Production of Monomethylol Urea for coating application: Effect of Temperature on Synthesis.

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Abstract

This work proposes Monomethylol urea (MMU) resin as a binder, MMU was synthesized using the one step process, was then subjected to FTIR analysis to confirm chemical reaction, and later investigated to determine the suitable temperature and its effect on the properties of MMU. Properties also determined include; gel time, elongation at break, moisture uptake, refractive index, formaldehyde emission, density, turbidity and solubility in water. All the properties investigated displayed its optimum at $60^{o}C$, with the exception melting point that exhibited optimum beyond $60^{o}C$. What this implies to the paint manufacturer is that the synthesis of MMU should be carried out at $60^{o}C$ for optimum result, because it is also at this temperature value that the resin is soluble, the formaldehyde emission and moisture uptake is low, density and viscosity is high.

Keywords: Monomethylol urea, temperature, coating, solubility. Resin.

Introduction

The individual molecules that make up polymeric materials are very large and have an extended chain-like shape that results in an entangled structure. This entanglement is beneficial in some respects, for instant the high levels of elongation that most polymers exhibit without breaking are due in large extent to chain entanglement. However, this entanglement also restricts the freedom required at a molecular level to organize into crystals. Consequently, no polymer under normal processing conditions is fully crystalline, and some polymers do not crystallize to any significant degree. This lack of a predictable and repeated structure gives rise to a situation where changes in temperature always influence the mechanical properties of the materials (Micheal *et al.*, 2011).

If the polymer is forced to change shape, it does so by breaking. Flexibility can occur when the chains and bulky side- groups that are tightly packed are subjected to temperature increase and some freedom of movement introduced (bulky side-groups, for example, may reduce the flexibility of a polymer, as they prevent the chains sliding past each other). Temperature increase reduces bulky side-groups influence, thereby making the amount of rotation that can occur around the linking bonds easier.

Clearly, the ability of a resin to spread without becoming overly thin, at the highest temperature, or overly viscous, at cold temperatures for both resin systems, is very important to be taken into account during resin synthesis. Therefore, understanding the composite material behavior under different temperatures is an important parameter to be considered because it can, in many cases, determine the upper bound on the temperatures at which a material has suitable properties (Weidong and Liangchi 2018).

Temperature has the most significant influence on flow properties/behaviors of the polymeric material. When a substance is heated, energy comes in and can be used to increase the kinetic energy of the molecules, causing an increase in temperature, or the heat can be used to increase the potential energy of the molecules, causing a change in the state. With increasing temperature, growing and propagating polymer chains become more flexible as a result of decreased viscosity and react to a greater extent, resulting in a more complete polymerization reaction and greater crosslinking. This increase in polymerization may lead to improved mechanical properties (letsch 1987).

The mechanical properties of polymer are dependent strongly on temperature and strain rate. This is due to the polymer amorphous microstructure which consists of the back bone molecular microstructure formed by the primary covalent bond and the sub-microstructures linked by the secondary bonds such as hydrogen bond and van der Waals' force. With increasing temperature, structure relaxation would become faster and in turn affect the conformation of polymer microstructure and its properties (Weidong and Liangchi 2018).

The dependency of thermoset properties with temperature and time is referred to as viscoelasticity and plays a vital role in the long term performance of thermosets. Accordingly, in this work the influence of varied temperatures on Monomethylol Urea synthesis by the one step as earlier described in our work resulted in a decrease in the number of UF particles around the MMU. Noticeably, the rate of hydrolysis was increased with temperature.

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 (6.0g) was made to react with one moles of formaldehyde (8.11ml) 37-41% (w/v), using 0.02g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 7.30 by using $0.1MH_2SO_4$ and $0.5MNaOH$ solutions. The solution was heated in a thermostatically controlled water bath at 50^0C. The reaction was allowed to proceed for 60min after which the resin was removed and kept at room temperature (30^0C).

Determination of Gel Time and Viscosity

Gel time was found out by gel-time meter. The temperature was set for 121°C in gel time meter and filled with liquid paraffin till the brim of the container. The heating system and stirrer were switched on. 10 gms of the sample was weighed and it was taken in a test tube and placed vertically in hot paraffin bath using wooden holder. Resin level in the tube was taken such that it was well within hot bath. A glass rod was placed in test tube and it was locked to the spindle drive with magnetic couple. The spindle was now rotated. When the top spindle rotates, magnetic coupling and bottom fin also started rotating along with glass rod. When the resin started solidifying, rotation of glass rod was resisted, which in turn stop rotation of bottom fin. Upper fin, still rotating freely, come into contact with static one, and the time was noted from the stopwatch. The gel-time was found out (Ganeshram etal., 2013).

