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EFFECT OF pH ON MONOMETHYLOL UREA SYNTHESIS FOR POSSIBLE APPLICATION AS AN EMULSION PAINT BINDER

S. A. Osemeahon[1] and C. S. Archibong[2]*
[1]Department of Chemistry, Modibbo Adama University of Technology, PMB 2076, Yola, Adamawa State, Nigeria
[2]Department of Chemical Sciences, Federal University Wukari, PMB 1020, Taraba State, Nigeria
*Corresponding author: archibong@fuwukari.edu.ng

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Abstract: Monomethylol Urea (MMU) was synthesized using the one step process. The MMU was characterized and evaluated, at different pH values. The viscosity, moisture uptake, formaldehyde emission, density as well as melting points were observed to decrease with increasing pH value while the gel time, elongation at break, refractive index and turbidity increased with increasing pH values. Observations on solubility test shows that MMU resins were soluble at pH value of 4 – 7.30, beyond this value it became insoluble, which is a pointer to the paint formulator that above this pH value, MMU should not be used for paint formulation.

Keywords: Monomethylol urea, binder, emulsion paint, pH

Introduction

Water based paints are used in a similar way as oil paints but it is comparatively much easier to remove water based paints from brushes and palettes while still wet. The vehicle or surface forming material (a synthetic resin) is dispersed in water by means of a dispersing agent acting as a binder. It may also have in it another vehicle or film forming constituent such as oil, Pigment and extenders that are dispersed in such an emulsion. In addition to these constituents, emulsion paint may also have emulsifying agents or surface active agents, stabilizers, driers, antifoaming agent, preservatives, etc. (Abdullah & Park, 2010).

Within the manufacturing process of a paint, there are several factors that can destabilize the product. This destabilization can be brought about by changes in pH with the existing consequences such as malfunction additives, generation of a film material with low adhesion, poor quality color, poor texture, low gloss, procreation of bacteria and consequently a bad smell of paint (Cakic *et al*, 2012). In this manufacturing process, paints pH should be controlled and the end of the process must be adjusted to suitable limits to achieve good stability. The pH can also affect the wetting of the paint on the surface, due to the pH sensitivity to the wetting aids. Corrosion can be accelerated if the pH is lower or higher, depending on the type of material been painted. Another major issue is on the hydrolytic stability to the resin, the pH can accelerate the rate of hydrolysis of the resin. One of the factors affecting the functionality of biocides is the pH, thus requires control according to the selected type of biocide (Menkiti & Onukwuli 2011).

Urea-formaldehyde (UF) resin, is a cheap water soluble resin, good technological characteristics, absence of colours in cured polymer, low cure temperature, resistance to micro-organism and abrasion, good hardness, good thermal properties and easiness of application. But In spite of these benefits, formaldehyde emission (FE) originated from either UF resin itself or composite products bonded by UF resins is considered a critical drawback as it affects human health particularly in indoor environment. UF hardness, brittleness, and poor water resistance also placed limitations on it usage and universal acceptability (Osemeahon *et al*., 2010).

However, Modification of the resin by controlling the pH and decreasing the molar ratio of formaldehyde can introduce stability to the paint sample and further decrease the present formaldehyde emission, brittleness and associated with tetra, tri, and dimethylol urea. This is where Monomethylol urea (MMU) comes in, it is a formaldehyde content form of UF resin obtained by the reduction of molar ratio of Urea to Formaldehyde, in order to reduce to the bearest minimum formaldehyde emission and harvest other advantages that comes with such reduction. In the work earlier reported by Akinterinwa *et al.* (2015), tetra, tri, and dimethylol ureas were synthesized and characterized. Although some of the drawbacks of MU decreased from tetra – dimethylol urea, there is still need to reduce the value of these factors (hardness, brittleness and formaldehyde emission) for this material to be suitable as an acceptable binder in the coating industry. In a quest to achieve this objective, this work set out to synthesis and characterize MMU for its possible application in the coating industry.

