



Application of methylol urea/natural rubber copolymer composite for emulsion paint formulation

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ABSTRACT

This work is a follow up to our quest to develop emulsion paint from amino resin. Both pure urea methylol (MU) and methylol urea/Nature rubber (MU/NR) blend were prepared. Some physico-chemical properties such as viscosity, melting point, moisture uptake, refractive index, density, elongation at break and formaldehyde emission of both MU and MU/NR were evaluated. The result revealed that MU/NR blend possesses better water resistant, hardness, flexibility and low formaldehyde mission while the pure MU gave better refractive index. Emulsion paints were also formulated from both resins and some physico-chemical properties namely pH, viscosity, flexibility, hardness, tackiness, resistance to blistering, dry time, gloss and storage stability were investigated. Emulsion paint derived from MU/NR binder except for gloss passed the entire test conducted while the one from pure MU binder failed flexibility, adhesion, hardness, tackiness and dry time. This work presents MU/NR paint as a high quality one and hence, may introduce a novel emulsion paint derived from MU/NR binder into the coating industry.

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Key words: Amino resin, methylol urea, natural rubber, binder, emulsion paint.

INTRODUCTION

The coating industry is in innovative mood. The innovation is driven by environment, health, safety, quality improvement and cost reduction. This is especially due to regulations with respect to volatile organic compounds (VOC), which is now challenging companies to find solutions in water-based systems.

With the advent of the regulations on air pollution, and for safety consideration, there have been continued interests in searching for alternative raw materials and new formulations to reduce the overall volatile organic compounds in surface coatings (Gan and Tan, 2001). Recently, much

research has focused on replacing solvent-based paints with water-based paints (Mohammed et al., 2001; Li and Zeng, 2002). The advantages of water-borne paint include being nonpolluting, easy to handle, quick drying, economic and environmentally friendly. However, although most household paints are water-based, this is not true of industrial paints. Because of the special requirements of the industrial coatings, satisfactory water-based polymers with the required properties have not yet been developed (Gooch, 1997). Therefore a significant challenge in this drive to reduce VOC is the need for the water-borne technology to deliver the enamel type

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properties characteristic of solvent-borne coatings.

The acceptance of urea formaldehyde resin (UF) as a universal material in many engineering areas such as in the coating industry is impeded by some of its inherent qualities such as brittleness, poor water resistance and formaldehyde emission (Barminas and Osemeahon, 2006; Osemeahon and Barminas, 2007). These disadvantages limit its uses. However, UF resins offer a wide range of conditions that make synthesis of these resins with important properties such as gel time, tack and spreading ability of the uncured resin possible. Also, formaldehyde emissions and the durability of the cured resin can be controlled and specifically tailored for the final use of the resins (Osemeahon and Barminas, 2006a, 2006b).

In our earlier experiments (Barminas and Osemeahon, 2007; Osemeahon and Barminas, 2007), we reported both the synthesis of UF through a new synthetic route and the successful copolymerization of the new class of urea formaldehyde with natural rubber resin as a way of developing a paint binder for emulsion paint formulation from amino resin. This work is a follow-up to this experiment (Osemeahon and Barminas, 2007). It involves preliminary evaluation on the application of the MU/NR composite as a binder for emulsion paint formulation.

MATERIALS AND METHODS

Chemicals

Urea, formaldehyde, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide pellets and sucrose were produced by British Drug House (BDH). Natural rubber (NR) (*Hevea brasiliensis*) was obtained as an exudate from Rubber Research Institute Benin City, Nigeria. All materials were used as received. Sodium benzoate, dispex, carboxymethyl cellulose (CMC) foamaster, rutile (TiO₂), China clay and parish white (CaCO₃) were obtained from Aba market, Nigeria. These chemicals were used as purchased.

Resin synthesis

Trimethylol urea was prepared by reacting one mole (6.0 g) of urea with three moles (24.3 ml) of 37% (w/v) formaldehyde using 0.2 g of sodium dihydrogen phosphate as catalyst (Osemeahon and Barminas, 2007). The pH of the solution was adjusted to 6 using 0.5 M H₂SO₄ and 1.0 M NaOH solutions. The solution was then heated in 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 MU-NR blend and films

Blend of MU and NR was prepared by adding 50.0 ml of NR to 50.0 ml of MU to give 50% of NR in MU. The mixture was stirred with a glass rod and left for 24 h at room temperature (30 °C). For film preparations, resins from MU and MU/NR were then poured into different glass petri dishes for casting using the solution casting method (Barminas and Osemeahon, 2006). The resins were also allowed to cure and set for seven days at 30 °C. The physical properties of the films were then investigated.