Viscosity was determined by adopting Ganeshram etal., 2013 method, using Brookfield viscometer. Spindle number was selected and the speed of motor was set. The temperature of the solution was measured using temperature probe. The spring cap was removed and the spindle was fixed. It was immersed upto the mark in the resin and the motor switched on. Spindle rotates inside the solution and produces shear, which gives value of viscosity. It was carried out at a temperature of 25°C.

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 was 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 5min after which the sample was removed and cooled for observation. The experiment was repeated three times

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 was 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 was 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 50mm long, 10mm wide and 0.15mm thick was brought to rupture at a clamp rate of 20mm/min and a full load of 20kg. Three runs were carried for each sample and the average elongation evaluated and expressed as the percentage increase in length.

Determination of formaldehyde emission using UV-Spectrophotometer

To determine any possible absorbance by formaldehyde, deionized water was used as the blank. The cuvette was rinsed several times with tap water followed by deionized water, it was then filled with deionized water, and placed in the holder, and the spectrophotometer was blanked at 563 nm. The sample was then put into another cuvette and the absorbance was noted at the same wavelength of 563 nm, with concentration recorded

Determination of Water Solubility

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

Results and Discussion
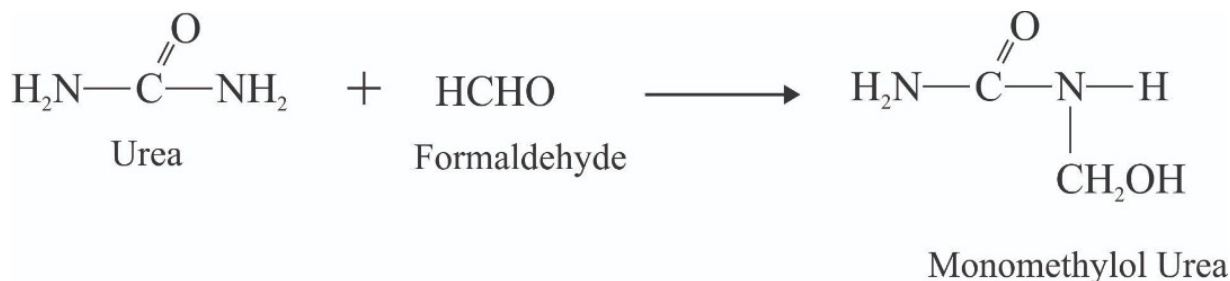
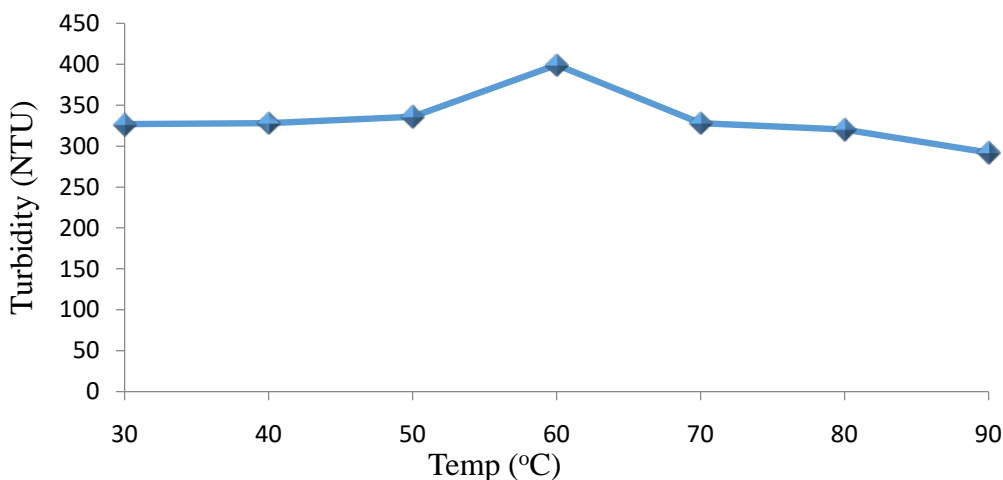

1 Effect of Temperature on Turbidity of MMU

Fig.1 Effect of Temperature on Turbidity of MMU

Fig. 1 stands for the graph of the effect of temperature on the turbidity of MMU. The turbidity of the resin is seen to increase at the onset with increasing temperature and later start declining. The polymer chains could possibly have experience a strong frustration in chain packing due to the formation of large loops at higher temperatures and inability of these loops to be incorporated in the crystalline structure, resulting in the decreasing turbidity (Bin *et al.*, 2016). The rise in turbidity may also be attributed to the progressive increase in crystallite size and changes in morphologies which is responsible for light scattering.

