



Comparison of some physiochemical parameters of emulsion Paint formulated from Monomethylol urea Resin, and that from di, and Trimethylol urea resins

Archibong, C.S

Department of Chemical Sciences Federal University Wukari Taraba state, Nigeria

Abstract

Monomethylol urea was synthesis, then compared with di and Tri methylol urea using standard organization of Nigeria as a reference standard. The physical properties of the three resins, saw monomethylol urea exhibiting improvement in terms moisture uptake, hardness and reduction of formaldehyde emission over di and Tri methylol urea. Paint products formulated from each of the polymer resins were further subjected to physical and chemical test to ascertain the paint quality and durability. Each of these paint products passed the stability and opacity test, their pH values were within the acceptable range in the coating industry. The paint products were also not affected when place in an acidic medium, they all show one form of defecation or the other when place in a salt medium, only paint product from Trimethylol urea was affected in an alkaline medium. This study presented monomethylol urea as a better binder for emulsion paint formulation than di and tri methylol urea.

Keywords: Monomethylol, dimethylol, Trimethylol urea, Emulsion paint, Resin.

Introduction

Presently, conventional paints are gradually and steadily replaced by environmentally friendly formulations whose use is recommended due to ecological considerations, specifically the reduction of VOCs emissions (Broek, 1993; Traumann *et al.*, 2014). The first coatings with water based paints were the emulsion paints containing different resins (Crespi *et al.*, 2007). They showed the disadvantages of not being suitable for metal (due to the small amounts of water remaining in film and on the support, which caused corrosion phenomena) and having a low mechanical stability. Their dissolution in water is related to the presence of easily ionizable hydroxyl and carboxyl groups.

Emulsion house paint is a water based paint principally used for internal and external surface coatings, mostly in buildings for appearance and protection. The processes involved in paint production, quality and performance of emulsion paint depends largely on the properties of its constituents and the ratios of these constitutions (Abdulassalam and Yahaya, 2010).

The most important paint constituent is the binder, and the higher the binder ratio in a paint formulation, the higher the paint quality. Urea Formaldehyde is a suitable binder for water paint, but intrinsic properties such as moisture uptake, brittleness and formaldehyde emission limits its application (Akinteriwa *et al.*, 2015). As a measure to checkmate these aforementioned setbacks

monomethylol urea (MMU) was synthesis by further reducing the formaldehyde to urea ratio during synthesis. Other constituents generally used for the production of emulsion house paints include; prime pigments, solvents, extenders pigments, and additives.

Water is present as a consequence of the emulsion polymerisation process used in preparing the latex, and provides liquidity and spreadability so that it may be distributed evenly. Water-based paints are much less harmful to the environment than solvent-based paints, and this is what drives the trend towards the use of water-based paints. The performance of oil-based paints is generally better because the solvent acts as a plasticiser, and aids in the film formation process. The performance of the water-based paints can approach that of the solvent-based paints through careful formulation of the latex. Paints are usually formulated to contain 60 to 70 volume percent water ((Lisa *et al.*, 2010).

The water used in the formulation process of an emulsion paint may lead to a longer drying period and support adherence issues. These drawbacks are caused by the water high dipole moment, because of its tendency to form hydrogen bonds and by the fact that it reduces the resistance duration of oxygen in the excited stage and the possibility of hydroperoxide stage formation (Dyer and Cummings, 2006). This may be curtailed by modification of the chemical structure of methylol urea by varying the pH, the temperature, catalyst and the time associated with the methylol urea synthesis, as earlier reported in my previous works (Archibong *et al.*, 2018) . These variations in the synthesis parameters of methylol urea synthesis can influence the water surface tension, ameliorating the support adherence.

The aim of the research therefore is to synthesis monomethylol urea resin and use the monomethylol urea to produce an emulsion paint, which is hoped to further reduced VOCs in coating materials.

MATERIALS AND METHODS

Resin Synthesis

MMU was prepared using the one step process (OSP) as reported by Archibong and Osemeahon (2019) 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 $^{\circ}C$. The reaction was allowed to proceed for 60min after which the resin was removed and kept at room temperature (30 $^{\circ}C$).

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 $^{\circ}C$ 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 $^{\circ}C$ and left for 5min after which the sample was removed and cooled for observation. The experiment was repeated three times

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 driven 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 *et al.*, 2013).

Viscosity was determined by adopting Ganeshram *et al.*, 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 Moisture Uptake

The moisture uptake of the resin films was determined gravimetrically, according to method described by Archibong and Osemeahon, 2019. 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°C). The degree of solubility was evaluated visually and the result recorded.

