

Polyesters From Chemically Modified Oil of Renewable Source

O.FOsagie¹, Oriji A.B²

*1*Department of Chemistry, Rivers State University of Science and Technology P.M.B 5080 Port Harcourt, Rivers State, Nigeria.

2 Department of Petroleum and Gas Engineering, University Of Port Harcourt, Port Harcourt, Nigeria.

Abstract: Rubber seeds, agricultural wastes without any known nutritional value, were blended to obtain oil. The oil was employed in the production of polyesters (alkyd resins) using alcoholysis method. The rubber seed oil (RSO) and its alkyd resins were characterized and evaluated by standard methods for their physicochemical properties, drying schedule and chemical endurance. RSO had an iodine value of 99.40, saponification values of 202.36, acid value of 22.16, viscosity of 25.72 free fatty acid of 11.20 and golden yellow colour. Also, the RSO prepared polyesters have coating properties whose values are comparable to those of commercial polyesters. It is therefore recommended that the oil obtained from the seeds of natural rubber (agricultural waste) be exploited in Nigeria for the production of environmentally friendly polyesters in order to optimize its application in non pigmented surface coating.

Keywords: Wastes, Rubber seeds, Environmentally friendly, Renewable source, polyesters

I. Introduction

Agricultural raw materials are known to be environmentally friendly, biodegradable, low cost and readily available. (Bakare et al. 2006). The use of these material resources in many applications has attracted the attention of many researchers due to their potentials to substitute petrochemical derivatives. Plant oils and animal fats belong to such agricultural resources with enormous applications. The world production of plant oils and animal fats rose from 58.4 million tons in 1980 to 114.5 million tons in 2000.

The development in organic chemistry, due to better and improved analytical equipment, has made it possible to perform comprehensive examination of chemical composition, the structure, and the property of natural products like vegetable oils, modification and application of improved consumer-based products has continuously evolved. (Carracher and Sperling 1983). This gradual increase in various applications of fats and oils has triggered the expansion of planted areas of these crops. Recently, cultivation by means of genetic engineering to develop high oleic acid soy bean and rapeseed oil as well as new oil seeds, is continuously being investigated and develop to meet growing demands (Warwel et al. 2001).

In Nigeria, vegetable oil dependent industries rely mostly on imported oils like linseed and soybean oil which are very expensive. The locally available oils like palm oil, palm kernel oil, groundnut oil and coconut oil are in short supply. (Akinayo et al. 2002).

Nigeria has the potential of producing over 13,000 tons of rubber seed oil annually. But to the best of our knowledge, rubber seed oil has no commercial value in Nigeria. Though previous research studies have shown that rubber seed oil is a potential raw material for alkyd resins used as binders for surface coatings. (Joseph et al. 2003).

The use of petroleum based monomers in manufacturing of petroleum based products is expected to decline in coming years because of the continuous rise in petroleum products and the high rate of oil depletion of known oil reserves. This coupled with strict governmental legislation all over the world on environmental protection against degradation, has inspired the investigation of renewable natural resources as a viable alternative. (Aigbodion et al. 2003). Because of this, plants and animals oils have long been identified as possible substitute for petrochemical derivatives in the production of polymers and Bio diesel.

To meet the increasing demands for these renewable agricultural raw materials, great attention has been shifted to chemical industries as it offer a large number of possible applications. The use of modern bio-technique and genetic approaches has proved successful for boiled plants such as rapeseed, walnut and soil bean. (Oguniyi and Njikang 2000). This modern universal approach for changing the amount and composition of the stored oil has enable the optimization of the resources for different specific applications, also, underused and used seed such as rubber seed, (agricultural waste), African locust bean seed and jathropha seed have continuously been sourced for non edible applications.

Rubber seed oil (RSO), an agricultural by product, abundantly available in Nigeria and rich in unsaturated hydrocarbons, is an excellent starting material for many products. An estimation of potential production, based on a world planted area of 9.37 million hectares and an average production rate of rubber seed of 287kg/ha/year is over 1.08 million tons of rubber seed oil per annum. This figure is expected to increase substantially with the expansion of natural rubber production. (Ikhuoria et al. 2004). Although rubber seed oil is a potential raw material for the production of commercially valued alkyd resins, the processing of polymers and the production of biodiesel.

Despite the production potential of alkyd resin from rubber seed oil, the produced resins are usually dark and this limits its application in non pigmented coatings. Chemical transformation of vegetable oils to fatty acid alkyl esters called transesterification or alcoholysis is one of the methods of modifying the quality of vegetable oils. Various components of vegetable oils which are glycerol esters of fatty acids and various amounts of solubilised impurities such as pigments, vitamins, sterols, phospholipids etc, which are capable of compromising the quality of the finished alkyd resins. Ester of rubber seed oil (RSO) would preclude some of these undesirable effects. (Oguniyi and Njikang 2000)

Polyesters are defined as the 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 (Aigbodion et al., 2000). The oils that are mostly employed for alkyd resin synthesis are linseed, soybean, castor and tall oils (Oguniyi and Njikang, 2000, Kildiran et al., 1996 and Majumder, 1999). 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 and tobacco oil (Adefarati, 1986). These drying oils owe their value as raw materials for decorative and protective coatings to their ability to polymerize or "dry" after they have been applied to surface to form tough, adherent, and impervious and abrasion resistance films. The advantages claimed in surface coating applications include excellent odour and heat bleach ability, good drying properties and more uniform

polymer structure (Kirk and Othmer, 1947).

The RSO is unique because of its relative abundance, level of unsaturation and possession of similar properties with linseed oil, which is traditionally employed in the manufacture of Alkyd Resins (Aigbodion, 1991). In addition, due to non use of RSO for edible purposes, it stands out as a veritable substitute for the linseed oil which is currently being imported into the country at a great cost.

