SYNTHESIS, FORMULATION AND CHARACTERIZATION OF PHENOL FORMALDEHYDE/CHITOSAN COMPOSITES

By

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Declaration

I declare that the work in the thesis entitled " Synthesis, Formulation and Characterization of Phenol Formaldehyde Composites" has been carried out by me in the Department of Polymer and Textile Engineering under the supervision of Prof. M. K Yakubu, Prof A. Danladi and Dr. A. A Kogo. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any University.

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Certification

This Thesis entitled "SYNTHESIS, FORMULATION AND CHARACTERIZATION OF PHENOL FORMALDEHYDE/CHITOSAN COMPOSITES" by Iliasu, Garba Baba meets the regulations governing the award of the degree of Doctor of Philosophy of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation,

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Abstract

The methodology of the experiment involves three main stages. The first part describes the synthesis of the PF (novolac) resins. Novolac (resins) were prepared with an excess of phenol over formaldehyde under acidic conditions. PF molar ratio were varied from 1P:2F to 1P:8F. The structure of the PF was determined using FT-IR techniques. The preparation and characterization was reported. The physicochemical properties tests carried out on the (novolac) resins include pH, viscosity, water-tolerance, density, resin solid content, gel time, cure time and yield%. Emission tests such as free formaldehyde content and free phenol content were determined . The second part involves synthesis of chitosan from commercial chitin with different degree of substitutions determined by potentiometric titration. Characterization using FT-IR of the fresh chitin and the deacetylated chitosan was carried out and functional groups were observed and compared with the standard values. The following analysis were carried out on the chitin: loss on drying, moisture content, % solubility, solubility in chemicals, density, pH value, and ash content. The solubility of the chitosan were tested in various solutions like distilled water, acetone, ethanol, acetic acid and lactic acid. The third part was the production of the composites with different P: F molar ratio 1P:2F to 1P:8F and filler loading were varied 10% to 50%. A total of thirty five composites were produced, fabricated and subjected to mechanical properties.from the physiochemical properties of density, water absorption and tensile strength/modulus of composites at different filler loading of 10% to 50% using 5%w/v Heaxemethylenetetramine (HMTA) as the hardener, loading of 40% with 1P:4F and 1P:2F gave excellent results in terms of mechanical properties. The results of the mechanical properties revealed that the tensile strength and the tensile modulus increases with the increase of the filler loading. Further analysis was carried out to determine the optimum from the composites at different filler loading. To prove the results, optimization of 1P:2F to 1P:4F were carried out with the filler at different degree of deacetylation (DD) % values. In this case, the DD% values were increased by increasing the concentration of the alkali (NaOH) at 30%, 40% and 50%w/v at a temperature of 120^{o}C. The approximate calculated values of 70%, 81.47% and 90.92% DD of the chitosan were obtained and composites using P: F molar ratio of 1P:2F and 1P:4F were prepared. The composites were then subjected to various analysis to obtain the optimization of the composites. In order to characterize the chitosan phenol formaldehyde composites, several analysis were carried out on the following sample, neat polymer (100%), untreated, 70%, 81.47% and 90.92% DD were carried out. Swelling behaviors tested using the following solvents water, carbon tetrachloride, ethanol and acetone, and the results obtained were reasonable. Chemical resistance on the 40% of 1P:4F and 1P:2F were carried out in 1N HCl and 1N NaOH at 72 hours. A very good results were obtained for samples 70%, 81.47% and 90.92% with an average result of around 7%. But the basicity behaviors was poor in 1N NaOH solution with the highest value in the untreated 12.5% were observed. Other tests carried out were density and water absorption, the densities were in the range of 1.8g/cm^3 for 60% to 0.82g/cm^3 for untreated.The water absorption measurement was found to be excellent in all the samples, lowest value was observed in 91% and highest for 70% DD. Neat matrix showed complete resistance to water absorption. Mechanical properties tests of: tensile strength/modulus (38% improvement), flexural strength/modulus (27% improvement), impact (65% improvement) and hardness (25% improvement) of filler loading of 40% at DD of 70% gave an excellent results. Formaldehyde emission test using flask method were carried out on the composites. The effect of DD on emission was found to be highest in 70% DD and lowest in 91% DD. The effect of chitosan in reduction of formaldehyde release in the production of chitosan/P:F composite mechanism of reaction between chitosan and novolac resin were drawn. The use of chitosan in the production of composite have significantly reduced the emission. The SEM studies of the samples were investigated and. morphological results clearly showed that when the polymer resin matrix was reinforced with the different loadings of chitosan 70% to 90.92% DD surface modification took place. Wide angle x-ray analysis (XRD) was carried out to investigate the effectiveness of the resin interaction Thermal analysis of the reinforced chitosan phenol formaldehyde composites as compared to the virgin polymer had improved from 330^{o}C to 615^{o}C. Improved stability was manifested throughout the whole range of temperature studied. The overall results of the research show that composites which were deacetylated, reinforced and cured with hardner (HMTA) gave excellent results than those without deacetylation and curing.

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List of Abbreviations

4-AAP	4- Anninoanti Pyrine
ADH	Alcohol Dehydrogenase
ADHES	Adhesive
AHMT	4 – Amino – 3 – Hydrazine – 5 – Mercapt To – 4h -1, 2, 4 – Triazole
ASTMD	American Society of Testing and Materials Standard.
BTEX	Benzene, Toluene, Ethylbenzene, and 0- Xylene
CA	Chromotrophic Acid
CE	Capillary Electrophoresis
DA	Degree of Acetylation
DD	Degree deacetylation
DDL	3, 5 – Diacetyl – 1, 4 – Dihydrolutidine
DMC	Dynamic Micro Chamber
DNPH	Dinitrophenylhydrazine
DO AS	Differential Optical Absorption Spectroscopy
EN	European Standard
EPA	European Particle Board Association

ESI	Electrospray Interface
FD	Formaldehyde
FID	Flame Lionization Detector
FT – IR	Fourier Transform Infrared Spectroscope
FTM	Formaldehyde Testing Materials
GA	Ghitaraldehyde
GC	Gas Chromatography
HDACS	Hexamethylene 1. 6 – Cycli (Aminocar Boxysulfonate).
HMTA	Hexamethylenetetramine
HODS	High- Order Derivative Spectrum
HPLC	High-Performance Liquid Chromatography.
IAQ	Indoor Air Quality
IARC	International Agency for Research on Cancer.
LC-MS	Liquid Chromatography/Mass Spectrometry.
LIFS	Laser Induced Fluorescence Spectroscopy
LOAEL	Lowest Observable Adverse Effect Levels
MBTH	3 – Methyl – 2 – Benzothiazoly Izone.

MDF	Medium Density Fiber Board
MMC	Metal Matrix Composite
MUPE	Melamine – Urea – Phenol – Formaldehyde
NOEL	No Observed Effect Level
PB	Particle Board
PCP	Parachlorophenol
PF	Phenol Formaldehyde
PFNR	Phenol-Formaldehyde Novolac Resin
PMC	Ceramic Matrix Composite
PTR – MS	Proton – Transfer – Reaction Mass Spectrometry
RP	Reverse Phase
SFC	Supercritical Fluid Chromatography
TDLS	Tunable Diode Laser Spectroscopy
UF	Urea – Formaldehyde
UV	Ultra – Violet
VOC	Volatile Organic Compounds
WHO	World Health Organization

CHAPTER ONE

1.0 INTRODUCTION

1.1 Resins

Resins are low molecular weight amorphous polymers. They normally have a melting or softening range, and are brittle at the solid state. Their main applications are in adhesives, inks, and chewing gum. Mostly, they are used together with larger polymers, which form the backbone of the adhesive and thus generate cohesion. Formulators use resins to create the best balance between adhesion and cohesion. Resin can be divided as synthetic and natural resins (Chretien , 1999).

Synthetic resins systems that are commonly used in advanced fibre-reinforced composites are namely, thermosets and thermoplastics. The difference between the two categories is that a thermosetting material undergoes an irreversible reaction during processing, where by it is permanently hardened due to the formation of cross-links between the monomer units. Thermosetting resins generally degrade if heating is continued . Major thermosetting resins for adhesive are phenol-formaldehyde (PF) resins, and melamine formaldehyde. Others are epoxy and polyester resins. Thermoplastic resins are polymers that soften and flow at elevated temperature and solidity at low temperatures. They are also called hot melt adhesives. Adhesives strengths with these thermoplastics resins are mainly from mechanical interlocking. Polypropylene and polyethene are examples of thermoplastics (Knop and Pilato 1985; Martin, 2013).

Rosin, a natural resin, is one of the oldest raw materials for the adhesives industry. There are three types of resin manufactured, gum rosin, wood rosin and tall oil rosin, all generated from the pine tree. Rosin resins, unlike hydrocarbon resins are not polymers. In fact, they are a blend of different molecules. They contain abietic acid and its double bond isomers as main components. Their molecules have poor stability caused by unsaturation. Stability can be improved by either disproportionation or hydrogenation. Phenolic resins are therefore often classified as “water-soluble”, “alcohol-soluble”, “oil-soluble”, etc ((Chretien, 1999; Pizzi, 2003).

1.1.1 Polymers

Phenolic resins (PF) are one of the most widely used thermosetting polymers. They are polycondensation products of phenol and formaldehyde. These are widely used because of their thermal stability, water resistance, binding strength, chemical resistance, electric insulation and dimensional stability. These have attracted special interest because of their large range of industrial applications, in adhesives, casting, molding and structural parts. PF are synthesized by reacting phenol with formaldehyde in the presence of an acid or alkali. Depending on the ratio of phenol (P) to formaldehyde (F) and the type of catalyst used, these are classified as resoles and novolacs. Novolacs are prepared with a formaldehyde to phenol (F/P) molar ratio <1.0 in presence of an acid catalyst where as resoles usually have F/P molar ratio >1.0 and employ an alkali catalyst (Christy, 2000).

Of these two types, resoles are reactive type resins and one – step process that are either liquid or brittle, soluble, fusible solids. They can be cross-linked by application of heat, without any catalyst (Knop and Scheih, 1979). Novolacs do not contain any reactive groups and hence require the addition of a crosslinking agent and heat to acheive cure. The novolacs are referred to as two-step process resins. The literature indicates that PF resin is a major adhesive used in exterior grade wood-based panels (Knop and Pilato, 1985; Christy, 2000). However, the marked disadvantages of the PF resin are relatively longer cure and press time, dark colour bond line, environmental issues of toxicity, and non-biodegradation. And also, the relationship between the synthesis conditions, the structure and the mechanical properties has not yet been completely clarified. One of the reasons for this is that the polymezation of the resins has a complicated reaction mechanism.

Chitosan is a modified carbohydrate polymer derived from chitin, one of the most abundant polysaccharides in nature, by deacetylation of chitin to different degrees. Chitin is present in crustacean shells, insect exoskeletons, fungal cell walls, microfauna, and plankton. It is formed by β-(1→4)-linked 2-amino-2-deoxy-D-glucopyranose and 2-acetamido-2-deoxy-D-glucopyranose units (Moiteiro and Airoidi, 1999). The presence of of amino groups in chitosan is responsible for its polycationic nature in acidic solutions. An important advantage of chitosan is the possibility of agents that perform chemical modifications on its structure by binding to amino and hydroxyl groups.

It is quite clear from the chemistry of chitosan and PF that crosslinking is possible between chitosan molecules and PF by methylene linkages. It was planned to utilize this possibility of cross-linking for the modification of PF resin by incorporating natural polymer like chitosan for the preparation of this composites.

1.1.2 Polymer Gel

Polymer gels are cross-linked networks of polymers which behave as viscoelastic solids. Because the polymer network is cross-linked, the gel network consists of a very large branched polymer which spans the entire gel. While gel can be soft and deformable, they also hold their shape like solid. Depending on the physical structure of the polymer network, gels can be strong, weak, or pseudo gels (Ross-Murphy, 1995). Chemically cross-linked gels are considered strong gels. Soft polymer gels can have excellent adhesion properties due to both the elastic and viscous properties (Zosel, 1991; Lenhart, 2006 ; Andrews and Jones, 2006).

A gel is dispersion of a three dimensional network that entraps a solvent medium. Classification of gels is based on the type of links that creates the three dimensional structures, the size and shape of the gel configuration and the type of solvent. Gels can form by covalent bonding, called chemical gels or by physical interactions at colloidal level, called physical gels. From the technical point of view, the determination of the gel time is important because it gives an indication of the curing process of the resin and the phase transition from the liquid to the solid state. Chemical cure of P: F resins as thermosetting polymers is associated with significant changes in their physical properties such as gelation and vitrification. As the condensation of resin commences, molar mass advancement occurs, leading to a gel state which is no longer soluble in water. While the water is evaporated during heating, the flexible phenolic intermediate becomes rigid and cross-linked (Gardziella, 2000).

