Development of an Emulsion Paint Binder from the Copolymerization of Dimethylol Urea and Hydroxylated Mahogany Seed Oil

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Abstract: Copolymerization of dimethylol urea (DMU) and hydroxylated mahogany seed oil (HMSO) was carefully studied in this work, the FTIR spectroscopy of the pure DMU and DMU/HMSO showed that chemical interaction took place. Some of the physico-chemical parameters such as melting point, gel time, moisture uptake, turbidity, viscosity, density, solubility, formaldehyde emission, and refractive index were investigated. Results of the composites showed remarkable improvements in formaldehyde emission, flexibility and softness, optical properties and water resistance compared to the hardness and brittleness, poor water resistance and formaldehyde emission associated with dimethylol urea. Therefore this composite (DMU/HMSO) resin can serve as a potential binder for emulsion paint formulation.

Keywords: composites, dimethylol urea, hydroxylated mahogany seed oil, binder, and emulsion paint.

Introduction

Paint was traditionally used to describe pigmented materials as distinct from clear films which are more properly called lacquers or varnishes. Paint is a loose word covering a whole variety of materials; enamels, lacquers, varnishes, undercoats, surface primers, sealers, fillers, stoppers and many others. If the pigment is omitted, the material is usually called a varnish. The pigmented varnish—the paint—is sometimes called an enamel, lacquer, finish or top coat, meaning that it is the last coat to be applied and the one seen when the coated object is examined (Surajudeen and Zebulu, 2015).

There are basically two types of paint. Oil paint, which is solvent-based, and emulsion paint which is water based. Solvent-based paint has good performance and durable qualities such as good chemical, water, weather and heat resistance, adhesion, full gloss, flexibility, etc. But the utility of oil paint has been gravely challenged by the evolution of volatile organic compounds (VOCs) being the solvents used in their formulation. The evolutions of volatile organic compounds which have health and environmental hazards have been considered.
seriously. This has led to the restrictions imposed by authorities, driving the industries towards the production of paints with little or no volatile organic compounds (Lee, et al, 2011; Yousefi, et al, 2011). Water based paints on the other hand are gaining popularity since they are environmentally friendly.

Urea formaldehyde (UF) resin adhesive is a polymeric condensation product of the chemical reaction of formaldehyde and urea, and is considered as one of the most important wood adhesives (Gurses et al., 2014). But its acceptance as a universal material in many engineering areas such as in the coating industry is impeded by some of its inherent qualities such as brittleness, poor water resistance and formaldehyde emission. These disadvantages limit its uses (Osemahon, 2011). Mahogany seed oil is bitter in taste and considered as a moderate drying oil, which can be useful in different chemical industries (Rana et al., 2015).

According to Okieimen and Eromosele (1999), mahogany (Khaya senegalensis) seed oil contains 52.5–67% oil content. This is a reasonable yield and according to Jibrail and Kaet (2013) this yield is desirable for biodiesel production. The unsaturation of MSO can be increased by epoxidation and then hydroxylation to create more bonding sites for the oil. When this is achieved, blending of the hydroxylated mahogany seed oil and the dimethylol urea will equally be achieved. The flexible and hydrophobic mahogany seed oil will reduce the rigidity and moisture uptake associated with dimethylol urea.

Materials and Methods

Urea, formaldehyde, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide, sucrose, distilled water, hydrogen peroxide, acetic acid, formic acid, iso-propanol, methanol (all of analytical grades), and mahogany seed oil.

Extraction of mahogany seed oil

Mahogany seed oil was extracted according to method described by Bamaiyi et al., (2007). Dry seeds of mahogany were collected from the farm. The seeds were removed from the pods and roasted in a wide source pan and pounded into a paste using pestle and mortar. The paste was mixed with cold water and allowed to stand for 3hrs. The mixture was then sieved to obtain the filtrate which is a brown liquid extract. The filtrate was heated again in a wide source pan until evaporation was completed and the pure oil was collected at the bottom of the pan, and kept at room temperature for use.