Paint Formulation

The method described by Karakas, *et al.*, (2011) was adopted with some modifications. The method splits the production process into three main stages as illustrated in the table below. The mixture in each stage will be stirred for 15mins using a mechanical stirrer.

First Stage

At the first stage, additives such as, dispersants, defoamer, thickener, anti-skin, drier, wetting agents, stabilizer, pH adjuster and preservatives were added. The basic purpose of this stage is to provide a favourable environment for wetting and dispersion of particles. A volume of 185 ml of

distilled water was introduced into a litter mixing tank and the overhead stirrer switched on after the addition of 12.7g of the additives as shown in Table 1. This mixture was stirred using a high speed stirrer for 15minutes.

Second Stage

In the second stage, also known as “Millbase”, pigments and extenders were dispersed in the mills. Immediately after dispersion, the stirrer speed in the millbase stage was increased to a very high speed and the mixture was stirred for another 15minutes. In millbase, binder was not added to avoid its structural deformation under the high mechanical forces.

Third Stage

Finally, binder plus the rest of the additives used in the first stage were mixed with 15ml of water. This stage is called “Letdown”. In this stage, the mixture was stirred at moderate speed for another 15 minutes. Energy losses in the mill base are minimized by adding thickeners before the dispersion stage of the production process. The above processes was repeated using pure MMU as binder.

Table 1. Recipe for the formulation of an emulsion paint

Stage	Material	Quantity (gr)
First	Water	100.00
	Anti-form	0.20
	Drier	0.02
	Calgon	1.16
	Genepour	1.16
	Bermocoll	2.50
	Troystan	1.14
	Dispersant	0.20
	Butanol	5.00
	Ammonia	054
Second [Millbase]	TiO ₂	27.00
	Al ₂ SiO ₃	11.20
	NaCO ₃	30.58
	Kaolin	2.52
	CaCO ₃	72.00
Third [Letdown]	Binder	100.00
	Water	50.00
	Dispersant	0.20
	Nicofoam	0.20
	Anti-Skinning agent	0.20

Test Procedures for Paint Samples

Paint samples were analyzed as described in Niger Cedar laboratory hand book of paint formulation recipe and standard organization of Nigeria methods

Viscosity

Viscosity of paint sample was determined by using an I.C.I. Rototinner viscometer. 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 oC. 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.

pH Measurement and Opacity Test

The pH of paint sample was determined by using phywe pH meter model 18 195.04. The paint sample was scooped with a palate knife and spread evenly across the width of a Mohest chart (black and white striped paper) about 4 cm from the edge of the paper. The paint was then evenly applied down the length of the paper by means of the K-bar (stainless steel bar) and left to dry. A second coat was applied using the same application technique but with a space of 5 cm left from the edge of the first coat. The opacity was assessed by the extent to which the black and white stripes were covered by the paint. Three determinations were made for each sample and mean value recorded for quality assessment.

Drying Time and Flexibility

Dry time was evaluated by applying the paint sample 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 was 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 chromate aluminium with the aid of paint applicator. The film was allowed to air dry under room temperature (27-30°C) for 7 days. The panel with the film was bent through 180° with a smooth action (taking 1-2 seconds). The panel was then removed and examined for cracking or loss of adhesion. Any crack or loss of adhesion indicates inflexibility or brittleness. Triplicate determinations were made at 27-30°C for each sample for quality assessment.

Chemical Resistance

The chemical resistance of the paint films was carried out thus; three flexible aluminium panels (150 mm x 0.3) were used as the test panels. A coat of paint with paint applicator was applied on the panels. One litter glass beaker was filled with 0.1 M NaOH solution to a depth of 150 mm and the test pieces was immersed for 48 hours to the depth of approximately 120 mm. The test piece was removed, washed with running water and stand to dry for 2 hours. The above procedure was repeated using 0.1M HCl and 0.1M NaCl respectively. Poor chemical resistance indicated by the presence of any surface defects such as cracking, blistering, peeling or changes in color.

Tackiness

This was carried out 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.

Adhesion Property

This was carried out by applying a coat of paint film 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 end and forcibly removed from the panel. Removal of more than 50% of square lines of the paint film indicates a poor adhesion. Triplicate determination were made

Resistance to Blistering

To determine 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 , which was allowed to dry for 24 hours. 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 determinations of each sample were made and quality assessment recorded as mean.