The main drawback preventing wider use of P: F resins in the manufacture of composites is its relatively slow cure rate. Many attempts have been made to cure P: F resins faster for the composite to be bonded at higher moisture contents and at lower press temperatures. Faster curing would also result in lower emission of volatile organic compounds during manufacturing of composites (Siimer and Kaljuvee, 2008). Different catalysis, additives, or modified resin formulations have been proposed as P: F resins cure accelerators (Astarloa-Aierbe, 1998; Lorenz and Conner, 2000). The fast curing process of PF resins may lead to changes in micro cross-linking within the cured resin system, which has implication with respect to the thermal properties, thermal stability, durability, and service life of the composites (Yuzhu-Chen *et al.,* 2014).

1.2 Polymer Composite

The first composite materials may have been bricks fashioned by the ancient Egyptians from mud and straw (Julien, 2011). Commercialization of composites can be traced to earlier this century when cellulose fibres were used to reinforce phenolic and later urea and melamine resins. Probably the most familiar composite materials is fiberglass, which is widely used to form large, lightweight reinforced structures.

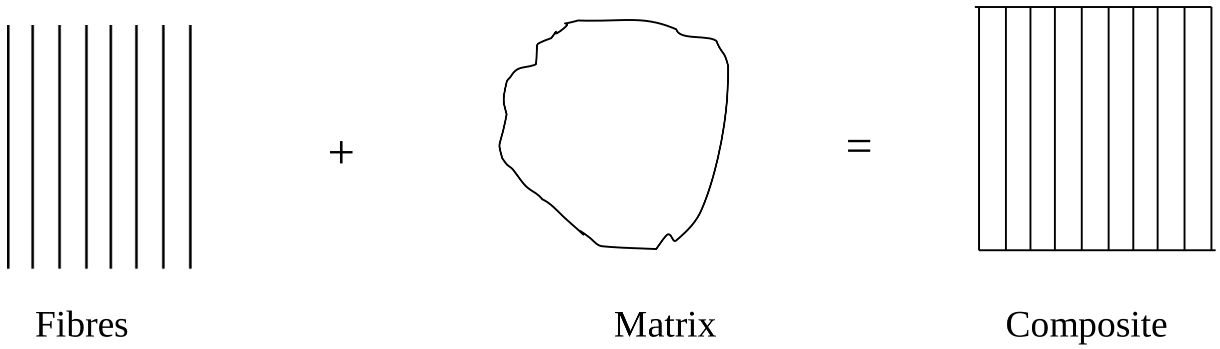
Polymer matrix composites are composites made from polymers or polymer along with other kinds of materials such as fibres (carbon, glass, cellulose, metal etc.) as reinforcement. The principal constituents of polymer matrix composites, which influence the strength and stiffness of the modern advanced polymer composites, are the reinforcing fibres, the matrix and interface. Each of these individual phases has to perform certain essential functions based on their mechanical properties so that a system containing them may perform satisfactorily as a composite.

Composites are used in a wide range of applications, wherever high strength – to – weight ratios are important. Principal uses are found in the automobile, marine and construction industries. In the majority of cases, especially those requiring high performance in the automotive and aerospace industries, the discontinuous phase or filler is in the form of a fibre. Typical fibres for composites applications include carbon or graphite, glass and aromatic polyamide (Knop and Pllato, 1985).

1.3 Composite Concepts

The desire for specified material properties has led to the unusual combination of materials. This is especially true for materials needed for many of our modern day technologies. This desire has led to the production of certain special materials known as composites. A composite material is made by combining two or more materials to give unique combination of properties. This definition is found to be more general and can include metal alloys, plastic co-polymers, minerals and wood. One of the most unique composites is fibre-reinforced. They differ from the earlier mentioned materials in that their constituent materials are different at molecular level and are mechanically separable. The constituent materials together provide the desired properties but remain in their original forms. The final properties of the composite materials are better than that of the constituent materials.

The main concept of a composite is that it is made up of matrix materials. Most composites are formed by reinforcing fibres in a certain matrix resin. The reinforcements can be fibres, particulates or whiskers and the matrix material can be metals, plastic or ceramics. The scheme 1.1 below shows a schematic diagram illustrating the formation of a composite.



Scheme 1.1: Formation of a composite material

In a composite, the fibres can be continuous, discontinues and particulate. The fibre carries the load and its strength is greatest along the axis of the fibre. The scheme 1.2 shows the fibre forms in a composite.

Continuous fibre composite discontinues fibre composite

Scheme 1.2: Fibre forms in a composite

Long continuous fibre in the direction of the load results in composite with properties far better than the plain matrix. The same is obtainable with the shorter fibres except that it provides properties less than that offered by the continuous fibre composites (Knop and Pilato, 1985). The fibre form is selected depending on the application and manufacture method.

1.3.1.0 Types of Composites Materials

Broadly, composite materials can be classified into three groups on the basis of matrix material. They are, metal matrix composites (MMC), ceramic matrix composites (CMC), and polymer matrix composites (PMC).

1.3.1.1 Metal Matrix Composites

Higher specific modulus, higher specific strength, better properties at elevated temperatures and lower coefficient of thermal expansion are the advantages of metal matrix composites over monolithic metals. Because of these attributes metal matrix composites are under consideration for wide range of applications viz combustion chamber nozzle (in rocket, space shutter), housings, tubing, cables, heat exchangers, structural members etc.

1.3.1.2 Ceramic Matrix Composites

One of the main objectives in producing ceramic matrix composites is to increase the toughness, naturally it is hoped and indeed often found that there is a concomitant improvement in strength and stiffness in ceramic matrix composites.

1.3.1.3 Polymer Matrix Composites

Polymeric matrix composites are the most commonly used matrix materials. The reasons for this are two-fold. In general the mechanical properties of polymers are inadequate for many structural purposes. In particular their strength and stiffness are low compared to metals and ceramics. By reinforcing other material with polymers, these difficulties can be overcome. Secondly high pressure and high temperature are not required in the processing of polymer matrix composites. For these reasons polymer composites developed rapidly and became popular for structural applications in no time. Polymer composites are used because overall properties of the composites are superior to those of the individual polymers. Modern composites are usually made of two components a fiber and a matrix (Ashish and Blbir, 2013).

1.3.2.1 Fibre

Fibres are polymers that have very high resistance to deformation-they undergo only low elongations(<10-50%) and have very high moduli (>35.000Ncm^2) and tensile strengths (>35.000Ncm^{-2}) (Kurita and Sannan, 1992). According to (Alves and Mano, 2008), fibre is a material made into a filament, a single fibre usually has a diameter up to 15μm. Bigger diameters generally increase the probability of surface defects. The main fuctions of fibres are to carry the load and provide stiffness, strength, thermal stability and other structional properties to the fibre reinforced polymer (Maron, 1998). To perform these functions, the fibres in fibre reinforced polymer composite must have high modulus of elasticity, high ultimate strength, and low variation of strength among fibres, high stability of their strength during handling and high uniformity of diameter and surface dimension among fibres (Warner and Rezau, 1997).

1.3.2.2 Matrix

The matrix materials is a polymer composed of molecules made of many simpler and smaller units called monomers (Bledzki *et al.*, 1993). The matrix must have a lower modulus and greater elongation than those of fibres, so that fibres can carry maximum load. The important functions of matrix material in fibre reinforced polymer composite include some of the following; binding the fibres together and fixing them in the desire geometrical arrangement; transferring the load to the fibres by adhesion and/or friction; provide rigidity and shape to the structural member; isolate the fibres so that they can act separately, resulting in slow or no crack propagation; provide protection to the fibres against chemical and mechanical damages; influence performance characteristic such as ductility, impact strength; and provide final colour and surface finish for connections. The fibre is embedded in the matrix in order to make the matrix stronger.

1.3.2.3 Reinforcements

Fillers with high aspect ratio (I/d), are classified as reinforcements. Where I: fibre length and d is the diameter of the fibre. The amount of fibre: the strength and stiffness of the composites increase with increasing the volume fraction: Orientation of the fibre has a great role in the strength of the composites. The strength and stiffness of polymers or composites are improved by adding fibres of glass, carbon, boron etc, as reinforcements for polymer composites.

1.3.3.0 Composite Fabrication

Composites are processed by a variety of methods, including compression and resin- transfer molding. Specialized processing operations for composite fabrication are filament winding and pultrusion (Rahman, 2008).

1.3.3.1 Filament Winding

In this process fibres are pulled from bobbing through a bath containing the composite resin, such as epoxy or polyester formulation, and then the impregnated fibres are wound on to a form (the mandrel) in some predetermined arrangement. Once the mandrel is uniformly covered to the desired thickness and fibre orientation, the composite is cured at elevated temperature and the mandrel may be removed or left as an integral part of the composite. Filament winding may be used to prepare corrosion-resistant (fibreglass) tanks and pipes. Employing advanced resin materials, filament winding is also being used to prepare high-performance composites for structural and other applications. The continuous reinforcement and controlled fibre orientation that can be achieved by filament winding to provide a higher level of reinforcement than discontinuous reinforcement using individual fibres (Knop and Pilato, 1985; Julien, 2011).

1.3.3.2 Pultrusion

A simple pultrusion operation is a completely continuous process since the cure is on-line. This makes pultrusion a suitable process for commercial production lines producing a variety of composite shapes or profiles. A roving of continuous fibres (e.g E.glass) and a continuous-strand met (typically glass/polyester) are combined and immersed in a resin both before passing, through a forming guide and the curing oven. The majority of composites that are pultruded are the fibre-glass variety prepared from unsaturated polyester resin and E – glass. Fibre loading in pultrusion may range from 20% to 80% (Kaith and Ashish, 2008).

1.4.1 Physical and Chemical Properties of Formaldehyde

Formaldehyde was first reported by Russion chemist Aleksandr Butlerov (1828-86) and was conclusively identified by August Von Hofmann, it is a colourless gas that is highly reactive. The compound is soluble in water, ethanol diethyl ether and acetone. In aqueous solution, methyleneglycol and polymethylene are formed. Formaldehyde is commonly purchased with a stabilizer. In a recent review an estimated output of 32 million tons of formaldehyde in 2006 with the highest producers being china (34%), the United States (14%), and Germany (8%). More than 65% of the total formaldehyde is used to synthesise- resins. Formaldehyde is more complicated than many single carbon compounds because it adopts different forms. Formaldehyde is a gas at room temperature, but the gas readily converts to a variety of derivatives, which are often used in place of the gas. One important derivative is the cyclic trimer formaldehydryde or trioxane (Julien *et al*., 2011).

Formaldehyde when dissolved in water combines with water to form methanediol or methylene glycol. The diol also exists in equilibrium with a series of didomers, depending on the concentration and temperature. A saturated water solution, that contains about 40% formaldehyde by volume or 37% by mass, is called Neat matrix formalin .usual a small amount of stabilization such as methanol, is added to limit oxidation and polymerization. A typical commercial grade formalin may contain 10 to 12% methanol in addition to various metallic impurities (Ko, 1976).

Formaldehyde is naturally occurring substantialy in the environment and in the upper atmosphere. Formaldehyde is an intermediate in the oxidation (or combustion) of methane as well as other carbon compound e.g. forest fires, in automobile exhaust, and in tobacco smoke. When produced in the atmospheric methane and other hydrocarbon it becomes part of smog. Formaldehyde has also been detected in outer space, as well as its oligomers and organisms. Formaldehyde is the primary cause of methanol's toxicity, since methanol is metabolized into toxic formaldehyde by methanol dehydrogenation. Formaldehyde does not accumulate in the environment, because it is broken down within a few hours by sunlight or by bacteria present in soil or water. Human's metabolism destroys formaldehyde quickly, so it does not accumulate, and is converted to dermic aid in the body (Knop and Pilato, 1985; Julien, 2011).

Small amounts of formaldehyde are produced in case of incomplete combustion of methane gas. Since formaldehyde is a colourless pungent irritating gas it is generally marketed as a mixture of oligomers of polymethylene glycols. Paraformal is a white solid containing mostly polymethylene glycols with 100 repeat units. It is prepared by distilling aqueous formaldehyde solution and generally contains 1-7 wt % water. Structure with 8- 100 formaldehyde units per molecule. The name *paraformaldehyde* describes polymeric structure with 8-100 formaldehyde units per molecule. The cyclic trimer of formaldehyde (C_3H_8) is called 1, 3, 5-trioxane. Formaldehyde has a dipolar resonance, which makes the molecule a typical electrophone (Julien *et al.*, 2011)..

1.4.2 Usage and Application of Formaldehyde

Formaldehyde is a chemical feedstock for numerous industrial processes. It is also used as a preservative, disinfectant, and biocide. As far as the indoor environment is concerned, its use as a component of thermosetting plastics is of particular significance (Knop and Pilato, 1985).

