

**DEVELOPMENT OF UREA FORMALDEHYDE AND POLYSTYERENE WASTE  
AS COPOLYMER BINDER FOR EMULSION PAINT FORMULATION**

**BY  
DIMAS, JEN BLESSED  
M.TECH/CH/011/0209**

**JULY, 2014**

**TITLE PAGE**

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**BEING A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY,  
SCHOOL OF PURE AND APPLIED SCIENCES, MODIBBO ADAMA UNIVERSITY  
OF TECHNOLOGY, YOLA  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF  
M.TECH INDUSTRIAL CHEMISTRY.**

**JULY, 2014**

## **DECLARATION**

I hereby declare that this thesis was written by me and it is a record of my own research work. It has not been presented before in any previous application for a higher degree. All references cited have been duly acknowledged.

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Dimas, Jen Blessed

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Date

## **DEDICATION**

This project is dedicated to my darleen Mike, for been absent when you need me most.

## APPROVAL PAGE

This project report entitled “Development of Urea Formaldehyde and Polystyrene Waste as Copolymer Binder for Emulsion Paint Formulation” meets the regulations governing the award of Master of Technology Degree of the Modibbo Adama University of Technology, Yola and is approved for its contribution to knowledge and literary presentation.

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Dr. S.A Osemeahon  
Supervisor

---

Date

---

Dr. I.I. Nkafamiya  
Internal Examiner

---

Date

---

External Examiner

---

Date

---

Dr. S.A. Osemeahon  
Head of Department

---

Date

---

Prof. D.T. Gungula  
Dean, Post Graduate School

---

Date

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## ABSTRACT

Urea formaldehyde that is trimethylol urea (TMU) resin was synthesized and blended with polystyrene (PS) waste to a developed (TMU/PS) copolymer binder for emulsion paint formulation. The resulting copolymer was analyzed for formaldehyde emission and other physical properties such as viscosity, gel time, density, turbidity, melting point, refractive index, moisture uptake, elongation at break and solubility in water. IR analysis of TMU, PS and TMU/PS showed chemical interaction between TMU and PS resins. This was observed in the TMU/PS spectra where the strong O-H peak at  $3437.36\text{ cm}^{-1}$  in TMU was almost absent due to the consumption of OH groups during condensation reactions. The level of formaldehyde emission decreased from 0.0905 ppm at 0% PS to 0.0120 ppm at 70% PS inclusion. Moisture uptake also decreased with increase in PS concentration from 4.72 % - 0.92%. The elongation at break on the other hand increased with increase in PS concentration from 140% - 570%. The resulting copolymer gave a better resin compared to pure TMU in terms formaldehyde emission, high water resistance and brittleness. 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. The emulsion paint formulated from both TMU and TMU/PS passed pH, viscosity, flexibility, opacity, gloss and storage stability test. Paint from pure TMU failed adhesion, hardness, tackiness, resistance to blistering and drying time test while the TMU/PS paint recorded a pass in all the tests. Both paint were unaffected by the salt medium but surface defect were observed in the case of TMU films in alkali and acid solutions. TMU/PS films were unaffected by both the acid and alkali solution. This study provides a potential route for both volatile organic compound (VOC) reduction in coating surfaces and environmental pollution from waste polystyrene disposal.

Keywords: Paint, binder, blending, urea formaldehyde, polystyrene waste.

## CHAPTER ONE

### INTRODUCTION

#### 1.1 Background of the Study

Paint making is an ancient human activity. The ancient mariners experimented with different methods of protecting the outer surface of their sea vessel. The use of tar, pitch, copper sheathing, lead sheathing, plant extracts, etc; as surface coatings were tried by them. The mahabharatha cites the use of shellac as protective coating. The Bible mentions the application of pitch in protecting wood. The ancient Indians and Egyptians were believed to have developed paints with coloured clays and use them for wall painting. The Greeks were well-versed in the manufacturing of white lead. The Chinese, even as early as 2000BC, use bees- wax for protecting certain articles from atmospheric degradation (Gopalan *et al.*, 2000).

Further, the paint technology was improved during the first millennium BC as the Greeks learnt to blend paints with hot wax, rather than water, making a paint that was both thicker and easier to spread and thus making it possible to blend colours. By this time many colours were available from both natural and synthetic sources, one of them being a purple pigment made from heating yellow earth until it turned red and then plunging it into vinegar. The technology then lapsed for many years, with techniques being passed down from generation to generation by travelling craftsmen. This continued until the eighteenth century, when paint factories began to be opened in Europe and America, and by the nineteenth century due to mass production the houses began to be painted. Now, the chemistry of paint manufacture and function are understood, such that paint manufacture has finally moved from being an art to being a science (Ravikumar *et al.*, 2012). The earliest development of the paint industry in the U.S. began with the first needs for coating and protecting residences. Paint companies were primarily pigment manufacturers who prepared powders of colouring by grinding naturally occurring materials. Until the middle of the nineteenth century, professional painters would combine pigments with an oil or varnish and thinners. In 1867, D.R. Averill prepared the first generation of ready mix paints. These emulsions of pigments in oil, zinc oxide, lead acetate, and lime water were initially found to be unacceptable by many painters. However, they set the stage for later developments by other manufacturers which increased the consistency and the quality of the product. These developments dramatically changed the market for paints. Consistency began to depend on the manufacturer and not the skills of the journeyman painter. Also, the door was opened to less sophisticated buyers performing do-it-yourself activities on their homes (Bonifant, 1994).

## 1.2 Paint

Paints consist essentially of pigments dispersed in a resinous binder reduced to an acceptable viscosity with a solvent. One or more additives may be incorporated to modify one or other of the film properties of the paint. The binding medium or binder which is the most important components in the majority of paint determines the physical and chemical properties of the paint (Opara *et al.*, 2013). The main function of the pigments is to impart the desired colour and to protect the film from penetrating radiation, such as UV rays. The pigments and the extenders are carried or suspended in drying oils called vehicle. The vehicle or drying oil is a film forming material, to which other ingredients are added in varying amounts. The purpose of paint may be protective or decorative or both (Sharma, 2011). Paint has an impact on the environment during the manufacturing process and on health during its use phase. Unused liquid paint is treated as 'hazardous' and requires appropriate disposal.

### Component materials

Most paint is made from three basic ingredients: (Myint *et al.*, 2010).

1. **Pigment** - provides colour and opacity
2. **Binder** - acts like a glue in holding the pigment to the surface
3. **Solvent** - maintains the pigment and binder in liquid form.

Paint may contain just the three components above, but some manufacturers will include small amounts of additives intended to affect the characteristics of the paint. Paint works by its application to a surface followed by the evaporation of the solvent, thus leaving a film comprising of the pigment and binder. Depending on the type of binder, paints are classified into two main categories i.e. oil paint which is oil based (such as high molecular weight fatty acids generally present in animals and vegetable oils) and emulsion paint which has synthetic resin as the binder and is water soluble as against oil paint which is solvent (organic solvent) soluble and higher performance or special type paint (Adetuyi *et al.*, 2012).

Oil-based paints display a lot of advantages such as water resistance, durability and flexibility over water borne paint. However, due to its use of volatile organic compound (VOC) as solvent and consequent of environmental pollution, the taste for oil-based paint is fast diminishing in many countries all over the world. For the purpose of both environmental and human survival, VOC reduction from coating surfaces is a task that must be done. VOCs are harmful materials to the environment, as they are partly responsible for air pollution, depletion of ozone layer, global warming and health risk to all living organisms (Yousefi *et al.*, 2011; Faucheu *et al.*, 2009).

Water borne paint are used in protection and decoration of most building nowadays because of their ease of applications, fast drying, non-odour, good-wash ability and excellent finish. However, water borne paints are limited in application due to the relatively low quality when compared to oil-based coatings. Although researches (Hasmukh and Sumeet, 2010; Kumthekar and Kolekar, 2011; Motawie *et al.*, 2010), have been directed towards eco-friendly water-thinnable paints, the dream of obtaining an emulsion paint with satisfactory service properties as compared to solvent based system has not been achieved (Karakas *et al.*, 2011).

### **Requirements or requisite of a good paint**

A good paint should essentially satisfy the following requirements;

1. It should be fluid enough to be spread on the metal surface easily.
2. It should have a high covering power.
3. It should form a quite tough, uniform, adherent and impervious film,
4. The film should not crack on drying,
5. It should be corrosion resistant and should protect the painted surface from corrosion effects of environment,
6. It should give a stable and decent colour to the surface painted with it. The colour should be stable to the effect of atmosphere and other agencies,
7. It should give a glossy film,
8. It should adhere well to the surface (Shashi, 2011)

### **Paint Failure**

According to Sharma (2011) failure of paints may be due to various causes, and in each case there is a special term to explain the failure. Progressive chalking or powdering of the paint film is called chalking and is caused by the destructive oxidation of the oil after drying of the paint on the surface. If chalking is very rapid, the term erosion is used. Poor attachment of the paint on the surface to be coated is called flaking or peeling and caused by the presence of dirt or grease on the surface or water entering from below the paint. If the centre peels off, a term alligating is employed. Fine surface cracking is called as checking and is due to the absence of plasticizers in the paint. Appearance of blisters on the coat applied to wood is generally known as blistering. Appearance of dull patches on the surface is called blooming. Discolouration of the film is known as bleeding. Refusal of some portions of the surface to be painted is called cissing.

### **Paint Failures can be avoided by;**

- a. Careful mixing of the constituents or ingredients in specified proportions,
- b. Proper processing of the surface to be coated before the paint is applied,
- c. Using a primer coat before the application of the paint.

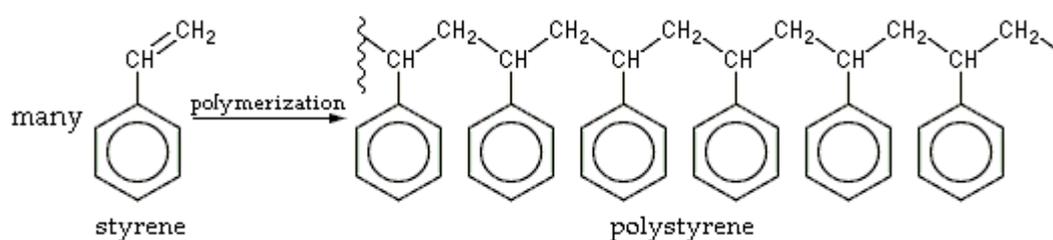
### **1.3 Urea Formaldehyde**

Urea-formaldehyde resins are poly-condensation products of urea and formaldehyde in either alkaline or neutral or acid or alkaline/acid medium. It is the most prominent example of the class of thermosetting resins usually referred to as amino resins. The resin is widely used as a moulding material and component of adhesive and protective finishing. They are available as viscous liquid or spray a dried powder which requires the addition of water prior to use. Urea formaldehyde resins are extremely tough, scratch resistant polymers which lend themselves ideally to a host of domestic and industrial applications. Low price, good technological properties, absence of colours in cured polymer, low cure temperature, resistance to micro organism and abrasion, hardness, excellent thermal properties and easiness of application for a variety of curing conditions are the advantages of urea formaldehyde (Akpabio, 2010; Ayoub *et al.*, 2013).

However, the structure of the thermosetting resin also leads to unwanted properties that restrict their application. Urea formaldehyde resin is too hard and brittle to be used alone as coating material. Urea formaldehyde resin also exhibit poor water resistance and formaldehyde emission hence creating problems of environmental pollution and inconsistency in the quality of product with age. Since Urea formaldehyde resin is soluble in water, it full utilization is needed to meet different requirements of the coating industry in terms of emulsion paint formulation and consequent reduction in VOC in our environment. This is only achievable if the inherent problems of brittleness, poor water resistance and formaldehyde emission associated with urea formaldehyde resin are taken care of (Cakir *et al.*, 2012; Osemeahon *et al.*, 2010). The coating industry is facing challenges and under pressures to meet environmental standard especially regarding the emission of volatile organic compoundVocs. Whether these challenges are driven by environmental requirements, performance, quality or lower cost, we know one thing for certain is that these challenges are real and only through research and innovations can the coating industry survive. The coating chemists recognize that these challenges and researches are ongoing in the world to provide new paint binders and paint formulations to support the changing face of the industry (Osemeahon *et al.*, 2011).

#### 1.4 Polystyrene (P S), Properties and Problem to the Environment

Polystyrene has a chemical composition of carbon and hydrogen ( $C_8H_8$ )<sub>n</sub>. Styrene is the naturally occurring monomer that makes up the polymer, polystyrene (American Chemistry Council, 2010). A chemical composition of polystyrene is illustrated in Scheme 1.



**Scheme 1:** Chemical composition of polystyrene

#### Properties

- a) Because of the presence of bulky phenyl groups, packing of polystyrene chains is not efficient and hence it is amorphous polymer. Its specific gravity (1.054) is also low.
- b) It has good optical properties like it is transparent polymer allowing high transmission of all wavelengths. Moreover, its high refractive index (1.592) gives it a particular high brilliance.
- c) Due to chain stiffening effect of benzene ring, polystyrene is hard but brittle. It emits a characteristic metallic sound when dropped.
- d) Being non-polar amorphous polymer, its softening temperature (82- 100 °C) is low. It cannot withstand the temperature of boiling water.
- e) As it is non-polar so it has low tendency for moisture absorption. Moreover, it has good electrical insulation characteristics.
- f) It has reasonable chemical resistance but mediocre oil resistance.

#### Application

Polystyrene is used for making Audio cassettes, Containers for talcum powder, House wares (small jars and storage containers), Bottle caps, combs and brush handles.

#### Important Derivatives

1. Expanded polystyrene: It is made by incorporating blowing agent in it and has foamed structure and it has the following properties; low density, low weight and less brittle.

It is use for packaging of cameras, electronic equipment, and thermoformed egg boxes.

2. High impact polystyrene (HIPS):It's made by suitable combination of polystyrene with rubbery materials like ethylene propylene diene monomer (EPDM), polybutadiene, styrene butadiene styrene (SBS) triblock thermoplastic rubber (TPR) and it has the following properties; improve impact strength, good dimensional stability, excellent resistance to weathering and low thermal conductivity. It s use for making electrical equipment housing like TV cabinet, knobs and switches, door and inner liners of refrigerators, disposable cups and tumbler (Shashi, 2011).

Polystyrene particle belongs to the family of latex particles that are used for a large variety 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). According to Ahmed *et al.*, (2012), Plastic has been used in great demand nowadays. Polystyrene product contributes to solid waste after use. Solid waste is defined as non-liquid and non-gaseous products of human activities, regarded as being useless (Babayemi and Dauda, 2009).

Polystyrene has a low scrap value and is difficult to transport. Because of this, most polystyrene are thrown into landfills instead of being recycled. Because polystyrene is not biodegradable, it remains in landfills with no value. This practice is not sustainable as there is limited land available for waste storage. Polystyrene continues to be a major problem for the world. Cost effectiveness is the key factor to the excessive use of the product. For this reason it is unlikely to see a reduction in the amount of polystyrene that will be produced in the future. Since the product is not biodegradable, disposing polystyrene waste in landfills is not a sustainable practice, and hence, recycling polystyrene becomes a needed alternative (Ricky *et al.*, 2010).

Polystyrene is recycled poorly throughout the world; therefore, there is great interest in recycling technologies to reduce the amount of polystyrene waste in landfills. Most of the world's polystyrene products are not recycled. Recycling programs for polystyrene are not currently in place on a large scale.

Solid waste management has emerged as one of the greatest challenges facing state and local government environmental protection agencies in Nigeria. The volume of solid waste being generated continues to increase at a faster rate than the ability of the agencies to improve on the financial and technical resources needed to parallel this growth. Solid waste management in Nigeria is characterized by inefficient collection methods, insufficient coverage of the collection system and improper disposal of solid waste (Ogueleka, 2009).

## 1.5 Blending of Polymer

Polymer blends are a mixture of chemically different polymers or copolymers with no covalent bonding between them. Polymer blends are classified as three types, namely, homologous, miscible and immiscible blends. Chemically identical polymers with differing molecular masses constitute homologous polymer blends. Miscible polymer blends exhibit single phase behaviour and immiscible polymer blends exhibit two or more phases at all compositions and temperatures. Preparation of polymer blends has received considerable importance in the recent past owing to the shorter time and lower cost of the product development than those of a new polymer. The performance of a polymeric material can be improved by selection of suitable ingredients and their ratios. Polymer blending imparts certain new characteristics leading to the formation of new materials with enhanced physical, chemical and mechanical properties. Blending of two polymers having different properties is used for producing a new polymeric material. These new polymeric material may possess the properties of both the polymers (Kaniappan and latha, 2011).

Polymer blending is a proven tool to obtain new types of materials with a wide diversity of properties intermediate between those of pure components. However, the properties of the polymer blend depend upon the compatibility of the individual polymers with each other and the method of mixing (Velu *et al.*, 2011). The two main objectives of making polymer blends are to maintain a proper cost performance ratio and reinforcement of properties, i.e., 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 advancing at a rapid pace. New blends are constantly being developed and characterized, and blends with metallocene resins, liquid crystal polymers, and biodegradable resins are now available. Blending technology is also proving to be of use in plastics recycling (Bhattacharya *et al.*, 2009).

Superior mechanical properties can be achieved via blending of PMMA with polystyrene (Kaniappan and Latha, 2011). Novel environmental protection urea-formaldehyde resin was synthesis by modifying urea-formaldehyde resin using keratin through adjusting factors of the mole ratio between formaldehyde and carbamide, adding time and adding amount of keratin (Shen *et al.*, 2011). Methylol urea has being blended with soybean oil, natural rubber and polyethylene waste. The results revealed that all these blends possesses better water resistance, flexibility and low formaldehyde emission compared to the pure urea formaldehyde (Osemeahon *et al.*, 2009; Osemeahon and Barminas 2007; Osemeahon and Archibong, 2011). According to Cakic *et al.*, (2012) properties of coating

base on alkyd resin can be improved via blending with other suitable resin. Recent studies assessed that many properties could be improve by blending alkyd resin with epoxy resins as well as melamine resins.

The properties of polymers depend upon the structure, molecular mass and its distribution and the interactions among polymer-polymer and polymer-solvent /molecules. Hence it is necessary to synthesize a polymer with required specification, which is a difficult, time consuming and costly process. A highly successful alternative is to blend/ mix the existing polymers for the purpose. This process needs detail knowledge about the interactions and miscibility of polymers with each other. Blending of polymers is widely accepted in the industry for the production of a polymeric materials with specific applications through an inexpensive route which otherwise not attainable with a single polymer. One of the important controlling parameter in this case is the degree of compatibility of the polymers blended. However, the degree of compatibility is very much dependent over the interaction between the polymeric phases of the polyblend. Therefore, by varying the interactive forces among the constituents of the system, one can get the material of required mechanical properties. This is one of the reasons that miscible polymer blends are receiving more importance in industrial applications. Miscible blends are usually clear and exhibit a single glass transition temperature ( $T_g$ ) usually intermediate between those of the individual component, where as immiscible blends exhibit separate glass transition temperature characteristic of each component. Some polymer pairs are almost impossible to mix with each other and form sea-island morphology. However, the main problem associated with blending polymers is the determination of degree of compatibility. Different techniques are presently being developed to produce polymer blends and/or determine their compatibility (Nawaz *et al.*, 2010; Ekwonu, 2011; Hwang *et al.*, 2012).

