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COPOLYMERIZATION OF DIMETHYLOL UREA WITH HYDROXYLATED WATERMELON SEED OIL AS BINDER FOR EMULSION PAINT FORMULATION

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Abstract
Watermelon Seed Oil was extracted, epoxidized and hydroxylated. Hydroxylated Watermelon Seed Oil (HWSO) was blended with Dimethylol Urea (DMU) in different ratio of 10 to 60% of hydroxylated oil, to develop DMU/HWSO copolymer binder for emulsion paint formulation. FT-IR analysis of copolymer resin (DMU/HWSO) showed chemical interaction between DMU and HWSO. Some physical properties of the copolymer resin such as viscosity, gel time, density, melting point, refractive index, moisture uptake, elongation at break and water solubility were determined. The results from studies indicate that viscosity, refractive index, gel time and elongation at break increases with increase in HWSO concentration in DMU/HWSO copolymer composite. However, density, melting point, water solubility and moisture uptake decreases with HWSO concentration in the composite. The results of the physic-chemical properties point to the fact that the traditional problems associated with DMU (formaldehyde emission, hardness and poor water resistance) can be addressed or reduced by DMU/HWSO blend.
Keywords: *Extraction, Epoxidation, Hydroxylation, Copolymerisation, Dimethylol Urea.*

Introduction

Paints are liquid or liquefiable substance of mastic composition which after application to a substrate in a thin layer, is converted to an opaque solid film (Stephanie, 2011). Painting has been known to be one of the most important aspects of building construction. It covers the block work and concrete rendering with attractive and beautiful colors giving the building a high aesthetic outlook. Paints usually consist of vehicle or binder, a pigment which contributes obscurities colour hardness and bulk to the film and a solvent or thinner which controls the consistency. (Rodger, 2007)
It is indispensable in building construction all over the world (Opara, 2014).
Painting and coatings are unique human activities that have helped the human race to contribute significantly in earning a better livelihood, building a better and more beautified world for ourselves. (Akinterinwa et.al., 2015).

Coating material items in our environment is done for different purposes which include: protection, decoration, durability and for special purposes (Van, *et al.*, 2007). The surfaces of many objects corrode in the air and are damaged by the effect of weather and wear if not protected and taken care through coating. For example, iron rusts and wood deteriorates in the atmosphere. As many materials become available, the need to modify the surface continues to grow. Many surfaces believed to be satisfactory without coating are attacked by weather, chemicals, atmospheric pollution or other factors and must be protected before certain uses. The wide variety of surfaces which must be protected and decorated has given rise to an infinite number of coating agents such as paints and varnishes. Not only to protect such surfaces but also to decorate them or to provide special purposes. It obliterates the surface on application and provides colour to it (Udeozo, *et al.*, 2013).

It is also the term used to describe a number of substances that consist of a pigment suspended in a liquid or paste vehicle such as oil or water with a brush, a roller or a spray gun. Paint is applied in a thin coat to various surfaces such as wood, metal or stone (Nkafamiya, 2017).

Paint is made up of three major constituents. Each type of finish has its own special blend of constituents that enhances its performance. The constituents includes;

1. Binder: the binder is the constituent that holds the pigment and other additives together and bind them onto the surface painted.
2. Pigment: the pigment gives paint its colour and opacity.
3. Solvent: the solvent enables the paint to be spread over a surface.
4. Other additives: these are other ingredients added to paint for a specific purpose (Igwebike, 2012).

Aim and Objectives

The aim of this research work was to develop a new binder for emulsion paint formulation from hydroxylated Citrullus vulgaris seed oil (Water melon seed oil) with Dimethylol urea copolymer

The aim was carried out through the following objectives.

1. Water melon seed oil (Citrullus vulgaris Seed oil) was extracted
2. Dimethylol urea was produced.
3. Epoxidation and hydroxylation of the extracted seed oil was carried out
4. Hydroxylated seed oil with the produced Dimethylol urea resin was copolymerized.
5. The copolymerized resin was characterized

Materials and Methods

Watermelon seed oil, Urea, formaldehyde, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide, sucrose, ammonia, hydrogen peroxide, acetic acid, formic acid, iso-propanol, methanol (all of analytical grade).

