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Effect of Polystyrene Acrylic on the Rheological Properties of Washable Paints Produced From Jatropha Seed Oil

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Abstract

Washable paints are less toxic due to the absence of organic solvent used in solvent based paints, but these paints were reported not to have excellent rheological properties as those of solvent based paint. This work studied the effect of polystyrene acrylic on the rheological properties of washable paints produced from jatropha seed (*Jatropha curcas)* oil. The oil was first converted to alkyd resin through alcoholysis and polycondensation reactions, and emulsified using isopropyl alcohol. Four samples of washable paints were produced using different quantities of alkyd emulsion and polystyrene acrylic in these combinations; 25% of polystyrene acrylic binder and 75% alkyd emulsion binder (JSO_1P), 50% each for polystyrene acrylic and alkyd emulsion (JSO_2P), a combination of 75% polystyrene acrylic binder and 25% of alkyd emulsion binder (JSO_3P), and a control sample which contains only polystyrene acrylic binder (PSNA). These paint samples were analyzed for the following performances; storage stability, sagging behavior, leveling and applicator loading. These performances were determined through rheological properties which include dynamic viscosity, yield stress and shear rates. The dynamic viscosities were measured at three different shear rates; 06 rpm, 12 rpm, 30 rpm and 60 rpm respectively. The rheological study shows that the viscosity of produced paints is within the range of 107.1mPa.s to 104.4mPa.s. At different shear rates, the viscosity of JSO_2P decreased from 1031mPa.s at 06rpm to 107.1mPa.s at 60rpm, that of JSO_3P decreased from 1052mPa.s at shear rate of 06rpm to 106.6 at the shear rate of 60 rpm, and that of PSNA decreased from 1055.9mPa.s to 106.7mPa.s at the shear rate of 60 rpm. The yield stress obtained include; 10567.2mPa for JSO_2P, 10812mPa for JSO_3P and 10801.8mPa for PSNA. The performance results indicated that polystyrene acrylic can be used to modify the flow properties of washable paints, but this can only be achieved at a ratio above 25% of polystyrene acrylic to jatropha based alkyd emulsion.

Keywords: Rheological properties, polystyrene acrylic, jatropha seed oil, washable paints and alkyd emulsion.

Nomenclatures

CP = commercial paint

JSO_1P = jatropha seed oil paint containing 25% polystyrene acrylic and 75% alkyd emulsion.

JSO_2P = jatropha seed oil paint containing 50% each of polystyrene acrylic and alkyd emulsion

JSO_3P = jatropa seed oil paint containing 75% polystyrene acrylic and 25% alkyd emulsion

HSV = high shear viscosity LSV = low shear viscosity

MSV = medium shear viscosity PSNA = paint sample containing polystyrene acrylic binder without alkyd emulsion.

VOC = volatile organic component. γ = share rate (rpm) and η = viscosity (mPa.s)

1. Introduction

Volatile organic compounds (VOCs) have aroused concern in many parts of the world especially in large cities due to their negative impact on the environment. Volatile organic compounds are those organic chemicals that have a high vapor pressure at room temperature (Wikipedia 2018). These VOCs pose long term health effects to humans. Most VOCs originate from plants, petroleum products and internal engine exhausts, but a significant amount is derived from solvent based coatings (Njuku, Mwangi &Thiong'o 2014). The routes to reduce VOC emission from coatings include the use of water-based polymers, higher solids content polymers, water reducible alkyd (Sorensen 2008), powder coatings *(*Erin et al. 2016) *a*nd the use of the novel technology which disperses highly hydrophobic alkyd resin into water (Malvern 2017). In this work, hydrophobic polymer was converted to water-based polymer, and was used together with a hydrophilic polystyrene acrylic in making paints.