## **1.6 Statement of the Problem**

The emission of volatile organic compound (VOCs) from oil based paint surfaces is presently a major challenge in the coating industry. This has resulted to the need to shift from oil based paint to emulsion (water) paint. However, present binders available for emulsion paint are inferior to those of oil based paint. Therefore, if emulsion paint must challenge the enamel and superior properties of oil paint, alternative binder for the emulsion paint must be sort.

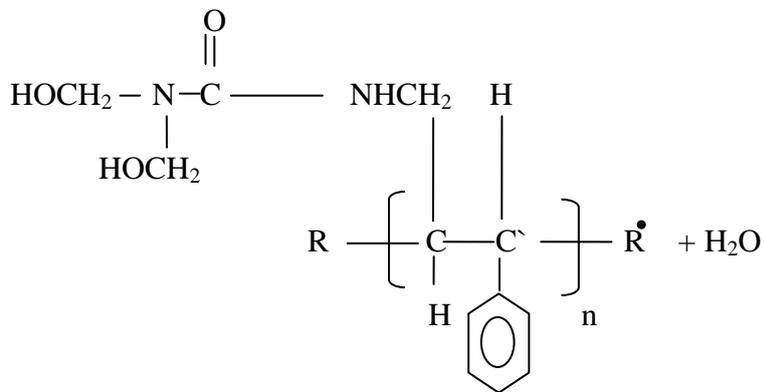
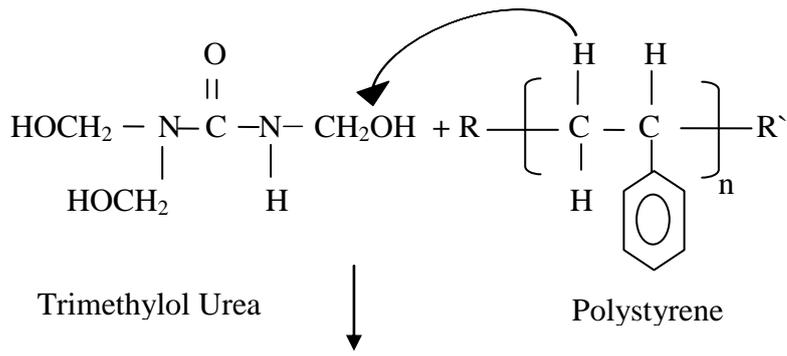
However, although most household paints are water-based, this is not true of industrial paints. Because of the special requirements of the industrial coatings, satisfactory

water-based polymers with the required properties have not yet been developed (Hasmukh and Sumeet, 2010; Osemeahon, 2011).

The acceptance of urea formaldehyde resin 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. These disadvantages limit its uses; hence creating problems of environmental pollution and inconsistency in the quality of product with age. However, urea formaldehyde 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. Formaldehyde emissions and the durability of the cured resin can be controlled and specifically tailored for the final use of the resins through blending (Osemeahon *et al.*, 2010).

In Nigeria, plastic wastes (PS) are dumped indiscriminately on roadsides and any available open pits irrespective of the health implication on people (Nwachukwu *et al.*, 2010). Therefore attempt to solve this problem through the utilization of this waste, as raw material for industrial product will be highly acknowledged.

Stephen *et al* (2010) reported that polymer blends continues to be a subject of investigations in both academia and industries because of their simplicity and effectiveness. Since blend involves the use of pre-existing material, without recourse to synthesis, they offer pecuniary advantage and time-saving economy. Trimethylol urea (TMU) has a lot of -OH groups in one hand and polystyrene (PS) 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.



Trimethylol Urea / Polystyrene Copolymer composite

**Scheme 2:** Reactive Blending of TMU/PS

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 the high water resistance properties of polystyrene and further reduce formaldehyde emission due to polystyrene inclusion in the composite. 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 pollution from disposal of waste polystyrene materials on the other hand.

### **1.7 Aim and Objectives**

This research intends to formulate emulsion paint using trimethylol urea (TMU) /polystyrene waste (PS) copolymer as binder. At the end of the research an emulsion paint that would be environment friendly and also acceptable to the coating industry will be formulated with view of reducing the problem of VOCs and waste polystyrene disposal in our environment.

The specific objectives of this research work include;

1. To synthesize trimethylol urea (TMU).
2. To constitute the waste polystyrene (PS) into liquid form.
3. To blend the synthesized trimethylol urea with waste polystyrene to produce TMU/PS composite.
4. To characterize the copolymer composite.
5. To formulate an emulsion paint using the pure TMU and TMU/PS composite.
6. To test the quality of the emulsion paint from TMU and TMU/PS composite.

### **1.8 Significance of the study**

If this blending is achieved, the resulting copolymer will share the properties of both trimethylol urea and 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. This study provides a potential route for both VOCs reduction in coating surfaces and environmental pollution from waste PS disposal

## **CHAPTER TWO**

### **LITERATURE REVIEW**

#### **2.1 Introduction**

Coatings are protective and/or decorative compositions that dry to a cohesive, adherent, tack free film upon application to a substrate. Technological advances have transformed coatings manufacture from an arts - and - crafts industry to a highly scientific branch of the chemical industry (Bhattacharya *et al.*, 2009). In most plants, the manufacturing processes are now carried out under careful laboratory control and are freely modified or revised, whenever revision is indicated, in accordance with known scientific principles. As a result, the industry has been able to offer a succession of constantly improved products through periods of fluctuation in the availability of many important raw materials, pressures for solvent replacement to meet emerging air quality standards, and extensive pigment reformulation to replace mercury and lead to conform to new federal regulations on toxicity. A most important development in the modern paint and varnish industry has been the introduction of synthetic resins as replacements for natural resins in the manufacture of coating materials. By using synthetic resins it has been possible to produce a variety of coatings that, in many cases, have important points of superiority over any of those compounded from natural resins. The synthetic vehicles are particularly distinguished by their hardness and durability and their high degree of resistance to the action of water, alkalies and other chemical (Lin, 2005).

Wood, metal, cement, bricks etc are well known construction materials for homes, offices, industries etc over period of time. Metal surfaces get scratched and warped, wooden surfaces get scratched and warped, walls crack and chips. Paint form a protective layer over these surfaces and keep them looking as good as new. The basic components of paint are a binder, a solvent and pigments. The basic properties of paint such as drying, gloss, hardness, durability, flexibility, abrasion resistance, impact resistance, chemical resistance and adhesion are governed by the binder system used in paint formulation, although some minor variations can be made by modifying other components of paints (Myint *et al.*, 2010 ; Shashi, 2011).

#### **1.7 Types of Paint**

##### **2.2.1 Oil-Based Paints**

The term “oil-based” is commonly used to refer to both oil and alkyl coating (Achi, 2003). Therefore oil-based paints are coatings in which the majority of the liquid content is a solvent

other than water. The binders in an oil-based coating are made from a vegetable oil that “dries” or oxidized, and crosslink’s when it is exposed to the air, and thus develops the desired properties of the paint product. Drying oils traditionally used in paints coating include linseed oil (squeezed from flax seed refined), Tung oil (from fruit of the china wood tree), and Soya oil (from soybean beans). Film formation of oil and alkyl-based coating is a two-step process; when the coating is applied to a surface;

1. The liquid evaporates and leaves the binder and pigment on the surface; and
2. The binder then “dries “or oxidizes as it reacts with the oxygen of the air.

It is this drying, or oxidation, that develops the hard, touch properties of oil or alkyl coating.

When working with oil-based paints, it is not advisable to use the same materials for both interiors and exteriors. For example Linseed-oil-based paints, yellow severely, when unexposed to light and outside weather. For this reason soyaphthalic alkyl resins is preferred as binders for interiors. High gloss interior paints are mainly contained in kitchens and bathrooms, where resistance to water and good wash ability are advantages. They are used in familiar area in industrial plants (Lowel, 1990).

### **2.2.2 Emulsion or Latex Paints**

Emulsion paints is an emulsion of two phase, one of which is water and this paint can readily be diluted or thinned with water, because water is the continuous phase present in it. The vehicle or surface forming material (synthetic resin later) is dispersed in water by means of a dispersing agent acting as a binder. It may also have in it another vehicle or film forming constituent such as oil. The binder may thus be oil, Oleo resinous varnish or other emulsifiable binders. Pigment and extenders are dispersed in such an emulsion. In addition to these constituents an emulsion paint may also have emulsifying agents or surface active agents, stabilizers, dries antifoaming agent, preservative etc (Sharma, 2011).

When a thin film of emulsion paint is applied on a surface, water undergoes evaporation from the surface and breaking of emulsion takes place. The resin particles coalesce to form a continuous homogenous clear film. The drying of emulsion film occurs in two stages. In the first stage, the film remains permeable to water, and moisture escapes, while in the second stage drying of resin takes place by oxidation. Emulsion paint can be applied on the surface of metal or wood very easily and they are quick drying, low odour, and impermeable to dust and dirt. These paint can be very easily applied with brush or roller and after painting the brush and roller can be easily wash with water. The surface, over

which emulsion paint is applied, can be easily washed with water. They are free from fire hazard also (Sharma, 2011).

Water based formulations are gaining market share due to the increasing demand for reduction or complete removal of solvents and volatile organic compound (VOCs). In the field of decorative coatings, formulators now have several decades of experience in the formulation of water-based high PVC (pigment volume concentration) paints and have developed some accurate knowledge of how to formulate lower PVC systems (Ruhlman, 2010). As mentioned earlier, a common limitation of waterborne coatings is that the hydrophilic groups stabilizing the resins in water adversely affect film properties such as weathering and water resistance. Bhattacharya *et al* (2009) proposed an ambient temperature cured 2K waterborne coating system in which the hydrophilic functional groups were consumed via cross linking during film formation. Technically, waterborne coatings are high tech products that are complex and delicate to formulate. This situation increases the demand for a more comprehensive toolbox to balance the various performance and handling requirements of waterborne coatings (Herold and Klaus, 2012).

### **2.2.3 Special paints**

In addition to the normal ingredients, some special chemicals are incorporated to paints for some specific purposes. They are known commonly as “special paints”. Following are some of the examples of special paints (Gopalan *et al.*, 2000; Mathiazhagan and Joseph, 2011).

**i. Heat-resistant and Fire-retardant paint:** When the surfaces are exposed to high temperatures such as in chimneys, exhaust pipes, furnaces, oil stills, etc oil paints tend to decompose or get charred, they being organic in nature. Then the surfaces become liable for corrosion. To overcome this problem, a suspension of graphite or lamp black in small amounts of drying oils and more thinner can be used. Other binders such as phenolic or epoxy are used to prepared high thermal resistance coating but at present silicon containing coating dominate the market. Recently developed silicon-based coatings are able to resist temperatures of up to 1000°C. Silicon derivatives such as silicone resins (siloxanes) or inorganic silicates are commonly used for high-temperature applications. Silicon containing materials are expensive; however, copolymers or blends of silicones with acrylate, epoxy or urethanes are very often used to save costs.

**ii. Fire-retardant paint:** The devastating nature of fire creates havoc and results in great loss of lives and property. Thus, the need to develop fire retardant coatings is constantly

growing. Although protection against fire by the use of coatings for indefinite periods is impossible, the use of fire-retardant coatings can delay the spread of fire or keep a structure intact against fire, thereby allowing sufficient time for safety measures to be taken. Today, several types of fire retardant are phosphorus containing, halogen-based and intumescent fire-retardant systems, each with a different principle of operation even expandable graphite are available commercially as fire retardant agents. Recently, polymer clay (layered silicates) nanocomposites have also been explored for the development of fire-retardant coatings.

**iii. Temperature indicating paints:** These paints contain ingredients which decompose and undergo colour changes when the temperature increases. Some examples of the active ingredients used are silver and mercury iodide, complex amine of Cu, Fe, Co, Ni, Mn, Cr, etc. These paints can be used in coating the outer walls of chemical reactors to indicate the temperature inside. Based on this, the reactions can be controlled or stopped at desired temperature ranges.

**iv. Water repellent paints:** The active ingredients used in these are silicones, cellulose dinitrate (pyroxylin), etc which are water-repellent.

**v. Anticondensation paints:** These types of paints are used to control high humidity as in ship cabins or constructions on the seashore or marshy places. The paints contain chemicals which absorb moisture and reduce dampness inside the housing.

**vi. Antifouling paints:** Oil paints are liable for attack by living organisms because of the organic content in them. So, in places where living organisms are handled or are present, such paints cannot be used. For use in breweries and biochemical laboratories, the paint is mixed with compounds having fungicidal properties. The active ingredients employed are HgO, Cu<sub>2</sub>O, Hg<sub>2</sub>Cl<sub>2</sub>, DDT, pentachlorophenol, etc. They are mixed either with the pigments or vehicles. Recently, a number of antifouling products have been developed using micro-encapsulation technology.

**vii. Luminous paints:** Luminous paints are used for visibility in the dark. They find application in inks, advertising signboards, road-marks, number plates of vehicles, watch dials, etc. The active components in luminous paints are specially prepared phosphorescent materials like CaS, ZnS, etc. These absorb light radiations and emit them in the dark. For colour effect in luminous paints, certain chemicals like copper salts (green), silver salts (blue), cerium and uranium salts (yellow), etc. are used. To protect the active ingredients from the attack by atmospheric moisture, the surface is coated with a thin and transparent water-proof film.

**viii. Anti-corrosive paint:** It is known that, when iron or steel is exposed to a natural atmosphere, then rust is formed. Although the rusting of iron or steel is usually termed as corrosion, the latter is a general term which is used to define the destructive interaction of a material with its environment. Corrosion usually refers to metals, though non metallic substrates such as plastics, concrete or wood also deteriorate in the environment. Corrosion causes enormous industrial losses with a depletion of our natural resources. In general, organic coatings are applied onto metallic substrates in order to avoid the detrimental effect of corrosion. Recent developments also include the use of nanoclay that can exchange anticorrosive agents with the corrosive species when needed.

## 2.3 Binders

Binders act to fix paint on the coated surface and provide tough, tenacious and glossy on the surface being painted (Sharma, 2011). They are non-crystalline liquid or solid material of relatively high molecular weight Polymer.

The binder is a very important ingredient that affects almost all properties of the coating, especially the following:

- Adhesion and related properties like resistance to blistering, cracking and peeling
  - Other key resistance properties like resistance to scrubbing, chalking and fading
- Application properties like flow, levelling and film build, and gloss development.

With no pigment present, most binders would dry to form a clear, glossy film; some binders are used without pigments to make clear finishes and varnishes. Pigment reduces the shininess, or gloss, of the binder ([www.paintquality.com](http://www.paintquality.com)).

The paint chemist uses a figure called the PVC (pigment volume concentration) to indicate the relative proportion of pigment to binder for the paint formulation. The PVC is a comparison of the relative volumes (not weights) of total pigment and binder, and is calculated as follows:

$$\text{PVC}\% = \frac{\text{Volume of Pigments}}{\text{Volume of pigments} + \text{Volume of Binder}} \times 100$$

### 2.3.1 Oil-based binders

The binder in an oil-based coating is made from a vegetable oil that “dries,” or oxidizes, and cross-links when it is exposed to the air, and thus develops the desired properties of the paint product. Drying oils traditionally used in paints and coatings include linseed oil, Tung oil and soya oil. Today, few paints are made with oil alone; rather, they are based on

modified oils called alkyds. Alkyds dry harder and faster than oils. Some coatings, particularly exterior primers, are made with combinations of oils and alkyds to achieve appropriate flexibility. The term “oil-based” are commonly used to refer to both oil and alkyd coatings ([www.paintquality.com](http://www.paintquality.com)). Linseed oil, the most common example of a drying oil, dries in 2 to 3 days while other oils, such as soya bean oil, may take up to 10 days (Ravikumar *et al.*, 2012).

### **2.3.2 Latex-based binders**

Most water- based paints are “latex” paints. The binder in a latex paint is a solid, plastic-like material dispersed as microscopic particles in water. This dispersion is a milky-white liquid, which is called latex in the paint industry, in that it is reminiscent of natural latex from the rubber tree. Latex is also called emulsion, and in some countries, such as England, latex paints are referred to as emulsion paints. Waterborne resins are polymeric materials whose composition enables them either to dissolve or to swell in water. They are of commercial interest principally because of their ability to alter advantageously the properties of aqueous systems or to deposit coatings from water solutions. Latexes are obtained either naturally, as for example natural rubber latex from *hevea brasiliensis* or by synthesis from raw materials based on petroleum or coal which are non renewable and must be used with economy (Motawie *et al.*, 2010 ; Stephen *et al.*, 2010 ).

While providing prompt development of a water- and weather-resistant, On the other hand, latex paints may blister from rain, dew or other sources of water on the outside of the coating, if the paint:

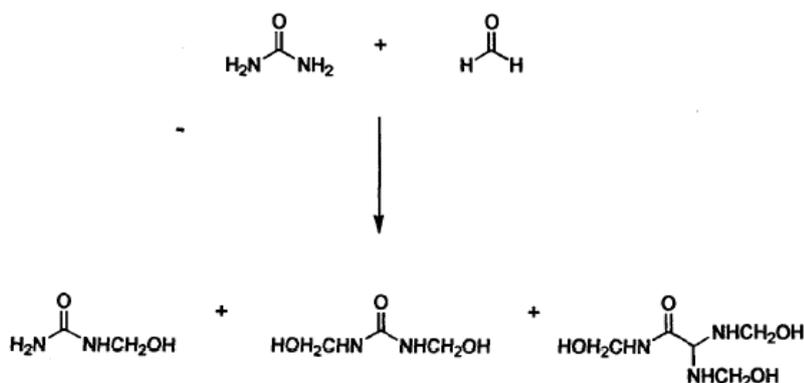
- I. has limited adhesion capability
- II. was applied over a chalky or otherwise unclean surface, such that the paint’s adhesion was compromised
- III. has not had enough time to dry thoroughly

Under any of these conditions, blistering tendency will be greater if the paint has high levels of tinting colour.

There are different broad chemical types of polymer used as latex paint binders. The two types used most commonly in North America are: 100 percent acrylic and vinyl acrylic. The formulator has many binders of each type from which to choose. A third category of latex binder is styrenated acrylic. Styrene is included in the binder for enhanced water resistance, gloss development and cost reduction ([www.paintquality.com](http://www.paintquality.com)).

## 2.4 Chemistry of Urea-formaldehyde

According to Conner (1996), urea-formaldehyde resins are formed by the reaction of urea and formaldehyde. The overall reaction of urea with formaldehyde is quite complex. The synthesis of a urea-formaldehyde resin takes place in two stages. In the first stage, urea is hydroxymethylated by the addition of formaldehyde to the amino groups (Scheme 3). This reaction is in reality a series of reactions that lead to the formation of Mono-, Di-, and Trimethylolureas. Tetramethylolurea is apparently not produced, at least not in a detectable quantity. The reaction rate is dependent on the pH. The rate for the addition of formaldehyde to successively form one, two, and three methylol groups has been estimated to be in the ratio of 9:3:1, respectively. The exact ratio, of course, is dependent on the reaction conditions employed in the addition reaction.



**Scheme 3.** Formation of Mono- Di- and Trimethylol urea by the addition of formaldehyde to urea. Tetramethylolurea has not been observed experimentally.

