



CHARACTERIZATION OF COMPOSITES FROM DIMETHYLOL UREA AND HYDROXYLATED BLACK SEED OIL FOR POSSIBLE APPLICATION AS AN EMULSION PAINT BINDER



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Abstract: The blending of dimethylol urea (DMU) and hydroxylated black seed oil (HBSO) was studied in this work. The FTIR spectroscopy of the pure DMU and DMU/HBSO showed that chemical interaction took place. Some of the physicochemical 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 copolymer composite (DMU/HBSO) resin can serve as a potential binder for emulsion paint formulation.

Keywords: Blending, dimethylol urea, hydroxylated black seed oil, emulsion paint

Introduction

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). Paint can also be defined as a solution or suspension (emulsion) of pigment, binder, and mineral solvent (or water) that on drying forms an adhering film on the surface. It is applied for protection and/or decoration. Painting has been known to be one of the most important aspects of building construction. It covers the block work and concrete rendering (plaster) with attractive and beautiful colours, giving the building a high aesthetic value and makes it decorative clean and habitable. It is indispensable in building construction all over the world (Opara, 2014).

Basically, there are two major types of paint. Oil paint or solvent-based paint, which is oil based, and emulsion paint which is water based (Surajudeen and Zebulu, 2015). 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 include; Binder, pigment, solvent and other additives for specific purposes (Igwebike, 2012). Solvent-based paint is of good performance and durable qualities (Lee *et al.*, 2011; Yousefi *et al.*, 2011), compared to water-based paint or emulsion paint. Despite this numerous advantages over the emulsion paint, solvent-based paint emits VOCs from its surfaces during the drying processes thereby polluting the environment, causing health hazards to man and giving rise to ozone depletion and the consequential climatic change.

Urea formaldehyde (UF) resin adhesive is a polymeric condensation product of 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 has been limited by some of its inherent qualities such as brittleness, poor water resistance and formaldehyde emission (Osemeahon, 2011).

Black seed oil (Nigella Sativa oil) is particularly rich in unsaturated and essential fatty acids. It contains conjugated linoleic (18:2) acid, thymoquinone, nigellone (dithymoquinone), melanthin, nigilline, and trans-anethole (Bharat, 2015).

Unsaturation of BSO could be increased by epoxidation and then hydroxylation to create more bonding sites for the oil, as well as reduce the brittleness associated with dimethylol urea. This experiment sets out to copolymerize DMU and HBSO with an expected outcome of minimizing the shortcomings of DMU and hence possible application as water repellent binder for emulsion paint binder.

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 black seed oil.

Extraction of black seed oil

Black seed oil was extracted using the method described by Nameer *et al.* (2016). The *N. sativa* L. seeds were pressed at room temperature (25°C) by mechanical pressing without any heating treatment. Crushed seeds were stored for one night at room temperature to separate oil phase from fibers, and the oil was filtered using filter paper, and stored ready for use.

Epoxidation of black seed oil

Epoxidation was carried out using the method described by Goud *et al.* (2007). 200 cm³ of the black seed oil was introduced in a 500 cm³ 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 black seed oil. A hydrogen peroxide of molar ratio 1.5:1 to the black 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 1600 rpm under isothermal condition at 50 – 60°C. The product was cooled and decanted in order to separate the organic-soluble compounds (epoxide black 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 black seed oil

Hydroxylation of the black seed oil was carried out using procedure described by Petrovic *et al.* (2003). The reaction was performed in a 1000cm³ three necked flask equipped with a reflux condenser and a thermocouple. The flask was placed on a hot plate with temperature control. 150 cm³ of the epoxidized black 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 5 h. 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) was adopted. One mole of urea (6.0 g) was made to react with two moles of formaldehyde (16.22 ml) 37 – 41% (w/v), using 0.2 g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 6 by using 0.5M H₂SO₄ 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 h 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 24 h at room temperature (30°C). For film preparations, resins from DMU and DMU/HBSO 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 2 h desiccator test as described by Osemeahon and Archibong (2011). The mold used was made from aluminium foil with a dimension of 69.9 x 126.5 mm and thickness of 12.0 mm. The emitted formaldehyde was absorbed in 25.0 ml 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/HBSO blends were determined by mixing 1ml of the resin with 5 ml 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 100 ml