However, doubts have been expressed about the sustained successful use of RSO for the large scale production of polyesters. Such doubts are attributed to fears that low percentage yield may result from the sourcing of oil from the rubber seed. Against this backdrop, many works had been conducted to verify the sustainability of RSO in the manufacture of alkyd resin. As a further step in this direction, this work attempts to contribute to the pool of scientific knowledge for the possible application of RSO in the production of alkyd Resin at industrial scale.

It is expected that the successful application of RSO as good substitute for linseed oil and other edible oils in the manufacture of alkyd resin will conserve the nation's foreign exchange and lessen the pressure on the demand for edible oils. This will ultimately translate to low prices for the edible oils and other associated products derivable from them.

II. Literature Review

Alkyd resins (polyesters) are often used in paints and varnishes industry. The alkyd resin is a prime candidate for surface coating materials. It is generally manufactured from phthalic anhydride, poly and drying oils. According to Formo et al. (1965), polyesters form the largest group of synthetic resins available to paint industries and it is widely used due to their low cost and versatility (Kirk and Othmer, 1947). In order to improve properties of alkyd resins, modification with various other materials is recommended. The other materials may be present in physical or chemical combination. The modification of polyesters with cellulose nitrate gives fast-drying, also, modification of alkyd resin with chlorinated rubber gives good fire-resistance. Alkyd resin is also used in coating application. Also they are compatible with most of the resin used on paint industries like rosin, epoxy, phenolic resin, amino resin, polyurethanes etc. Alkyd resins are used in both clear and pigmented, industrial and trade coating to protect and decorate a wide variety of substances. The industrial coatings or finishes generally are applied during the manufacturing process of the item which they cover. Often they are specifically formulated to meet both conditions desired for their application and the endless use of the article of manufacture. The industrial finishes include primers and top coats for refrigerators, furniture, and electrical equipment. There are many significant efforts that have been made to increase alkyd resin production. Many researchers have attempted to search the different sources for alkyd resin preparation. Aigbodion et al (2004) studied enhancing the quality of alkyd resins using methyl esters of rubber seed oil in 2004.

III. Sources and Composition of Rubber Seed Oil (RSO)

Rubber seed oil is the oil obtained from the seed of rubber trees. The oil is unsaturated and comprise mainly of oleic, linoleic and linolenic acids. The function of oils and fats in alkyd is to provide the site for free radicals cross linking, which is the mechanism of drying of oil modified polyesters (Stevens, 1999).

IV. Properties of fat and Oil

Table 1: Physicochemical Properties of Seed Oils as Found in Literatures

| Oil source/Seed | OC | AV | SV | IV | SG | RI | V | HV | FFA | Reference/source |
|-----------------|-------|---------|---------|----------|---------------|---------------|---------|--------|------|--|
| | % | mgKOH/g | mgKOH/g | gI2/100g | dimensionless | dimensionless | mm2/s | MJ/kg | % | |
| Moringa | 40.39 | NR | 186.67 | 69.45 | NR | 1.4608 | NR | NR | 0.40 | Anwar & Bhanger (2003). |
| C. pepo | 41.59 | 0.39 | 190.69 | 104.36 | 0.915 | 1.4662 | 93.65cp | NR | 0.39 | Duhan, (2012). |
| Cashew nut | 49.1 | 10.7 | 137.0 | 41.3 | 0.962 | 1.458 | 56.0cp | NR | 6.1 | Akinhanmi, Atasie, & Akintokun (2008). |
| Fluted rubber | NR | 7.59 | 179.02 | 85.12 | 0.926 | NR | NR | NR | NR | Duhan, (2012). |
| Black beniseed | NR | NR | 158.04 | 106.26 | NR | NR | 33.2 | 41.1 | 0.73 | Fariku, Ndongya, Bitrus (2007). |
| C. maxima | 43.69 | 0.53 | 185.20 | 105.12 | 0.913 | 1.4656 | 48.09 | NR | 0.27 | Alfawaz, (2004). |
| Agusi | 30.0 | 40.0 | 189.5 | 104.4 | 0.874 | 1.4670 | NR | NR | NR | Mabaleha, Mitei & Yeboah (2007). |
| Desert melon | 28.0 | 2.5 | 182.1 | 124.0 | 0.954 | 1.468 | NR | NR | NR | Mabaleha, Mitei & Yeboah (2007). |
| Rubber seed | 68.17 | 13.46 | 28.07 | NR | NR | 585.41 | NR | 0.5854 | 4.11 | Eka, Aris and Nadiyah (2010). |

Source: Bwade et al; 2013.

Where OC= Oil Content, AV= Acid Value, SV= Saponification Value, IV= Iodine value, SG= Specific gravity, RI= Refractive index, FFA= Free fatty acid and HV= heating value

V. Purification of Oil

Crude fats and oils are obtained directly from the extraction of the oil seed. Crude fats and oils contain varying substances that may influence undesirable flavour, colour, or keeping quality of the oil. These substances are removed through a series of purification and processing steps.

1.5.1 Degumming

Degumming is defined as the treatment of additives that are used for the removal of waxes, phosphates, and other impurities in oil. The process of degumming converts the phosphatides to the hydrated gums that are highly insoluble in oil and are quickly separated as the sludge. For the crude lecithin processing, all the hydrated gums are completely vacuum dried. In this process, phosphoric acid and water are added at the temperatures of 60°C (140°F).

1.5.2 Alkali Refining

Alkali refining involves the reaction of free fatty acids in oil with alkaline solution such as caustic soda and potassium hydroxide. In alkali refining, alkaline solution is used to neutralize the free fatty acid present in the oil.

1.5.3 Bleaching

Bleaching is the process of removing colour pigments and metal ions from oil. The purpose of bleaching (or decolorizing) is to reduce the levels of pigments such as carotenoids and chlorophyll, but it also further removes residues of phosphatides, soaps, traces of metals, oxidation products, and proteins. These trace components interfere with further processing. They reduce the quality of the final product and are removed by adsorption with activated clay and silica.

