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Research paper

Synthesis, characterization and antimicrobial evaluation of silver nanoparticles embedded alkyd resin derived from pine seed oil

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Abstract

Silver nanoparticles were synthesized by reducing 0.1mmol silver Nitrate salt with 5ml of neem leaf extract, in an environmental friendly process. The nanoparticles were tested to have strong zones of inhibition on the antibacterial and antifungal isolates; E. Coli, staphylococcus aureus, Aspergillus fumigatus, and mucor species used. UV-visible spectrophotometric analysis was carried out on both the silver nitrate salt and silver nanoparticles, which show bathochromic shift from 221nm (AgNO3) to 440nm (AgNPs). Pine seed oil was condensed to alkyd resin via two step reactions; alcoholysis and esterification reactions respectively, and was characterized by FTIR, acid value and viscometric measurement. Antimicrobial evaluation was carried out on the pine seed oil with its alkyd resin. Pine alkyd resin was used in the formulation of paints with percentage Pigment Volume Concentrations (%PVC) 4 and 5% respectively, and is classified as automotive clearcoat. Chemical resistance, scratch resistance, light fastness, and drying schedule tests were conducted on the paints and are found to exhibit good properties which are similar to commercial paints. Antimicrobial evaluation of the paints incorporated with silver nanoparticles revealed more inhibition zones than those without silver nanoparticles.

Keywords: *AgNO3; AgNPs; %PVC; Paints; PSO; PSOR.*

1. Introduction

Alkyd resin is an essential material used in paint formulation and other surface coatings as a binder. However, because of its non-availability, alkyd resin is largely being imported for industrial consumptions. Vegetable oil is an important raw material for alkyd resin production. They are polyester products formed from the polymeric condensation of polyhydric alcohol, polybasic acid and monobasic fatty acids.

Formation of organic coatings may be simple or complex in composition of variety of materials, each having a specific function. Formulation has three major components; Pigments, binder/ vehicle and additives. The pigment provides colorant and other functions. The binder sticks together the pigments with substrate and to each other. And additives are substances which modify or improve the properties of a coating.

The type or class of alkyd resin to be produced is another main consideration for the choice of modifying oil. Alkyd resins have been classified based on the kind and amount of oil used for its production (Kirk & Othmer, 1966), it can be regarded as drying and non-drying based on the oil length, i.e. short oil 35%, medium oil 40-55%, long oil 56-70% and very long oil alkyd having an oil content of more than 70%. Most drying alkyds are modified using semi-drying or drying oils. High degree of unsaturation enables thin film of alkyds to polymerize in the presence of oxygen at room temperature to give a solid film. However, non-drying alkyds based on non-drying oil are used as blending agents for other resins (Odetoye et al, 2012).

2. Materials and methods

2.1. Materials

The reagents used were prepared using standard analytical method of preparation. Pine seed oil was purchased from National Board for Technology Incubation Centre kano, Nigeria, Neem leaf (Azaradichta indica) was obtained from the abundant neem trees in Bayero University Kano, Nigeria. Some of the materials used are; UV-Visible spectrophotometer, FTIR machine, Autoclave, agar plates.

2.2. Methods

2.2.1. Green synthesis of the silver nanoparticle

Neem leaves obtained were washed thoroughly with tap water followed by rinsing with distilled water and then air dried. 10g of the finely cut neem leaves were weighed and heated to boil with 100mL of distilled water, the extract is then filtered and cooled. 15ml of 1mmol $AgNO_3$ was then reacted with 5ml of neem leaf extract, and the colour changed slowly at room temperature overnight to deep brown.

2.2.2. Physico-chemical analysis of pine seed oil with its alkyd resin and characterization of silver nanoparticle

The physico-chemical properties such as; acid value, refractive index, iodine value, saponification number, specific gravity, percentage free fatty acid and characterization of the silver salt, silver nanoparticle through FTIR and UV-Visible analysis and FTIR characterization of the pine seed oil sample was determined in accordance with American Oil Chemists Society method (AOCS).

2.2.3. Synthesis of the pine alkyd resin

Synthesis of pine alkyd resin was carried in two step reactions; alcoholysis and esterification reactions. In the alcoholysis reaction, measured amounts of the triglycerides(pine oil) were placed into 1000mL of three neck round bottom flask fitted with dean and stark apparatus and heated to 120^{o}C to expel the moisture content of the oil. To this a measured quantity of glycerol and calcium carbonate (catalyst) were added and continued heating for 40mins at a temperature of 230^{o}C, until a monoglyceride forms when an aliquot of the solution dissolved completely in a methanol. In the esterification reaction, the temperature of the solution was lowered to about 180^{o}C, and the flask is connected with $N_{2,}$ to this a weighed phthalic anhydride, 10grams of xylene were added in each synthesis to aid distilling off of water of esterification by forming an azeotrope. The solution was heated for 2hrs at 240-250^{o}C and an aliquot was drawn at an interval of 30mins to check for the drop in acid value, as shown from the table of formulation below.

