Synthesis and Characterization of Water- Reducible Alkyd Resin from Cottonseed Oil

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Abstract— **Medium oil water-reducible alkyd resin was synthesized by polyesterification reaction of commercially refined cottonseed oil with glycerol and maleic anhydride patially substituted with trimellitic anhydride in lithium hydroxide catalytic process and copolymerized with polyethylene glycol. A predictive mathematical model was obtained to predict the acid value and viscosity as functions of polybasic acid/oil molar ratio, catalyst concentration, reaction temperature, reaction time, and rate of mixing. The optimal conditions for the production of alkyd resin was found to be MA/oil ratio 0.38:1, temperature 240.61^{0}C; catalyst concentration 0.38% reaction time 150mins and mixing rate 600rpm.At these conditions 87% conversion was achieved producing water- reducible alkyd resin with acid value of 15mgKOH/g. Pyscochemical and performance evaluation of the resin showed that it can satisfactorily substitute for convetional alkyd resins in situations where minimal volatile organic compound emission is desired.**

Keywords: Polycondensation reaction, Copolymerization, Water-reducible.

I. INTRODUCTION

Alkyd resins are low molecular weight esters resulting from polycondensation reaction of polyhydric alcohols, Polybasic acids and monobasic acids (oils and fats). These resins are predominantly the most versed used solvent-born binder in the paints and coatings industry because of their desirable attributes such as versatility in solvent solubility and compatibility with other polymer systems (Athawale, et al, 2000).

In recent times, most commercial alkyd resins were produced from the popular edible seed oils such as soybean oil , peanut oil etc. Alkyd resins formulated and produced using any of these oils are usually expensive because most of the oils are expensive as they are competitively demanded for food and for non-edible industrial product purposes. Moreover, the resins are mainly reducible in organic solvents such as toluene, acetone, butanol, xylene, naphtha solvents, etc. which are non-biodegradable and environmentally unfriendly. Thus, they introduce a lot of undesired volatile organic compounds (VOC) into our environment hence causing several health, safety and environmental problems. They also make our coatings and paints hazardous during end applications. These consequences, jointly considered with the regulations to limit the amount of volatile organic compounds in paints and coatings have encouraged several researches and developments directed towards ensuring reduction in volatile solvent emission into the environment via organic solvent based paints and coatings. A major prospective technology in this endeavor was the replacement of organic solvents in coatings with water considering the obvious advantages of water such as availability, cost and environmental acceptability. These attractive attributes, besides other considerations have encouraged research into water reducible alkyds which has in recent times received considerable attention from some authors.

Stable emulsion with micro and nano scale particles of polymer in water medium was reportedly achieved by incorporating some water soluble monomers into an alkyd resin structure via copolymerization (Yousefi, 1991). Mini-emulsion polymerization was used in preparation of stable water-based alkyd-acrylic hybrid resins. The resulting hybrid resins not only have many advantages of both alkyd and acrylic resins but also are water-based resins (Yousefi, 2011). Hybrid resin consisting of two different oils and water soluble polymers and dispersible in water medium was achieved from copolymerization of alkyd with stable acrylic emulsion (Pishvaei, 2008). Mini-emulsion technique was used to copolymerize alkyd resin with methyl -methacrylate and butyl-acrylate to obtain a stable emulsion possessing satisfactory binder properties (Asua,2002, Chern, 2006, Ouzineb, et al ,2006, Guyot, et al, 2007, and Landfester, 2009). A water- reducible alkyd-acrylic resin resulted from a copolymer of 15 to 40% n-butyl-acrylate and maleic anhydride polymer-grafted on modified palm kernel oil (Saravari, et al,2005. Thus many researches have been successfully conducted on synthesis of water-soluble alkyd resin. However, there is yet no reported literature on synthesis and evaluation of water reducible cottonseed oil modified alkyd resin based on partial substitution of maleic anhydride with trimellitic anhydride in glycerol and polyglycol polyesterification.