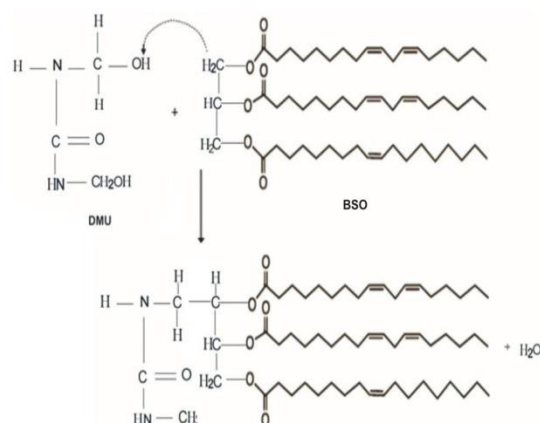
Phywe made of graduated glass macro-syringe was utilized for the measurement. The apparatus was standardized with 60% (W/V) sucrose solution whose viscosity is 5.9 mpa.s at 30°C. The viscosity of the resins was evaluated in relation to that of the standard sucrose solution at 30°C. Three different readings 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 50 mm long, 10 mm wide and 0.15 mm thick was brought to rupture at a clamp rate of 20 mm/min and a full load of 20 kg. 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 black seed oil.



FTIR spectral analysis

Figure 1a and 1b show the FTIR spectra of pure DMU, BSO, EBSO, HBSO, and a blend of DMU/HBSO. The DMU spectra shows predominately the amine (NH₂), and the carbonyl (C = O) of an aldehyde. Others are C – H of an alkane that is attached to a hydroxyl group between 3400 and 1642 cm⁻¹. The C = O of the carbonyl and C – H of a fatty acid (Chemmanur and Rohman, 2013). The BSO shows a signal predominately the C = O of a carbonyl and an ether. The C – O stretching of aromatic ether was observed between 1260 – 1028 cm⁻¹ in the BSO (Chemmanur and Rohman, 2013). At 1649 and 798 cm⁻¹ shows the presence of C = C which shows that a diene is present. The epoxidation of the BSO (EBSO) shows that the C – O – C group of the BSO is unaffected, though the C – O stretching becomes unsaturated and is shown at 1730 cm⁻¹. The O = C = O is also observed to be a prominent signal at 2869. This can be due to the oxygen of the carbonyl group which is oxidized. The hydroxylation of the BSO introduces a hydroxyl group on the BSO. This is due to the peak at 3449 cm⁻¹. The C = O stretching in the BSO remains unreactive with the rocking vibrational bending of C – H of a methyl alkane present. At 1098 cm⁻¹ CO – O – CO stretching of an anhydride shows the basic backbone of the BSO (Mahmood *et al.*, 2009).

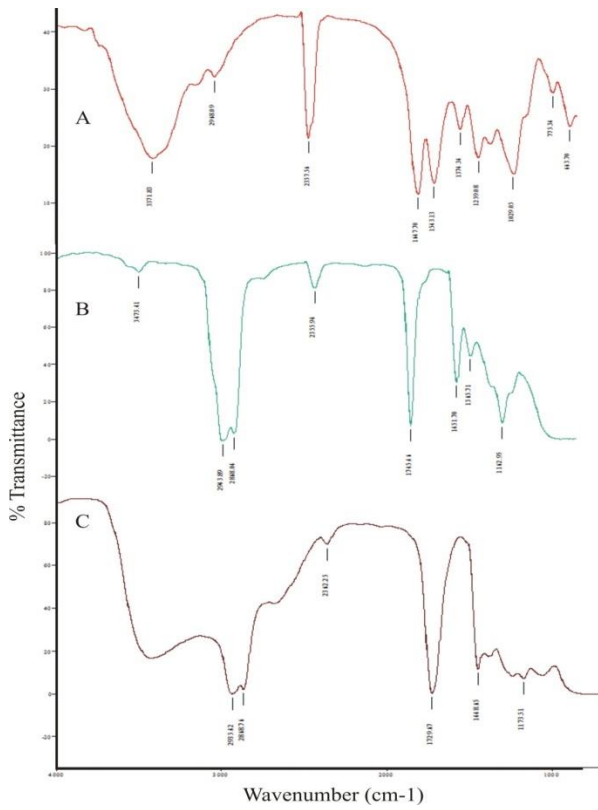


Fig. 1a: A – FTIR Spectra of DMU, B – FTIR Spectra of HBSO, C – FTIR Spectra of DMU/HBSO