Epoxidation of the mahogany seed oil

Epoxidation was carried out using the method described by Goud et al., (2007). 200cm$^3$ of the mahogany seed oil was introduced in a 500cm$^3$ three necked flask equipped with a reflux condenser and a thermocouple. The flask was placed on a hot plate with temperature control. Acetic acid and formic acid at a molar ratio of 0.5:1 to the oil and sulphuric acid catalyst 3% weight of hydrogen peroxide as an oxygen carrier was added into the mahogany seed oil. A hydrogen peroxide of molar ratio 1.5:1 to the mahogany oil was added drop wise into the mixture. This feeding strategy is required in order to avoid overheating the system since epoxidation is an exothermic reaction. The uniformity of the reaction was maintained by using a magnetic stirrer which runs at 1600rpm under isothermal condition at 50-60°C. The product was cooled and decanted in order to separate the organic-soluble compounds (epoxide mahogany seed oil) from water-soluble compounds. Warm water was used to wash the epoxidized oil (in small aliquots) in order to remove residual contaminants. This procedure was repeated in triplicates.
Hydroxylation of the epoxidized mahogany seed oil

Hydroxylation of the mahogany seed oil was carried out using procedure described by Petrovic et al., (2003). The reaction was performed in a 1000cm$^3$ three necked flask equipped with a reflux condenser and a thermocouple. The flask was placed on a hot plate with temperature control. 150cm$^3$ of the epoxidized mahogany seed oil was hydroxylated using alcohol (methanol and isopropanol) with a molar ratio of 4:1 to the oil and water at a molar ratio of 2:1 was mixed with the epoxidized oil and sulphuric acid catalyst in the reactor. The reaction was performed at a fixed temperature of 60°C for 5hrs. Uniformity was maintained by using a magnetic stirrer which runs at 1600rpm. The product (polyol) was cooled and decanted in order to separate the organic-soluble compounds from water-soluble compounds. Warm water was used to wash the polyol (in small aliquots) in order to remove residual contaminants. This procedure was repeated in triplicates.

Resin synthesis

The one step process (OSP) as reported by Osemeahon and Barminas (2007). One mole of urea (6.0g) was made to react with two moles of formaldehyde (16.22ml 37-41% (w/v), using 0.2g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 6 by using 0.5M H$_2$SO$_4$ 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 2hrs after which the resin was removed and kept at room temperature (30°C).

Copolymerization

This was carried out by blending different concentrations (10-60%) of oil in DMU. The mixture was stirred with glass rod and left for 24hrs at room temperature (30°C). For film preparations, resins from DMU and DMU/HMSO were poured into different petri dishes for casting using the solution casting method (Osemeahon and Archibong 2011). The resins were also allowed to cure and set for three days at 30°C. the physical properties of the film were investigated.

Determination of formaldehyde emission

Formaldehyde emission was carried out using the standard 2hr desiccator test as described by Osemeahon and Archibong (2011). The mold used was 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 was analyzed by a refractometric technique using Abbe refractometer. Triplicate determinations were made for the samples and the average value taken.

Determination of moisture uptake

The moisture uptake of the resin films were determined gravimetrically, according method described by Osemeahon and Archibong, 2011. Known weights of the samples were 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 for each sample and the average value recorded.

Determination of water solubility

The solubility of DMU and DMU/HMSO blends were determined by mixing 1ml of the resin with 5ml of distilled water at room temperature (27-30°C).
Determination of density, turbidity, melting point and refractive index

The densities of the resins were 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 for each sample and average value calculated. The turbidity of the samples were determined by using Supertek digital turbidity meter (Model 033G). The melting points of the film samples were determined by using Galenkamp melting point apparatus (Model MFB600-010F). The refractive indexes of the samples were determined with Abbe refractometer. The above properties were determined according to standard methods (AOAC, 2000).

Determination of viscosity and gel time

Viscosity and gel time were carried out according to method described by Osemeahon and Archibong (2011). A 100ml Phywe made of graduated glass macro-syringe was utilized for the measurement. The apparatus was standardized with 60% (W/V) sucrose solution whose viscosity is 5.9mpa.s 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 profile was obtained.