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 *and* Osemeahon, 2019). The refractive index gives indication of the turbidity. Light interaction

with a colloidal system is its turbidity. Turbidity actually derived its principle from light scattering.
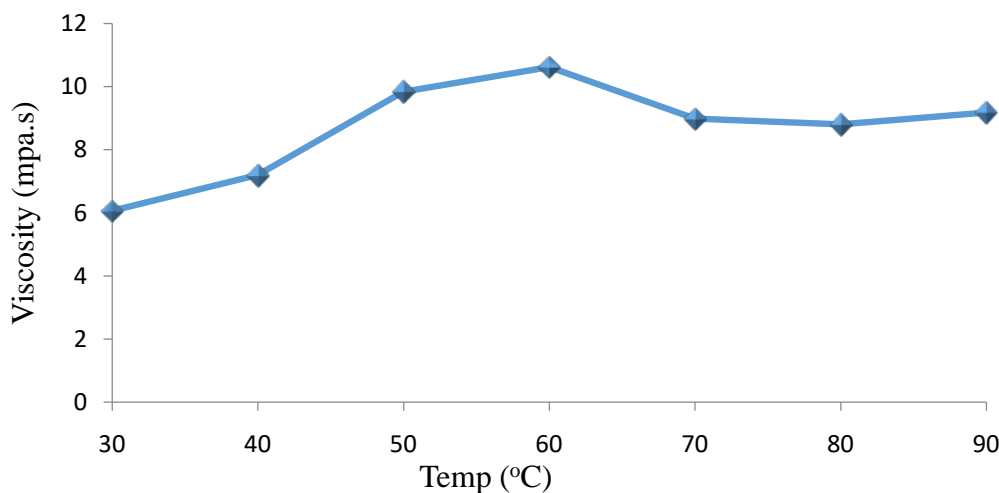
2 Effect of Temperature on the Viscosity of MMU

Fig 2. Effect of Temperature on the Viscosity of MMU

Fig, 2 is a graph of viscosity of MMU against Temperature. The viscosity is observed to increase with increasing temperature until at $60^{o}C$, when it starts to decrease. This could be attributed to the fact that cross-linked molecular chains of thermosets are further linked to each other by entanglements and strong secondary bonds especially at low temperatures. During temperature elevation, the secondary bonds break and the entanglements between polymer chains loosen, so that the cross-linking molecular structure becomes weak. Also at higher temperatures the particles that were abinitio associated, due to the possible function of hydrogen bonds, Vander waal forces, and other weak forces will begin to dissociate (Adhikari *et al.*, 2010).

The increase in viscosity at the onset may also be attributed to the variation of the different chain lengths, and the increase in molecular weight of the polymer which in turn gives rise to increase in viscosity (Afzal *et al.*, 2013).

The knowledge of viscosity 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 determining the physical and mechanical properties of polymer system (Hussain and Nasr, 2010).

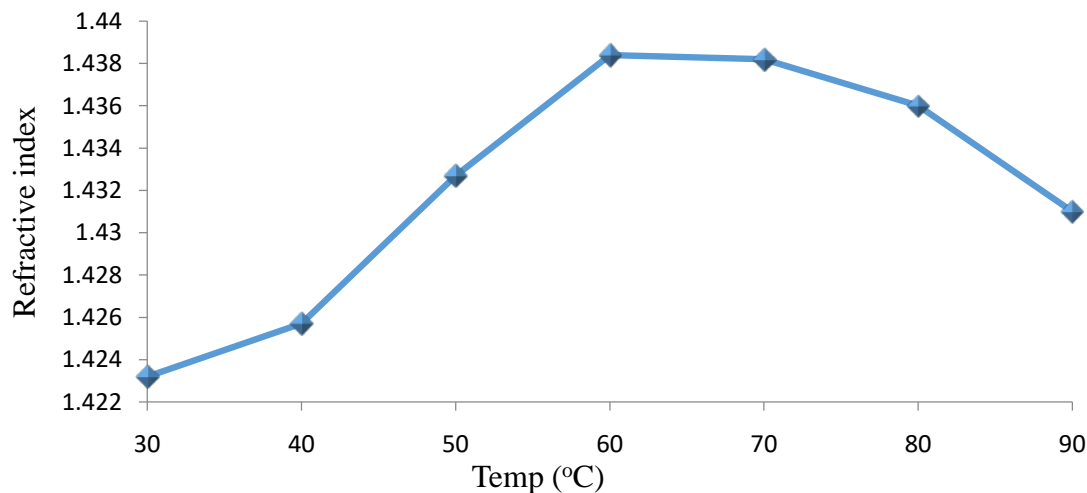## 3 Effect of Temperature on the Refractive index of MMU

