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Full Length Research Paper

Utilization of amino resin for emulsion paint formulation: Effect of urea formaldehyde viscosity on urea formaldehyde and soybean oil copolymer composite

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In our continuous desire to develop a paint binder from amino resin, the effect of urea formaldehyde (UF) viscosity on a copolymer composite derived from the copolymerization reaction between urea formaldehyde (UF) and soybean oil (SBO) to give urea formaldehyde/ soybean oil copolymer composite (UF/SBO) was investigated. Some physical properties of (UF/SBO) obtained at different viscosities (5.11 - 260.04 mPa.s) were evaluated. The melting point, density and formaldehyde emission were found to increase with increase in UF viscosity while the dry time, moisture uptake refractive index and elongation at break were found to decrease with increase in UF viscosity. UF viscosity below 150.00 mPa.s was found to produce UF/SBO copolymer composite that is soluble in water. The processing of UF/SBO copolymer resin for emulsion paint formulation should be carried out below this viscosity level. The copolymer composite was found to be ductile throughout the viscosity range studied (5.11 - 260.04). This takes care of the inherent brittleness associated with the traditional UF and will give paint formulators freedom of choice as regards processing viscosity of UF/SBO. The results obtained from this experiment will offer formulator different options and to control formulation processes towards developing UF/SBO copolymer composite as a paint binder for emulsion paint formulation.

Key words: Copolymerization, viscosity, amino resin, paint binder.

INTRODUCTION

With the advent of the regulations on air pollution, and for safety consideration, there have been continued interests in the search for alternative raw materials and new formulations to reduce the overall volatile organic compounds in surface coatings (Osemeahon et al., 2009). Recently, much research has been focused on replacing solvent-based paints with water based paints (Mohammed et al., 2001; Li et al., 2001). The advantages of water borne paint include being nonpolluting, easy to handle, quick drying, economic and environmentally friendly. However, although most household paints are water-based, this is not true of industrial paints. Because of the special requirements of the industrial coatings, satisfactory water-based polymers with the required properties have not yet been developed (Osemeahon et al., 2009). Therefore a significant challenge in this drive to reduce VOC is the need for the water-borne technology to deliver the enamel type properties characteristic of solvent-born coating.

The acceptance of urea formaldehyde resin 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 (Barminas and Osemeahon, 2006; Osemeahon et al., 2008). These disadvantages limit its uses. However, UF resins offer a wide range of conditions that make synthesis of these resins with important properties such as gel time, tack and spreading ability of the uncured resin possible. Also, formaldehyde emissions and the durability of the cured resin can be

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controlled and specifically tailored for the final use of the resins (Osemeahon and Barminas, 2006).

Osemeahon et al. (2008) reported that the ultimate performance of a fully cured amino resin largely depends on its synthesizing parameters, including the ingredient mole ratio, catalyst, viscosity, reactivity and so on. These parameters are frequently adjusted empirically to tailor the resin properties to specific production requirements such as the resin reactivity, formaldehyde emissions, water resistance etc.

In the coating industry an understanding of the viscosity of the paint binder is very important because it controls factors such as flow rates, leveling and sagging, thermal and mechanical properties, dry rate of paint film and adhesion of the coating to substrate (Osemeahon and Barminas, 2007). Osemeahon et al. (2009), reported that the polymerization reaction in urea formaldehyde resin synthesis is normally ended when the viscosity of the reaction mixture obtain the established optimal. Thus 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 (Osemeahon and et al., 2008).

In our previous experiments (Barminas and Osemeahon et al., 2007; Osemeahon and Barminas, 2007a), we reported both the synthesis of UF through a new synthetic route and the successful copolymerization of this new class of methylol urea (MU) resin with soybean oil (SBO) as a way of developing a paint binder for emulsion paint formulation from amino resin. In order to optimize the copolymerization reaction between MU and SBO, this experiment is set out to investigate the effect of UF viscosity on the UF/SBO copolymer composite. This will offer formulators with varied options to tailor quality performance.

MATERIALS AND METHODS

Materials

Urea, formaldehyde, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide pellets and sucrose were reagent grade products from the British Drug House (BDH). Soybean oil was obtained from Yola market, Nigeria. All materials were used as received.

Resin synthesis

Trimethylol urea was prepared by the method described by Barminas and Osemeahon, (2006). One mole (6.0 g) of urea was reacted with three moles (24.3 ml) of 37% (w/v) formaldehyde using 0.2 g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 6 by using 0.5 M H_2SO_4 and 1.0 M NaOH solutions. The solution was then heated in a thermostatically controlled water bath at 70°C. The reaction was allowed to proceed for 2 h after which the sample was removed and kept at room temperature (30°C).

