxyl group is quicker than that of a secondary hydroxyl group, the decline in acid value in a short period in the initial phases of reaction is thought to lead to the time when the primary hydroxyl group reacts¹⁴. The acid value for alkyd resin I was observed to be more than that of II. This could be due to the amount of oil used since more percentage of oil was used for the production of alkyd resin II. The rate at which the acid value decreases is said to be proportional to the amount of oil used in the formulation. It denotes the start of the

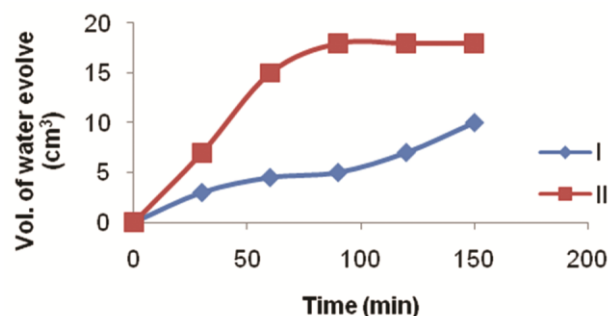


Fig. 1 — Plot of water condensed against time

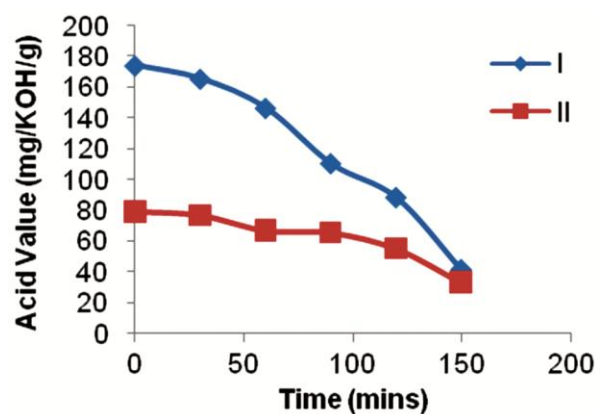


Fig. 2 — Plot of change in acid value against time

Table 2 — Physicochemical properties of watermelon seed oil

Physicochemical properties	Watermelon oil
Colour	Brown
Odour	Mild
Specific gravity (25°C) g/cm ³	0.875
Acid value (mg KOH/g)	2.54
Viscosity (mm ³ /sec)	2.58
Saponification value (mg KOH/g)	185.13
Iodine value (mg KOH/g)	119.3
Peroxide value (mg KOH/g)	2.50
Oil content (% by weight)	51.10

creation of a three-dimensional network as a result of the alkyd chain's cross-linking¹⁵.

Extent of reaction and degree of polymerization

The acid value was proportional to the reaction extent P_n and the average degree of polymerization D_p , as follows:

$$P_n = \frac{C_0 - C_t}{C_0} \quad \dots(1)$$

and

$$D_p = \frac{1}{1 - P_n} \quad \dots(2)$$

where C_0 is the initial acid value and C_t is the acid value after time, t , of the reaction. "Equation 2," which relates the degree of polymerization to the level of reaction, is commonly referred to as the Carothers equation¹⁶.

As expected, the extent of reaction increased as the reaction progressed for both alkyd resin prepared. The extent of the reaction at the point of termination for the reaction (150 min) for alkyd I was 76.23% while that of alkyd II was lower (58.32%) (Table 3). This might also be due to the oil chain length.

Figure 3 illustrates the variation in the average degree of polymerization (D_p) as a function of reaction time. The first region of these graphs portrays the time when glycerol's primary hydroxyls reacted with phthalic anhydride's carboxyl groups to form linear chains. Esterification of the primary hydroxyl groups was done right away, the acid value decreases, and the reaction slows down before a temperature is reached at which the secondary hydroxyl groups react¹⁵. When the D_p of the alkyd chains increases, the viscosity of the reaction medium increases.

Drying properties of alkyd resin film

Table 4 illustrates the drying time at different stages for alkyd I and II compared to commercial alkyd resin. Alkyd resin I was found to have good

drying efficiency when compared with commercial alkyd resin at all stages of drying, both in the absence and presence of mixed drier. Alkyd II films took a long time to hard dry (with drier) and this might be due to the presence of more linolenic acid due to longer chain length. However, it is also worthy to note that the time for hard dry for both alkyds was the same as that of the commercial one (72h). In a research done by Ekpa & Isaac, the dry through time for long oil alkyd resin synthesized from Melon (*Colocynthis vulgaris Shrad*) seed oil using lead drier was found to be 1800mins (30hrs) indoor¹⁷ while Alkyd II (long oil alkyd from watermelon seed oil) synthesized in this experiment took 24hrs to dry through. Based on their drying ability, undoubtedly, the prepared resins might be acceptable binders in alkyd paint formulation. The drier, which contains cobalt, calcium, and aluminum as main, secondary, and auxiliary driers, greatly improved the drying

