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Research Article

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Synthesis and Characterization of Monomethylol Urea (MMU) for possible application as an Emulsion Paint Binder

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Abstract In our quest to further reduced formaldehyde emission, improve water resistance properties, and introduce more flexibility into amino resin binders, monomethylol urea (MMU) was synthesized and compared with dimethylol urea (DMU) and trimethylol (TMU) urea using the one step process with some modifications. The chemical structure of MMU was characterized with FTIR spectroscopy which shows interactions took place. The cured polymer resin showed improvement in moisture uptake, elongation at break, refractive index, turbidity, dry time and viscosity. Such properties makes monomethyol urea (MMU) resin a more highly promising binder for emulsion paint application.

Keywords Monomethylol Urea, Dimethylol urea, Trimethylol urea, Binder, Emulsion Paint

Introduction

The modern household presents a wide range of conditions which the paint must protect against. The bathroom and kitchen are moist, warm areas which may promote the growth of mould. The living area needs to be bright, comfortable and, where young children or pets are around, easily cleaned. Paints are made for all of these situations as well as other paints for cars, lane markings on roads and for the protection of ships, underground storage vessels etc.

Many surfaces believed to be satisfactory without coating are actually attacked by weather, chemicals, atmospheric pollution or other factors and must be protected before certain uses. The wide variety of surfaces which must be protected and decorated has given rise to an infinite number of coating agents such as paints and varnishes. Not only to protect such surfaces but also to decorate them or to provide special purposes. It obliterates the surface on application and provides colour to it [1].

Water based paints are gaining popularity with the public’s efforts to avoid using paints that involve harmful solvents and dangerous chemicals in its application and cleanup. Whereas water based paints grip well to almost any surface and are weather- resistant. Also, doesn’t dry, crack or fade in the sunlight. They are less likely to attract the growth of mildew. It can be used on almost all types of surfaces without any pre-treatment. They have a less potent odor and take less time to dry. They don’t become brittle over time and require less ventilation than oil paints. They also have more elasticity than oil based paints. They are eco-friendly in nature, have better colour retention than oil based paints which fade and chalk with time. Water is used as a medium to carry the colour pigment to the surface that is being painted. By the time the paint dries, the solvent evaporates completely. These paints have very little risks for humans and animals around because the only thing that evaporates and enters the air is hydrogen and oxygen [2].

Paints are essentially a mixture of a solvent, a binder (that sticks to the surface) and a pigment (which provides colour, opacity and protection of the surface concerned). Paint quality is majorly determine by the quality of its binder, it also follows that the higher the quantity of a binder in a paint formulation the better the quality of that paint. It is the constituent that holds the pigments and other additives together and bind them onto the surface painted

Urea formaldehyde (UF) hardness, brittleness, Formaldehyde emission and poor water resistance places limitations on it usage and general acceptability. Typically, this resin compositions contain a substantial molar excess of formaldehyde, some of this excess is released upon curing of the resin during the manufacture. It is also well known that formaldehyde continue to be released from panels even after the manufacturing process is completed. It is therefore necessary and urgent to propose an efficient solution to avoid these drawbacks, allowing manufacture of paint with low formaldehyde emission, as well as introducing flexibility and water resistance to paint [3].

Modification of the resin by decreasing the molar ratio of formaldehyde will further decrease the present formaldehyde emission and brittleness associated with tetra, tri, and dimethylol urea. These actions will therefore introduce MMU as a promising candidature for paint formulation while producing a flexible, water resistant and non-brittle paint binder. Also, changing synthesis conditions of resins provides relatively good possibilities of designing the structure and technical properties of resins (Kim, M.G. 2011). Very broadly, the chemical structure of UF resins can be alter by varying conditions like it pH, Temperatures, catalyst and the kinetics.

Materials and Methods

Resin Synthesis

MMU was prepared using the one step process (OSP) as reported by Osemeahon and Barminas [4] 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 0.1M $H_2SO_4$and 0.5M NaOH solutions. The solution was heated in a thermostatically controlled water bath at 50 °C. The reaction was allowed to proceed for 60min after which the resin was removed and kept at room temperature (30 °C).

Determination of Formaldehyde Emission

Formaldehyde was carried out using the standard 2h desiccator test as described by Osemeahon and Dimas, 2014. The mold used was made from aluminium foil with a dimension of 69.9 x 126.5mm and thickness of 12.0mm. The emitted formaldehyde will be absorbed in 25.0ml of water and was analyzed by a refractometric technique using Abbe refractometer. Triplicate determinations was made for the samples and the average value taken.