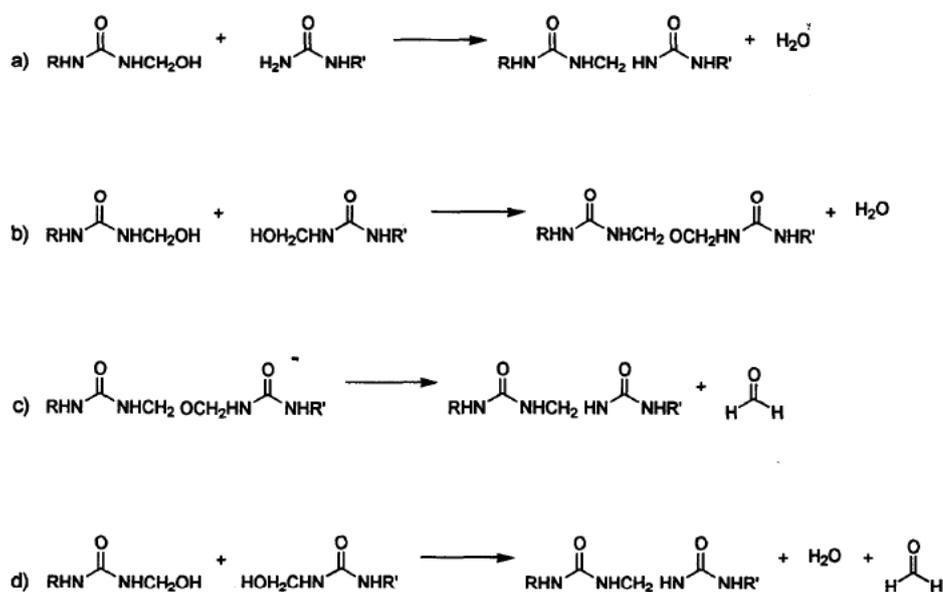
The reaction between urea (U) and formaldehyde (F) is basically a two step process, comprising of the methylation and condensation stage. Methylation refers to the addition of up to three molecules of the bi functional formaldehyde to one mole of urea to give to so-called methylolureas. The formation of methylol groups mostly depends on the F/U molar ratio, with higher molar ratio increasing the tendency to form highly methylolated species.

Urea formaldehyde resins are based on a manifold reaction of two monomers, urea and formaldehyde. By using different reaction and preparation conditions, a more or less innumerable variety of condensed structures is possible. Such structures consist of linear or branched polymeric molecules of various molecular masses. After hardening, urea formaldehyde resins form insoluble three-dimensional networks of thermosetting duromers.

Although urea formaldehyde resins consist of only two main components, i.e, urea and formaldehyde, they present a broad variety of possible reactions and structures. This variety leads to a wide range of molar mass distributions in urea formaldehyde resins, from low molar mass molecules up to more or less polymeric structures (Ivana *et al.* , 2010).

The second stage of urea-formaldehyde resin synthesis consists of the condensation of the methylolureas to low molecular weight polymers. The increase in the molecular weight of the urea-formaldehyde resin under acidic conditions is thought to be a combination of reactions leading to the formation of:

1. methylene bridges between amido nitrogens by the reaction of methylol and amino groups on reacting molecules (Scheme 4a);
2. methylene ether linkages by the reaction of two methylol groups (Scheme 4b);
3. methylene linkages from methylene ether linkages by the splitting out of formaldehyde (Scheme 4c);
4. methylene linkages by the reaction of methylol groups splitting out water and formaldehyde in the process (Scheme 4d) (Conner, 1996; Zorba, *et al* 2008).



**Scheme 4:** Condensation reactions of methylolureas to form (a) methylene bridges between amido nitrogens, (b) methylene ether linkages, and (c) and (d) methylene linkages. Reactions of these types produce higher molecular weight oligomers and polymers. Formaldehyde emission and durability of cured resin can be controlled and specifically tailored for the final use of the resin (Osemeahon, 2011).

## 2.5 Green Chemistry

Green chemistry can be defined as the practice of chemical science and manufacturing in a manner that is sustainable, safe, and non-polluting and that consumes minimum amounts of materials and energy while producing little or no waste material. The practice of green chemistry begins with recognition that the production, processing, use and eventual disposal of chemical products may cause harm when performed incorrectly. In accomplishing its objectives, green chemistry and green chemical engineering may modify or totally redesign chemical products and processes with the objective of minimizing wastes (Manahan, 2006).

Green chemistry is the universally accepted term to describe the movement towards more environmentally acceptable and sustainable chemical processes and products. The substitution of volatile organic solvent is an important target for almost all chemical manufacturers both in reaction and in work-ups and product purification (Dara *et al.*, 2012).

During the approximately two centuries that chemical science has been practiced on an ever-increasing scale, it has enabled the production of a wide variety of goods that are valued by humans. These include such things as pharmaceuticals that have improved health and extended life, fertilizers that have greatly increased food productivity and semiconductors that have made possible computers and other electronic devices. Without the persistent efforts of chemists and the enormous productivity of the chemical industry, nothing approaching the high standard of living enjoyed in modern industrialized societies would be possible. Even with these improvements, the impact of industrial processing, use and disposal of chemicals on environment is staggering. Green chemistry is already demonstrating the potential and promise to develop new techniques and methodologies to enable industries to pursue their traditional innovations and at same time minimizing environmental impacts (Manahan, 2006; Dara *et al.*, 2012).

Green chemistry is sustainable chemistry. There are several important respects in which green chemistry is sustainable:

- **Economic:** At a high level of sophistication green chemistry normally costs less in strictly economic terms (to say nothing of environmental costs) than chemistry as it is normally practiced.
- **Materials:** By efficiently using materials, maximum recycling, and minimum use of virgin raw materials, green chemistry is sustainable with respect to materials.
- **Waste:** By reducing it as far as possible or even totally eliminating their production, green chemistry is sustainable with respect to wastes (Manahan, 2006).

### **2.5.1 Volatile organic compound (VOCs)**

VOC is defined as Volatile Organic Compound. These are *almost all* the solvents or thinners in paint. The amount of VOC is usually expressed as a ratio of weight of VOC to the volume of coating - such as grams per litre or pounds per gallon (McGlennon, 2012). The presence of VOCs or volatile organic compounds is also a major environmental problem in regular paints.

VOCs are harmful materials to the environment, polluting the air and causing health risks to humans. To address this problem, paint manufacturers make it one of their stringent goals to develop new products that contain little to zero VOCs. The demand for green buildings is driving painting contractors to use only green paints and coatings. In response, paint manufacturers and their suppliers develop eco-friendly paints made out of environmentally-safe materials. These layered responses allow for a successful implementation of the green building trend to most commercial and residential facilities in the country (Parker, 2009).

The presence of VOCs in paint is significant both in terms of environmental impact and to health. Volatile Organic Compounds, VOCs, are organic compounds that have high enough vapour pressures to enable them to vaporise into the atmosphere. Organic solvents used in paint are a rich source of VOCs - White spirit, for example, contains the 'aromatic hydrocarbons' xylene, methyl benzene and ethyl benzene. Though solvents are the main source, VOCs are also emitted from other components such as some pigments (tints), fungicides and biocides - leading to a degree of variance amongst brands and colours of paint described as low-VOC. VOCs are emitted both during application and for extended periods afterwards. One study demonstrated that less than 50% of the VOCs in latex paint are emitted in the first year (Greenspec, 2012).

A recent study by Herbarth and Matysik (2010) shows that personal activities of residents related to indoors such as furniture, carpets, paint and varnishes contribute to VOC exposure and also alkanes with longer chain length are mostly emitted indoors by the interior materials, e.g. paint and varnish. As most people spend the majority of time indoors, the indoor exposure plays an important role in the overall personal exposure and therefore in any health risk assessment.

### **2.5.2 Formaldehyde Emission**

The evolution of formaldehyde from urea-formaldehyde material is incontrovertible. Over the past 40 years investigators have examined extensively the structure of the components of urea-formaldehyde resin systems and the chemistry of their formation and degradation in

aqueous solutions. Classical Kinetic, chromatographic and NMR have been applied (Conner, 1996). The reactions which lead to the formation of urea-formaldehyde products formed during urea-formaldehyde resin synthesis and cure are reversible. In the forward direction, water is eliminated; therefore, the reverse reaction can be viewed as hydrolysis, which leads to the release of formaldehyde. Because most, if not all, of these reactions are catalysed by acid, the use of an acid catalyst to hasten bond cure, unfortunately also increase the rate of hydrolysis and formaldehyde liberations (Osemeahon, 2008).

The issue of formaldehyde exposure in homes is long-standing and has been studied over time. Formaldehyde is frequently used in plywood, fibreboard, resins, glues, and several other construction components. Acute and chronic health effects of formaldehyde vary depending on the individual. The typical threshold for development of acute symptoms due to inhaled formaldehyde is 800 ppb; however, sensitive individuals have reported symptoms at formaldehyde levels around 100 ppb. These sensitized individuals can have exacerbations of symptoms without the appreciation of odour, giving the individual little or no warning of exposure. The common symptoms from acute exposure to formaldehyde manifest as irritation of the throat, nose, eyes, and skin. This upper respiratory tract irritation can potentially exacerbate asthma symptoms and other respiratory illnesses. In addition to acute health effects of formaldehyde, chronic exposures in occupational settings also have been extensively studied. Respiratory symptoms of chronic runny nose, chronic bronchitis, and obstructive lung disease all have been suggested (CDC, FEMA, USEPA, 2008). Tang *et al* (2009) reported that Formaldehyde levels between 0.1-0.5 ppm are detected by human senses; between 0.5-1.0 ppm can cause eye irritation and above 1.0 ppm can irritate the nose and throat. World health organization (WHO) recommends a limit of 0.08 ppm as residential indoor formaldehyde maximum allowable concentration (MAC).

The EU (European Union) paint directive has reduced the proportion of volatile organic compounds allowed in paints and varnishes, to conform, domestic paint manufacturers have cut back on organic solvent content, or turned to water-based products. Manufacturers have changed the binding molecules in their products to meet legislation though organic solvent are important because of smooth, glossy, durable finish but the waves have changed (Houlton, 2012). Top Green Projects reflect the multifaceted nature of design and materials that contribute to sustainable-building objectives. Top Green Coatings Projects (2009) report where low-emitting paint are clearly stamped on the green-building package.

The main strategy to reduce the formaldehyde emission of urea formaldehyde resins has been the change on its formulation by decreasing the molar ratio of formaldehyde to urea. However, the reduction weakens the mechanical properties of particleboard and moreover it increases the time required for hardening under the action of current hardeners (latent acids) (Ferra *et al.*, 2011). Recent development work with the formaldehyde-free reducing agent Bruggolite FF6 in emulsion redox systems has shown that it is capable of substantially reducing free monomers, reaction time and yellowing. It offers other benefits as well (Matthias and Paul, 2012).

The result of paint manufacturers' paint reformulation efforts is apparent in the wide array of green paints that painting contractors can choose from. One product is a result of many years of polymer research leading to a new and improved latex paint that eliminates the use of toxic solvents. Without the inclusion of such harmful solvents, air quality is maintained during and after painting application projects, protecting painting contractors and building tenants at the same time (Ferra *et al.*, 2011).

## 2.6 Pigments

Pigments are finely ground particles or powders that are dispersed in paints. Many of the same pigments are utilized in latex- based and oil-based paints. There are two primary categories of pigments: prime and extenders (Hall, 2010).

### 2.6.1 Prime pigments

These are the pigments that provide whiteness and colour. They are also the main source of hiding capability.

1. **Titanium Dioxide** ( $\text{TiO}_2$ ) is a white synthetic inorganic pigment existing in two crystalline forms: rutile and anatase. Titanium dioxide has high refractive index (anatase 2.52, rutile 2.76). Anatase is photo chemically active but provides clear white colour therefore its main application is interior paints. Photo chemically inert rutile is used for protection of paints from degradation by light. Titanium oxide is the most widely used pigment.
2. **Zinc Oxide** ( $\text{ZnO}$ ) is a white synthetic inorganic pigment having refractive index 2.01.
3. **Zinc Yellow** (**Yellow 36**) is zinc chromate ( $\text{ZnCrO}_4$ ).
4. **Yellow Dyes** are stable yellow non-toxic organic pigments with good opacity.

5. **Benzidine Yellows** are yellow-to-red organic pigments for interior applications. They are resistant in chemicals and stable at elevated temperatures (up to 300°F / 150°C).
6. **Chrome Oxide Green** is olive-green inorganic pigment with a high level of opacity. Chrome Oxide Green is the most stable green pigment.
7. **Phthalocyanine Green** imparts green-blue color. It is used as the pigment for decorative applications. The pigment is resistant to heat, solvents and alkalis.
8. **Phthalocyanine Blues** are widely spread pigments. They provide a wide spectrum of color: from reddish-blue to yellowish-green. The pigments are non-toxic and resistant to solvents, chemicals and elevated temperatures.
9. **Ultramarine Blue** is natural pigment made of the semiprecious mineral lapis lazuli. The pigment is resistant to fading. It is stable at elevated temperatures.
10. **Vermilion** is a natural orangish red pigment consisting of toxic mercuric sulfide (HgS).
11. **Pigment Brown 6** is red inorganic pigment based on Iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>).
12. **Red 170** is a synthetic organic pigment widely used in automotive industry.
13. **Dioxazine Violet** is organic synthetic pigment. It is non-toxic and has high tinting strength.
14. **Carbon Black** is the pigment obtained from organic materials (wood, bones) by charring (thermal decomposition in a limited amount of Oxygen). Large quantities of Carbon Black are used for colouring and reinforcing automobile tires.
15. **Iron (II) Oxide (FeO)** is inorganic black pigment (Kopeliovich, 2012).

### 2.6.2 *Extender pigments*

Extenders provide bulk at relatively low cost. They add much less hiding than TiO<sub>2</sub> and impact on many properties, including sheen, scrub resistance, exterior colour retention and others. Some commonly used extenders are noted below.

1. **Clay:** Aluminium silicates (also called kaolin and china clay) are used mainly in interior paints, but also in some exterior paints. Calcined (heated to drive off water and create air-particle interfaces) clay provides more hiding than most extenders; delaminated clay enhances stain resistance.
2. **Silica and silicates:** These provide scrub and abrasion resistance. Many of these exhibit excellent durability in exterior paints.
3. **Diatomaceous silica:** This is a form of hydrous silica consisting of ancient fossilized single-cell organisms. It is used to limit sheen in paints and varnishes.

4. **Calcium carbonate:** Also called chalk, this is a general purpose, low cost, low hiding pigment used in both interior and exterior paints.
5. **Talc:** Magnesium silicate a relatively soft general purpose extender used in interior and exterior paints.
6. **Zinc oxide:** This is a reactive pigment helpful with mildew resistance, corrosion inhibition and stain blocking. It is used mainly in primers and in exterior paints ([www.paintquality.com](http://www.paintquality.com)). New found interest in fillers from agro-waste is having potential applicability as extenders in paint. This is as a result of transition to renewable (plant-based) resources. Rice-husks ash, an agro-waste product, has a high silica content, which makes it an alternative to natural quartz, and synthetic silica. It is applied as a flattening (matt) extender to produce Red oxide primer (industrial paint). It showed superiority in flattening effect that surpassed that of calcium carbonate and silica flour (Ossi, 2012).

## 2.7 Solvent

The liquid portion of the paint (also referred to as the “carrier”) provides a way to get the pigment and the binder from the container onto the surface that is to be painted.

- For most oil-based and alkyd paints, the liquid component is paint thinner, which is a combustible solvent made primarily of mineral spirits, a petroleum distillate of aliphatic hydrocarbons.
- For shellac-based primers and varnishes, the liquid is denatured alcohol.
- For clear and pigmented lacquers, the liquid is usually lacquer thinner or another solvent that is “stronger” and more flammable than paint thinner.
- For latex paints, the liquid is primarily water

The pigments and the binder are what is left on the surface when the paint dries and the liquid portion evaporates. Together, they are called the solids portion of the paint:

PIGMENTS + BINDER = SOLIDS

The coating (e.g., paint, stain, primer) consists of the solids and the liquid:

SOLIDS + LIQUID = COATING ([www.paintquality.com](http://www.paintquality.com))

## 2.8 Paint Additives

Additives are additional ingredients that affect and enhance many paint properties. Additives belong to a broad and diffuse category of key components in a coating formulation. They

comprise a small percentage of the coating formulation - their use level rarely exceeds 1 or 2%, and the total level of all additives in a formulation seldom exceeds 5% of the total product. Their impact, however, is significant as they contribute to the ease of manufacture, the stability of the coating in the package, ease of application, quality and appearance of the final film (Joseph *et al.*, 2012).

These additives often explain why paints of different manufacturers behave differently (Hall, 2010). As the paint and coatings industry continues to fall under pressure by environmental regulations, manufacturers of coatings and paints are endlessly reformulating their products. As a result, demand for novel additives continues to increase. The rapid economic growth in most of the emerging countries in the recent years resulted in rampant architectural construction and industrial activity, which created significant demand for paints and additives that, in turn, rocketed demand for paint additives (Tim, 2012).

### **2.8.1 *Thickeners and rheology modifiers***

Rheology is the science of how a liquid tends to flow. Without thickeners and rheology modifiers it would be impossible to create water borne composition that will perform satisfactory as a coating. It is generally interpreted that thickening agents are used to prevent pigment settling and provide 'in can' stability and rheology modifiers are used to adjust application properties, film flow and levelling.

- a) provide adequate viscosity (thickness), so the paint may be applied properly
- b) Impact how thick the paint goes on and how well it flows out when applied
- c) Modern rheology modifiers help latex paints to:
  - resist spattering when applied by roller
  - flow out smoothly
  - be less likely to spoil than those modified with older-generation thickeners (With spoilage, the paint may smell putrid and/or lose viscosity).

Rheology additives are indispensable for good effect pigment orientation in waterborne paint systems. They help to optimize the viscoelastic properties of the paint. Rheology-modifying wax additives give particularly good results (Buhne *et al.*; 2009). Rheology plays a major role both in production and application stages of paints. Na-Bentonite, clay based thickening agent, is generally used to modify the viscosity of paints since it is more economical and environmentally friendly compared to polymer based thickening agents. Na-Bentonite and MgO mixture was evaluated as an additive in waterborne paints. It is determined that the bentonite – Mgo mixture can perform as well, or better

than other thickening agents (Karakas *et al.*, 2011). Bermocoll is used as a thickener, stabilizer and water retaining agent for water-based decorative paints. Bermocoll cellulose ethers can be regarded as polymeric surface active agents. They can contribute to the dispersion of pigments by improving the flow during grinding; it also helps to stabilize the pigments from flocculation. Bermocoll, like all other cellulose ethers, has good water retention properties (Akzonobel, 2008).

### **2.8.2 *Anti-settling agents (surfactants)***

The primary functions of an anti-settling or a pigment dispersant is to surround a suspended pigment particle with a barrier that either ionic repulsion or steric hindrances prevents random contact with other particles. This in turn avoids adhesion and flocculation. Anti-settling agents tend to differ from emulsifiers in that the anti-settling or dispersing agent attaches itself to the outside solid surface of the pigment. Whereas in the case of an emulsifier, a portion of the emulsifying agent tends to be submerged and becomes part of the liquid surface of the dispersed phase. The prevention of setting of pigment when a solvent-based paint is stored is often a matter of compromise. Good dispersing agents and deflocculants aid gloss and opacity but not favourable to setting (Osemeahon, 2008).