Urea-formaldehyde (UF) adhesives (so-called aminoplasts) are still the most commonly used products in the manufacturing of wood-based materials and furniture due to their rapid curing, their compatibility with additives, and their low price. In the first step, mono-, di-, and trimethylolurea are formed from formaldehyde and urea in a Mannich reaction. This is followed by condensation reactions to build up the polymer. UF adhesives have poor water resistance: the presence of water results in a hydrolysis of the C-N bond and, as a consequence, the release of formaldehyde ((Julien *et al.*, 2011).

Melamine-urea-formaldehyde (MUF) adhesives are similar to UF adhesives. They are produced by mixing portions of UF and melamine-formaldehyde (MF) or by condensation of all monomers in one batch. Melamine-formaldehyde resins are excellent exterior wood adhesives because of their water resistance (Mano, 1992).

Phenol-formaldehyde (PF) adhesives (so-called phenoplasts) are made by electrophilic substitution to methylol phenol in the first step. In alkaline solution, the reaction results in highly viscous resins of low molecular weight, called resoles. A novolac with a high degree of crosslinking is formed in acidic solution. PF adhesives are very stable and water-resistant and have a high adherence to wood. In the past, plastics made of PF resins were also known as *Bakelite* and were, among other things, used as casings for telephones, radios, etc (Knop and

Melamine-urea-phenol-formaldehyde (MUPF) adhesives are used for the production of moisture-proofed wood based products and for construction materials. Like MUF adhesives, they are produced by the addition of small amounts of phenol (Mano , 1992).

1.4.3 Formaldehyde and Health Effects

Formaldehyde (FD) is naturally occurring substance which is widely met both in human and plant. It is also used in the production of other chemical products and material (i.e. dyes fabrics, medicines). Indoors formaldehyde can be emitted from the furniture that contain composite wood products, by various sheds, in sulfating materials, wall papers, paints etc. Formaldehyde is a colourless, but strong smelling gas and thus can be easily detected. When present in the air at levels above 0.I ppm, it can cause watery eyes burning sensations in the eyes, nose and throat nausea, coughing, chest tightness, whetting and headache, can affect people differently, some people are very sensitive to formaldehyde while others may not have any noticeable reaction to same levels. Most of these symptoms disappear via exposure in clean air. Some people may also show skin rashes, and allergic reactions. It is pointed out that FD is neither accumulated in the environment nor in the human organism because it is quickly oxidized and biodegraded (Mari, 1983; Julien *et al*., 2011).

It is argued that there are more severe effects at long – term exposure. Scientific studies in the early 1980s have demonstrated that formaldehyde is a strong nasal carcinogen (Richardson, 1999). Recently, FD was classified as a probable" human carcinogen (category 2A) by the international Agency for Research on cancer (IARC), under the world health organizations (WHO). In June 2004, ARC decided to reclassify formaldehyde to known" human carcinogens. This was based on studies of reducing carcinogenicity in industrial or exposed to high FD comes 30 to 60 years ago. In the European Union, FD is classified in category 3, and it varies from one country to another (Mari, 1983; Julien *et al*., 2011).

1.4.4 Formaldehyde as Indoor Pollutant

Discussion about formaldehyde as a possible carcinogen started in 1980 when the carcinogenicity of formaldehyde in rats and mice after long-term inhalation exposure was reported. These publications and the results of studies of human exposure assessment for formaldehyde triggered an avalanche of scientific work as well as stories in the yellow press. Although electronic databases and powerful search engines are now available, it is still difficult to survey all papers in the technical and medical literature. Notwithstanding this, formaldehyde is definitely the most common and the best-known indoor air pollutant (Salthammer *et al.*, 2010).

Over the years, the release of formaldehyde from building products has been decreasing. On the other hand, formaldehyde concentrations in ambient air are increasing continuously, especially in the urban environment. The number of articles on indoor pollution with formaldehyde is more as compared to outdoor. This high number of articles is because of the various resources of formaldehyde and also low air exchange rates in the indoor environment (Salthammer *et al.*, 2010). A relation between wood based products and formaldehyde emission was recognized by scientists during 1960 to 1970. Particle board, could release high concentration of formaldehyde into the homes and offices because of reversibility of reaction between urea and formaldehyde. Sevaral European standard committee for formaldehyde and other regulated dangerous substances have laid down permissible expore levels of formaldehyde by inhalation. And these include the formaldehyde in the Indoor Environment Chemical Reviews, (2010), formaldehyde emission from furniture coatings in Germany, 1992 and high formaldehyde concentrations in mobile homes in the United States 2006.

However, in 2004, formaldehyde discussions were generally taken up again when formaldehyde was considered as carcinogenic for humans. As a consequence, various authorities and institutions have proposed new indoor air guidelines, giving values that are nearly ubiquitous. Although a prioritized ranking of chemicals and exposures that cause concern is difficult and uncertain, the Scientific Committee on Health and Environmental Risks (SCHER) states that formaldehyde (like carbon monoxide, nitrogen dioxide, benzene, naphthalene, environmental tobacco smoke (ETS), radon, lead, and organophosphate pesticides) is a compound of concern in the indoor environment (Salthammer *et al.,* 2010).

1.5.0 Phenol

Phenol compounds are some of the most important contaminants present in the environment as a result of various processes, such as the production of plastics, dyes, pesticides, paper and petrochemical product (Connnzalez-Toledom, 2001 ; Penalver, 2002). They are often found in waters (LJompart, 2002), soils Baciocchi (2001), and sediments, because of their toxicity, phenols are included in the list of proxity pollutants in many countries and are required to be determined. Therefore phenols are monitored as important organic pollutants in the world (Deutsche, 1984; APHA, 1985). There are many kinds of phenols (e.g. mono-, binary-, polyhydric – phenols, polysubstituents and polysubstituted phenols and their isomer etc.

1.5.1 Physical and Chemical Properties of Phenol

Phenol is a member of a homologous series of compounds containing a hydroxyl group bound directly to the aromatic ring. Phenol, or PhOH, belongs to the family of alcohol due to the presence of the OH group. The hydroxyl group of phenol determines its acidity whereas the benzene ring characterizes its basicity. Thus, it is formally the enol form of the carbonyl group. Phenol has a low melting point, it crystallizes in colourless prisms and has a characteristic, slightly pungent odour. In the molten state, it is clear, colourless, mobile liquid. In the temperature range $T<68.4^{o}C$, its miscibility with water is limited: above this temperature it is completely miscible. The melting and solidification points of phenol are quite substantially lowered by water (Knop and Pilato, 1985; Mo *et al*., 2014) .

A mixture of phenol and 10% water is called phenolum liquefactum, because it is actually a liquid at room temperature. Phenol is readily soluble in most organic solvents (aromatic, hydrocarbons, alcohols, ketones, ethers, acids, halo-generated hydrocarbons etc.) and somewhat less soluble in aliphatic hydrocarbons. Phenols form azeotropic mixtures with water and other substances. Phenol can be considered as the enol of cyclohexadienone. While the tautometric keto-enol equilibrium lies far to the ketone side in the case of aliphatic ketones, for phenol it is shifted almost completely to the enol side. The reason of such stabilization is the formation of the aromatic system. The resonance stabilization is very high due to the contribution of the ortho- and para-quinonoid resonance structures which stabilize the negative charge (Mo,. *et al*, 2014).

In contrast to aliphatic alcohols, which are mostly less acidic than phenol, phenol forms salts with aqueous alkali hydroxide solutions. The contribution of ortho- and para-quinonoid resonance structures allows electrophilic substitution reactions such as chlorination, sulphonation, nitration, nitrosation and merceration. The reaction in the presence of acid catalyst is used to remove impurities from synthetic phenol. Phenol readily couples with diazonium salts to yield coloured compounds. Alkylation and acylation of phenols can be carried out with aluminium chloride as catalyst: methyl groups can also be introduced by the Mannich reaction. Diaryl ethers can be produced under extreme conditions (Knop and Pilato, 1985; Julien *et al*., 2011).

1.5.2 Phenol Usage and Production

Phenol is one of the most versatile and important industrial organic chemicals. Until World War II, phenol was essentially a natural coal-tar product. Eventually, synthetic methods replaced extraction from natural sources because its consumption had risen significantly. For instance, as a metabolic product, phenol is normally excreted in quantities of up to 40 mg/ L in human urine. Currently, small amounts of phenol are obtained from coal tar. Higher quantities are formed in coking or low-temperature carbonization of wood, brown coal or hard coal and in oil cracking. The earlier methods of synthesis (via benzenesulphone acid and chlorobenzene) have been replaced by modern processes, mainly by the Hock process starting from cumene, via the Raschig–Dow process and by sulphonation. Phenol is also formed during petroleum cracking (Moder and Frank, 1997; Julien *et al*., 2011)..

Phenol has achieved considerable importance as the starting material for numerous intermediates and final products. Phenol occurs as a component or as an addition product in natural products and organisms. For example, it is a component of lignin, from which it can be liberated by hydrolysis. Lignin is a complex biopolymer that accounts for 20 to 30% of the dry weight of wood. It is formed by a free-radical polymerization of substituted phenyl propane units to give an amorphous polymer with a number of different functional groups including aryl ether linkages, phenols and benzyl alcohols. Most pulp-processing methods involve oxidative degradation of lignin, since its presence is a limitation to the utilization of wood pulps for high end uses such as print and magazine grade paper. Such limitation is due to the photo induced yellowing of lignin-rich, high-yield mechanical pulps and, as a result, the photooxidative yellowing has been extensively studied in the hope of understanding its mechanism and ultimately preventing its occurrence. Phenoxyl radicals are produced during the photo oxidation of lignin and their subsequent oxidation ultimately leads to quinones, which are actually responsible for the yellow colour (Knop and Sheih, 1979 ; Rebecca, 2003).

Phenol was first used as a disinfectant in 1865 by the British surgeon Joseph Lister at Glasgow University, Scotland, for sterilizing wounds, surgical dressings and instruments. He showed that if phenol was used in operating theatres to sterilize equipment and dressings, there was less infection of wounds and, moreover, the patients stood a much better chance of survival. By the time of his death, 47 years later, Lister's method of antiseptic surgery (Lister spray) was accepted worldwide. Its dilute solutions are useful antiseptics and, as a result of Lister's success, phenol became a popular household antiseptic. Phenol was put as an additive in a so-called carbolic soap. Despite its benefits at that time, this soap is now banned. In (Salthammer et al, 2010), Dangerous Properties of Industrial Materials, one finds frightening phrases like 'kidney damage', 'toxic fumes' and 'co-carcinogen'. Clearly, phenol is totally unsuitable for general use, but the benefits 130 years ago plainly outweighed the disadvantages. However, because of its protein-degenerating effect, it often had a severely corrosive effect on the skin and mucous membranes (Christy, 2000; Julien *et al.*, 2011).

In the US, phenols are ranked in the top 50 major chemicals. In 1995 the total annual production of phenols was estimated at 4 to 5 billion pounds. In Japan the production of phenols in the late nineties was estimated approximately on the same level -1,200,000 tons per year. In 1995, 95% of US phenol production was based on oxidation of cumene, the exception being one company that used toluene oxidation and some companies that distilled phenol from petroleum. Two major uses of phenols in 1995 were the production of Bisphenol-A [4, 4-isopropylidenediphenol] (35%) and the production of phenolic resins (34%). Other uses include production of caprolactam (15%), aniline, (5%), alkylphenols (5%), xylenols (5%) and other miscellaneous compounds (1%). Bisphenol A is one of the raw materials widely used in the production of epoxy resins. Being inert, strong and adhesive with high insulator properties these polymers found their application in construction, coatings and bonding. In addition, Bisphenol A is used for the production of polycarbonate plastics, found in such products as baby food bottles, food cans, dental sealants, food packing and coatings. In the US alone, 1.65 billion pounds of this polymeric compounds are produced each year, and in Japan its production is estimated nowadays at over 200,000 tons per year (Moder and Frank, 1977).

Another group of very widely used compounds is phenols with long aliphatic chains R like octyl or nonyl as shown below. These compounds are important intermediates in the production of polyethoxylate surfactants, which are compounds consisting of alkyl chains attached to a phenol ring and combined with a variable number of ethylene oxides. In 1994 their production in EC countries reached 110,000 tons, mainly for industrial, agricultural and household uses. Moreover, the annual production in all developed countries has been estimated at 0.35 Mton. Environmental effects of substituted phenols owing to their poor ultimate biodegradability and the possible environmental hazard of their metabolites, alkylphenol ethoxylates have been replaced in household applications, mainly by alcohol ethoxylates. However, for industrial applications, this replacement has not been carried out yet due to the excellent performance of alkylphenol ethoxylates and their low production costs (Julien *et al*., 2011).