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-examine or any change in viscosity or coagulation of the emulsion paint. Absence of coagulation or any change in viscosity is regarded as pass. Triplicate samples were used for each determination and average recorded

Results and Discussion

Table 2. Comparison of some physical properties of Monomethylol Urea (MMU), Dimethylol Urea (DMU) and Trimethylol Urea (TMU) 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)	(Akinterinwa et al., 2015)
Viscosity(mpa.s)	12.20	10.30	11.40	3.11-38.00	(Akinterinwa et al., 2015)
Elongation at break (%)	32	26	23	124	(Akinterinwa et al., 2015)
Formaldehyde Emission (ppm)	0.0330	0.0860	0.1051	0.08 (maximum)	(Osemeahon et al., 2010)
Moisture Uptake (%)	2.5	3.0	4.102	3.00 maximum	(Osemeahon et al., 2010)
Density (g/cm ³)	1.183	1.184	1.1870	1.07(Minimum)	(Osemeahon et al., 2010)
Melting Point (°C)	226.20	240.4	246.1	200(Minimum)	(Osemeahon et al., 2010)
Solubility	Soluble	Soluble	Soluble	-	(Osemeahon et al., 2010)
Turbidity	326	112	111	-	(Idowu-Oyewole et al., 2016)
Gel Time(hrs)	264	216	210	-	(Idowu-Oyewole et al., 2016)
Appearance	Clear	Clear	Clear	-	(Idowu-Oyewole et al., 2016)

Table 2. Shows some physical parameters of MMU, DMU, TMU and also comparing them with the acceptable standards in the coating industries. The refractive index gradually decreases as one moves from TMU to MMU. The decrease in refractive index could be attributed to the microphase separation between urea and formaldehyde with decreasing formaldehyde addition (Archibong *et al.*, 2018). The viscosity on the other hand is observe to increase from TMU to MMU, this effect may probably be induced by the intrinsic shear-thinning properties of the MMU resin, whose viscosity is sensitive to shear rate, with a newtonian behavior at lower formaldehyde content (Julien *et al.*, 2012). It could also be attributed to the fact that cross-linked molecular chains of methylol urea are further linked to each other by entanglements and strong secondary bonds especially at low formaldehyde inclusions. 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, 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 (Sunday and Christopher, 2018). Formaldehyde emission, moisture uptake, density and melting point decrease from TMU to MMU, reduction in formaldehyde emission may be as a result of the gradual reduction in formaldehyde inclusion as one moves along the route (TMU, DMU, MMU), the drop in moisture uptake could be attributed to the transport of water in a polymer network which is related to the availability of molecular-sized holes in the polymer structure and this holes tends to close up with decreasing formaldehyde content (Hui *et al.*, 2018). The decrease in density may also be due 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 (Bin *et al.*, 2016), while decreasing melting point signals decreasing hardness and increasing flexibility of the different thermosets resin. This behaviour may be attributed to urea serving as a flexible spacer, crosslink modifier and/or formaldehyde resin condensation inhibitor (Akinterinwa et al., 2015). The increase in turbidity may be due to the growth of large inter-polymer aggregate which results in light scattering, because at a lower formaldehyde inclusion there's tendency towards sedimentation (Sahad S.M. 2015). The gel time increase 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 (Lihui *et al.*, 2007).

Table 3. Some Physical Parameters of Paint Synthesis from MMU, DMU, and TMU Binder

Parameters	MMU	DMU	TMU	SON Standard
pH	8.30	8.22	7.3	7-8.5
Flexibility	Fail	Fail	Pass	Pass
Viscosity (poise)	8.8	8.6	6.5	6-15
Opacity	Pass	Pass	Pass	Pass
Adhesion	Fail	Fail	Fail	Pass
Hardness test	Fail	Fail	Fail	Pass
tackiness	Pass	Pass	Fail	Pass
Blistering	Fail	Fail	Fail	Pass
Drying Time				
Touch	50	55	167	20
Hard	73	88	700	120
Storage stability (6 months)	Pass	Pass	Pass	Pass