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 was brought to rupture at a clamp rate of 20mm/min and a full load of 20kg. Three runs were carried out for each sample and the average elongation evaluated and expressed as the percentage increase in length.

Result and Discussion

Reaction between dimethylol urea and pure mahogany seed oil.

FTIR spectral analysis

Figure 1a and Figure 1b show the FTIR spectras of pure DMU, MSO, EMSO, HMSO, and a blend of DMU/HMSO. The overlay of the DMU, MO and EMO show the presence of a hydroxyl group on all the three spectras. The C-H bending of alkane was also observed in DMU, MO and EMO. O=C=O peak was only observed in EMO. The C=O of DMU, MO and EMO was also observed due to the carbonyl of an unsaturated ether in mahogany oil. C=C was observed in MO and EMO. This is due to the unsaturation in the backbone of MO (Coates, 2000). Upon epoxidation, the degree of unsaturation increases. For hydroxylated
mahogany oil (HMO), an O-H was introduced at 3500-3300cm\(^{-1}\) with a bending reflected at 1366cm\(^{-1}\), and a C-H bending vibration of a methyl group at 2869cm\(^{-1}\). The blend of DMU/MO Shows O-H stretching at 2933cm\(^{-1}\) of an intramolecularly bonded alcohol. Others are C-O of a carbonyl at 1261cm\(^{-1}\). This shows that blending MO with DMU affects the positions of source peaks by the induction of the hydroxyl group of the DMU. Other functional groups are C–H, C–C and C=O of an aldehyde (Coates, 2000).

Infrared spectroscopy helps us read infrared absorption and transmission, and create a molecular “fingerprint” of a material. Just like people, no two unique molecular structures produce exactly the same infrared fingerprint. FTIR is more powerful, because it allows us to collect and process large quantities of spectrometric data using a mathematical formula called the Fourier transform. It has many advantages over other spectrometry tests (Eric, 2015).

![Figure 1a. A–FTIR Spectra of DMU, B–FTIR Spectra of MSO, C–FTIR Spectra of EMSO](image-url)
Effect of HMSO concentration on the viscosity of DMU/HMSO copolymer composite
In the coating industry, an understanding of the viscosity of the binder is important because it controls factors such as flow rates, levelling and sagging, thermal and mechanical properties, dry rate of paint film and adhesion of the coating to the substrate (Osemeahon and Barminas, 2007).

Figure 2 shows the effect of viscosity on DMU/HMSO copolymer composite. At the beginning, it is observed that there is a gradual increase in the viscosity with no inclusion of HMSO. A sharp increase is observed at 50cm$^3$ inclusion of HMSO, after which the viscosity decreases. This could be attributed to the segmental factor of the resin. From the beginning up to 50cm$^3$ HMSO, the DMU or hard segment formed a continuous phase, and the soft segments were dispersed in the matrix of the hard segments. This is as a result of strong interchain association forming large aggregates with large hydrodynamic volumes. Therefore the high viscosity was observed. Between 50 and 60cm$^3$ inclusion of HMSO, a sharp decrease in viscosity is observed. This is because the soft segment formed the continuous
phase, and the hard segments were dispersed in the matrix of the soft segments which produced a large decrease in viscosity.

**Figure 2. Effect of HMSO concentration on the viscosity of DMU/HMSO copolymer composite**

**Effect of HMSO concentration on the density of DMU/HMSO copolymer composite**

The density of a binder influences such properties as the dispersion and stability of pigment and can be used to determine the critical pigment volume concentration, spreading capacity and consistency of the paint (Akinterinwa et al., 2015).

Figure 3 shows the effect of HMSO concentration on the density of DMU/HMSO copolymer composite. The gradual decrease in density can be attributed to a rise in the molecular weight of the blend due to non-homogeneity with DMU, hence the possibility of physical interaction leading to no rise in the molecular weight of the blend (Osemeahon and Archibong, 2011). Density depends on free volume and packing efficiency of molecular chains. Therefore decrease in density with increase in concentration of HMSO indicates inefficient molecular chain packing. In addition, the physical properties of polymer depend on its chain length and the hard and soft segments. Increase in soft segments in the blend will lead to a decrease in the density of the copolymer composite (Osemeahon and Dimas, 2014).