Resin Synthesis

Dimethylol Urea (DMU) was prepared using the method described and adopted by Akinterinwa *et al.,* 2015. The one step process (OSP) as reported by Osemeahon and Barminas (2007) with some modifications was adopted. One mole of urea (6.0g) was made to react with two moles of formaldehyde (16.22ml) 37-40% (w/v), using 0.2g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 6by using 0.5M H_2SO_4 and 1.0M NaOH solutions. The solution was heated in a thermostatically controlled water bath at 70°C. The reaction was allowed to proceed for 2 hours after which the resin was removed and kept at room temperature 30°C.

Extraction of Watermelon Seed Oil

The rotten watermelon fruits (*Citrullus vulgaris*) were purchased from Jalingo main market, Taraba State of Nigeria. The seeds were removed from the pulp and washed. The seeds were selected to remove those damaged and sundried for a week to get rid of moisture. They were ground mechanically to a particulate size and extraction of *Citrullus vulgaris* seed oil was equally done mechanically.

Epoxidation of *Watermelon* Seed Oil

Epoxidation was carried out using the method described by Goud *et al.,* 2007.

Hydroxylation of Epoxidized *Watermelon* Seed Oil

Hydroxylation of the vegetable oil was carried out using procedure described by Patrovic *et al.,* 2003.

Copolymerisation of DMU with HWSO

The DMU/HWSO copolymer was prepared by carried out different blends (0-60%) of the HWSO in DMU. 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 (Osemeahon *et al.*, 2013).

Determination of Formaldehyde Emission

Formaldehyde emission was carried out using the standard 2 h desiccator test as described by Osemeahon and Archibong, 2011. The mould used will be made from aluminium foil with a dimension of 69.9 x 126.5mm and thickness of 12.0mm. The emitted formaldehyde was absorbed in 25.0ml of water and will be analyzed by a refractometric technique using Abbe refractometer. Triplicate determination were made for the samples and the average value taken.

Determination of Water Solubility

The solubilities of DMU and Dimethylol Urea/Vegetable Oil (DMU/VO) blends was determined by mixing 1ml of the resin with 5ml of distilled water at room temperature (27-30%)

Determination of Viscosity and Gel Time

Viscosity and gel time were carried out according to method described by Osemeahon and Archibong, 2011. A 100ml graduated glass macro-syringe was utilized for the measurement. The apparatus was standardized with 60% (w/v) sucrose solution whose viscosity is 5.9mpa at 30°C. The viscosity of the resins was evaluated in relation to that of the standard sucrose solution at 30°C. Three different readings were taken for each sample and the average value calculated. The gel time of the resin was determined by monitoring the viscosity of the resin with time until a constant viscosity is obtained.

Determination of Moisture Uptake

The moisture of the resin film was determined gravimetrically according to method described by Osemeahon and Archibong, 2011. Known weight of the sample was introduced into desiccators containing a saturated solution of sodium chloride. The increase in weight (wet weight) of the sample was monitored until a constant weight was obtained. The difference between the wet weight and dry weight of the sample was recorded as the moisture uptake by the resin. Triplicate determinations were made and the average value recorded.

Determination of Density, Turbidity, Melting Point and Refractive Index

The density of the resin was determined by taking the weight of a known volume of resin inside a density bottle using pioneer (Model PA64) weighing balance. Three readings were taken and average value calculated. The turbidity of the sample was determined by using Supertex digital turbidity meter (Model 033G). The melting point of the film sample was determined by using Galenkamp melting point apparatus (Model MFB600-010F) while the refractive index of the sample were determined with Abbe refractormeter. The above properties will be determined according to standard methods (AOAC, 2000).

Determination of Elongation at Break

The elongation at break was determined using Inston Tensile Testing Machine (Model 1026). Resin films of dimension 50mm long, 10mm wide and 0.15mm thick were brought to rupture at a clamp rate of 20mm/min and a full load of 20kg. Three runs were carried out and the average elongation evaluated and expressed as the percentage increase in length.

FTIR Analysis

The infra-red (IR) analysis of vegetable oil (VO), Dimethylol urea (DMU), epoxidized watermelon seed oil (EWSO), hydroxylated watermelon seed oil (HWSO) and Dimethylol urea/hydroxylated watermelon seed oil (DMU/HWSO) was carried out using infra-red spectrophotometer (PerkinElmer Spectrum Version 10.03.06) between 400 and 4000 cm.

