



OPTIMIZATION OF PROCESSING VISCOSITY OF REACTIVE BLENDING OF DIMETHYL UREA AND EPOXIDIZED COTTON SEED OIL FOR EMULSION PAINT PRODUCTION



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Abstract: The effect of dimethyl urea (DMU) viscosity on a composite obtained from the reactive modification of DMU and epoxidized cotton seed oil ECSO was successfully investigated in this work. Some physico-chemical parameters of the Dimethyl urea obtained at different DMU viscosities (13.75 – 27.80 mpa.s) were evaluated. The Density, formaldehyde emission, melting point, refractive index were seen to increase with increasing DMU viscosity. DMU viscosity below 22.08 mpa.s was seen to produce DMU/ECSO blend soluble in water and beyond this value the composite became insoluble. The processing of DMU/ECSO composite by formulators for the development of an emulsion paint could therefore be suggested below the value.

Keywords: Dimethyl urea, viscosity, epoxidized cotton seed oil, reactive blend

Introduction

In view of the emphasis on pollution prevention by regulatory agencies and the chemical industry (majorly, in the area of emission of volatile organic compound VOC) (Nawaz *et al.*, 2010), and with the skyrocketing costs of waste disposal, waste treatment, and regulatory compliance, the practice of evaluating a particular synthetic method based on maximum yield alone is no longer fashionable. The amalgamation of two organic functionalities into a single polymer offers a unique combination of distinctive properties of both constituents viz reduction in the emission of volatile organic compound, good processability, improved toughness, flexibility, chemical resistance and some other properties like weatherability, UV resistance and thermo oxidative stability (Dinda *et al.*, 2008). Vegetable oil represents one of the cheapest biological feedstock available in large quantities. Its use as a blending tool offers numerous advantages such as low toxicity, availability, renewability and inherent biodegradability (Velu *et al.*, 2011). The double bonds in the vegetable oil are used as reactive sites in the coating industry and they can also be functionalized by epoxidation.

Dimethylol urea (DMU) has –OH as its functional group while epoxidized cottonseed oil (ECSO) has oxirane or epoxy functional groups along its chains (Kim, 2011). Because of the presence of these functional groups in both polymers and other physico-chemical properties, physical and chemical interactions will be feasible when they are mixed. When blending is achieved, the resulting composite (ECSO/DMU) will exhibit both properties of pure dimethylol urea and epoxidized cottonseed oil (Devi & Maidivanne, 2012). Rigidity and brittleness of Urea Formaldehyde (DMU) will be eliminated due to the high flexibility of epoxidized cottonseed oil, moisture uptake of DMU will be greatly reduced because of the high water resistance properties of ECSO oil (Akinterinwa *et al.*, 2015). Drastic reduction of formaldehyde emission will be achieved due to the inclusion of ECSO and subsequent reduction of DMU in the composites. Thereby, solving those problems that have impeded urea formaldehyde usage. This study sets out to determine the viscosity at which the copolymer composite DMU/ECSO will be most suitable for the formulation of an emulsion paint

Materials and Method

The materials used were Urea, formaldehyde, sodium dihydrogen phosphate, water, sulphuric acid, sodium hydroxide pellets, cottonseed oil, hydrogen peroxide (6 wt%), formic acid, 0.1MNa₂S₂O₃, 0.1MNaOH solution, lithium aluminate, dam's reagent, starch indicator and

phenolphthalein. They were used as received from the suppliers.

Epoxidation of cottonseed oil

The method as describe by Dinda and Patwadhan (Dinda *et al.*, 2008) was adopted for the epoxidation and steps were as follows; cottonseed oil in the amount of 200 ml was placed in a 500 ml three neck flask equipped with reflux condenser. Acetic acid of mole ratio of 0.5:1 to the oil and sulfuric acid catalyst together with hydrogen peroxide were added into the cottonseed oil. A hydrogen peroxide molar ratio of 1.5:1 to the oil was then added drop-wise into the mixture. This feeding strategy was to avoid over heating the system as the epoxidation reaction is highly exothermic. The reaction was well mixed and was performed at a stirring speed of 1600 rpm under isothermal conditions. The product of the reaction was then cooled and decanted to effect a separation of the organic-soluble compound (epoxidized oil) from water-soluble phase. The epoxidized oil was then washed with warm water (in small aliquots) to remove residual contaminants.

Dimethylol urea resin synthesis

Dimethylol urea was prepared by using one mole (6.0 g) of urea to react with two moles (16.22 ml) of 37-41% (w/v) formaldehyde 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 1 h after which the sample was removed and kept at room temperature (30°C)

Determination of physical properties

Determination of viscosity and gel time

The standard method of viscosity determination was employed using the viscometer bath capillary inserted into the viscometer bath. About 20 ml of the sample was poured into the U-tube viscometer with capillary and then corked. The U-tube was suspended into the viscometer bath containing water and the temperature of the bath was 33°C. The cork was removed and the time taken for the content to run up starting from the top mark to the middle mark was noted using a stop watch. Five different readings were taken for each sample and the average value calculated. The gel time of the resin was determine by monitoring the viscosity the resin with time until a constant viscosity profile was obtained (Mirmohseni & Hassanzadeh, 2000).