VI. Classification of Alkyd Resin

There are several types of alkyds. One classification is into oxidizing and nonoxidizing types. Oxidizing alkyds cross-link by the same mechanism as drying oils. Nonoxidizing alkyds are used as polymeric plasticizers or as hydroxy-functional resins, which are cross-linked by melamine-formaldehyde (MF), by urea-formaldehyde (UF) resins, or by isocyanate cross-linkers. A second classification is based on the ratio of monobasic fatty acids to dibasic acids utilized in their preparation (oil lengths). Oil length is the amount of fatty acid present in the resins (in percentage). Alkyds are short oil if fatty acid percentage is less than 45%, medium oil if fatty acid percentage is between 45-55% and long oil if fatty acid percentage is greater than 55% (Prane and Joseph, 2002).

VII. Aim of the Study

This research work is anchored on the following aims and objectives:

- To partially refine rubber seed oil, synthesize alkyd resins
- To determine the physicochemical properties and chemical resistance of the RSO prepared alkyd resins

Experimental

2.1 Collection of Samples

The Rubber (*Hevea brasiliensis*) seeds were obtained from a rubber plantation at Omagwa Town in Ikwere Local Government Area of Rivers State, Nigeria. Other reagents used for the study was obtained from laboratory in the Department of Chemistry, Rivers State University of Science and Technology.

2.2 Preparation of rubber seed oil

The shells was removed from the rubber seed, cleaned and dried under the sun for a day. The kernel was later dried to constant weight in the oven for three hours at 35°C to ensure that water and moisture were removed. 1000g of the kernel was immediately grounded using mortar and pestle into a paste in order to weaken and rupture the cell. The paste was stored in a labeled airtight container for oil extraction. n-hexane was added to the paste in the container and mix for oil extraction. The mixture was filter using a filter paper to separate the paste from the oil. The extracted oil was put in an evaporating dish for 24 hours to evaporate the n-hexane. The oil was later put in an oven at 60°C for another 24 hours to remove any remaining n-hexane. Finally, the oil was collected and stored in a label airtight container for further used.

2.3 Degumming of rubber seed oil

300g of crude rubber seed oil was weighed. 100ml of acetic acid was then mixed with the weighed crude rubber seed oil in a 500ml beaker. The mixture was stirred and allowed to settle in a separating funnel over-night and finally, the gums were separated from the rubber seed oil and thereafter washed with water and dried.

2.4 Physico-chemical characterization of crude and degummed rubber seed oil

Saponification Value

2g of RSO was dissolved into a 25ml ethanolic potassium hydroxide solution in 250ml round bottom flask with a reflux condenser. The flask was heated in a steam bath and occasionally swirled to effect saponification as the solution starts to boil, the heating was effected for 30mins, after heating: the soap solution formed was titrated with standard. 0.5m hydrochloric acid using phenolphthalein as indicator. A blank titration was also done in the same manner. The saponification value (S.V) was expressed as:

$$S.V = \frac{56.1M(u-v)}{W}$$

Where:

| | | |
|---|---|---|
| M | = | Molarity of hydrochloric acid |
| W | = | Weight of samples in grammes used |
| U | = | Volume in ml of hydrochloric acid titrated in blank and |

V = Volume in ml of hydrochloric acid titrated in test.

Iodine Value

The sample under determination was weighed and dissolved in 25ml of carbon tetrachloride and agitated thoroughly and then allowed to stand for about 30 mins in dark. 100ml of distilled water and 20ml 10% (w/v) potassium iodide was added to the mixture and filtered with 0.1M standard sodium thiosulphate using 0.5% (w/v) starch solution as indicator. Blank solution was also carried out in similar manner. The iodine value (IV) was calculated as follows:

$$IV = \frac{(b - a) \times M \times 12.69}{W}$$

Where M = Molarity of standard sodium thiosulphate
 W = Weight of sample in grams used
 b = Volume in ml of sodium thiosulphate titrated in blank
 a = Volume in ml of sodium titrated in test.

Acid Value

2g of the RSO was dissolved in 50ml of neutralized solvent of equal volume of diethyl ether and absolute ethanol. The resultant solution was titrated with 0.1M KOH solution using phenolphalein as indicator. The acid value was calculated using the expression;

$$\text{Acid Value (AV)} = \frac{(V \times M \times 56.1 \times 0.142)}{W}$$

Where V = Volume of titrant (KOH) in ml
 M = Molarity of standard KOH
 W = Weight of grams of samples

Refractive Index

$$RI = \frac{W_s}{W_w}$$

Ws = Wight of samples (CRSO and DRSO) Ww = Weight of distilled water

Refractive Index

It was determined using refractometer, in the determination of refractive index, the prison of a refractometer was cleaned using soft paper and acetone after which 5 drops of the RSO were placed on it. The prison was closed firmly and the lamp was swung against it. The switch button at the back of the instrument was used to adjust the alignment mark until the centre mark was aligned on the cross hair and the reading was taken.

Colour

The colour of both crude rubber seed oil and the degummed rubber seed oil samples were determined by the physical eye identification.

Specific gravity

The specific gravity (SG) of both samples was obtained by using a 25ml capacity density bottle at 20⁰C. The SG was calculated as the ratio of the weight of equal volume of the samples to that of water equal temperature i.e. SG Where:

2.5 Preparation of Rubber seed oil based Polyesters (Alkyd resins)

RSO was reacted with glycerol at a temperature range of 230-250⁰ C in a three-necked flask, fitted with motorized stirrer, nitrogen gas inlet, a dean and stark trap carrying a water condenser. Alcoholysis was complete when one part of the reaction mixture dissolved in three parts of anhydrous methanol and formed a clear solution. The reaction temperature was cooled to about 180⁰ C and then phthalic anhydride and xylene was introduced to the flask. The reaction temperature was elevated and then monitored to completion by determination of the acid value periodically, until it dropped to below 7.