Fig.3 Effect of Temperature on the Refractive index of MMU

Fig. 3 represents the graph of the refractive index of MMU with changes in temperature. The refractive index rises first until it got to its peak at 60°C where it began to fall. Refractive index been the resistance under which light passes through a material, at a low temperature there is a greater resistance of the flow of light into the MMU, that translate to increase in refractive index, but as the temperature increases the resistance to flow becomes less and the refractive index thus decreases. It could also be as a result of density of the MMU, when the temperature is increased, the density drops which results in the refractive index decreased (Yumiko *et al.*, 2010). The fall could also be as a result of decreasing of crystallite sizes that changes the speed of light which caused it to bend as the temperature increases (Meydeneri *et al.,* 2017). The gradual fall in the refractive index with increasing temperature value, may also be due to the decreasing discontinuities in the molecular structure of the blend, and the differences in the level of specific interaction in the resin mixture thereby creating less light scattering (Qi *et al.,* 2002; Liem *et al.,* 2002). They may also have been an alteration in the crystallinity of the system with increasing temperature due to decrease in the number of various chain lengths that make up the copolymer (Jain, 2008).

Refractive index is a surface phenomenon, which is expressed as a function of the incidence angle and refractive index of the material, the surface roughness and a geometrical shadowing function. Gloss is a necessary coating property when the purpose is for surface aesthetic or decoration (Kaygin and Akgun, 2009; Yumiko *et al.*, 2010). Glossiness of the paint shows how it

reflects light and shininess, in short, gloss is a measure of the ability of coated surface to reflect light.

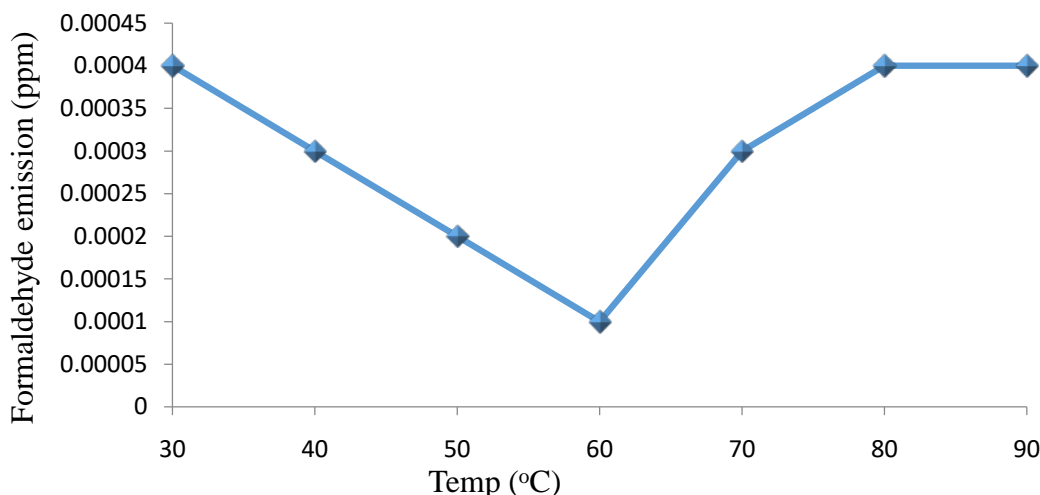## 4 Effect of Temperature on the Formaldehyde Emission of MMU

Fig. 4 Effect of Temperature on the Formaldehyde Emission of MMU

Fig 4 is a representation of the effect of temperature on the formaldehyde emission of MMU with increasing temperature. The formaldehyde emission is noticed to decrease with increasing temperature until it reaches its minimum at $60^{o}C$, then it began to rise. The probable explanation for this may be that low temperature 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 at lower temperature resulting in lower formaldehyde emission but at higher temperatures the reverse is the case (Abdullahi and Park, 2010; Ezeriba *et al.,* 2014).

It may also be that there was a reduction in stress during cure which reduces emission resulting from improved flexibility with increasing temperature until after $60^{o}C$ where stress tends to increase and rigidity sets in, because the higher the temperature, the better the interfacial adhesion, possibly resulting in tight matrix (Pracella *et al.*, 2006).

A serious drawback of urea formaldehyde resin is the emission of the hazardous formaldehyde during cure. The issue of formaldehyde exposure in homes is longstanding and has been studied overtime. It is therefore important to determine the formaldehyde emission from synthesized urea-formaldehyde resin before its application application (Derkyi *et al*., 2008).