Determination of density

The mettle Toledo XS 64 was used in determining the density of the cured resin via Archimedes principle, four readings were taken for each sample and average value was calculated.

Determination of refractive index and turbidity

The refractive indexes of the composite were determined using abbe refractometer. Turbidity of the resin samples was measured using Hanna microprocessor turbidity meter (Model, H19370). The above properties were determined according to standard method (AOAC, 2000)

Determination of moisture uptake

The classic laboratory method of measuring high level moisture of solid or semi-solid material loss on drying (LOS) was adopted. In these techniques a sample of material is weighed, heated in an oven for an appropriate period, cooled in dry atmosphere of a desiccator and then reweighed. The difference between the weighed and the reweighed sample were then recorded as the moisture intake by the resin. Triplicate determinations were made for each sample and mean value recorded.

Determination of melting point

The melting point of the different copolymer samples were determined by using Galenkamp melting point apparatus (Model MFB600-010F) (Osemehon & Archibong, 2011). The different copolymer samples were ground into powder and some quantity of each sample was poured into capillary tubes. The melting point was then taken one after the other for all the samples.

Determination of formaldehyde emission

Formaldehyde test was performed by using the standard 2h desiccator method (Kim, 2001). The evaluation of the absorbed formaldehyde by the 25.0 ml water was obtained from standard calibration curves derived from refractometric technique using Abbe refractometer. In brief, the prepared resin was aged for two (2) days. At the end of the period, the resin was poured into a mold made from aluminium foil with a dimension of 69.6 × 126.5 mm and thickness of 1.2 mm. The mold and its content were then allowed to equilibrate for 24 h in the laboratory after which it was then placed inside a desiccator along with 25 ml of water, which absorbed the formaldehyde emitted. The set up was allowed to stay for 2 h after which the 25 ml water was removed and analyzed for formaldehyde content. Triplicate determinations were made for each sample and mean value record.

Water solubility

The solubility of Dimethylol Urea in water was obtained by mixing 1 ml of the resin with 5 ml of distilled water at a temperature of 30°C

Preparation of DMU-ECESO composite film

Blending of dimethylol urea (DMU) with epoxidized cottonseed oil (ECESO) was done by preparing 10% of epoxidized cottonseed oil in dimethylol urea at room temperature (30°C). The solution was mixed thoroughly using magnetic stirrer. The above procedures were repeated at different epoxidized cottonseed oil concentrations (10 – 70%) and were cast in petri dishes by using solution casting method (Mirmohseni & Hassanzadeh, 2000). The resins were then allowed to cure and set for seven days at 30°C. The physical properties of these films were then investigated.

Results and Discussion**Effect of DMU viscosity on the formaldehyde emission of DMU/ECESO**

Table 1 shows the effect of DMU viscosity on the formaldehyde emission of DMU/ECESO composite. It is observed that the formaldehyde emission increases with increase in DMU viscosity. This trend can be attributed to two reasons; (a) It may be due to the result in the rate of condensation reactions with increase in DMU viscosity thereby increasing the rate of emission of formaldehyde in the process (Kaniappan & Lathan, 2011). (b) It may be as a result of increase in stress during resin cure with increase in DMU viscosity. Low DMU viscosity gives rise to low molecular

weight which favours molecular chain mobility that enhances flexibility of polymer network; flexibility reduces stress during curing, and reduction in stress reduces emission (Kaniappan & Lathan, 2011). Even when an increase in formaldehyde emission was recorded with increase in DMU viscosity in this work. The maximum value (0.0435 ppm) recorded is still within acceptable limit of 0.1 ppm as stipulated by agency against environmental pollution (Devi & Maidivanne, 2012).

Table 1: Effect of DMU viscosity on the formaldehyde emission of DMU/ECESO

DMU Viscosity (mpa.s)	Formaldehyde emission (ppm)
13.75	0.0422
18.50	0.0426
22.08	0.0427
24.44	0.0431
27.80	0.0435

Table 2: Effect of DMU viscosity on the water solubility of DMU/ECESO copolymer composite

DMU viscosity (mpa.s)	solubility
13.75	Soluble
18.50	Soluble
22.08	Partially soluble
24.44	Insoluble
27.80	insoluble

Effect of DMU viscosity on the solubility of DMU/ECESO in water

The development of amino resin for emission paint formulation requires an understanding of the solubility of the resin in water (Osemehon & Archibong, 2011). It is important both from technical and processing ground. This is more so because the solubility of dimethylol urea decreases with increase in viscosity (Devi & Maidivanne, 2012). Table 2 showed the effect of DMU viscosity on the solubility of DMU/ECESO composite in water. Below a viscosity of 22.08 mpa.s, the DMU/ECESO composite is soluble in water and beyond this point the copolymer resin is insoluble in water. This is attributed to differences in molecular weight and cross link density (Akinterinwa *et al.*, 2015). 22.08 mpa.s seems to represent the gel point of the copolymer resin, thus processing of DMU/ECESO composite for emulsion paint formulation is recommended below this viscosity.

