

Full Length Research Paper

Optimization of the copolymerization reaction between methylol urea and polyester: Effect of viscosity on some physical properties of the 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 methylol urea (MU) and triethanolamine (TEA) to give methylol urea/triethanolamine copolymer composite (MUT) was investigated. Some physical properties of MUT obtained at different viscosities (4.11 - 255.00 mPa.s) were evaluated. The melting point, refractive index, density and formaldehyde emission were found to increase with increase in UF viscosity while the dry time, moisture uptake and elongation at break were found to decrease with increase in UF viscosity. UF viscosity below 155.00 mPa.s was found to produce MUT copolymer composite which is ductile and soluble in water. The processing of MUT copolymer resin for emulsion paint formulation should be carried out below this viscosity level. The results obtained from this experiment will offer formulator different options and to control formulation processes towards developing MUT copolymer composite as a paint binder for emulsion paint formulation.

Key words: Copolymerization, viscosity, 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 (VOC) in surface coatings (Gan and Tan, 2001). 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 (Gooch, 1997). 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-borne coatings.

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

Park et al. (2002) reported that the ultimate performance

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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 (Kim, 2001). Kim (2001) 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, 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).

In our earlier experiment (Osemeahon and Barminas, 2007), reported the successful *in situ* esterification of the toxic formaldehyde byproduct emitted during the cross-linking reactions of UF resin by using a polyol (triethanolamine) (TEA) and the copolymerization of methylol urea (MU) with the polyester to give methylol urea/triethanolamine (MUT) composite. Although, flexibility was introduced into the traditional hard UF resin and formaldehyde reduced to a safe level in that study, that of poor water resistance was unfortunately worsened because the moisture uptake of MUT was higher than that of the pure MU. This problem therefore disqualified MUT as a good binder for the coating industry. However, it is our felt thought that this problem of poor water resistance may be addressed if the synthesis parameters of the copolymer composite are optimized. This experiment is set out to investigate the effect of UF viscosity on the properties of MUT copolymer composite.

MATERIALS AND METHODS

Materials

Urea, formaldehyde, triethanolamine, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide pellets and sucrose were reagent grade products from the British Drug House (BDH). All materials were used as received.

Resin synthesis

Trimethylol urea was prepared by the method described by Chen et al. (2001). 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 H₂SO₄ 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.

Preparation of MUT composite films

Copolymer composite film of UF and TEA film was obtained as reported by Mirmohseni and Hassanzadeh, (2000). In brief, 50 ml of UF was added to 5 ml of TEA to form MUT 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 (4.11 - 254.00 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. A 100 ml Phywe made graduated glass macrocygringe (Phywem, Gottingen, Germany) was utilized for the measurement. The apparatus was standardized with a 20% (w/v) sucrose solution whose viscosity is 2.0 mPa.s at 30 °C (Lewis, 1987). 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 (GmbH, Greifensee, Switzerland) weighing balance. Five readings were taken for each sample and average value calculated. The turbidity of the resin samples was determined by using Hanna microprocessor turbidity meter Model, H193703 (Villafranca Padovana, Italy). The melting points of the different film samples were determined by using Galenkamp melting apparatus Model, MFB600-010F (Loughborough, UK). The refractive indices of the resin samples were determined with Abbe refractometer (Bellingham and Stanley, Tunbridge well kent, UK). Five readings were taken for each sample and average value calculates for each of the aforementioned parameters.

Determination of moisture uptake

The moisture uptakes of the different resin film were determined gravimetrically (Osemeahon and Barminas, 2007). 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 differences between the wet weight and dry weight of each sample were then recorded as the moisture intake 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 reported by 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 2 days. At the end of this period, the resin was poured into a mold made from aluminum foil with a dimension of 69.6 × 126.5 mm and thickness of 1.2 mm. The mold and its content was 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 recorded.

Tensile test

Tensile properties (tensile strength and elongation at break) were measured as described by Wang and Gen (2002) using Instron Testing Machine Model 1026 (USA). Resin films of dimension 50 mm long, 10 mm wide and 0.15 mm thick were brought to rupture 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 qualitative 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) and solubility ascertained by physical observation (Osemeahon and Barminas, 2006).