1.5.3 Phenol and Health Effect

Wide use of phenol and its derivatives led to studies of its occupational exposure and toxicity. Phenol toxicity in humans is not a big surprise, as this compound is toxic to most microorganisms, which explains its common use as a general disinfectant. This fact complicates treatment of phenol-containing wastewater by conventional biological processes. Phenol genotoxicity was determined using Syrian hamster embryo cells. Phenol induced morphological transformation, gene mutation, chromosomal aberrations, sister chromatid exchanges and unscheduled DNA synthesis. 2, 4, 6-Trichlorophenol induced mononuclear cell leukemia in male rats and liver tumors in mice (Gonzales-Cosado *et al.*, 1998). In another study, genotoxicity of this compound was established in V79 Chinese hamster cells. Conversely, 2, 4-dichlorophenol did not cause any increase in tumors in rats or mice in the 2-year study. In fact, mononuclear cell leukemia in rats and lymphomas in mice were decreased in these studies (Stich, 1991).

The damaging effect of long-term exposures (6+ months) to pentachlorophenol (PCP) on the immune system was studied in 190 patients. The distribution of PCP levels in blood was: 0–10 μg l−1 (69%), 11–20 μg l−1 (20%), and >20 μg l−1 (11%). The patients had various clinical symptoms and complained of the following: general fatigue (64%), rapid exhaustion (59%), sleeplessness (53%), headache (44%), mucous membrane, throat and noise irritation (39%), frequent common diseases (36%), bronchitis (30%) and nausea (13%). Analogous symptoms were described in previous studies. Blood levels of PCP were associated negatively with total lymphocyte counts and several other blood immune parameters (Colosia *et al.*, 1993). These data provide clear evidence that immunological abnormalities are associated with high levels of PCP in plasma of individuals with long-term exposure. PCP also induces chromosomal aberrations in mammalian cells *in vitro* and in lymphocytes of exposed persons in vivo (Gonzalez *et al.*,1998).

Several case-control studies have shown significant associations of polychlorophenols with several types of cancer, with the most consistent findings being non-Hodgkin lymphoma and soft-tissue sarcoma. Occupational exposure to chlorophenols can be a risk factor for nasal and nasopharyngeal cancer.

In the studies of polychlorophenols, great importance is attached to a compound's purity as its contaminants can include very toxic and carcinogenic dioxins. One has to be sure that the observed toxicity effect is connected with the main compound and not with the impurity. Polychlorophenols are also known to uncouple oxidative phosphorylation, alter the electrical conductivity of membranes and inhibit cellular enzymes, such as ATPase, β-galactosidase etc. The genotoxicity of the rodent carcinogen 2, 4, 6-trichlorophenol was studied in V79 Chinese hamster cells (Richardson *et al.*, 1999). This compound did not induce mutation or structural chromosome aberrations; however, it did produce dose-related increases in hyperdiploidy and micronuclei. It appears that it causes chromosome malsegregation as a major mode of genotoxic action. As mentioned above, pentachlorophenol has different solubility at acid and neutral pH. It was shown that this compounds toxicity also depends on pH. Studies of wastewater from a Baikalsk pulp and paper mill allowed one to evaluate a 'pure' cellulose bleaching process pollution at Lake Baikal, where it is located, has no agriculture and only little municipal pollution. Although mutagenic activity was effectively decreased during 1960 Victor Glezer biological and chemical treatment, even modern wastewater purification systems do not totally abolish potential toxicity and mutagenity of the effluents (Cristina *et al*., 2009).

Chlorinated phenols can degrade with formation of highly carcinogenic dibenzo-*p*dioxin and dibenzofuran derivatives. It can occur by thermolysis, slow combustion, photocatalytically, by photochemical degradation and by photolysis. Even in the presence of TiO_2, which in many cases leads to the total degradation of organic compounds, photocatalytic degradation includes formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. It was shown that the level of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in commercial animal products, raised near incinerators, are elevated compared to products from areas with no such industrial sources. It is related primarily to meat, milk from cows and eggs from chicken. Some phenol derivatives can act like hormones (e.g. estrogens) and interact with the human hormonal system (Knop and Pilato, 1985; Cristina *et al.*, 2009).

Two main phenol groups must be mentioned here—Bisphenol A and octyl- and nonylphenols. Bisphenol A might be a factor in decreasing sperm count in males and increasing rates of breast cancer in women. It was also shown that increased sensitivity to Bisphenol A during the perinatal period causes an increase in body weight soon after birth and in adulthood and a decrease of plasma luteinizing hormone level in adulthood. Octyl- and nonylphenols are formed during anaerobic biodegradation of the corresponding alkylphenol ethoxylates. These compounds are known to cause proliferation of breast cancer cells by acting as estrogenic mimic. They also cause endocrine-disrupting effects and 'feminization' of male species. In the context of health effects with an emphasis on cancer, phenols, as an independent class of organic compounds, are generally not genotoxic. This means that they cannot modify genes and therefore are not considered to be a direct cancer risk (Richardson *et al.*, 1999).

Laboratory studies have demonstrated that while not genotoxic, phenols can be co-carcinogens or promoters, increasing the effect of environmental genotoxic carcinogens. This promoting effect is highly dependent on the dosage and chronicity of exposure. Recent studies have demonstrated that some phenols found in fruits and vegetables, as well as synthetic phenolic antioxidants, exert protective effects against cancer, demonstrating antimutagenic, anticarcinogenic properties, and can also antagonize the effect of promoters. However, in a high dose range some of them can cause cancer in animals through mechanisms like cytotoxicity, regenerative cell duplication and hydroxyl radical generation. Generally, the neoplastic effects of phenolic antioxidants can be observed at high dietary levels and occur only after effective biological defense mechanisms are overloaded. Therefore, the public needs to be much more aware of the importance of dosage and exposure time (Lee, 2005; Liu *et al.*, 2008; LWPF, 2009).

1.6.1 Physical and Chemical Properties of Phenolic Resins

Phenolic resins are yellow to brown in colour, and the colouration can be very intense. Pale phenols resins become coloured immediately after production during storage or processing. The colouration is less intense only in the case of phenolic resins from para-alkyl-substituted phenolics they are typically brown in colour, and novolacs are lighter in colour than resoles. Resoles are dark yellow, orange reddish, or brownish even when made with pure raw materials. However, if the alkali is neutralized resoles become almost colourless. Characteristic UV absorption maxima lie at 254nm and 280nm (Lin *et al*., 2005).

Phenolic resins which are not crosslinked are commercially available as solids or solutions. For particular application e.g. in themoset, the polycondensation can be driven so far that the resins are no longer soluble but can only be swelled by organic solvents (Lee, 2005).

The softening point of solid resins can be determined by the capillary melting point according to DIN53244, by the ring and ball methods or similar procedures. Simple PF resins are readily soluble in alcohol,, esters, ketones, phenols, and some ethers, and insoluble in hydrocarbons and oils. As a class, resoles tend to be more soluble in alcohols and water, and novolacs tend to be more soluble in hydrocarbons. In the early stages of condensation resoles are often soluble in water, owing to the presence of methylol phenols, especially polyalcohol (Gardziiella *et al*., 2000).

The miscibility with solvents, usually described as ‘’ solubility’’ depends on the structure of the resin ranging from solubility in water to that in naphtha. Resins often have limited miscibility with certain solvents. Soluble phenolic resins have a broad molecular mass distribution; determination usually by gel permeation chromatography and have values of more than 50,000 depending on the type of phenol monomer. The viscosity of phenolic resins or their solutions is measured at high concentrations in 30 to 80% solution.

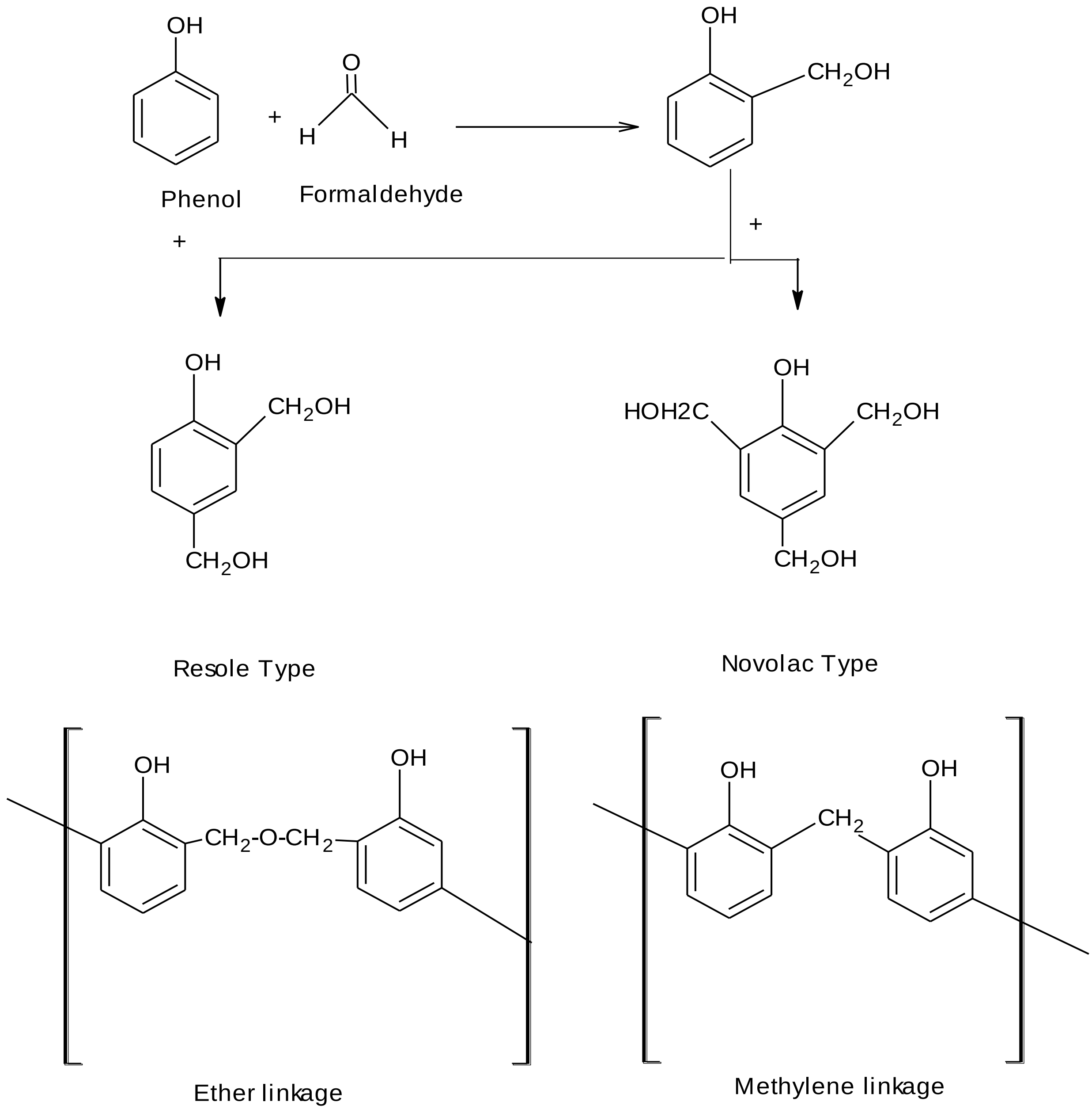
Cross-linked phenolic resins are hard substances which only have a small fracture strain and cannot be melted. Decomposition reactions begin at 120 to 250°C, depending on the molecular structure, although oxidative degradation takes the form of attack at the methylene bridges to produce substituted, dihydroxy benzophenones. Above this temperature, they begin to char slowly, and at higher temperatures charring is more rapid at about 400°C decomposition is rapid, yielding phenols and aldehydes, and leaving a coke like residue There are, however also some type of phenolic resin (ether resins) which are stable for some time up to 300°C. Hardened PF resin have a specific gravity of approximately 1.2 to 1.3, a refractive index of 1.6, and a specific heat of 0.5. The phenolic resins can be plasticized, their compatibility with plasticizers can be adjusted by introduction of hydrophilic or hydrophobic groups (Moder and Frank,1997 ; Gardziiella *et al*., 2000 ; Pistin, 2002)..

1.6.2 Formation and Structure of Phenol Formaldehyde Resin

Phenol-formaldehyde resins, as a group are formed by a step-growth polymerization reaction that can be either acid or base catalyzed by condensing phenol and formaldehyde. Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycol oligomers, the concentration of the reactive form of formaldehyde depends on temperature and pH. Phenol is reactive towards formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. The initial reaction in all cases involves the formation of a hydroxymethyl phenol;

$$HOC_6H_5 + CH_2O \longrightarrow HOC_6H_4\,CH_2OH$$

The hydroxymethyl group is capable of reacting with either another free ortho or Para site, or with another hydroxymethyl bridge and the second forms an ether bridge (Knop and Pilato, 1985) (Scheme 1.3).