In developed countries, increasing concerns about the impact of chemical paints on health and the environment have led to a growing market in non-toxic paints (EPA 2017) such as washable paints. Toxic paints release organic compounds during manufacturing, storage, application, drying and after drying. The concentration of these compounds can remain in the air long after the activity is completed. Waterborne coatings are non-toxic though they do not have the same advantageous rheological properties as solvent-based coatings. Waterborne coatings include those paints in which water is used as their solvent. These paints, if not formulated correctly, display inferior characteristics with regard to flow properties, leveling, application properties, film build and stability (TA Instrument 2015). Therefore, it is necessary to study and determine the performance of these paints before they get to the consumers, of which rheological tests become very important. Two rheology modifiers; alkyd emulsion and polystyrene acrylic were used in producing the washable paints under study. Rheological tests are used widely to evaluate functional coatings in terms of their properties and performance. These tests portray the behavior of fluid during manufacturing as they are mixed and transferred, and during application by spraying, brushing, coating, or dipping, as they are subjected repeatedly to different rates of shearing over a range of durations. Three basic parameters which include; shear stress, shear rate and shear viscosity are necessary in studying the rheological properties of any material. Rheological testing provides a convenient way to measure performance as critical rheological changes occurring during the life cycle of decorative and protective coatings (TA Instrument 2015). .

According to (Malvern 2015) rheological studies can predict paint behavior without large costly batch studies. It also predicts the behavior during storage, stirring, application and after application. Paint samples which will suffer deformation during pumping, application and storage can be fished out and reformulated before it gets to the consumers. Different paint sample has its own unique rheological behavior when subjected to stress. These behaviors are affected by the interaction between droplets. According to (Lewandowska 2006), who studied the rheological behavior of polymer, experimental conditions such as polymer concentration, temperature, solvent quality, and shear rate applied can affect the rheological behavior of polymer. Rheological behavior of samples can also be effected by particle content, polymer concentration and molecular weight, and water temperature, pH, and salinity (Jamal 2012). Therefore, each paint sample will behave differently based on the influencing parameters. This work is therefore aimed at studying the rheological behavior of washable paint samples produced from jatropha seed oil (JSO) based alkyd emulsion modified with polystyrene acrylic at different shear rates.

2.0 Material and methods

2.1 Conversion of jatropha seed oil into alkyd emulsion

Jatropha seed oil was converted into alkyd emulsion through alcoholysis, polycondensation and emulsification processes.

***Alcoholysis process*:** This is the first stage involved in alkyd resin production. This process was carried out at a temperature of 260^{o}C for 1 hour using a heating mantle. In this stage, 58.19 g of jatropha seed oil and 21g of glycerol were heated together in the presence of 0.1g lithium hydroxide as a catalyst. Nitrogen was purged at a rate of 0.06ft^3/sec. This process converts the oil into reactive monoglyceride which can easily take part in polycondensation reaction.This process was completed when the mixtures became soluble in anhydrous methanol (1:3) (w/v).

***Polycondensation reaction*:** This is the second stage involved in alkyd emulsion production**.** The reactions were carried out in a half litre three-necked flask fitted with a nitrogen in-let tube, stirrer, digital heating mantle and temperature loop. After alcoholysis, the temperature of the reactants was reduced to 120 ˚C before polycondensation reaction. 23.46 g of phthalic anhydride and 3.40 g of benzoic acid was added to the reactor, and the reaction temperature was set to 230–250 ˚C for the polycondensation process. Nitrogen was purge at a rate of 0.1ft^3/sec. The progress of the reaction was monitored at every 10 mins interval by diluting an aliquot of the reacting mixture in toluene. This was then titrated with 16 ml – 2.2 ml of 0.1M ethanolic potassium hydroxide solutions to phenolphthalein end-point (Agbodion et al 2003; Ikhuora, Aigbodion & Felix 2004).

Emulsification process: After polycondensation reaction, the resultant alkyd resin was diluted with water (50-100% v/w) at a temperature of 120^{o}C in the presence of isopropyl alcohol (10% v/w) to give alkyd emulsion. The mixture was thoroughly agitated using a motorized stirrer.

2.2 Production of washable paints

Four samples of washable paints were produced using the composition of polystyrene and alkyd emulsion in table 1.