### **2.8.3 *Plasticizers***

In order to reduce certain aspect of cracking in paints, plasticizers are added to the paint by proper choice of the oils. Plasticizers provide elasticity to the film and thus prevent cracking of the paints. Plasticizers are low melting solid or liquid of low volatility, which prevent cracking of the paints by increasing elasticity. Chemically plasticizers are mostly esters; Tricresyl phosphate, triphenyl phosphate, dibutyl tartarate and tributyl phthalate and oil etc.

### **2.8.4 *Anti-skinning agents***

Certain anti-skinning agents are also added to the paints in order to prevent gelling and skinning of the finish product before application of the paints by brushing, spraying or dipping. Polyhydroxy phenols are usually employed as anti-skinning agents (Sharma, 2011).

### **2.8.5 *Anti-foaming agents (defoamers)***

These are products used to diminish the tendency for the formulation of air bubbles during the manufacture of water-base coating system. Latex paints are stabilized with surfactants and colloids, which unfortunately also helps to stabilize air introduced during manufacture or

during application and thus produce stable foam (Achi, 2003). Non-aqueous paints may also show bubbling. Antifoam are usually of high surface activity and good mobility whilst not being actually soluble in the foaming liquid. They work by lowering the surface tension in the neighbourhood of the bubbles causing them to coalesce to large, less stable bubbles which then break. At their simplest, the additives may be solutions of large; less stable bubbles which then break. At their simplest, the additives may be solutions of single substances such as pine, oil, dibutyl phosphate, or short chain (C<sub>6</sub>-C<sub>6</sub>) alcohols. Complex ones may be undisclosed compositions comprising mineral or silicone oils carried on fine-particle silica in the presence of surfactants. Many work by providing an element of incompatibility and thus create centre from which bubbles collapse.

### **2.8.6 Driers**

A drier is a material that promotes or accelerates the drying, curing, or hardening of oxidizable coating vehicles. Driers are divided into two classes: those that affect the oxidation of oil and those that affect the polymerization process itself (Ibekwe and Ibemesi, 2012). The most common driers are metal soap of carboxylic acid and include Cobalt, Manganese, Cerium, Zirconium and Calcium. Concern is expressed about the possible impact of metal driers on health in general. A recent work by Ibekwe and Ibemesi, (2012) shows that melon seed oil (MSO) is susceptible to auto-oxidation, which forms the basis of the drying effect employed in the paint industry.

The film formation process of one-component waterborne formulations involves a sequence of water evaporation, coalescence and further solidification. The length of this process determines when the coated substrate can be further processed or used. A long drying time lengthens the total coating process until finished parts can be used, further processed or stacked. Accelerating the development of a coating's early performance characteristics allows for increased productivity if a coating line can run faster, or if the interval between multi-layer coatings can be shortened. The drying of various waterborne formulations for different applications were compared and specific film stability was reached after a significantly shorter time when a nanoparticle-based additive was added (Herold and Klaus, 2012).

### **2.8.7 Biocides**

Biocides prevent growth and attack of fungi, bacteria and insect. There are two type of biocide used in latex paints as;

- a. A preservative to keep bacteria from growing in the paint. (This is especially important for paint stored in containers that are repeatedly opened and closed, because contamination can occur.)
- b. A mildewcide, to discourage mildew from growing on the surface of the paint after it has been applied. (This is used mainly in exterior products, although some interior paints, such as those formulated for use in damp areas, e.g., kitchens and baths, may also contain mildewcide). Fungal spoilage and algal defacement of industrial and private structures has been an ongoing challenge to the coatings industry for decade (Dow Microbial Coating, 2012).

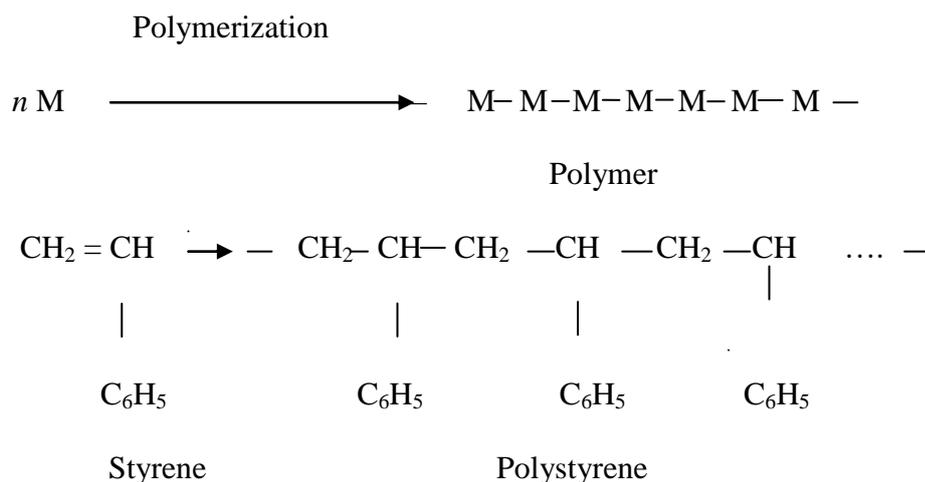
A recent article by Holtz *et al.*, (2012) report the use of nanostructured silver vanadate as a promising antibacterial additive to water-based paints that has potential for applications in bathrooms, kitchens, and hospital environments.

### **2.8.8 Fire retardant additives**

Polymeric materials have become more widely used in areas such as, home furnishings, construction, and various industrial applications. However most polymers contain high carbon and hydrogen contents, which are flammable to various degrees. Fire retardant coatings are designed to prevent the heat, flames or fire from spreading. This coating has an ability to expand for many times of its original thickness to produce insulation layer of char when heated. An increased char yield reduced amount of combustible gases reaching the flame, which in turn leads to extinction (Muriel *et al.*, 2010; Zaharuddin *et al.*, 2011).

## **2.9 Polymer**

A polymer is a large molecule made by linking together repeating unit of small molecules called monomers. The process of linking them together is called polymerization (Paula, 2011).



**Scheme 5**

In this modern world, polymers are an integral part of everyone's life style. They have very diverse structures and applications ranging from domestic articles to sophisticated and medical instruments. These materials have penetrated into almost all the applications like, transportation, agriculture, construction, education etc. These materials are used as Fibers, Rubbers, plastics, Adhesives, Paints etc. In fact, the very existence of life is virtually the formation, transformation and decomposition of biopolymers VIZ. carbohydrate, proteins, and nuclei acids. Therefore, in view of their importance, a proper understanding of polymeric materials is very essential (Shashi, 2011).

Polymers can be of biological and synthetic origin, and are very important in our daily lives. Synthetic polymers can be prepared by addition and condensation polymerization using a variety of polymerization processes to yield polymers with differences in their stereo-regularity, organization of their constituents, molecular weight and crystallinity. All these differences yield polymers with different mechanical properties. Since the number of monomers available is very high, the variety of the polymers theoretically possible is also high. Some become viscoelastic and some are just plastic. Polymers are not always linear like noodles but can be made to have branches either of the same monomer or by adding other monomers to change the chemistry and the crystallinity of the product (Hasirci *et al.*, 2011).

Modification of polymers has received greater attention in light of the scarcity of starting materials required for the synthesis of new monomers to deliver better polymeric materials. The next generation awaits polymer modification as it opens up new possibilities. Sometimes, balancing of properties is needed, and this is possible only through modification of polymers (Bhattacharya *et al.*, 2009).

### 2.9.1 Copolymerization

Often, it is possible to obtain polymers with new and desirable properties by linking two or more different monomers or repeating unit during polymerization. Polymers with two different repeating units in their chains are called copolymers and the process copolymerization (Joel, 2010). Both chain growth polymers and step growth polymers can be copolymers. Many of the synthetic polymers used today are copolymers example, Saran from Vinyl Chloride monomers and Vinylidene Chloride monomer and butyl rubber from Isobutylene monomers and Isoprene. There are four types of copolymers. In an alternating copolymer, two monomers alternate. A block copolymer consists of blocks of kind of monomer. A random copolymer has a random distribution of monomers. A graft copolymer contains branches derived from one monomer grafted onto a backbone derived from another monomer. These structural differences extend the range of physical properties available to the scientist designing a copolymer (Paula, 2011).

An alternating copolymer	ABABABABABABABABABABABA
A block copolymer	AAAAABBBBBAAAAABBBBBAAA
A random copolymer	AABABABBABAABBABABBAAB
A graft copolymer	AAAAAAAAAAAAAAAAAAAAAAAAA
	B            B            B
	B            B            B
	B            B            B
	B            B            B

### 2.9.2 Synthetic resin and plastic

The emergence of synthetic resins and plastic industry from primitive beginnings a century ago to an international multi-billion dollars per year industry today has profoundly changed the way people live. Plastic can perform in ways that are not possible with traditional materials and therefore have become an essential component in our technological based society. The word “plastic” was originally used as an adjective to denote formability. In the 1920s it began to be used as a noun to refer to synthetic materials such as Bakelite and celluloid. Now it is use generically to refer to a larger class of manufactured organic polymeric material. The American Society for testing materials (D1695-77) has define plastic as “a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in it finished state and at some stage in it manufacture or in its processing into

finished articles, can be shaped by flow". The word plastic has its roots in the Greek word *plastikos* which means being able to be moulded into different shape (Mangizvo, 2012).

Although the words "plastic" and "resins" sometimes are used interchangeably, workers in the polymer industry generally make a distinction between them. Originally "resins" refer to the natural exudates of plant and trees such as rosin, copal, amber, elemi, kaure, manila, mastic and batu. The word also became to be used for resin like substances of animal origin such as shellac and casein. In the synthetic polymer field "resins" also refers to unblended, synthetic polymeric raw materials from which a finished adhesive, coating or plastic product is made. In the manufacture of polyethylene irrigation pipe, for example, the raw product synthesis from ethylene monomer is called a resin. It is consider a plastic material after the resin is blended with fillers, pigment, antioxidant or other substances and then extruded.

Plastic and resins can be classified in several different ways. They can be grouped according to chemical composition (polyolefin, polyacrylate) according to physical characteristic (elastomeric, thermoplastic, thermoset) according to form (sheet, film, fiber) and according to function (packaging film, structural adhesive, engineering thermoplastics) (Riegels, 1997).

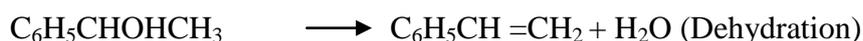
### 2.9.3 Chemistry of Polystyrene

Styrene is prepared by first producing ethyl benzene by the catalytic combination of benzene with ethyl.



Ethyl benzene

Ethylbenzene is then dehydrogenated to give styrene monomer.

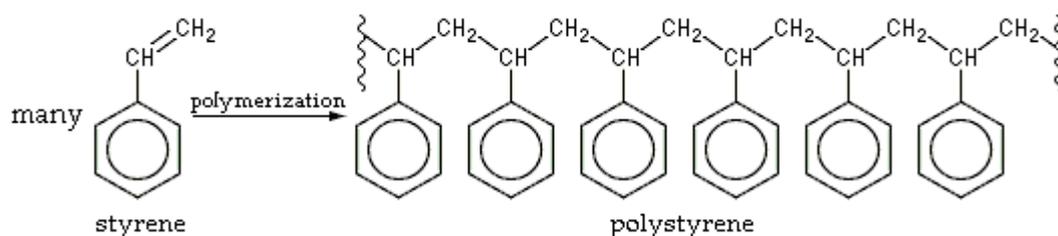


**Scheme 6**

Styrene

Styrene is then polymerised to polystyrene in presence of benzoyl peroxide catalyst. Polystyrene for injection moulding and extrusion can be made by pear polymerisation (in which monomer in powder form is finely dispersed in dispersing medium by means of a

dispersing agent in presence of a catalyst). Polymer pearls are obtained by heating and stirring of the dispersion in the closed vessel and solution polymerisation (in which styrene is dissolved in ethyl benzene).



### Scheme 7

Polystyrene is an important polymer of immense use industrially as it is highly resistance to shock, chemicals and weather conditions. It dissolves in many solvent and has a lot of uses as plastic in industry for domestic purposes (Al-bermany, 2011).

### 2.10 Solid Waste

Solid waste is synonymous with the word refuse. The wastes generated and discarded from human and animal activities that are normally solid are called as solid wastes. There are two components of solid wastes: garbage and rubbish. Garbage or food waste is the animal and plant residue produced as a result of the handling, cooking, and eating of foods. Rubbish is the combustible and non-combustible portion of solid waste, excluding food waste. Trash is the combustible portion of rubbish. White goods are the bulky portions of rubbish, such as refrigerators, air conditioners, and the like. Construction and demolition debris, rock fragments, and the like are specially called rubble. Solid waste can be classified into different types depending on their sources:

1. Household waste is generally classified as municipal solid waste (MSW).
2. Industrial waste as hazardous
3. Biomedical waste or hospital waste as infectious waste (Viswanathan, 2009)

The amount of waste discharge into the environment is related to the population composition, size and per capital income. A remarkable growth in population and income give rise to the production and consumption of goods and services and thus, the discharge rate is increased. The majority of substances composing MSW include paper, vegetable matter, plastics, metals, textiles, rubber and glass. MSW disposal is an enormous task in the developing countries across the world, as poverty, population growth and high urbanization

rates combine an effectual and under-funded government to prevent efficient management of wastes. Collection and disposal of wastes differs from country to country. In USA, the methods of disposal are landfills and incineration, disposal method in Australia is landfill, while in Japan its incineration and Recycling which started in April 2001. In Nigeria, the common method of disposal is open dump. The amount of trash that accumulates in a matter of hours would be more than waste collectors could haul in a day, these garbage “dumps” are located on the side of the highway at the fringe of cities and slums (Nwachukwu *et al.*, 2010).

Trend of solid waste generation shows an increase in the composition of plastic waste. Plastic solid waste (PSW) is categorized into seven groups, namely: Polyethylene terephthalate (PETE), High-density polyethylene (HDPE), Polyvinylchloride (PVC), Low-density polyethylene (LDPE), Polypropylene (PP), Polystyrene (PS) and others. PSW had increased significantly because of changing of life style (Dhokhikah and Trihadiningrum, 2012). Plastics are resistance to moisture; hence they do not break easily. Therefore they block drains during rains, recognized as threat to oceans, soil, domestic animals, wildlife and marine life. In marine environments, bags can entangle, suffocate or cause blockage in digestive tracts in marine animals (Mangizvo, 2012; Isiya, 2012).

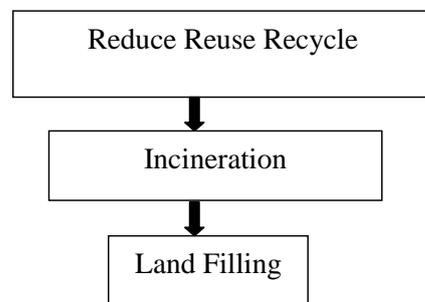
With the development of new synthetic polymers, plastics have found applications in every field of life. A worldwide increase in the use of these materials has generated issue of solid waste disposal. Millions of tons of solid waste are disposed off annually in the world and a large proportion consists of plastics. 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; Borghei *et al.*, 2010).

The quantity of solid waste generated in urban areas in industrialized countries is higher than in developing countries; still municipal solid waste management remains inadequate in the latter. Solid waste in developing countries differs from developed countries. Most developing countries, Nigeria, inclusive have solid waste management problems different from those found in industrialized countries in areas of composition, density, political, and economic framework, waste amount, access to waste for collection, awareness and attitude. The wastes are heavier, wetter and more corrosive in developing cities than developed cities (Ogueleka, 2009).

Recycled plastics can be incorporated into conventional bituminous road surfacing mixtures; greater durability and fatigue life have been reported for these modified mixtures, enhance various engineering properties (Bindu and Beena, 2010). Chemical recycling of

polystyrene (PS) waste by sulfonation is one of the ways to change the original chemical and physical properties of waste PS. It is possible to receive a water-soluble PS derivative which can be used as a flocculent agent or as a concrete plasticizer through sulfonation from polymer insoluble in water (Sulkowski *et al.*, 2009).

In recent years, the building community has taken a more active role in the sustainable design of buildings. The concept of environmentally-conscious building design (“green building”) has already been incorporated into tools that measure environmental performance of buildings and building materials. Optimizing material selection is a key component in building “green”. The increasing costs of material disposal and land filling make the reusability of expanded polystyrene (XPS) a very attractive option. The hierarchy of waste management for green building design is as follows:



Recycling has traditionally been seen as the most effective way to protect and preserve the environment. Recycling has been viewed by much of the public as primarily a social issue. Incineration is seen as less desirable but even it can have some benefits when XPS is involved. Land filling is usually viewed as the last viable option to be considered for waste management (Fabian *et al.*, 2004). In a recent work by Sabnis *et al.*, 2012, Poly(ethylene) terephthalate (PET) which leads to polymer wastes is recycle and utilized for coating application and the paint showed excellent gloss, flexibility, pencil hardness, adhesion, no cracks and good resistance to acids. An up-cycling of the post consumer blend wastes for value-added goals remains a challenge for the scientific community. Many scholars had work on recycling of thermoplastic elastomers, which makes polymer life virtually endless. Blending have been developed aiming to upgrade the polymer recyclates during reprocessing (Jermy *et al.*, 2011).

## **CHAPTER THREE**

### **MATERIALS AND METHODS**

#### **3.1 Materials/reagents**

Urea, formaldehyde, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide pellets, ammonia, butanol and sucrose were reagent grade products from the British Drug House (BDH). Titanium dioxide, calcium carbonate, sodium carbonate, kaolin, aluminium silicate, calgon, anti-skinning agent, anti-foam, genepour, drier, bermocoll, nicofoam, troystan, dispersant, water and gasoline were obtained from Yola market, Nigeria. All the materials were used as received. Polystyrene waste was collected from refuse dumps located in Yola, Nigeria.

#### **3.2 Methods**

The methods used for the resin synthesis and determination of the film properties were done as described by Osemeahon and Archibong (2011).

##### **3.2.1 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 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M NaOH solutions. The solution was heated in a thermostatically controlled water bath at 70°C. The reaction was allowed to proceed for 2 h after which the sample was removed and kept at room temperature (30°C).

##### **3.2.2 Formation of liquid PS**

Solid (polystyrene) PS was constituted into liquid form by dissolving 5 g of PS waste in 25 mL of gasoline. The mixture was stirred continuously and allowed to stay for 24 h to achieve a homogenous solution.

##### **3.2.3 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.

### **3.2.4 Determination of viscosity and gel time**

A 100 ml Phywe 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. 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.

### **3.2.5 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).

### **3.2.6 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.

### **3.2.7 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.

### **3.2.8 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.

### 3.2.9 Water solubility

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

### 3.3 Fourier transform infrared spectrophotometric Analysis

The infra-red (IR) analysis of TMU, PS and TMU/PS was carried out using infra-red spectrophotometer (Buck Scientific Inc. Norwalk, CT USA, Model M500 to 4000 cm<sup>-1</sup>

### 3.4 Statistical Analysis

The degree of spread of the data around the mean was calculated using standard deviation to measure the extent to which the data differ among themselves.