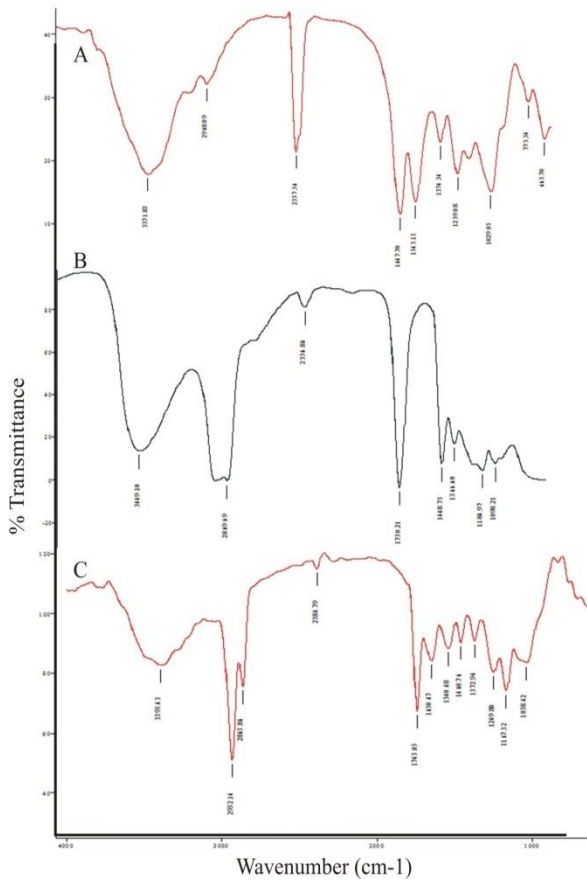


Fig. 1b: A - FTIR Spectra of DMU, B – FTIR Spectra of HBSO, C – FTIR Spectra of DMU/HBSO

Effect of HBSO concentration on viscosity of DMU/HBSO copolymer composite

In the coating industry, an understanding of the viscosity of the paint binder is very important. This is because it controls factors such as flow rates, levelling and sagging, thermal and mechanical properties, dry rate of paintfilm and adhesion of the coating to the substrate (Osemeahon and Barminas, 2007). The polymerization reaction in urea formaldehyde is ended when the viscosity is optimal (Kim, 2001). Therefore, in the coating industry, a knowledge of the viscosity of the binder is of considerable importance both from the manufacturing processes, pot stability and rate of cure of the paint film (Achi, 2003). Fig. 2 shows the effect of HBSO concentration on the viscosity of DMU/HBSO copolymer composite. An increase in the viscosity is observed with increase in concentration of HBSO at the beginning, with a sharp increase reached at 50 cm³ inclusion of HBSO. This is then followed by a decrease with 60 cm³ inclusion. The increase in viscosity can be explained in terms of differentials in the molecular weight and crosslinked density among the different amino resins (Markovic *et al.*, 2001). As the alkyl chains increases, the molecular weight also increases. At a critical point, the crosslink density reached its optimal giving rise to dissociation of polymer crosslink which in turn gave rise to a more linear polymer, hence the decrease observed at 60cm³ inclusion of HBSO (Osemeahon *et al.*, 2007).

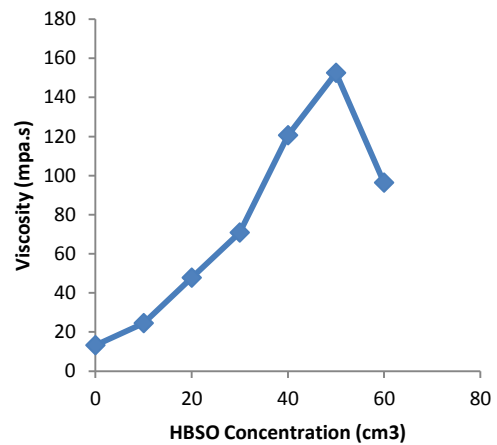


Fig. 2: Effect of HBSO concentration on the viscosity of DMU/HBSO copolymer composite

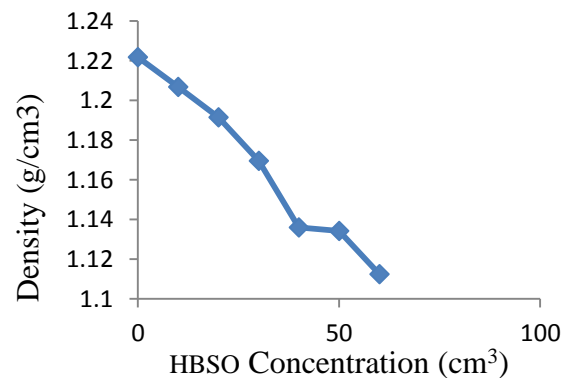


Fig. 3: Effect of HBSO concentration on the density of DMU/HBSO copolymer composite

