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Development of urea formaldehyde and polystyrene waste as copolymer binder for emulsion paint formulation

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Urea formaldehyde, that is, trimethylol urea (TMU) resin was synthesized and blended with polystyrene waste (PS) to develop TMU/PS copolymer binder for emulsion paint formulation. The resulting copolymer was analysed for formaldehyde emission and other physical properties such as viscosity, gel time, density, turbidity, refractive index, melting point and moisture uptake, elongation at break and solubility in water. Infrared (IR) analysis of TMU, PS and TMU/PS showed chemical interaction between TMU and PS resins. The level of formaldehyde emission and moisture uptake were found to decrease with increase in PS concentration while, that of elongation at break on the other hand increase with increase in PS concentration. The three problems (hardness, low water resistant and formaldehyde emission) traditionally associated with TMU resin can be addressed with TMU/PS copolymer. Some physical properties of the copolymer are in agreement with the literature values of other type of binders use in paints with values within the acceptable level in the coating industry. Thus this study provides urea formaldehyde and polystyrene as a potential binder for the coating industry. Polystyrene which leads to polymer wastes is recycled and utilised for coating application.

Key words: Binder, blending, polystyrene waste, solid waste, urea formaldehyde.

INTRODUCTION

The introduction of synthetic resins as replacement for natural resins in the formulation of coating materials has transformed the modern paint industry. It is now possible to produce a variety of coatings using synthetic resin, because of its superiority over any of those from natural resins. The synthetic resins are particularly distinct due to their hardness, durability and resistance to water, alkalies and other chemical (Lin, 2005). The need for environmental conservation and pollution prevention arising from volatile organic compounds (VOC) in oil paint has increased steadily. This has motivated chemists to modify

coatings, hence solvent are reduced or totally omitted from the coating formulation and replaced with water.

Urea formaldehyde resins are poly-condensation products of urea and formaldehyde in either alkaline or neutral or acid or alkaline/acid medium. Urea formaldehyde are thermosetting polymers which accounts for over 80% of amino resins, mostly used as a moulding material, component of adhesive and protective finishing. Low price, good technological characteristic, absence of colours in cured polymer, low cure temperature, resistance to micro organism and abrasion,

hardness, good thermal properties and easiness of application are the outstanding qualities of urea formaldehyde (Akpabio, 2012; Ayoub et al., 2013).

The structure of thermosetting resins also leads to some unwanted mechanical properties which limits their application (Cakir et al., 2012). In spite of the afore-mentioned advantages accredited to urea formaldehyde, it is far too hard and brittle to be use alone as coating material. Urea formaldehyde resin also exhibit poor water resistance and formaldehyde emission; thus, creating problems of environmental pollution and inconsistency in the quality of product with age.

Since urea formaldehyde resin is soluble in water, its full utilization is needed to meet different requirements of the coating industrially in terms of emulsion paint formulation and consequent reduction in VOC in the environment. This can be achieved if the inherent problems of brittleness, poor water resistance and formaldehyde emission associated with urea formaldehyde resin are addressed (Osemeahon, 2008). Hence, this study seeks solution to the problem, by copolymerization of urea formaldehyde, that is, trimethylol urea (TMU) resin and polystyrene waste (PS).

Polymer blending is a proven tool to obtain new types of materials with a wide range of properties intermediate between those of pure components. Polymer blends are made to maintain a proper cost performance ratio and reinforcement of properties, which is compensation of the demerits of a polymer by blending it with a second one that is rich in the aspects lagging in the initial one. The technology of blending is now moving at a rapid pace and blending technology is also proving to be of use in plastics recycling (Arthanareeswana et al., 2011; Bhattacharya et al., 2009). An up-cycling of the post consumer blend wastes for value-added goals remains a challenge for the scientific community. Recycling of thermoplastic elastomers makes polymer life almost endless. Blending has been developed in order to improve polymer recyclates during reprocessing (Leib et al., 2011). Polystyrene particle is a member of the family of latex particles that are used for different types of industrial products and biological assays. Bare latex particles are used as binders of pigment in paint and in the process paper coating (Thormann et al., 2008). With the development of new synthetic polymers, plastics have found applications in every field of life.

A worldwide increase in the use of these materials has generated the issue of solid waste disposal. Synthetic plastics do not biodegrade in natural environments due to the complexity of their structure, high molecular weight and hydrophobic nature (Atiq et al., 2010). According to Ahmed et al. (2012), Plastic has been used in great demand nowadays. Plastics do not break easily because they are resistance to moisture. They block drainage during rains; they are recognized as threat to oceans, soil, domestic animals, wildlife and marine life.

In marine environments, plastic can entangle, suffocate or cause blockage in digestive tracts of marine animals (Magizvo, 2012; Isiya, 2012).

Polystyrene product contributes to solid waste after use. Polystyrene has a low scrap value and is difficult to transport, so most polystyrene are thrown into landfills instead of being recycled.

Since the product is not biodegradable, disposing polystyrene waste in landfills is not a sustainable practice, so recycling polystyrene becomes a needed alternative (Ricky et al., 2010). Polystyrene is recycled poorly throughout the world; hence, the interest in re-cycling technologies to reduce the amount of polystyrene waste in landfills. Recycling programs for polystyrene are not currently in place on a large scale. The development of an effective recycling process is required for waste polystyrene.

Since blend involves the use of pre-existing material, without recourse to synthesis, they offer pecuniary ad-vantage and time-saving economy. Trimethylol urea has a lot of -OH groups in one hand and polystyrene having –H atoms along it framework on the other hand. Therefore, both chemical and physical interactions are possible when these two different polymers are mixed as shown in scheme 1. If this blending is achieved, the resulting composite will share the properties of both pure methylol urea and pure polystyrene.

This will then introduce flexibility into the TMU due to high flexibility of polystyrene, reduce moisture uptake due to hydrophobicity of polystyrene and further reduce formaldehyde emission due to polystyrene inclusion in the blend.

This process will eventually produce an acceptable emulsion paint binder from amino resin on one hand and then help to reduce the problem of environmental pollu-tion from disposal of waste polystyrene materials on the other hand.