Standard Deviation (SD)

$$SD = \sqrt{V} = \left[ \sum_{i=1}^N \frac{(x_i - \bar{x})^2}{N-1} \right]^{\frac{1}{2}}$$

### 3.5 Paint formulation

The method described by Karakas *et al* (2011); was adopted for the paint formulation. Paint production process involves three main stages:

#### 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 12.7 g of the additives as shown in Table 1. This mixture was stirred using a high speed stirrer for 15 min.

#### 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 15 min. 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 min. Energy losses in the mill base are minimized by adding thickeners before the dispersion stage of the production process. The above processes were repeated using pure TMU as binder. The details of the formulations are shown in Table 1.

### **3.6 Test procedures for paint samples**

Paint sample was analysed as described in Niger Cedar laboratory hand book of paint formulation recipe and to standard organization of Nigeria methods (SON, 1990).

#### **3.6.1 Viscosity**

Viscosity of paint sample was determined by using an I.C.I. Rotothinner 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<sup>0</sup>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 allowed to run until a steady state is reached (5 min). At the end of the required time, the viscosity was recorded in poises. Triplicate determinations were made for each sample and mean value recorded.

#### **3.6.2 pH and Opacity**

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

#### **3.6.3 Drying time and flexibility**

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 is 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 chromate aluminium with the aid of paint applicator. The film was allowed to air dry under room temperature (27<sup>0</sup>C) for 7 days.

**Table 1:** Recipe for the formulation of emulsion paints from TMU and TMU/PS binders.

Stage	Materials	Quantity in g
First	Water	185
	Anti-foam	0.2
	Drier	0.2
	Calgon	1.16
	Genepour	1.16
	Bermocoll	2.5
	Troystan	1.14
	Dispersant	0.2
	Butanol	5
	Ammonia	0.54
Millbase	TiO <sub>2</sub>	50
	Al <sub>2</sub> (SiO) <sub>3</sub>	11.2
	Na <sub>2</sub> CO <sub>3</sub>	0.58
	Kaolin	2.52
	CaCO <sub>3</sub>	123.0
Letdown	Binder	100
	Water	15
	Dispersant	0.2
	Nicofoam	0.2
	Anti-skinning agent	0.2
<b>Total</b>		<b>500 g</b>

The panel with the film was inserted into the conical Mandrel Bend Tester and the panel bent through 180° with a smooth action (taking 1-2 seconds). The panel was 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.

#### **3.6.4 Adhesion property**

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 h. 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 intersections of the perpendicular line. The adhesive tape were 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.

#### **3.6.5 Specular gloss**

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 pre clean glass panel and the film allowed to dry for 24 h. The ASTM gloss-meter was allowed to warm 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 held against the pot-hole in three separate positions along its length and the mean gloss calculated in percentage 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.

#### **3.6.6 Stickiness and pencil hardness**

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. Pencil hardness of the paint films was also determined according to ASTM standard methods (ASTM D 3363-74 3363-74).

#### **3.6.7 Resistance to blistering**

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 min indicates poor water resistance. Triplicate samples were used for each determination and the average quality assessment recorded.

### **3.6.8 *Stability test***

The paint sample was fully sealed in a container and allowed to stay at room temperature (27<sup>0</sup>C) for 4 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.

### **3.6.9 *Chemical resistance***

To evaluate the chemical resistant of the paint films, three flexible aluminium panels (150 mm x 0.3) were used as the test panels. A coat of paint with paint applicator was applied to the panel. One litter glass beaker was filled with 0.1 M NaOH solution to a depth of 150 mm and the test pieces immersed for 48 hours 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 0.1 M NaCl respectively. The presence of any surface defects such as cracking, blistering, peeling or change in colour will indicate poor chemical resistance.

## CHAPTER FOUR

### RESULTS AND DISCUSSION

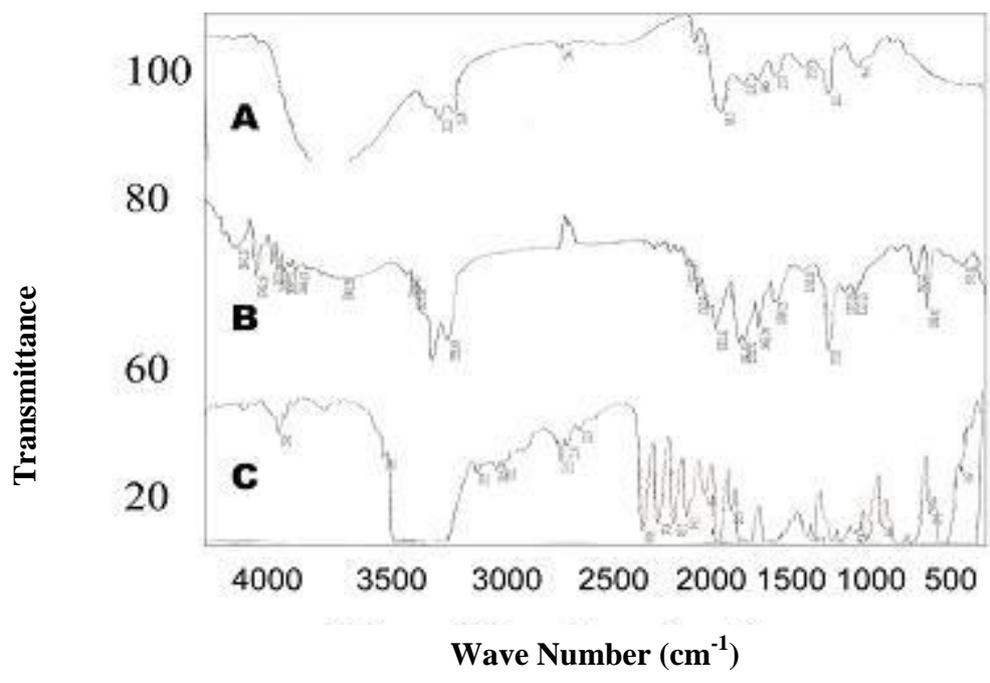
#### 4.1 Fourier transform infrared Spectrophotometric Analysis (FTIR).

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 IR spectra of A (TMU), B (TMU+PS) and C (PS). In the spectra of TMU, the broad band stretching from  $3600\text{ cm}^{-1}$  through  $3100\text{ cm}^{-1}$  is due to O-H of methylol urea,  $2922.89\text{ cm}^{-1}$  is due to C-H,  $1742.81\text{ cm}^{-1}$  is due to C=O of urea,  $1630.80\text{ cm}^{-1}$  is due to N-H bending motion of the amine,  $1460.29\text{ cm}^{-1}$  is due to  $-\text{CH}_2$  of methylene bridge and  $1252.29\text{ cm}^{-1}$  due to C-O-C of ether linkage (Osemeahon, 2011). The IR spectrum of PS showed absorption bands at  $3160.57\text{ cm}^{-1} - 2908.64\text{ cm}^{-1}$  corresponding to aromatic and aliphatic C-H stretching respectively. The peaks at  $1600.68\text{ cm}^{-1}$  and  $1448.90\text{ cm}^{-1}$  were assigned to C=C stretching of phenyl group. The C-H deformation vibration band of benzene ring hydrogen was seen at  $755.68\text{ cm}^{-1}$  and ring deformation was observed at  $698.13\text{ cm}^{-1}$  (Naghash *et al.*, 2007; Kaniappan and Latha, 2011). In the TMU+PS spectra, the strong O-H peak at  $3437.36\text{ cm}^{-1}$  in TMU is almost absent. This reduction may be ascribed to the consumption of OH groups during condensation reactions. The peak at  $3060.53\text{ cm}^{-1} - 2928.08\text{ cm}^{-1}$  were assigned to aromatic and aliphatic (alkanes) C-H stretching, proofing the disappearance of O-H peak in the copolymer. The C=C, C=O, N-H, C-O-C, C-H and  $-\text{CH}_2$  bands of TMU and PS all shifted to different frequency because of polycondensation, in the copolymer. This observation indicates a chemical reaction between trimethylol urea (TMU) and polystyrene (PS).

#### 4.2 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.



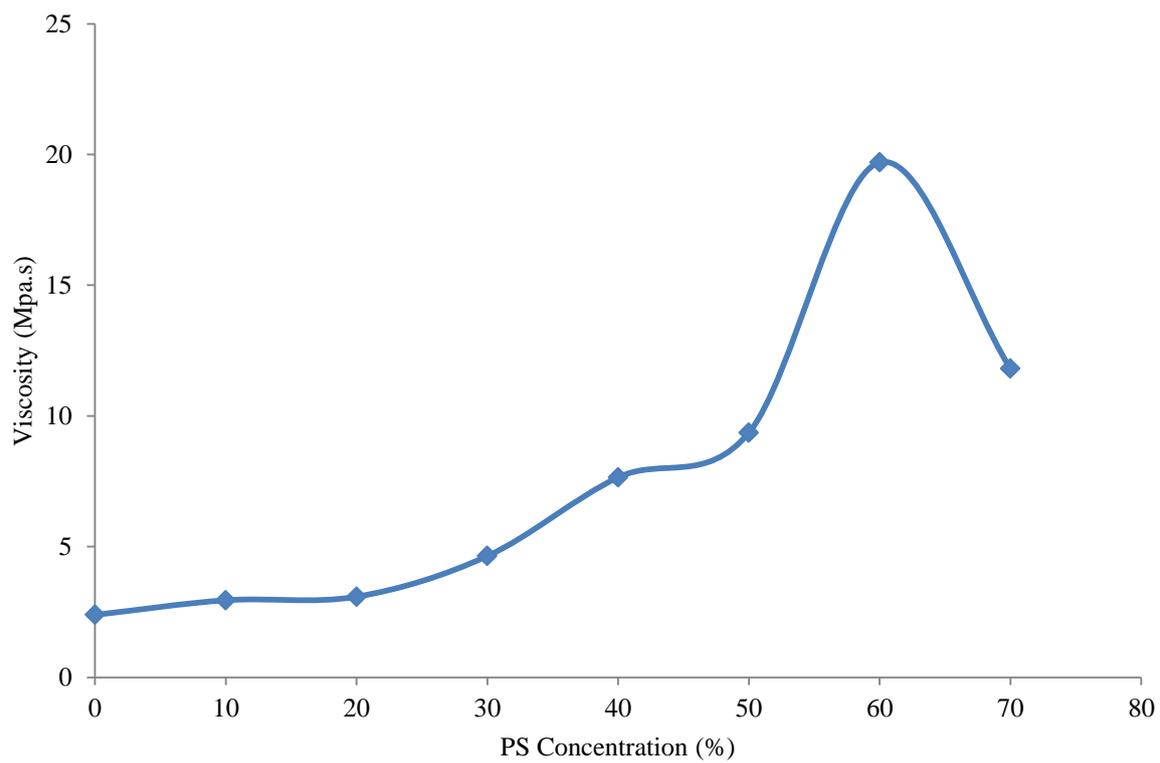
**Figure 1:** IR Spectra of (A) TMU, (B), TMU + PS and (C) PS)

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 (Stabik *et al.*, 2009). 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 arose as a result of variation in respective chainlength. As the PS loading increased, the molecular weight of the coploymer increased, this increase in molecular weight gave rise to increase in viscosity due to increase in cross-linking density. This explains the regime from 0-60% PS loading (Afzal *et al.*, 2013; Reddy *et al.*, 2012). After 60% PS loading, further inclusion of PS into the copolymer results in polymer dissociation, signaling overloading above the optimal level. Polymer dissociation result to fragmentation of long chain polymer into shorter chain oligomers with corresponding decrease in viscosity. This explains what happen at 70% loading of PS (Osemeahon and Barminas, 2007).



**Figure 2:** Effect of PS concentration on the viscosity of TMU/PS resin.

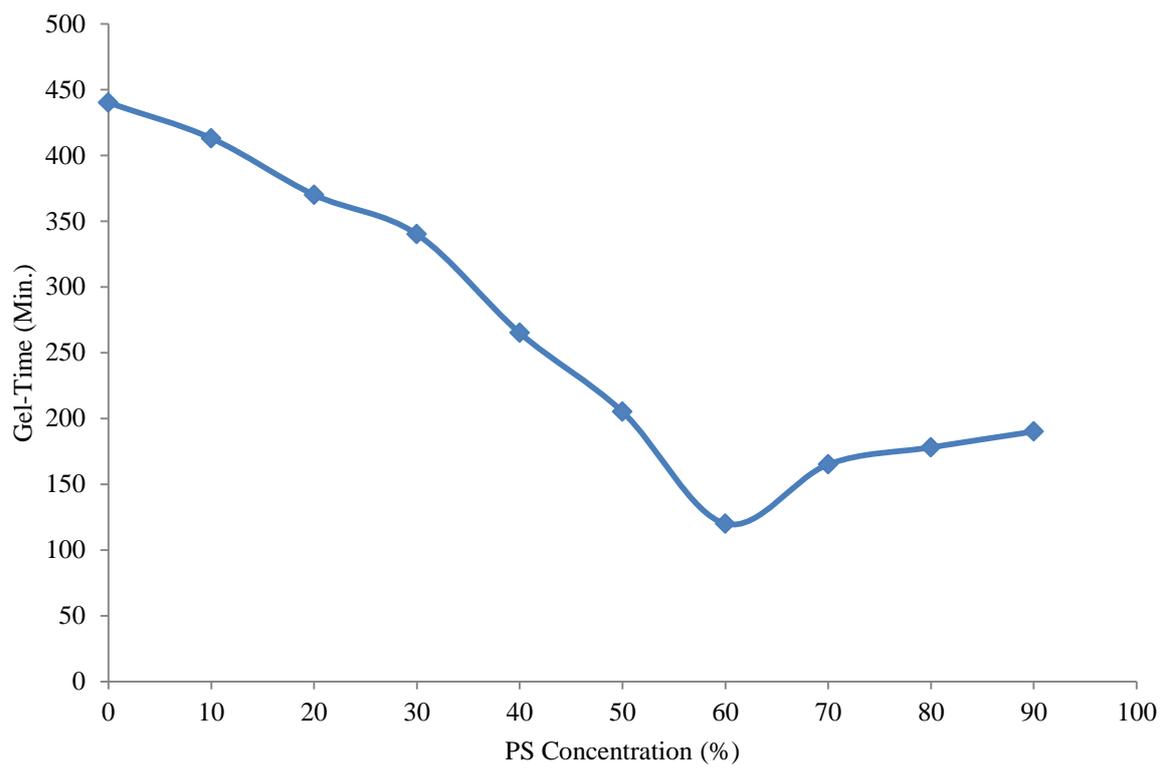
### 4.3 Effect of PS concentration on the gel-time of TMU/PS resin

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 (Suupere *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's 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 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 increased 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.



**Figure 3:** Effect of PS concentration on the gel time of TMU/PS resin.

#### **4.4 Effect of PS concentration on the density of TMU/PS resin**

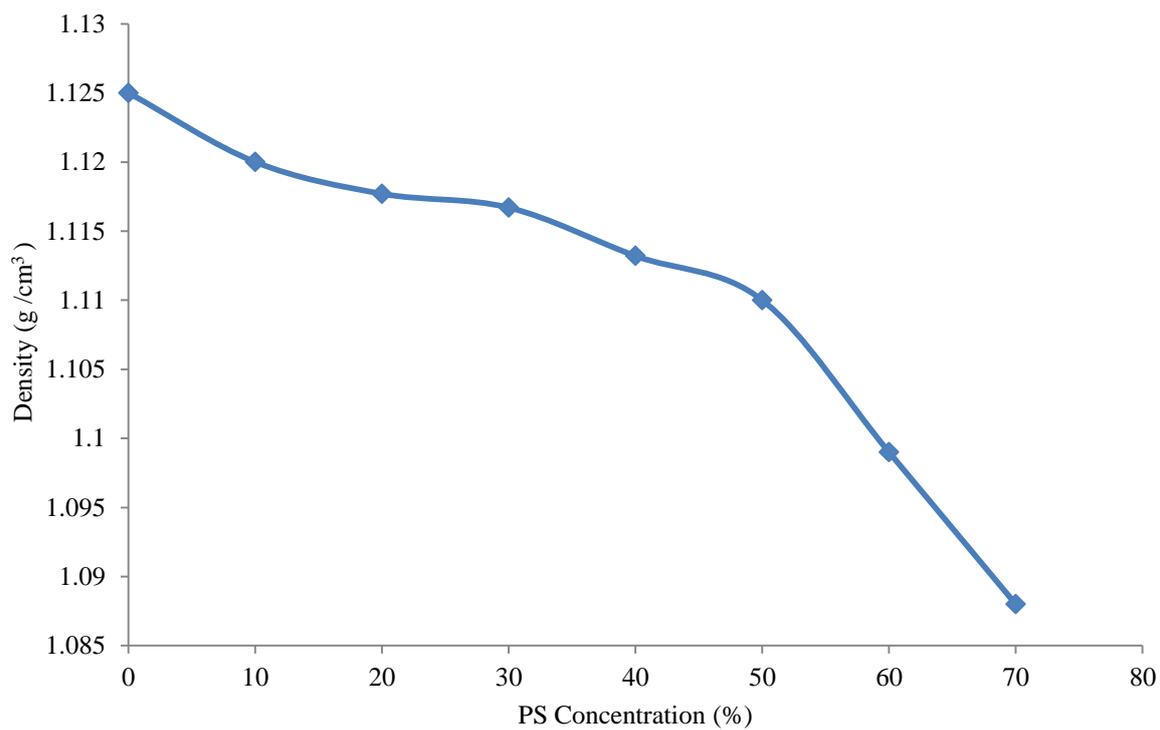
Density is a physical property of matter that expresses a ratio of mass to volume and is an important physical parameter in polymer engineering processes. Density depends on the atomic mass of an element or compound. Since different substances have different densities, density measurements are very useful 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 Rekuviene, 2011). The density of a paint binder in the coating industry has an important influence on factors such as pigment dispersion, brushability of paint, flow, leveling and sagging.

The gradual decrease observed in density with increase in PS concentration 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 with PS loading is due to increased in the 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).