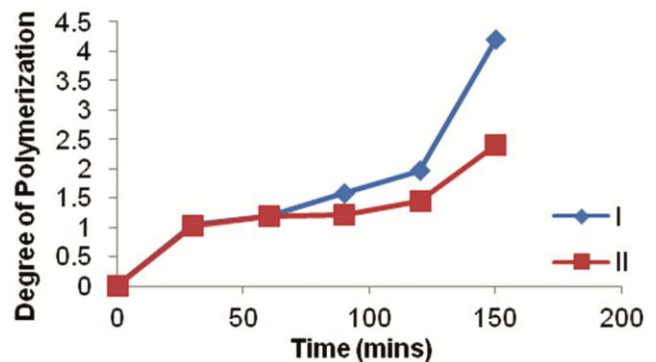


Fig. 3 — Changes in average degree of polymerization (D_p) versus reaction time

Table 4 — Drying time of prepared alkyd resins of I, II and commercial alkyd resins in the presence and absence of mixed driers

Drying time stages	Alkyd resins samples in the absence of mixed driers		
	I	II	Commercial ¹⁴
Tack free (h)	12	14	10
Surface dry (h)	22	24	20
Dry through (h)	48	50	40
Hard dry (h)	72	72	72

Drying time stages	Alkyd resins samples in the presence of mixed driers		
	I	II	Commercial ¹⁴
Tack free (h)	5	6	4
Surface dry (h)	9	10	8
Dry through (h)	20	24	18
Hard dry (h)	42	48	40

Table 3— Extent of reaction (% P_n) and average degree of polymerization (D_p)

Time	I			II		
	AV	% P_n	D_p	AV	% P_n	D_p
0	174.3	-	-	79.28	-	-
30	165.66	5.21	1.05	76.84	3.07	1.03
60	146.65	15.86	1.19	66.84	15.69	1.19
90	110.52	36.59	1.58	65.55	17.31	1.21
120	88.47	49.24	1.97	55.05	31.26	1.45
150	41.42	76.23	4.2	33.04	58.32	2.4

Table 5 — Analysis of chemical resistance of samples of prepared 30%, 60% alkyd resins oil lengths and commercial alkyd resins in different service media after 24 H

Alkyd resin samples	Different service media			
	Distilled water	5% NaCl solution	0.1M H ₂ SO ₄ solution	0.1M NaOH solution
I	1	2	3	4
II	1	2	3	4
Commercial	1	2	3	4

1 = No effect
2 = Softening of film,
3=Shrinkage of film
4 = Removal of film

Table 6 — Scratch hardness of alkyd resin sample

Properties	Alkyd resin sample	
	I	II
Pencil hardness		
Scratch	6B	2B
Gouge	3B	HB

properties of alkyd resins prepared, according to the results.

Chemical resistance

Analysis of the chemical resistance of samples of the prepared alkyd in different service media after 24 h of immersion was compared with that of commercial alkyd resin and the result is shown in Table 5. The result showed that the behavior of the prepared alkyd in the solvents used is the same as that of the commercial alkyd. Alkyd I and II were unaffected by the distilled water, moderately affected by the salt solution, less severely affected by acid solution and more severely affected by alkaline solution. Alkyd resins contain ester group constituents that function as bond linkages that are susceptible to alkali hydrolysis, which explains their low alkaline resistance¹⁸.

Scratch/Gouge hardness

Table 6 shows the scratch and gouge hardness determined by pencil hardness for the alkyd films of alkyd samples I and II. The result showed that alkyd I produced a stronger film than that of alkyd II.

Mechanical properties

The alkyd resin sample I and II showed good flexibility properties (Table 7). There was no airline crack in the coating on the bent edges when viewed with a magnifying glass. Also, the impact resistance on the coated panel was observed and there was no

Table 7— Mechanical properties of alkyd resin

Properties	Alkyd sample I	Alkyd sample II
Flexibility	1	1
Impact resistance	1	1

1 = Passed
2 = Failed

crack on the coated panel. The coated panels were observed for water, acid, alkali and solvent resistance and there was no effect on distilled water, the films were softened on the salt solution, the acid solution caused shrinkage of the film and alkali solution caused the removal of the film for both 30% and 60% oil length alkyd resin samples. This is consistent with the results of the chemical resistance experiment.

Conclusion

The suitability of watermelon seed oil for the production of alkyds was investigated in this study. Short and long alkyd resins were successfully synthesized using watermelon seed oil. The iodine value of the oil determined in this study indicates that the oil extracted from watermelon seeds is semi-drying, making it ideal for modifying alkyd resin for surface coating applications. The short oil alkyd resin was found to have better drying time and hardness. Better properties observed for alkyd I may be due to the better extent of reaction and degree of polymerization. Both alkyds prepared showed good mechanical properties with good chemical resistance properties similar to that of the commercial alkyd.

The short and long oil length alkyds from watermelon oil have satisfactory properties that can make it considerable for the production of alkyd resins. Thus, this study suggests that the watermelon seed oil is a suitable material for alkyd resin.

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