Materials and Methods

Resin synthesis

MMU was prepared using the one step process (OSP) as reported by Osemeahon and Barminas (2016) with some modifications. One mole of urea (6.0 g) was made to react with one moles of formaldehyde (8.11 ml) 37-41% (w/v), using 0.02 g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 7.30 by using 0.1M H_2SO_4 and 0.5M NaOH solutions. The solution was heated in a thermostatically controlled water bath at 50^0C. The reaction was allowed to proceed for 60 min after which the resin was removed and kept at room temperature (30^0C).

Determination of gel time and viscosity

The standard method of determining viscosity was employed using the viscometer bath and the u-tube viscometer with capillary inserted into the viscometer bath (Rey *et al*, 2018). A quantity of the sample of MMU resins was poured into the u-tube viscometer with capillary and then corked. The U-tube was suspended into the temperature of the viscometer bath containing water and the temperature was maintained constant. 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 stopwatch. Gel time was measured by having a spindle rotate in the liquid until the time when rotation stops because the viscosity is too high, i.e. the material has gelled. Three different readings were taken for each sample and the average value calculated.

Determination of moisture uptake

The moisture uptake of the resin films was determined gravimetrically, according to method described by Osemeahon and Dimas (2014). 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 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 for each sample and the average elongation evaluated and expressed as the percentage increase in length.

Determination of density, turbidity, melting point and refractive index

The density of the resins was 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 was determined by using Supertek digital turbidity meter (Model 033G). To determine the effect of melting point on monomethylol urea (MMU), a melting point differential macrophase separation technique was developed. In this technique, MMU was introduced into a porcelain dish. The dish with it content was transferred into an oven set at $120^{o}C$ for curing. The mixture was removed periodically from the oven and stirred until the mixture gelled and finally solidified. The temperature was then raised to $150^{o}C$ and left for 5 min after which the sample was removed and cooled for observation. The experiment was repeated three times

Determination of formaldehyde emission

Formaldehyde 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 will be 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 water solubility

The solubility of MMU was determined by mixing 1 ml of the resin with 5 ml of distilled water at room temperature ($30^{0}C$).

Results and Discussion

Effect of pH on the gel time of MMU

Figure 1 shows the effect of pH on the gel time of MMU. The gel time of MMU increases with increase in the pH. This tendency can be explained in terms of separation of charges or double layer tendency due to the excess positive and negative charges in the colloidal system of MMU resin. At a low pH, the crosslinking reaction and the resultant MMU polymer have high molar mass and results in formation of solid polymer initially moldable solid but ending in infusible hard plastics. In the high pH of the alkaline condition, the tendency is formation of larger molecular methylol urea derivatives with crosslinks, hence, a more plastic solid capable of bonding with the adherends. Thus, at high pH the MMU are not just suitable for binder but are functional binder at mildly alkaline (Akpabio, 2012). Gel time is the time it takes for a mixed resin system to gel or become so highly viscous that it can no longer be considered workable or able to be handled. A thermoset resin system converts from a liquid mixture of chemicals to a solid material that has a highly cross-linked polymer as the major structural material. The gel time is the time when the polymer formation is in its early stages of cross-linking to the point that if the polymer gel state is disturbed then the final polymer will have properties that are not well established.