Table 1: Compositions of Alkyd Resin of Pine Seed Oils

Raw Materials	Alkyd Resin of Pine Seed Oil
Oil(g)	85.84
Pthalic anhydride(g)	43.42
Glycerol(g)	18
Oil length	58.29

2.2.4. Antibacterial and antifungal evaluation

The activity was carried out by employing paper disc diffusion method, in which the agar plates were incubated with test organisms (E. Coli, staphylococcus aureus, Aspergillus fumigatus, and mucor species) by spreading uniformly. One disc from each sample was placed in the petri-dishes with sterile forceps. The dishes were incubated for 24 hours at 37^{o}C. After 24 hours, the antibacterial activity of test compound was found by measuring the zone of inhibition.

2.2.5. Alkyd paints formulation and performance evaluations

The paint was formulated based on pigment volume concentrations (PVC) which guides the manufacture of paint in desired properties. PVC is the concentration by volume of the pigment expressed as a percentage of the total non-volatile volume of the paints.

$$\%PVC = \frac{Vp}{Vp+Vb} \times 100\%$$

Where;
V_p = Volume of pigment dispersion
V_b = Volume of binder.
Paint is applied on a glass slides to taste the drying through period of the paints. The dried paints each on a glass slide are immersed in to water, hydrochloric acid, and sodium hydroxide to test their chemical resistance. Scratch resistance, flexibility and light fastness were also tested

3. Results

Table 2: UV-Visible Spectrophotometry of the $Agno_3$ and Agnp

Materials	λmax (nm)
Aqueous solution of Silver Nitrate salt	221
Silver nanoparticle colloidal solution	440

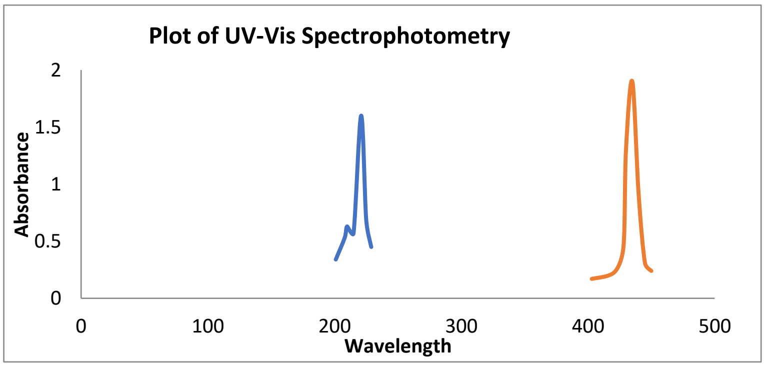

Fig. 1: UV-Visible Spectroscopy of $AgNO_3$ and AgNP.

Silver nanoparticles were synthesized by weighing 10g of the finely cut neem leaves and heated to boil with 100ml of distilled water. The extract was then filtered and cooled. 15ml of 1mmol $AgNO_3$ was then reacted with 5ml of the neem leaf extract, and the colour changed slowly at room temperature overnight to deep brown. The AgNP was then characterized using UV-Vis spectrophotometer. Table 2 and Figure 1 showed a bathochromic shift from 221nm ($AgNO_3$) to 440nm (AgNP). Shifting of absorption band from UV region to visible region confirmed the formation of the nanoparticle, which typically attributed to plasmon resonance of silver nanoparticles. Silver nanoparticles were synthesized according to the method described in the previous section, the colloidal solution turned pale brown, pale yellow and pale red indicating that the silver nanoparticles were formed. The UV-Visible spectroscopy revealed the formation of silver nanoparticles by exhibiting the typical surface plasmon absorption maxima at 418-420nm (Maribel et al, 2009).