RESULTS AND DISCUSSION

The chemistry of esterification of formaldehyde and copolymerization of amino resin with polyester

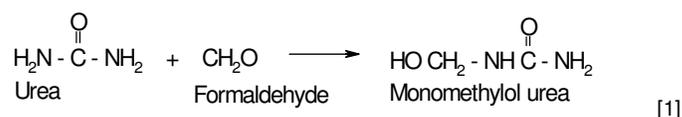
The synthesis, use and chemistry of polyurethane are well documented (Osemeahon and Barminas, 2007). Some of the end products derived from Polyurethane include rigid foam, flexible foam, surface coatings, cast elastomers etc. Polyurethane syntheses are based on simple diisocyanate (OCN-R-NCO) -and polyol (OH-R'-OH).

The beauty of polyurethane polymer is that it consist of both rigid (isocyanate block) and flexible (polyol block) segments (Osemeahon and Barminas, 2007).

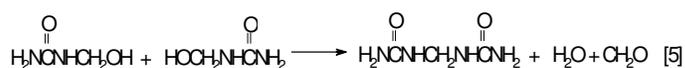
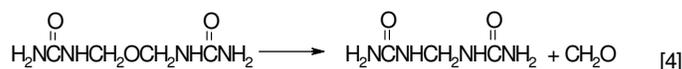
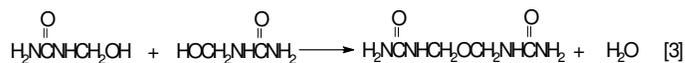
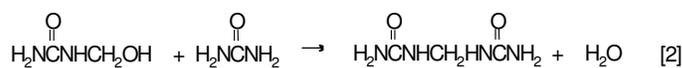
With this segmented polymer structure, polyurethane can vary its properties over a wide range of strength and stiffness by modification of its basic building blocks the polyol, diisocyanate and chain extender (Osemeahon and Barminas, 2007). Essentially the hardness range covered is that of soft jelly-like structure to hard rigid plastics and properties are related to segmented flexibility, chain entanglement, inter-chain forces and cross-linking.

During the condensation reactions of methylol urea resins into polymer chains, formaldehyde (H₂CO) is released at two of the four major steps (Equations 4 and

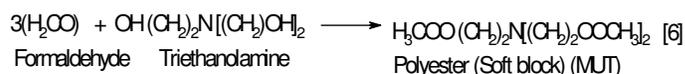
5) which is eventually emitted as a toxicant to the surroundings (Conner, 1996). However, this H₂CO contains carbonyl group just like isocyanate (NCO). In analogy, it may be possible for the carbonyl group in H₂CO to react with polyol. If this happens, the following may be expected to take place: (i) The hazardous formaldehyde will be captured and removed from the system by the polyol, (ii) *In situ* etherification of the emitted formaldehyde will take place, (iii) The polyester produced will be incorporated into the backbone of the urea formaldehyde as a copolymer resin and (iv) Segmented flexibility will be introduced into urea formaldehyde resin, a situation akin to polyurethane (Barminas and Osemeahon, 2010).



During curing, the amino resin undergoes crosslinking as result of the following condensation reactions:



Therefore during the condensation reactions of methylol urea resins into polymer chains, formaldehyde CH₂O was released (Equations 4 and 5). However, this CH₂O contains carbonyl group just like isocyanate (—N=C=O) used in the formation of polyurethanes. It may be possible therefore, for the carbonyl group in CH₂O to react with polyols such as triethanolamine (TEA) to start a sequence of reactions leading to the formation of methylol urea/triethanolamine (MUT) copolymer composite. More importantly the hazardous formaldehyde will be captured from the system by the polyol through *in situ* esterification:



The polyester produced will be incorporated into the backbone of the methylol urea as a copolymer resin through copolymerization process and segmented flexibility will be introduced into urea formaldehyde resin. This is shown below (Barminas and Osemeahon, 2010):

