



Formulation of Emulsion Paint Using Hydroxylated Mahogany Seed Oil/Polyvinyl Acetate Copolymer as Binder.

¹Jildawa, Daniel, ²Nkafamiya Iliya .I And ¹Uzoh, Raymond D*

¹Materials Science Technology Department, Federal Polytechnic, Mubi, Adamawa State. ²Chemistry Department, Modibbo Adama University, Yola, Adamawa State, Nigeria

Abstract

This research study developed a copolymer binder for paint production using conventional polyvinyl acetate(PVA) and hydroxylated ,epoxidized mahogany seed oil(MSO). Seed oil from mahogany was extracted, epoxidized and hydroxylated and was blended and copolymerized with conventional polyvinyl acetate in different ratio of 10 to 60% of hydroxylated oil to form HMSO/PVA copolymer binder. The copolymer binder formed was characterized, and subsequently used as a binder in formulation of emulsion paint. The important physico-chemical parameters of the formulated paint were analyzed and compared with paint formulated using only PVA and acceptable value in quality was achieved comparable to commercial paints. Paint produced from the copolymer binder was found to be of good consistency, smoothness and uniformity and conformed to coating standards. The formulated paint using HMSO/PVA copolymer binder showed increase in gloss, adhesion and flexibility, which are major drawbacks in paints produced using conventional PVA as binder. The study further proved that paint produced from the HMSO/PVA copolymer showed good resistance to acids, alkalis and salt medium compared to the pure PVA binder based paint.

Keywords: Extraction, Epoxidation, Hydroxylation, Copolymer, Polyvinyl acetate

Introduction

Paint, according to Nkafamia (2018) is defined as a number of substances that consist of a pigment suspended in a liquid or paste vehicle such as oil or water and spread with a brush, a roller or a spray gun. It is applied in a thin coat to various surfaces such as wood, metal or stone. Paint is defined as any liquid, liquefiable, or mastic composition that after application to a substrate in a thin layer, converts to a solid film. It is most commonly used to protect, add colour, or provide texture to objects (Gidigbi *et al.*, 2019). Paint is further defined as a stable mechanical dispersive mixture of one or two pigments in a vehicle. It is a mixture of binder, pigments and solvents that form a continuous film that can be protective or decorative. It is a liquid that dries to form a protective film on the surface. For instance Crowley, *et al.*, (2008) reported that, paint provides surface protection, preservation, decoration, as well as aesthetics and adds functionality to structures. It is observed that this has come with quite few limitations, as paint thinned with solvent, though prove to be of better qualities like good water resistance, glossiness, and durable among other things, but was found of efflorescing volatile organic compounds (VOCs), which is inimical to safe environment, as VOC depletes the ozone layer of the atmosphere resulting to global warming and hence, has a negative consequence on environment. Previous study by Kumthekar and Kolekar, 2011;

Yelwa *et al.*, 2017 & Gidigbi *et al.*, 2019 showed that emulsion paints are environment- friendly, though, lack some qualities found in oil-based paint.

The binder is one of the most important ingredients in paint formulation because it is a film-forming material (Gopalan *et al.*, 2000; Yelwa *et al.*, 2017; Gidigbi *et al.*, 2019).

Polyvinyl Acetate (PVA) is one of the common binder used in the formulation of emulsion paint. However, the major setback usually experienced in emulsion paint produced using PVA as a binder is fundamentally due to inadequacies in PVA, such as inflexible, poor water resistance and evanescent. Therefore, in order to cater for these inadequacies, hydroxylated epoxidized mahogany seed oil (HMSO/PVA) copolymer binder is synthesized and subsequently used to formulate an emulsion paint with improved properties. Mahogany seed oil is a vegetable oil found in a plant seed. Generally vegetable oils and their derivatives obtained through functionalization have great potentials as renewable and sustainable raw materials for the production of bio-based polyols which serve as precursor to paint binders and polyurethanes for coatings and foam production (Musik *et.al.*,2021). Vegetable oils are modified by various chemical reactions such as epoxidation, hydroxylation, hydrogenation, acrylation, hydroformylation, e.t.c. These reactions result in products that are

actively used as binders in coating materials due to their unique structural properties. Triglycerides of vegetable oils contain active sites (double bonds) which can be functionalized and used for polymerization using appropriate processes (Musik et.al.,2022).