**Figure 3. Effect of HMSO concentration on the density of DMU/HMSO copolymer composite**
Effect of HMSO concentration on the gel-time of DMU/HMSO copolymer composite

Gelation which is the time required for a polymeric material to reach infinite viscosity has also been marked to be the point at which a polymer substance can attain an infinitely large molecular weight (Achi, 2003). Gel-time can be used to determine the dry time of a binder, hence an optimum operational condition for the paint formulated (Akinterinwa et al., 2016). The effect of HMSO concentration on the gel-time of DMU/HMSO copolymer composite is shown in Figure 4. It is observed that the gel-time of the copolymer increases with increase in the concentration of HMSO. This is due to the decrease in reactivity which is a function of the increase in the size of the alkyl group attached to the carbonyl carbon resulting from the copolymerization of DMU with HMSO (Osemeahon, 2011). The two regimes in the graph can be explained in terms of the interaction between oligomers of the resin as viscosity increases and gel-point approaches.

Figure 4. Effect of HMSO concentration on the gel-time of DMU/HMSO copolymer composite

Effect of HMSO concentration on the turbidity of DMU/HMSO copolymer composite

Figure 5 shows the effect of HMSO concentration on the turbidity of DMU/HMSO copolymer composite. It is observed that turbidity increases with increase in the concentration of HMSO. At the beginning, the turbidity is low. But with increase in the concentration of HMSO in the blend, an increase in turbidity is observed. The rise in turbidity may be attributed to the progressive changes in crystalline orientation and morphologies responsible for light scattering. Light scattering and hence turbidity is relatively used to determine average molecular weight of polymeric materials (Moreno et al., 2000).

Figure 5. Effect of HMSO concentration on the turbidity of DMU/HMSO copolymer composite
Effect of HMSO concentration on the refractive index of DMU/HMSO copolymer composite

Gloss which is known to be a very good property of paint has been reported to be a function of the refractive index (Nadal et al., 2006). The binder plays an important role in exhibiting the gloss property of paint.

Figure 6 presents the effect of HMSO concentration on the refractive index of DMU/HMSO copolymer composite. The gradual rise in the refractive index with increase in HMSO inclusion may be due to the increasing changes in the molecular structure of the blend, and the differences in the level of specific interaction between the two polymers thereby creating light scattering (Qi et al., 2002; Liem et al., 2002). It may also be attributed to a possible rise in crosslinking density as the concentration of the HMSO increases (Osemeahun and Archibong, 2011).

Effect of HMSO concentration on the formaldehyde emission of DMU/HMSO copolymer composite

Formaldehyde emission in the curing process is one of the major disadvantages of urea formaldehyde resin which has led to restrictions on its use by regulatory organizations (Witold et al., 2008).

Figure 7 shows the effect of HMSO concentration on the formaldehyde emission of DMU/HMSO copolymer composite. It is observed that formaldehyde emission decreases with increase in the concentration of HMSO.

This behaviour can be attributed to the reduction in the concentration of urea formaldehyde in the composite as HMSO is added. The decrease in formaldehyde emission may also be due to possible interaction between DMU and HMSO resins, which may hinder the condensation reactions in the urea formaldehyde resin, hence hindering the release of formaldehyde from the reaction (Akinterinwa et al., 2015).
Figure 7. Effect of HMSO concentration on the formaldehyde emission of DMU/HMSO copolymer composite

Effect of HMSO concentration on the melting point of DMU/HMSO copolymer composite

Rigidity and flexibility which can be determined from the thermal property of paint’s binder, is a critical factor in their processing and application (Akinterinwa et al., 2016).