Determination of Moisture Uptake

The moisture uptake of the resin films was determined gravimetrically, according to method described by Osemeahon and Dimas [3]. 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 Water Solubility

The solubility of MMU was determined by mixing 1ml of the resin with 5ml of distilled water at room temperature (27-30 °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 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 ^oC 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 ^oC

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

Determination of Viscosity and Gel Time

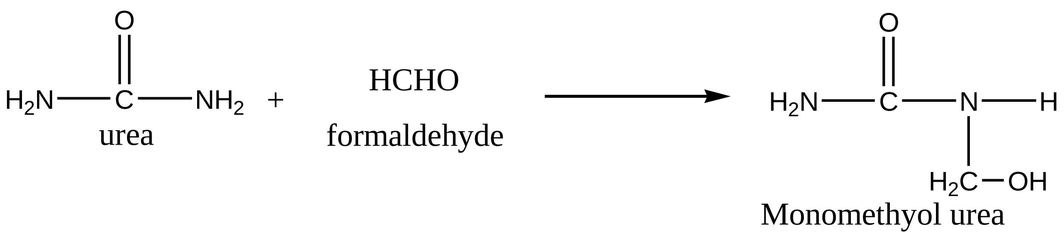
Viscosity and gel time was carried out according to method described by Osemeahon and Archibong [5]. A 100ml Phywe made of graduated glass macro-syringe was utilized for the measurement. The apparatus was standardized with 60% (W/V) sucrose solution whose viscosity is 5.9mpa.s at 30 °C. The viscosity of the resins was evaluated in relation to that of the standard sucrose solution at 30 °C. Three different readings were taken for each sample and the average value calculated. The gel time of the resin was determined by monitoring the viscosity of the resin with time until a constant viscosity profile is obtained.

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.