Results and Discussion

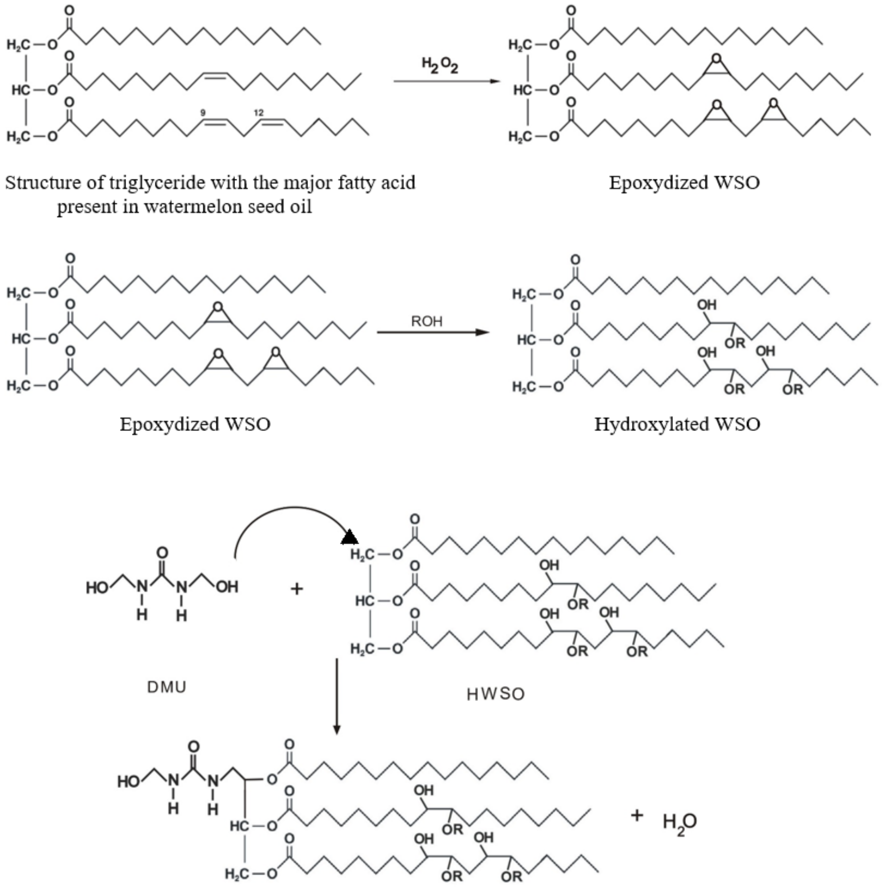


Figure 1: Reaction Scheme for the Synthesis of DMU/HWSO resin

FTIR Spectra Analysis

Figure 2 shows the IR spectra of A (DMU), B (Blend DMU/HWSO) and C (HWSO). The FTIR spectrum of DMU, showing a broad band stretching from 3600 cm^{-1} through 3100 cm^{-1} is due to O-H of Dimethylol urea, 2924.46 cm^{-1} is due to N-H, 1742.81 cm^{-1} is due to C=O of urea, 1460.29 cm^{-1} is due to $–CH_2$ of methylene bridge (Osemeahon, 2011).

For the hydroxylated oil (HWSO) an O-H was introduced at 3500-3300cm^{-1}. The dual sharp transmitted at 2853cm^{-1} - 2923.91cm^{-1} produced by stretching of the C-H group of alkane in the spectrum of HWSO can be remarkable distinguished. The peak at 1749.59 cm-1 indicates C=O stretching vibrations of the saturated ester present in the oil (Yelwa *et al.*, 2017).