Table 3: Physico-Chemical Analysis of PSO

Properties	Pine Seed Oil
Acid Value	2.08
Iodine Value	118.41
Saponification Number (mg/g)	193.7
Refractive Index	1.465
PFFA (%)	1.04
Specific Gravity (g/cm^3)	0.8791
Viscosity (MPa at 28ºC)	15.41
Moisture Content (%)	0.22
pH	5.2

The physico-chemical analysis result in Table 3 showed that, iodine values of pine seed oil was 118.41(cg/g) , and have been identified to possess high degree of unsaturation and therefore higher tendency to undergo oxidative rancidity (Ayo et al 2007). The saponification value of the pine seed oil was 179.8(mg/g) which is the indication of the average molecular mass of fatty acid present in the oil, and is found to be slightly above the range reported by (Ogunniyi et al 2006). Acid value of pine seed oil as obtained from the result of analysis was 2.08(mgKOH/g), and it's the measure of the extent to which the constituent glycerides have been decomposed by lipase action, and has shown to be the general indication of the edibility of the oil (AOCS 1996). The refractive index of the oil was found to be 1.465, specific gravity of the oil was 0.63(g/cm^3) which implies that they are less dense than water (Momodu et al 2011). Percentage free fatty acids of pine seed oil obtained was 1.04%, while the viscosity of the oil at 28^{0}C was found to be 15.41Mpa, moisture content of the pine seed oil was found to be 0.22%.

Table 4: FTIR Spectral Absorption of PSO and PSOR

Bands(cm^{-1})	FTIR Peak
3478	O-H stretch due to alcohol
2961	C-H stretch due to alkane
1449	C-C stretch due to aromatic ring
1112	C-O stretch due to ester
2922	C-H stretch due to alkane
1723	C=O stretch due to ester
1451	C-C stretch due aromatic ring
1259	C-O stretch due to ester

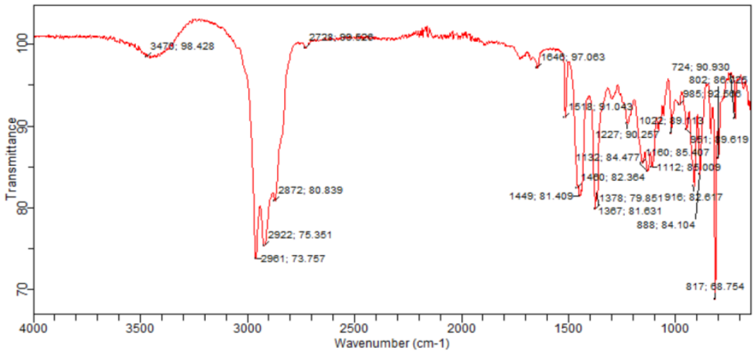

Fig. 2: FTIR Analysis of PSO.

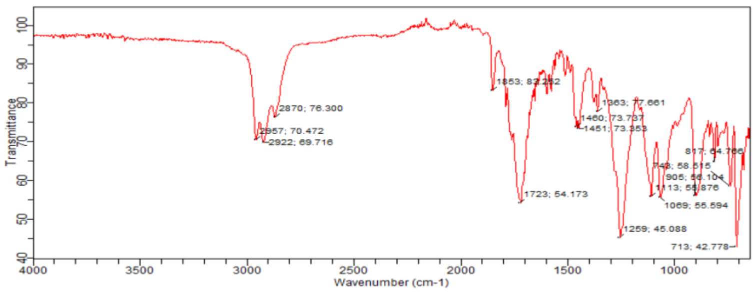

Fig. 3: FTIR Analysis of PSOR.

Table 6, figures 2 and 3 shows FTIR result of pine seed oil and its respective alkyd resin with spectral absorption at band positions; 3478cm^{-1}, indicates O-H stretching due to alcohol, 2961 cm^{-1}, indicates C-H stretching due to alkane, and 1449 cm^{-1}, indicates C-C stretching due to aromatic ring, and 1112cm^{-1}, indicates C-O stretching due to ester. Alkyd resin of pine seed oil with spectral absorption at band positions; 2922 cm^{-1}, indicates C-H stretching due to alkane, 1723 cm^{-1}, indicates C=O stretching due to ester, 1451cm^{-1}, indicates C-C stretching due to aromatic ring, and 1259cm^{-1}, indicates C-O stretching due to ester.

Table 5: Result of Acid Values (mgKOH/g) of PSOR

Neem	Time(min)
32.8	30
23.0	60
15.0	90
9.3	120

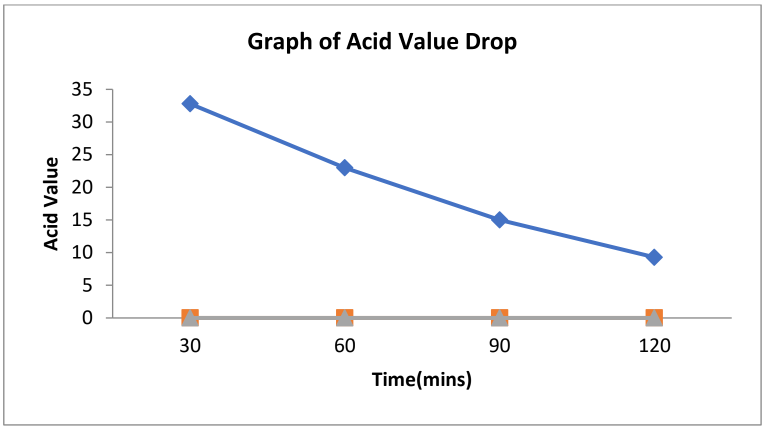

Fig. 4: Acid Value Drop of PSOR.

