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Effect of Different Polyols on the Esterification of Monomethylol Urea with Polyol.

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ABSTRACT

In this study, the effect of different types of polyol (PL) on some physical properties of monomethylol urea (MMU) resin is reported. Monomethylol Urea/diethylene glycol (MMU/DG), monomethylol urea/glycerol (MMU/G) and monomethylol urea/polyethylene glycol (MMU/PG) resins were prepared. Some physical properties namely refractive index, moisture uptake, melting point, viscosity, density, elongation at break and formaldehyde emission were investigated. Differences were recorded between the pure MMU and the monomethylol Urea/Polyol (MMU/PL) on one hand and among the different MMU/PL resins on the other hand. The values of viscosity, density, elongation at break, moisture uptake (MMU/G) and refractive index were higher than that of pure MMU resin while those of formaldehyde emission, melting and moisture uptake of MMU/PG and MMU/DG decreased with respect to MMU resin. This result present MMU/PG as the resin with the highest level of flexibility (elongation at break = 400% and melting point = 1600C) compared to the pure MMU moiety. This development will help to address the present problem of hardness associated with pure MMU resin and hence a potential binder for the coating industry.

Keywords: Monomethylol urea, different polyols, copolymerization, paint binder.

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INTRODUCTION

Paints and coatings occupy a prominent place in the cultural history of mankind. People have always been fascinated with colour and use paints to decorate and beautify themselves and their environment. Today, coatings not only protect and beautify the substrate, they also have functional properties. Paints and coatings play an indispensable role in our modern world and cover virtually everything we use including household appliances, buildings, cars, ships, aeroplane, computers, circuit boards etc.

However, despite the glorious history of the coating industry towards the provision of better life for the modern society, the use of oil based paints have come under increasing environmental pressure over the years. This is because oil based paint uses solvent which is responsible for the emission of volatile organic solvent (VOCs) from coating surfaces. The toxicity of their VOCs affects human, depletion of ozone layer in the atmosphere, and one of the factors responsible for the global climatic change. The above health and environmental concerns have driven the world coating industry to focus attention on research towards replacing oil paint with water-based paints [1].

The advantages of water borne coating include nonpolluting, easy to handle, quick drying, economical and environmentally friendly. However, although most household paints are water-based, this is not true of industrial paints. Because of the special characteristics of industrial coatings, satisfactory water-based polymers with the required properties have not yet been developed [2]. Therefore, the present challenge in this drive to reduce VOCs is the need for the water-borne technology to deliver the enamel type characteristics of solvent coatings.

Methylol urea is an amine resin. It is colourless, water soluble, low cost, good thermally and mechanical properties etc. since is water soluble, it makes a potential candidate as a binder for water-based paints. Despite the various advantages of this resin, its use in many engineering fields is limited by its inherent drawbacks namely poor water resistance, hardness and brittleness and formaldehyde emission [3]. If MMU is to be considered for use as a binder for the coating industry, the above disadvantages must be addressed.

In our previous experiment [4], it was revealed that the degree of substitution of methylol urea (mono-tetra) affects some of its physical properties such as moisture uptake and formaldehyde emission. In this report, MMU had the least moisture uptake and formaldehyde emission. However, the ductility of the monomethylol resins was too low and hence its disqualification as a binder for the coating industry. Also, it was reported [5] that trimethylol Urea can be esterified with polyol to introduce a soft moiety into the hard methylol Urea domain. In order to harness the potential of MMU, this experiment was set out to investigate the effect of using different type of polys on the esterification of MMU and their effect on some physical properties of MMU with the aim of introducing flexibility into the polymer resin.

MATERIALS AND METHODS

Materials

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

Resin Synthesis

Monomethylol urea was prepared by the method described by Chen et al. [6]. One mole (6.0 g) of urea was reacted with three moles (8.1 ml) of 37% (w/v) formaldehyde using 0.2 g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 6 by using 0.5 M H_2SO_4 and 1.0 M NaOH solutions. The solution was then heated in a thermostatically controlled water bath at 70° C. The reaction was allowed to proceed for 2 h after which the sample was removed and kept at room temperature (30° C).