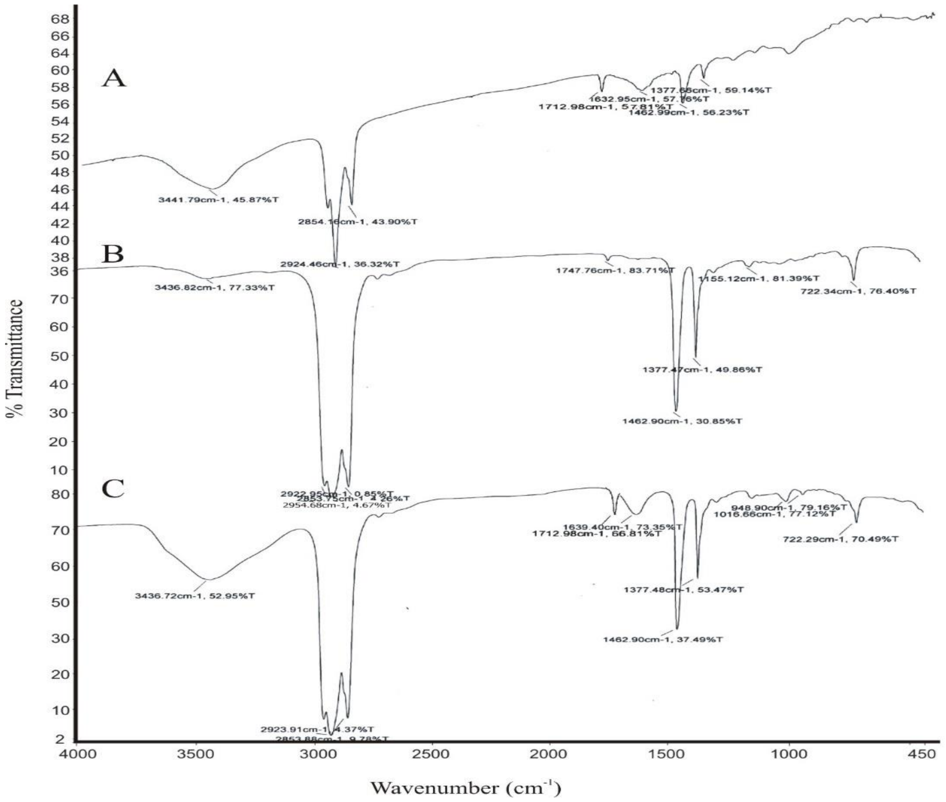


***Figure 2**: FTIR spectra of A (DMU), B (Blend DMU/HWSO) and C (HWSO)*

The blend DMU/HWSO shows the presence of hydroxyl (OH) and a secondary amine from the DMU (-NH). Others are C – O stretching of an aldehyde which is a carbonyl compound with numerous C –H, C – C of methyl group and a rocking symmetry of CH_2.

Effect of HWSO Concentration on the Viscosity of DMU/HWSO Resin

The relationship between the structure and rheology of a polymer is of practical interest for two reasons: firstly, rheological properties are very sensitive to certain aspect of structure and they are simple (Oluranti *et al.*, 2011).

Figure 3 is a graph that shows the effect of HWSO concentration on the viscosity of DMU/HWSO copolymer resin. From the graph, it is observed that viscosity increases with increase in inclusion of HWSO. This is attributable to the increase in molecular weight as DMU copolymerizes with the relatively large molecular weight of HWSO (Markovic, *et al.*, 2001). From the graph, it is observed that viscosity reaches its peak with 30% inclusion of HWSO after which it begins to fall. This is due to the dissociation of the molecules in the blend.

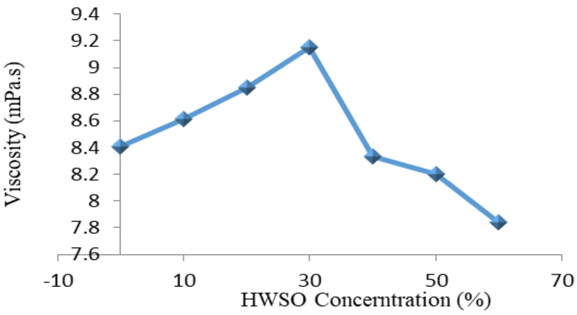


***Figure 3**: Effect of HWSO concentration on the viscosity of DMU/HWSO resin.*

Gel-Time of DMU/HWSO Resin

Figure 4 shows the effect of HWSO concentration on the gel-time of DMU/HWSO composite. From the graph, it can be observed that the gel-time increased with increase in inclusion of HWSO. This is attributed to increase in molecular weight which leads to increase in viscosity of the composite resin (Osemeahon and Dimas 2014). Therefore, continuous increase in HWSO will lead to increase in cross-linking of the molecules where the gel-time will become steady.

Gelation is the change in macromolecular structure of resin, which is usually expressed as an increased of viscosity and leads finally to the loss of flow-ability.