Table 7 and figure 4, showed acid value of pine seed oil with reaction time. It was found that the acid values decreases with increasing the reaction time, due to the reactivity of primary and secondary hydroxyl groups of glycerol with carboxyl groups of the phthalic anhydride as reported by (Oladipo et al 2013).

Table 6: Viscosity Results for PSOR at 25±0.1^{0}C in 15ml of Acetone Using Ostwald Viscometer.

Conc.(g/L)	t_o(sec)	t(sec)	$\eta_r = t/t_o$	$\eta_{sp} = \frac{t-to}{to}$	$\eta_{sp/C}$
0.125	126	128	1.016	0.016	0.128
0.25	126	129	1.023	0.023	0.092
0.50	126	133	1.056	0.056	0.112
1.00	126	145	1.150	0.150	0.150

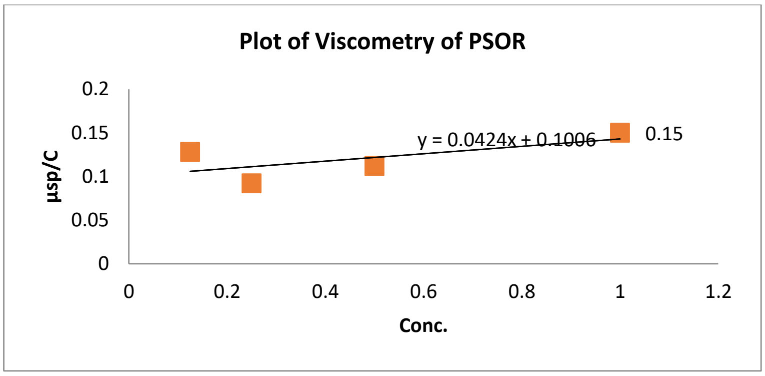

Fig. 5: Viscometric Analysis of PSOR.

Table 8 and Figure 5 showed viscometric analysis of PSOR, and was found that the time flow of the alkyd resin dissolved in acetone in the viscometer, increases with increasing the amount of the alkyd resin, while volume of the solvent was maintained. Hence, the viscosity of the resin was found to be increasing.

Table 7: Antibacterial and Antifungal Evaluation of $AgNO_3$ and AgNPs

Test organisms	Zone of inhibition (mm)/concentration(μg/ml)						Control (X)
	1x10^3	2x10^3	3x10^3	1x10^3	2x10^3	3x10^3	3x10^3
Eschricia coli	12	13	15	16	18	20	Ampicilline 21
staphylococcus aureus	13	14	16	19	21	22	24
Aspergillus fumigatus	13	15	16	20	23	26	Ketoconazole 34
Mucor specie	11	13	15	17	18	22	25

Tables 7 shows the antibacterial and antifungal screening of $C_7H_5O_2Ag$ and AgNPs, with strong activities in silver nanoparticles than the silver salt, but all increases with increasing the concentrations of the salts and AgNPs respectively. Sondi & Alopek, (2007) reported that the antibacterial activity of silver nanoparticles on Gram-negative bacteria was dependent on the concentration of Ag nanoparticle, and was closely associated with the formation of 'pits' in the cell wall of bacteria. Then, Ag nanoparticles accumulated in the bacterial membrane caused the permeability, resulting in cell death and they reported degradation of the membrane structure of microorganism with silver nanoparticles

Table 8: Antimicrobial and Antifungal Activity of Alkyd Resin of PSO and PSOR

Test organisms	Zone of inhibition(mm)/Concentration(µg/ml) Control					
	$1x10^3$	$2x10^3$	$3x10^3$	$4x10^3$	$5x10^3$	$5x10^3$
Staphylococcus aureus	6	6	6	6	6	Ampicilline 26
Eschericia coli	6	6	6	7	9	21
Aspergillus fumigatus	6	6	6	7	10	Ketoconazole 38
Mucor specie	6	6	6	7	8	25
Staphylococcus aureus	6	6	6	7	8	Ampicilline 26
Eschericia coli	6	6	7	8	11	21
Aspergillus fumigatus	6	6	6	7	11	Ketoconazole 38
Mucor specie	6	6	7	8	10	25

Tables 8 showed antibacterial and antifungal properties of pine seed oil with its respective alkyd resin. In PSO, absence of activities was observed in all the four organisms used at lower concentrations (1×10^3 - 3×10^3), and very poor activities at higher concentrations (4×10^3 - 5×10^3) as compared with the control. While in the PSOR result, absence of activities was observed in all the four organisms used at lower concentrations (1×10^3 - 2×10^3), a very poor and even zero activity activities was recorded at higher concentrations (3×10^3 - 5×10^3) as compared with the control.