Effect of DMU viscosity on the reactive index of DMU/ECESO

Gloss is an important factor of many coating products. The gloss of a coating with or without pigment is a function of refractive index of the surface. The angle of incidence of the beam of light and the nature of material (Velu *et al.*, 2011). Table 3 shows the effect of viscosity on the refractive index of DMU/ECESO composite. It is noticed that the refractive index increases with increase in DMU viscosity. This is due to the increases in molecular weight and cross link density of the different viscosity (Velu *et al.*, 2011).

Table 3: Effect of DMU viscosity on the refractive index of DMU/ECESO

Viscosity (mpa.s)	Refractive index
13.75	1.4260
18.50	1.4280
22.08	1.4300
24.44	1.4330
27.80	1.4434

Table 4: Effect of DMU viscosity on the density of DMU/ECSO

DMU Viscosity (mpa.s)	Density/g/cm ³
13.75	1.1670
18.50	1.1685
22.08	1.1689
24.44	1.1695
27.80	1.1699

Effect of DMU viscosity on the density of DMU/ECSO

The density of a paint binder in a coating industry has a profound influence on factors such as pigment dispersion, brushability of the paint, flow leveling and sagging. Table 4 shows the effect of DMU viscosity on the density of DMU/ECSO composite. The density increases with increase in DMU viscosity which is as a result of the increase in molecular weight. This observation suggests that when the copolymer resin is applied in paint the distance behavior may be established readily (Vaidya *et al.*, 2012).

Effect of DMU viscosity on the melting point of DMU/ECSO

The melting point of a polymer is related to its molecular weight, degree of cross linking and the level of rigidity of the polymer (Vaidya *et al.*, 2012). Table 5 shows the effect of DMU viscosity on the melting point of DMU/ECSO composite. The melting point of DMU/ECSO composite is observed to increase with increase in the Viscosity of DMU, this is attributed to differences in the molecular weight and cross link density of the copolymer networks at different DMU viscosities. At the onset the differences between the melting point and increase in DMU viscosity is much but stabilizes as optimum growth is obtained.

Table 5: Effect of DMU viscosity on the melting point of DMU/ECSO

DMU viscosity (mpa.s)	Melting point (°C)
13.75	148
18.50	154
22.08	159
24.44	160
27.80	162

Table 6: Effect of DMU viscosity on the moisture uptake of DMU/ECSO

DMU Viscosity (mpa.s)	Moisture uptake (%)
13.75	0.0060
18.50	0.0170
22.08	0.0180
24.44	0.0190
27.50	0.0196

Effect of DMU viscosity on the moisture uptake of DMU/ECSO

The interaction of structural-network of polymer resin with water is both of fundamental and technical interest. Water uptake affect vital properties of the polymer material such as physical, mechanical, thermal and structural properties. One of the major drawbacks of DMU resin is their poor water resistant. In paint making industry, the moisture uptake of the paint binder is very crucial because it is responsible for blistering and broominess of the paint film.

From Table 6, the effect of DMU viscosity on the moisture uptake of DMU/ECSO copolymer composite is presented. The copolymer exhibit a gradual increase in moisture uptake with increase in DMU viscosity. This trend is attributed to increase in molecular weight and cross link density as the

viscosity of DMU resin increases (Nikje *et al.*, 2011; Toloei *et al.*, 2013).

Effect of DMU viscosity on the elongation at break of DMU/ECSO

One of the short coming of DMU resin is that it is too hard and brittle and hence poor resistance to crack propagation (Akinterinwa *et al.*, 2015). Table 7 shows the effect of DMU viscosity on the elongation at break of DMU/ECSO composite. It is observed that that the elongation at break reduces gradually with increase in DMU viscosity until after DMU viscosity of 22.08 mpa.s that a rapid reduction of elongation at break is observed. This trend of result is attributed to the increase in molecular weight and hence cross link density of DMU/ECSO copolymer with increase in DMU viscosity.

Conclusion

The effect of DMU viscosity on some physico-chemical parameters of DMU/ECSO were been investigated. The result obtained showed that DMU viscosity has a pronounced influence on the the properties of DMU/ECSO copolymer composite. The processing of DMU/ECSO composite for emulsion paint formulation could be suggested below viscosity of 22.08 mpa.s because at a viscosity beyond this value the copolymer composite becomes insoluble in water. Also at a viscosity beyond 22.08 mpa.s the ductility of the composite is lost

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