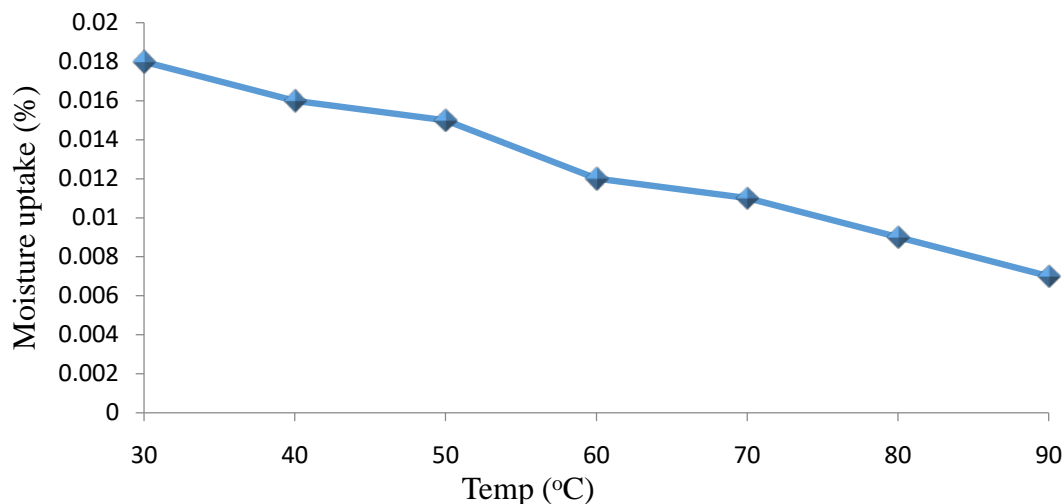## 5 Effect of Temperature on the Moisture Uptake of MMU

Fig. 5 Effect of Temperature on the Moisture Uptake of MMU

Fig.5 is the graph of the effect of moisture uptake of MMU against temperature. The moisture uptake is seen to decrease with increasing temperature, this is to be expected as the increasing temperature causes polymerization and crosslinking to form a tighter network and therefore increasing the density and reduces moisture uptake. Such observations can also be ascribed to a reduced chain length of the oligomers between crosslinks, this shortening of the chains between crosslinks enhances the elastic resistance to the swelling stress and therefore lowers the degree of moisture uptake (Mohsen, 2016). It could also be that as the temperature increases there is also increase in reaction rate and agglomeration resulting in a smaller surface area of MMU exposed to water, this is because the higher the temperature, the better the interfacial adhesion, possibly resulting in tight matrix (Pracella *et al.*, 2006).

Polymeric binders play a major role in moisture transport properties of paint, because it is one of the major constituent. Waterborne coatings are susceptible to durability issues pertaining poor water resistance. The functional groups on polymers or copolymer resins that are used can undergo hydrogen or ionic bonding, unless the hydrophilic character is balanced with that of the hydrophobic, the coating will either be water sensitive or the formulation will not have colloidal stability

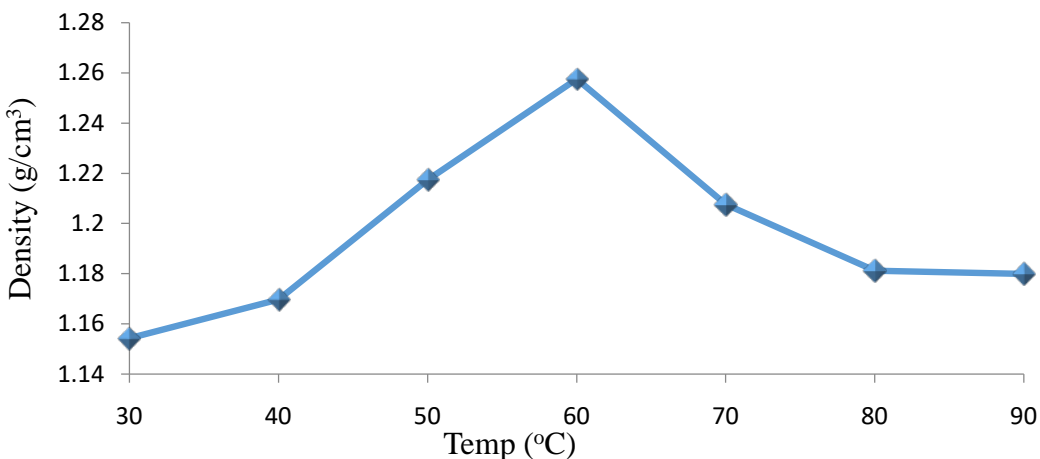## 6 Effect of Temperature on the Density of MMU

Fig.6 Effect of Temperature on the Density of MMU

Fig. 6 is a graph representing the effect of temperature on the density of MMU. The density initially increases with increasing temperature until it got to $60^{o}C$ then it starts sloping down. The initial increased in density could be owing to the effect of polymerization proceeding with crystallization simultaneously. The rate of polymerization becomes larger due to the activation of effectives sites and thus the initial increase in density with temperature. This is to be expected as the increasing crosslinking temperature causes the polymerization to form a tighter network and therefore increasing the density (Park *et al.,* 2002; Ayuob *et al.*, 2013; Archibong *et al.*, 2018). The density of MMU decreases gradually from $60^{o}C$ upward, this may be as a result of rearrangement of molecular chains during chain folding. ''This reeling in'' of chains during crystallization makes the disentanglement of the chain from the solution more pronounce, resulting in a lower density (Bin *et al.*, 2016). Meanwhile, with increment of the size of polymer crystals, the gap between crystals as well as the membrane porosity increase which also result in a density decrease. The effects of saturated temperature are complex, higher saturation temperatures not only enhances the free volume of polymer and the mass transfer, it also result in decrease in densities (Yajun and Sanjiu, 2015). Apparently at higher temperature long polymer chains become entangled and are less easy to crystallize which can also be seen as lower density (Hamed *et al*., 2010).