Table 1: Compositions Of Alkyd Emulsion and Polystyrene Acrylic Used for Washable Paint Production

S/N	Samples	Composition of Binders (g)		Composition of Binders (%)	
		Alkyd Emulsion	Styrene	Alkyd Emulsion	Styrene
1	JOS_1P	37.5	12.5	75	25
2	JOS_2P	25	25	50	50
3	JOS_3P	12.5	37.5	25	75
4	PSNA	0	50	0	50

Table 1 shows the composition of alkyd emulsion and polystyrene acrylic binders used for the formulation of washable paints. The paint samples were made up of 50% binders which include; polystyrene acrylic and jatropha seed oil based alkyd emulsion. The samples were formulated according to the procedure below.

100g of different samples of washable paints were prepared according to the formulation in table 1, and the procedure below using jatropha seed oil based alkyd emulsion. The samples were named as follow; JOS_1P, JOS_2P, JSO_3P and PSNA respectively. Commercial washable paint purchased from New market Owerri, Imo state and PSNA were used for control and comparison. 5 ml of water, 0.28 g antifoaming agent and 30 g titanium dioxide were first mixed in a 250 ml beaker to form paste. 50 g binder, 8.14 g calcium trioxocarbonate iv and 5.6ml of water were mixed with the paste to form a paint sample which was modified with1.8g of cobalt drier. The sample was preserved with 0.8g ammonia. Polystyrene acrylic was used to modify the paints' properties at different proportions.

2.3 Rheological characterization of washable paints

The rheological characterization of paints were carried out using Techmel and Techmel USA brand of Brookfield rotational viscometer at low shear viscosity (LSV) of 6rpm,12rpm and 30rpm respectively and a medium shear viscosity (MSV) of 60rpm. The consistency of a coating (i.e., in-can appearance, pouring and mixing behaviour) are processing properties defined by medium shear viscosity (MSV). The LSV correlates to all low rate processes like levelling, sagging, settling and sedimentation (TA Instrument 2015).

3.0 Results and Discussions
3.1 Alkyd emulsion

Jatropha seed oil was successfully converted to alkyd emulsion with an acid value of 5.90 mgKOH/g.

3.2 Washable paint production

Sample $JOSP_1$ showed poor interaction with polystyrene acrylic and cobalt drier. Samples, $JOSP_2$, and $JOSP_3$ showed good interaction with styrene and driers. PSNA and commercial paint (CP) were used for comparison and control respectively.

3.3 Rheological properties of washable paints

Different rheological properties studied include; yield stress, viscosity and yield stress. Sagging, leveling, bleeding and stability are some of paint properties determined by rheological characterization.

a. Viscosity of the paint samples

Table 2: Average Viscosity of Washable Paint Samples at Different Time and Shear Rate Of 60RPM

Time(mins)	Viscosity(mPa.s)			
	JOS_2P	JOS_3P	PSNA	CP
5	107.1	106.8	106.7	522.5
10	107.0	106.6	106.2	522.0
15	106.9	105.7	106.0	522.0
20	106.5	105.2	105.9	521.8
25	106.0	105.2	105.5	521.3
30	105.5	105.0	104.2	520.4

Table 2 shows the average viscosity of JOS_2P, JOS_3P, PSNA and CP samples. The samples viscosity readings at a shear rate of 60rpm taken at interval of 5mins for a period of 30mins showed slight change in viscosity with time; this is a pseudoplastic behavior. The results of JOS_2P and JOS_3P are comparable with PSNA and CP. As reported by (Clifford 2019), if the viscosity of paint is above 100cps (100mPa.s), the brush drag will be so high that the painter will end up with a sore wrist, but viscosity much below 100 cps is likely to cause misting, and high viscosity probably will give ropiness and other unwanted surface pattern. Also, (TA Instrument 2015) reported that typical paints are adjusted to 50–150mPa.s for low drag during application.

b. Stability: flow and shear rate

Table 3: Variation Of Viscosity With Shear Rate

γ(rpm)	JOS_2P η(mPa.s)	JOS_3P η(mPa.s)	PSNA η (mPa.s)	CP η (mPa.s)
06	1031	1052	1055.9	5149
12	518	530	528.3	2597
30	209.1	212.7	211.8	1040
60	107.1	106.8	106.7	522.5

γ(rpm) is share rate and η is viscosity (mPa.s)

Table 3 is the average viscosity readings for JOS_2P, JOS_3P, PSNA and CP at different shear rates. The readings show that the paints viscosities change with shear rates. A change in viscosity with increase in shear rate indicates thixotropic behavior of the samples. The values in table 3 were used to plot the graphs of figure 1 through 4.