Some Physical Properties of MMU, DMU and TMU paints are tabulated in Table 3. As seen from the Table, some properties such as pH, viscosity, flexibility and opacity of MMU, DMU and TMU were within acceptable ranges for paints (SON, 1990). MMU, DMU and TMU all fail adhesion, hardness test, tackiness and resistance to blistering. This behaviour of these three paint product produced from MMU, DMU, and TMU can be due to low molecular weight and hence low crosslink density of the binders (Naghash *etal.*, 2007; Zorba *etal.*, 2008), the low cross linking density give rise to more free volume solvent molecules pass easily through the crosslinked network, also because of their hydrophilic nature (Hasmukh *etal.*, 2010; Motawie *etal.*, 2010). The drying time of MMU, DMU and TMU paint fail specification, the long drying time is attributed to the low molecular weight and hence low crosslink density of the three binder which delayed drying (Jain, 2008). The Touch-dry and hard-dry are respective stages in the coating dry-film formation. The touch-dry time is the period of particle coalescence and cohesion as the solvent evaporates. While hard-dry is the period of optimum adhesion and cohesion of the film to a stage if desired further coat can be satisfactorily applied (Egbewat *etal.*, 2014). Stability in storage is an important factor for coating system. Amino resin when use as a paint binder can undergo self-condensation making the system too viscous and gel like for coating application. From the above, all the paint formulation passed the standard stability test because of the addition of butanol (stabilizer) during formulation.

Table 4. Result and comparison of Chemical Resistance of MMU, DMU and TMU paint Film

Sample	Media		
	0.1M Hcl	0.1MNaOH	0.1MNacl
MMU	No effect	Blistering	No effect
DMU	No effect	Blistering	No effect
TMU	No effect	Cracking	Blistering

Chemical Resistance

The ability of a paint product to resist attack by chemical is one of the desirable quality of a good paint. Table 4 presents the effects of the three different media (i.e. NaCl, NaOH, and HCl) where a coat of each of the paint on an applicator was inserted into each of the media. All paint samples show no effect, in the HCl (acidic) medium hence a good resistance to this medium, all three paint sample were affected by the NaOH medium showing poor resistance in this medium. While in the alkaline medium MMU and DMU were not affected, but the TMU paint developed blisters in this medium. At a low pH (acidic medium), the crosslinking reaction and the resultant MMU, DMU and TMU polymer have high molar mass and results in formation of solid polymer initially moldable solid but ending in infusible hard plastics (Akpabio, 2012). 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 and DMU are suitable for a functional paint but TMU is not just suitable for functional binder at mildly alkaline (Akpabio, 2012). At a neutral pH the charges are neutralized and the MMU, DMU and TMU resin loses their tendency to behave as a resin and at above pH of 7 it starts building up again (Akpabio, 2012).

Conclusion

Waterborne paints represent an impressive alternative to paint based on organic solvents especially due to the fact that the organic base paint require expensive ingredients and are majorly responsible for emitting significant amounts of VOCs known to be affecting the environment and the human health. In our continuous search to better the formaldehyde emission and other properties like poor water resistance, brittleness and hardness associated with UF which has been manifesting in different dimensions, we synthesis monomethylol urea compared its parameters with that of di and tri methylol urea. We went further and formulated emulsion paint using the various resins as binders, monomethylol urea exhibited far better paint qualities, surpassing di and tri urea paint in terms of the viscosity, pH, tackiness and opacity, resistance to chemical attack. It would therefore, not be out of place to conclude that monomethylol urea would make a better emulsion paint binder than any of the other members of urea formaldehyde (di, tri, and tetra) family.

References

1. A M Alakrach , R Hamzah, N Z Noriman, Omar S Dahham1, Z Shayfull, S Z Syed Idrus , S Sudin (2018). Recycled Natural Rubber Latex Gloves Filled Chloroprene Rubber: Effects of Compatibilizers J. Phys.: Conf. Ser. 1st International Conference on Green and Sustainable Computing.