Preparation of MMU/PL Bends and Composite Films

Copolymer composite film of UF and EG film was obtained as reported by Mirmohseni and Hassanzadeh [7]. In brief, 50 ml of MMU was added to 5 ml of DG to form MMU/DG 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 for different polyols. The physical properties of these films were then investigated.

Determination of Density, Turbidity, Melting point and Refractive Index

The above properties were determined according to standard methods [8]. The density of the different resins were 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 sample was determined by using Hanna microprocessor turbiditymeter Model, H193703 (VillafrancaPadovana, 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 (Bellinglam and Stanley, Tunbridge well kent, UK) and the viscosity of the resins were determined by using Brookfield digital viscometer (Model Dv-E). Five readings were taken for each sample and average value calculate for each of the aforementioned parameters.

Determination of Moisture Uptake

The moisture uptakes of the different resin films were determined gravimetrically [5]. Known weight of the sample was introduced into a desiccator containing a saturated

solution of sodium chloride. The increase in weight (wet weight) of the sample was monitored until a constant weight was obtained. The difference between the wet weight and dry weight of each sample was then recorded as the moisture 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 2h desiccator method [9]. The evaluation of the absorbed formaldehyde by the 25.0 ml water was obtained from standard calibration curve 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 mm x 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 property (tensile strength and elongation at break) was determined as described by Wang and Gen[10] 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.

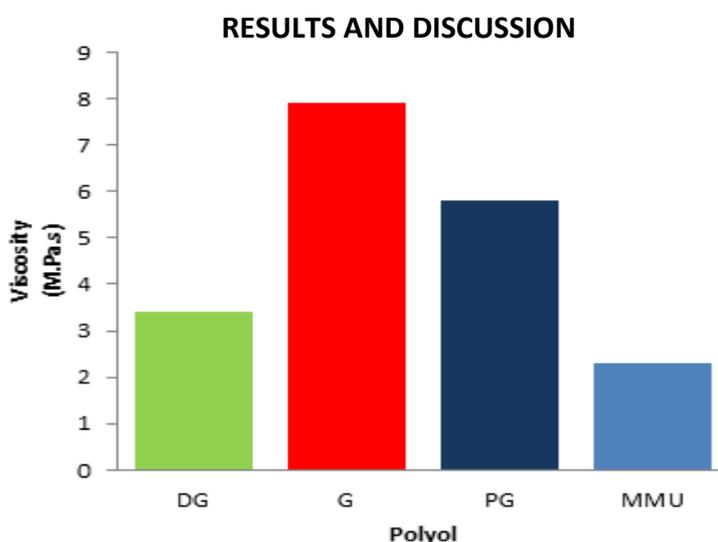


Figure 1: Effect of different polyols on the viscosity of MMU resin.

Viscosity

Viscosity is the resistance of a substance to flow. It is a measure of the resistance of a fluid to deformation under shear stress. In the development of a binder for the coating industry, an understanding of the viscosity of such resin is an indispensable factor. This is so

because the viscosity of a paint binder controls crucial factors of the paint such as flow rates, leveling and sagging, thermal and mechanical properties, dry rate of paint film and adhesion of the coating to substrate [9]. Thus, in the coating industry a good knowledge of the binder viscosity is desirable both from manufacturing point of view, stability and rate of cure of paint film.

Figure1 shows the effect of using different polyols on the viscosity of MMU. It is observed that the inclusion of polyol to MMU polymer domain resulted to an increase in the viscosity of MMU resin. Different viscosity values were also recorded among the different MMU/polyol resins. The above observation can be explained in terms of differential in molecule weight and crosslink density between pure MMU and MMU/polyol on one hand and among the different MMU/polyol resins from the different polyols on the other hand [11, 12].