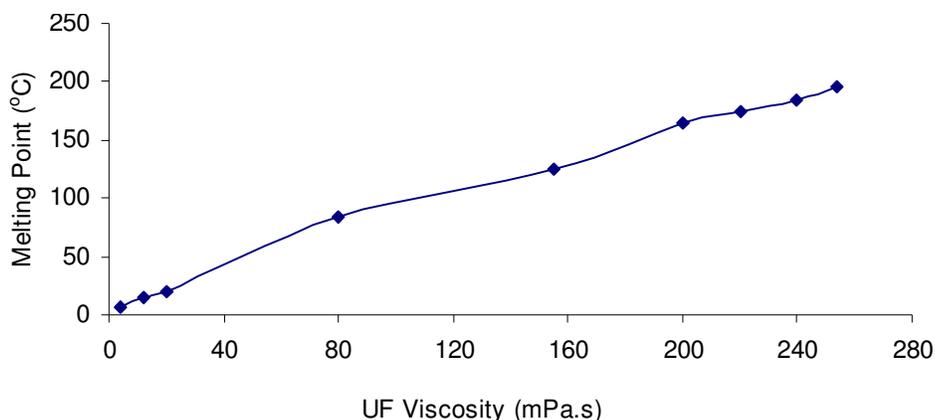


Figure 1. Effect of UF viscosity on melting point of MUT copolymer composite.

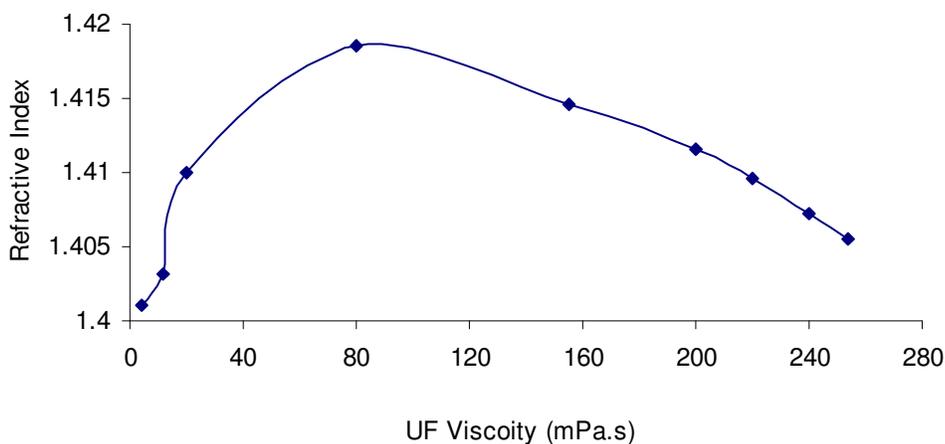
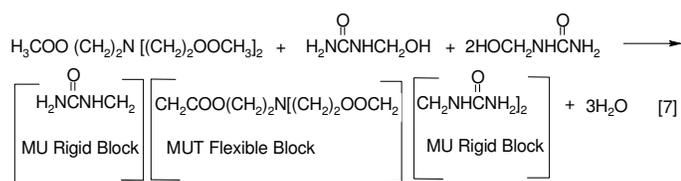


Figure 2. Effect of viscosity on the refractive index of MUT copolymer composite.



Melting point

The melting point of a polymer is related to its molecular weight, degree of cross-linking and the level of rigidity of the polymer (Bindu et al., 2001). Figure 1 presents the effect of UF viscosity on the melting point of MUT copolymer composite. An increase in melting point is observed with increase in UF viscosity. This type of behaviour can be explained on the basis of increase in molecular weight which gave rise to increase in viscosity and hence, the corresponding increase in melting point. As the viscosity of the UF resin approaches the gel point, the rate of polymerization reaction decreases and hence

the observed little increase in melting point at higher viscosities (200 - 254 mPa.s) (Ma et al., 2002).

Refractive index

Gloss is an important quality factor of many coating products. The gloss of paint coatings with or without pigment is among other things a function of the refractive index of the surface (Sekaran et al., 2001). Figure 2 shows the influence of UF viscosity on the refractive index of MUT composite. The refractive index of the copolymer resin increases with increase in UF viscosity reaching maximum value at 80 mPa.s after which a decrease in the refractive index was observed with increase in UF viscosity. This observation suggests that the aggregates of MU formed in the polyester matrix reached maximum size at the viscosity of 80 mPa.s after which dissociation occurred forming resins with differences in molecular weight, features and orientations. This gave rise to the corresponding