2. A.M. Motawie, M.H. Sherif, M.M. Badr, A.A. Amer and A.S. Shehat, Synthesis and characterization of waterborne epoxy resins for coating application. *Austr.J of Basic and Appl. Sci.*, 4(6), 2010, 1376-1382.
3. Abbas Kazaure Adamu, Muhammed Kabir Yakubu, and Olufemi Kassim Sunmonu (2014) International Conference on Biological, Chemical and Environmental Sciences (BCES-2014) Penang (Malaysia Characterization of Emulsion Paints Formulated using Reactive – Dyed Starch as a Pigment)
4. Afsoon F, Laleh R, Faramarz A (2011). DSC analysis of thermosetting polyimide based on three bismaleimide resin eutectic mixtures. *Iranian Polym. J.* 20(2):161-171
5. Akinterinwa, A., Osemeahon S.A., Nkafamiya., I.I and Dass P.M (2015). Formulation of emulsion paint from a copolymer composite of Dimethylol urea/polystyrene. *Journal of chemistry of chemistry and material research*, 7(7):20-25
6. Al-Manasir N (2009). Preparation and characterization of crosslinked polymeric nanoparticles for enhanced oil recovery applications. University of Oslo, Norway. pp. 12-85
7. Archibong, C.S, Osemeahon, S.A., Ushie O.A and Ugwuja, D.I (2018). Trimethylol urea and polystyrene waste composite as binder for emulsion paint formulation. *International journal of modern chemistry* 10(1):1-13
8. Archibong, C and Osemeahon S. (2019). Development of monoethylol urea urea for coating application: effect of time on synthesis. *Current trends in biomedical engineering and Bioscience* 18(2)55-72
9. Broek A.D., (1993), Environment-friendly paints: their technical im(possibilities), *Progress in Organic Coatings*, 22, 55-68.
10. Crespi M.S., Hikosaka M.Y., do Amaral G.C.A., Ribeiro C.A., (2007), Kinetic parameters obtained for thermal decomposition of acrylic resins present in commercial paint emulsions, *Journal of Thermal Analysis and Calorimetry*, 88, 669-672
11. E.M. S. Sanchez, C.A.C. Zavaglia, M.I. Felisberti (2000). Unsaturated polyester resins: influence of the styrene concentration on the miscibility and mechanical properties. *J. Polymer* 41 765-769.
12. Fahad AlObaidi, Zhibin Ye, Shiping Zhu (2004). Ethylene Polymerization with Homogeneous Nickel-Diimine Catalyst: Effect of catalyst structure and polymerization conditions on catalysts activity and polymer properties. *J. pol.* 45:6823-6829
13. Fatma Meydeneri Tezel, Ishak Atsin Karper (2017). Effect of pH on Optical and Structural Characterization of Chemical Deposit AgI thin films. *Mat. Res. J.* 20(6):8-25
14. Ferrándiz-Mas V., García-Alcocel, E. (2013). Durability of expanded polystyrene mortars. *Construction and Building Materials* 46, 75-182
15. Ganesshram, V. and Achudhan, M (2013). Synthesis and characterization of phenol formaldehyde resin as a binder used for coated abrasives. *Industrial journal of science and technology* 6(6):4814-4823
16. G. Astarloa-Aierbe, J.M. Echewerria, A. Vazquez, I. Mondragon (2000). Influence of the amount of Catalyst and pH on the Phenolic Resol Resin Formation. *J. pol.* 41:3311-3315
17. G.A.H. Nooijen., B.V., Amsterdam (2001). Ziegler/Natta catalysts in particle form ethylene polymerization: The effect of polymerization start-up on catalyst activity and morphology of the produced polymer. Elsevier Science Publishers (11):35-46
18. Gonzalez GM, Cabanelas JC, Baselga J (2012). Application of FTIR on epoxy resins- Identification, monitoring the curing process, phase separation and water uptake. *Infrared Spectrosc. – Mater. Sci. Eng. Technol.* 261-283.
19. Hamad, K., Kaseem, M., and Deri, F. (2010) Effect of recycling on rheological and mechanical properties of poly (lactic acid)/ polystyrene polymer blend, Springerlink.