2.6 Recipe for Alkyd formulation

The recipe for alkyd resins formulation is presented in table 2.1 below.

Table 2.1:Recipe for Alkyd formulation

| Ingredient | Quantity |
|------------------------|-------------|
| RSO (g) | 151.13 |
| Glycerol (g) | 60 |
| Phthalic anhydride (g) | 90.13 |
| Calcium Oxide (g) | 0.5 |
| Oil length (%) | 50 (medium) |

2.7. Physico-chemical analysis of polyesters samples

The physico-chemical properties of alkyd resins prepare was determined using ASTM standard methods (ASTM D 1639-90, (1994), AOAC, (1997). Similar procedure was used for the determination of physicochemical parameter of the oil.

2.8 Drying Schedule of the RSO

The drying schedule was achieved by applying thin spread of the polyesters on clear glass panel and dried at room temperature. The drying process was monitored in terms of the time of set-to- touch, surface-dry and dry-through.

2.9 Chemical Endurance

The chemical endurance was determined using ASTM (D 1308-67) standard test method at room temperature. The resistance of the films to different solvent media (water, brine, KOH, HCl) was determined.

Polyesters From Chemically Modified Oil of Renewable Source

VIII. Results

Table 3.1: Physico-chemical properties of Refined and Crude rubber seed oil (RSO)

| Properties/parameters | Crude RSO | Refined RSO |
|-------------------------------------|-------------|---------------|
| Colour | Light brown | Golden yellow |
| Acid value (mgKOH/g) | 22.40 | 22.16 |
| Saponification Value (mgKOH/g) | 202.62 | 202.36 |
| Iodine Value (g ₂ /100g) | 99.40 | 98.42 |
| Specific gravity | 0.900 | 0.889 |
| Viscosity (Stokes) | 26.84 | 25.72 |
| Free fatty acid (mg/KOH/g) | 11.70 | 11.20 |
| Refractive index | 1.47 | 1.46 |

Table 3.2: Physico-chemical properties of the finished Polyesters

| Properties/parameters | Alkyd resins |
|----------------------------|--------------|
| Colour | Dark brown |
| Specific gravity (S.G) | 0.935 |
| Acid value | 5.97 |
| Saponification value (S.V) | 283.20 |
| Iodine value | 89.60 |
| Refractive index | 1.604 |
| Free fatty acid | 3.00 |

Table 3.3: Drying schedule for formulated alkyd resin

| Characteristic | Medium Alkyd Resin |
|---------------------|--------------------|
| Set to touch (mins) | 45 |
| Surface dry (min) | 140 |
| Dry through (min) | 660 |

Table 3.4: Chemical Endurance of polyesters film

| Solvent Media | Resistance |
|---------------------|----------------------|
| Alkali (0.1MKOH) | Film was removed |
| Acid (0.1MHCl) | Film was not removed |
| Brime (5% w/w NaCl) | Film was not removed |
| Water (Cold) | Film was not removed |

IX. Discussion

The refractive index of 1.467 obtained in this study falls within the standard value for refractive index of organic oil which is between 1.3 – 1.6 (Kovo and Bawa, 2007). The value is also in the range found for common oils such as castor seed (1.47), butyrospermumparki (1.453), sterculiasetegera (1.465), blighiasapida (1.449) and shear butter oils (1.60) (Asuquo et al, 2010; Kyari, 2008). Refractive index is an indication of the level of saturation of the oil.

The viscosity value (25.72 stoke) obtained for RSO is higher than those of other oils e.g. castor oil (13.02 stoke), shear butter oil (17.78 stoke) and lower than crambe oil (27.20 stoke) (Asuquo et al, 2010).

The specific gravity of RSO was found to be 0.900 indicating that the oil is less dense than water. This value is quite comparable to the linseed oil, which is recommended standard in the production of alkyd resin. Also, the value seems to indicate that no heavy element is present in the oil (Aigbodion and Bakare, 2005). The specific gravity obtained for RSO in this study is similar to those of other oils e.g. shea butter oil (0.92) and castor seed oil (0.96) (Asuquo, 2008).

Peroxide value of 15.2 was obtained for RSO in this study. Peroxide value is an indication of deterioration of oils. Oils with higher peroxide values are more unsaturated than those with lower peroxide values. More unsaturated oils are known to absorb more oxygen and develop higher peroxide values, and oils with higher peroxide values are prone to rancidity (Asuquo, 2008). Therefore, the oil in this study may not be suitable for consumption since it has a peroxide value above 10.

The saponification value (202.36) in table 3.1 obtained for RSO in this study is above those of common oils such as soybean (189 – 195), peanut (187 – 196) and cotton seed oil (189 – 198) (Codex, 1993) which suggest that the oil has high lauric acid content. The lauric acid content and the saponification value of oil serve as important parameters in determining the suitability of oil in soap making and alkyd production. The saponification value obtained for RSO in this study (Table 3.1) projects the oil as good in alkyd synthesis. The saponification value obtained for RSO in this study is also in the range of 203 reported for RSO obtained from (RRIN) Edo State Nigeria and 182.12 ± 0.27 reported for Malaysian rubber seed oil (Abdullah and Salimon, (2009).

From the results in Table 3.1, crude RSO has a light brown colour similar to the dark colour reported for RSO obtained from the rubber research institute of Nigeria (Aigbodion and Bakare, 2005). This indicates that in its natural form, RSO is only suitable in applications where bright color is not the major consideration e.g. pigmented coatings.