Determination of physical properties

Determination of viscosity, density, melting point and refractive index

The viscosity of the polymer blend and that of the pure MU resins were obtained from a previous method (Barminas and Osemeahon, 2006). In brief, a 100 ml Pyhwe made graduated glass macro-syringe was utilized for the measurement. The apparatus was standardized with 20% (W/V) sucrose solution whose viscosity is 2.0 mPa.s at 30 °C. The viscosity of the resin was evaluated in relation to that of the standard sucrose solution at 30 °C. Other physical properties were determined according to AOAC Method of Analysis (AOAC, 2000). The densities of the different resins were determined by taking the weight of a known volume of resin inside a density bottle using Metler At400 weighing balance. Five readings were made for each sample and average value calculated. The

melting point of the different film samples were determined by using Galenkamp melting point apparatus model MFB600-010F. The refractive index of resin samples were determined by using Abbe refractometer. For each test, triplicate determinations were made and mean value recorded.

Determination of moisture uptake

The moisture uptakes of the different resin films were determined gravimetrically. Known weight of each of the samples were introduced into a desiccator containing a saturated solution of sodium chloride. The wet weights of each sample was then monitored until a maximum weight was obtained. The difference between the wet weight and dry weight of each sample was then recorded as the moisture intake by the resin (Barminas and Osemeahon, 2007). Triplicate determinations were made for each sample and mean value recorded.

Tensile test

Tensile properties (tensile strength and elongation at break) were measured as described by Osemeahon *et al.* (2007), using Instron Tensile Testing Machine (Model 1026). 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. A number of five runs were done for each sample and the average elongation evaluated and expressed as the percentage increase in length.

Determination of formaldehyde emission

Formaldehyde emission test was performed by using the standard 2 h desiccator test as earlier reported (Osemeahon and Barminas, 2007). The mold used was made from aluminium foil with a dimension of 69.6 mm x 126.5 mm and thickness of 12.0 mm. The emitted formaldehyde was absorbed in 25.0 ml water and analyzed by a refractometric technique using Abbe refractometer. Triplicate samples were used and average value taken.

Paint formulation

The method described by Eze and Uwakwe (2004) was adopted for the paint formulation. A volume of 180 ml of distilled water was introduced into a liter mixing tank and the overhead stirrer switched on. An amount of 0.2 g of the antifoam was added followed by the addition of the dispersant and the suspenders with the temperature of the mixture maintained at 60 °C for 5 minutes. Rutile (TiO₂), China clay and Paris white (CaCO₃) were then added. This was followed by the addition of thickener, binder (MU) and the stabilizer (Butanol). The mixture was then made up to 500 ml with distilled water. This process was repeated for MU/NR binder. The details of the formulations are shown in Table 1.

Test procedures for paint samples

Paint samples were analysed according to standard organization of Nigeria methods (SON, 1990). Viscosity of paint sample was determined by using an I.C.I. Rotoviscometer. The 500 ml tin sample container of the instrument was filled with paint sample under test to 0.3 mm of the top rim of the dept gauge. The sample was stirred with a thermometer and the temperature maintained at 27 °C. The container with the paint sample was placed in the processing ring on the turntable and the lever pulled down to switch on the motor automatically. The disc was then allowed to run until a steady state was reached (5 minutes). At the end of the required time, the viscosity was recorded in poises. Triplicate determinations were made for each sample and mean value recorded. The pH of paint sample was determined by using Phywe pH meter model 18 195.04.

Opacity was determined by using the standard Mohest Chart. The paint sample was applied on Mohest Chart (i.e. hiding power chart) and allowed to dry for 24 h. The opacity was then evaluated by comparing the dried sample film with the hiding power chart. Three determinations were made for each sample and mean value assessment recorded.

Table 1: Recipe for the formulation of emulsion paints from MU and MU/NR binders.

Raw Material	Amount used (g)	
Sodium benzoate	0.2	0.2
Dispex	0.4	0.4
Carboxyl methyl cellulose (CMC)	2.5	2.5
Foamaster	0.2	0.2
Rutile (TiO ₂)	54.64	54.64
China Clay	32.21	32.21
Parish white (CaCO ₃)	68.20	68.20
Binder (v/v)		
MU	160	-
MU/NR (1:1)	-	85
Butanol	5	5

To evaluate the dry time, paint sample was applied on a glass panel with the aid of bar applicator and allowed to dry. Dry to touch was taken when the paint film was no longer sticking to the finger and dry to hard taken when the film resisted finger print. Triplicate evaluations were made for each sample and mean value assessment recorded. For flexibility test, paint sample was applied on a freshly degreased and chromated aluminum with the aid of paint applicator. The film was then allowed to air dry under room temperature (27 °C) for 7 days. The panel with the film was then inserted into the conical Mandrel Bend Tester and the panel bent through 180° with a smooth action (taking 1 – 2 seconds). The panel was then removed from the tester and examined for cracking or loss of adhesion. Any crack or loss of adhesion indicates inflexibility or brittleness. Triplicate samples were made and average evaluation taken.