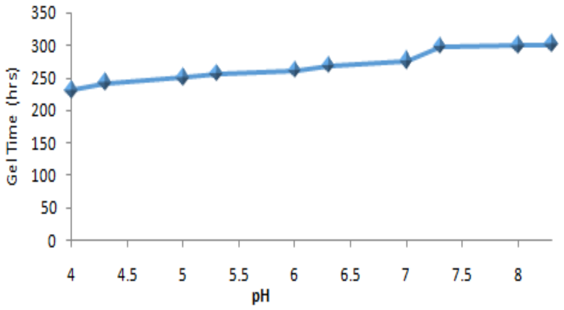

Fig. 1: Effect of pH on the gel time of MMU

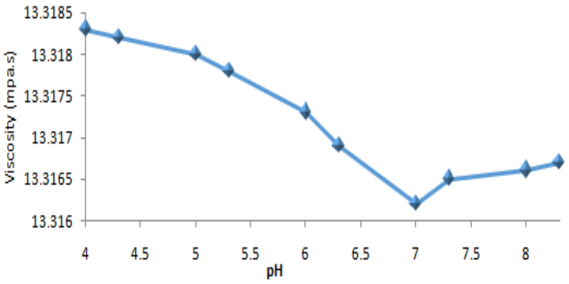

Fig. 2: Effect of pH on the viscosity of MMU

Effect of pH on the Viscosity of MMU

From the Fig. 2 above, the viscosity of MMU is seen to decrease with increase in the pH value of MMU. At a lower pH values, electrostatic repulsions are weak, and the particles present a higher association due to the possible function of hydrogen bonds, Vander Waal forces, and other weak forces (Adhikari *et al.*, 2010). When the pH increases, the association of the particles is destroyed due to the increase in electrostatic repulsion that are greater than the weak forces, and the aggregates break up because any sort of rearrangement disperses the fully ionized molecules to form small discrete particles. On the other hand, the decrease of viscosity values with increasing value of pH may be as a result of the greater significance of polymer compaction by shielding than the hydrophobic associations in an environment increasingly hostile to the hydrophobes (Stephanie, 20011). As revealed by the graph in Fig. 2, the viscosity of MMU decreases until a minimum is reached at 7, at pH 7 the charges are neutralized and the MMU resin loses its tendency to behave as a resin and at above pH of 7 it starts building up again (Akpabio, 2012). Another probable reason for this is that the reaction activity is low, because of less active site in the MMU molecules, thus, the higher the value of pH in the resin the lower the viscosity.

The knowledge of viscosity can help to characterized polymers and to determine indirectly molecular mass. It is the key for design processing operations that depend on the way that the product flows; for example, creaminess, thickness, smoothness, spreadability, pour-ability, brittleness and hardness. Control of the morphology and viscosity of lattice particles has been a well-practiced art within the industry for sometimes now, given its great importance in the determining the physical and mechanical properties of polymer system (Elham & Kamal, 2018).

Effect of pH on moisture uptake of MMU

Figure 3 is a graph of moisture uptake of MMU with changes in pH. The effect of moisture uptake is observed to decrease as the pH concentration increase, this could be as a result of the pseudo-hydrophobic build up as one moves from acidic to alkaline region on the pH value. In general hydrophilic polymers such as MMU contain a few hydrophobic units which can form temporary hydrophobically associating network in aqueous system in low concentration as pH increases (Udeozo *et al*., 2013). In large concentration rate, the pseudo-hydrophobicity, and the intermolecular network interactions becomes more significant and effective. The behavior may also likely, be attributed to reduction in hydroxonium ion charge density as the pH value increases because the polymer-water affinity is related to the presence of hydrogen bonding sites along the polymer chains, which create attractive forces between the polymer and the water molecules (Rey *et al*., 2001). The transport of water in a polymer network is related to the availability of molecular-sized holes in the polymer structure and this holes tends to close up with increasing pH value.

Waterborne coatings are susceptible to durability issues pertaining poor water resistance. The functional groups on polymer or copolymer resins that are used can undergo hydrogen or ionic bonding, unless the hydrophilic character is balanced with that of hydrophobic, the coating will either be water sensitive or the formulation will not have colloidal stability (Archibong *et al*., 2018)