The iodine value of 99.40 (table 3.1) obtained for RSO in this study is lower than 136 and 135.79±0.33 reported by

the Rubber Research Institute of Nigeria (Abdullah and Salimon, 2009). This value is below the standard of iodine value for organic oil which is between 125 and 150 (Asuquo, 2008). Based on the iodine value obtained in this study, RSO can be classified as semi-drying oil (with iodine values of 100 – 150) (Asuquo, 2008). Also, this result is indicative of the fact that RSO is quite suitable in alkyd synthesis and its level of unsaturation will accommodate the cross-linking reactions for alkyds to form dry, hard solid film (Sullivan, 1976).

The acid value of 22.16 obtained for RSO in this study is higher than those reported for Malaysian RSO (15.03±0.04) but lower than RSO obtained from the RRIN (43.62) (Abdullah and Salimon, 2009). It corresponds to the amount of potassium hydroxide needed to neutralize free fatty acids.

The physico-chemical properties of medium oil length formulated alkyd resin are presented in Table 3.2.

The dark brown colour of the alkyd resins could be attributed to the colour of RSO and also to high temperatures of reaction, oxidation and catalyst. This alkyd can be utilized in the production of pigmented coatings where very bright colour is not a major requirement.

The iodine values of the alkyds were observed to be 89.60mgKOH/g for the medium alkyd resins as compared to that of RSO (99.40mgKOH/g). The decrease in level of unsaturation of the alkyds could be attributed to the dimerization and polymerization reactions at the reactive double bonds of the oil during alkyd synthesis.

The saponification value of the alkyd resin was observed to have increased greatly considerably to 283.20mgKOH/g for alkyd resin as compared to that of RSO (202.36). This was due to polymerization reaction. The alkyds were essentially polyesters.

The drying schedule of RSO prepared alkyd resin is shown in Table 3.3.

It was observed that the medium alkyds was set to touch at 45 mins, surface dry after 140mins, and completely dried after 660mins. The drying schedule for alkyd resins in this study is closely related to the result of 45mins, 2hrs and 10hrs for set to touch; surface dry and dry through respectively, obtained by Umoebika et al., (2013). Based on this result, it can be inferred that RSO prepared alkyd resin could be used as binder in surface coating formulation as it showed comparable coating properties to other reported oil modified alkyd.

Film of the prepared alkyd resin showed excellent resistance to acid, brine, water but poor resistance 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 (Momodu, 2011).

X. Conclusion

Rubber seed oil was used in the preparation of alkyd resin. Generally, there are increase in the values of acid value, saponification value and iodine value for the alkyd resin when compared to that of RSO. RSO seems to be more promising in the production of alkyd resin as indicated by physico-chemical analysis of the finished alkyd resin. The alkyd resin films have properties that will make it to be highly resistant to acid, brine, and water. Therefore, it can be useful in formulation of non-polluting coatings. However, it has its short coming which is poor resistance to alkali.

References

- [1]. Abdullah B. M.; Salimon O (2009) Physicochemical characteristics of Malaysian rubber (*Hevea brasiliensis*) seed oil. *Eur. J. Sci. Res.*, 31, 431-445.
- [2]. Abulude, F. O., Ogunkoya, M. O., & Ogunleye, R. F. (2007). Storage properties of oils of two Nigeria oil seeds *Jatropha curcas* (physic nut) and *Helianthus annuus* (sunflower). *Amer. J. Food Tech.*, 2, 207-211. <http://dx.doi.org/10.3923/ajft.2007.207.211>
- [3]. Adefarati, F.B., (1986): Development of Non-Edible Oils for use in the Nigerian Surface Coating Industry with particular reference to Rubber (*Hevea brasiliensis*) Seed Oil for manufacture of Air-Drying Oil modified Alkyds. In: Enabor EE (ed.) *Industrial Utilization of Natural Rubber (Hevea brasiliensis) seed, latex and wood*, Rubber Research Institute of Nigeria. 27-38.
- [4]. Aigbodion, A.I (1991): Preliminary Studies on the preparation of rubber seed oil, *Indian journal of Natural Rubber Research*, 4(2): 114-117.
- [5]. Aigbodion, A.I and Pillai, C.K.S (2001); Synthesis and molecular weight characterization of Rubber Seed Oil- modified Alkyd Resin; *Journal of Applied Polymer Science*. Vol. 32, No9, pp 1105-1108.
- [6]. Aigbodion A.I & Okieimen, F.E (2002); Kinetics of the Preparation of Rubber seed Oil Alkyd ; *European Polymer Journal*, Vol. 32 No 9; Pp 1105-1108
- [7]. Aigbodion AI, Okieimen FE, Ikhuoria EU, Bakare IO, Obazee EO (2003a). Rubber seed oil modified with maleic anhydride and fumaric acid and their alkyd resins as binders in water-reducible coatings. *J. Appl. Polym. Sci.* 89: 3256-3259.
- [8]. Aigbodion AI, Okieimen FE, Obazee EO, Bakare IO (2003b). Utilization of maleinized rubber seed oil and its alkyd resin as binders in waterborne coatings. *Progress Org. Coat.* 43: 28-31.
- [9]. Aigbodion, A.I. and Spillai, C.K., (2000): Preparation, Analysis and Application of Rubber Seed Oil and its Derivatives in Surface Coatings. (98) 187-192.
- [10]. Aigbodion A. I.; Bakare I. O (2005) Rubber seed oil quality assessment and authentication. *J. Am.Oil Chem. Soc.*, 82, 465-469.
- [11]. Aigbodion A. I.; Bakare I. O (2005) Rubber seed oil quality assessment and authentication. *J. Am.Oil Chem. Soc.*, 82, 465-469.
- [12]. Akinmawo, G., (1989). Local materials in the paint industry: problems and prospects. Seminar on Raw Materials for the Domestic: Industrial Plastics, Rubber and Coating Sector, Lagos, pp. 60–70.
- [13]. Akintayo, C. O. (2004). Synthesis and Characterization of Albiziabenth medium oil modification of alkyd resin and its chemically modified derivatives. PhD thesis. University of Ibadan, Ibadan, Nigeria.
- [14]. Akpan, U.G., Jimoh, A. and Mohammed, A.D. (2006). "Extraction, Characterization and 'Modification of Castor Seed Oil'".
- [15]. Leonardo *Journal of Sciences*, vol. 8:43-52
- [16]. AOAC (1997). *Official Methods of Analysis*, 17th Ed. Washington, DC.
- [17]. Aremu, M. O.; Olaofe, O.; Atolaiye, B. O.; Amos, V. A (2008) The physicochemical properties and fatty acid composition of sponge luffa (*Luffa cylindrica*) kernel oils. In: *Proceedings of the Chemical Society of Nigeria*. Petroleum Training Institute, Effurum-Warri, Delta State, Nigeria.
- [18]. ASTM D 1639-90, (1994): Standard Method for Acid Value of Organic Materials. In: *Annual Book of American Society for Testing and Material Standards*. 6: 260-261.
- [19]. ASTM D 1962-1967, (1979): Test for Saponification Value of drying oils, fats and polymerized fatty acids. In: *Annual Book of American Society for Testing and Material Standards*. 29: 259-61.
- [20]. ASTM D 1541-60, (1979), Test for Iodine Value of drying oils and their derivatives. In: *Annual Book of American Society for Testing and Material Standards*. 29: 186-189.
- [21]. Asuquo J. E.; Anusiem, A. C. I.; Etim, E. E (2010) Extraction and characterization of shear butter oil. *World J. App. Sci. Tech.*, 2, 282-288.
- [22]. Asuquo J. E (2008) Studies on the Adsorption of Some Selected Metallic Soaps onto Hematite. Ph.D. Dissertation, University of Port Harcourt, Nigeria.
- [23]. Bajpai, M. And Seth S., (2000): Use of Unconventional Oils in Surface Coating: Blends of alkyd resin with epoxy esters. *Journal of Pigment and Resins Technology*. 29(2): 82-87.
- [24]. Boxall J. (1982) The development in modern coating technology. *Journal of progress in organic costing*.
- [25]. Bwade, K.E., B. Aliyu, and A. M. Kwaji (2013) Physicochemical Properties of Pumpkin Seed Oil Relevant to Bio-diesel Production and other Industrial Applications. *International Journal of Engineering, Business and Enterprise Applications*, 4(1): 73
- [26]. Cocks, L.V and Rede, C.V., (1966): *Laboratory Handbook for Oil and Fat Analysis*, London Academy Press, London. 305-309.