The central focus of this research, therefore, is to synthesize and characterize water reducible alkyd resin from cottonseed oil.

II. MATERIALS AND METHODS

A. Source Review

The commercial refined, edible grade cottonseed oil was purchased from Shoprite Enugu. Research grade of Maleic anhydride ($C_4H_2O_3$) with minimum assay >97%, Trimellitic anhydride ($C_9H_4O_5$) with assay 98%, glycerol ($C_3H_8O_3$) with assay >99%, sodium bisulphate (Na_2CO_3) with assay 97.5%, Polyethylene glycol (PEG 4000) with assay 97%, and Lithium

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hydroxide (LiOH) with assay >96.8% were purchased from Gerald Chemical Services Ltd, Ogbete Main Market. Four-neck flat-bottom round flask and condenser were procured from Federal Science Equipment Development Institute (FSEDI) Enugu. Other equipments include electronic weighing balance, heating mantle equipped with magnetic stirrer and general laboratory glasswares. Xylene, White spirit, Naphtha solvent and distilled water were obtained from Conraws Science equipment and chemicals Ltd Enugu.

B. *Characterization of Cottonseed Oil*

The physical and chemical properties of the refined cottonseed oil and that of neutralized/ dehydrated oil were determined following the method described by AOAC, (2004).

C. *Synthesis of Water- Reducible Alkyd Resin*

In the synthesis of the alkyd resin, three stages were involved. The stages were alcoholysis, esterification and copolymerization. The basic reagents utilized for the coupled operations include neutralized and dehydrated cottonseed oil, glycerol, Maleic anhydride (MA), Trimellitic anhydride (TA), Polyethylene glycol (PEG) and Lithium hydroxide (LiOH) as catalyst. The method suggested by Hlaing and MyaO, (2008) for alkyd resin synthesis was utilized to implement a central composite rotatable design, formulated based on the factor setting indicated in table 1. The details on the experimental design may be found in Uzoh, et al, (2013).

D. *Alcoholysis*

Monoglyceride was first synthesized by reacting neutralized and dehydrated cottonseed oil with glycerol. The oil was heated maintaining agitation speed of 600 rpm. Glycerol and selected catalyst (0.1% LiOH) wt was added and alcoholysis reaction was allowed to progress at 230-240^{o}C. The reaction was continued for 120 miutes at the end of which, sample of the reaction mixture became soluble in 3 volume of anhydrous methanol. After alcoholysis was completed, the reaction mixture was cooled to 140^{o}C

E. *Esterification*

Maleic anhydride (MA) and Trimellitic anhydride(TA) at 8:1 ratio was added to the monoglyceride mixture and followed by introduction of calculated quantity of xylene. The temperature of the mixture was maintained at the range of 220 – 260^{o}C. Progress of the reaction was monitored by intermittent measurement of the acid value (AV) and viscosity (V). These parameters were measured off-line for all reaction durations after a uniform delay period of 30minutes. The conversion to alkyd resin(Y) calculated analytically in terms of measured reduction in AV equation (1), for a given reaction phase using equation (2), relying on data obtained from normal titration while the viscosity was measured instrumentally for cold sample using viscometer.

F. *Copolymerization*

Polyethylene glycol was heated up to 230^{o}C and introduced into the reaction mixture and maintained at 230-240^{0}C while at constant agitation speed of 600rpm. Progress of the reaction was monitored again by checking the acid value at 20mins interval until and acid value of 13mgKOH/g was attained.

$$Acid \quad Value(AV) \equiv \frac{MV * 40}{W} \quad (1)$$

$$Y \equiv 1 - \frac{AV_j}{AV_o} \equiv 1 - \frac{V_j}{V_o} \quad (2)$$

AV_0 and AV_j are the acid values of the mixture determined at the initial time (t=0) and later time t=j respectively while V_0 and V_j are the corresponding volumes of KOH used in the titration.