MATERIALS AND METHODS

Reagents

Urea, formaldehyde, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide pellets and sucrose were reagent grade products from the British Drug House (BDH), Gasoline. All materials will be used as received. Polystyrene waste was collected from refuse dumps around Yola, Nigeria.

Resin synthesis

Trimethylol urea (TMU) was prepared by using one mole (6.0 g) of urea to react with three moles (24.3 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 0.5M H_2SO_4 and 1.0M NaOH solutions. The solution was heated in a thermostatically controlled water bath at 70°C. The reaction was allowed to proceeds for 2 h after which the sample was removed and kept at room temperature (30°C).

Formation of liquid PS

Solid PS was constituted into liquid form by dissolving 5 g of PS

waste in 25ml of gasoline. The mixture was stirred continuously and allowed to stay for 24h to achieve a homogenous solution.

Preparation of TMU/PS blends and films

Blend of TMU and PS was prepared by adding varying amount of PS (0-70%) in TMU resin. 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 resin was allowed to cure and set for seven days at (30°C). The physical properties of the resin films were investigated.

Determination of viscosity and gel time

A 100 ml Phywe made of 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. Five different readings were taken for each sample and the average value calculated. The gel point of the resin was determined by monitoring the viscosity of the resin with time until a constant viscosity profile was obtained

Determination of density, turbidity, melting point and refractive index

The density of the resin was determined by taking the weight of a known volume of resin inside a density bottle using metler (Model, AT400) weighing balance. Five readings were taken for each sample and average value calculated. The turbidity of the resin samples was determined by using Hanna microprocessor turbidity meter (Model, H193703). The melting points of the film samples was determined by using Galenkamp melting point apparatus (Model, MFB600-010F).The refractive indices of the resin samples was determined with Abbe refractometer. The above properties were determined according to standard methods (AOAC, 2000)..

Determination of moisture uptake

The moisture uptakes of the resin films were determined gravimetrically. Known weight of the sample 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 is obtained. The difference between the wet weight and dry weight of the sample was then recorded as the moisture uptake by resin. Triplicate determinations were made for the sample and the average value recorded.

Determination of formaldehyde emission

Formaldehyde emission test was performed by using the standard 2 h desiccator test. The mold used was made from aluminium foil with a dimension of 69.6 x 126.5 mm and thickness of 12.0 mm. The emitted formaldehyde was absorbed in 25.0 ml of water and analyzed by a refractometri technique using Abbe refractometer. Triplicate determinations were made for the samples and the average value taken.

Elongation at break

The elongation at break was measured using Inston Tensile Testing Machine (Model 1026). Resin films of dimension 50 mm long, 10 mm wide and 0.15 mm thick was brought to rapture at a clamp rate of 20 mm/min and a full load of 20 kg. A number of five runs were carried out for each sample and the average elongation evaluated and expressed as the percentage increase in length.

Water solubility

The solubility of the TMU and TMU/PS blend in water was obtained by mixing 1ml of the resin with 5ml of distilled water at room temperature (30°C).

FTIR analysis

The infra-red (IR) analysis of TMU, PS and TMU/PS was carried out using infra-red spectrophotometer (Thermo Electron Corporation. Version 2.6.0, builds 2.5225 Verona Road Madison, WI, 53711. USA) within 500 to 4000 cm-1.

RESULTS AND DISCUSSION

FTIR spectral analysis

FTIR spectroscopy is one of the powerful tools used in identifying and investigating the presence of functional groups in a molecule, as each specific chemical bond often has a unique energy absorption band, and can obtain structural and bond information on a complex to study the strength and the fraction of hydrogen bonding and miscibility (Kaniappan and Latha, 2011; Saravanan et al., 2011).

Figure 1 shows the FTIR spectra of TMU, PS, and TMU/PS. Figure 1 shows the IR spectra of A (TMU), B (TMU+PS) and C (PS). In the spectra of TMU, the broad band stretching from 3600 cm^{-1} through 3100 cm^{-1} is due to O-H of methylol urea, 2922.89 cm^{-1} is due to N-H, 1742.81 cm^{-1} is due to C=O of urea, 1460.29 cm^{-1} is due to –CH$_2$ of methylene bridge and 1252.29 cm^{-1} due to C-O-C of ether linkage (Osemeahon, 2011).

The IR spectrum of PS showed absorption bands at 3160.57 to 2908.54 cm^{-1} corresponding to aromatic and aliphatic C-H stretching, respectively. The peaks at 1600.68 and 1448.90 cm^{-1} are assigned to C=C stretching of phenyl group. The C-H deformation vibration band of benzene ring hydrogen was seen at 755.68 cm^{-1} and ring deformation was observed at 698.13cm^{-1}. The C-H stretching vibration of ring hydrogen appeared at 3000 to 3100cm^{-1} (Naghash et al., 2007; Kaniappan and Latha,2011).

