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Formulation of Alkyd-Based Polymer Coating from Treated Seed of Tsada (Ximenia Americana) Seed Oil: Physiocochemical and Mechanical Characterization

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Abstract:
The purpose of this work is to synthesized Tsada oil-based alkyd coating and investigate the parameters that affect coating performance. The method used for the alkyd resin synthesis is the alcoholysis method combined with azeotropic esterification with refluxing xylene which carries away the reaction water (Marvin et al., 1954). Alkyds were formulated from Ximenia americana seed oil (XASO), glycerol, phthaleic anhydride and maleic anhydride. Performances of the cured coatings were tested in terms of film hardness, adhesion, drying time and chemical resistance test.The experimental result shows that, the synthesized coatings possess coating performance properties in terms of viscosity, chemical resistance, and adhesion. The viscosity of the alkyd increases with increase in the reaction time and concentration of maleic and pthaleic anhydride. The viscosity increase followed the trend $MA_2 < MA_1 < PA$*. The chemical resistant test reveals that the alkyds from* MA_1 *and* MA_2 *have poor resistance towards acid and alkalis as the coating exhibit severe whitening during the soaking period. The result of the adhesion property test showed that alkyd PA has excellent adhesion performance relative to alkyd* MA_1 *and* MA_2*.The experimental test shows that, alkyd PA can be applicable to spraying technology due to its low viscosity. The resistance of the alkyd to alkali, peeling, flaking and blistering makes it to be used for exterior applications. However, alkyds* MA_1 *and* MA_2 *have higher viscosity and drying time, which makes them to form thicker dry film for better hiding and durability. The experimental results suggest that, XASO which is non-drying oil can make tremendous improvement in coating industry because its (XASO) better film performance which is indicated by excellent adhesion to substrate.*

Keywords: *Tsada seed oil, coating, alcoholysis, alkyds*

1. Introduction

The term “alkyd” originally comes from “al”, referring to alcohol, and “kyd”, referring to acid. Nowadays, the term alkyd refers to polyesters modified with fatty acids. Alkyds are prepared via condensation polymerization of three types of monomers: polyalcohols, polybasic acids, and fatty acids or triglyceride oils to obtain fatty-acid containing polyesters (Weiss, 1997). In the surface coating industries, oil-modified polyesters or alkyds dominates as the most widely used solvent borne binder (Bognar *et al.*, 1991). These low molecular weight esters which are products of polycondensation reaction of polyol, diacid, and mono-acid (oils or fats) are very flexible and versatile and have been found to be compatible with other polymer systems (Anthawale *et al.*, 2000). Furthermore, developments in organic chemistry and fundamental knowledge on the physics and chemistry of paints and coatings enabled some problems encountered before in vegetable oil based products to be solved. This resulted in the development of coatings formulations with much improved performance that are based on renewable resources.

Vegetable oil such as linseed, Pongamia, Soybean and Rubber seed have been used in the preparation of different low molecular weight polymers varying from alkyd (Wang *et al.*, 2000), polyepoxides (John *et al.*, 2002), polyesterimides (Ahmad *et al.*, 2003), to polyurethanes (Ahmad *et al.*, 2002). Some of these oils are medicinal while others are edible; due to their competitive use the oils are scarce and expensive. The use of renewable but non edible oils provides an opportunity to make value added products like polymeric resins for the paint coating industry. There is thus a compelling reason to explore low priced and unconventional sources such as Tsada (*Ximenia Americana)* seed oil *(XASO)* to supplement available sources. *Ximenia americana* is a medicinal plant that is bushy and spiny shrub, 4-5m high with an open crown. The fruits are green but turn golden-yellow or red when ripe. The physico-chemical properties of *XASO* by Eromosele 1993, shows some level of unsaturation due to its Iodine Value. The iodine value 96.52g/100g, is a clear indication that the oil is non-drying and may substantially be a polyunsaturated (Eromosele, 1993). Tsada seed oil which contains significant amount of saturated bonds that presumably contribute to the non-drying property of the resin synthesized. The non-drying alkyds have made tremendous improvement in quality of nitrocellulose lacquers (Williams, 2000).

The main aim of this work is to develop a new bio-based polymeric coating fromTsada (*Ximenia americana*) seed oil as renewable resources. To achieve this goal, the experimental work focused on formulation of *XASO* alkyd polymer coating from glycerol and dicarboxylic acids (maleic and phthaleic anhydrides) using the in-situ alcoholysis method (Marvin *et al*., 1954).