Scheme1.3 : Illustration of the formation of the Resole and Novolac type structure respectively

1.6.2.1 Resole Type (Base Catalysed)

Base-catalysed phenol-formaldehyde resins are made with formaldehyde to phenol ratio of greater than one (usually around 1.5). These resins are called resoles. Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, and are then heated. The first part of the reaction at round 70^0C, forms a thick reddish-brown tacky material, which is rich in hydroxymethyl and benzylic ether groups. The rate of base catalysed reaction initially increases with pH, and reaches a maximum at about pH 10. The reactive species is the phenoxide ($C_6H_5O^-$) formed by de protonation of phenol. The negative charge is delocalized over the aromatic ring activating sites 2, 4 and 6, which then react with the formaldehyde. Being thermosets, hydroxymethyl phenols will crosslink on heating to around 120^0C to form methylene and methyl ether bridges. At this point the resin is a 3 – dimensional network which is typical of polymerized phenolic resins. The high cross linking gives this type of phenolic resin its hardness, good thermal stability, and chemical imperviousness (Young and lovell, 1991).

1.6.2.2 Novalac Type (Acid catalysed)

Novalac are phenol-formaldehydes resins made where the molar ratio of formaldehyde to phenol is less than one. The most common precursors for preparing novolac oligomers and resins are phenol, formaldehyde sources and to a lesser extent, cresols. Three reactive sites for electrophilic aromatic substitution are available on phenol which give rise to three types of linkages between aromatic rings i.e. ortho-ortho, ortho-para, and para-para. The polymerization is brought to completion using acid-catalysis. Typically, 1 to 6wt% catalyst is used. Approximately 4 to 6wt% phenol can typically be recovered following novolac reactions. Free phenol will be removed by washing with water repeatedly. The importance of an acid catalyst is attributed to facilitated decomposition of any dibenzyl ether groups formed in the process. The phenol units are mainly linked by methylene groups. Novalacs are commonly used as photo resists. The molecular weights are in the low thousands, corresponding to about 10 to 20 phenol units. Hexamethylene tetramine or “hexamine” is a hardener that is added to crosslink novalac. At $\geq 180^0$C, the hexamine forms cross links to form methylene and dimethylene amino bridges. Oxalic acid is preferred since resins with low colour can be obtained. Oxalic acid also decomposes at high temperature [>180^oC] to CO_3, CO and water, which facilitates the removal of this catalyst thermally (Megson, 1972 ; Nabi and Jog, 2004) .

1.7.0 Chitosan

Chitosan is typically obtained by deacetylation of chitin under alkaline condition. It is one of the most abundant organic materials being second only to cellulose in the amount produced annually by biosynthesis. Chitin is an important constituent of the exoskeleton of insects and marine animals, such as crustaceans, mollusks etc. It is also the principal fibrillar polymer in the cell wall of certain fungi. Chitosan is a linear polysaccharide, composed of glucosamine and N- acetyl glucosamine .Chitosan displays interesting properties such as biocompatibility biogradability, and its degradation products are non-carcinogenic. Therefore chitosan has prospective applications in many fields such as biomedicine, waste water treatment, functional membrane, and flocculation. However, chitosan is only soluble in few dilute acid solutions which limit its applications. Recently there has been a growing interest in the chemical modification of chitosan in order to improve its solubility and widen its application Derivatization by introducing small functional groups to the chitosan structure such as alkyl or Chelat carboxymethyl groups can drastically reduce the solubility of chitosan at neutral and alkaline pH values without affecting its cationic character(Kurita, 1988; Kumar, 2000).

1.8.1 Statement of the Research Problems

Many of our modern technologies require composite materials, because of their unusual combination of properties, which are not found in conventional materials (metals, alloys, ceramics, and polymeric materials). In line with these demands, the need for continuous research in composite materials is paramount towards improving the existing and developing new materials.

In fact, free formaldehyde in any product is undesirable for health reasons. The main drawback of the Phenol formaldehyde (PF) resins is its slow release of formaldehyde in finished product to the environment, contributing to worsening the indoor air quality, hence there is great desire of producing PF resins with low free formaldehyde content. The marked disadvantages of synthesized PF resins are relatively longer cure , dark colour , toxicity, and non-biodegradation. The composite industry continues to look for eco-friendly processes that substitute for toxic chemicals. In this point of view, chitosan is an excellent candidate of an eco-friendly materials. PF is suitable for use in a wide number of applications due to the abundant hydroxyl groups on the phenolic resins leading to strong intra- and intermolecular hydrogen bonds with a number of materials containing electron donors such as carbonyl and amide groups. The presence of free amino groups in chitosan is responsible for its polycationic nature in acidic solutions. The degree of deacetylation is an important property in chitosan production as it affects the physiochemical properties, hence determining appropriate applications

1.8.2 Research Questions

This research work asked the following questions:

i. Is there any need for the research work on the existing chitosan polymer composites?
ii. How to synthesize different novalac/prepolymer resins with different phenol/formaldehyde (P/F) mole ratios (1P:2F to 1P:8F).
iii. How to analyze and characterize the chitosan and synthesized novolac resins.
iv. What percentage of deacetylation (%DD) of Chitosan is the best for synthesizing Chitosan composite?
v. What method can be used to fabricate the different polymer composites?
vi. How to analyse the fabricated polymer composites ?
vii. How to determine the optimum composite from different filler loading.

viii. How to determine the mechanical properties of chitosan reinforced phenolic composites.

ix. How to characterize the chitosan phenol formaldehyde composites.

x. What are the areas of application of the composite produced?

xi. How can these researches bring development in the area ?

1.8.3 Justification of the Present Study

1. The Phenol formaldehyde (PF) polymers are the oldest commercial synthetic polymers over 100 years ago. PF is a synthetic adhesive which, when its two components are combined, produces a thermosetting polymer with properties completely distinct from the phenol or formaldehyde.
2. They possesses, many advantages, such as readily available raw materials, simple production processes, highly durable, more stable and good mechanical and hygroscopic strength. The versatility that makes phenol formaldehyde suitable for use in wide number of factories applications was soon recognized (Knop and Pilato 1985; Sellers 1985).
3. This is due to the abundant hydroxyl groups on phenolic resins causes these materials to form strong intra- and intermolecular hydrogen bonds with a number of materials containing electron donors such as carbonyl and amide groups.
4. An important advantage of chitosan is the possibility to perform chemical modifications on its structure by binding to amino and hydroxyl groups.
5. It is quite clear from the chemistry of chitosan and Phenol formaldehyde (PF) that crosslinking is possible between chitosan molecules and PF by methylene linkages. It was planned to utilize this possibility for the preparation of this composites with low emission of formaldehyde.

1.8.4 Aim of the Research Work

This research work is aimed at synthesizing phenol formaldehyde resin with low emission and then reinforced with Chitosan and determine its characterization. The physical and chemical characterization of the composite will suitable end use of application?

1.8.5 Objectives of the Present Works

The objectives of this research will include the following:

1. To synthesize and characterize novalac/prepolymer resins with different phenol/formaldehyde (P/F) mole ratios (1P:2F to 1P:8F) to optimize production.

2. To prepare chitosan with different degrees of deacetylation 70%, 81% and 91% [DD] and to determine its physical and chemical properties. FT-IR, SEM, and XRD of the chitosan.

3. To fabricate and characterize PF/chitosan composite to optimize the production.

4. To analyze and study Infrared spectroscopy (FT-IR), X-ray diffraction study Scanning Electron Microscopy (SEM) (XRD), and thermo gravimetric analysis (TGA/DTA) of the composite .

1.8.6 Scope and Limitation of the Research

The research work is limited only to the synthesis of PF (novolac) as well as the physical and chemical characterization of chitosan phenol formaldehyde composite.Production of composite using PF and chitosan, optimization of composite and its characterization Area of utilizations and applications of the polymer composite will be reported. Seven prepolymer resins of different molar ratios of novalac phenol formaldehyde (P: F) will be prepared. These P: F resins will be reinforced with Chitosan to form the composites.

1.8.7 Expected Results

The Standard values specified for phenol formaldehyde properties are tensile strength 76 MN/m^2, flexuaral modulus 8.3 GN/m^2, Impact strength 1.1 J/cm, resin solid content 49.6%, formaldehyde content 30mg/kg or 2.5mg/L, denisity 0.671g/cm^3 and water absorption 1.5%. The application of PF is in the production of plastics. It is expected that the phenolic resins when reinforced with chitosan will give excellent results in terms of mechanical properties enhancement and better physical and chemical properties than those without chitosan. The results of the optimum PF/composites are to be compared with standard values and works of the other researchers in the subject or closely related areas. The results obtained will form the basis for further research work in this area and also to assess the possibility of using these polymers composite in a number of applications.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Physical, Chemical and Toxicology Properties of Formaldehyde

Formaldehyde is a colourless, reactive, strong-smelling gas at room temperature. It is one of chemical in a large family of chemical compounds called volatile organic compounds (VOCs). Formaldehyde can be released into the air. Formaldehyde, a major indoor pollutant, originates mainly from the formaldehyde resins, which are used in the production of composite. Due to the stronger sources and low air exchange rates in the indoor environment, exposure to formaldehyde is higher indoors than outdoors. Formaldehyde is very active, and is transported in air, water and contaminated soils U.S (EPA, 1989). In a aqueus systems, atmospheric deposition is a significant source of formaldehyde.The high solubility of formaldehyde in water causes rapid absorption in the respiratory and gastrointestinal tract. Here, it can be oxidized to form formate and exhaled as carbon dioxide or incorporated in biological matrices. The biological half-life is extremely short at about 1 min (McGregor *et al.*, 2004). As an electrophile, formaldehyde can react with nucleophilic biogenic compounds in the body (Kotzas *et al.*, 2005) Formaldehyde itself is produced in small amounts from methanol via the enzyme alcohol dehydrogenase (ADH), (Nelson and Lehmminger, 2004) which is a human metabolite and can be measured in urine (Takenchi *et al.*, 2007).

Formaldehyde exposure may potentially cause a variety of symptoms and adverse health effects. According to a report published by “Health Canada”(2005), which is based on human clinical studies and animal experiments, the primary effects of acute exposure to formaldehyde are irritation of the mucosa of the upper respiratory tract and the eyes The RD50 values (exposure concentration producing a 50% respiratory rate decrease as an indication of respiratory tract irritation) of male mice are 3.1 to 5.3 ppm for an exposure time of 5 to 10 min. The lowest observable adverse effect levels (LOAEL) for human sensory irritation range from 0.4 ppm (rhinitis) to 3 ppm (eye, nasal, and throat irritation) (Kawaora *et al.*, 2007). A recent study of formaldehyde and sensory irritation in humans showed that eye irritation is the most sensitive parameter. A no observed effect level (NOEL) of 0.5 ppm was derived in the case of constant exposure (Lung *et al,* 2008). Different threshold values are available for the odor perception of formaldehyde. (Devos *et al.*, 1992) have calculated a standardized human olfactory threshold of 0.87 ppm (1.07 mg m^{-3}).

The WHO has estimated absolute odour thresholds (defined as the concentration at which 50% of the panel detects the odour) between 0.06 and 0.22 mg m^{-3}.10 In the report (Kostinen *et al.*, 2008) very low odour thresholds of 0.03 and 0.035 mg m^{-3} are specified, which refer to an updated world health organization (WHO, 2002) report and an unavailable paper from 1917 cited in (Devos *et al.*, 1992) respectively. In 2004, the International Agency for Research on Cancer (IARC, 2004) has classified formaldehyde as carcinogenic for humans (Group 1), this evaluation is based on information regarding the relationship between nasopharyngeal cancer and leukemia related to the exposure to formaldehyde. In the European Union (EU), formaldehyde is classified under Category 3 as a suspected carcinogen (Directive 2001/58/ CEE). Since 1991, the U.S. EPA (European Particle Board Association) has regarded formaldehyde as a probable human carcinogen (B1) (http://cfpub.epa.gov/ ncea/iris).

2.2 Physical and Chemical Properties of Phenol Toxicity and Health Effects

The current emphasis on the biological properties of natural or anthropogenic compounds depends on studies of possible health hazards or beneficial effects of agents to whom humans are exposed in everyday life. Phenolic compounds, which are ubiquitous among plants, used as food additives and ingested daily in milligram quantities, are a complicated system from this point of view. On the one hand, phenols induce DNA double-strand breaks, DNA adducts, mutations and chromosome aberrations in a great variety of test systems. On the other hand, they suppress the genotoxic activity of carcinogenic compounds *in vitro* as well as *in vivo* studies (Stich, 1991) The dual function of dietary phenols also becomes evident from the studies of their carcinogenic or, the opposite,1358 Victor Glezer anticarcinogenic potential.