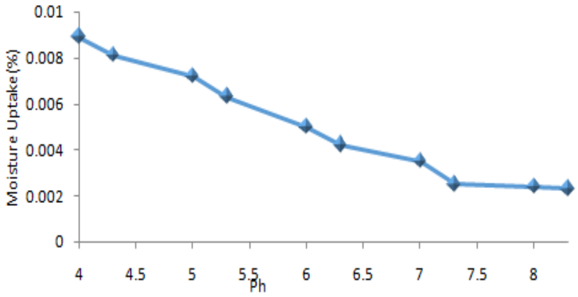

Fig. 3: Effect of pH on moisture uptake of MMU

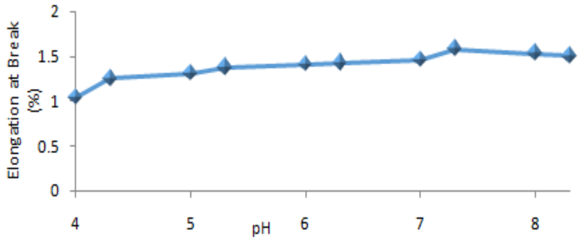

Fig. 4: Effect of pH on elongation at break of MMU

Effect of pH on Elongation at break of MMU

The effect of Elongation at break with changes on pH of MMU is shown in Figure 4. The elongation at break increases with increasing pH value, this may be due to intermolecular electrostatic repulsion which lead to lowering of the degree of cross-linking, thereby, leading to decrease in rigidity and increase in flexibility of MMU as the pH value increases. The further the pH deviates from pH7, the greater the loss in tenacity of a polymer, of which acidic conditions cause more severe degradation than basic conditions at pH levels equidistant from neutral (Kevlar.com 2017). This explains why at lower pH the elongation at break tends to be low compared to the higher pH value, as evidence on the sudden shot at the elongation at break value above pH 7 in basic condition on the figure above.

Elongation also known as fracture strain, is the ratio between change length and initial length after breakage of the test specimen. It expresses the capacity of a material to resist changes of shape without crack formation. The tensile strength is an important property for polymers that are going to stretched, resins for instance must have good tensile strength. Elongation at break can be a propel tool to determine the adhesion between phases, because of its sensitivity for load transfer between phases (Cakir *et al*., 2012; Hwang *et al*., 2012).

Effect of pH on the density of MMU

Figure 5 shows the effects of pH on the density of MMU, as the pH value increases the density of MMU decreases. The gradual decrease in the density of MMU with increasing pH, could be attributed to the fact that, methylolation reactions are favored at higher pH values, while, the condensation reactions are favored at lower pH, which are paused by increasing the pH. Condensation reactions result in the formation high molecular weight compounds with cross linkages, methylene linkages are also favoured by decreasing the pH (Akpabio, 2012). The formation of UF dimers with ether linkages had a minimum yield at high pH (Elham *et al.,* 2018). Molecular weight and viscosity build more during condensation stage. Density depends on free volume and packing efficiency of molecular chains. The reduction in density with increasing pH may also be as a result of the molecular features and morphology of MMU with increasing pH value. Density measurement is useful for the identification and characterization of different substances and a significant factor that affects the production cost and profitability of the manufacturing process (Kazys and Rekuviene, 2011).

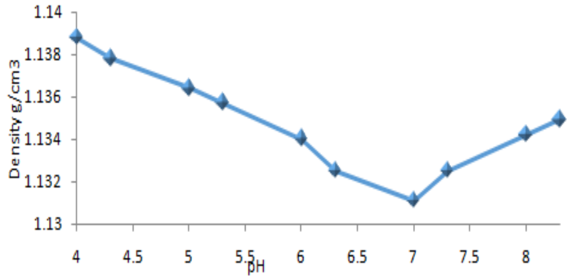

Fig. 5: Effect of pH on the density of MMU

Effect of pH on the turbidity of MMU

Figure 6 is a graph of the turbidity of MMU against the changes in pH. The turbidity tends to increase with increasing pH concentration. This may be due to the growth of large inter-polymer aggregate, because at a higher pH there's tendency towards sedimentation and fundamentally alkaline is a suitable place for sedimentation (Fatima & Ishak, 2017). The rise in turbidity can also be attributed to the progressive inrease in crystallite size and changes in morphologies responsible for light scattering. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted with no change in the direction or flux through the sample. When we have homogeneity and few particles, there will be less scattering; hence, higher scattering is observed when there is a non-homogenous system with lots of particles (Archibong *et al.* 2018).