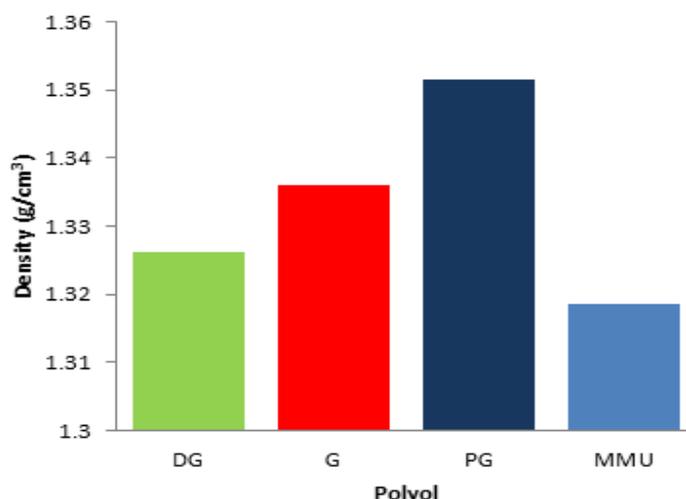


Figure 2: Effects of different polyols on the density MMU resin.

Density

Density is an important physical parameter in polymer processing. It affects production cost and profitability of the manufacturing process [12]. In the case of paint manufacturing processes, density influence factors such as pigment dispersion, brushability of paints flow, leveling and sagging [13].

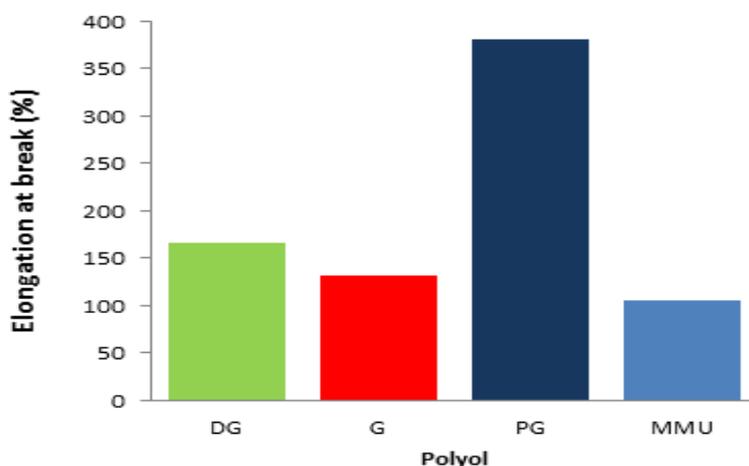


Figure 3: Effect of polyols on the elongation at break of MMU resin.

The effect of different polyols on the density of MMU is shown in figure 2. It is observed that the density of MMU resin is increased in the presence of each of the different polyols. The increase in the density of MMU resin with polyol inclusion is due to increase in molecular weight among the different polymer systems [14, 15]. Density is a function of free volume and packing efficiency of molecules.

Elongation at Break

Elongation at Break measures the extent to which a polymer material stretches before it breaks. It therefore defines the ductility or flexibility of the materials. One of the drawbacks of MMU resins is that it is too hard and brittle resulting to the resin derived from it having poor resistance to crack propagation [16].

From figure 3, the effect of different polyol on the elongation at break of MMU can be seen. It is observed that the introduction of each of the respective polyol into the matrix of MMU resin gave rise to an increase in elongation at break. The reason for this phenomenon can be attributed to the in situ esterification which occurred between the generated formaldehyde (from MMU condensation reactions) and the OH- groups of the polyols. This chemical interaction gave rise to the introduction of ester Chains (soft segment) into the hard MMU domain hence the increase in flexibility of the MMU Chain [17, 18]. The differences in the elongation among the different polyols is due to their differences in terms of crystallinity, orientation and Chain length.

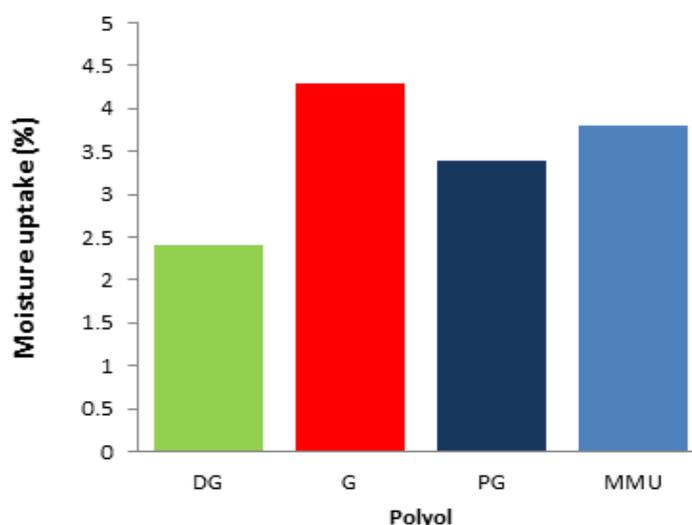


Figure 4: Effects of different polyols on the moisture uptake of MMU resin.