Some phenols induce precancerous lesions, papillomas and cancers, or act as cocarcinogens, but there are others which are potent inhibitors of carcinogenesis at the initiation and promotion stages (Stich, 1991). One example of this latter group is vitamin E (tocopherol), which plays an important role in blood cells and nervous system tissues. It must be concluded that health hazard versus protective activity of phenols contained in dietary mixtures remains an unresolved problem and their multiple, occasionally contradictory functions make it difficult to propose their use as chemopreventative agents. This means that each group of phenols has to be examined separately for its biological and toxicological activity. Taste and odour complaints from consumers are an important issue for drinking water suppliers. Taste and odour threshold concentrations in water were determined for 59 drinking water contaminants, including phenols. Their determinations are usually based on the WHO drinking water guidelines (1993), European Standards HMSO, 1996 or US EPA, (1994 ; 2011)). The odour and taste description can change with concentration: for example, at 0.09 ppm the odor of 2-chlorophenol was described as 'musty, sweet, floral', but in the 0.5 to 1 ppm range as 'chemical, medical'.

In the case of 2, 4, 5-trichlorophenol, the description changed on increasing its concentration from 'fruity' to 'antiseptic'. While the odour and taste threshold of 2-chlorophenol is 0.1 ppb, the US EPA guideline for drinking water recommends 40 ppb. This shows that there is no correlation between a compound's taste and odour threshold and its health effects. (Young *et al.*, 1996) show that phenols can produce taste or odor in drinking water at concentrations much lower than health based regulations. This does not mean that it is acceptable to supply water that has an offensive taste or smell. Possible psychomatic effects, such as headaches, stress or upset stomach, must to be taken into account. Although there is an incomparable variation in the level and quality of taste and odor that consumers would regard as acceptable, such effects cannot be ignored and in particular cases a warning to the public not to drink the water

2.3 Phenolic Degradation / Pyrolysis

The pyrolysis of phenolic-formaldehyde (PF) resins was studied by TG-MS technique (Chen *et al.*, 2013). The structure changes of pyrolysis of PF resin heated to different temperatures were investigated by foorier transform in frared rays (FT-IR). The experimental results shows that the pyrolysis of PF can be divided into three stages. Ether bonds and untreated terminal hyrox methyl groups of the cured resin degradate in the first stage. In the second stage, crosslinking are broken, involving formation of a thermally crosslinked intermediate structure and the breaking of methylene bridges into methyl groups. Cyclodehydration and forming char of phenolic hydroxyl occurs in the third stage. The thermal stability and char yield of resin are depended in the pyrolysis of methylene bridges (Chen *et al.*, 2013).

phenolic Phenolic networks have been shown to possess moderate non-flammability and low smoke generation with a self-ignition temperature of 482°C (Sunshine, 1973). They are currently used in the interiors of airplanes such as the DC-10 because of their excellent flame retardance and low smoke emission. Their excellent flame retardance promoted interest in understanding the mechanisms behind the degradation of phenolics. To understand the flame retardance of phenolics it is important to consider the degradation pathways in both oxygen (oxidative degradation) and in an inert atmosphere (thermal degradation). (Madorsky and Straus, 1964) studied the mechanisms and kinetics of the thermal degradation (without oxygen) of cured phenolic resoles. In the study the phenolic materials were pyrolized in a vacuum at several different temperatures ranging from 355°C to 1200°C to analyze the mechanisms of degradation as a function of temperature. The apparatus used in the test was capable of collecting the volatiles given off during pyrolysis in three separate fractions: (Knop and Pilato, 1985) material volatile at the pyrolysis temperature but not at room temperature, (Hshieh and

Beeson, 1997) material volatile at room temperature, and (Sunshine, 1973) material volatile at -190°C. Each fraction as well as the char were analyzed to help understand the mechanisms of thermal degradation. At lower temperatures the main products of degradation were propanols, acetone, propylene, butanols and only a small amount of carbon dioxide. However, at higher temperatures (800 and 1200°C) significant amounts of carbon monoxide as well as methane were produced. These products could be formed from a complete breakdown of the benzene ring occurring at high temperature.

It was hypothesized that such a degradation pathway could lead to free radicals capable of stripping the residue of hydrogen and oxygen leading to a more carbonized char. From the analysis of the the char, 99.2 % carbon after pyrolysis at 1200°C was estimated. Molecular weight analysis of the fraction volatile at the pyrolysis temperature but solid at room temperature indicates cross-linked phenolic fragments with an average of three to four benzene rings per chain. Based on the results of pyrolysis, Madorsky suggested that the primary mechanism for thermal degradation of phenolics is thermal scission at the bond between the methylene and the phenolic ring. In addition to thermal degradation, oxidative degradation is important to understand the mechanisms of flame retardance of phenolics. (Conley and Bieron, 1963) investigated the low temperature (100 to 200°C) oxidative degradation of phenolics using infrared spectroscopy.They observed no changes in the infrared spectra with heating fully cured phenolic resin in either nitrogen or vacuum up to 200°C for 50 hours, suggesting no degradation. However at the same temperatures in air several changes in the infrared spectra were observed. Therefore, (Conley and Bieron, 1963) concluded that "the initial degradation is dependent on the presence of oxygen and that the products of degradation are oxygenated species. In the temperature range investigated (100 to 200°C) the rate of oxidation increased with increasing temperature, however the mechanism was unchanged.

In addition, no differences were observed between the infrared spectra of the degradation of resoles compared with that of novolacs. This similarity between the resole and novolac degradation pathways was also shown to be true for the high temperature degradation of phenolics (Lochte *et al.*,1965). Conley and Bieron (1963) went on to show that the oxidation observed at these temperatures was a surface phenomenon. After a detailed analysis of the changes in functional groups in the IR along with some chemical analyses, a mechanism for the low temperature thermal degradation of phenolics was proposed.

Jackson and Conley, (1964) investigated the high temperature (greater than 200°C) oxidative degradation of phenolics using infrared spectroscopy, vapor phase chromatography, as well as thermogravimetric and X-ray analysis. The major volatile products of extended oxidation of the resin were carbon dioxide and carbon monoxide. However, water, paraformaldehyde, methane, and aromatic products were also produced. Water and paraformaldehyde were major products at temperatures up to 400°C, which suggests a high temperature post-curing reaction. These products could be the result of the loss of methylol groups. However, this reaction should be minor for fully cross linked resins. This high temperature post curing reaction imparts improved oxidative stability and resistance to thermal pyrolysis due to the complete crosslinking of the resin.

Jackson and Conley proposed three types of degradation mechanisms (oxidative degradation, fragmentation, and formation of benzoid species) to account for all the observed products produced during high temperature oxidative degradation. The first describes the oxidative degradation of phenolics in generalized form, which accounts for the production of carbon monoxide and carbon dioxide. The second accounts for the formation of methane, phenol, cresol and other methyl substituted species by radical bond rupture during thermal pyrolysis. And the third one accounts for the formation of benzene, toluene, benzaldehyde, and methane as a result of loss of the hydroxyl from the phenolic species generated in first and second.

Although products from both oxidation and thermal pyrolysis (fragmentation) were observed at high temperatures, oxidative degradation is the predominant mechanism for the degradation of phenolics. Lochte *et al*., (1965) suggested that "the resin itself can act as an oxygen source for the oxidative process. The hydroxyl radical produced in third way can act as the source of oxygen for further oxidation.

Jackson and Conley (1964) studied the mechanisms of char formation at higher temperature and found that the degradation mechanisms of the char Infrared analysis of the char indicated the appearance of hydroxyl and carbonyl groups at 700°C. In addition, gas chromatograms of the volatile components indicated that carbon monoxide is produced only at elevated temperatures and is produced simultaneously with the formation of graphite like char. Infrared analyses indicated that the char formation reactions proceed through the initial formation of quinone-type species. Elemental analysis indicated a drastic loss of oxygen from the char at temperatures above 450°C, confirming the production of carbon monoxide during char formation (Lochte *et al*,1965).

The proposed mechanism of char formation is consistent with the appearance of hydroxyl and carbonyl groups at 700°C as well as the production of carbon monoxide at higher temperatures. Based on these degradation studies Lochte suggested that "the elevated temperature degradation is fundamentally associated with the chemical stability of the dihydroxydiphenylmethane unit (Lochte *et al*, 1965).

The Incorporation of phosphorus into phenolic resins to improve flame retardance. (Sunshine, 1973) to phenolic is directly related to their structure and thermal degradation mechanisms. The production of a structural char, as explained above, results in remarkably low flame spread rates. In addition, they have low smoke production and low toxicity of the smoke produced due to the low carbon monoxide production during degradation. They have significantly less carbon monoxide, hydrogen chloride, and hydrogen bromide production than flame retardant polyester resins.

2.4.0 Chemistry of Phenolic Resin

Phenolic materials have extensive industrial importance due to their high flame retardance and low cost .Phenolic thermosets were the first major plastic materials used by industry. They are still among the most widely used thermosets because they are some of the lowest-cost engineering material on a cost-per-volume basis. Applications range from construction to electronics and aerospace. Phenolic are formed from the condensation polymerization reaction between phenol and formaldehyde. The condensation reaction for phenolics can be carried out under two different conditions, resulting in two different intermediate materials. One of the intermediates is called resoles and the other novolacs (Kaith and Ashish, 2008). The reaction mechanism to form the prepolymers is controlled by the pH and the reactant ratio of phenol to formaldehyde. In strongly acidic conditions with an excess of phenol, novolac s are formed; whereas in basic conditions with an excess of formaldehyde, resoles are formed. Novolacs are soluble and fusible, and require an external curing agent, such as hexamethylenetetramine (HMTA), to form the phenolic networks. On the other hand, resoles will crosslink with heat to form insoluble, infusible networks (Young and lovell, 1991).

2.4.1 Resole Chemistry

Resoles are prepared under alkaline conditions with an excess of formaldehyde. The ratio of phenol to formaldehyde ranges from 1:1 to 1P:3F (Sheng, 2010). The mechanism of the phenol formaldehyde reaction is a base catalyzed electrophilic aromatic substitution to form a combination of the mono, di and trihydroxymethylphenols (Figure 2.1). These hydroxymethylphenols are then reacted to form the prepolymers. There are two distinct pathways of prepolymer formation that depend on pH and temperature (Figure 2.2.). The first pathway, which leads to dihydroxydibenzyl ether, is more predominant under neutral to weakly acidic conditions and at temperatures less than 130°C. At higher temperatures dihydroxydibenzyl ether will eliminate formaldehyde to produce dihydroxydiphenylmethane. The second pathways, which leads to dihydroxydiphenylmethane, is predominant under alkaline conditions and temperatures between 130 and 150°C. At temperatures greater than 150°C many other side reactions are present (Young and Lovell, 1991).

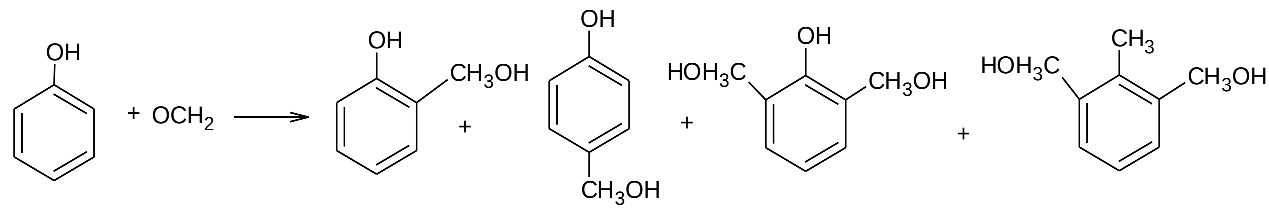


Figure 2.1 : Base catalyzed reaction of phenol with formaldehyde

Once the prepolymers are formed the resole resin can be crosslinked with heat. Usually a pH of 9 or greater and temperatures between 130 and 180°C are used. In order to prevent premature curing the resins should be stored under cold conditions. The prepolymers are heated to promote crosslinking of the resin by further reaction of hydroxymethylphenols. Water and formaldehyde are produced and volatilized during curing (Figure 2.2.). This release of volatiles results in networks with asignificant amount of voids that detract from the mechanical properties.