2. Experimental

2.1. Materials

The fruits of *Ximenia americana* seed were collected locally from the forest around Yola metropolis of Adamawa State. The fruits were then washed, air-dried at room temperature and cracked to remove the hard shell in other to obtain the seed. *Ximenia americana* seed oil (XASO) were extracted using n-hexane in a Soxhlet apparatus (Eromosele *et al*., 1994) and solvent removed on a rotary evaporator at 50^0C. Followings are commercially available chemicals, which were used without further treatment: maleic anhydride (MA), phthaleic anhydride (PA), glycerol, calcium hydroxide, and xylene were obtained at chemistry Department, Modibbo Adama University of Technology Yola, Adamawa State.

2.2. Alkyd synthesis

The method used for the alkyd resin synthesis is the alcoholysis method combined with azeotropic esterification with refluxing xylene which carries away the reaction water (Marvin *et al*., 1954). The method consists of two stages as follows:

2.2.1. Stage I: Synthesis of Monoglycerides

Alcoholysis is a transesterification reaction between a triglycerides (oil) and glycerol (polyols) to form a monoglycerides (Patton, 1962; Elliot, 1993). The *XASO* and glycerol were added into a three neck flask in a ratio of 1:2 respectively. The mixture was then heated to a temperature of 120^0C for 0.5 hours, and then $Ca(0H)_2$ was added as a catalyst. The temperature was further raised for 1 hour at 240^0C until the alcoholysis was realized. The completion of the alcoholysis was indicated by a simple solubility test, where one part of the reaction mixture was mixed with three parts of ethanol. A clear solution indicates conversion to monoglycerides has been achieved (Elliot, 1993).

2.2.2. Stage II: Synthesis of alkyds

At the onset of the second phase, the temperature was lowered to about 180^0C and a measured quantity of pthalic and maleic anhydrides were added (see *table1* below), followed by addition of xylene (10% of total weight charge) into the reaction mixture to remove the water of esterification by forming an azeotrope (Onukwuli and Igbokwe, 2008; Ikhuoria *et al.,* 2007).As the reaction progresses, the viscosity was monitored for every 30 minute. Finally, the synthesized alkyd was cool down to a temperature of 150^0C, diluted with white spirit and thoroughly mixed to achieve homogeneity.

The above procedure was repeated with different diacid composition ranging from using PA alone (ALKYD PA), PA/MA_1 at 1:0.43 (Alkyd MA_2). The total amount of PA in the three formulations was maintained constant.

	Alkyd Compositions		
Raw Materials	PA	MA_1	MA_2
XASO (mL)	15.00	15.00	15.00
Glycerol (mL)	30.00	30.00	30.00
PA (g)	1.00	1.00	1.00
MA (g)	-	0.25	0.43
Xylene (mL)	60.00	60.00	60.00

Table 1: Alkyd resins compositions

2.3. Characterization of Alkyd Samples

All the alkyd samples were evaluated for their physico-chemical properties in accordance with ASTM techniques. Performance characteristics of the alkyds were determined thus: Crosshatched adhesion tape test (ASTM D3359), Chemical resistance test (ASTM D1647), Drying schedule (ASTM D1640-69), Viscosity (Barminas and Osemeahon, 2006), Acid value (Volumetric analysis) and Solid content (Gravimetric analysis).

3. Results and Discussion

3.1. Alcoholysis

The completion of alcoholysis was indicated by a simple solubility test, where one part of the reaction mixture was mixed with three parts of ethanol. A clear solution indicates conversion to monoglycerides has been achieved and ready for the subsequent esterification reaction with diacids (Patton, 1962; Elliot, 1993). The chemical interaction between the triglycerides and glycerol is shown at Figure 1.