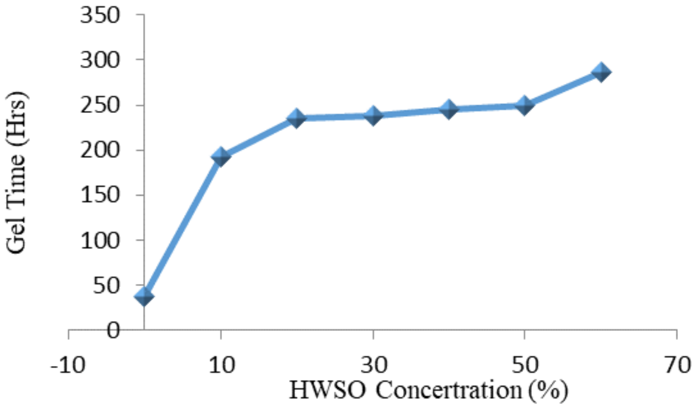


Figure 4*: Effect of HWSO concentration on the gel-time of DMU/HWSO resin.*

Density of DMU/HWSO Resin

The gradual decrease observed in density with increase in HWSO concentration in Figure 5 can be as a result of differences in the molecular features and morphology which influenced the packing nature of resin molecules as the concentration of HWSO increases. Physical properties of polymer depend on chain length and content of soft and hard segments. The decrease observed with HWSO loading is due to increase in the amount of soft segment (Mavani *et al.*, 2007). The density of DMU as can be seen is higher than that of HWSO. Therefore, it is expected that with increase in HWSO concentration, there will be decrease in the density (Osemeahon and Dimas, 2014).

Density is a physical property of matter that expresses a ratio of mass to volume and is an important physical parameter in polymer engineering processes. The density of a paint binder in the coating industry has an important influence on factors such as pigment dispersion, brush-ability of paint, flow, leveling and sagging.

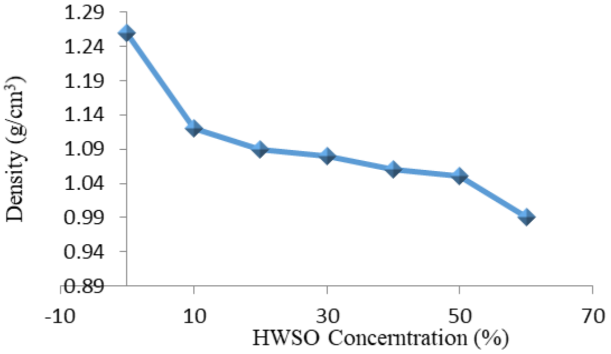


Figure 5: *Effect of HWSO concentration on the density of DMU/HWSO resin.*

Turbidity of DMU/HWSO Resin

Figure 6 shows the effect of HWSO concentration on the turbidity of DMU/HWSO resin. Turbidity is relatively low at 0% HWSO because pure DMU is clear and transparent. However on addition of HWSO it becomes colloidal and light scattering increases. As the concentration of HWSO increases, the growth of large inter-polymer aggregate increase and the turbidity increased, hence turbidity of the system can be used as an indicator of the level of inter-chain cross-linking (Nodar, 2009). The higher the HWSO concentration, the higher the light scattering and the higher the turbidity (Osemeahon and Dimas, 2014).

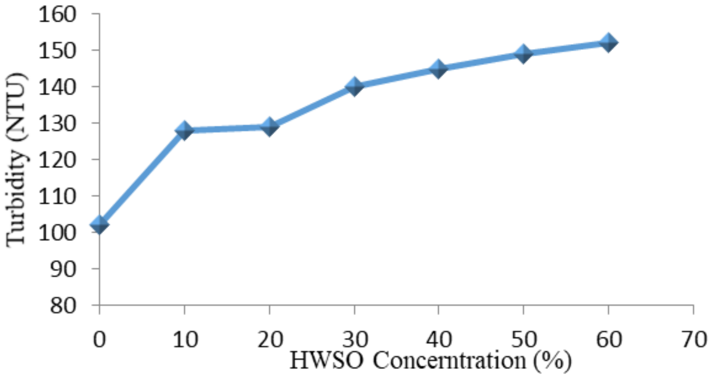


***Figure 6**: Effect of HWSO concentration on turbidity of DMU/HWSO resin.*

Refractive Index of DMU/HWSO Resin

The effect of HWSO concentration on the refractive index of DMU/HWSO composite is shown in Figure 7. From the graph, it can be observed that refractive index increases with increase in HWSO concentration. Pure DMU has a low refractive index. As HWSO is added to DMU, the optical property of DMU is increased. There is an alteration in the crystallinity of the system with HWSO loading which gives rise to higher crystallinity of DMU/HWSO composite. This explains the above behavior (Jain, 2008).