Table 9: Composition of Alkyd Resin Paints of Pine Seed Oil with their %PVC

	Resin(g)	Fe_2O_3(g)	TiO_2(g)	Solvent(ml)	AgNP(ml)	Thickner(g)	Extender(g)	Drier(ml)	PVC%
P_1	10	7	0	30	1	0.2	0.4	0	4
P_2	10	0	7	30	0	0.2	0.4	0	5

Where;
P_1 = Paint of alkyd resin of pine seed oil with nanoparticle
P_2 = Paint of alkyd resin of pine seed oil without nanoparticle
Table 9 showed a composition and amounts of the components used in the formulation of alkyd paint and their respective %PVCs. Quantities of alkyd resin of pine seed oil was maintained in each formulation, two different types of pigments were used and silver nanoparticle was used in one of the formulations, to test the influence of the additives in the properties of the paint formed. In P_1 formulation, silver nanoparticle was used as an additive, and the pigment used was Fe_2O_3. While in P_2 paint no nanoparticle was added, and the pigment used was TiO_2. The PVC% of paints formulated are all <5% and are used in automotive clearcoats. (Uppal, 2006).

Table 10: Evaluation Tests of the PSOR Paint

Alkyd Resin	Chem. Resist.		Scratch Resist.	Drying Period	Light Fastness
P_1	NaOH	Fair	Excellent	35mins	Excellent
	HCl	Good			
	Brine	Good			
	Water	V.Good			
P_2	NaOH	Poor	Good	40mins	Good
	HCl	Fair			
	Brine	Fair			
	Water	Good			

Tables 10 showed the evaluation and performance tests carried out on different alkyd paints formulated. Resistance to chemical attacks by HCl, H_2O and Brine on P_1 alkyd paint was found to be generally good, but poor with NaOH. While in P_2 alkyd paint, fair resistance was observed with the chemical with exception of NaOH which is poor. This is because nanomaterials represent almost the ultimate in increasing surface area and they are chemically very active because the number of surface molecules or atoms is very large compared with the molecules or atoms in the bulk of the materials, and because of greater surface activity of nanoparticles, they can absorb more resins compare to conventional pigments and thus reduce the free space between the pigment and the resin (Mathiazhagan and Rani, 2011). Scratch resistance in P_1 and P_2 shows performances of excellent and good respectively, and this is due to higher iodine value 118.41(cg/g) of pine seed oil, which have been identified to possess high degree of unsaturation and therefore higher tendency to undergo oxidative rancidity (Ayo et al, 2007). The drying schedule of the alkyd paints; P_1 and P_2 were found to be 35mins and 40mins respectively, this also due to the level of unsaturation. Light fastness rating of the alkyd paints P_1 and P_2 were; excellent and good respectively, Silver nanoparticles have application in some spectrally selective coating and enhance raman scattering (Kim et al, 2011).

Table 11: Antibacterial and Antifungal Evaluations of Alkyd Paints of PSO

Test Organism	Zone of inhibition (mm)/ Concentration(µg/ml) with and without AgNP						Control
	PSO			PSOR			
	1×10^3	2×10^3	3×10^3	1×10^3	2×10^3	3×10^3	3×10^3
							Ampicilline
Staphylococcus aureus	6	6	6	17	19	21	26
Eschericia coli	6	6	6	16	17	18	21
							Ketoconazole
Aspergillus fumigatus	6	6	6	18	20	21	34
Mucor specie	6	6	6	15	17	20	25

Tables 11 expressed the Antibacterial and Antifungal evaluations of Pine alkyd resin paints, with strong inhibition zone in the organisms incorporated with various concentrations of the silver nanoparticles.

4. Conclusion

Synthesis of silver nanoparticles using an eco-friendly green synthetic method has been successful as confirmed by UV-visible spectrophotometry and colour transformation. The nanoparticles were incorporated into the synthesized alkyd resin derived from Pine seed oil.

The nanoparticles embedded alkyd resin was found to be active against some bacterial and fungal isolates. The resin was also used to formulate oil-based paints. The paints formulation have a %PVC range of 3-5%, hence are classified as automotive clear coats.

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