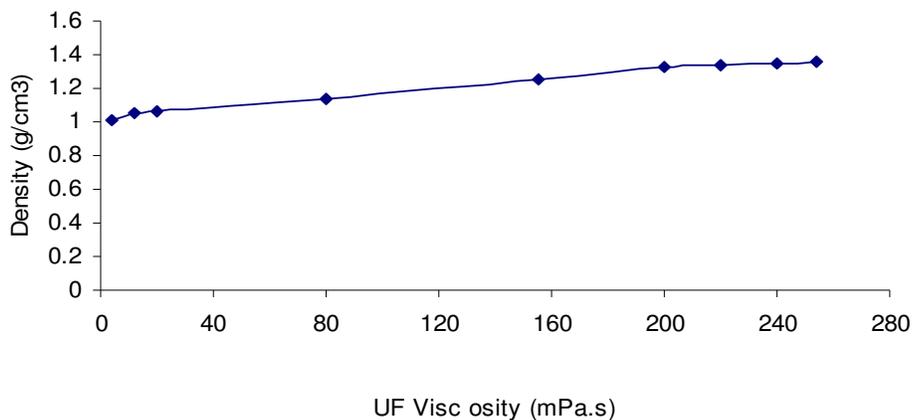


Figure 3. Effect of viscosity on the density of MUT copolymer composite.

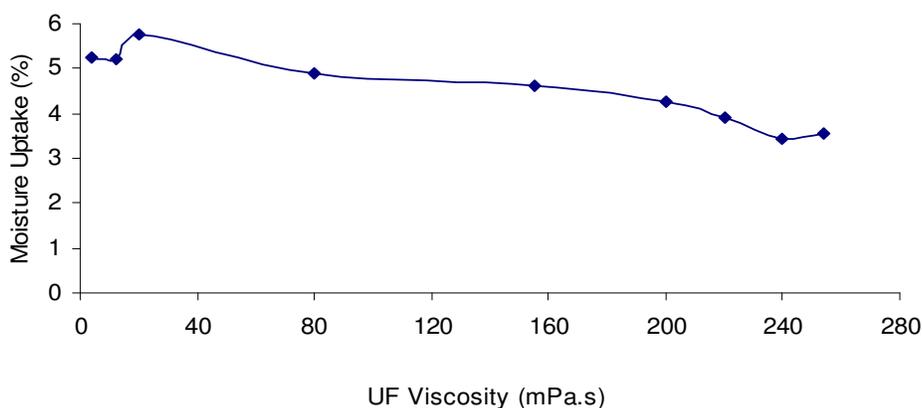


Figure 4. Effect of UF viscosity on the moisture uptake of MUT copolymer composite.

differences in their respective level of interaction with light (Trazza and Krochta, 2001; Hepburn, 1982).

Density

In the coating industry, the density of the paint binder has a profound influence on factors such as the pigment dispersion, brushability of paint flow, leveling and sagging (Lowel, 1990). The influence of UF viscosity on the density of MUT composite is shown in Figure 3. The graph indicates increase in density with increase in UF viscosity. This observation is due to increase in molecular weight which gave rise to the increase in viscosity. This in turn, influenced the packing nature or level of crystallinity of the resin molecules. The density of a polymer system is a function of the free-volume availability. The free-volume of a material is the summation of the spaces or holes that exist between the molecules of that very material. An increase in free-volume give rise to a decrease in density (Hepburn, 1982; Sekaran et al., 2001).

Moisture uptake

The interaction of structural – network of polymer resins 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 (Nogueria et al., 2001). One of the major drawbacks of UF resins is their poor water resistance (El-Naggar et al., 2001). In the paint making industry, the moisture uptake of the paint binder is very crucial because it is responsible for blistering and broominess of paint film.