Result and Discussion

Formation of Monomethylol urea



IR Spectroscopy of MMU

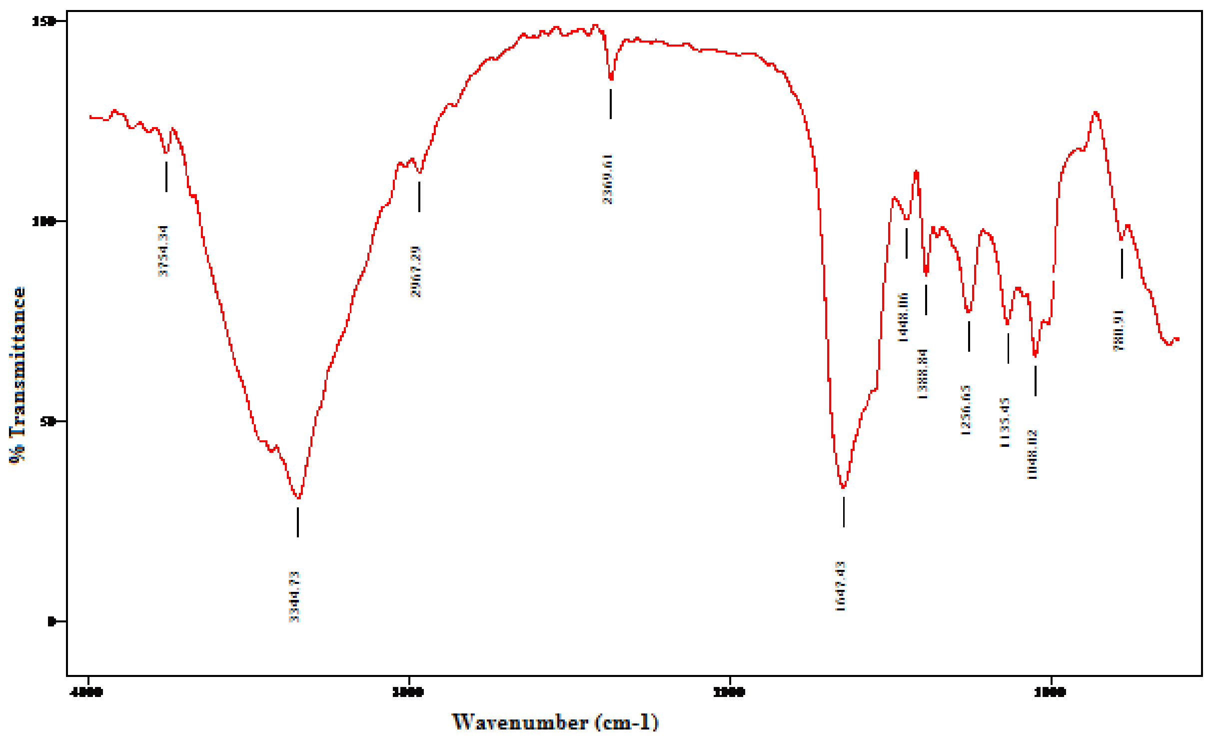


Figure 1: FTIR Spectra of Monomethylol urea

Figure 1 shows the spectral of MMU. In the spectra, the broad band stretching from 3700 through 2700 cm^{-1} can be attributed to O-H group which overlapped with that of water and N-H group of the methylol Urea and the small narrow peaks attributed to non- bonding O-H stretching vibration. The peaks at 2967-2369 cm^{-1} can be associated with sp^3 C-H stretching vibration, while the sharp peaks at 1648-1388 cm^{-1} can be associated with aliphatic nitriles, while. Peaks between 1256-1135 cm^{-1} can be progressively associated to the stretching carbonyls (C=O) [6]. This has given credence to the fact that reaction actually took place during the synthesis of urea and formaldehyde.

Comparism of some physical properties of Trimethylol Urea (TMU), Dimethylol Urea (DMU) and Monomethylol Urea (MMU) with acceptable standard in the coating industry

Properties	MMU	DMU	TMU	Accepted Level in the coating industry	Reference
Refractive Index	1.4187	1.4210	1.4400	1.4000(minimum)	
Viscosity(mpa.s)	12.20	10.30	11.40	3.11-38.00	
Elongation at break (%)	32	26	23	124	[7]
Formaldehyde Emission (ppm)	0.0330	0.0860	0.1051	0.08 (maximum)	
Moisture Uptake (%)	2.5	3.0	4.102	3.00 maximum	
Density (g/cm3)	1.183	1.184	1.1870	1.07(Minimum)	
Melting Point (^{o}C)	226.20	240.4	246.1	200(Minimum)	
Solubility	Soluble	Soluble	Soluble	-	[8]
Turbidity	326	112	111	-	
Gel Time(hrs)	264	216	210	-	
Appearance	Clear	Clear	Clear	-	[6]

Refractive index

Reflectiveness which is known to be a very good property of paint has been reported to be a function of the refractive index [7]. The binder plays an important role in exhibiting the reflective property of paint. The refractive index is seen to decrease gradually as one move from TMU–MMU and falls still within the acceptable level in the coating industry, this may be due to the increasing changes in the molecular structure of the resin, and the differences in the level of specific interaction in polymer product as the molar ratio of urea to formaldehyde in the constituents decreases, due to less light scattering. It may also be attributed to a possible fall in crosslinking density as the concentration ratio decreases.

Viscosity

Viscosity is a fundamental rheological parameter of macromolecular compounds, a property that defines resistance to flow and is related to the characteristics of composite materials widely used in many fields of industry. The knowledge of viscosity can help to characterize polymers and to indirectly determine molecular mass. Understanding the viscosity of the binder is quite important because it controls factors such as flow rates, levelling and sagging, thermal and mechanical properties, dry rate of paint film and adhesion of the coating to the substrate [3]. From the table above, it is observed that viscosity increases as the molar ratio of urea to formaldehyde decreases, with MMU having the higher viscosity. This may be as a result of strong interchain association forming large aggregates with small hydrodynamic volumes. This difference in viscosity is attributed to the variation of the different chain lengths, and the increase in molecular weight of the copolymer. Therefore, increase in molecular weight gives rise to increase in viscosity [9].

Moisture uptake

Moisture induces chemical degradation of the polymer network and also generates stress because of swelling and hence blistering of the coating film. It deteriorates thermo-mechanical properties as well as adhesion [10-11]. It is that property responsible for blistering, alligatoring, brooming etc, of paint film, affecting its mechanical properties in a way that might lead to the paint's failure [7]. From the table above the moisture uptake is highest in TMU but lowest in MMU, this could be attributed to the reduction in the quantity of hydrophilic hydroxyl (OH) component of the formaldehyde presentin MMU.

Density

Density is a physical property of matter that expresses the ratio of mass to volume, and is an important physical parameter in polymer engineering processes. Therefore, density measurements are very useful for the identification and characterization of different substances. It is a factor that affects the production cost and profitability of the manufacturing process [12]. The density of a binder influences such properties as the dispersion and stability of pigment and can be used to determine the critical pigment volume concentration, spreading capacity and consistency of the paint [7]. From the table above, it is observe that the density decreases from TMU down to MMU this behavior may be attributed to the difference in molecular features and morphology which influences the packing nature of the composite molecules as the concentration of formaldehyde decreases from TMU to DMU and down to MMU.