G. *Characterization of Water- Reducible Alkyd Resin*

Standard test methods of ASTM, (2689-93) were used to determine some significant properties such as acid value, saponification value and iodine value of the synthesized water reducible alkyd resin. The color and specific gravity were determined following the American Oil Chemists Society methods, (AOAC, 2004). The viscosity was measured at 25^{0}C using Hake Rotary Viscometer PK 100.

H. *Performance Evaluation of Water-Reducible Alkyd Resin*

Performance evaluation tests were carried out on the synthesized resin by formulating the resin into paint following the recipe in table 1 and evaluating the drying characteristics and chemical resistance following methods of (ASTM 1640-83) and (ASTM 3363-74) respectively. Film hardness and abrasion resistance tests were performed with Blinckel HA 300. Methods described by Ekpa and Isaac, (2008) were followed in determining other characteristics such as specific gravity and adhesion. These properties were compared with that of paint prepared with conventional soyabean oil medium alkyd obtained from Intecil Resin plant Emene Enugu using a recipe for the production of standard alkyd gloss paint, (Ibanga and Edet, 2013), as also indicated in table 5.

III. Results and Discussion

Table I: Physicochemical properties of Cottonseed Oil

Properties	Commercially Refined Oil	Neutralized/ Dehydrated Oil
Color	Golden Yellow	Goilden Yellow
Specific gravity	0.912	0.98
Viscosity (cp)	63.90	42.80
Acid Value (mgKOH/g)	0.29	0.20
Idine Value (gI_2/100goil)	22.10	98.20
Saponification Value	63.19	194
Free fatty acid	0.15	-
Moiture content (%)	0.16	-

Table II: Recipe for Synthesis of Water-Reducible Alkyd Resin

Chemicals	Mass (g)
Cottonseed oil	121.20
Glycerol	54.30
Lithium hydroxide	0.82
Maleic Anhydride	46.03
Trimellitic Anhydride	5.75
Polyethylene Glycol (PEG 4000)	71.90
Total	300.00

Table III: Physicochemical Properties of Water-Reducible Alkyd Resin

Propertis	Value
Color	Dark Brown
Specific gravity	1.05
Acid Value (mgKOH/g)	13
Iodine Value (gI_2/100g oil)	43.86
Saponification Value	372
Viscosity (cP)	8896

Table IV: Result of Solubility Test on Water-Reducible Alkyd Resin

Solvent	Observation after 24hrs
Xylene	Clear solution
Naphtha solvent	Clear solution
Distilled water	Cloudy solution

Table V: Recipes for Production of Sample Paints

Ingredients	Standard	Specimen
Water-reducible Alkyd resin	-	50.22
Intecil Alkyd resin	50.22	-
Titanium (IV) Oxide	16.55	16.55
Calcium carbonate	6.0	6.0
Distilled Water	-	7.39
Calcium drier	0.60	0.60
Cobalt drier	0.59	0.59
Lead drier	0.80	0.80
Formalin	2.03	2.03
Total	92.70	100.0

Table VI: Result of Hardness and Abrasion Test

Height (m)	Standard sample	Specimen
1	No effect	No effect
2	No effect	Noeffect
3	Scratch / thickness reduction	No effect
4	Pronounced effect	Minor effect

Table VII: Result of chemical Resistance Test

Chemical	Obervation Period (hrs)	Effect on Standard	Effect on Specimen
2%Na_2CO_3	24	Film removal	Film removal
2%H_2SO_4	24	Color change	Color change
Distilled water	48	No effect	No effect

Table VIII: Result of Drying Characteristics Test

Drying Stage	Standard	Specimen
Dust free	6hrs	8hrs
Set-to-touch	18hrs	20hrs
Hard dry	24hrs	38hrs