To evaluate the adhesion property of paints, a coat of paint film was applied with film applicator on a degreased metal panel and allowed to dry for 48 hours. Two sets of lines, one crossing perpendicularly over the other were drawn with a crosshatch tester on the paint film. An adhesive tape was pressed firmly with the thumb covering all the interactions of the perpendicular line. The adhesive tape was held at its loose ends and forcibly removed from the panel. Removal of

more than 50% of the square lines of the paint film indicates poor adhesion. Triplicate determinations were made at 27 °C for each sample and average assessment recorded. Specular gloss at 85° of paint sample was determined by using gloss meter (Digital instruments, model RSPT-20). Paint film was prepared by using 4mesh (100 microns) applicator over a precleaned glass panel and the film allowed to dry for 24 h. The ASTM gloss-meter was allowed to warmed up for 10 min and using the black glass standard held against the pot-hole, the meter was adjusted to read 92.5%. The sample cast on the glass panel was then held against the pot-hole in three separate positions along its length and the mean gloss calculated in % with a difference of not more than 5% between the highest and the lowest. Triplicate measurements were made for each sample and mean value recorded.

This was done qualitatively on the dried film by hand feeling to find out if the paint film is sticky or not. Stickiness of a dried paint film is an indication that the film is tacky. Triplicate samples were used for each determination and the average quality assessment recorded. To test for resistance to blistering, undiluted paint sample was applied to a glass panel with an applicator to give a wet film thickness of about 120 µm and was allowed to dry for 24 h. At the end of this period 4 ml of distilled water in the form of

circular drop was placed on the film. The presence of blistering, wrinkling, swelling or cracking within a period of 30 minutes indicates poor water resistance. Triplicate samples were used for each determination and the average quality assessment recorded. For the stability test, the paint sample was fully sealed in a container and allowed to stay at room temperature (27 °C) for 12 months. At the end of this incubation period, the sample was re-examined for any change in viscosity or coagulation of the emulsion paint. Absence of coagulation or any change in viscosity is regarded as a pass. Triplicate samples were used for each determination and the average value recorded.

To evaluate the chemical resistant of the paint films, three flexible aluminum panels (150 mm x 150 mm x 0.3 mm) were used as the test panels. A coat of paint with paint applicator was applied to the panel. One liter glass beaker was filled with 0.1 M NaOH solution to a depth of 150 mm and the test piece immersed for 48 h to the depth of approximately 120 mm. The test piece was removed, washed with running water and stood to dry for 2 h. The above procedure was repeated by using 0.1 M HCl and 0.1M NaCl respectively. The presence of any surface defects such as cracking, blistering, peeling or change in color indicates poor chemical resistance. Pencil hardness of the paint films was also determined according to ASTM standard method (ASTM D 3363-74).

RESULTS

Table 2 compares some physical properties of pure methylol urea (MU) and MU/NR copolymer composite. It was observed that the viscosity, melting point and elongated at break of MU/NR blend are very high compared to those of MU. The increase in viscosity is due to increase in molecular weight, which is a consequence of the reactive, blending between MU and NR (Osemeahon and Barminas, 2007). The relatively high melting point of MU/NR is due to the high molecular weight and cross density of MU/NR composite as reflected in the high

viscosity value. The density, moisture uptake, refractive index and formaldehyde emission of MU/NR are relatively very low compared to those of MU. The decrease in density with NR presence in MU/NR blend can be ascribed to inefficient molecular chain packing as density depends on free volume and packing efficiency of molecular chain (Chain and Yi, 2001).

The low moisture uptake and formaldehyde emission recorded in MU/NR blend is explained by the reduction in MU loading in the presence of the hydrophobic NR resin. Cured NR is resistant to moisture uptake (Osemeahon and Barminas, 2007). The relative low refractive index of MU/NR blend agrees with literature reports (Gupta *et al.*, 2001; Osemeahon and Barminas, 2007). This is due to micro phase separation between MU and NR.