MATERIALS

Mahogany seed oil, PVA, NaOH, HCl, Sodium dihydrogen phosphate, Sulphuric acid, Acetic acid, Formic acid, Hydrogen peroxide, Kaolin, Butanol, Petri dishes, Beakers, Conical flasks, Measuring cylinders, three neck flask, hot plate, thermocouple, condenser, stirrer

METHODOLOGY

EXTRACTION OF MAHOGANY SEED OIL

Mahogany seed oil was extracted manually, according to the method described by Evwierhoma and Ekop, 2016.

EPOXIDATION OF MAHOGANY SEED OIL

Epoxidation was carried out on the extracted mahogany seed oil using the method described by Goud *et al.*, 2007; Gidigbi *et al.*, 2019.

HYDROXYLATION OF EPOXIDISED MAHOGANY SEED OIL

Hydroxylation was carried out on the epoxidised mahogany seed oil, using the procedure described by Petrovic *et al.*, 2003; Yelwa *et al.*, 2017.

COPOLYMERIZATION OF PVA WITH HMSO.

The HMSO/PVA copolymer was prepared using different blends (0-60%) of the HMSO in PVA. The mixture was stirred and then poured into a glass Petri dish for casting. The resin was also allowed to cure and set for seven days at (30°C). The physical properties of the resin films were investigated according to Osemeahon et. al., 2013.

EMULSION PAINT FORMULATION RECIPE WITH PVA AND PVA/HYDROXYLATED EPOXIDIZED MAHOGANY OIL AS BINDER.

Stage	Materials	Quantity(grams)
1 st stage	Water	185.00
	Ant-foam	0.20
	Drier	0.20
	Calgon	1.16
	Genepor	1.16

	Bermocoll	2.50
	Tryostan	1.14
	Dispersant	0.20
	Butanol	5.00
	Ammonia	0.54
2 nd Phase Millbase	TiO ₂	50.00
	Al ₂ SiO ₃	11.20
	Na ₂ CO ₃	0.58
	Kaolin	2.52
	CaCO ₃	123.00
3 rd Stage (letdown)	Binder	100.00
	Water	15.00
	Dispersant	0.20
	Nicofoam	0.20
	Anti-skinning agent	0.20
Total		500

DETERMINATION OF MOISTURE UPTAKE

The resin films moisture uptake was determined gravimetrically as described by Osemeahon and Archibong, 2011. Average value of triplicate determinations of each sample was recorded.

DETERMINATION OF VISCOSITY AND GEL TIME

Viscosity and gel time was carried out according to method described by Osemeahon et al., 2013. Average value for the triplicate measure was recorded. The gel point of the resin was determined by measuring the viscosity of the resin with time until a constant viscosity profile was obtained (Osemeahon et al., 2013).

WATER SOLUBILITY

Solubility of the resins in water was determined by mixing 1ml of the resin with 5ml of distilled water at room temperature (30°C).

DENSITY, TURBIDITY, MELTING POINT AND REFRACTIVE INDEX

Density was determined using density bottle of standard volume as described by Gidigbi *et al.*, 2019. Average value of three readings was taken for each sample. The turbidity of the sample was determined using Supertek digital turbidity meter (Model 033G).

The melting point of the film sample was determined by using Galenkamp melting point apparatus (Model MFB600-010F).

The refractive index of the sample was determined with Abbe refractometer. The above properties was determined according to standard methods.

DETERMINATION OF ELONGATION AT BREAK

The elongation at break was determined using Instron Universal Testing Machine (model 1026). Resin films of dimension 50mm long, 10mm wide and 0.15 mm thick was brought to rupture at a clamp rate of 20mm/min and at a full load of 20kg. Average value of triplicate was recorded.

RESULTS AND DISCUSSION

Table 1: Comparison of some physical properties of PVA and HMSO/PVA resins.