From Figure 4, the effect of UF viscosity on the moisture uptake of MUT copolymer composite is presented. The copolymer exhibits a relatively gradual decrease in moisture uptake initially and then followed by rapid decrease in moisture uptake with increase in UF viscosity. This trend is attributed to molecular weight and crosslink density as the viscosity of UF resin increases (Osemeahon and Barminas, 2007). The gradual increase in the molecular weight of UF segment with increase in

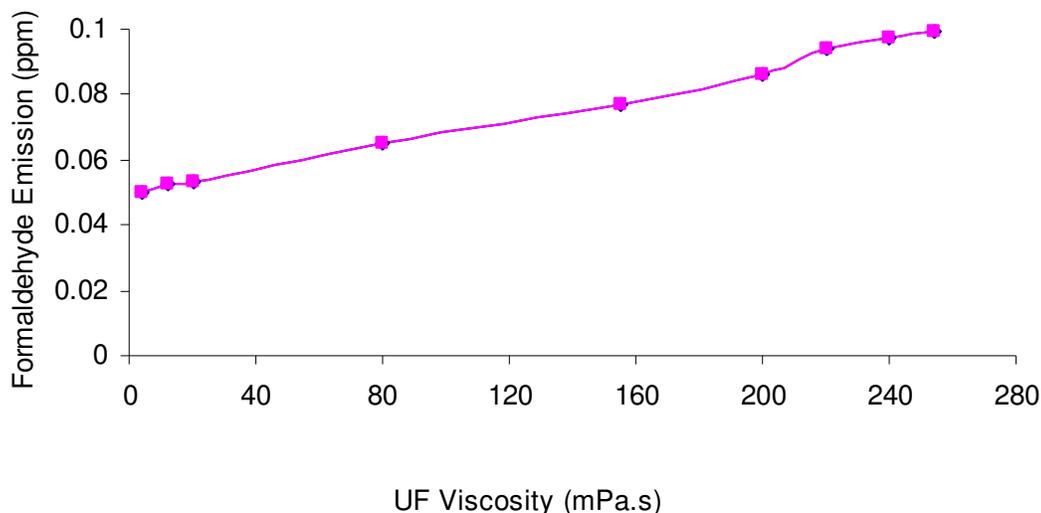


Figure 5. Effect of UF viscosity on the formaldehyde emission of MUT copolymer composite.

UF viscosity, resulted in resins with differences in chain topology, molecular size holes in the polymer morphology and crosslink density (Nogueria et al., 2001). This result suggests that high viscosity of UF is required for the copolymerization of MU and Polyester in order to obtain MUT composite of low moisture uptake for emulsion paint formulation.

Formaldehyde emission

One of the major drawback of urea formaldehyde resin is the emission of the hazardous formaldehyde during cure. In the development of paint binder from urea formaldehyde resin, serious effort must be made to reduce the formaldehyde levels to acceptable ones (Osemeahon et al., 2008).

Figure 5 shows the effect of UF viscosity on the formaldehyde emission of MUT composite. It is observed that formaldehyde emission increases with increase in UF viscosity. This trend can be ascribed to two reasons; firstly, it may be due to increase in the rate of condensation reaction with increase in UF viscosity thereby, increasing the rate of emission of formaldehyde in the process (Nakason et al., 2001). Secondly, it 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 this enhances flexibility of polymer network; flexibility reduces stress and reduction in stress reduces formaldehyde emission (Chain and Yi, 2001). This experiment therefore suggests that low UF viscosity favor low formaldehyde emission from MUT copolymer composite.

Dry time

The time it takes for a paint to dry (reaction time) after application is an important factor for the paint formulation (Osemeahon and Barminas, 2006b). 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 pickup dirt (Trumbo et al., 2001).

Figure 6 shows the effect of UF viscosity on the dry time of MUT composite. The result shows that the dry time decreases with increase in UF viscosity in the copolymer. This can be explained in terms of increase in the rate of polymerization which in turn gave rise to increase in molecular weight, crosslink density, UF viscosity and hence the rate of cure of the resin (Hepburn, 1982).

Tensile test

Elongation 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 in that it is too hard and brittle and hence poor resistance to crack propagation (Lowel, 1990) 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.