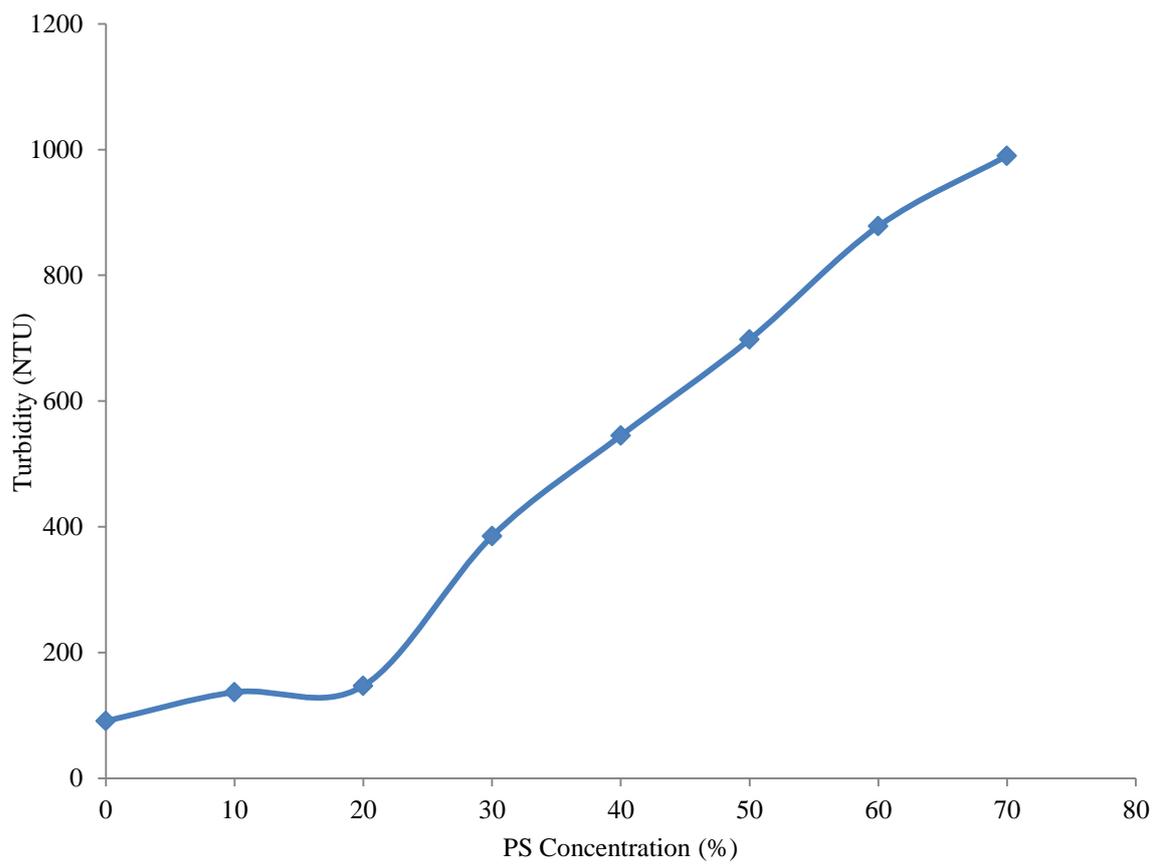
#### **4.5 Effect of PS concentration on the turbidity of TMU/PS resin**

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 is 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.

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 (Nodar, 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 as observed in Figure 5.



**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.

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

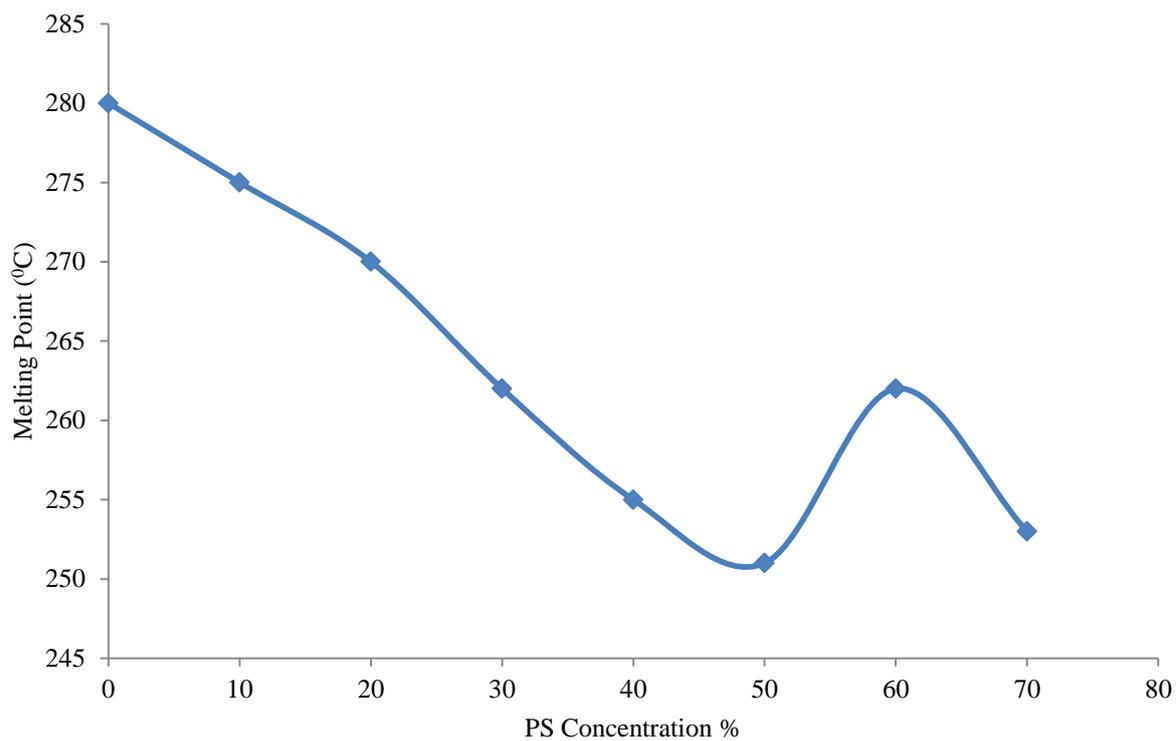
Thermal property, molecular weight, degree of cross linking and the level of rigidity of the polymer is related to its melting point. The melting points of the two polymers are very different which probably result from different contributing factors. In general, the melting point of a compound increases 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 brittleness. 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 0-50% concentration of PS in the blend. This can be explained on the basis of increase flexibility as a result of increase in the concentration of PS which gives rise to increase in molecular mobility. The increase in the melting point observed at 60% PS 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 (Osemeahon and Barminas, 2007).

#### **4.7 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 result from light penetration to the surface undergoing multiple reflections and refractions, 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 shininess. 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 that of the oil paint. The refractive index of the binder is a crucial factor in the ultimate gloss property of the the paint formulation.



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

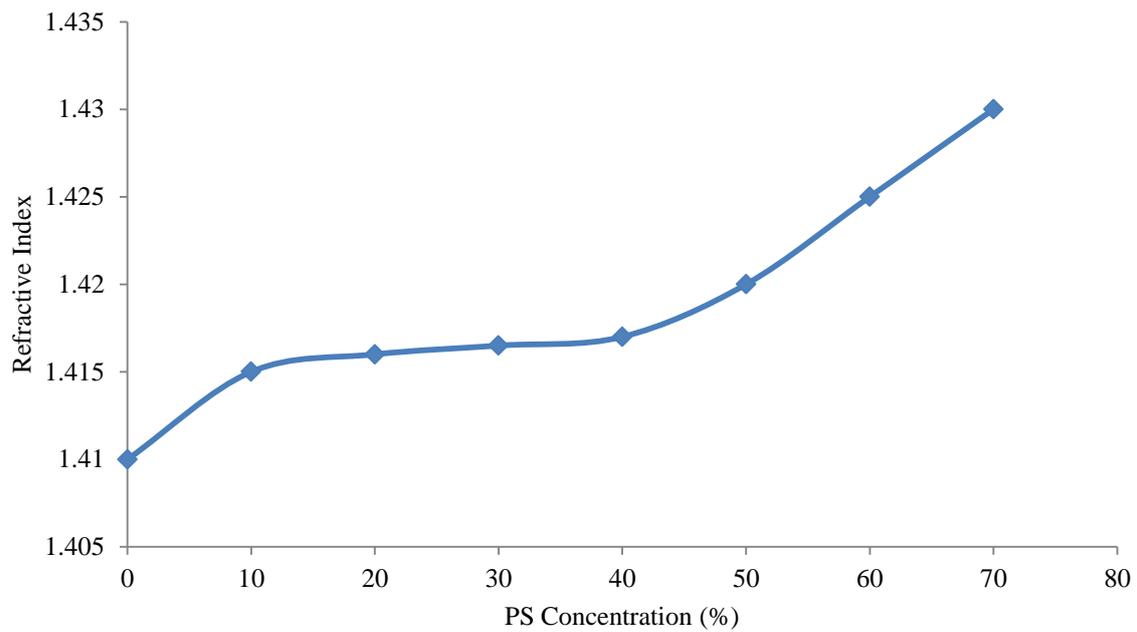
The effect of PS concentration on the refractive index of urea formaldehyde resin is shown in Figure 7. It is observed that, the refractive index increases with PS concentration. TMU has lower refractive index than PS. As the PS is added to TMU, the optical property of TMU as regard refractive index 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).

#### **4.8 Effect of PS concentration on the moisture uptake of TMU/PS resin**

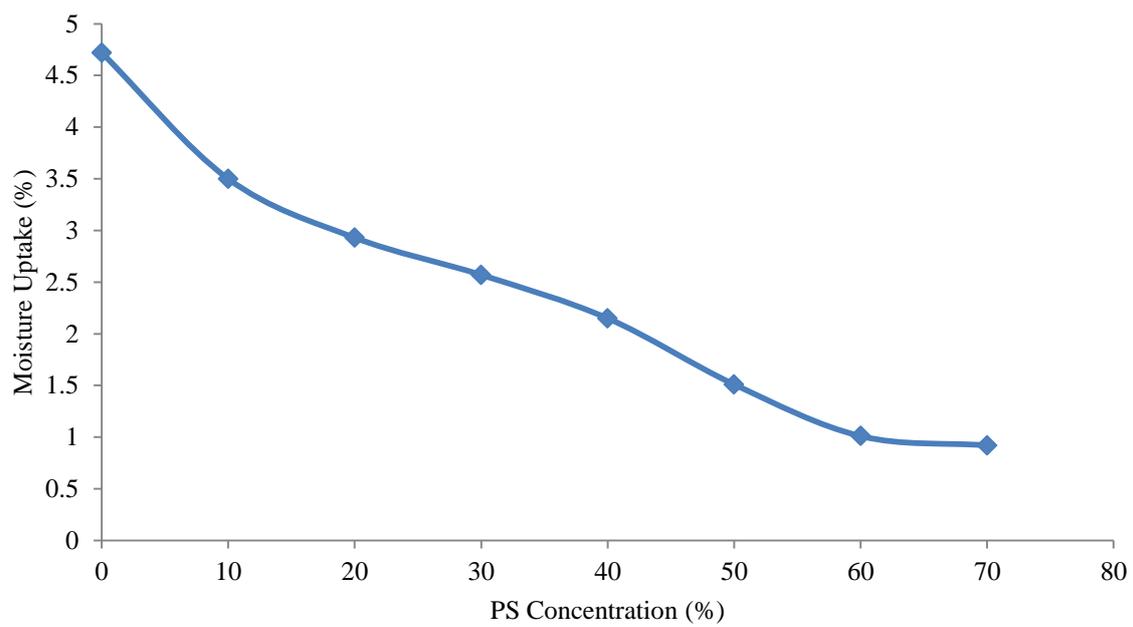
Polymeric binders play a major role in moisture transport properties of paint because it is one of the major constituent. Waterborne coatings are susceptible to durability issues pertaining poor water resistance. The functional groups on polymers or copolymer resins that are used can undergo hydrogen 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 hydro-phobicity of the binder.

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 coploymer 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 void 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.



**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.

#### **4.9 Effect of PS concentration on the formaldehyde emission of TMU/PS resin**

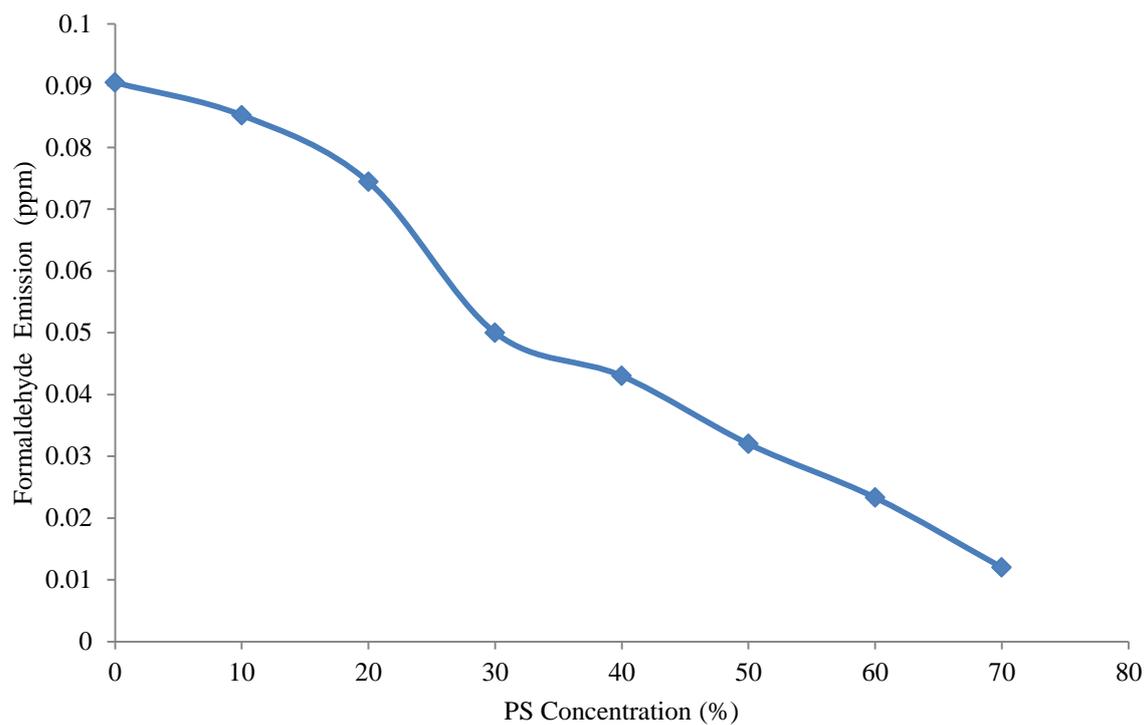
A serious drawback of urea formaldehyde resin is the emission of the hazardous formaldehyde during cure. The issue of formaldehyde exposure in homes is long-standing and has been studied overtime. It is therefore important to determine the formaldehyde emission from synthesized urea-formaldehyde resin before its application (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 Salthammer *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 (Abdullah and Park, 2010; Lee *et al.*, 2011; Ayoub *et al.*, 2013). The formaldehyde emission in this study has been reduced to 0.01 ppm, which is even lower than the world health organization (WHO) recommendation limit (0.08 ppm).

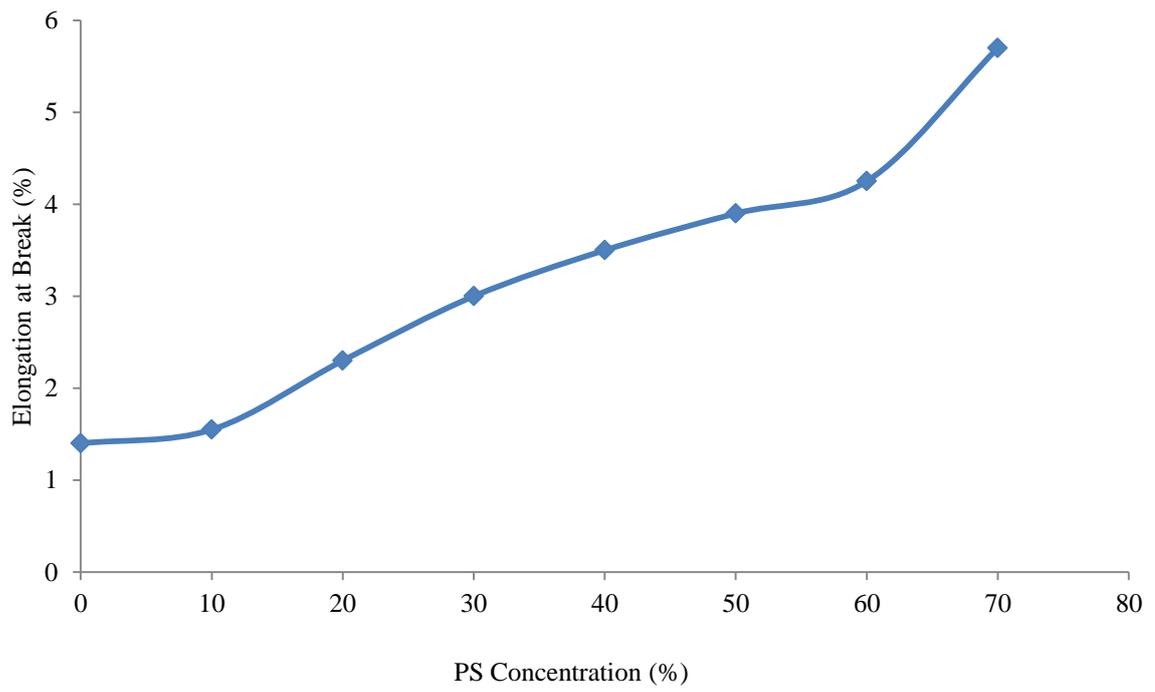
#### **4.10 Effect of PS concentration on the elongation at break of TMU/PS resin**

Elongation, the increase in length of the sample at the breaking point is a useful property for the characterization 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 given in Figure 10. The blend results showed increased 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.



**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.

#### 4.12 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. The binders in oil paint are water insoluble, while for emulsion is water soluble.

It can be seen that at 0-40% low PS loading, the copolymer is in a hydrophilic state, with hydrophilic TMU dominating (Table 2). 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 3 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 emission are also within the same range with other binders. The elongation at break is a little higher than other binders, indicating improved flexibility. This results place TMU/PS copolymer resin as a competitive binder among other traditional resins for the coating industry.

The comparison between TMU, TMU/PS resins and the acceptable level in the coating industry is shown in Table 4. A decrease was observed in density, formaldehyde emission, moisture uptake and melting point between the TMU and TMU/PS; this signals 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 seen from Table 4, 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 TM/PS are within the acceptable level. The melting point of both resins is higher than the required value; therefore further research is necessary to address this shortcoming.

**Table 2:** Effect of PS concentration on the solubility in water of TMU/PS resin

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

**Table 3:** Comparison of some physical properties of TMU/PS film with films from other Paint binders

Types of Resin	Physical Properties								Literature
	Gel Time (sec.)	Viscosity (mpa. s)	Refractive Index	Density (g/cm <sup>3</sup> )	Melting Point (oC)	Moisture Uptake (%)	Elongation at Break (%)	Formaldehyde Emission (ppm)	
TMU/PS	120	19.70	1.4250	1.0990	262	1.01	450	0.0233	This study
Polyvinyl acetate	ND	0.40	1.40	0.929	ND	ND	ND	ND	Habibu (2011)
Palmoil/Alkyd	ND	499	ND	1.278	ND	ND	ND	ND	Blaise et al (2012)
Commercial UF	54.2	451	ND	ND	ND	2	ND	ND	Suurpere et al (2006)
Polyvinyl Butyral	ND	9-16	1.485	1.03	ND	0.3	110	ND	Solutia (2008)
Acrylic/Methacrylic ester	ND	2500	ND	ND	ND	ND	ND	ND	Dumitru (2011)
Innovative UF	ND	365	ND	ND	ND	0.25	ND	0.07	Zorba et al (2008)
MU/NR	ND	248	1.3411	0.641	255	1.341	350.43	0.058	Osemeahon et al (2009)
UF / PE	190	32.60	1.432	1.3362	130	0.0080	250.0	0.0142	Osemeahon and Archibong (2011)
Alkyd from cater oil resin	ND	4	1.474	ND	ND	ND	ND	ND	Hlaing and Oo (2008)

**Table 4:** Comparison of some physical properties of TMU and TMU/PS resins.

	TMU	TMU/PS	Acceptable Level in the coating industry (Osemeahon et al., 2013).
Density (g/cm <sup>3</sup> )	1.125± 0.001	1.099 ± 0.002	1.07 (min.)
Refractive index	1.4100± 0.11	1.4250± 0.1010	1.4000 (min.)
Formaldehyde emission (ppm)	0.0905± 0.10	0.0 233± 0.0011	0.1 (max.)
Moisture uptake (%)	4.72± 0.1000	1.01 ± 0.0010	3.10 (max.)
Viscosity (mpa.s)	2.39 ±0.0300	19.70 ± 0.120	3.11- 38.00
Elongation at break (%)	116± 0.1011	425.00 ± 0.01	125(min.)
Melting point ( °C)	280 ± 0.150	262 ± 0.100	200(max.)