The density is a very significant factor affecting the production cost and profitability of the manufacturing process. A reduction in the density reduces the raw material cost and therefore

decreases the manufacturing costs. So, it is very important to measure the density of coating material with a good accuracy during processing.

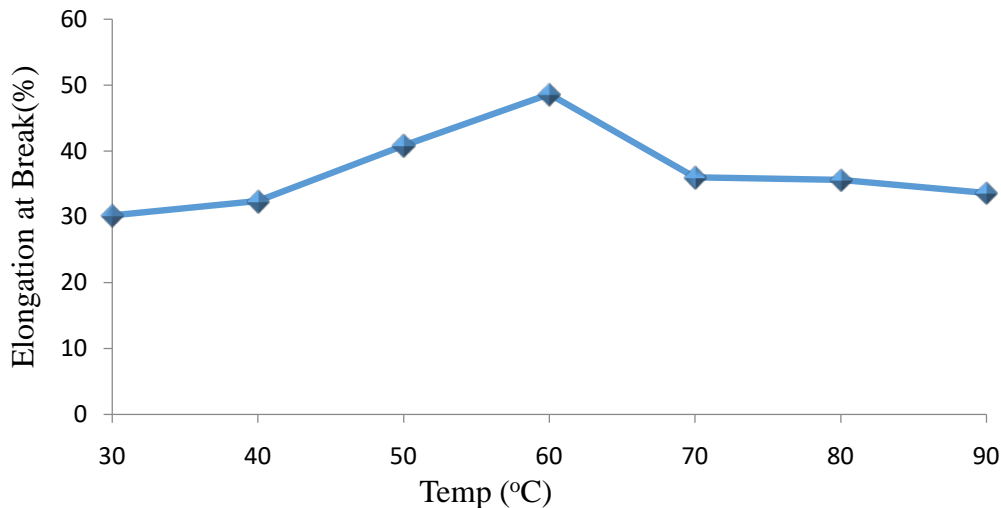## 7 Effect of Temperature on the Elongation at Break of MMU

Fig.7 Effect of Temperature on the Elongation at Break of MMU

Fig.7 represent the graph of the effect of temperature on the elongation at break of MMU. The elongation at break increases at first then begin to decline. The elastic moduli of polymers are controlled by binding forces (mainly Van-der-Waals forces), and unfreezing of molecular mobilities (dispersion steps). The former is responsible for the elastic behavior, the latter for viscoelasticity (Bascheka et al., 2009). At low temperatures, the stiffness of sub-microstructures formed by entanglement of side groups is large enough so that they can vibrate together with the main chains, thereby resulting in increase in elongation at break. However, with increasing temperatures, the secondary bond starts to fail due to β-relaxation, making the entanglement effect weaker and thus elongation at break decreases (Weidong and Zhang, 2018). This slight reduction in elongation at break of the MMU composites with temperature increase can also be attributed to relative increase of urea/formaldehyde matrix amount reducing adhesion force against shear fracture of polymer interface under load. The brittle character of these composites is dominated by the matrix fraction, the higher this fraction, the steeper is the composite britility (Manchado et al., 2001).

The elongation at break is an important property for polymers that are going to stretched, resins for instance must have good elongation at break. The structure of thermosetting resins also leads to some unwanted mechanical properties that limit their structural applications because they are

relatively brittle. 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).

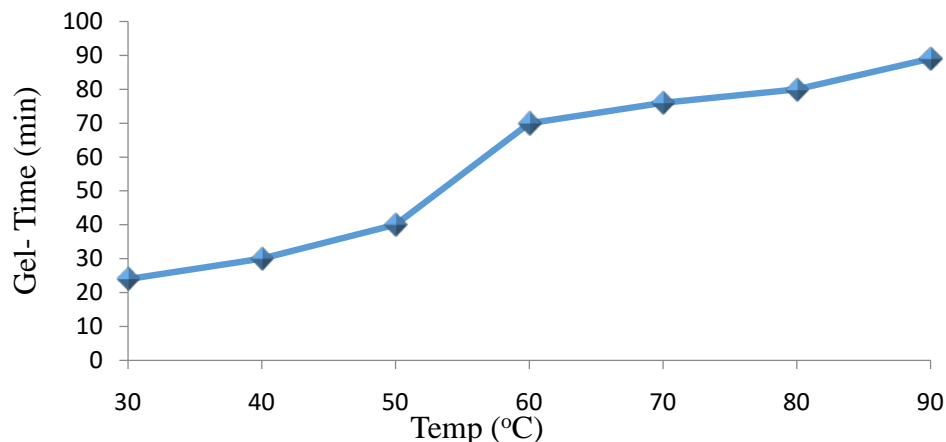## 8 Effect of Temperature on the Gel-Time of MMU