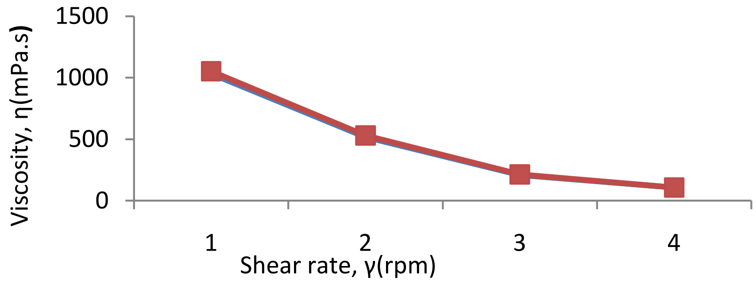

Figure 1: Variation Of Viscosity With Shear Rate for JOS_2P & JOS_3P

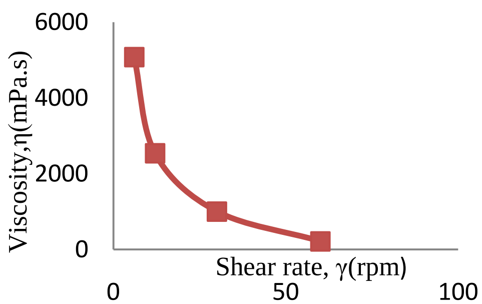

Figure 3: Variation Of Viscosity With Shear Rate for CP

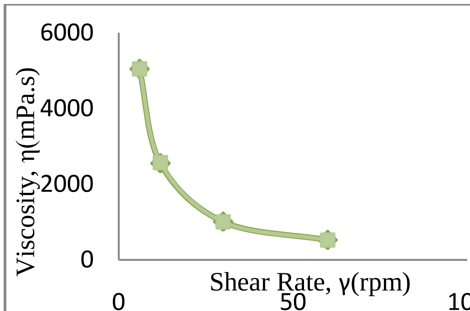

Figure 4: Variation Of Viscosoty With Shear Rate for PSNA

From figures 1 through 4, the viscosity shear rate curves show drop or shear thinning behaviour of the paint samples; JOS_2P, JOS_3P, PSNA and CP with increasing shear rate. Hence, as the shear rate increases, the viscosity dropped. The samples are said to show high-low shear viscosity. The ease of structure breakdown of these paints at medium shear viscosity means that they are more likely to flow in to the bristles of a paint brush when dipped into the paint. The high low shear viscosity of the samples, will enable the samples withstand the force of gravity causing particles to sediment as reported by (Malvern 2005). Therefore, JOS_2P,

JOS_3P, PSNA and CP are not susceptible to sedimentation and hence will maintain good consistency during storage. At high shear rate, a low viscosity is also beneficial for brushing: a too high viscosity will lead to undesired brush drag. According to (Viguerie et al 2009), good brushing properties are obtained if the viscosity at high shear rates does not exceed 200 – 500 Pa s. This means that JOS_2P, JOS_3P, PSNA and CP will not show poor brush drag during application.

c. Yield stress: sagging and levelling

The results for variations of stress with rate for each of the samples were calculated from the viscometer readings and are recorded in table 4. This was used to study the stress evolution of JOS_2P, JOS_3P, PSNA and CP respectively as shown in figures 5 through 9.