Effect of HBSO concentration on the density of DMU/HBSO copolymer composite

Density depends on the free volume and packing efficiency of molecular chains. In the coating industry, the density of the paint binder influences factors such as pigment dispersion, flow, leveling and sagging, and brushability (Osemeahon and Barminas, 2006). Fig. 3 shows the effect of HBSO concentration on the density of DMU/HBSO copolymer composite. The density of the copolymer is observed to decrease with increase in concentration of HBSO. This behavior may be attributable to the packing nature of the resin molecules (Chain and Yi, 2001). The decrease in density with increase in molecular weight also indicates inefficient molecular packing (Osemeahon and Barminas, 2007b).

Effect of HBSO concentration on the gel-time of DMU/HBSO copolymer composite

Gel-time can be used to determine the dry time of a binder. The time it takes for a paint to dry after application to a surface is an important factor to the paint formulator (Osemeahon and Barminas, 2006a). This is because if the paint dries too fast, it will be prone to brittleness. And if it dries too slowly, the paint film may be subjected to pick up dirt (Trumbo *et al.*, 2001).

Figure 4 shows the effect of HBSO concentration on the gel-time of DMU/HBSO copolymer composite. It is observed that the gel-time of the copolymer increases with increase in concentration of HBSO inclusion, with a sharp increase observed between 40 to 60 cm³. This result is due to decrease in reactivity which is a function of the increase in the size of the alkyl group attached to the carbonyl carbon resulting from copolymerization of DMU with HBSO. The greater the size of the alkyl group attached to the carbonyl carbon, the less the reactivity of the carbonyl group. This is because the large groups around carbonyl group may hinder the attacking reagent due to steric hindrance (Teware, 2000).

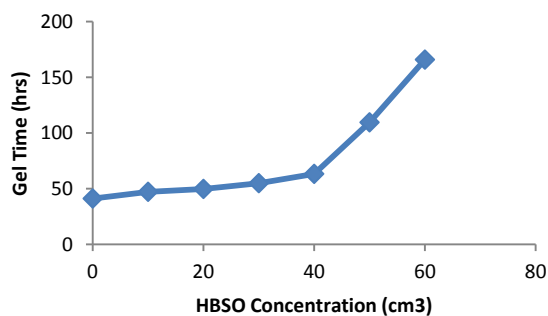


Fig. 4: Effect of HBSO concentration on the gel-time of DMU/HBSO copolymer composite

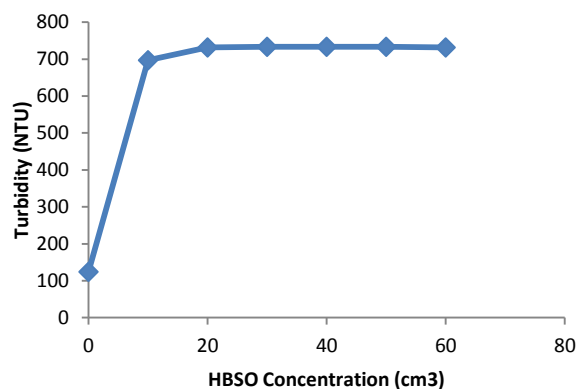


Fig. 5: Effect of HBSO concentration on the turbidity of DMU/HBSO copolymer composite

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

Turbidity in addition to the pigment is a factor that enhances the opacity of paint films (Akinterinwa *et al.*, 2016). Turbidity is the cloudiness or haziness of a fluid caused by large numbers of individual particles that are generally invisible to the naked eye. The optical properties of the binder such as turbidity are very important in the coating industry. This is because it is related to the gloss properties of the paint (Trezza and Krochta, 2001).

Figure 5 shows the effect of HBSO concentration on the turbidity of DMU/HBSO copolymer composite. Turbidity is relatively low before the introduction of HBSO. This is because pure DMU is clear and transparent. However, with increase in the concentration of HBSO, the copolymer became colloidal and light scattering increased, leading to an increase in turbidity (Osemeahon and Dimas, 2014). The increase in turbidity can also be associated with the gradual increase in the molecular weight of the blend with the increasing incorporation of HBSO.