The UF samples with different viscosities used in this experiment were obtained by removing 60 ml of resin from the synthesized UF resin at 24 h intervals for the period of 168 h and their viscosities determined (Osemeahon et al., 2007).

Preparation of UF/SBO composite films

Copolymer composite film of UF and SBO film was obtained as reported earlier (Osemeahon and Barminas, 2007a). In brief, 50 ml of UF was added to 25 ml of SBO to form UF/SBO copolymer composite. The mixture was stirred and left for 24 h at room temperature (30°C) and then poured into a glass Petri dish for casting. The composite was also allowed to cure and set for seven days at (30°C). The above procedure was repeated at different UF viscosities (5.11 - 260.04 mPa.s). The physical properties of these films were then investigated.

Determination of viscosity

The method reported by Barminas and Osemeahon, (2007) was adopted for the determination of the viscosity of UF resin. In brief, a 100 ml Phywe made graduated glass macro-syringe was utilized for the measurement. The apparatus was standardized with 20% (W/V) sucrose solution whose viscosity is 2.0 mPa.s at 30°C. The viscosity of the resin was evaluated in relation to that of the standard sucrose solution at 30°C. Five different readings were taken for each sample and the average value calculated.

Determination of density, turbidity, melting point and refractive index

The above properties were determined according to standard methods (AOAC, 2000). The density of the different resins was determined by taking the weight of a known volume of resin inside a density bottle using metler (Model, AT400) weighing balance. Five readings were taken for each sample and average value calculated. The turbidity of the resin samples were determined by using Hanna microprocessor turbidity meter (Model, H193703) (Barminas and Osemeahon, 2006). The melting points of the different film samples were determined by using Galenkamp melting point apparatus (Model, MFB600-010F).The refractive indices of the resin samples were determined with Abbe refractometer (Barminas and Osemeahon, 2006).

Determination of moisture uptake

The moisture uptakes of the different resin film were determined gravimetrically (Osemeahon and Barminas, 2007a). Known weight of the sample was introduced into a desiccator 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 each sample was then recorded as the moisture uptake by resin. Triplicate determinations were made for each sample and the average value recorded.

Determination of formaldehyde emission

Formaldehyde emission test was performed by using the standard 2 h desiccator test as earlier reported (Osemeahon and Barminas, 2007a). The mold used was made from aluminium foil with a dimension of 69.6 x 126.5 mm and thickness of 12.0 mm. The emitted formaldehyde was absorbed in 250 ml of water and analyzed by a refractometric technique using Abbe refractometer. Triplicate samples were used and average value taken.

Tensile test

Tensile properties (tensile strength and elongation at break) were

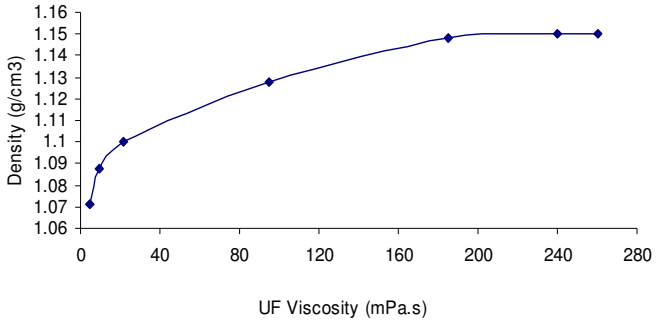

Figure 1. Effect of viscosity on the density of UF/SBO copolymer composite.

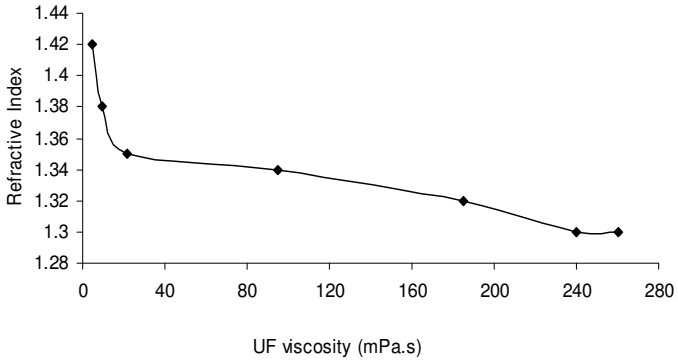

Figure 2. Effect of UF viscosity on the refractive index of UF/SBO copolymer composite.

measured as described by Osemeahon et al, (2007), using Instron Testing Machine (Model 1026). Resin films of dimension 50 mm long, 10 mm wide and 0.15 mm thick were brought to rapture at a clamp rate of 20 mm/min and a full load of 20 kg. Five runs were done for each sample and the average elongation evaluated and expressed as the percentage increase in length.