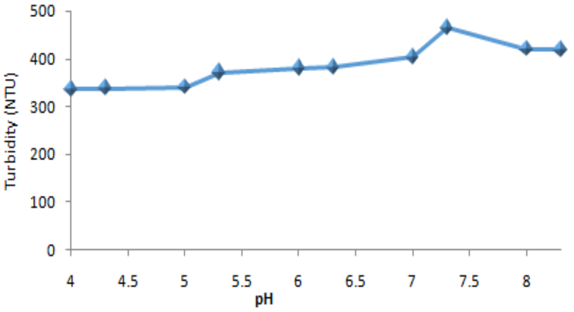

Fig. 6: Effect of pH on the turbidity of MMU

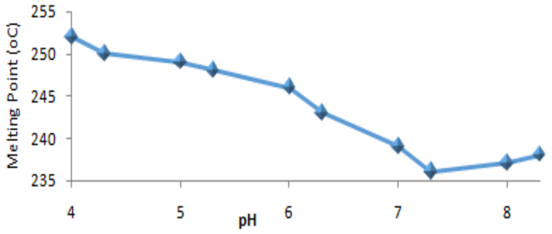

Fig. 7: Effect of pH on the melting point of MMU

Effect of pH on the melting point of MMU

Figure 7 shows that the melting point of MMU decreases with increase in pH value. The melting point of MMU is seen to decrease with increase in pH concentration of MMU. The steady decrease in melting point may be related to decrease in crystallinity and increase in atactic nature of MMU resin with increasing pH values. Atactic brings randomness and makes polymer amorphous that cannot crystallized and crystallinity brings about increase in melting point (Kim *et al*, 2011).

Akpabio (2012) opined that the proportion of higher molecular weight product in UF resin decreased substantially as the reaction pH increases, the decrease in melting point as observed may therefore, be a result of decreasing molecular weight with increasing pH value. And Ming Cao *et al.* (2017), also shows that at very low pH, the cross linking reaction is dominant, and as the number of cross-links increases, the polymer becomes rigid and so is its melting point, hence the decrease in melting point as the cross-link density decreases with increasing pH values. The opposing effect of gelation and viscosity relaxes at pH above 7.30 and allow rapid crosslinking and rigidity to kick start at pH 8 and above (Akpabio, 2012).

Thermal property, molecular weight, degree of cross linking and the level of rigidity of the polymer is related to the melting point. Rigidity and flexibility which can be determined from the thermal property of paint's binder, is a critical factor in their processing and application (Akinterinwa *et al*, 2015.

Effect of pH on the refractive index of MMU

Figure 8 is a graph of the refractive index of MMU against pH. It is observed that the refractive index of MMU increases with increase in pH value of MMU. This can be explained in terms of increasing of crystallite sizes that changes the speed of light which caused it to bend as the pH increases (Meydeneri and Karper, 2017). The gradual rise in the refractive index with increasing pH value, may also be due to the increasing discontinuities in the molecular structure of the blend, and the differences in the level of specific interaction in the resin misture thereby creating light scattering (Abdullah & Park, 2010). Refractive index is a fundamental physical quantity of materials. It describes how light or electromagnetic waves propagate through an optical medium. It is express as a function of the incidence angle and the refractive index of the material (Osemeahon and Dimas, 2014). The glossiness/shininess of a paint is a direct reflection of the refractive index of the binder.