Effect of HBSO concentration on the refractive index of DMU/HBSO copolymer composite

Paints are known to have varying degrees of opacity or transparency depending on the quantity of light transmitted through or reflected from the surface of the paint. The gloss of paint is a function of refractive index of the surface and particle size (Osemeahon, 2011).

The effect of HBSO concentration on the refractive index of DMU/HBSO copolymer composite is shown in Fig. 6. An increase in the refractive index of the copolymer is observed with increase in concentration of HBSO. This behavior can be explained in terms of the differences in molecular weight and molecular features of the copolymer (Trezza and Krochta, 2001). Increase in the concentration of HBSO in the copolymer, increases the molecular weight of DMU/HBSO, hence the difference in the interaction with light. This implies that high gloss emulsion paint can be produced from DMU/HBSO copolymer binder.

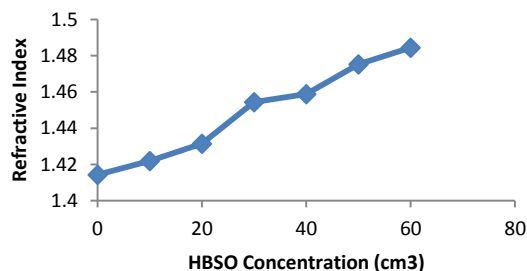


Fig. 6: Effect of HBSO concentration on the refractive index of DMU/HBSO copolymer composite

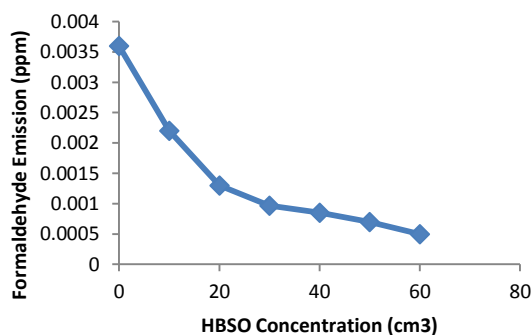


Fig. 7: Effect of HBSO concentration on the formaldehyde emission of DMU/HBSO copolymer composite

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

The emission of formaldehyde in the curing process of urea formaldehyde is said to be one of the major setbacks of urea formaldehyde resin (Kim, 2001). Therefore, in the development of paint binder from urea formaldehyde resin, efforts must be made to reduce formaldehyde to an acceptable level (Osemeahon, 2011).

Figure 7 shows the effect of HBSO concentration on the formaldehyde emission of DMU/HBSO copolymer composite. It is observed that formaldehyde emission decreases with increase in the concentration of HBSO. This behaviour can be attributed to the gradual reduction in the concentration of DMU, with increase in HBSO concentration (Osemeahon, 2011). The formaldehyde emission level is drastically reduced by limiting the problem at source (pizzi *et al.*, 2001).

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

The melting point of a polymer has a direct bearing on its thermal property, molecular weight, degree of crosslinking and the level of rigidity of the polymer. The hardness and brittleness of urea formaldehyde resins is one of its disadvantages. This makes it difficult to be used as a paint binder (Osemeahon, 2011).

Figure 8 shows the effect of HBSO concentration on the melting point of DMU/HBSO copolymer composite. A gradual decrease in melting point of the copolymer is observed with increase in the concentration of HBSO. The decrease in melting point can be explained in terms of increase in molecular mobility due to the increase in flexibility as a result of increase in concentration of HBSO in the blend, differences in molecular feature, crystallinity and crystalline orientation (Sekaran *et al.*, 2001; Chain and Yi., 2001; Min *et al.*, 2002). The softness of the amino resins increase with increase in alkyl length of aldehydic group. Thus the softness of the copolymer increases with increase in alkyl length of the aldehydic group. The result in this experiment mirror the decrease in density with increase in aldehydic group (Osemeahon *et al.*, 2007).