Dry time and water solubility

The relative degree of cure (Reaction time) was expressed in the form of dry time (dry to touch). This was measured by the quail-tative finger-making test (Ali et al., 2001). The solubility of methylol urea in water was obtained by mixing 1 ml of the resin with 5 ml of distilled water at room temperature (30°C) (Osemeahon and Barminas, 2006).

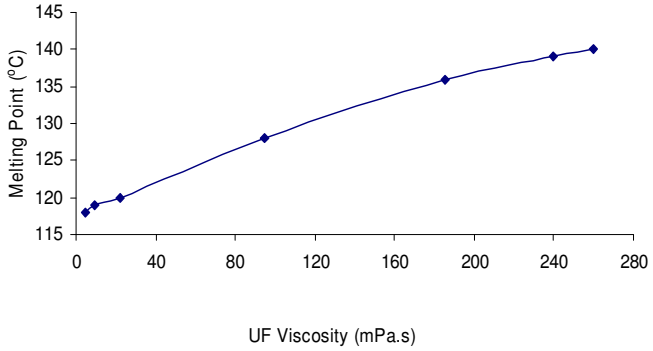

Figure 3. Effect of viscosity on the melting point of UF/SBO copolymer composite.

RESULTS AND DISCUSSION

Density

In the coating industry the density of a paint binder is important because it influences factors such as pigment dispersive, brushability of paint, flow leveling and sagging (Osemeahon and Barminas, 2007a; Osemeahon et al., 2008). Figure 1 shows the effect of UF viscosity on the density of UF/SBO copolymer composite. The density increases with increase in UF viscosity. This trend is due to increase in molecular weight and packing nature of resin molecules (Osemeahon et al., 2007; Sakaran et al., 2001)

Refractive index

Gloss is an important factor of many coating products (Osemeahon et al., 2009). The gloss of a paint coating with or without pigments is a function of refractive index of the surface, the angle of incidence of the beam of light and the nature of the material (Trezza and krochta, 2001; Osemeahon and Barminas, 2006).

Figure 2 present the effect of UF viscosity on the refractive index of UF/SBO copolymer composite. It is observed that the refractive index of UF/SBO copolymer decreases rapidly from 5.10 - 22.00 mPa.s viscosity levels. After this, gradual decrease in refractive index is observed with further increase in UF viscosity. This result is due to differences in the level of specific interaction between the two polymers (Qi et al., 2002) this gave rise to molecules with differences in molecular weight, molecular features and molecular orientations (Osemeahon and Barminas, 2007).

Melting point

The melting point of a polymer has a direct bearing to its thermal property. It is also related to its molecular weight, degree of crosslinking and the level of rigidity of the polymer (Park et al., 2002; Osemeahon et al., 2008). In the case of the coating industry, the melting point of a binder is related to its thermal resistance as well as to the brittility of the coating film (Osemeahon and Barminas, 2006). Figure 3 indicates the effect of UF viscosity on the melting point of UF/SBO copolymer composite. It is observed that the melting point increases with increase in UF viscosity. This trend is in agreement with earlier report

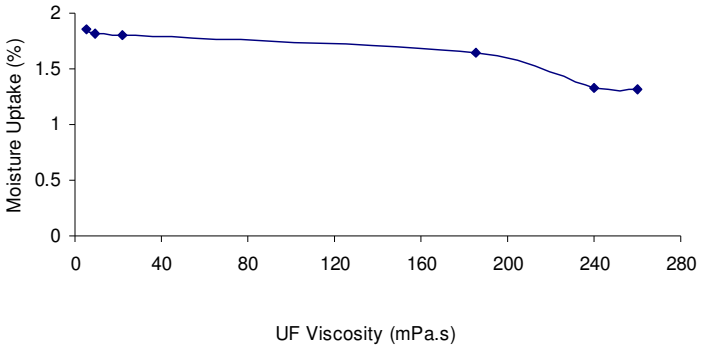

Figure 4. Effect of viscosity on the moisture uptake of UF/SBO copolymer composite.