#### **4.13 Some physical properties of paints formulated from TMU and TMU/PS binders**

Some physical properties of TMU and TMU/PS paints are shown in Table 5. As seen from the Table, some properties such as pH, viscosity, flexibility and opacity of both TMU and TMU/PS fall within the the acceptable ranges for paints (SON, 1990). TMU/PS paint exhibited good adhesion, tackiness and hardness properties, but the paint from pure TMU showed poor adhesion, hardness and tack properties. This behaviour of TMU paint can be due to low molecular weight and hence low crosslink density of the pure TMU binder (Purwantiningsih and Mas ud, 2012 ; Xu *et al.*, 2009).

Resistance to blistering of the different paints formulated are also provided in Table 5. The paint from the TMU/PS binder passed resistance to blistering test while those formulated with the pure TMU binder failed the test. These results indicate that PS segment has been cross linked into the TMU/PS copolymer thereby impacting hydrophobic character. The higher degrees of cross-linking give rise to less free volume and solvent molecules hardly pass through the crosslinked network (Naghash *et al.*, 2007; Hasmukh and Sumeet, 2010; Motawie *et al.*, 2010). This implies that the paint can perform well when exposed to environmental conditions such as rain and sun. The pure TMU paint failed water resistance test as a result of the inherent property of urea formaldehyde resin in addition to low molecular weight of the TMU binder used in the paint formulation (Ayoub *et al.*, 2013; Zorba *et al.*, 2008).

The drying time of TMU/PS paint met specification, while that of TMU paint is outside the specified range (SON, 1990). The long drying time displayed by TMU paint is attributed to the low molecular weight and hence low crosslink density of the TMU binder while the TMU/PS has high crosslinked density due to increased in molecular weight which enhanced drying (Onukwli and Igbokwe, 2008). The gloss results shows that both TMU and TMU/PS have gloss value within the range specified, but TMU/PS has a higher gloss due to the higher refractive index of PS incorporated into the blend ( Jain, 2008). Stability in storage is an important factor for coating system. Amino resin when used as a paint binder can undergo self-condensation making the system too viscous and gel like for coating application. All the paint formulated passed the standard stability test because of the addition of butanol (stabilizer) during formulation (Table 5). The TMU/PS paint has better resistance to scratching than TMU paint. Resistance of coated material against scratching is a function of surface hardness. TMU/PS paint has better pencil hardness because the more the network formed in the polymer matrix, the higher the cross-linking density and the harder the resulting coating film (Kaygin and Akgun, 2009; Purohit *et al.*, 2013).

**Table 5:** Some physical properties of paint formulated from TMU/PS Binders

Parameter	TMU	TMU/PS paint	SON Standard
pH	7.1	7.3	7-8.5
Viscosity (poise)	6.5	13	6-15
Flexibility	P	P	P
Opacity	P	P	P
Adhesion	F	P	P
Hardness test	F	P	P
Tackiness	F	P	P
Resistance to blistering	F	P	P
Drying time(min)			
Touch	168	10	20
Hard	700	35	120
Storage Stability (4 month)	P	P	P
85 <sup>0</sup> Gloss	29.0	32.0	16-50
Pencil Hardness	2B	2H	-

P and F means Pass and fail SON test respectively.

#### **4.14 Chemical resistance**

The ability of a paint film to resist chemical attack is one of the desirable qualities of a good coating film. Table 6 shows the resistance of the TMU/PS coating system on exposure to a number of chemicals. From the results, both TMU and TMU/PS are unaffected by the salt medium. TMU/PS films are also unaffected by both the acid and alkali solutions, while surface defect were observed in the case of TMU films in alkali and acid solutions. TMU/PS has better chemical resistance due to high crosslinked density of network which decreases their exposure to environment (Motawie *et al.*, 2010).

**Table 6:** Chemical resistance of TMU and TMU/PS paint films

Samples	Media		
	0.1M NaCl	0.1 M HCl	0.1 M NaOH
TMU	a	b	c
TMU/PS	a	a	a

a= No effect      b= Cracking      c= Blistering

## **CHAPTER FIVE**

### **SUMMARY, CONCLUSION AND RECOMMENDATION**

#### **5.1 Summary**

In this work, TMU was synthesized and copolymerized with PS waste to form a copolymer binder for emulsion paint formulation. The resulting copolymer addressed the problem of urea formaldehyde resin which includes brittleness, low water resistance and formaldehyde emission. The copolymer binder is comparable with other binders used for paint with values within the acceptable level in the coating industry. The emulsion paint formulated from both TMU and TMU/PS passed pH, viscosity, flexibility, opacity and storage stability test. Paint from pure TMU failed adhesion, hardness, tackiness, resistance to blistering and drying time test while the TMU/PS paint passed those entire standard tests. Both paints have gloss values within the specified range and TMU/PS has higher pencil hardness than TMU. This work may introduce a new binder for the coating industry.

#### **5.2 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. Thus, this class of resin may introduce a novel paint binder in the coating industry.

Polystyrene which leads to polymer wastes is recycle and utilised for coating application. The emulsion paint formulated using TMU/PS binder exhibit good consistency, it was smooth and uniform. The paint showed excellent gloss, adhesion and flexibility. The pH, viscosity, opacity and drying time of the TMU/PS paint conform to SON standard. It showed good pencil hardness, no cracks and good resistance to acidic, alkaline and salt medium compared to the pure TMU paint.

#### **5.3 Recommendation**

For the full development of the TMU/PS binder for emulsion paint formulation and other products, this study recommends that:

- The effect of viscosity of urea formaldehyde on the physical properties of the blends should be investigated.
- The PS binder should be developed from polystyrene variety different from the one used in this study.

#### **5.4 Contribution to knowledge**

Emulsion paints can be formulated from TMU/PS as binder. This study offers the following benefit and opportunities:

- A. The study has answered the quest for indigenous technology and self reliant for the economic emancipation of our country, also lowering cost effect.
- B. Most of conventional paint binders used today in our coating industry are imported. This research is providing an economic future for this country.
- C. This study provides a novel class of 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.
- D. This study provides a simple economic route for the recycling of waste polystyrene and hence an important practice for sustainable recycling. Recycling of polystyrene does not only serve as a source of raw material to the coating industries, it also contributes to the conservation of raw petrochemical products and energy.
- E. This study also shows the role of latex in coating formulation as a key in bringing the desired performance in order to meet VOCs regulation by reducing the dependence on oil based by formulating emulsion paint.
- F. The use of polystyrene waste for coating will open new market of recycled polymer and a potential solution to the problem of solid waste management.

## REFERENCES

- Abdullah, Z.A. and Park, B.D. (2010). Influence of acrylamide copolymerization of urea-formaldehyde resin adhesives to their chemical structure and performance. *J. Appl. Polym.Sci.*, 117 (6): 3181-3186.
- Achi, S.S. (2003). Basic principles of coating technology. Shemang Graphics, Zaria Nigeria :1-2.
- Adetuyi, O.A., Ajekwene, K.K. and Jabar, J.M. (2012). Production and performance evaluation of insecticide base coatings. *J. Chem.Soc. Nigeria*, 37 (2):20-26.
- Afsoon, F., Laleh, R. and Faramarz, A. (2011). DSC analysis of thermosetting polyimide based on three bismaleimide resin eutectic mixtures. *Iranian Polymer J.*, 20 (2): 161-171.
- Afzal, A., Siddiqi, M.H., Saeed, S. and Ahmed, Z. (2013). Explorin resin viscosity effect in solventless processing of nano-SiO<sub>2</sub>/epoxyl polymer hybrids. *RSC Adv.* 2013, 3, 3885-3892.
- Ahmed, H., Bahaa, H., Majeed, A., Nahida, A. and Athraa, S. (2012). Synthesis and study electrical properties of (PS-CAO) composite. *American j. Scientific Research*, 75: 5-8.
- Ahmed, S., Ashraf, S., Kumar, S., Alam, K. and Hasnat, A. (2005). High performance paint from a sustainable resource. *Indian J. Chemical Tech.*, 12: 193-197.
- Akpabio, U.D. (2010). Retention of urea formaldehyde resin finish on cellulosic fabric and its effect on water absorbent capacity of the treated fabric. *Int. J. of Advanced Sci. & tech. Research*, 2 (5): 31-39.
- Akzonobel, (2008). *Bermocoll in latex paint*; Tomorrow's answers today. ([www.akzonobel.com.cs](http://www.akzonobel.com.cs)), pp.1-20.
- Al-bermany, J.E.D. (2011). Study some physical properties of post-irradiation for polystyrene dissolved in Toluene. *American J. Sci. Research.* 29: 130-141.
- American Chemistry Council (2010). Polystyrene facts. Retrieve from <http://www.americanchemistry.com/s.-plastic/sec-pfpg.asp>
- AOAC, (2000). Official Method of Analysis international ( Horwitz, W, Editor) Gaithersburg Mongland,USA, 1 (41) : 1-68.
- Atiq, N., Ahmed, S., Ali, M.I., Andleeb, S., Ahmed, B. and Roson, G. (2010). Isolation and Identification of PS biodegrading bacteria from soil. *African J. microbiology Research*, 4 (14):1537-1541.
- Ayoub, S., Taghi, T., Abolghasem, K. and Ahmadreza, S. (2013). Improving some of applied properties of oriented strand board (OSB) made from under-utilized low quality paulownia (*Paulownia fortunei*) wood employing nano-SiO<sub>2</sub>. *Industrial Crops and Products*, 42 (2013): 1-9.

- Babayemi, J.O. and Dauda, K.T. (2009). Evaluation of SWG, categories and disposal options in developing countries: a case study of Nigeria. *J. Appl. Sci. Environ. Manage.*, 13 (3) : 83-88.
- Bharath, N.K. and Swamy, P.R. (2009). Adhesive tensile and moisture absorption characteristics of natural fibers' reinforced urea formaldehyde composites. *Int. J. of recent Trends in Engineering*, 1 (5): 60-62.
- Bhattacharya, A., James, W. and Rawlins, P.R. (2009). Poly grafting and crosslinking. Published by John Wiley & Sons, Inc., Hoboken, New Jersey, pp.276-281.
- Bindu, C.S. and Beena, K.S. (2010). Waste plastic as a stabilizing additive in stone mastic asphalt; *Inter. J. of Engr'g and Tech.*, 2 (6): 379-387.
- Blaise, V.I., Ogunniya, D.S., Ongoka, P.R., Moussounga, J.E. and Ouamba, J.M. (2012). Physio-chemical properties of alkyd resin and palm oil. *Malaysian Polymer Journal*, 7 (2): 42-45.
- Bonifant, B. (1994). Competitive implications of environmental regulation in the paint and coating industry. *Paint and Coating Industry*, pp 196-197.
- Borghei, M., Abdolreza, K., Sharhrzad, K., Abdolrasoul, O. and Amir, H.J. (2010). Microbial biodegradable potato starch base low density polyethylene; *African j. Biotechnology*, 9 (26): 4075-4080.
- Buhne, S., Axel, W. and Anne, L. (2009). Influence of rheology in water borne paint systems. Technical paper. *European Coating J.*, Sept issues: 28-33.
- Cakic, M.S., Ivana, S.R., Vladislav, M.J., Radmilaz, R., Olivera, Z.I and Jao, K.B. (2012). Investigation of the curing kinetics of alkyd-melamine-epoxy resin system. *Progress in Organic Coatings*, 73(4): 415-424.
- Cakir, M., Kartal, I., Demirer, H. and Samur, R. (2012). Effect of water absorption on the wear behaviour of sol-gel processed epoxy/silica hybrids. *Scientific Research and Essays*, 7 (7): 805-812.
- CDC, FEMA, USEPA. (2008). Environmental Health; Formaldehyde exposure in homes: A Reference for State Officials to Use in Decision-making. *Chemistry World*, March Issue.
- Conner, H.A. (1996). Urea-formaldehyde adhesive resins in Encyclopedia of Adhesive resins in Encyclopedia of Polymeric Material.ed ( Joseph. Salamone), 2: 8495- 8500.
- Dara, S.S., Mishra, D.D. and Chand, S. (2012). A Textbook of Environmental Chemistry and Pollution Control. Ram Nagar, New Delhi, Revised Edition, pp. 446-447.
- Derkyi, N.S., Darkwa, N.A. and Yartey, J.G. (2008). Effect of cassava flour as urea formaldehyde adhesive extender on the bonding strength of plywood. *Ghana Journal of Forestry*, 23&24: 25-34

- Desai, D.S., Patel, V.J. and Sinha, K.V. (2003). Polyurethane adhesive system from biomaterial-based polyol for bonding wood. *Int. J. of Adhesion and Adhesives*, 23 (2003):393-399.
- Dhokhikah, Y. and Trihadiningrum, Y. (2012). Solid waste management in Asian Developing countries: challenges and opportunities. *J. Appl. Environ. Biol.Sci.* 2 (7): 329-335.
- Dow microbial coating. (2012). New antimicrobial meets performance and low-VOC requirement; *Paint and Coating Industry Magazine*, Feb issues.
- Ekonu, A.M. (2011). Additives effects of the bonding strength of polyisoprene Rubber (Natural rubber). *Oasis J. Research & Dev.*, 1 ( 2 ) : 79-85.
- Emile, G. (2003). Moisture transfer properties of coated gypsum. Eindhoven University Press, Eindhoven, Netherlands, 2-6.
- Fabian, B., Herrenbruk, S. and Hoffee, A. (2004). The environmental and societal value of extruded polystyrene formulation (*Earth Tech Forum 200*), April issues: 6-10.
- Faucheu, J., Chazeau, L., Gauthier, C., Cavaillé, J., Goikoetxea, M., Minari, R. and Asua J.M. (2009). Latex imaging by Environmental STEM: Application to the study of the surfactant outcome in hybrid alkyd/acrylate systems. *Langmuir* 25, 17 (2009) 10251-1025.
- Ferra, M., Joao, M., Martin, O., Adelio, M.M., Mario, R.N., Luisa, H., Carvalho, F. and Magalhaes, D. (2011). Evaluation of urea-formaldehyde adhesive performance by recently developed mechanical tests. *Inter.J. Adhesion & Adhesive*, 31:127-134.
- Gonzalez, G.M., Cabanelas, J.C. and Baselga, J. (2012). Application of FTIR on epoxy resins- Identification, monitoring the curing process, phase separation and water uptake. *Infrared Spectroscopy-Material Science, Engineering and Technology*, 261-283.
- Gopalakrishnan, S., Nevaditha, N. T. and Mythili, C.V. (2012). Synthesis and characterization of bifunctional monomers for high performance polymers from renewable resource. *Int. J. of ChemTech Research*, 4 (1): 48-54.
- Gopalan, R., Venkappyya, S. and Nagarajan, S. (2000). Engineering Chemistry (Rev. ed.) Vikas publishing house, PVT : 7.10-7.19.
- Greenspec. (2012). Paint: Materials; manufacture use and impact. Data protection Act (DPA) registered.
- Habibu, U. (2011). Production of trowel paints using polyvinyl synthesis from vinyl acetate monomer as binder. *Leonardo J. Sci.*, 19: 49-56.
- Hall, P. (2010). (Paint and weathering) paint types. *The manual for scale modellers guide* Jan : 1-4.

- Hasirci, V., Yilgor, P., Endogan, T., Eke, G. and Hasirci, N. (2011). Polymer Fundamentals; polymer synthesis. *Comprehensive Biomaterials*, 1: 349-371.
- Hasmukh, S.P. and Sumeet, J.P. (2010). Novel surface coating system based on maleated shellac. *E-Journal of chemistry*, 7(S1): S55-S60.
- Hemant, K., Tripathi, S., Mistry, S. and Bajpai G, 2009. Synthesis, characterization and application of coatings based on epoxy novalac and liquid rubber blend. *E- journal of Chemistry*, 6. (4) 1253-1259.
- Herbarth, O. and Matysik, S. (2010). Decreasing concentrations of volatile organic compounds (VOC) emitted following home renovations. *Indoor Air*, 20:141-145.
- Herold, M.P. and Klaus, S.R. (2012). Nano particles additives accelerates drying time of waterborne coating. *PCI Magazine*, Aug issues: 2-6.
- Hlaing, N.N. and Oo M.M. (2008). Manufacture of alkyf resin from castor oil. *World Academy of Science , Eng.& Tech.*, 24,155-161.
- Holtz, R.D., Bruna, A.L., Antonia, G., Souza, F., Marcelo, B. and Oswaldo, L.A. (2012). Nanostructured silver vanadate as a promising antibacterial additive to water-based paints. *Nano medicine; Nano technology; Biology and Medicine*, 8(6) : 935-940.
- Houlton, S. (2012). Painting the town green: royal society of chemistry, *Chemistry World*. March issues.
- Hussain, A.I and Nasr, H.E. (2010). The role of carboxylic acid on the characterization and evaluation seed emulsion of styrene/butyl acrylate copolymers lattices as paint. *Nature and Science*, 8 (8): 94-103.
- Hwang, Y., Sangmook, L., Youngjae, Y., Kwangho, J. and Lee, W. (2012). Reactive extrusion of polypropylene/polystyrene blends with Supercritical carbon dioxide. *Macromolecular Research*, 20 (6): 559-567.
- Ibekwe, N.N. and Ibemesi, J.A. (2012). Preliminary investigation in the use of melon seed oil fatty acids as paint drier. *J. Chem. Soc. Nigeria*, 37 (2): 1-3.
- Igwe, O.I. and Ezeamaku, U.L. (2010). The Use of Some Local Clays in Alkyd Paint Formulations. *Malaysian Polymer Journal*, 5(1): 81-94.
- Isiya, A.D. (2012). *Waster Management: (A look into Biodegradable and non Biodegradable Materials)*. Proceeding of International Conferences on Science and Sustainable Development, 4 (3): 35-40.
- Ivana, G., Olivera, N., Diporovic-momcilovic, M. and Popovic, M. (2010). Molar-mass distribution of urea-formaldehyde resins of different degrees of polymerisation by MALDI-TOF mass spectrometry. *J.Serb. Chem.Soc.*, 75 (5): 689-701.
- Jain, V.V. (2008). Evaluation of second generation indirect composite resins. ( Master's thesis, Indiana University). Unpublished.