The effect of UF viscosity on the tensile strength and elongation at break are shown in Table 1. It is observed that the tensile strength increases while the elongation at break decreases initially, increased at the viscosity of 220 mPa.s and again decreases with further increase in UF

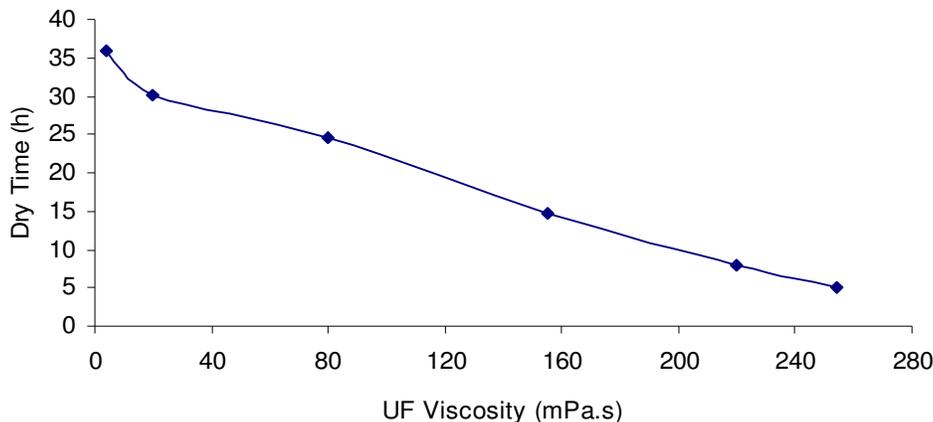


Figure 6. Effect of UF viscosity on the dry time of MUT copolymer composite.

Table 1. Effect of UF viscosity on the tensile strength and elongation at break of MUT copolymer composite.

UF viscosity (mPa.s)	Tensile strength (Kg/cm ³)	Elongation at break (%)
4.11	0.032 ± 0.002	174.08 ± 0.11
20.1	0.038 ± 0.001	132.00 ± 0.31
80.00	0.039 ± 0.001	126.25 ± 0.13
155.04	0.040 ± 0.001	115.09 ± 0.24
220	0.043 ± 0.001	181.22 ± 0.11
240	0.046 ± 0.001	168.55 ± 0.54
254	0.051 ± 0.001	161.22 ± 0.18

viscosity. This trend of result is attributed to the differences in molecular weight, crosslink density and molecular orientation experienced at different viscosities (Ma et al., 2001). Increase in molecular weight and hence crosslink density give rise to increase in viscosity. Low viscosity produces weaker molecular interchain attractive forces, increase in molecular slippage and mobility, hence increase in elongation at break. As the viscosity increases, molecular freedom or mobility reduces, thus, the decrease in the elongation at break. The sharp increase in the elongation at break recorded at 220 mPa.s is due to polymer dissociation (Hepburn, 1982). This gave rise to smaller chains, molecular movement and increase in elongation at break. The observed second decrease in elongation at break at higher viscosities is attributable to another regime of polymerization of the earlier dissociated oligomers (Hepburn, 1982).

Solubility in water

In the development of amino resin for emulsion paint formulation, the solubility of the resin in water is paramount. It is important both from the technical and processing point of view. This is more so because the

solubility of urea formaldehyde in water decreases with increase in viscosity (Park et al., 2001). The effect of UF viscosity on the solubility of UF in water is shown in Table 2. Below a viscosity of 155.04 mPa.s, The MUT composite is soluble in water and beyond this point the resin is insoluble in water. This trend is attributed to differences in molecular weight and crosslink density (Lowel, 1990). The viscosity of 155.04 mPa.s seems to present the gel point of the copolymer resin. Thus, processing of MUT copolymer resin as a binder for emulsion paint formulation could be suggested below this viscosity level.

Conclusion

This experiment examined the effect of UF viscosity on some physical properties of MUT copolymer composite. It shows that UF viscosity has a significant influence on the properties of MUT composite. At a viscosity below 155.00 mPa.s, the copolymer film is ductile and soluble in water. Beyond this viscosity value, the copolymer resin is brittle and insoluble in water. This suggests that the processing of MUT composite for emulsion paint formulation could be carried out below this viscosity level. While the level of formaldehyde emission was found to increase with

Table 2. Effect of UF viscosity on the water solubility of MUT copolymer composite.

UF viscosity (mPa.s)	Solubility in water
4.11	Soluble
12.03	Soluble
20.1	Soluble
80.12	Soluble
155.00	Slightly Soluble
200.00	Insoluble
220	Insoluble
240	Insoluble
254	Insoluble

increase in UF viscosity, that of moisture uptake decrease with increase in UF viscosity. The result from this study will contribute greatly to the optimization of the copolymerization reactions between methylol urea and triethanolamine.

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