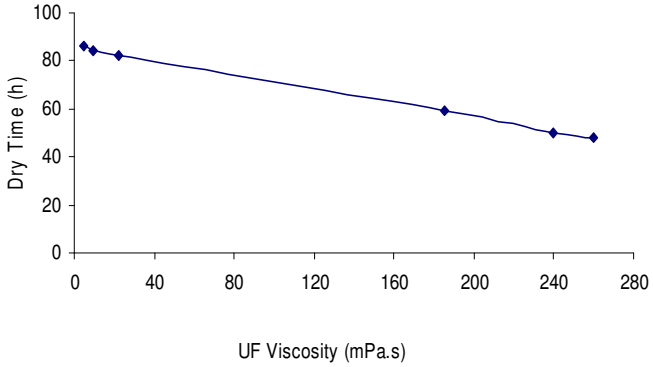

Figure 5. Effect of viscosity on the dry time of UF/SBO copolymer composite.

(Osemeahon et al., 2008). The trend is due to different in molecular weight and crosslink density.

Moisture uptake

The interaction of structural network of polymer resin with water is both of fundamental and technical interest (Osemeahon et al., 2008). Water uptake affects vital properties of the polymer such as, mechanical, thermal and structural properties (Hu et al., 2001). One of the major drawbacks of UF resin is their poor water resistance (Osemeahon et al., 2008). In the coating industry, the moisture uptake of the paint binder is very crucial because it is responsible for blistering and broominess of paint film (Barminas and Osemeahon, 2006).

Figure 4 shows the effect of UF viscosity on the moisture uptake of UF/SBO copolymer composite. It is observed that the moisture uptake decreases with increase in UF viscosity. This result can be explained in terms of the differences in crosslink density at different UF viscosities (Osemeahon et al., 2008). As the viscosity of UF increases, the molecular weight and hence crosslink density also increases. The higher the crosslink density the lower the void spaces available for moisture accommodation (Osemeahon et al., 2007). This results suggested that a better water resistant UF/SBO copolymer composite can be obtained at high UF viscosity.

Dry time

One of the drawbacks of UF/SBO copolymer Composite is that the dry time is relatively too high when compared to the traditional paint binder. This factor limits the amount of SBO inclusion into UF/SBO composite to a maximum value of 30% (Osemeahon and Barminas, 2007a).The time it takes for a paint to dry (reaction time) after application is an important factor for the paint formulator (Osemeahon et al., 2007). This is because if the paint dries too fast, it will be prone to brittleness and if it dries too slowly, the paint may be subjected to pick up dirt (Trumbo et al., 2001). The effect of UF viscosity on the dry time of UF/SBO copolymer composite is shown in Figure 5.The result shows that the dry time decreases with increase in UF viscosity. This is attributed to increase in molecular weight and crosslink density (Osemeahon and Barminas, 2007a). Thus a UF/SBO copolymer resin with high rate of drying, increase in the percentage (more than the present 30%) inclusion of SBO in the composite (Osemeahon and Barminas, 2007a) and better water resistance may be obtained at high viscosity of UF resin.

Table 1. Effect of UF viscosity on the formaldehyde emission of UF/SBO copolymer composite.

UF viscosity (mPa.s)	Formaldehyde emission (ppm)
5.11	0.052 ± 0.002
9.55	0.057 ± 0.001
22.07	0.062 ± 0.001
95.03	0.071 ± 0.003
240.41	0.079 ± 0.003
260.04	0.079 ± 0.002

Formaldehyde emission

The emission of formaldehyde during resin cure is one of the drawbacks of urea formaldehyde resin (Kim, 2001; Osemeahon et al., 2008). In the development of paint binder from urea formaldehyde resin, serious effort must be made to reduce formaldehyde levels to acceptable ones (Barminas and Osemeahon, 2006).

Table 1 shows the effect of UF viscosity on formaldehyde emission of UF/SBO copolymer composite. It can be seen that the formaldehyde emission increases with increase in UF viscosity. This trend can be ascribed to two reasons (Osemeahon et al., 2008); firstly**,** it may be due to increase in the rate of condensation reactions with increase in UF viscosity thereby increasing the rate of emission of formaldehyde in the process. Secondly, it

Table 2. Effect of UF viscosity on the tensile properties (Tensile Strength and Elongation at Break) of UF/SBO copolymer composite.

UF viscosity (mPa.s)	Tensile strength (kg/cm^2)	Elongation at break (%)
5.11	0.050 ± 0.03	170.55 ± 0.01
9.55	0.055 ± 0.01	162.28 ± 0.01
22.07	0.060 ± 0.02	150.07 ± 0.01
95.03	0.086 ± 0.02	131.43 ± 0.02
240.41	0.090 ± 0.04	127.001 ± 0.03
260.04	0.095 ± 0.03	126.08 ± 0.01

Table 3. Effect of UF viscosity on the water solubility of UF/SBO copolymer composite.