The results of the property evaluation of the refined cottonseed oil and that of the further treated (neutralized and dehydrated) one are tabulated in table 1. There was no remarkable change in color as a result of the neutralization and dehydration. The golden yellow color of the oil remained stable. The viscosity dropped from 63cP to 42.81cP. This is in trend with the drop in acid value, moisture content and free fatty acid content. These drastically affected the specific gravity which appreciated from 0.91 to 0.98, the iodine value which improved from 22.10gI_2/100g oil to 98.20gI_2/100g oil and also the saponification value that showed remarkable increase from 63.19 to 194. These are attributable to the molecular condensation of the triglycerides following the loss of water molecules during dehydration and also loss of the free fatty acid converted to soap during neutralization. Obviously, the neutralization and dehydration processes imparted immensely on the iodine and saponification values of the oil. These properties were known to impart remarkably on the drying properties and molecular weight of alkyd that may be synthesized from the oil.

In the alcoholysis stage of the synthesis process, dehydrated cottonseed oil was reacted with glycerol at 220-230^oC using 0.20% by mass of Lithium hydroxide as catalyst. Alcoholysis was achieved within 120mins as the mixture became soluble in three volume of anhydrous methanol. The mixture was cooled to 140^oC before Maleic anhydride was introduced. The cooling was to ensure that the acid went into the monoglyceride, otherwise, part of it may sublime if it is introduced at a temperature far above the boiling point of the acid. The mixture was subsequently heated to 180^oC at which trimellitic anhydride was introduced before it was further heated and maintained at 220- 260^oC as shown in table 2 This second stage of the reaction was continued at constant temperature and long chain molecules were formed which contain excess hydroxyl group. At this state water was released. Removal of water from the mixture was facilitated by a solvent extraction method using Xylene The mixed vapor generated was then condensed and collected. Xylene was suitably applied for this process considering its boiling point and solubility in water at such elevated temperature. The reaction progress was monitored by intermittent measurement of the acid value (AV), viscosity and water off. The acid value and viscosity were measured off-line for all reaction durations after a uniform delay period of 30minutes. The conversion to alkyd resin(Y) calculated analytically in terms of measured reduction in AV (1) for a given reaction phase using equation (2), relying on data obtained from normal titration while the viscosity was measured instrumentally for cold sample using viscometer. At 87% conversion the acid value had reduced to 13mgKOH g from its initial value of 154mgKOH/g. The reaction was stopped at such considerably high acid value to avoid gel formation as the viscosity was rapidly appreciating with the reducing acid value. The high viscosity is in conformity with observations earlier made by Kirk and Othmer, (1947), the presence of Maleic anhydride (MA) up to 10 mol % of the total dibasic acid in resin formulation accelerates viscosity increase during resin manufacturing process. However, despite this obvious challenge, maleic anhydride was used in this synthesis because it is known to possess the ability to impart vinyl unsaturation to the backbone chain of the resin molecules and thus allows the resin to be grafted with vinyl and other monomers. On the other hand, Trimellitic anhydride (TMA) was used to substitute part of the maleic anhydride in the formulation becauuse it imparts a measurable quantity of pendent carboxyl groups for water solubilization of the resulting resin, (Kirk and Othmer, (1947). These vital properties imparted to the resin structure by the combined application of the dibasic acids allowed its fast copolymerization with Polyethylene glycol (PEG) to achieve the desired water-reducible alkyd resin.

Table 3, showed the physicochemical analysis of the water–reducible alkyd resin .The color of the alkyd is dark-brown compared to the golden- yellow color of dehydrated cottonseed oil. The dark-brown coloration may have been caused by side reactions due to atmospheric oxygen inlet into the reactor during the process, as one of the

necks was intermittently opened for introduction of materials. The acid value of 13mgKOH/g is considerably high even at a considerably high acid conversion of 87% achieved in the process. However, further processing was not advisable to avoid gel formation considering the already attained high viscosity of 8896cp. The high acid value is however attributable to the high acid values of 1142mgKOH/g and 865mgKOH/g respectively for (maleic anhydride (MA) and trimellitic anhydride (TMA)), polybasic acids used in the synthesis. The high iodine value of 43.866gI_2/100g oil is an indication that there is high degree of unsaturation in the molecules of the ester formed. This is likely as a result of conjugated bond culminating from the benzene rings of the TMA and double bonds in the structure of MA. The high iodine value implies that the alkyd will produce coatings with good drying characteristics.