Figure 8 shows the effect of HMSO concentration on the melting point of DMU/HMSO copolymer composite. A decrease in the melting point of the copolymer is observed at the beginning with inclusion of up to 20cm³ of HMSO, after which a steady regime is observed up to 30cm³ inclusion, with a sharp decrease observed at 40cm³ addition. The melting point is observed to have risen again at 50 to 60cm³ inclusion of HMSO. Decreasing melting point signals decreasing hardness and increasing flexibility of the blend compared to the pure DMU. This behaviour may be attributed to HMSO serving as a flexible spacer, crosslink modifier and/or urea formaldehyde resin condensation inhibitor (Akinterinwa et al., 2015). The sharp decrease observed at 40cm³ inclusion of HMSO is due to polymer dissociation which takes place, while the sudden increase observed at 50 to 60cm³ inclusions is due to polymer association (Osemeahon and Dimas, 2014).

Figure 8. Effect of HMSO concentration on the melting point of DMU/HMSO copolymer composite
Effect of HMSO concentration on the moisture uptake of DMU/HMSO copolymer composite

Moisture uptake in polymeric materials is very important on both physical and structural levels. In synthetic resins used as binders, it is responsible for blistering, alligatoring, brooming etc, of paint film, affecting its mechanical properties in a way that might lead to the paint’s failure (Akinterinwa et al., 2016).

Figure 9 shows the effect of HMSO concentration on the moisture uptake of DMU/HMSO copolymer composite. A decrease in moisture uptake of the copolymer is observed with increase in HMSO concentration. DMU is hydrophilic while HMSO is hydrophobic. This decrease in moisture uptake can be attributed to the decrease in concentration of DMU with increase in HMSO in the blend (Akinterinwa et al., 2015). A possible interaction between DMU and HMSO can also reduce the OH groups in the copolymer resin, thereby reducing its affinity for water molecules (Cakir et al., 2012; Akinterinwa et al., 2015).

Effect of HMSO concentration on the elongation at break of DMU/HMSO copolymer composite

Elongation at break is a significant factor recounting the rupture performance of composites. It is the ratio between increased length and initial length after breakage of a tested material (Wu et al., 2000).

The effect of HMSO concentration on the elongation at break of DMU/HMSO copolymer composite is shown in Figure 10. The increase in the elongation at break may be attributed to the increase in flexibility of the copolymer composite as the concentration of HMSO is increased, since the stiffness associated with DMU is gradually reduced with increase in HMSO which makes the copolymer softer.
Figure 10. Effect of HMSO concentration on the elongation at break of DMU/HMSO copolymer composite

Effect of HMSO concentration on the solubility of DMU/HMSO copolymer composite
In the development of amino resins for emulsion paint formulation, resin solubility or dispersability in water is an important factor in the resin’s acceptability (Barminas and Osemeahon, 2006). Table 1 presents the effect of HMSO concentration on the solubility of DMU/HMSO copolymer composite. It is observed that the blends are soluble in water up to 40cm$^3$ inclusion of HMSO, after which the blends form dispersions in water. The increasing hydrophobic behaviour is expected as the concentration of the hydrophobic HMSO resin increases in the blends (Akinterinwa et al., 2016).

Table 1. Effect of HMSO concentration on the solubility of DMU/HMSO copolymer composite

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<thead>
<tr>
<th>DMU/HMSO concentration</th>
<th>Solubility in water</th>
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<tbody>
<tr>
<td>0</td>
<td>Highly soluble</td>
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<tr>
<td>90/10</td>
<td>Soluble</td>
</tr>
<tr>
<td>80/20</td>
<td>Soluble</td>
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<tr>
<td>70/30</td>
<td>Soluble</td>
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<tr>
<td>60/40</td>
<td>Slightly soluble</td>
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<tr>
<td>50/50</td>
<td>Insoluble</td>
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<tr>
<td>40/60</td>
<td>Insoluble</td>
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Conclusion
The copolymerization of dimethylol urea (DMU) and hydroxylated mahogany seed oil (HMSO) has further reduced the moisture uptake, hardness/brittleness, and formaldehyde emission that are common attributes associated with dimethylol urea binders.

This is due to the hydrophobicity of mahogany seed oil, flexibility of mahogany seed oil, and molar reduction of dimethylol urea by subsequent inclusion of mahogany seed oil. Therefore, DMU/HMSO resins can be recommended for use as binder for emulsion paint formulation.

References