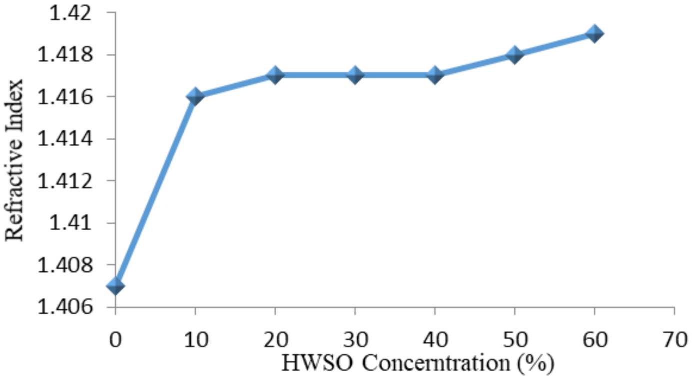


Figure 7: Effect of HWSO concentration on the refractive index of DMU/ HWSO resin.

Formaldehyde Emission of DMU/HWSO Resin

Figure 8 shows the effect of HWSO concentration on the formaldehyde emission of DMU/HWSO copolymer composite. It is observed that formaldehyde emission decreases with increase in the concentration of HWSO. This behaviour is attributed to the gradual reduction in the concentration of DMU, with increase in HWSO concentration (Osemeahon, 2011). The formaldehyde emission level is drastically reduced by limiting the problem at source (pizzi *et al.*, 2002).

The emission of formaldehyde during the curing process of a resin is known to be one of the major drawbacks of urea formaldehyde (Kim, 2001; Osemeahon et al, 2008). Serious efforts must be made to reduce formaldehyde to acceptable levels in the development of paint binders from urea formaldehyde resins (Osemeahon et al, 2010).

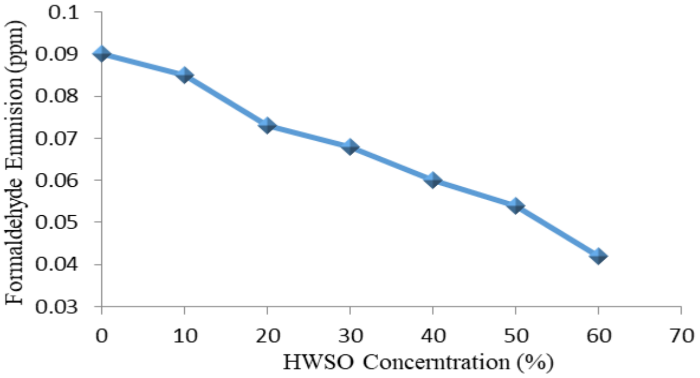


***Figure 8**: Effect of HWSO concentration on the formaldehyde emission of DMU/ HWSO resin*

Moisture Uptake of DMU/HWSO Resin

In Figure 9, the percentage water absorption of the films was greatly influenced by the HWSO content. The moisture uptake decreased with increase in the concentration of HWSO, this is as a result of the excellent hydrophobicity of HWSO. Increase in HWSO into the copolymer give rise to corresponding increase in hydrophobicity of the polymer matrix (Naghash *et al.*, 2007). Also interaction between DMU and HWSO results in an increase in cross-linking density, this narrows down the intermolecular spacing. The smaller intermolecular spacing give rise to lower viol spaces within the matrix hence the reduction in moisture uptake (Nouailhas *et al.*, 2011). The reduced sensitivity to moisture due to HWSO inclusion in DMU matrix provides benefits in property retention as a function of environmental conditioning. This will also address one of the shortcomings of pure DMU, which is high moisture uptake.

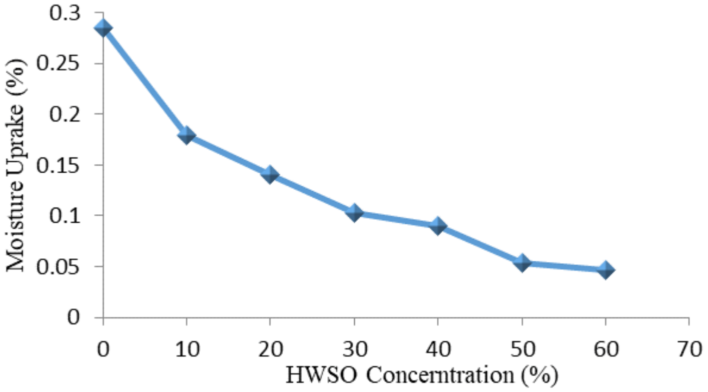


***Figure 9**: Effect of HWSO concentration on the moisture uptake of DMU/ HWSO resin*

Elongation at Break of DMU/HWSO Resin

Figure 10 shows the effect of HWSO on the elongation at break of DMU/HWSO resin. A steady increase in elongation at break was observed from 0 to 30% HWSO and an abrupt increase at 40% due to compatibilization effect and improved interfacial adhesion, hence flexibility is improved and brittleness reduced. Also, a decrease was observed after 40%. This non-linear behavior in terms of the mechanical property is caused by the difference in intimate physical interlocking, and the extent of phase separation (Hwang *et al.*, 2012)