Fig.8 Effect of Temperature on the Gel-Time of MMU

Fig 8 represent the effect of temperature on the gel-time of MMU. The gel time is observed to increase with increasing temperatures, at first the increase is slow then it shots upward. This behavior may be the result of the interaction of urea and formaldehyde enabling the formation of 3D network structures contributing to mechanical properties including covalent bonding, crystallization, and molecular secondary forces such as hydrogen bonding, molecular entanglements, and hydrophobic interactions as the temperature increases (Lihui *et al.,* 2007). At higher temperatures, 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.

Gelation marks the end of the "working time" of the resin, resin is no longer liquid, any attempts to "work" it shape and make it smooth-- is ineffective and may compromise the properties of the composite.

Thus, gel time is an important factor in the manufacture of all composites, especially with paint binders. The gel point is the temperature or time at which the first set of covalent bonds connects across the sample (the onset of a three dimensional network) and the molecular weight becomes infinitely large (Holly *et al.,* 2004).

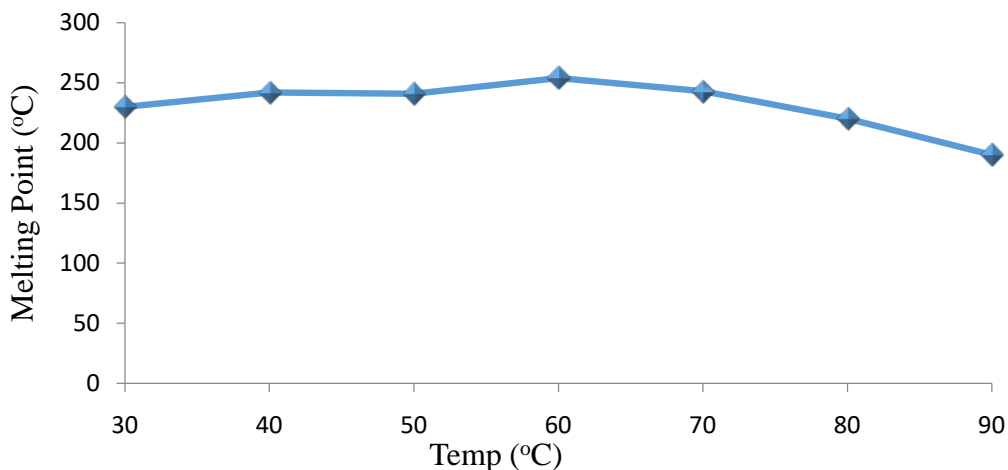## 9 Effect of Temperature on the Melting Point of MMU

Fig.9 Effect of Temperature on the Melting point of MMU

Fig 9 represent the graph of effect of temperature on the melting point of MMU. The melting point is seen to increase continuously as temperature increases up until $60^{o}C$ then at above this temperature it starts descending with further temperature increase. The increased in melting point with increasing temperature may be as a result of the fact that crystallinity increases resulting to increasing melting point until above a critical temperature, this crystallinity also decreases with increasing branch length, and then the inability of the longest chains to be incorporated in the crystalline structure (Lihui *et al*., 2007). The decrease in melting point as observed may also be as a result of decreasing molecular weight with increasing temperature. It may also be that at very low temperature, the cross linking reaction is dominant, and as the number of cross-links increases, the polymer becomes rigid and so is its melting point (Ming Cao *et al.,* 2017). The decrease in melting point with increasing temperature interval above $60^{o}C$, may also be attributed to molecular disentanglement, debonding and decrystallization since there are many non- interacting segments such as dangling ends, stray chains, and loops existing within the MMU system (Weng *et al*., 2007).

Thermal property, molecular weight, degree of cross linking and the level of rigidity of the polymer is related to its melting point. The melting points of the two extrems appear different which probably could result from different contributing factors. In the coating industry, the melting point of a binder is related to its thermal resistance as well as to the brittlity. Urea formaldehyde resins are made-up of molecules that cross-link into clear hard plastics (Afsoon *et al*., 2011).