Moisture Uptake

Moisture or water uptakes by polymer materials influence the swelling of such materials. This development leads to weakening of the material which has a detrimental effect on its chemical, physical, mechanical, thermal and structural properties. One of the limiting factors of MMU resins is poor water resistance [19].

Figure 4 shows the effect of different polyols on the moisture uptake of MMU. It is observed that the moisture uptake by MMU decreased in the presence of diethylene glycol

and polyethylene glycol while experiencing an increase with glycerol. This phenomenon is due to the difference in chain topology, molecular size holes in the polymers, morphology and cross link density [18]. Differences in the number of OH-group among the different resins may also be a factor.

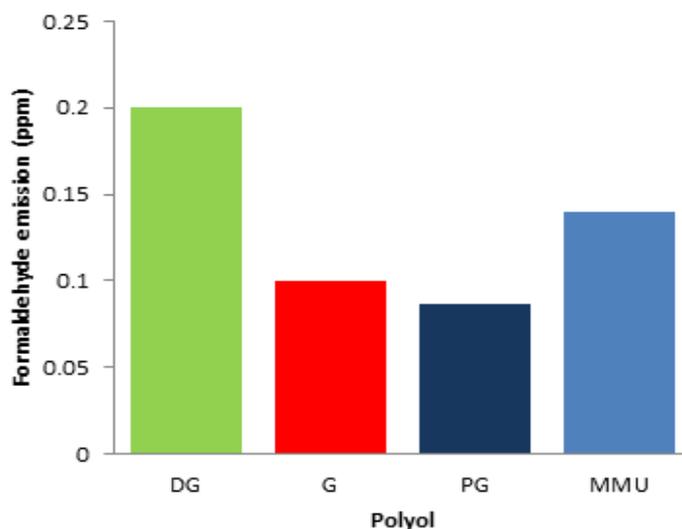


Figure 5: Effect of different polyols on the formaldehyde emission of MMU resin.

Formaldehyde Emission

The emission of toxic formaldehyde during the various condensation reaction stages of MMU has continue to be a disturbing issue to many industrialists using the polymer resin. Despite the various attractive advantages of this resin, the problem of Formaldehyde emission has continued to be its challenger toward harnessing its full potential.

Therefore, to utilize MMU as a binder for the coating industry, the emission of this toxic byproduct fromMMU condensation reaction must be kept within acceptable level.

Figure 5 displays the effect of different polyol on the formaldehyde emission of MMU. It shows a high reduction in the formaldehyde emission when MMU was interacted with each of the different polyol. The level of reduction is also observed to be different from one type of polyols to another. The conversion of the emitted formaldehyde into polyester is implicated in this development [5].

The differences observed among the different polyols can be explained on the basis of differences in the number of OH-group and the position of the hydroxyl group in the polyol backbone. Primary OH-groups are more reactive than secondary OH-Group [20]. The result from this experiment gives a good promise toward the utilization of MMU as binder for the coating industry.

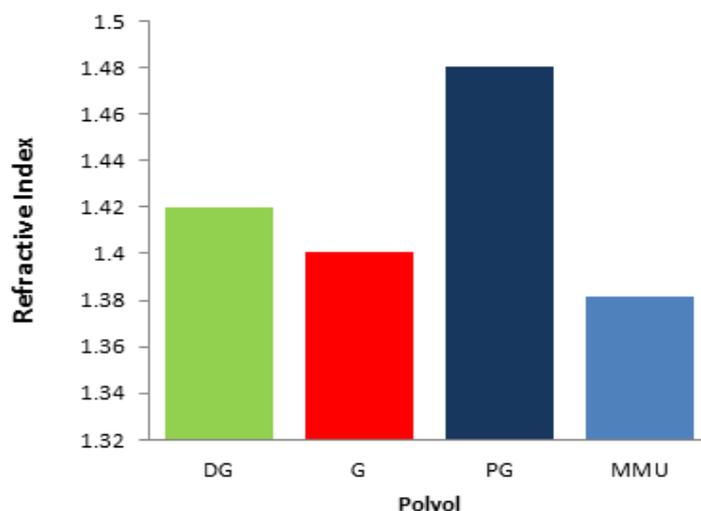


Figure 6: Effect of different type of polyols on the refractive Index of MMU resin.