UF viscosity (mPa.s)	Solubility in water
5.11	Soluble
9.55	Soluble
22.07	Soluble
95.03	Soluble
150.10	Soluble
240.41	Slightly soluble
260.04	Insoluble

may be due to increase in stress during resin cure with increase in UF viscosity. Reduction in stress during cure reduces emission (Osemeahon and Barminas, 2006).

Low UF viscosity gives rise to low molecular weight which favors molecular chain mobility and enhances flexibility of polymer network; flexibility reduces stress during cure and reduction of stress reduces emission (Osemeahon et al., 2008; Cain and Yi, 2001). Although an increased formaldehyde emission is recorded with increase in UF viscosity in this experiment, the maximum value (0.079ppm) recorded is however within acceptable limit (0.10ppm) as stipulated by the environmental safety regulation (Osemeahon et al., 2008). Therefore the effect of UF viscosity on formaldehyde emission of UF/SBO copolymer even at high viscosity is within levels of comfort and can be tolerated.

Tensile test

Elongated at break determines to what extend a material stretches before breaking and hence the ductility or flexibility of the material. One of the shortcomings of UF resin is that it is too hard and brittle and hence poor resistance to crack propagation (Osemeahon et al., 2009). In the coating industry, a paint binder must be able to withstand stress emanating from variation in environmental factors. Therefore in developing paint binder from amino resin, tensile property such as elongation at break must be considered (Osemeahon et al., 2008).

The effect of UF viscosity on the tensile strength and elongation at break are shown in Table 2. It is observed that the tensile strength increases while the elongation at break decreases with increase in UF viscosity. This trend of result is attributed to the increase in molecular weight and hence crosslink density of the UF/SBO with increase in UF viscosity (Ma et al., 2002). Differences in crystallinity or crystalline orientation of the resin molecules with increase in UF viscosity may also be responsible for the result (Osemeahon et al., 2008). From these results, UF/SBO copolymer composite retained its ductility even at the highest viscosity level (260.04mPa.s). This is an important and plausible development for the paint formulator as it allows freedom of choice of UF/SBO composite at any UF viscosity level.

Solubility in water

Development of amino resin for emulsion paint formulation requires an understanding of the solubility of the resin in water (Osemeahon and Barminas, 2006). It is important both from the technical and processing point of view. This is more so because the solubility of urea formaldehyde resin decreases with increase in viscosity (Osemeahon et al., 2007). Table 3 shows the effect of UF viscosity on the solubility of UF/SBO copolymer resin in water. Below a viscosity of 150.10 mPa.s, the UF/SBO copolymer is soluble in water and beyond this point the resin is insoluble in water. This result is attributed to differences in molecular weight and crosslink density (Osemeahon and Barminas, 2006). Perhaps, the viscosity of 150.10 mPa.s seems to represent the gel point of the copolymer resin. Thus processing of UF/SBO copolymer composite for emulsion paint formulation could be suggested below this viscosity value.

Chemical resistance

The ability of a paint film to resist chemical attack is one of the desirable qualities of a good coating film (Osemeahon and Barminas, 2007b). Table 4 present the effect of UF viscosity on the chemical resistance of UF/SBO copolymer composite. It is observed that the chemical resistance of the copolymer film increases with increase in UF viscosity for all the chemicals used. This behavior is explained by the increase in molecular weight

Table 4. Effect of UF viscosity on the chemical resistance of UF/SBO copolymer composite.

UF Viscosity (mPa.s)	Chemicals		
	Acid (HCl)	Alkali NaoH	Xylene
5.11	Poor	Poor	Poor
9.55	Poor	Poor	Poor
22.07	Fair	Fair	Fair
95.03	Good	Good	Good
240.41	Very good	Very good	Very good
260.04	Very good	Very good	Very good

and crosslink density as UF viscosity increases.

Conclusion

This study examined the effect of UF viscosity on some physical properties of UF/SBO copolymer composite. The result obtained from this study revealed that UF viscosity has a significant influence on the properties of UF/SBO blend. At a viscosity below 150.10 mPa.s, the copolymer composite is soluble in water while flexibility was maintained throughout the viscosity range (5.11 – 260.04). At a viscosity above 150.10 mPa.s the copolymer composite became insoluble in water. Emulsion paint formulation could be suggested below this viscosity level. While the level of formaldehyde emission was found to increase with increase in UF viscosity that of moisture uptake on the other hand decreases with increase in UF viscosity. The result from this study will help in the optimization of the blending reaction between UF and SBO.

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