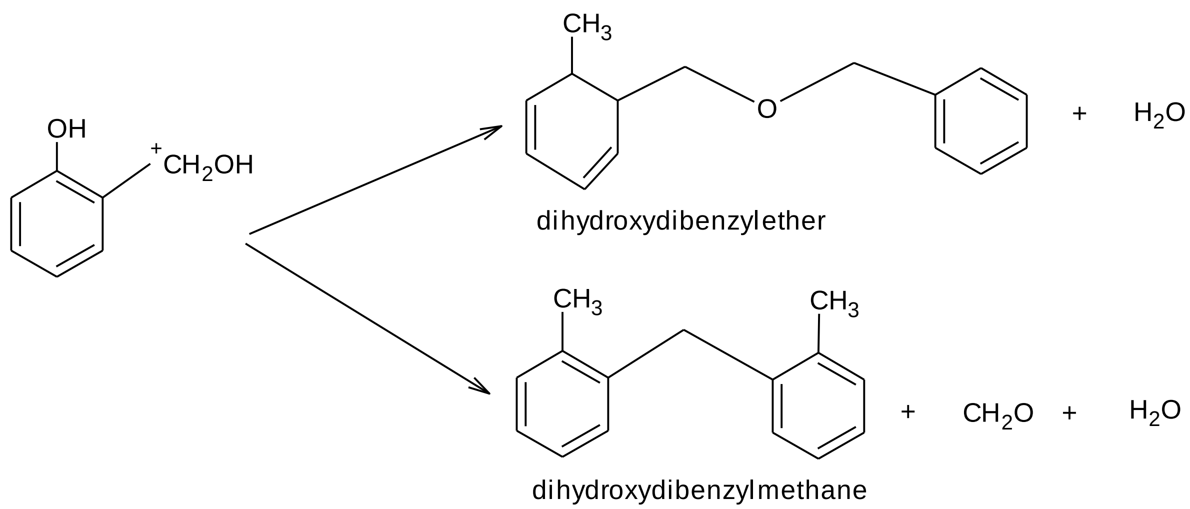


Figure 2.2 : Prepolymer formation

2.4.2 Novolac Chemistry

Novolacs are prepared under acidic conditions with an excess of phenol. This procedure produces relatively linear chains with molecular weight typically between 500 and 1000g/mol. The catalyst most frequently used are oxalic acid, hydrochloric acid, sulphuric acid, or phosphoric acid. Most commonly, oxalic acid is preferred because resins of low colour may be prepared. In addition, oxalic acid decomposes at high temperatures to CO_2, CO and water, which facilitates the removal of the catalyst thermally about, 1-6 weight % is used. Cross-link novolacs are processed together with curing agents, mainly hexamethylenetetramine. Cross-linking occurs at a sufficient rate at 140 to 160^{o}C and can be carried out within a few minutes, particularly if a part of the polycondensation reaction has already taken place. The use of nololacs which are not cross-linked is less important and is based particularly on their solubility and compatibility properties. As polyakyllidenephenols they have strong inter- and intramolecular interactions and can be adapted to the most varying requirements by alkyl substitution (Collins 1973; Christy, 2000).

The novolacs are formed by reacting phenol and formaldehyde in an acid solution but with insufficient formaldehyde to complete the reaction at 100^{o}C (the opposite of forming resoles). About one mole of phenol is reacted with 0.7 to 0.85 mole of formaldehyde. This is the first stage of the reaction and a brittle thermoplastic resin is produced which can be melted but cannot crosslink to form a solid network. The addition of hexamethylenetetramine (hex), a basic catalyst, to the firs t stage phenolic resin makes it possible to create methylene cross linkages to form a thermosetting material. When heat and pressure are applied to the hex-containing novolac resin, the hex decomposes, producing ammonia which provides methylene cross linked to form a network structure. On account that hexa, a second material, must be added to novolacs, they are called two-stage resins. The temperatures require for the cross-linking of the novolac resin ranges from 120 to 177°C. The various fillers used can vary from 50 to 80% by weight. The fillers reduce shrinkage during molding, lower cost and improve strength (Collins 1973; Knop and Pilato, 1985; Christy, 2000; Sheng, 2010).

Novolacs are mixtures of isomeric polynuclear phenols of various chain lengths with an average of five to six phenolic nuclear per molecule. They contain no reactive methylol group and consequently cross-link and harden to form infusible and insoluble resins only when mixed with compounds that can release formaldehyde and form methylene bridges (such as paraformaldehyde or hexamethylenetetramine). As with novolacs, the methylolphenols formed condense with more phenols to form methylene-bridge polyphenols. The latter, however, quickly react in an alkaline system with more formaldehyde to produce methylol derivatives of the polyphenols. In addition to this method of growth in molecular size, methylol groups may interact with one another, liberating water and forming dimethylene ether links (CH_2-O-CH_2). This is particularly evident if the ratio of formaldehyde to phenol is high. The average molecular weight of the resins obtained by acid condensation of phenol and formaldehyde decreases hyperbolically from over 1000 to 200, with increases in the molar ratio of phenol to formaldehyde from 1.25:1 to 10:1 (Gardziella *et al.*, 2000 ; Sheng, 2010).

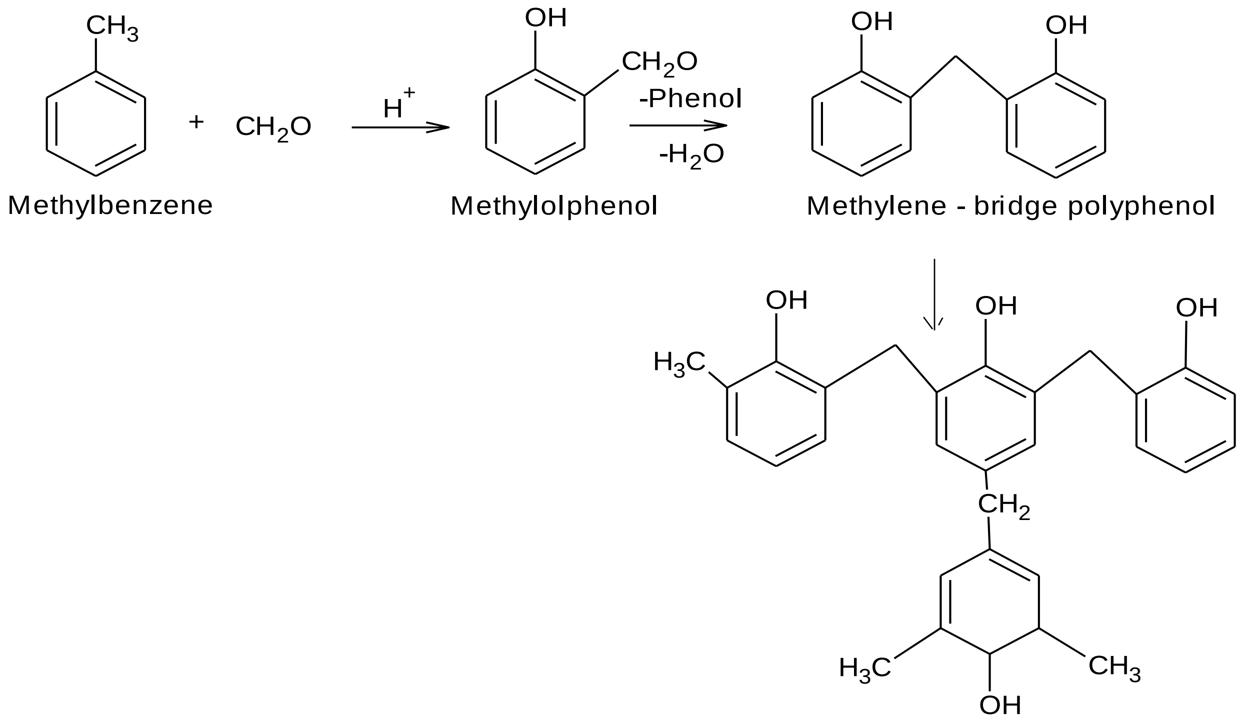


Figure 2.3 : Novolac prepolymer preparatic

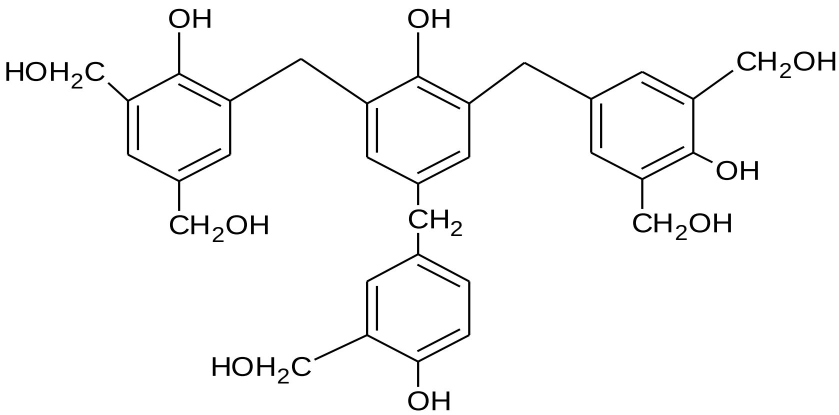


Figure 2.4 : Representative structure of a resol

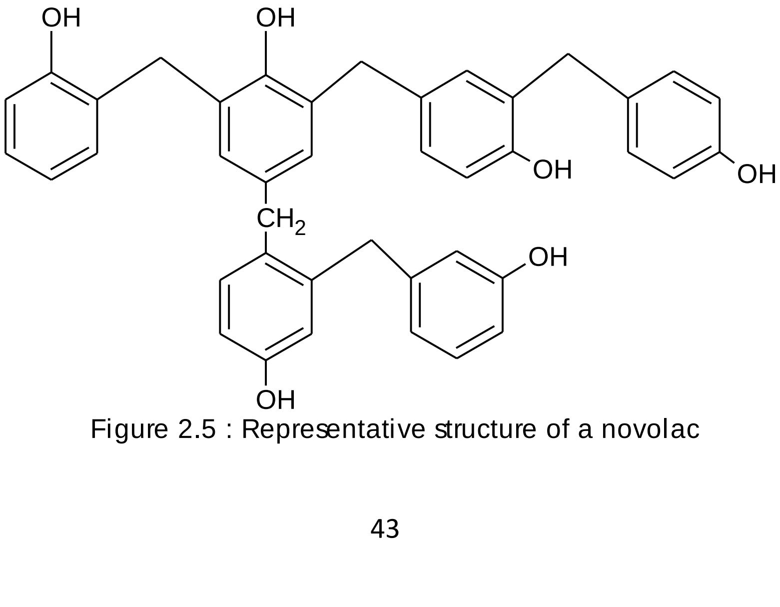


Figure 2.5 : Representative structure of a novolac

2.5.0 Reaction of Phenol-Formaldehyde Novolac Resin and Hexamethylenetetramine

The reaction of hexamethylenetetramine (HMTA) with phenol-formaldehyde novolac resin (PFNR) has been studied in different papers in the past (NIOSH, 1994; Cardoso and Pererare 1999; Sakiara *et al.*, 1999). Of particular interest is the release of the gaseous products during the curing process and the way to minimize it at the technological operations (Bricker and Varl, 1950). The curing mechanism of the PFNR with HMTA is described in details using different classic methods (1R, Spectroscopy, DTA, TG, ‘H NMR, ^{13}C NMR, GPC) measurements etc (Feigl, 1966; Pickard and clark, 1984; Georghiou *et al.*, 1989; NIOSH, 1995). The different transient intermediates of this interaction in solid state were specified (Georghiou., 1989). The earliest appeared product of the model reaction between phenol and HMTA as designated by (Sakiara, 1999) has been found at 103^{o}C to be benzoxazine. In another study by (Cardoso and Pererare, 1999) it was suggested that during the curing process at higher temperature (up to 150^{o}C) the reaction passes throughout benzylamine to form in a presence of excess of phenol a cross-linked structure with the evolution of ammonia.

Further investigations has shown among the variety of transient intermediates the prevateme of the benzoxazine ones (Georghiou, 1989; Sakiara, 1999) especially in the presence of free phenol. It has been reported by (Mosiewickki, 2004) composite made from tannin, pinewood flour reinforced with HMTA hardener before the filler leads to inhomogeneous materials, with gel-like lumps of resin.

2.5.1 Synthesis of Hexamethylenetetramine (HMTA)

HMTA used for cross linking novolac or catalyzing resole synthesis is prepared by reacting formaldehyde with ammonia Figure 2.6. The reaction is reversible at high temperatures, especially above 250^{o}C. HMTH can also be hydrolyzed in the presence of water (Sheng, 2010).