Refractive index

The refractive index of a coating surface defines its gloss power. One of the advantages of oil paints over emulsions paint is its superior gloss power. Therefore if the quest for emulsions paint to challenge the enamel property of oil paint is to be achieved, the enhancement or improvement of the present gloss power of emulsions paint must not be forsaken.

Figure 6 shows the influence of different polyols on the refractive index of MMU. It is revealed that the different polyols enhanced the refractive index of MMU resin on one hand and at different levels on the other hand. This phenomenon can be explained on the basis of differences in molecular structure, weight, features and orientation among the different polymer systems [17, 20]. The refractive index of a polymer system is a function of the fineness of the dry film formed. While a fine surface will generate high refractive index a rough surface will result in low refractive index and hence the resulting gloss power.

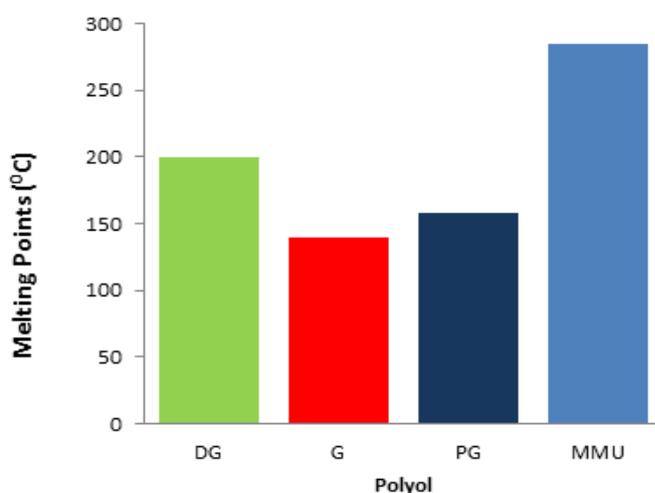


Figure 7: Effect of different types of polyol on the melting point of MMU resin.

Melting point

The melting point of a polymer reflects its level of rigidity or flexibility. It measures the degree of resistance of the polymer film to friction and scratches. While it is necessary for coating film to resist wear caused by friction and scratches on one hand, it is equally very important that the film exercise good level of flexibility so as to withstand crack propagation occasioned by seasonal vibration on the other hand. One of the shortcomings of the methylol urea is that it is too hard and brittle with an average melting point of about 280° C [21].

Figure 7 indicates the effect of using different polyol on the melting point of methylol urea. It can be observed that the introduction of polyol into the moiety of MMU resulted in the reduction of MMU melting point in all cases of the different polyols used. This is a consequence of the introduction of soft ester segment into the MMU domain resulting from the in situ esterification of the emitted MMU [2]. The differences observed among the different polyols can be explained on the basis of differences in the number of hydroxyl group and polyol chemical structure. A higher number of hydroxyl increases the liability of bond formation with the emitted formaldehyde byproduct. The more networks formed in the polymer matrix, the harder is the resulting polymer film [15].

CONCLUSION

The effect of different polyols on some physical properties of MMU/PL composite has been examined. It is revealed that the type of PL used in the synthesis of MMU/PL resin has a great influence on the physical properties of the polymer resin. The values of formaldehyde emission, melting point and uptake (except for MMU/G) were lower than that of pure MMU resin while those of elongation at break and refractive index were higher than that of pure MMU resin. Differences among the MMU/PC composites in terms of viscosity, density, elongation at break, refractive index, moisture uptake, melting point and formaldehyde emission were also recorded. MMU/PG present itself as a resin with the highest level of flexibility (elongation at break = 400%, melting = 1600C) compared to MMU and other MMU/PL. therefore, introduction of PG into MMU will help to address the present problem of hardness associated with pure MMU and hence a potential builder for the coating industry.

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