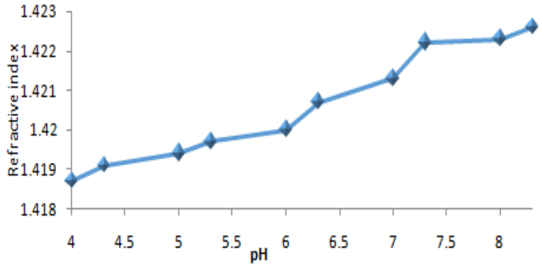

Fig. 8: Effect of pH on the Refractive Index of MMU

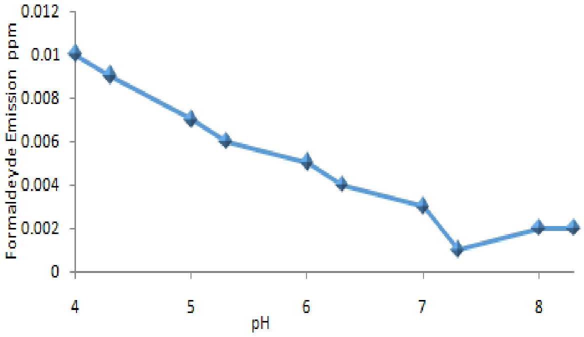

Fig. 9: Effect of pH on the formaldehyde emission of MMU

Table 1: Effect of pH on the water solubility of MMU

pH	Solubility
4.00	Soluble
4.30	Soluble
5.00	Soluble
5.30	Soluble
6.00	Soluble
6.30	Soluble
7.00	Soluble
7.30	Soluble
8.00	Insoluble
8.30	Insoluble

Effect of pH on the formaldehyde emission of MMU

Figure 9 shows the effect of pH on the formaldehyde emission of MMU. It is observed that as the pH value increases, there is a gradual reduction in formaldehyde emission until it reaches it optimum at pH 7.30. This may be as a result of reduction in stress during cure which reduces emission resulting from improved flexibility. In addition, pH increase behaves as an obstacle disrupting the MMU matrix and therefore, making it more difficult for the reactive group of urea and formaldehyde to come close and interact (Lee *et al*., 2011, Abdullahi and Park, 2010).

The decrease in formaldehyde emission may also be due to possible interaction between MMU wither either the acidic or alkaline pH, which may hinder the condensation reactions in the urea formaldehyde resin, hence hindering the release of formaldehyde from the reaction (Akinterinwa *et al*., 2015). It is important to determine the formaldehyde emission from synthesized urea formaldehyde resin before its application most especially because of the health challenge it poses to human and its environs. High emission of formaldehyde from latex paint has been reported by Salthmalmer *et al.* (2010). Recently much effort has been made to reduce formaldehyde from building materials (Lee *et al*., 2011).

Table 1 presents the effect of pH on the solubility of MMU composite. It is observed that the resin is soluble in water up to pH of 7.30, after which the blends form dispersions in water. When the net charges of an ionic polymer approaches zero, attractions between oppositely charged units leads to globule-like conformation that most often lead to insolubility in pure water Also, the effect of interchain repulsions due to a higher proportion of negatively charged with increase pH value allows hydrophobes to take part at least to some extent in intramolecular associations. This increasing hydrophobic behavior is expected as the pH value increases (Fatima & Ishak, 2017). In the development of amino resins for emulsion paint formulation, resin solubility or dispersability in water is an important factor in the resin's acceptability.

Conclusion

Experiment was conducted on the effect of pH on synthesis of MMU. The viscosity and gelation were observed to move in alternate direction, the trend was such that the gel time is increasing with pH but the viscosity is decreasing, from these observations, it shows there must be a compromised between gelation and viscosity of the MMU preparation for it to act as a binder. Others physico-chemical parameters like the melting point, moisture uptake, formaldehyde emission, were observed to decrease with increase in pH value, while Turbidity, Refractive index, Elongation at break increases with increasing pH value which are in consonance with literature (Osemeahon and Archibong, 2011). MMU resin therefore, can be a suitable binder at pH 7.3 in the alkaline condition, because at this pH value the opposing effect of gelation and viscosity relaxes and beyond this point the binder is insoluble in water and rapid crosslinking and rigidity kick start above this pH.

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