In the TMU+PS spectra, the strong O-H peak at 3437.36 cm-1 in TMU is almost absent. It appears at a lower frequency 3361.58 cm-1. This reduction may be ascribed to the consumption of OH groups during condensation reactions. The C=C, C=O, N-H, C-O-C, C-H and –CH$_2$ bands of TMU and PS all shifted to different frequency, because of polycondensation, in the co-polymer. These observation indicates a chemical reaction between TMU and PS.
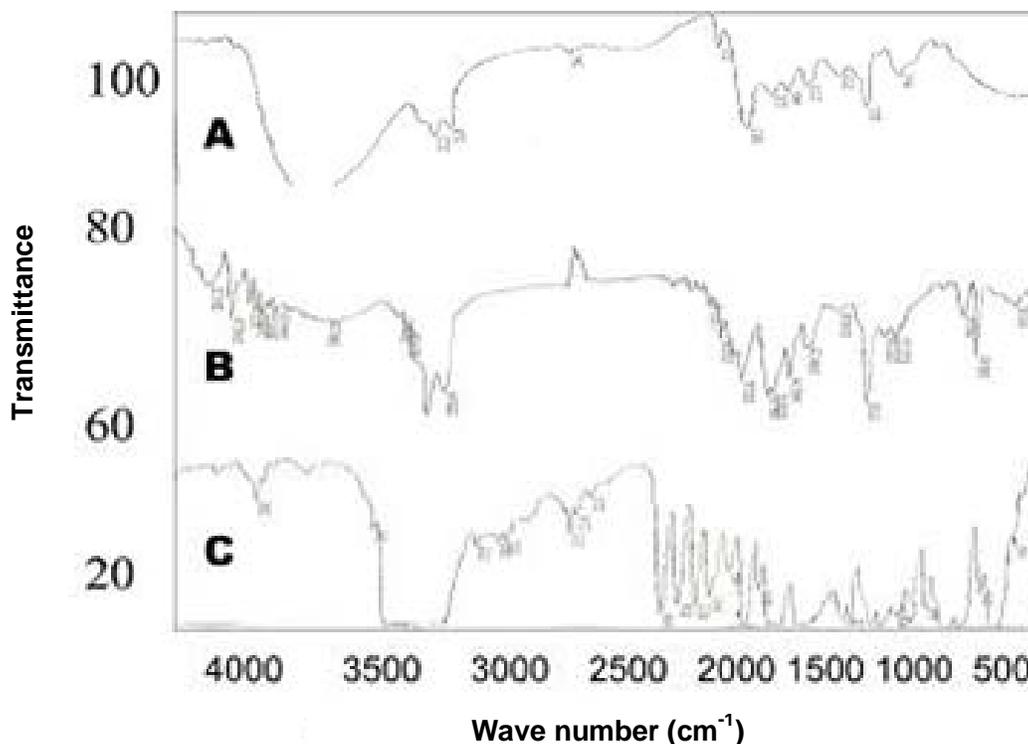
**Figure 1.** IR Spectra of (A) TMU, (B) TMU+PS, and (C) PS.

Effect of PS concentration on the viscosity of TMU/PS resin

Rheology is a branch of physics that deals with the deformation and flow of matter under stress. The results from rheological investigations provide the mathematical description of the visco-elasticity behaviour of matter. For many years, rheology has been used as semi-quantitative tools in polymer science and engineering. The relationship between the structure and rheology of a polymer is of practical interest for two reasons: firstly, rheological properties are very sensitive to certain aspect of structure and they are simple (Oluranti et al., 2011).

An important rheological property of fluids is viscosity. Viscosity is a fundamentally rheological parameter of macromolecular compounds (polymer) properties that defines resistance to flow and is related to the characteristics of composite materials widely used in many field of industry. The knowledge of viscosity can help to characterize polymers and to determine indirectly molecular mass. The term viscosity is defined as the measure of internal friction of a liquid. The time required for a liquid to drain out of a capillary tube is directly proportional to its viscosity. The SI unit of viscosity is the Pascal times second [Pa s] but also in poise [P]. In processing technologies of polymeric materials, viscosity is the most important technological characteristic (Stabik et al., 2009).

It is well known that studying rheological properties of fluids and gels are critically important since, it is the key for design processing operations that depend on the way that the product flows, for example, flow through a pipe, stirring in a mixer, and packaging into containers. Many of the sensory attributes of emulsions lattices are directly related to their rheological properties, for example, creaminess, thickness, smoothness, spread-ability, pour-ability, flow-ability, brittleness, and hardness. Control of the morphology and viscosity of lattices particles has been a well practiced art within industry for some time now, given its great importance in determining the physical and mechanical properties of polymer system (Hussain and Nasr, 2010).

Figure 2 shows the effect of polystyrene waste on the viscosity of TMU/PS resin. At the beginning with low level of PS and high level of TMU, we have relatively low viscosity. Difference in viscosity arises as a result of variation in respective chain length. As the PS loading increases, the molecular weight of the copolymer increased, this increase in molecular weight gave rise to increase in viscosity due to increase in cross-linking density. This explains the regime from 0 to 60% PS loading (Afzal et al., 2013). After 60% PS loading, further inclusion of PS into the copolymer results in polymer dissociation, signalling overloading above the optimal level. Polymer dissociation results to fragmentation of long chain polymer into shorter chain oligomers with
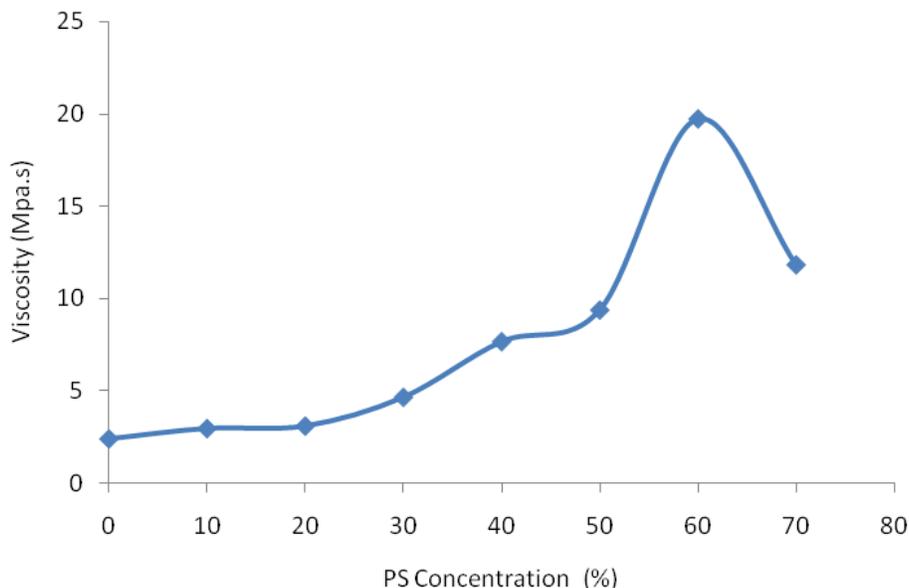
Figure 2. Effect of PS concentration on the viscosity of TMU/PS resin.

corresponding decrease in viscosity. This explains what happen at 70% loading of PS

Effect of PS concentration on the gel-time of TMU/PS resin

Gelation is the change in macromolecular structure of resin, which is usually expressed as an increased of viscosity and leads finally to the loss of flow-ability. Gelation has two processes: the initial period of slow viscosity growth and the period of fast structuration (Suurpere et al., 2006). The gel time or pot life is the maximum length of time the system remains in sufficiently fluid condition to be applied to a substrate, it is also the point at which network formation commenced. The dry time of any paint is a function of its binders gel time among other factors. On the technical front, gel time enable paint formulator to ascertain the optimum storage period of a binder before its utilization for paint formulation and is important in determination of adhesion (Desai et al., 2003; Menkiti and Onukwuli, 2011; Ayoub et al., 2013).