- [27]. Eka, H. D.; Aris, T.Y. and Nadiyah, W.A. (2010). Potential use of Malaysian Rubber (*Hevea brasiliensis*) Seed as Food, Feed and Biofuel. *International Food Research Journal*, vol.17: 527-534
- [28]. Fariku, S., Ndongya, A.E., and Bitrus, P.Y. (2007). "Biofuel Characteristics of Beniseed (*sesamum indicum*) Oil". *African Journal of Biotechnology* 6(21):2442-2443
- [29]. Formo, M.W. (1965). Esters reaction of fatty materials. *Journal of America Oil Chemist Society* 31:548-559.
- [30]. Ihekoronye, A. and Ngoddy, P. (1985). *Integrated food science and technology in the Tropics*, MacMillan Education Limited, pp: 338-339.
- [31]. Ikhuria, E. U., Maliki, M., Okieimen, F. E., Aigbodion, A. I., Obazee, E. O., & Bakare, I. O. (2007). Synthesis and characterization of chlorinated rubber seed oil alkyd resins. *Prog. Org. Coat.*, 59, 134-137. <http://dx.doi.org/10.1016/j.porgcoat.2007.02.001>
- [32]. Ikhuria, E.U. and Aigbodion, A.L., (2006). Determination of Solution of Viscosity Characterization of Rubber Seed Oil Based Alkyd Resins. *J. Appl. Polym. Sc.* 101: 3073-3075.
- [33]. Ikhuria, E.U., Aigbodion, A.I and Okieimen, F.E., (2005). Preparation and Characterization of water reducible alkyds with fumarized rubber seed oil. *Progress in Org. Coatings*, 52:238-240.
- [34]. Kildiran, G., Yucek, S.O. and Turkay, S., (1996): In-situ alcoholysis of soyabean oil. *J. Amer. Oil Chem.Soc.* 73(2): 252-8.
- [35]. Kirk, R.F and Othmer, D.F. (1947). *Alkyd Resin: Encyclopedia of Chemical Technology*. Vol 9. New York: John Wiley and Sons, Inc.
- [36]. Kovo, A. G.; Bawa, A. A (2007) Extraction and characterization of oil from *Accianiloticiaseeds* by different solvents. *J. Eng. App. J.*, 2, 572-575.
- [37]. Kyari, M. Z. (2008) Extraction and characterization of seed oils. *Int. Agrophysics*, 22: 139-142.
- [38]. Majumder, S., Kumar, D., Nirvan, Y.P.S., (1999): Acrylate grafted dehydrated castor oil alkyd. A binder for exterior paints. *Paint India*. 60:57-65.
- [39]. Marvin W. Formo (1954) "Ester reactions of fatty materials" *Journal of the American Oil Chemists' Society* 1954, 31 (11), pp 548-55
- [40]. MacDonald, P., Edward, R.A. and Greenhalg, J.F.D., (1994): *Animal Nutrition*, 4th Edition, Longman Publishers. 22-28, 32-36.
- [41]. Micciche, F. (2005). The combination of ascorbic acid derivative/iron salts as catalyst for the oxidative drying of alky-paints: A Biomimetic approach. *Technische Universiteit Eindhoven*. <http://alexandria.tue.nl/extra2/200512801.pdf>
- [42]. Momodu, V.M., Omorogbe, S.O, Ikhuria, E.U., and Aigbodion, A.I. (2011): Synthesis and Evaluation of Performance Characteristics of Walnut (*Tetracarpidium conophorum*) Seed Oil-Modified Alkyd Resin. *Researcher*; 3(7): 63-66.
- [43]. Nwakwo, B.A., Aigbekaen, E.O. and Sugay, G.A., (1986): Estimates of Natural Seed Production in Nigeria. In: Enabor EE (ed.) *Industrial Utilization of Natural Rubber Seed, Latex and Wood*. Rubber Research Institute of Nigeria, Benin City, Pp 78-87.
- [44]. Nzikou, J.M., Mvoula-Tsieri, M. Pambou-Tobi, N.P.G. Ndangui, C.B. Kimbonguila, A. Silou, Th. M. Linder, Scher, J. and Desobry, S. (2010). Proximate Composition and Seed Oil from Terminalia Catappa L. and Their Kinetics of Degradation of the Oil during Heating. *Australian Journal of Basic and Applied Sciences*, Vol.7:2039-2047
- [45]. Ogunyi, D.S. and Njikang, G.N., (2000): Preparation and evaluation of alkyd resin from Castor Oil. *Pak J. Sc. Res.* 43(6): 378- 80.
- [46]. Okieimen .E F., Bakare, O.I and Okieimen, C.O., (2002): Studies on the epoxidation of rubber seed oil. *Ind. Crops Prod.* 15: 139-144.
- [47]. Okieimen .E F. and Ebhoaye, J.E., (1992): Studies in the thermal degradation of polyvinyl chloride in the presence of metal soaps of rubber seed oil. *Eur. Polym. J.* 28(1): 1423-1425.
- [48]. Onwuka, G.I. (2005). "Food analysis & instrumentation". Naphthali publishers, Lagos, Nigeria.
- [49]. Patton, T. C. (1962) *Alkyd resin technology* Wiley Interscience Publisher, New York, 1962.
- [50]. Prane and Joseph J. (2002) *Introduction to polymers and Resins*. Federation of societies on coating technologies, New York.
- [51]. Stevens, M.P., (1999). *Polymer Chemistry: An Introduction*. In: *Polyester*. 3rd ed. Oxford University Press, 335-58.
- [52]. Umeobika U.C., Onuegbu T.U., Iloamaeke M.I., Ekwueme I.J (2013) synthesis and evaluation of performance characteristics of rubber seed oil-modified short and medium alkyd resins. *International Journal of Science Innovations and Discoveries*
- [53]. Wicks, JR, Frank N. Jones and Peter S. Pappas (1999) *Organic Coating Science and Technology*, 2nd ed, Wiley -Inter science Publication, Canada.
- [54]. Akpan, U.G., Jimoh, A. and Mohammed, A.D. (2006). "Extraction, Characterization and Modification of Castor Seed Oil".
- [55]. *Leonardo Journal of Sciences*, vol. 8:43-52
- [56]. AOAC (1997). *Official Methods of Analysis*, 17th Ed. Washington, DC.
- [57]. Aremu, M. O.; Olaofe, O.; Atolaiye, B. O.; Amos, V. A (2008) The physicochemical properties and fatty acid composition of sponge luffa (*Luffa cylindrica*) kernel oils. In: *Proceedings of the Chemical Society of Nigeria*. Petroleum Training Institute, Effurum-Warri, Delta State, Nigeria.