Table 4: Variation Of Shear Rate γ(rpm) With Shear Stress τ (mPa)

γ(rpm)	JOS_2P τ (mPa)	JOS_3P τ (mPa)	PSNA τ (mPa)	CP τ (mPa)
06	10516.2	10730.4	10770.18	52519.8
12	10567.2	10812	10777.32	52978.8
30	10664.1	10847.7	10801.8	53040
60	10924.2	10893.6	10883.5	53295

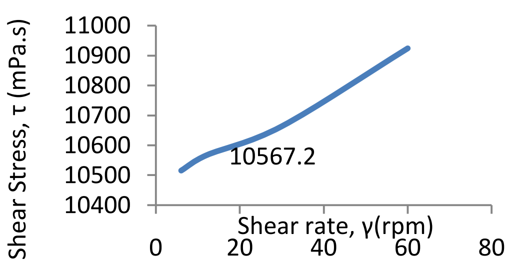

Figure 5: Shear Stress/ Rate for JOS_2P

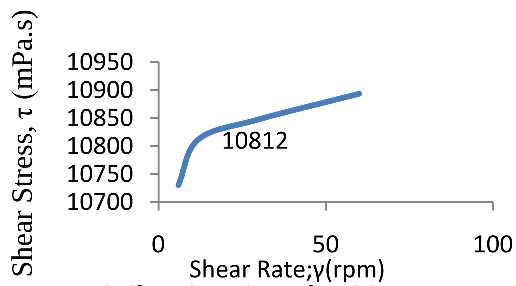

Figure 6: Shear Stress/ Rate for JOS_3P

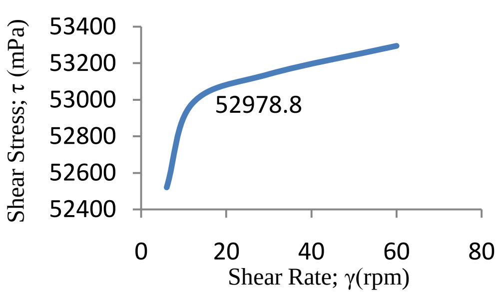

Figure 7: Shear Stress/Rate for CP

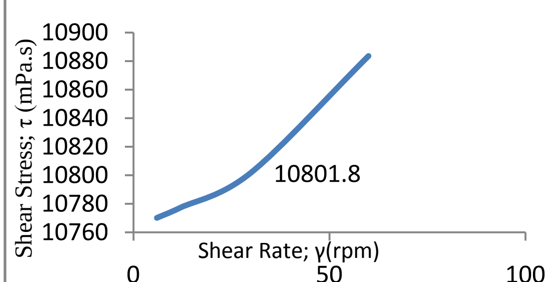

Figure 8: Shear Stress/Rate for PSNA

Figures 5 through 8 show the yield stresses for samples JOS_2P, JOS_3P, PSNA and CP as 10567.2mPa, 10812mPa, 10808.8mPa and 52978.8mPa respectively. The samples have large yield stresses greater than 1000mPa. Coatings with high yield stress will regain their elastic structure after leveling is completed. This is an indication of good sagging and leveling properties as reported by (TA Instrument 2015). This means that these coatings; JOS_2P, JOS_3P, PSNA and CP will show good leveling behavior.

Results should be clearly described in a concise manner. Results for different parameters should be described under subheadings or in separate paragraph. Table or figure numbers should be mentioned in parentheses for better understanding.

4.0. Conclusion

This research has proven that jatropha seed oil can take the place of edible oils used in coating industry, if properly modified. It can be successfully converted to alkyd emulsion: a binder for making washable paints.

Blending the washable paints produced from jatropha seed oil with polystyrene acrylic has proven to be effective in the rheological behavior of these paint samples. Incorporating alkyd emulsion up to 75% of the total binders used in the paint production with 25% of polystyrene proved to show poor interaction with the system. In essence, more than 25% polystyrene is needed to get a washable paint with good rheological behaviors. This study showed that the paint samples; JSO_2P, JSO_3P and PSNA behaved as non Newtonian and are also thixotropic fluids. This implies that during storage the paints will become thicker, but on application of stress they will become thinner which is a common characteristic of paints. The paint samples also showed good performances in terms of brush drag, consistency during storage, sagging and leveling properties. These are the performances improved by incorporating polystyrene acrylic binder in washable paints.

5.0 Recommendation

1. Further research in using lower proportion of acrylic as a rheology and film modifier in washable paint production is also recommended.
2. Since jatropha seed oil is non-edible oil which is good in alkyd emulsion production. It is recommended that jatropha plants be extensively cultivated and utilized for this and other purposes, hence reducing the cost in importation of linseed.
3. Awareness should be created on the use of non toxic paints.

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