- Jesmy, J. Jyotishkumar, P. Sajeev, M.G. and Sabu, T. (editors Leib A, Grigoryeva O) (2011). Recycling of polymer blends. *Recent Dev. in Polymer Recycling*, 2011:187-214.
- Joel, R.F. (2010). *Polymer Science and Technology*, 2<sup>nd</sup> Edition, PH Learning private limited. New –Delhi pp.10.
- Joseph, K.V., Springate, R. and Brezinski, D. (2012). Additive hand book, *Paint and Coating Industry*, June Issue, pp.4-12.
- Kaniappan, K. and Latha, S. (2011). Certain Investigations on the formulation and characterization of polystyrene/poly(methylmethacrylate) blends. *Inter. J. Chemtech Research*, 3 (2): 708-717.
- Karakas, F., Pyrgiotakis, G., Celik, M.S. and Brij, M.M. (2011). Na-Bentonite and Mgo mixture as a thickening agent for waterbased paints. *Kona Powder & Particle J.*, 29:96-106.
- Kaygin, B. and Akgun, E. (2009). A nano-technological product: An innovative varnish type for wooden surfaces. *Scientific Research and Essay*, 4 (1): 001-007.
- Kazys, R. and Rekuviene R. (2011). Viscosity and density measurement methods for polymer melts. *Ultragarsas "Ultrasound"* 66 (4): 20-25.
- Kopeliovich. (2012). Composition of paints ; *Sub.Tech. Forum Article*, July Issue.
- Kumthekar, V. and Kolekar, S. (2011). Attributes of the latex emulsion processing and its role in morphology and performance in paint. *Progress in Organic Coatings*, 72 (2011) : 380-386.
- Lee, J., Jeon, J. and Kim, S (2011). Green adhesives using tannin and Cashew nut shell liquid for environment-friendly Furniture Materials. *Journal of the Korea Furniture Society*, 22 ( 3 ): 219-229.
- Lin, K.F. (2005). *Paints, Varnishes and Related Products*. Bailey's Industrial Oil and Fat Products, Sixth Edition, Six Volume Set (Edited by Fereidoon Shahidi) John Wiley & Sons, Inc.
- Lowel, H.J., Kroschwitz, B. and Mark, H.F. (1990). Coating, In; *Encyclopedia of Polymer Science and Engineering*, pp.615.
- Magizvo, R.V. (2012). The incidence of plastic waste and their effect in Alice, SA. *Plastic W. Management*, 1(2): 49-53.
- Manahan, S.E. (2006). Green chemistry and the ten commandments of sustainability. ChemChar Research, Inc Publishers Columbia, Missouri U.S.A. 2<sup>nd</sup> Edition, pp.2-12.

- Mathiazhagan, A. and Joseph, R. (2011). Nanotechnology-A New Prospective in Organic Coating–Review. *International Journal of Chemical Engineering and Applications*, 2(4):225-237.
- Matthias, L. and Paul, F. (2012). Voc-free alternative for green coatings; The future of emulsion polymerisation. *Paint Coating Industry*. pp 1-4.
- Mavani, I.S., Mehta, M.N. and Parsania, H.P. (2007). Synthesis and physico-chemical study of polyester resin of 1,1- bis (3- methyl-4-hydroxy phenyl). cyclohexane and rinioleic acid and its polyurethanes with polyethylene glycol. *J. Sci. & Ind. Res.*, 66: 377-384.
- Mcglennon, R.J. CO. Inc. (2012). *Maclac Guide to Paint: VOC definitions and calculations*. pp 1-2.
- Menkiti, M.C. and Onukwuli, O.D. (2011). Utilization potentials of rubber seed oil for the production of alkyd resin using variable base oil lengths. *New York Sci. Journal*, 4 (2): 51-59.
- Motawie, A.M., Sherif, M.H., Badr, M.M., Amer, A.A. and Shehat, A.S. (2010). Synthesis and characterization of waterborne epoxy resins for coating application. *Austr.J of Basic and Appl. Sci.*, 4(6):1376-1382.
- Muriel, R., Sebastian, W. and Manfred, D. (2011).Recent Developments in Halogen Free Flame Retardants for Epoxy Resins for Electrical and Electronic Applications. *Materials*, 3: 4300-4327.
- Myint, S., Zakaria, M.S.B. and Ahmed, K.R. (2010). Paint based on waste expanded polystyrene. *Progress in Rubber, Plastic and Recycling Technology*
- Naghash, J.H., Karimzadeh, A., Momeni, R.A., Massah, R.A. and Alian H (2007). Preparation and properties of triethoxyvinylsilane-modified styrene-butyl acrylate emulsion copolymers. *Turk. J. Chem.*, 31(2007):257-269.
- Nawaz, M., Rehman, W. and Baloch, M.K. (2010). Investigating the compatibility of polymers in common solvent. *J. of the Chilean Chemical Society*, 55 (1): 90-93.
- Nkwachukwu, O.I, Chidi, N.I. and Charles, K.O. (2010). Issues of Road disposed habit of municipal solid waste, environmental impacts and implementation of sound management practices in developing countries”Nigeria”. *Int. J. Environs. Sci and Deve.*, 1 (5): 2010-0264.
- Nodar, A. (2009) Preparation and characterization of crosslinked polymeric nano particles for enhanced oil recovery applications. University of Oslo.
- Nouailhas, H., Aouf, C., Guerneve, C., Caillol, S., Boutevin, B. and Fulcrand, H. (2011). Synthesis and properties of biobased resin.Part 1. Glycidation of flavonoids by epichlorohydrin. *J. Polym .Sci. Part A: Polym. Chem.*, 49 (2011): 2261-2270.
- Ogwueleka, T. (2009). Municipal solid waste characteristics and management in Nigeria. *Iran journal on Environmental Health Science Eng.* 6 (3): 173-180.

- Oluranti, S.A., Emmauel, R.S., Adesola, T.A. and Olusesan, F.B. (2011). Rheological properties of polymers: structure and morphology of molten polymer blends. *Materials Sciences and Applications*, 2:30-41.
- Onukwli, D.O. and Igbokwe, K.P. (2008). Production and characterization of castor oil-modified alkyd resins, *J. Eng. Appl. Sci.*, 3 (2): 161-165.
- Opara, C.C., Sokore, B. and Ugwo, P.N. (2013). Production and study of factors affecting the flexibility of polyester paint using local materials. *Int .J. of Eng. & Sci. Research*, 3 (3):2582-2588.
- Osemeahon, S.A. (2011). Copolymerization of methylol urea with ethylol urea resin for emulsion paint formulation. *Afri. J. Pure and Applied Chemistry*, 5 (7): 204-211.
- Osemeahon, S.A. and Archibong, C.A. (2011). Development of urea formaldehyde and polyethylene waste as a copolymer binder for emulsion paint formulation. *J.of Toxi. & Environm. Health Sciences*, 3 (4): 101-108.
- Osemeahon, S.A. and Barminas J.T. (2007). Study of a composite from reactive blending of methylol urea resin with natural rubber. *Afri. J. Biotech.*, 6 (6) : 810-817.
- Osemeahon, S.A., Ilesamin, J.O.Y., Aliyu, B.A. and Mishelia, I.E. (2011). Copolymerization of methylol urea with vegetable oil; Effect of using different types of vegetable oil on some physical properties of the copolymer composite. *Int. J. Phy. Sci.*, 6 (15): 3629-3635.
- Osemeahon, S.A., Nkafamiya, I.I. and Fai, F.Y. (2009). Application of methylol urea/natural rubber copolymer composite for emulsion paint formulation. *Int. J. Bio. Chem. Sci.*, 3 (6):1491-1498.
- Osemeahon, S.A., Nkafamiya, I.I., Milam, C. and Modibbo, U.U. (2010). Utilization of amino resin for emulsion paint formulation: Effect of urea formaldehyde viscosity on urea formaldehyde and Soybean oil copolymer composite. *Afri. J.Pure and Applied Chem.* 4 (1): 001-006.
- Ossi, I.C.D. (2012). Rice Husk ash as a new flattening extender in red oxide primer. *J. Chem. Soc. Nig*, 37 (2): 59-64.
- Park, B-D., Jeong, H-W. and Lee, S-M. (2010). Morphology and chemical elements detection of cured urea formaldehyde resins. *J. Appl. Polym. Sci.*, 120 (3): 1475-1482.
- Parker, S.A. (2009). Green paint technology for painting contractors ; *Ezine articles*.
- Paula, Y. (2011). Organic chemistry, 6<sup>th</sup> edition, pearson education. Inc. Publishing as Prentice Hall. pp.1178-1180.
- Pizzi, A., Zhoa, C., Kamo BGun, C. and Heinrich, H. (2002). TTT and CHT Curing Diagrams of Water Borne Polycondensate Resins on Lignocelluloses Substrate. *J. Appl.Polym. Sci.*, 80: 2128-2139.

- Purohit, J., Chawada, G., Choubisa, B., Patel, M. and Dholakiya, B. (2012). Polyester polyol derived from waste poly (ethylene terephthalate) for coating application on mild steel. *Chemical Sci. J.*, 2012: Pg. 1-7.
- Purwantiningsih, H.S. and Mas'ud, Z.A. (2012). Synthesis and Application of Jatropha Oil based Polyurethane as Paint Coating Material. *Makara Journal of Science*, 16 (2): 134-140.
- Rahmat, A.R., Rahman, W.A., Sin, L.T. and Yussuf, A.A. (2009). Approaches to improve compatibility of starch filled polymer system. *A Rev.Mat. Sci. Eng. C.*, 29: 2370-2377.
- Raquez, J.M., Deleglise, M., Lacrampe, M.F. and Krawczak, P. (2010). *Progress in Polymer Science*, 35 (2010): 487-509.
- Ravikumar, H.R., Shwetha, S.R. and Karigar, C.S. (2012). Biodegradation of paints: a current status. *Indian J. Science & Technology*, 5 (1) :1-11.
- Reddy, M.M., John, K. and Naidu, V.S. (2008). Study of viscosity & refractive index of nylon 6, 6 and Poly(methyl methacrylate) in formic acid. *Indian J. of pure & Appl. Physics*, 46: 209-211.
- Reddy, S.K., Prabhakar, N.M., Babu, K.P., Venkatesulu, G., Rao, K.U., Rao, C.K. and SubhaS.M.(2012). Miscibility Studies of Hydroxypropyl Cellulose/Poly(Ethylene Glycol) in Dilute Solutions and Solid State. *International Journal of Carbohydrate Chemistry*, 2012(2012): 1-9.
- Ricky, G., Oscar, L. and Yusef, S. (2010). An Investigation into Polystyrene Recycling at UBC. Dawn Mills APSC 262. The University of British Columbia. PP. 1-18.
- Riegel's, A.J. (1997). Hand book of industrial chemistry; S.K Jain for CBS publishers and distrutors, India. pp. 633-634.
- Ruhlman, D. (2010). Reflection on water: New dispersant and rheology modifiers for gloss emulsion system (waterborne alkyds). *European Coating Journal*, pp.18.
- Sabnis, A.S., Bhave, V.G., Kathalewar, M.S., Mare, S. and Raut, P.P. (2012). New polyester polyol derived from recycled poly (ethylene terephthalate) for coating application. *Archives of Applied Science Research*, 2 4 (1) : 85-93
- Salthammer, T., Mentese, S. and Marutzky, R. (2010). Formaldehyde in the indoor environment. *Chem. Rev.*, 110 (4): 2536-2572.
- Saravanan, D., Gomathi, T. and Sudha P.N. (2011). Synthesis, Characterization and Thermal Behavior of Natural Polymer Blend. *International Journal of Chemical and Analytical Science*, 2 (12):1265-1269.
- Sharma, B.K. (2011). Industrial chemistry (including chemical engineering), 6<sup>th</sup> edition, Goel publishing house. pp. 984-1360.

- Shashi, C. (2011). A textbook of engineering chemistry. Dhanpat Rai & CO (PVT) LTD. pp. 71-72.
- Shen, D., Kkai, K., Welie, X., Weiming, C. and Yueming, J. (2011). Synthesis of a novel environmental protection urea-formaldehyde resin, transportation, mechanical and electrical engineering (TMEE), international conference, PP. 2142-2149.
- Shinde, N., Kathalewar, M. and Sabnis, A. (2012). Synthesis and characterization of emulsion polymers using isopropenyl acetate. *Int. J. Ind.Chem.*, 3 (28): 3-8.
- SON. (1990). Standard for Paints and Varnishes part 6: Test Methods for paints for Decorative purpose, pp1-24.
- Stabik, J., Dybowska, A., Szczepanik, M. and. Suchon, £. (2009). Viscosity measurements of epoxy resin filled with ferrite powders. *Archives of Materials Science and Engineering*, 38 (10): 34-40
- Stephen, O., Fatima, R. and Ikechukwu, A. (2010). Adhesive formulations with ternary blends using simplex lattice design. *Inter. J. of Phy. Sci.*, 5 (13): 2098-210.
- Sulkowski, Wieslaw, nowak W, Krzysztof Sulkowska, Anna/Wolinka Agnieszka/Bajdure wioletta M ; Pertak Danuta/Mikula Barbara(2009). Study of the sulfonation of expanded polystyrene waste and of properties of the product obtained. *Pure and Applied Chemistry (Report)*.
- Suurpere, A., Christjanson, P. and Siimer, K. (2006). Rotational Viscometry for the study of urea formaldehyde resins. *Proc. Estonian Acad. Sci. Eng.*, 12 (2) : 134-146.
- Tang, X., Bai, Y., Duong, A., Smith, M., Li, L. and Zhang, L. (2009). Review article: Formaldehyde in China: production , consumption, exposure levels and health effects. *Environ. Int.*, 35 (2009): 1210-1224.
- The Rohm and Hass; paint quality institute. [www.paintquality.com](http://www.paintquality.com), ingredient of paint and their impact on paint properties.
- Thormann, E., Simonsen, A.C., Hansen P.L. and Mouritsen O.G. (2008). Interaction between a polystyrene particle and hydrophilic and hydrophobic surfaces in aqueous solutions. *Langmuir*, 24: 7278-7284.
- Tim, W. (2012). *Coating world, article on growing paint additives market*; environmental pressure and the growing shift toward water based system.
- Toloei, A., Atashin, S. and Bahrololoom, M.E. (2013). A New Approach in Modifying Polymeric Coating to Increase Corrosion Resistance Properties. *ISRN Materials Sci.*, 2013: 1-7.
- Top green coating project. (2009). The many shades of Green; *J. of Architectural Coating*.
- University of British Columbia Sustainability (2010). Green Research Programme. Retrieved June, 2012 from <http://www.sustain.ubc.ca/campus-sustainability/greening-the-campus/green> Research Programme

- Velu, S., Muruganandam, L. and Arthanareeswana, G. (2011). Performance enhancement of polysulfone ultrafiltration membrane by blending with polyurethane hydrophilic polymer. *Inter.J. of Chem. & Analytical Sci.*, 2 (7): 87-92.
- Viswanathan, B. (2009). Pollution control strategies; a chemist's perspective. National center for catalysis Research. Indian Institute of Technology-Madras.
- Wirongong T, Lisa M, Sasitorn W, Pensiri S, Pornchai R (2011). Effect of carboxymethyl cellulose concentration on physical properties of biodegradable cassava starch based films. *Chem. Cent. J.* 5:6.
- Xu, K., Zhou, S. and Wu L (2009). Preparation and properties of thermosetting acrylic coatings using titanium-oxo-cluster as a curing agent. *Chinese J.Polym. Sci.*, 27 (3):351-358.
- Yousefi, A.A., Pishvae, M. and Yousefi, A. (2011). Preparation of water-based alkyd/acrylic hybrid resins. *Progress in Color, Colourant and Coatings*, 4 (2011): 15-25.
- Yumiko, H., Takanobu, S., Tetsuo, O., Toshiaki, O., Masashi, M. and John, M. (2010). Effects of specular component and polishing on color resin composites. *J. of Oral Science*, 52 (4): 599-607
- Zaharuddin, W., Wan, A., Bambang, A.J. and Pattihi, H. (2011). Effect of vermiculite addition on thermal characteristic of water-based acrylic fire retardant coating formulation. *J. Appl. Sci.*, 11: 1763-1769.
- Zorba, T., Papadopoulou, E., Hatjiissaak, A., Paraskevopoulos, K.M. and Chrissafis, K. (2008). Urea-formaldehyde resins characterized by thermal analysis and FTIR method. *J. Thermal Analysis and Calorimetry*, 92: 29-33.

## APPENDIX

### APPENDIX 1: Effect of PS concentration on the viscosity of TMU/PS resin

Concentration (%)	0	10	20	30	40	50	60	70
Viscosity(mpa.s)	2.39 ±0.0300	2.95 ± 0.0100	3.085±0.1000	4.64 ±0.1000	7.65 ±0.0100	9.36±0.0220	19.70± 0.1200	11.81±0.0410

**APPENDIX 2:** Effect of PS concentration on the gel-time of TMU/PS resin.

<b>Concentration</b>	0	10	20	30	40	50	60	70	80	90
Gel-Time (Min.)	440 ±0.0101	413 ±0.0220	370 ±0.0544	340±0.0441	265±0.011	205 ±0.010	120 ±0.0121	165 ±0.011	178 ±0.021	190 ±0.055

**APPENDIX 3:** Effect of PS concentration on the density of TMU/PS resin

Concentration (%)	0	10	20	30	40	50	60	70
Density (g/cm <sup>3</sup> )	1.1250±0.001	1.1200±0.0100	1.1177±0.0100	1.1167±0.0121	1.1132±0.0020	1.1100 ±0.0115	1.0990±0.002	1.0880 ±0.0100

**APPENDIX 4:** Effect of PS concentration on the turbidity of TMU/PS resin

Concentration (%)	0	10	20	30	40	50	60	70
Turbidity (NTU)	91±0.1014	137±0.0112	147±0.0110	385±0.0110	545 ±0.1010	698±0.0120	878 ±0.1022	990±0.111

**APPENDIX 5:** Effect of PS concentration on the melting point of TMU/PS resin

Concentration (%)	0	10	20	30	40	50	60	70
Melting Point ( $^{\circ}\text{C}$ )	280 $\pm$ 0.1500	275 $\pm$ 0.1110	270 $\pm$ 0.1010	262 $\pm$ 0.0222	255 $\pm$ 0.121	251 $\pm$ 0.113	262 $\pm$ 0.100	253 $\pm$ 0.132

**APPENDIX 6:** Effect of PS concentration on the refractive index of TMU/PS resin

Concentration (%)	0	10	20	30	40	50	60	70
Refractive Index	1.4100 $\pm$ 0.110	1.4150 $\pm$ 0.0310	1.4160 $\pm$ 0.0110	1.4165 $\pm$ 0.0122	1.4170 $\pm$ 0.0113	1.4200 $\pm$ 0.0220	1.4250 $\pm$ 0.1010	1.4300 $\pm$ 0.0110

**APPENDIX 7:** Effect of PS concentration on the moisture uptake of TMU/PS resin

Concentration (%)	0	10	20	30	40	50	60	70
Moisture Uptake (%)	4.72 ±0.1000	3.5±0.1200	2.93 ±0.1221	2.57±0.0300	2.15 ±0.0009	1.51±0.0122	1.01±0.001	0.92±0.0040

**APPENDIX 8:** Effect of PS concentration on the formaldehyde emission of TMU/PS resin

Concentration (%)	0	10	20	30	40	50	60	70
Formaldehyde Emission (ppm)	0.0905±0.010	0.0852±0.110	0.0744±0.1250	0.0500±0.1010	0.0430±0.0001	0.0320±0.0011	0.0233±0.0011	0.0120±0.0220

**APPENDIX 9:** Effect of PS concentration on the elongation at break of TMU/PS resin.

Concentration (%)	0	10	20	30	40	50	60	70
Elongation at Break (%)	140 ±0.1011	155 ±0.0023	230 ±0.0009	300 ±0.1501	350 ±0.2001	390±0.1330	425 ±0.010	570 ±0.141