Parameters	PVA	HMSO/PVA	Acceptable Level in the coating industry
			(Osemeahon <i>et al.</i> , 2013).
Density (g/cm³)	1.201	1.087	1.07u (min.)
Refractive index	1.401	1.417	1.4000 (min.)
Moisture uptake (%)	0.413	0.248	3.10 (max.)
Viscosity (Mpa.s)	34.55	24.00	3.11- 38.00
Melting point (°C)	181	165	200(max.)
Elongation at break (%)	310	417	125(min)
Turbidity (NTU)	1641	1636	-
Gel time (Min)	155	250	-
Solubility	Soluble	Soluble	-

Some physical properties of paints formulated from PVA and HMSO/PVA binders

Table 2 shows the results of some physical parameters tested for the paint samples formulated using PVA, and HMSO/PVA. The Table also inter-compared the results for the different binders, and with the Standard Organization of Nigeria's (SON) specifications. Both paint samples passed the stickiness/tackiness test, indicating a good adhesion potential for all the paint samples (Gopalan, *et al.*, 2007). Both paint samples are alkaline with the pH within the SON specification range.

The pH of the HMSO/PVA paint is however higher than that of the PVA, and this was due to hydroxyl group present in copolymer matrix. Paint pH value can be used to inhibit microbial activities. (Olusanya, 2008).

Both HMSO/PVA and acrylic PVA paint samples passed the adhesion test. The viscosity of both HMSO/PVA and PVA fall within the acceptable range, as paint from PVA being viscous than paint from HMSO/PVA. This may be due to higher molecular weight and crosslinking density.

Both paint samples pass the opacity test, indicating their ability to stabilize pigment dispersion.

Also, both paint samples pass the stability test, which indicates good storage characteristics for the paint. Both also pass flexibility test, which indicate good application of paint on substrate.

Both the paints from the PVA and HMSO/PVA binders passed resistance to blistering test. These results indicate that HMSO segment has been cross linked into the HMSO/PVA copolymer there by impacting hydrophobic character (Yelwa *et al.*, 2017). The higher degrees of cross-linking give rise to less free volume and solvent molecules hardly pass through the cross linked network (Osemeahon and Dimas, 2014). This implies that the paint can perform very well against environmental degradation. The pure PVA paint failed water resistance test as a result of the inherent property of the resin in addition to low molecular weight of the PVA binder used in the paint formulation (Wikipedia, 2018).

Table 2: Some physical properties of paints formulated from PVA and HMSO/PVA Binders

Parameter	PVA	HMSO/PVA paint	SON Standard
pH	7.32	8.07	7-8.5
Viscosity (poise)	14.5	12.09	6-15
Flexibility	Pass	Pass	Pass
Opacity	Pass	Pass	Pass
Adhesion	Pass	Pass	Pass
Hardness test	Pass	Pass	Pass
Tackiness	Pass	Pass	Pass
Resistance to blistering	Pass	Pass	Pass
Drying time (min)			
Touch	32	41	20
Hard	51	72	120

Chemical Resistance

The ability of paint to resist chemical attack or staining is one of the desirable qualities of a good coating film (Standardcon, 2018). Chemical resistance test determines the ability of a coating film to resist discoloration from chemical agents and other

materials common in our environment. Table 4 shows the resistance of the HMSO/PVA and PVA coating film when exposed to acid, alkaline and salt solutions. From the results, both PVA and HMSO/PVA were unaffected by salt medium. PVA and HMSO/PVA film were also unaffected by both the acidic and alkaline solutions. HMSO/PVA has a better chemical resistance due to high cross-linked density of network which decreases their exposure to environmental condition (Yelwa *et al.*, 2017, Gidigbi *et al.*, 2019).h

Table 3: Chemical Resistance of PVA and HMSO/PVA Paint Films

Samples	Media		
	0.1M NaCl	0.1 M HCl	0.1 M NaOH
PVA	A	A	A
HMSO/PVA	A	A	A

Key word

A= No effect

B= Cracking

C= Blistering

CONCLUSION

The copolymer HMSO/PVA resin was synthesized by blending polyvinyl acetate with hydroxylated mahogany seed oil. The effect of the concentration of the blends, on the miscibility of HMSO/PVA blends were studied, based on, the viscosity, gel time, density, melting point, turbidity, moisture uptake, elongation at break, and refractive index. It is concluded that HMSO/PVA blend is found to be completely miscible from 0 to 40% of hydroxylated oil, sparingly miscible at 50% of hydroxylated oil, while it is immiscible from 60% to 100% of hydroxylated oil composition.