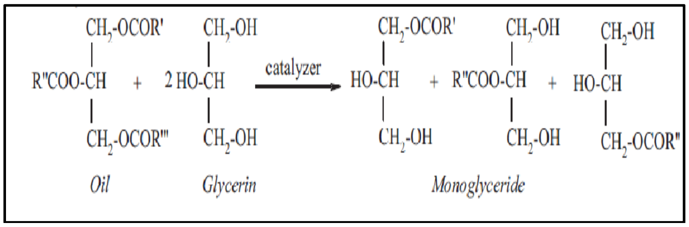

Figure 1: Conversion of triglycerides to Monoglycerides (Patton, 1962; Elliot, 1993)

3.2. Acid Value vs. Water Collected

The extent of conversion during the synthesis of the alkyds at the stage of the condensation of the monoglycerides with the diacids was monitored from the acid number of the reaction mixture. Table 2 shows the changes in acid number and the amount of water collected at different reaction time. As the reaction progress, the acid number decreased and amount of water collected gradually increased owing to the condensation between the monoglycerides with diacids. The decrease in acid value is explained as arising from the desperate reactivities of primary and secondary hydroxyl groups of glycerol with carboxyl groups of phthalic anhydride. It is also attributable to incorporation of almost all reactants in the polymer chain at the initial stage of reaction, characteristics of step-growth polymerization. It has been reported that the primary hydroxyl groups of the monoglyceride reacts more rapidly than the secondary hydroxyl groups with carboxyl groups of phthalic anhydride. It is established that at a temperature of about 160ºC, primary hydroxyl groups of glycerol react rapidly with carboxyl groups of phthaleic anhydride, while secondary hydroxyl groups react at temperature above 230ºC (Goldsmith, 1948). In confirmation of the above, the acid value for all the samples decreased, consistent with high amounts of di- and triglyceride present in the reaction mixture and the concentration of the acid anhydride (Onukwli & Igbokwe, 2008). However, in polyesterification reactions, the reactivity of the functional group does not depend on the size of molecule to which it is attached (Aigbodion & Okieimen, 1996).

Parameter		**Time (min)**		
	30.0	60.0	90.0	120.0
Acid value (mgKOH)	15.5	10.2	9.0	8.4
Water collected (mL)	4.10	3.00	2.80	2.00
Temperature (^oC)	120	240	260	300

Table 2: Acid values of alkyd PA

3.3. Viscosity and Acid Values of Synthesized Alkyds

In coating industry an understanding of the viscosity of the binder is very important because it controls factors such as flow rates, leveling and sagging, thermal and mechanical properties, dry rate of paint film and adhesion of the coating to substrate (Barminas and Osemeahon, 2007). Because of the presence of functional groups in the polymeric backbone, inter-polymeric specific interactions have long been known to result in unusual behavior and material properties that are dramatically different from those of the nonfunctional polymers (Qi *et al*., 2002). These interactions include ion-ion columbic interaction, hydrogen bonding and transitional metal complexation. Specific interactions between polymers cause aggregation or complexation of the component polymer chains, resulting in solution viscosity variation (Qi *et al*., 2002).

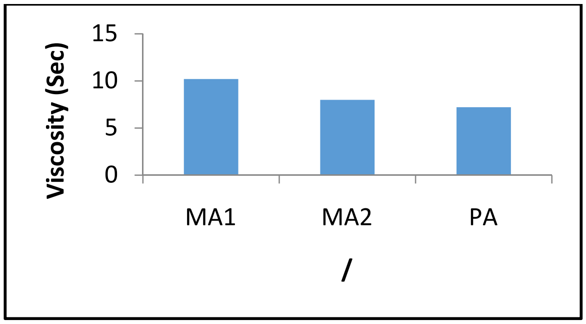

Figure 2: Variation in viscosity of alkyds

Figure 2 shows the variation in viscosity of alkyd PA, MA_1 and MA_2. The increase in viscosity is attributed to the increase in amount of maleic anhydride and also the complexity of the molecular structure of the alkyd formed. Furthermore, the viscosity of ALKYD MA_1 and ALKYD MA_2 rises as a result of the polymerization degree. This is due to the fact that viscosity is highly dependent on amount of cross linking in polymer (Osemeahon and Barminas, 2007). Viscosity increases with the amount of cross-links, which means the formation of longer and branched polymer chains. Slight decrease in the cross-linking density of the coating results in low porosity of the coating. The extent of polymerization directly affects the viscosity of polymers. XASO is classified as non-drying oil which contains a higher proportion of saturated bonds and leads to a ,lower degree of polymerization. However, the high molecular weight of the resin also causes the resin to have an unsuitably high viscosity, thereby necessitating low-solids formulations for coating applications. In many paint systems, low viscosity is a desirable attribute in spraying lacquers and penetrating sealers and stains. Low viscosity entailed their penetrative ability while concomitant with binding or consolidation of the substrate surface.