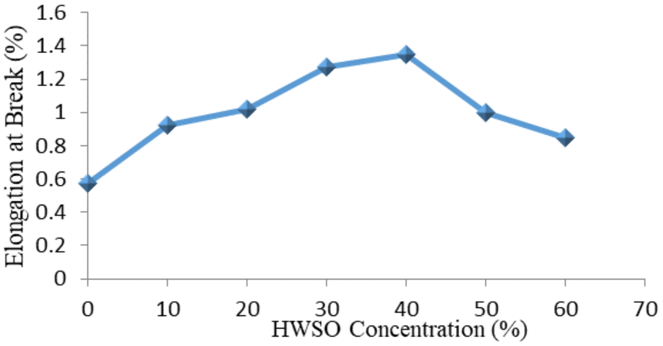


***Figure 10**: Effect of HWSO concentration on the elongation at break of DMU/ HWSO resin*

Melting Point of DMU/HWSO Resin

Figure 11 exhibits the effect of HWSO concentration on the melting point of DMU/HWSO resin. The result shows a gradual decrease in melting point from 0-40% concentration of HWSO in the blend. This can be explained on the basis of increase flexibility as a result of increase in the concentration of HWSO which gives rise to increase in molecular mobility. The increase in the melting point observed at 50% HWSO inclusion in the blend is due to increase in molecular weight which makes the material harder in nature due to the increased cross-linking density. From the Figure, optimal hardness was obtained at 50% HWSO loading; however at 60% regime of HWSO inclusion polymer dissociation takes place resulting to the decrease in melting point observed (Osemeahon and Barminas, 2007).

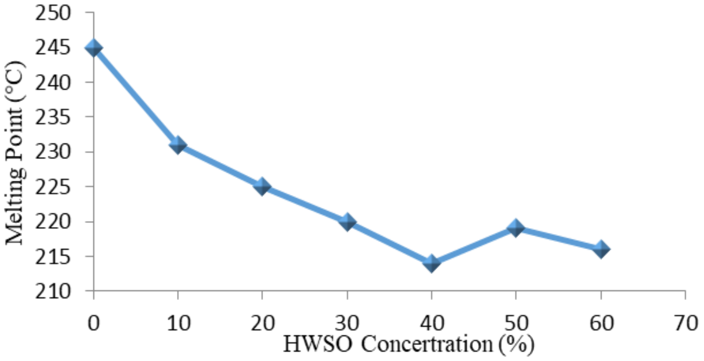


Figure 11: Effect of HWSO concentration on the melting point of DMU/ HWSO resin

SOLUBILITY OF DMU/HWSO RESIN.

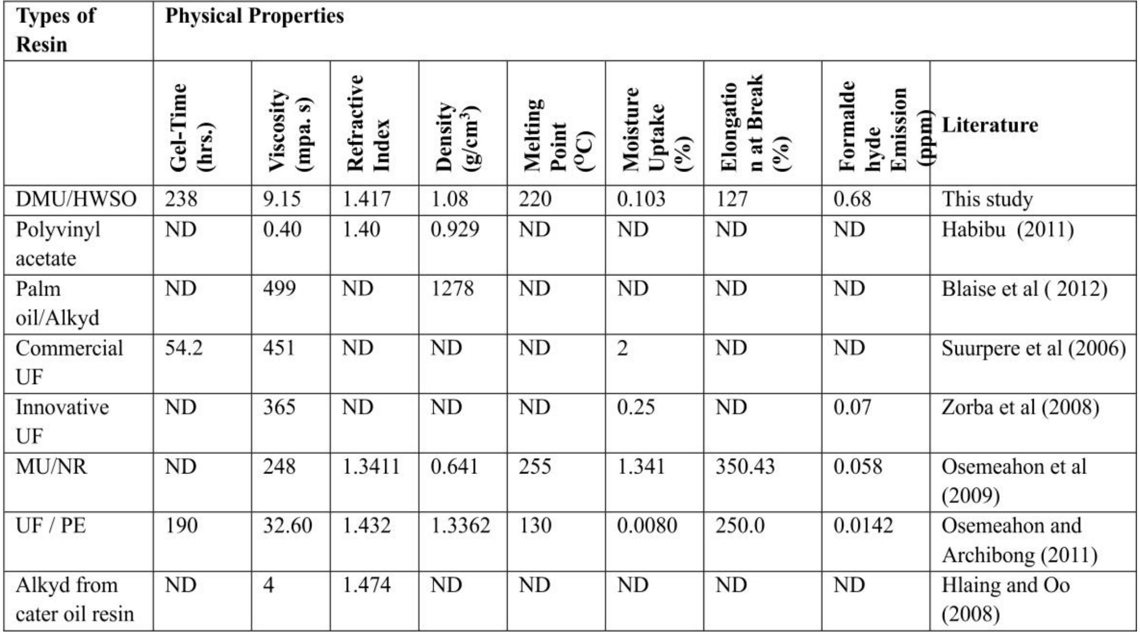
Water solubility is an important parameter in the consideration of any resin as a binder for emulsion paint formulation. The binders in oil paint are water insoluble, while for emulsion is water soluble.