Gelation is characterized by the incipient formation of a material of an infinite molecular weight and indicates the conditions of the process-ability of the material. Prior to gelation, the system is soluble, but after gelation, both soluble and insoluble materials are present. As gelation is approached, viscosity increased dramatically and the molecular weight goes to infinite. The reaction between monomers leads to the formation of network, hence gelation. Both molecular weight and poly-dispersity increase until one single macromolecule is formed. At this point, the behavior of the system changes from liquid-like to

rubber- like thus the reactive system becomes a gel (Gonzalez et al., 2012). Figure 3 shows the effect of PS concentration on the gel-time of TMU/PS composite.

From the graph, it can be seen that the gel time decreased with PS inclusion up to 60% PS. This behaviour is attributed to increase in molecular weight and cross-linking density which leads to increase in viscosity and reached a stage where nucleation process begins producing microgel particles which enhanced increase in viscosity build up (Menkiti and Onukwli, 2011). An increase was observed at 70% PS. This result agrees with the viscosity result where phase inversion and dissociation occurred at 70% PS. In the paint industry, the gel time is typically refers to as dry time of the paint. The longer the time its takes a polymer to gel, the same time it will take for the paint to cure or dry. Short dry time is harmful to the paint film just like if the dry time is too long. This factor must be monitored in order to ascertain the rate it will take a paint formulated from a particular binder to dry.

Effect of PS concentration on the density of TMU/PS resin

Density is a physical property of matter that expresses a ratio of mass to volume and is an important physical parameter in polymer engineering processes. Density depends on the atomic mass of an element or compound. Since different substances have different densities, density measurements are very useful for the identification and characterization of different substances and a significant factor that affects the production cost and profitability of the manufacturing process (Kazys and
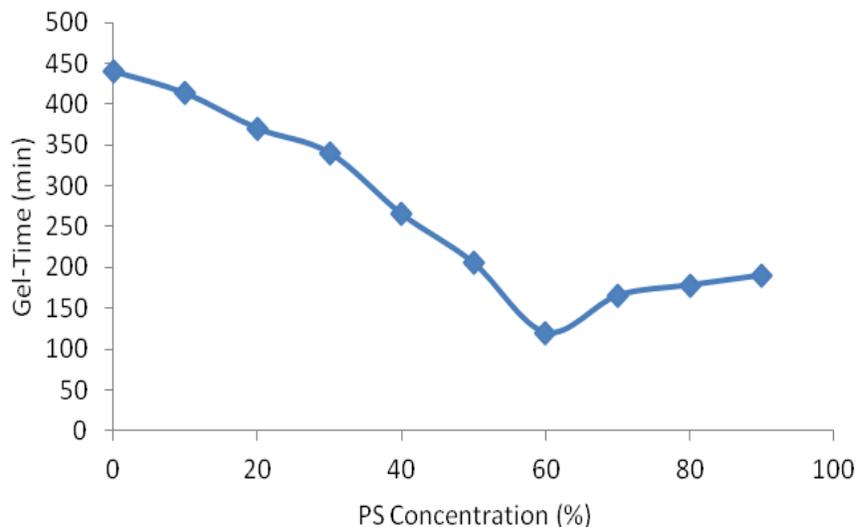
Figure 3. Effect of PS concentration on the gel time of TMU/PS resin.

Rekuviene, 2011). The density of a paint binder in the coating industry has an important influence on factors such as pigment dispersion, brush-ability of paint, flow, levelling and sagging.

The gradual decrease observed in density with increase in PS concentration as shown in Figure 4 can be as a result of differences in the molecular features and morphology which influenced the packing nature of resin molecules as the concentration of PS increases. Physical properties of polymer depend on chain length and content of soft and hard segments. The decrease observed from 0 to 70% PS loading is due to increasing amount of soft segment (Mavani et al., 2007). It is expected that the density of the blends will fall between the density of urea formaldehyde resin and polystyrene, since the pure PS has a lower density relative to pure TMU (Blaise et al., 2012).

Effect of PS concentration on the turbidity of TMU/PS resin

The measurement of turbidity of the binder was performed in order to characterize the optical properties of the binder as related to gloss property. The refractive index gives indication of the turbidity. Light interaction with a colloidal system is its turbidity. Turbidity actually derived its principle from light scattering. When we have homogeneity and few particles, there will be less scattering; hence, higher scattering is observed when we have a non homogenous system with a lot of particles. Figure 5 shows the effect of PS concentration on the turbidity of TMU/PS resin.

Turbidity is relatively low at 0% PS, because pure TMU

is clear and transparent. However, on addition of PS it becomes colloidal and light scattering increases. As the concentration of PS increases, the growth of large interpolymer aggregate increase and the turbidity increased, hence turbidity of the system can be used as an indicator of the level of interchain cross-linking (Al-Manasir, 2009). The more the PS loading, the more the light is scattered and this consequently leads to corresponding increase in the turbidity of the system.