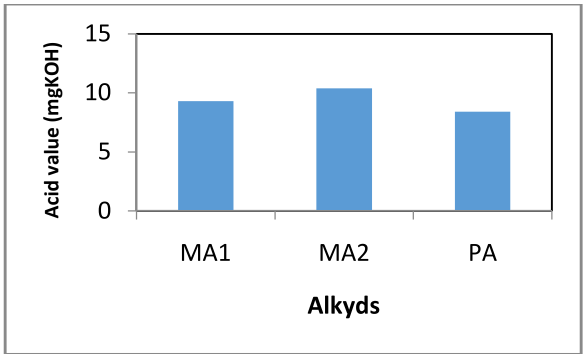

Figure 3: Variation in acid values of alkyds

The variation in acid value of the different synthesized alkyds is shown in Figure 3. The result shows an increase in acid values owing to the incomplete or partial polycondensation reaction between the acids and monoglycerides. Furthermore, increase in concentrations of maleic anhydride lead to the formation of gel-like intermolecular complex structure, making very difficult to control the viscosity (Qi *et al*., 2002). The described phenomenon above causes partial condensation of the different alkyds (MA_1 and MA_2).

3.4. Film Properties

3.4.1. Chemical Resistant Test

The ability of a paint film to resist chemical attack is one of the desirable qualities of a good coating film (Osemeahon and Barminas, 2007b).The results for acid, alkali, water and solvent resistance test are summarized in Table 3 The coatings from ALKYD MA_1 and ALKYD MA_2 have poor resistance towards acids and alkali as the coatings exhibited severe whitening during the soaking period. This may be due to the poor cross-linking of the alkyds film during film autoxidation reactions and the absence of function groups which helps to promotes film adherence to the substrate. Results from alkali test shows that alkyd coatings have poor resistance towards alkali solution where film defects start to appear in less than 1 hr of immersion in the alkali solution. This is not totally unexpected as ester linkages in the alkyd are susceptible to alkali hydrolysis.

		Alkyds	
Reagents resistance (Hours)	PA	MA_1	MA_2
Acid (24)	1	2	2
Alkali (2)	2	0	0
Water (72)	1	3	2
Solvent (72)	1	2	2

Table 3: Chemical resistance test

0= Completely removed; 1= Unaffected; 2= Partially cracked; 3= Loss in gloss.

3.4.2 Physico-Mechanical Properties

3.4.2.1. Dry Time

The results of the drying time and surface dry of the various alkyds are shown in Figure 4. The time it takes for a coating to dry (reaction time) after application is an important factor for the paint formulator (Osemeahon *et al*., 2007). This is because if the coating dries too fast, it will be prone to brittleness and if it dries too slowly, the coating may be subjected to pick up dirt (Trumbo *et al*., 2001). From the results given it suggests that ALKYD PA gives a good surface dry and good tack-free dry relative to ALKYD MA_1 and ALKYD MA_2 respectively. The good drying time can be attributed to the presence of carbonyl groups in the polymer backbone, which activate the methylene groups in the ALKYD PA resin. Therefore, in the presence of suitable driers, the oxygen activation of the methylene group is further accelerated, which results in faster drying time. The drying time is further improved by the presence of

C=C units which in the presence of oxygen, serve as an initiator for the oxidative cross-linking reaction and its related to the amount of the double bonds present in the oil as measured by the iodine value (Muizebelt et al., 1998; Agbenyega et al., 1991).

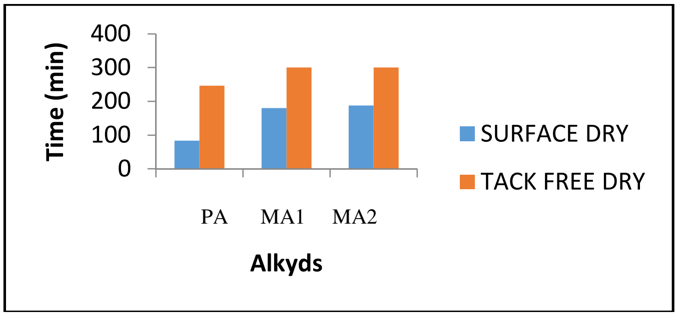

Figure 4: Drying time of alkyds

However, the alkyds in general have high drying time. This is so because XASO is a non-drying polyunsaturated fatty acid which contains a high degree of saturations. Furthermore the high level of saturation causes the oil to have high induction period in connection to the presence of phytochemicals present in the oil (Eromosele and Eromosele, 2002; Mevy et al., 2009) which acts as free radical scavengers.