The emulsion paint formulated using HMSO/PVA binder indicates a good consistency, smoothness and uniformity. The paint showed increase in gloss, adhesion and flexibility. It further revealed that paint produced from the HMSO/PVA copolymer showed good resistance to acidic, alkaline and salt medium compared to the pure PVA paint.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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REFERENCES

- Afsoon, F., Laleh, R., and Faramarz, A. (2011). DSC analysis of thermosetting polyimide based on three bismaleimide resin eutectic mixtures. *Iranian Polym. J.*, 2(20), 161-171.
- Akinterinwa, A., Osemeahon, S., Nkafamiya, I., and Dass, P. (2015). Formulation of emulsion paint from composite of Dimethylol Urea/Polystyrene. *chemistry and materials reseach*, Vol. 7(No. 7).
- Al-Manasir, N. (2009). Preparation and characterization of crosslinked polymeric nanoparticles for enhanced oil recovery applications. . *University of Oslo, Norway.*, 12-85.
- AOAC. (2000). Official methods of analysis international (Horwitz W. edition). *Gaithersur, USA.*, 17th edition, (14): 1-68.
- Barminas, J., and Osemeahon, S. (2007). Properties of Low Viscosity urea- formaldehyde Resin. *Bulletin of Pure and Applied Sciences.* , Vol. 25c (no. 2). Pp 8-15.
- Biresaw, G., and Carriere, C. (2004). Compatibility and mechanical properties of blends of polystyrene with biodegradable polyester. (33), 313-320.
- Crowley, J., League, J., Jack, W., and and Lowe, J. (2008). A three dimensional approach to solubility. *Journal of Paint Technology*, Vol. 38(No. 2), 20-28.
- Desai, D., Patel, V., and Sinha, K. (2003). Polyurethane adhesive system from biomaterial-based polyol for bonding wood. *Int. J. Adh. Adhes.*, 3(5), 393-399.
- Emile, G. (2003). Moisture transfer properties of coated gypsum. . *Eindhoven University Press, Eindhoven, Netherlands.*, pp. 2-6.
- Evwierhoma, E. T., and Ekop, I. E. (2016). extraction and characterisation of oils from some local seeds. *Int. Journal of scientific and engineering research*, Vol. 7(5).
- Gidigbi, J.A., Osemeahon, S.A., Ngoshe, A.M., and Babanyaya, A. (2019). Modification of Polyvinyl acetate with Hydroxylated Avocado Seed Oil as a Copolymer Binder for possible Application in Coating Industry. *International Journal of Recent Innovations in Academic Research*, 3(2), 231-244.
- Gopalan, R., Venkappavy, A., and Nagarajan, S. (2000). *Engineering Chemistry: Surface Coatings*. Vileas Publishing House.
- Goud, V., Patwardhan, A., and Dinda, S. a. (2006). studies on the epoxidation of mahua oil (Madhumica Indica) by hydrogen peroxide. *Bioresource Technology*, 97, 1365-1371.
- Habibu U. (2011): Production of trowel paints using polyvinyl acetate synthesized from vinyl acetate monomer as a binder. *Leonardo journal of sciences*. P. 49-56.
- Hussain, A., and Nasr, H. (2010). The role of carboxylic acid on the characterization and evaluation seed emulsion of styrene/butyl acrylate copolymers lattices as paint. . *Nature Sci.*, 8(8), 94-103.
- Hwang, Y., Sangmook, L., Youngjae, Y., Kwangho, J., and Lee, W. (2012). Reactive Extrusion of Polypropylene/Polystyrene Blends with Supercritical CarbonDioxide. . *Macromolecular Res.*, 6(20), 559-567.
- Jain, V. (2008). Evaluation of second generation indirect composite resins. . *A thesis Submitted to the Faculty of the University Graduate School in partial fulfillment of the requirements*

for the degree, Master of Science in the Department of Dental Materials, Indiana University, Indianapolis., 1-94.