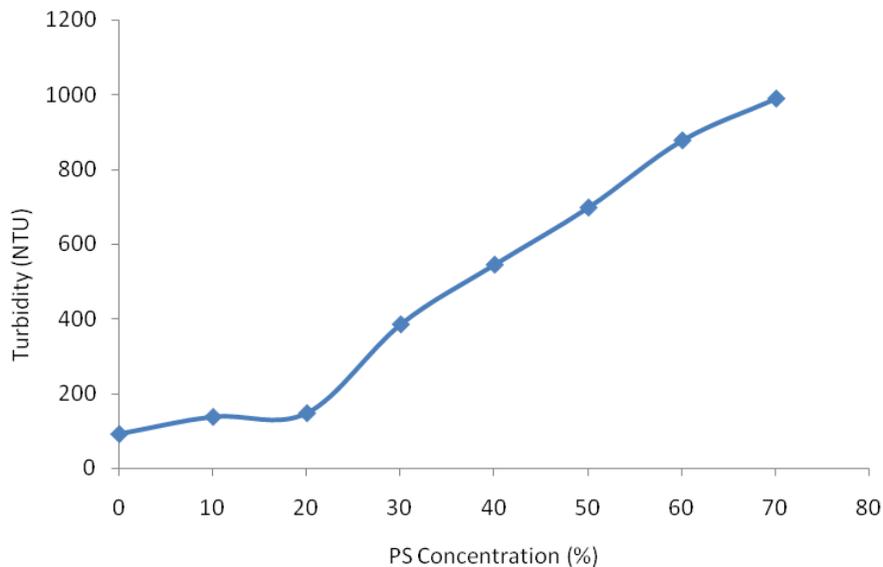**Effect of PS concentration on the melting point of TMU/PS resin**

Thermal property, molecular weight, degree of cross linking and the level of rigidity of the polymer is related to its melting point. The melting points of the two polymers are very different which probably result from different contributing factors. In general, the melting point of a compound increases with its molar mass, intermolecular Van der Waals interactions and also the intrinsic structures that affect the rigidity. In the case of coating industry, the melting point of a binder is related to its thermal resistance as well as to the brittlity. Urea formaldehyde resins are made-up of molecules that cross-link into clear hard plastics (Afsoon et al., 2011).

Figure 6 exhibits the effect of PS concentration on the melting point of TMU/PS resin. This is the mirror of the viscosity behaviour of the polymer composite. The result shows a gradual decrease in melting point from 0 to 50% concentration of PS in the blend. This is due to increase flexibility as a result of increase in the concentration of PS which give rise to increase in molecular mobility.

The increase in the melting point observed at 60% PS
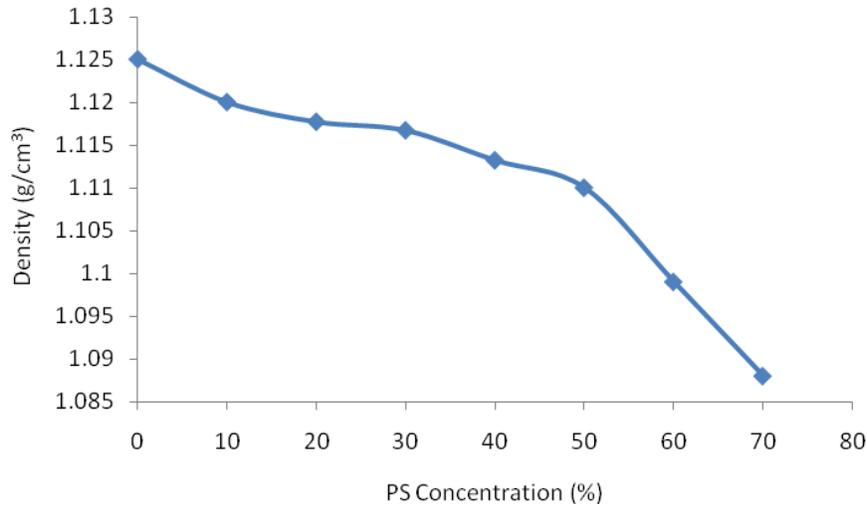
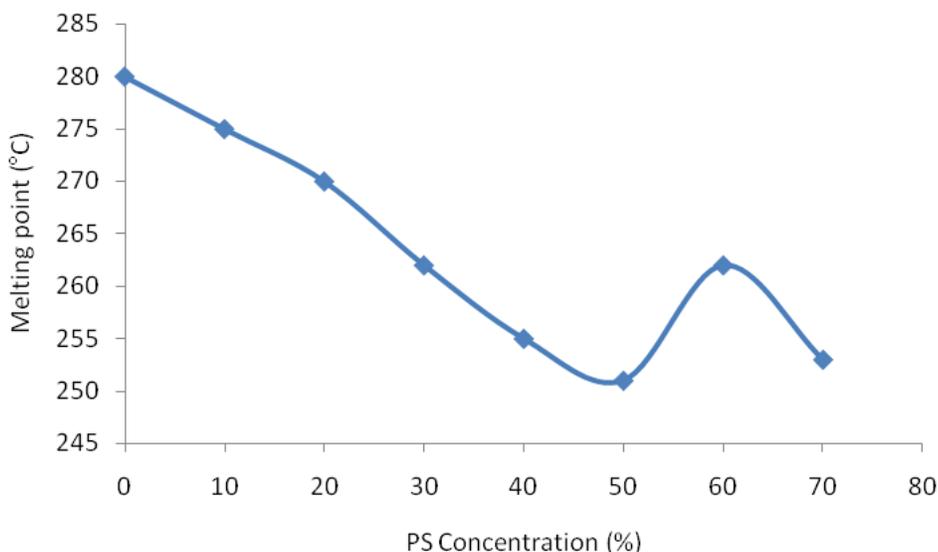**Figure 4.** Effect of PS concentration on the density of TMU/PS resin.

Figure 5. Effect of PS concentration on turbidity of TMU/PS resin.

inclusion in the blend is due to increase in molecular weight which makes the material harder in nature due to the increased cross-linking density. From the figure, optimal hardness was obtained at 60% PS loading, however, at 70% regime of PS inclusion, polymer dissociation takes place resulting to the decrease in melting point observed.

Effect of PS concentration on the refractive index of TMU/PS resin

Gloss is a measure of the ability of coated surface to reflect light. Reflection of light from surfaces can be classified according to the diffuse component or the specular component. The diffuse component results from light penetration to the surface, undergoing multiple reflections and refractions, and then re-emerging again at the surface. The specular component is a surface phenomenon, which is expressed as a function of the incidence angle and refractive index of the material, the surface roughness and a geometrical shadowing function. Gloss is a necessary coating property when the purpose is for surface aesthetic or decoration (Kaygin and Akgun, 2009; Yumiko et al., 2010). Glossiness of the paint shows how it reflects light and shineness. One of the advantages of oil paint is gloss. If water paint is to challenge the oil paint, the gloss property of emulsion paint must challenge

Figure 6. Effect of PS concentration on the melting point of TMU/PS resin.

index of the binder is a crucial factor in the ultimate gloss property of the paint formulation.