3.4.2.2. Adhesion Property

Results from adhesion tape test showed that ALKYD PA has excellent adhesion performance relative to alkyds MA_1 and MA_2. The observed film detachment of the adhesion tape of ALKYDS PA, MA_1 and MA_2 was not >5%. The good adhesion to the substrate is attributed to the inherent chemical structure, flexibility of the alkyd resin and high viscosity (Barminas and Osemeahon, 2007). Certain polar groups in a film such as carboxylic groups (—COOH) are very active promoters of adhesion, due to their attraction to the substrate, or by their influence in improving the wetting properties. Good initial wetting of a surface by a coating and the maintenance of wetting during the process of film formation are essential for good film adhesion.

3.5. Chemistry of Alkyd Structures

The join addition of maleic anhydride happens to the double bond at the chain extremity. The products of the addition of one or two molecules of maleic anhydride with oils are presented with structures (2) and (3). Structure 3 presents a product according to Diels-Alder synthesis (Boyd, 1994).

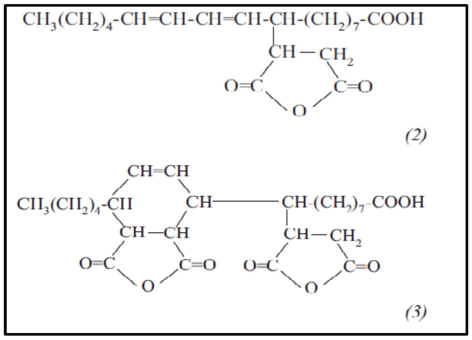

Figure 5

3.5.1. Esterification with Phthalic Anhydride (Boyd, 1994)

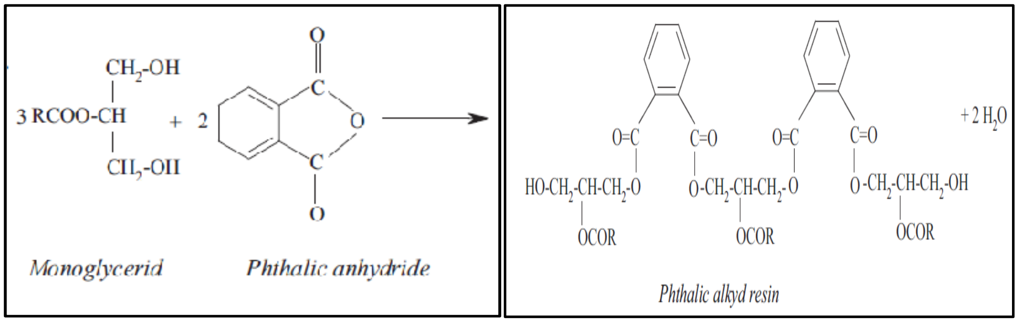

Figure 6

3.5.2. Esterification with Maleic Anhydride (Boyd, 1994)

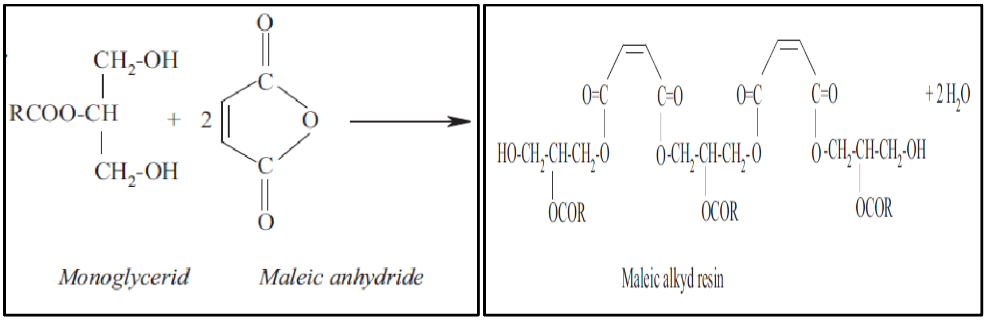

Figure 7

4. Conclusion

Alkyd-based polymer coating was successfully synthesized and characterized. The experimental test shows that, alkyd PA can be applicable to spraying technology due to its low viscosity. The resistance of the alkyd to alkali, peeling, flaking and blistering makes it to be used for exterior applications. However, alkyds MA_1 and MA_2 have higher viscosity and drying time, which makes them to form thicker dry film for better hiding and durability.

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