- Kaniappan, K., and Latha, S. (2011). Certain Investigations on the formulation and characterization of polystyrene/poly(methylmethacrylate) blends. *Int. J. Chem. Res.*, 3(2), 708-717.
- Kazys, R., and Rekuviene, R. (2011). Viscosity and density measurement methods for polymer melts. . *Ultragarsas "Ultrasound"*, 66(4):20-25.
- Kumthekar, V., and Kolekar, S. (2011). Attributes of the Latex Emulsion Processing and its role in morphology and Performance in Paint. *Journ. of Prog. organic coating*, 72, 380-386.
- Mavani, I., Mehta, M., and Parsania, H. (2007). Synthesis and physico-chemical study of polyester resin of 1,1- bis(3- methyl-4-hydroxy phenyl)cyclohexane and rininoic acid and its polyurethanes with polyethylene glycol. *J. Sci. Ind. Res.* , 66:377-384.
- Montemor, M. (2014). Functional and smart coatings for corrosion protection: A review of recent advances. *Surface and Coatings Technology. SCT-19492. In press.*
- Musik, M, Bartkowiak, M, Milchert, E (2022). Advanced Methods For Hydroxylation of Vegetable Oils, Unsaturated Fatty Acids And Their Alkyl Esters. *Coatings 12(13)*.
- Naghash, J., Karimzadeh, A., Momeni, R., Massah, R., and Alian, H. (2007). Preparation and properties of triethoxyvinylsilane-modified styrene-butyl acrylate emulsion copolymers. *Turk. J. Chem.*, 31, 257-269.
- Nkafamiya, I. I. (2017). CHM 702 Enterprenurship Skill Lecture Note. *Chemistry Department, Mautech, Yola.*
- Osemeahon, S. (2011). Copolymerization of methylol urea with ethylol urea resin for emulsion paint formulation. . *Afr. J. Pure Appl. Chem.*, 5(7), 204-211.
- Osemeahon, S., and Archibong, C. (2011). Development of of urea formadehyde and polystyrene waste as copolymer binder for emulsion paint formulation. *J. Toxicology and Environmental Health Science.*, 3(4): 101-108.
- Osemeahon, S., and Dimas, B. (2014). Development of urea formaldehyde and polystyrene waste as a copolymer binder for emulsion Paint formulation. *Jour. of Toxicology and Environmental Health Science*, 49-56.
- Osemeahon, S., Maitera, O., Hotton, A., and Dimas, B. (2013). Influence of starch addition on properties of urea formaldehyde/starch copolymer blends for application as a binder in the coating industry. *Journal of Environmental Chemistry and Ecotoxicology*, 5(7), 181-189.
- Petrovic, Z., Zlantanic, A., Lava, C., and Sinadinovic-fiser, S. (2003). Epoxidation of Soybean oil in toluene with peroxy acetic acid and peroxy formic-acids-kinetics and side-reactions. *European Journal of Lipid Science and Tech.*, 293-299.
- Petroudy, D. (2017). *Advanced high strength natural fibre composites in construction*. Science Direct.
- Shashidhara, Y., and Jayaram, S. (2010). Vegetable oils as a potential cutting fluid - an evolution. *Tribology international*(43), 1073-1081.

- Sudharsan R. K., P. M., Venkatesulu, G., Sajan, K. U., Chowdoj, i. R., and Subha, M. C. (2012). Miscibility Studies of Hydroxypropyl Cellulose/Poly(Ethylene Glycol) in Dilute Solutions and Solid State. *International Journal of Carbohydrate Chemistry*.
- Suurpere, A., Christjanson, P., and Siimer, K. (2006). Rotational Viscometry for the study of urea formaldehyde resins. *Proc. Estonian Acad. Sci. Eng.*, 2(12), 134-146.
- Yelwa, J. M., Osemeahon, S. A., Nkafamiya, I. I., and Abdullahi, S. (2017b). Synthesis And Characterization Of Hydroxylated Sunflower Seed Oil/ Poly Vinyl Acetate Copolymer As A Binder For Possible Application In The Coating Industry. *International Journal of Innovative Research and Advanced studies*, 4(7).
- Yumiko, H., Takanobu, S., Tetsuo, O., Toshiaki, O., Masashi, M., and John, M. (2010). Effects of specular component and polishing on color resin composites. *J. Oral Sci.*, 4(52), 599-607.