The effect of PS concentration on the refractive index of urea formaldehyde resin is as shown in Figure 7. It is observed that, the refractive index increases with PS concentration. TMU has lower refractive index than PS. As the PS is added to TMU, the optical property of TMU as regard refractive index increases. This explains the observed behaviour of the copolymer resin. The alteration of the crystallinity of the system with PS loading give rise to higher crystallinity to the TMU/PS resin, which also explains the above behaviour (Jain, 2008).

Effect of PS concentration on the moisture uptake of TMU/PS resin

Polymeric binders play a major role in moisture transport properties of paint, because it is one of the major constituent. Waterborne coatings are susceptible to durability issues pertaining poor water resistance. The functional groups on polymers or copolymer resins that are used can undergo hydrogen or ionic bonding, unless the hydrophilic character is balanced with that of the hydrophobic, the coating will either be water sensitive or the formulation will not have colloidal stability. Hydrophobic components in the binder give the best combination of improving water resistance of water-borne coating. A detailed knowledge of moisture transport is also essential for understanding the resistance of a material against attacks from its environment (Emile, 2003; Bharath and Swamy, 2009).

One of the main drawbacks of urea formaldehyde resin is its high water uptake and this has to be improved in order for the resin to satisfy the coating industry. Water

deteriorates thermo-mechanical properties and adhesion; it induces chemical degradation of the network and also generates stresses, because of swelling and hence blistering of the coating film (Gonzalez et al., 2012; Toloei et al., 2013). The water absorption ratio of latex films is an important parameter for characterization of hydrophobicity of the binder.

As shown in Figure 8, the percentage water absorption of the films was greatly influenced by the PS content. The moisture uptake decreased with increase in the concentration of PS, this is as a result of the excellent hydrophobicity of PS. Increase in PS into the copolymer give rise to corresponding increase in hydrophobicity of the polymer matrix (Naghash et al., 2007). Also, interaction between TMU and PS results in an increase in cross-linking density, this narrows down the intermolecular spacing. The smaller intermolecular spacing give rise to lower voil spaces within the matrix, hence the reduction in moisture uptake (Nouailhas et al., 2011). The reduced sensitivity to moisture due to PS inclusion in TMU matrix provides benefits in property retention as a function of environmental conditioning. This will also address one of the shortcomings of pure TMU, which is high moisture uptake.

Effect of PS concentration on the formaldehyde emission of TMU/PS resin

A serious drawback of urea formaldehyde resin is the emission of the hazardous formaldehyde during cure. The issue of formaldehyde exposure in homes is long-standing and has been studied overtime. It is therefore important to determine the formaldehyde emission from synthesized urea-formaldehyde resin before its application
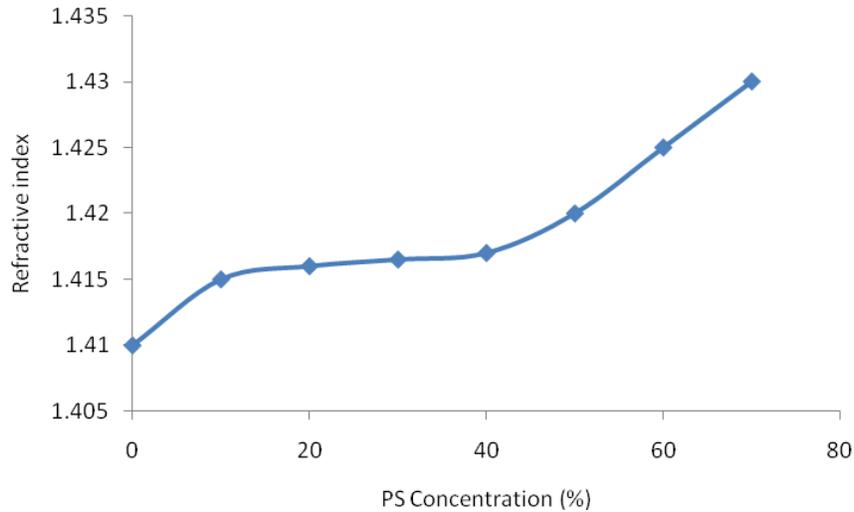
Figure 7. Effect of PS concentration on the refractive index of TMU/PS resin.
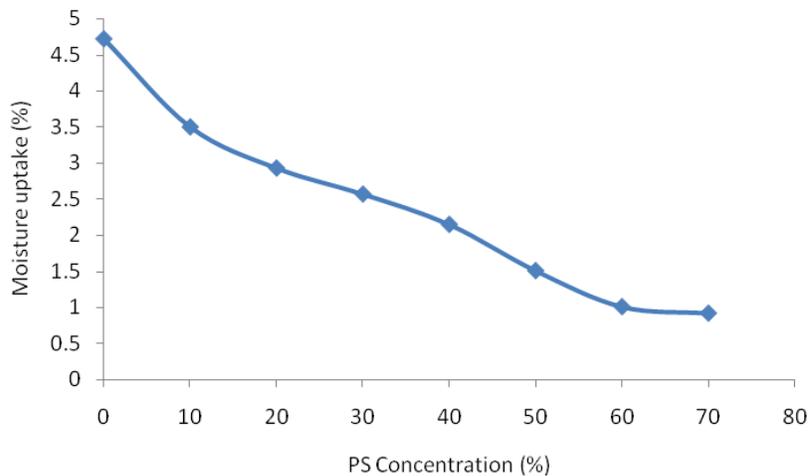
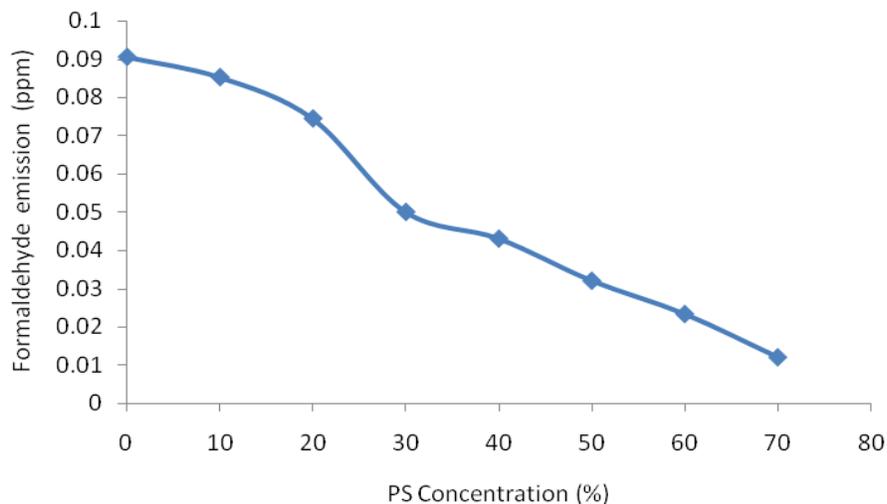**Figure 8.** Effect of PS concentration on the moisture uptake of TMU/PS resin.