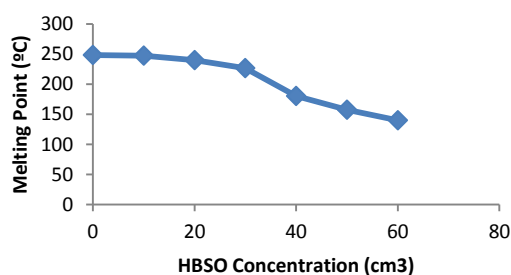


Fig. 8: Effect of HBSO concentration on the melting point of DMU/HBSO copolymer composite

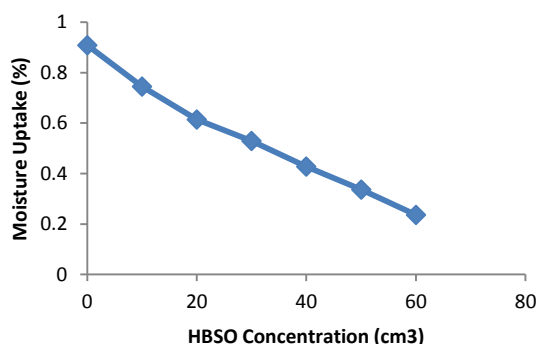


Fig. 9: Effect of HBSO concentration on the moisture uptake of DMU/HBSO copolymer composite

Effect of HBSO concentration on the moisture uptake of DMU/HBSO copolymer composite

Water uptake affects vital properties of the polymer material such as physical, mechanical, thermal and structural properties (Hu *et al.*, 2001; Nogueira *et al.*, 2001). Many resins and other polymer matrices absorb moisture by instantaneous surface absorption and diffusion (Barminas and Osemeahon, 2006). Urea formaldehyde resins exhibit poor water resistance (Osemeahon *et al.*, 2008). The moisture uptake of a binder is of very crucial importance in the coating industry because it is responsible for blistering and broominess of paint film (Osemeahon, 2011).

The effect of HBSO concentration on the moisture uptake of DMU/HBSO copolymer composite is shown in Fig. 9. the moisture uptake of the copolymer is observed to decrease with increase in the concentration of HBSO. The decrease in moisture uptake may be due to the differences in chain topology which is related to the molecular size holes in the polymer structure, which also depends on morphology and crosslinked density (Nogueira *et al.*, 2001; Hu *et al.*, 2001). This is also due to the hydrophobic nature of HBSO.

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

Elongation at break is also known as fracture strain or tensile elongation at break. It measures how much bending and shaping a material can withstand without breaking. It is reciprocal to the stiffness of a material (Yetgin *et al.*, 2013).

Figure 10 shows the effect of HBSO concentration on the elongation at break of DMU/HBSO copolymer composite. The increase observed with increase in the concentration of HBSO in the blend may be attributed to some of the factors that affect elongation at break which include increase in soft segments, velocity of testing, orientation level, temperature.

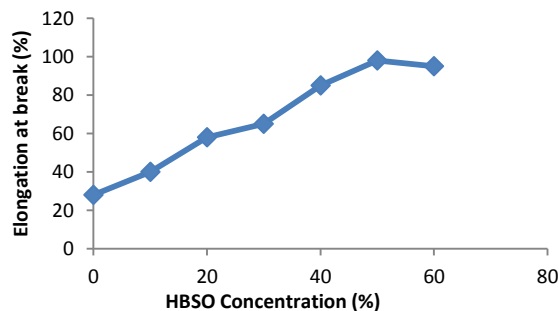


Fig. 10: Effect of HBSO concentration on the elongation at break of DMU/HBSO copolymer composite

Table 1: Effect of HBSO concentration on the solubility of DMU/HBSO copolymer composite

DMU/HBSO 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

Effect HBSO concentration on the solubility of DMU/HBSO copolymer composite

Table 1 presents the effect of HBSO concentration on the solubility of DMU/HBSO copolymer composite. The solubility is observed to decrease with increase in HBSO concentration. From the beginning up to 30 cm³ inclusion of HBSO, DMU has a dominating effect and thus allows the copolymer to stay in aqueous solution because of the hydrophilic nature. But above 30cm³ inclusion of HBSO, the copolymer is no longer soluble. This is due to the hydrophobic nature of HBSO. The insolubility could also be due to conversion of the polymer samples to gel immediately with increase in HBSO loading (Naghash *et al.*, 2007).

In the consideration of any resin as a binder for emulsion paint formulation, water solubility is of paramount importance. This is because the binders in oil paint are insoluble, while those for emulsion paints are soluble.

Conclusion

The copolymerization of dimethylol urea (DMU) and hydroxylated black seed oil (HBSO) has further reduced the moisture uptake, hardness/brittleness, and formaldehyde emission that are common attributes associated with dimethylol urea binders. This is because of the hydrophobicity, flexibility of black seed oil, and molar reduction of dimethylol urea by subsequent inclusion of black seed oil. Therefore DMU/HBSO resins can be recommended for use as binder for emulsion paint formulation.

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