- [58]. Akpan, U.G., Jimoh, A. and Mohammed, A.D. (2006). "Extraction, Characterization and Modification of Castor Seed Oil".
- [59]. *Leonardo Journal of Sciences*, vol. 8:43-52
- [60]. AOAC (1997). *Official Methods of Analysis*, 17th Ed. Washington, DC.
- [61]. Aremu, M. O.; Olaofe, O.; Atolaiye, B. O.; Amos, V. A (2008) The physicochemical properties and fatty acid composition of sponge luffa (*Luffa cylindrica*) kernel oils. In: *Proceedings of the Chemical Society of Nigeria*. Petroleum Training Institute, Effurum-Warri, Delta State, Nigeria.
- [62]. ASTM D 1639-90, (1994): Standard Method for Acid Value of Organic Materials. In: *Annual Book of American Society for Testing and Material Standards*. 6: 260-261.
- [63]. ASTM D 1962-1967, (1979): Test for Saponification Value of drying oils, fats and polymerized fatty acids. In: *Annual Book of American Society for Testing and Material Standards*. 29: 259-61.
- [64]. ASTM D 1541-60, (1979), Test for Iodine Value of drying oils and their derivatives. In: *Annual Book of American Society for Testing and Material Standards*. 29: 186-189.
- [65]. Asuquo J. E.; Anusiem, A. C. I.; Etim, E. E (2010) Extraction and characterization of shear butter oil. *World J. App. Sci. Tech.*, 2, 282-288.
- [66]. Asuquo J. E (2008) Studies on the Adsorption of Some Selected Metallic Soaps onto Hematite. Ph.D. Dissertation, University of Port Harcourt, Nigeria.
- [67]. Bajpai, M. And Seth S., (2000): Use of Unconventional Oils in Surface Coating: Blends of alkyd resin with epoxy esters. *Journal of Pigment and Resins Technology*. 29(2): 82-87.
- [68]. Boxall J. (1982) The development in modern coating technology. *Journal of progress in organic costing*.
- [69]. Bwade, K.E., B. Aliyu, and A. M. Kwaji (2013) Physicochemical Properties of Pumpkin Seed Oil Relevant to Bio-diesel Production and other Industrial Applications. *International Journal of Engineering, Business and Enterprise Applications*, 4(1): 73
- [70]. Cocks, L.V and Rede, C.V., (1966): *Laboratory Handbook for Oil and Fat Analysis*. London Academy Press, London. 305-309.
- [71]. Eka, H. D.; Aris, T.Y. and Nadiyah, W.A. (2010). Potential use of Malaysian Rubber (*Hevea brasiliensis*) Seed as Food, Feed and Biofuel. *International Food Research Journal*, vol.17: 527-534
- [72]. Fariku, S., Ndongya, A.E., and Bitrus, P.Y. (2007). "Biofuel Characteristics of Beniseed (*sesamum indicum*) Oil". *African Journal of Biotechnology* 6(21):2442-2443
- [73]. Formo, M.W. (1965). Esters reaction of fatty materials. *Journal of America Oil Chemist Society* 31:548-559.
- [74]. Ihekoronye, A. and Ngoddy, P. (1985). *Integrated food science and technology in the Tropics*, MacMillan Education Limited, pp: 338-339.
- [75]. Ikhuria, E. U., Maliki, M., Okieimen, F. E., Aigbodion, A. I., Obazee, E. O., & Bakare, I. O. (2007). Synthesis and characterization of chlorinated rubber seed oil alkyd resins. *Prog. Org. Coat.*, 59, 134-137. <http://dx.doi.org/10.1016/j.porgcoat.2007.02.001>
- [76]. Ikhuria, E.U. and Aigbodion, A.L., (2006). Determination of Solution of Viscosity Characterization of Rubber Seed Oil Based Alkyd Resins. *J. Appl. Polym. Sc.* 101: 3073-3075.
- [77]. Ikhuria, E.U., Aigbodion, A.I and Okieimen, F.E., (2005). Preparation and Characterization of water reducible alkyds with fumarized rubber seed oil. *Progress in Org. Coatings*, 52:238-240.
- [78]. Kildiran, G., Yucek, S.O. and Turkay, S., (1996): In-situ alcoholysis of soyabean oil. *J. Amer. Oil Chem.Soc.* 73(2): 252-8.
- [79]. Kirk, R.F and Othmer, D.F. (1947). *Alkyd Resin: Encyclopedia of Chemical Technology*. Vol 9. New York: John Wiley and Sons, Inc.
- [80]. Kovo, A. G.; Bawa, A. A (2007) Extraction and characterization of oil from *Accianiloticiaseeds* by different solvents. *J. Eng. App. J.*, 2, 572-575.
- [81]. Kyari, M. Z. (2008) Extraction and characterization of seed oils. *Int. Agrophysics*, 22: 139-142.
- [82]. Majumder, S., Kumar, D., Nirvan, Y.P.S., (1999): Acrylate grafted dehydrated castor oil alkyd. A binder for exterior paints. *Paint India*. 60:57-65.
- [83]. Marvin W. Formo (1954) "Ester reactions of fatty materials" *Journal of the American Oil Chemists' Society* 1954, 31 (11), pp 548-55
- [84]. MacDonald, P., Edward, R.A. and Greenhalg, J.F.D., (1994): *Animal Nutrition*, 4th Edition, Longman Publishers. 22-28, 32-36.
- [85]. Micciche, F. (2005). The combination of ascorbic acid derivative/iron salts as catalyst for the oxidative drying of alky-paints: A Biomimetic approach. *Technische Universiteit Eindhoven*. <http://alexandria.tue.nl/extra2/200512801.pdf>
- [86]. Momodu, V.M., Omorogbe, S.O, Ikhuria, E.U., and Aigbodion, A.I. (2011): Synthesis and Evaluation of Performance Characteristics of Walnut (*Tetracarpidium conophorum*) Seed Oil-Modified Alkyd Resin. *Researcher*; 3(7): 63-66.
- [87]. Nwakwo, B.A., Aigbekaen, E.O. and Sugay, G.A., (1986): Estimates of Natural Seed Production in Nigeria. In: Enabor EE (ed.) *Industrial Utilization of Natural Rubber Seed, Latex and Wood*. Rubber Research Institute of Nigeria, Benin City, Pp 78-87.