application (Derkyi et al., 2008). Hydrolysis of cured urea resins has been known to be responsible for formaldehyde emission leading to sick building syndrome (Park et al., 2010). Formaldehyde is higher indoors than outdoors. High emissions of formaldehyde from latex paint have been reported by Salthalmmer et al. (2010). Recently, many efforts have been made to reduce formaldehyde emission from building materials (Lee et al., 2011).

Figure 9 shows the effect of PS concentration on formaldehyde emission of TMU/PS resin. As the concentration of PS increases, the formaldehyde emission decreases. This important promising trend is due to the gradual decrease in the TMU content with increase in the PS loading in the blend. This may also be as a result of reduction in stress during cure which reduces emission

resulting from improved flexibility. Furthermore, PS behave as a physical obstacle disrupting the continuity in the TMU matrix and therefore, making it more difficult for the reactive groups of urea and formaldehyde to come close and interact (Abdullahi and Park, 2010; Lee et al., 2011; Ayoub et al., 2013). The formaldehyde emission in this study has been reduced to 0.02 ppm, which is even lower than the world health organization (WHO) recommendation limit (0.08 ppm).

Effect of PS concentration on the elongation at break of TMU/PS resin

Elongation, the increase in length of the sample at the breaking point is a useful property for the characterization

Figure 9. Effect of PS concentration on formaldehyde emission of the TMU/PS resin.
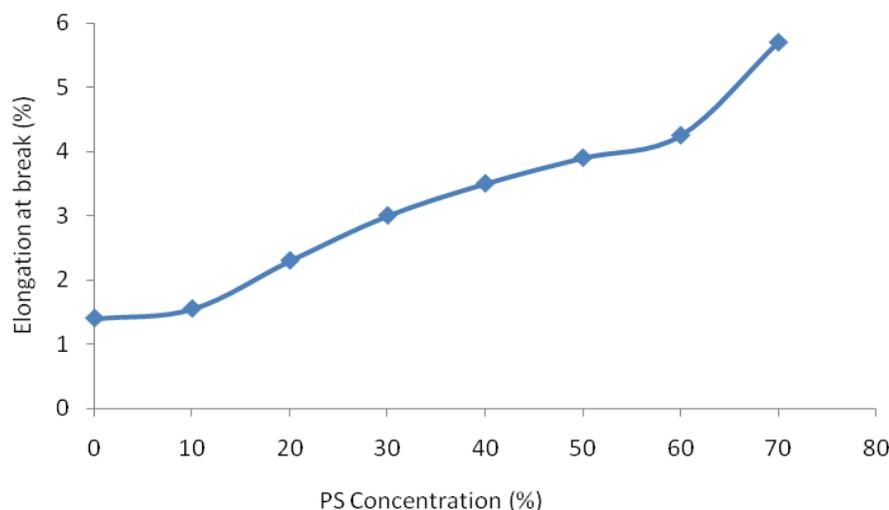
Figure 10. Effect of PS concentration on the elongation at break of TMU/PS resin.

of resins for paint formulation. Elongation gives a picture about how much the material will be stretched before it breaks. The structure of thermosetting resins also leads to some unwanted mechanical properties that limit their structural applications. They are relatively brittle. Elongation at break can be a propel tool to determine the adhesion between phases, because of its sensitivity for load transfer between phases (Cakir et al., 2012; Hwang et al., 2012).

The effect of addition of PS on elongation at break is as shown in Figure 10. The blends results showed increase in elongation at break with increase in PS inclusion. Elongation increased due to increase in concentration of soft segment (PS) that impacts flexibility. The flexibility

improvement may also be due to the presence of some dissolved polystyrene particles inside the urea formaldehyde matrix (Hemant et al., 2009; Shinde et al., 2012). Sharp increase at 70% is due to phase inversion observed at that regime.

Effect of PS concentration on the solubility in water of TMU/PS resin

Water solubility is an important parameter in the consideration of any resin as a binder for emulsion paint formulation. paint formulation.

From Table 1, it can be seen that at 0 to 40% low PS

Table 1. Effect of PS concentration on the solubility in water of TMU/PS resin.

PS concentration (%)	Solubility
0	Soluble
10	Soluble
20	Soluble
30	Soluble
40	Slightly soluble
50	Insoluble
60	Insoluble
70	Insoluble
80	Insoluble
90	Insoluble

Table 2. Comparison of some physical properties of TMU/PS film with films from other paint binders.