20. Hwang, Y., Sangmook, L., Youngjae, Y., Kwangho, J., and Lee, W (2012). Reactive extrusion of polypropylene/polystyrene blends with supercritical carbon dioxide. *J. of Macromol. Res.* 20(6):559-567.
21. Jain W (2008). Evaluation of second generation indirect composite resins. A thesis submitted to the faculty of the University Graduate School in partial fulfilment of the requirements for the degree, Master of Science in the Department of Dental Materials, Indian University, Idianapolis. Pp. 1-94.
22. J.H. Naghash, A. Karimzadeh, R.A. Momeni, R.A. Massah and H. Alian, Preparation and properties of triethoxyvinylsilanemodified styrene-butyl acrylate emulsion copolymers. *Turk. J. Chem.*, 31(2007), 2007, 257-269.
23. Joakin Jeremeseff (2012). Investigation of UF-resin-the Effect of Formaldehyde/
24. Jon won Kang and yun-kyoo Han (1997). Polymerization of Tetrahydrofuran with new transition metal catalyst and its mechanism: (p-methylbenzyl)-o-cyanopyridium Hexafluoroantimonate. *Bull Koren Chem. Soc.*18(4):1-16
25. Kaniappan K, Latha S (2011). Certain Investigations on the formulation and characterization of polystyrene/poly(methylmethacrylate) blends. *Int. J. Chem. Res.* 3(2):708-717.
26. Karakas F., Pyrgiotakis G., Celik M.S. and Moudgil B.M. (2011). Na-Bentonite and MgO Mixture as Thickening Agent for Water-Based Paints. *KONA Powder and Particle J.* No 29: 96-106.
27. Kazys, R., and Rekuviene, R (2011). Viscosity and density measurement methods for polymer melts. *Ultragarsas "Ultrasound"* 66(4):20-25.
28. Kim, M.G., Kanatzidis, M.G., Facchetti A., Marks T.J (2011). Low-Temperature Fabrication of high Performance Metal Oxide Thin-Film electronics via combustion Processing. *US Nat. Lib. Of Med. Natural instistute of Health.* 10(5):382-8
29. kirana, suswato, and sigit T. Nicaksmo (2018). Effect of thermoset plastic addition in physical and mechanical properties of plastics waste composite for construction material application. *AIP conference proceedings*
30. Lee J. Jeon. Kim S.(2011). Green adhesives using tannin and Cashew nut shell liquid for environmental-friendly furniture materials. *J. Korean Furniture society.* 22(3):219-229
31. Liem, H., Etchegoin, P., Whitehead, K.S., and Bradley, D.DC (2002). Raman Scattering as a probe of morphology in conjugated polymer thin films. *Journal of Applied Physics.* 92(2):1154-1161.
32. Lisa G., Curteanu S., Lisa C., (2010), Artificial neural network for prediction of excess refractive indices of some binary mixtures, *Environmental Engineering and Management Journal*, 9, 483-487
33. Luis Alexandro, Francisco J.E., Horlesian M.T., Florentino S.C., Hector R.C., Claude S.T., Francisco H.G., Jose L.C., Ramon E.D. (2016). The Influence of co-catalyst in the polymerization of 1,3-butadiene catalyzed by Neodymium chloride Tripentanoate. *J.Mex. Chem. Soc.* 60(3):56-62
34. Menkiti M.C., Onukwuli O.D (2011). Utilization potentials of rubber seed oil for the production of alkyd resin using variable base oil lengths. *New York Sci. J.* 4(2):51-59.
35. Menkiti MC, Onukwuli OD, (2011). Utilization potentials of rubber seed oil for the production of alkyd resin using variable base oil lengths. *New York Sci. J.* 4 (2):51-59.
36. Ming Cao, Taohong Li, Jiankun Liang and Guanben D.U. (2017). The influence of pH on Melanine-Dimthylurea-Formaldehyde Co-condensations: A Quantitative ¹³C-NMR Study. *MDPI J. of Polymer* 10(9): 1-12

37. Ming Liu, Rooban Venkatesh K.G. Thirumalai Yiqiang Wu and Hui Wan (2017). Characterization of the Crystalline Region of Cured Urea Formaldehyde Resin. R.S.C. 7:49536-49541
38. MM Alavi Nikje; F Abedinifar; and A Idris (2016). Epoxidized Soybean Oil Ring Opening Reaction under MW Irradiation, 3 (3):383-388.
39. S. Abdulsalam, and Yahaya, Y. U. (2010), "Effectiveness of Gum Arabic as a Binder in Emulsion House Paint", Global Journal of Engineering Research, 10 (1 & 2): pp. 83-89, 2010
40. S.P.Hasmukh and J.P. Sumeet, Novel surface coating system based on maleated shellac. E –Journal of chemistry, 7(S1), 2010, S55S60
41. Salthammer T, Mentese S, Marutzky R (2010). Formaldehyde in the indoor environment. Chem. Rev. 110(4):2536-2572.
42. SON, Standard for Paints and Varnishes part 6: Test Methods for paints for Decorative purpose, 1990, pp1-24
43. T. Zorba, E. Papadopoulou, A. Hatjiissaak, K.M. Paraskevopoulos and K. Chrissafis, Urea-formaldehyde resins characterized by thermal analysis and FTIR method. J. Thermal Analysis and Calorimetry, 92, 2008, 29-33.
44. Traumann A., Reinhold K., Tint P., (2014), Environmental and occupational impact on human health of dust and chemicals from modern technologies, Environmental Engineering and Management Journal, 13, 22332241.
45. Yelwa, J.M., Osemeahon, S.A., Nkafamiya, I.I. and Abdullahi, S. (2017). Synthesis and Characterization of Hydroxylated Sunflower Seed Oil/Poly Vinyl Acetate Copolymer as a Binder for Possible Application in the Coating Industry, 4(7): International Journal of

© GSJ