Table 1 presents the effect of HWSO concentration on the solubility of DMU/HWSO copolymer composite. The solubility is observed to decrease with increase in HWSO concentration. From the beginning up to 30% inclusion of HWSO, DMU has a dominating effect and thus allows the copolymer to stay in aqueous solution because of its hydrophilic nature. But above 30% inclusion of HWSO, the copolymer is no longer soluble. This is due to the hydrophobic nature of HWSO. The insolubility could also be due to conversion of the polymer samples to gel immediately with increase in HWSO loading (Naghash *et al.*, 2007).

Table 1 Effect of HWSO concentration on the solubility of DMU/HWSO resin.

DMU/HWSO Concentration	Solubility in Water
0	Highly soluble
90/10	Soluble
80/20	Soluble
70/30	Soluble
60/40	Slightly soluble
50/50	Insoluble
40/60	Insoluble

Table 2: Comparison of some physical properties of DMU/HWSO film with films from other Paint binders



Types of Resin	Physical Properties								
	Gel-Time (hrs.)	Viscosity (mpa. s)	Refractive Index	Density (g/cm^3)	Melting Point (^{0}C)	Moisture Uptake (%)	Elongation at Break (%)	Formaldehyde Emission (ppm)	Literature
DMU/HWSO	238	9.15	1.417	1.08	220	0.103	127	0.68	This study
Polyvinyl acetate	ND	0.40	1.40	0.929	ND	ND	ND	ND	Habibu (2011)
Palm oil/Alkyd	ND	499	ND	1278	ND	ND	ND	ND	Blaise et al (2012)
Commercial UF	54.2	451	ND	ND	ND	2	ND	ND	Suurpere et al (2006)
Innovative UF	ND	365	ND	ND	ND	0.25	ND	0.07	Zorba et al (2008)
MU/NR	ND	248	1.3411	0.641	255	1.341	350.43	0.058	Osemeahon et al (2009)
UF / PE	190	32.60	1.432	1.3362	130	0.0080	250.0	0.0142	Osemeahon and Archibong (2011)
Alkyd from cater oil resin	ND	4	1.474	ND	ND	ND	ND	ND	Hlaing and Oo (2008)

KEY:
MU = Methylol Urea; UF = Urea Formaldehyde; PE = Polyethylene; NR= Natural Rubber;
ND = Not Detected

Table 3: Comparison of some physical properties of DMU and DMU/HWSO resins.

	DMU	DMU/HWSO	Acceptable Level in the coating industry (Osemeahon *et al.,* 2013).
Density (g/cm^3)	1.26	1.08	1.07 (min.)
Refractive index	1.407	1.417	1.4000 (min.)
Formaldehyde emission (ppm)	0.09	0.068	0.1 (max.)
Moisture uptake (%)	0.285	0.103	3.10 (max.)
Viscosity (mpa.s)	8.41	9.15	3.11- 38.00
Melting point (^{0}C)	245	220	200(max.)

Summary

In this work, DMU was synthesized and copolymerized with HWSO to form a copolymer binder for emulsion paint formulation. The resulting copolymer addressed the problem of urea formaldehyde resin which includes brittleness, low water resistance and formaldehyde emission. The copolymer binder is comparable with other binders used for paint with values within the acceptable level in the coating industry.

Conclusion

The copolymerization of urea formaldehyde and watermelon seed oil was successfully carried out. The formaldehyde emission level, moisture uptake and elongation at break in the experiment after blending were within the acceptable levels required in the coating industry in term of environmental safety, water resistance and flexibility respectively. Thus, this class of resin may introduce a novel paint binder in the coating industry.

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