| Type of resin | Physical property | | | | | | | Literature |
	Viscosity (mpa. s)	Refractive index	Density (g/cm^3)	Melting point (°C)	Moisture uptake (%)	Elongation at break (%)	Formaldehyde emission (ppm)	
TMU/PS	19.70	1.425	1.0990	262	1.01	425	0.0233	This study
Polyvinyl acetate	0.40	1.40	1.25	ND	ND	ND	ND	Habibu (2011)
Palmoil/Alkyd	499	ND	0.929	ND	ND	ND	ND	Blaise et al. (2012)
Commercial UF	451	ND	1278	ND	2	ND	ND	Suurpere et al. (2006)
Polyvinyl butyral	9-16	1.485	ND	ND	0.3	110	ND	Solutia (2008)
Acrylic/Methacrylic ester	2500	ND	1.03	ND	ND	ND	ND	Dumitru (2011)
Innovative UF	365	ND	ND	ND	0.25	ND	0.07	Zorba et al. (2008)
MU/NR	248	1.3411	0.641	255	1.341	350.43	0.058	Kazys and Rekuviene (2011)
UF/PE	32.60	1.432	1.3362	130	0.0080	250.0	0.0142	Osemeahon and Archibong (2011)
Alkyd from cater oil resin	4	1.474	ND	ND	ND	ND	ND	Hlaing and Oo (2008)

loading, the copolymer is in a hydrophilic state, with hydrophilic TMU dominating. This allows it to stay in aqueous solution, but above 40% inclusion of PS, the copolymer seems to adopt hydrophobic stand with the hydrophobic now dominating; hence, the insolubility in water experienced in this particular state. This insolubility could also be due to conversion of the copolymer samples to

gelation immediately with increase in PS concentration (Naghash et al., 2007).

Table 2 compares some physical properties of TMU/PS copolymer binder with other paint binders. The viscosity of the copolymer (TMU/PS) as observed is within the values of other polymer resins, while the density, refractive index, melting point, moisture uptake and formaldehyde emi-

ssion are also within the same range with other binders. The elongation at break is a little higher than other binders, indicating improved flexibility. This result place TMU/PS copolymer resin as a competitive binder among other traditional resins resins for the coating industry. The comparison between TMU, TMU/PS resins and the acceptable level in the coating industry is shown in Table 3. A

Table 3. Comparison of some physical properties of TMU and TMU/PS resins.

Property	TMU	TMU/PS	Acceptable level in the coating industry (Osemeahon et al., 2013)
Density (g/cm)	1.1250	1.0990 ± 0.002	1.07 (min)
Refractive index	1.4100	1.4250± 0.1010	1.4000 (min)
Formaldehyde emission (ppm)	0.0905	0.0233± 0.0011	0.1 (max)
Moisture uptake (%)	4.72	1.01 ± 0.001	3.10 (max)
Viscosity (mpa.s)	2.39	19.70 ± 0.1200	3.11- 38.00
Elongation at break (%)	116	425.00 ± 0.01	125 (min)
Melting point (°C)	280.00	262 ± 0.10	200 (max.)

Trimethylol Urea / Polystyrene Copolymer composite
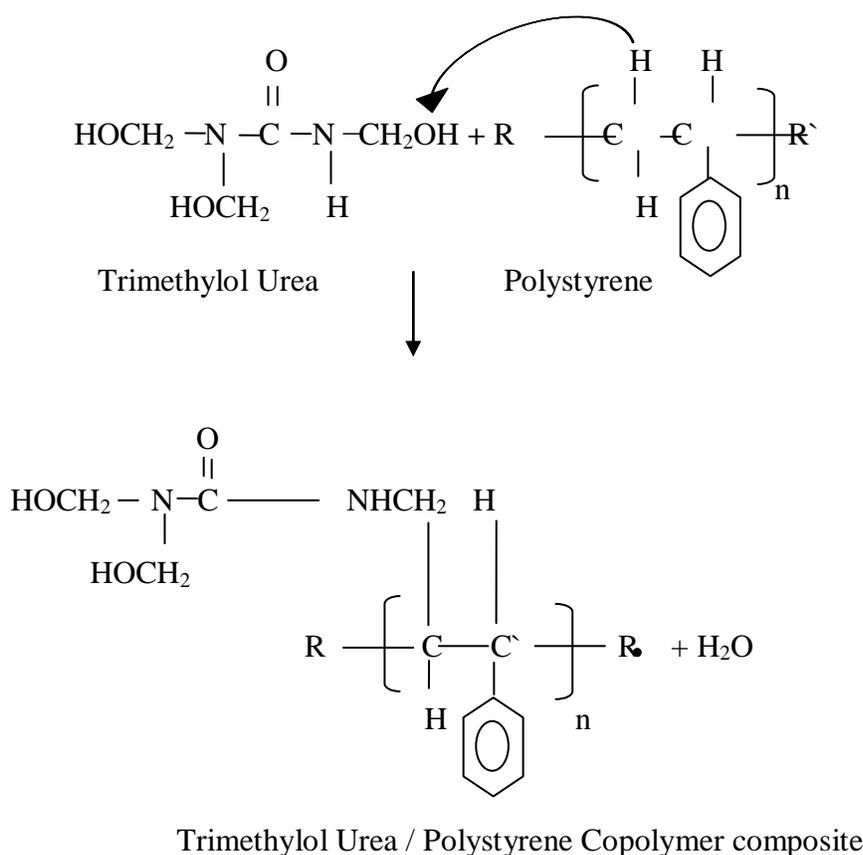
Scheme 1. Reactive blending of TMU/PS.

decrease was observed in density, formaldehyde emission, moisture uptake and melting point between the TMU and TMU/PS, these signal positive developments in terms of film adhesion, emission of VOC, water resistance and hardness, respectively. The refractive index, viscosity and elongation at break increased as shown in Table 3; this indicates better gloss, consistency and high ability to withstand weather or service condition. The density and refractive index of both TMU and TMU/PS are within the acceptable range in the coating industry. Although both TMU and TMU/PS binders meet formaldehyde emission level, TMU/PS resin showed lower emission than TMU resin. The moisture uptake, viscosity and elongation at break of the TMU did not meet the requirement, while that of TMU/PS are within the acceptable level. The melting point of both resins is higher than the require value, therefore further research is necessary to address this shortcoming.

Conclusion

The copolymerization of urea formaldehyde and polystyrene waste was successfully carried out. The

formaldehyde emission level, moisture uptake and elongation at break in the experiment after blending were within the acceptable levels required in the coating industry in term of environmental safety, water resistance and flexibility, respectively. This study provides a novel class of polystyrene modified urea formaldehyde resin with low formaldehyde emission, high water resistant and ductile properties. This creates initiatives for new opportunities towards developing various target paint products for different field of engineering, thus providing a simple economic route for the recycling of waste polystyrene and hence an important practice for sustainable recycling.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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