- [88]. Nzikou, J.M., Mvoula-Tsieri, M. Pambou-Tobi, N.P.G. Ndangui, C.B. Kimbonguila, A. Silou, Th. M. Linder, Scher, J. and Desobry, S. (2010). Proximate Composition and Seed Oil from TerminaliaCatappa L. and Their Kinetics of Degradation of the Oil during Heating. Australian Journal of Basic and Applied Sciences, Vol.7:2039-2047
- [89]. Ogunyi, D.S. and Njikang, G.N., (2000): Preparation and evaluation of alkyd resin from Castor Oil. Pak J. Sc. Res. 43(6): 378- 80.
- [90]. Okieimen .E F., Bakare, O.I and Okieimen, C.O., (2002): Studies on the epoxidation of rubber seed oil. Ind. Crops Prod. 15: 139-144.
- [91]. Okieimen .E F. and Ebhoaye, J.E., (1992): Studies in the thermal degradation of polyvinyl chloride in the presence of metal soaps of rubber seed oil. Eur. Polym. J. 28(1): 1423-1425.
- [92]. Onwuka, G.I. (2005). "Food analysis & instrumentation".Naphthali publishers, Lagos, Nigeria.
- [93]. Patton, T. C. (1962) Alkyd resin technology Wiley Interscience Publisher, New York, 1962.
- [94]. Prane and Joseph J. (2002) Introduction to polymers and Resins. Federation of societies on coating technologies, New York.
- [95]. Stevens, M.P., (1999). Polymer Chemistry: An Introduction. In: Polyester. 3rd ed. Oxford University Press, 335-58.
- [96]. Umeobika U.C., Onuegbu T.U., Iloamaeke M.I., Ekwueme I.J (2013) synthesis and evaluation of performance characteristics of rubber seed oil-modified short and medium alkyd resins. International Journal of Science Innovations and Discoveries
- [97]. Wicks, JR, Frank N. Jones and Peter S. Pappas (1999) Organic Coating Science and Technology, 2nd ed, Wiley –Inter science Publication, Canada