Table 1. Effect of Temperature on the Water solubility of MMU

Temperature (^{o}C)	Solubility
0	Soluble
30	Soluble
40	Soluble
50	Soluble
60	Soluble
70	Insoluble
80	Insoluble
90	Insoluble

Table 1 above is a representation of the effect of temperature on the solubility of MMU. MMU is observed to be soluble in distilled water to about 60°C and it becomes insoluble at temperatures beyond this values. The solubility of a given polymer in a given solvent is favored if the solubility parameters of polymer and solvent are nearly equal, at higher temperatures the solubilty parameters of MMU resins and that of the solvent are far apart (Ming *et al.,* 2017). Also, the effect of interchain repulsions due to increasing temperature may allow hydrophobes to take part at least to some extent in intramolecular associations.

The development of amino resins for emulsion paint formulation requires an understanding of the solubility of the resin in water, it is important from both the technical and processing point of view.
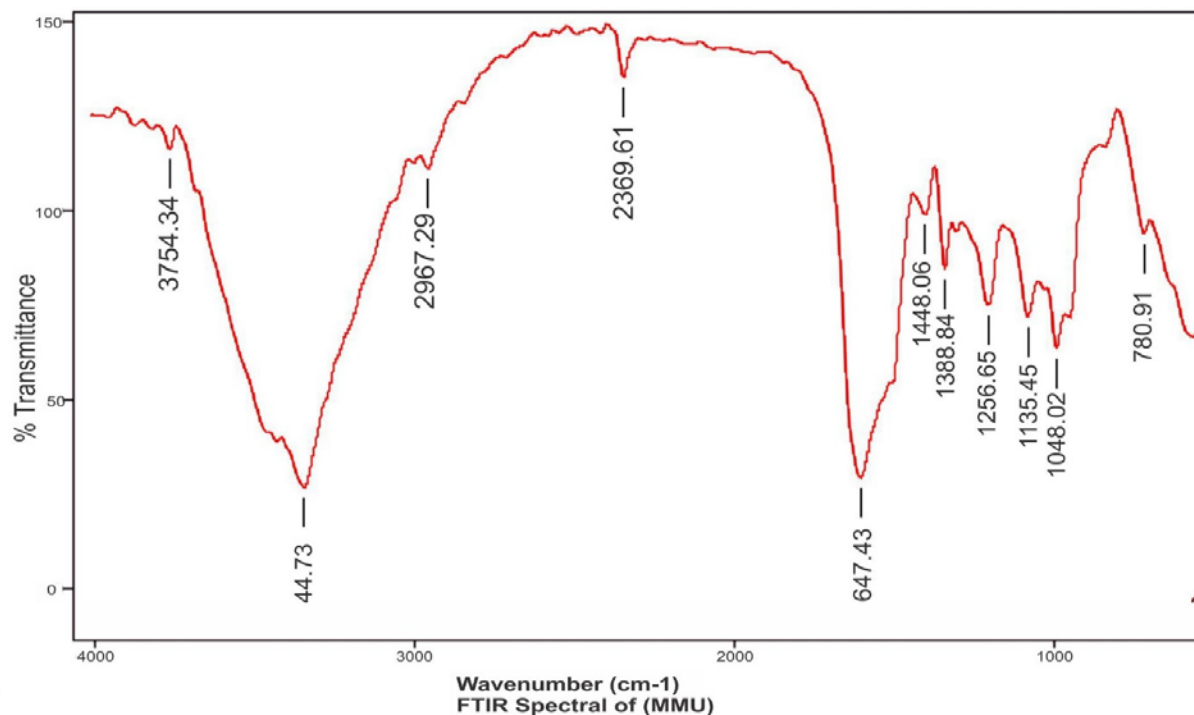
10 FTIR Spectroscopy of MMU

Fig. 10 FTIR spectra of Monomethylol Urea

The FT-IR spectra of MMU shows the appearance of a broad band in the region 3754.34 cm^{-1} through 3344.73 cm^{-1} indicating the presence (OH) on the monomethylol urea. The appearance of strong bands 2967.29 cm^{-1} and 2369.61 cm^{-1} indicates the presence N-H, the peak at 1647.43 cm^{-1} is due to C=O of urea, the bands at 1448.06 cm^{-1} and 1388.84 cm^{-1} is due to CH$_2$ of methylene bridge and the bands at 1256.55 cm^{-1} through 1048.02 cm^{-1} was due to characteristic C-O-C ether linkage stretching (Abbas *et al.*, 2014).

Conclusion

The search to better the hampering factors like, poor water resistance, formaldehyde emission, brittleness and hardness associated with UF is undergoing trials from different dimensions. In this paper, the effect of processing temperature on the synthesis of Monomethylol urea was studied in conjunction with some physical properties that can be harness for a better paint formulation.

The formaldehyde emission, moisture uptake and elongation at break were within environmentally friendly level in the coating industry in terms of safety, water resistance and flexibility.

This work will allow processing of MMU binder with low formaldehyde emission, more flexible and resistance to water be design at optimal temperature for paint formulation.

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