Solubility test result in table 4 indicates that the resin is soluble in both organic solvents and water. At the end of 24hrs, the sample prepared with xylene and naphtha solvents respectively retained the color of the resin while the sample made with water was cloudy. This indicates that there was emulsion formation resulting from the mixing of remnants of the azeotropic solvent, other organic constituents and the water use as dilution solvent.

Result of performance evaluation conducted on the sample paint formulated with the synthesized alkyd and the sample formulated with the conventional medium oil soybean alkyd (Ibanga and Edet, 2013), are as shown in table 5. The color of the paint sample was off-white compared to the brilliant white color of the standard sample. The off-white color is attributable to the dark-brown color of the synthesized resin. The higher specific gravity possessed by the water-reducible alkyd based paint sample is in trend considering the fact that the specific gravity of paint is a function of the type of resin and the degree of cross linkage and depends on other ingredients (Ibanga and Edet, 2013). In the present situation, the use of water as the dilution solvent also contributed to the higher specific gravity considering the higher specific gravity of water compared to that of organic solvents used in the standard sample.

The dust-free, set-to-touch, and hard dry time test results were as shown in table 6. The sample produced with the water-reducible resin exhibited longer drying time despite the high iodine value of the resin. The longer drying time properties could be attributable to the low volatility of water used as the dilution solvent.

Paint based on the water-reducible resin showed an excellent adhesion property. This is in trend with expectations considering that the resin contains some polar groups such as (–COOH) remnants of the polybasic acids and (O-H) largely introduced by the PEG grafted in the resin structure during synthesis. These polar groups are very active promoters of adhesion due to their attraction to substrate or by their influence in improving the wetting properties, (Issam and Chuen, 2009). Good initial wetting of a surface by coating and maintenance of the wetting during the process of film formation are essential for the good film adhesion.

Film hardness and abrasion test result shown in table 7 revealed that the film exhibited a good degree of hardness and abrasion resistance as it showed neither scratches nor thickness reduction even at 3meters height. This indicates an advantageous quality over the standard on which minor scratches and film thickness reduction were observed even at 2meters. The excellent hardness and abrasion resistance properties are attributable to the nature of the polybasic acids, (Maleic and Trimellitic anhydrides), used in the synthesis of the resin. This confirms the assertion by Kirk and Othmer, (1964), alkyd resins based on maleic anhydride gives harder and resistant film than that based on phthalic anhydride.

Chemical resistance test results in table 8 revealed that the water-reducible alkyd based paint showed poor resistance to alkali, moderate resistance to acid, and excellent resistance to water. Poor resistance of the film to alkali is traceable to the fact that the resin composed mainly of ester linkages which according to Aigbodion, et al, (2001) are liable to alkaline hydrolysis. The excellent resistance to water is due its high affinity with the high concentration of the hydroxyl polar group grafted into the resin structure by the polyethylene glycol (PEG) during resin synthesis.

IV. Conclusion

Water reducible alkyd resin has been synthesized from cottonseed oil. The physcochemical and performance evaluation of the resin showed that it possessed the necessary qualities that could enable it be used as binder in paints and coatings when zero emission of volatile organic compounds is desired. The rate at which the acid value of the reacting mixture drops in the course of the process was shown to follow linear curves with approximately uniform gradient within the optimum isotherm in the first 20mins of the polyesterification process. This trend was subsequently opposed at the later stages of the reaction due to fast depletion of primary hydroxyl group and the uprising of the secondary hydroxyl group. The findings of this research presented a result showing that cottonseed oil has a high potential as a vital triglyceride for water reducible alkyd synthesis.

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