Formaldehyde Emission

The emission of hazardous formaldehyde during the curing process of urea formaldehyde resins has continued to pose a serious setback. Therefore, it is matter of necessity to determine the formaldehyde emission from synthesized urea-formaldehyde resin prior to its application [7,13]. It is observed that formaldehyde emission is highest in TMU followed by DMU and the lowest in MMU. This behaviour can be attributed to the reduction in the concentration of formaldehyde along that route (i.e TMU, DMU, MMU). It may also be attributed to the reduction in stress during the curing process which reduces emission resulting from their reactions as we descend from TMU to MMU. This experiment therefore present MMU as a better resin in the methylol urea(MU) family for application in paint formaulation.

Melting Point

In the coating industry, the melting point of a binder is related to its thermal resistance as well as its brittleness. The thermal property, degree of cross linking, level of rigidity and molecular weight of the polymer is related to its melting point [14]. The melting point is observed to have decrease again as one move from TMU through DMU to MMU. Decreasing melting point signals decreasing hardness and increasing flexibiliity of the different polymer. This behaviour may be attributed to urea serving as a flexible spacer, crosslink modifier and/or formaldehyde resin condensation inhibitor [7]. Also at MMU blend, polymer degradation might have occurred as the rigid structure of the polymer became flexible therefore making the molecules to gain mobility resulting in the decrease in melting point. This again addresses one of the fundamental drawback of MU which is brittleness and rigidity.

Elongation at break

Elongation at break is a significant factor recounting the rupture performance of composites. It is the ratio between increased length and initial length after breakage of a tested material. Elongation tells how much a material will stretch before it breaks. It determines the adhesion between phases because of its sensitivity for load transfer between the phases [15-16]. The gradual increase in the elongation at break with decrease in the concentration of formaldehyde as shown on the table above may be attributed to the ability of formaldehyde to enhance rigidity spacing, thereby decreasing the free volume in the blend. Also, it may be due to the increase in the soft segments in the polymer blend as the rigidity factor decreases.

Gel Time

Gelation which is the time required for a polymeric material to reach infinite viscosity. It has also been marked to be the point at which a polymer substance can attain an infinitely large molecular weight [6]. The function of a binder's gel-time among other factors determines the dry time of paint. Technically, gel-time enables a paint formulator to ascertain the optimum storage period of a binder before its utilization for paint formulation. It is also important in the determination of adhesion [17]. It is observed from the above table that the gel-time of the polymer increases with decrease in the concentration of formaldehyde. This may be due to the decrease in reactivity which is a function of the increase in the size of the alkyl group attached to the carbonyl carbon resulting from the polymerization of urea and formaldehyde.

Solubility

Resin solubility or dispersability in water is an important factor in the resin's acceptability [18]. It is important from the technical point of view as well as from the processing point of view. But their solubility's is observed to increase with decrease in concentration of formaldehyde the rigidity and hardness factor. It therefore means for a paint formulator using these binders, MMU can better be used for paint formulation, as it is the resin that goes into solution faster.

Turbidity

The essence of knowing the turbidity of a binder is in order to characterize the optical properties of the binder as it relates to the gloss property. The refractive index gives indication of the turbidity. The principle of turbidity was derived from light scattering. When there is homogeneity and there are few particles, there will be less scattering; hence higher scattering is observed when we have a non-homogenous system with a lot of particles. The rise in turbidity as observed from the table as one progresses from TMU to DMU and down to MMU may be attributed to the progressive changes in crystalline orientation and morphologies responsible for light scattering. Light scattering and hence turbidity is relatively used to determine average molecular weight of polymeric materials [18].

Conclusion

Monomethylol urea (MMU) was successfully synthesized, characterized and compared with other amino resins like Trimethylol urea (TMU), Dimethylol urea (DMU) and then with the acceptable standard in the industry. Results show MMU having more remarkable improvement in terms of formaldehyde emission, moisture resistance, and flexibility than the other two resins. Therefore, tapping on the aforementioned qualities of MMU would be a welcome idea, for MMU appears a more promising binder for the paint industry. It's our believe that the brilliant qualities of MMU could further be enhanced/magnified by copolymerizing it with other polymer material.

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