Some physical properties of paints formulated from MU and MU/NR binders

Some physical properties of MU and MU/NR paints are tabulated in Table 3. In this table, some properties such as pH, viscosity, flexibility and opacity of both MU and MU/NR paint falls within acceptable ranges for paints (SON, 1990). MU/NR paint displayed good adhesion, tackiness and hardness properties, but the pure MU paint presented poor adhesion, hardness and tack properties. The behavior of the MU paint can be attributed to low molecular weight and hence low crosslink density of the pure MU binder (Osemeahon and Barminas, 2007).

The results of resistance to blistering (water resistance) of the different paint formulations are also provided in Table 3. The paint from the MU/NR binder passed resistance to blistering test while those formulated with the pure MU binder failed the test. The above results indicate that NR segment has been cross linked into the MU/NR copolymer thus making the resulting binder water resistant. Also, the presence of cured NR in MU/NR binder, presents hydrophobic segment, which helped to increase the water resistance of the resulting

Table 2: Some physicochemical properties of the synthesized MU and MU/NR binders.

Property	MU	MU/NR
Viscosity (mPa.s)	3.41 ± 0.04	248.03 ± 2.51
Melting point (°C)	214.00 ± 2.41	255.00 ± 2.57
Density (g/cm ³)	1.102 ± 0.020	0.641 ± 0.010
Moisture Uptake (%)	3.261 ± 0.021	1.341 ± 0.020
Refractive index	1.4104 ± 0.0061	1.3411 ± 0.0057
Formaldehyde emission (ppm)	0.948 ± 0.001	0.058 ± 0.000
Elongation at break (kg/cm ²)	1 15.03 ± 1.02	350.43 ± 2.18

Figure 3: Some Physical Properties of Paints Formulated From MU and Modified MU Binders.

Parameter	MU	MU/NR	SON Standard
pH	7.1	7.6	7-8.5
Viscosity (poise)	6.5	11.5	6 – 15
Flexibility	P	P	P
Opacity	P	P	P
Adhesion	F	P	P
Hardness	F	P	P
Tackiness	F	P	P
Resistance to blistering	F	P	P
Drying time (min)			
Touch	180	18	20
Hard	720	110	120
Storage Stability (12 months)	P	P	P
85 ⁰ Gloss	28.4	15.2	16-50
Pencil hardness	2B	H	-

P and F means pass and fail SON test, respectively

paint formulation (Wu *et al.*, 2001). The inability of the pure MU paint to pass the resistance to blistering test can be attributed to the inherent property of urea formaldehyde resin couple with the low molecular weight of the MU binder employed in the paint formulation (Conner, 1996; Noguera *et al.*, 2001).

The drying times of MU/NR paint presented in Table 3 is within acceptable standard range while that of MU paint is outside the range (SON, 1990). The long period of drying exhibited by MU paint is attributable to the low molecular weight and hence low crosslink density of the MU binder (Lowel, 1990). The gloss of MU is within

acceptable standard range. The low gloss of MU/NR is expected and it is due to low refractive index of the MU/NR binder. Stability in storage is an important consideration for coating systems (Lowel, 1990). In the usage of amino resin as a paint binder the resin can undergo self-condensation and if this happens, the system may become too viscous and gel-like for use in the coating application intended. This, therefore, calls for the addition of a stabilizer (Butanol) into the formulation. From Table 3, all the formulations passed the standard stability test meaning that this problem has been successfully controlled.

Table 4: Chemical resistance of paint films.

Samples	Media		
	0.1 M NaCl	0.1 M HCl	0.1 M NaOH
MU	a	b	c
MU/NR	a	a	a

a = No effect, b = cracking, c = blistering

Chemical resistance of paint films

The chemical resistance of the paint films to different solvent media are shown in Table 4. From the results, both MU and MU/NR are unaffected by the salt medium. MU/NR films are also not affected by both the acid and alkali solutions. However, surface defects were observed in the case of MU films both in alkali and acid solutions. These results indicate that MU/NR paint has better chemical resistance than MU paint. These differences are attributable to the differences in the different binders to resist pH changes in the various media (Barminas and Osemeahon, 2007).

Conclusion

We prepared raw methylol urea and methylol Urea/Natural rubber blend. Some physical properties of both MU and MU/NR were studied. The result revealed that MU/NR blend possesses better water resistant, hardness, flexibility and lower formaldehyde emission while the pure MU gave better refractive index. Both MU and MU/NR binders were also used to formulate emulsion paints. Emulsion paints from MU/NR gave better quality paint in terms of the physical and chemical tests conducted. This work may, therefore, introduce a novel emulsion paint derived from MU/NR binder into the coating industry.

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