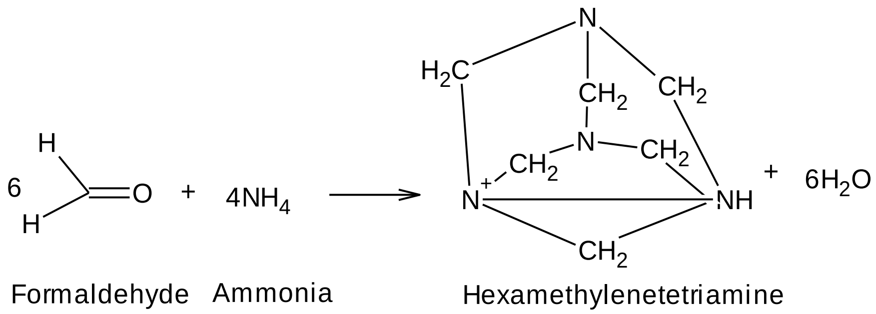


Figure 2.6 : Synthesis of HMTA

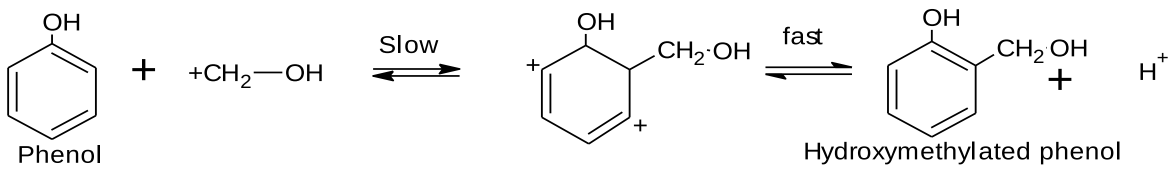
2.6.0 Ssynthesis of Novolac Resin

Novolac oligomers are prepared in acidic media using an excess of phenol over formaldehyde Figure 2.3. The mechanism associated with this reaction can be described in four steps Figure 2.7. First, a methylene glycol is protonated by an acid to form the reaction medium, which then releases water to form a hydroxymethylene carbonium [step-1].

1) $$HO{\cdot}CH_2\text{-}OH + H^+ \rightleftharpoons {}^{+}CH_2{-}OH + H_2O$$

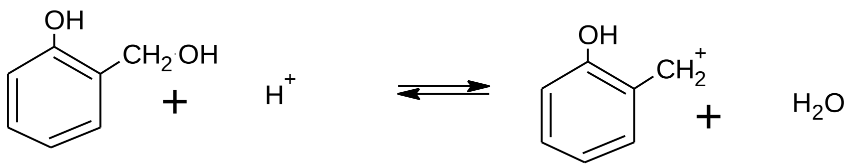
This ion acts as a hydroalkylating agent by reacting with phenol via electrophilic aromatic substitution. The rate determining step of the sequence occurs in [step-2].

2)



A pair of electrons from the benzene ring attacks the electrophile, followed by deprotonation and a gain of aromaticity. The methylol group of the hydroxymethylated phenol is unstable under acidic conditions and looses water readily to form a benzylic carbonium ion [step-3].

3)



This ion then reacts with another phenol to form a methylene bridge in another electrophilic aromatic substitution in the ortho and para position [step-4].

4)

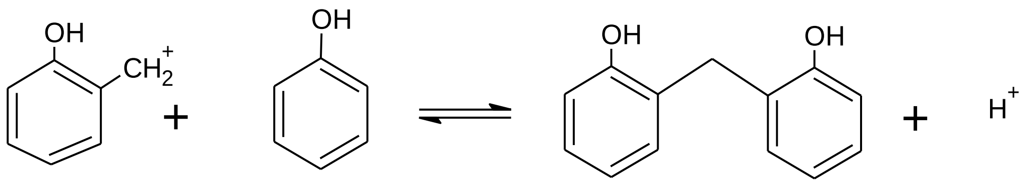


Figure 2.7: (step1, 2, 3, &4) Mechanism of novolac synthesis via electrophilic aromatic substitution.

This major process repeats itself until the formaldehyde is exhausted (Pizzi *et al*, 2003). These prepolymers are thermally stable and can be stored effectively. Novolac cross linking is usually achieved by introducing a source of methylene groups to form additional methylene bridges between aromatic rings. Hexamethylenetetramine [HMTA] is the most widely used curing agent [source of formaldehyde] for these reactions (Sheng, 2010).

2.6.1 Mechanism of Synthesis of Novolac Resin

In the formation of novolac substitution and condensation reaction occur simultaneously. In large reaction vessels formaldehyde is metered to a phenol catalyst mixture and the rate of addition is controlled depending on the heat evolved for safety reasons. When using small vessels, even under laboratory conditions, care must be taken, because of the exothermic reaction. Phenolic resins are the polycondensation products of the reaction of phenol with formaldehyde. Phenol resins were the first true synthetic polymers to be developed commercially. Phenols condense initially with formaldehyde in the presence of either acid or alkali to form a methylolphenol or phenolic alcohol, and then dimethylolphenol (Knop and Pilato, 1985; Sheng, 2010).

The initial attack may be at the 2-, 4-, or 6-position. The second stage of the reaction involves methylol groups with other available phenol or methylolphenol leading first to the formation of linear polymers (Cascaval. *et al* .,1994) and then to the formation of hard-cured, highly branched structures .three reactive sites for electrophilic aromatic substitution are available on phenol which give rise to three types of linkages between aromatic rings, i.e, ortho – orho, ortho –para, and para- para. The complexity of the isomers leads to amorphous material. For novolac chain with ten phenol groups 13,203 isomers (Megson, 1972), can statistically form, making the separation of pure phenolic compounds from novolacs only impossible.

2.6.2 Curing Behavior in the Synthesis of Novolac

The curing agent or hardener is a substance added to a plastic composition to promote or control the curing action, or a substance added to control the degree of hardness of the cured film (Nabi. and Jog, 2004) . Novolacs are mixtures of isomeric polynuclear phenols of various chain lengths with an average of five to six phenolic nuclei per molecule. They contain no reactive methylol groups and consequently cross-link and harden to form methylene bridges (such as paraformaldehyde or hexamethylenetetramine). Novolac resins which are thermoplastic in nature must generally be cured by addition of cross-linking agents a formaldehyde source. The most widely used curing agent is hexamethylenetetramine (HMTA or hexa). Paraformaldehyde or trioxane is of only limited importance. Most commonly 5 to 15 weight % of HMTA is used. The properties of cured parts are determined to a great extent by the ratio of the two reactants.

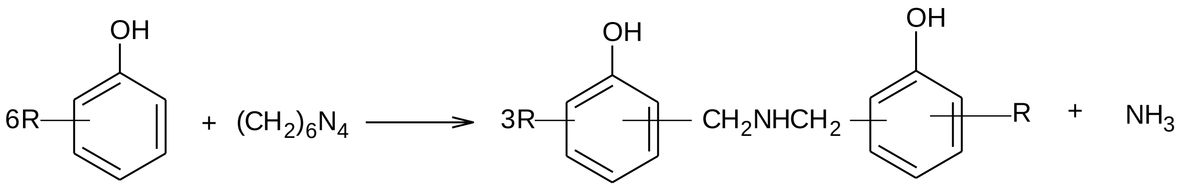


Figure 2.8 : Novolac Crosslinked With HMTA

The iniatial cure reaction of a novolac with HMTA were studied by heating reactants at 90°C for 6 hours, then rising the temperature incrementally to a maximum of 205°C. This leads to mostly hydroxybenzylamine and benzoxazine intermediates Figure 2.9 (Sojka *et al.,* 1981). Hydroxybenzylamines formed via repeated electrophilic aromatic substitutions of the active phenolic ring carbons on the methylenes of the HMTA (and derivatives of HMTA). Since, novolac resins form strong intermolecular hydrogen bonds with electron donors, a plausible mechanism for the initial reaction between novolac and HMTA involves hydrogen and nitrogen between phenolic hydroxyl groups and an HMTA nitrogen. Such hydrogen bonding can lead to proton transfer where a phenolate ion is generated. A negatively charged ortho or para carbon can attack the methylene of a C-N bond. Benzoxazines form by nucleophilic attack of the phenolic oxygen on HMTA-phenolic intermediates, upon further reaction, methylene linkages form as the major product of both types of intermediates through various thermal decomposition pathways (Megson, 1972; Sheng, 2010).

Since a small amount of water is always present in a novolac resins, it has also been suggested that some decomposition of HMTA proceeds by hydrolysis, leading to the elimination of formaldehyde and aminomethylol compounds step 1 and 3, Figure 2.7 (Ogata and Kawasaki, 1977) phenolic can react with the formaldehyde elimination product to extend the novolac chain or form methylene bridged intermediates in combination with formaldehyde to produce ortho or para-hydroxybenzylamines (i.e. Mannich type reaction Figure 2.22).

The hydrolysis of HMTA leads to aminomethylated products and formaldehyde. These aminomethylated products, formaldehyde and dihydroxydiphenylmethane undergo a Mannich type reaction Figure 2.22. Substituted benzoxazines and benzylamines are the major first-formed intermediates produced during the curing process, further reaction of these intermediates leads to a highly cross-linked network (Christy 2000; Zhang, 2007; Sheng 2010).

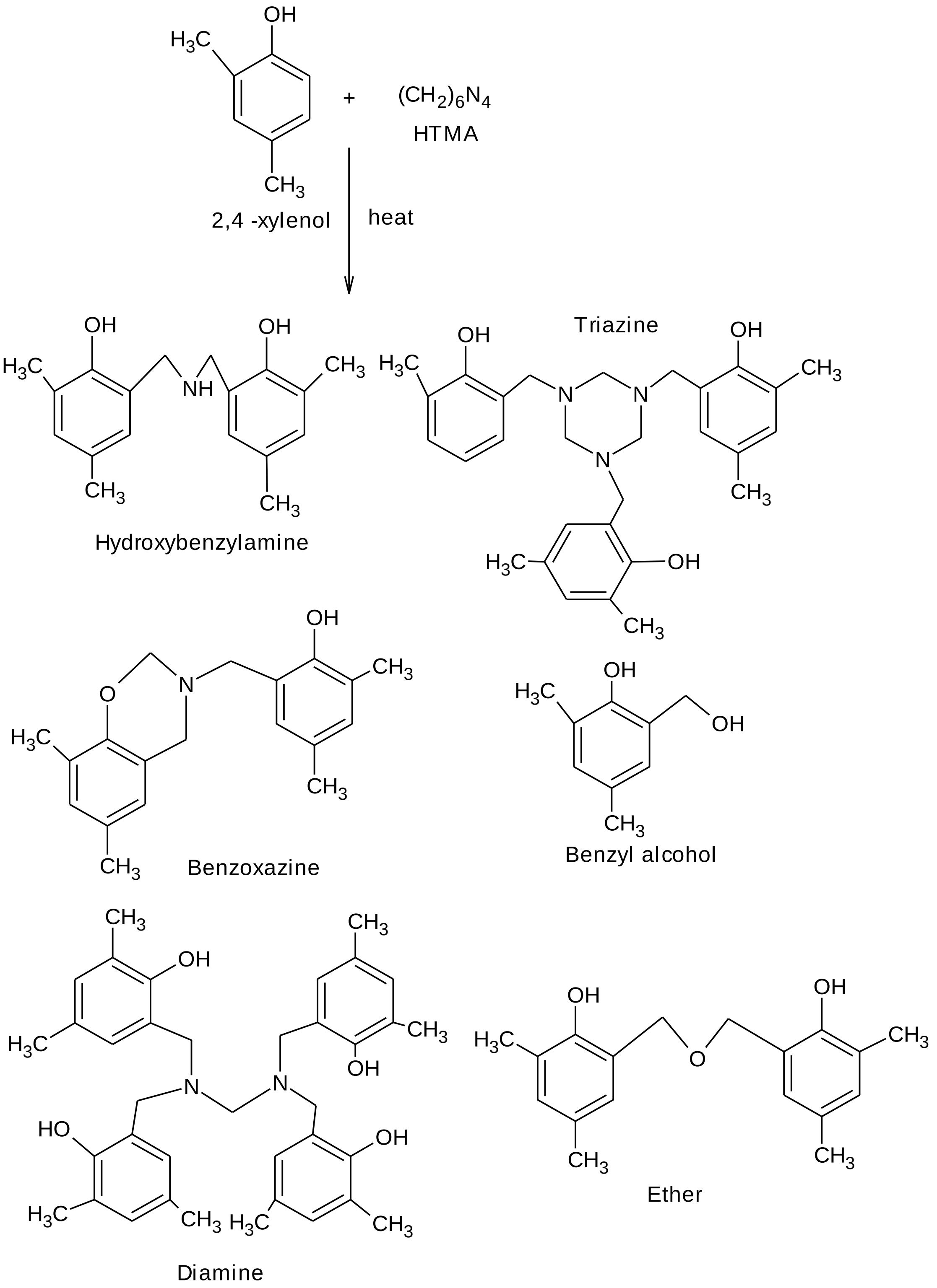


Figure 2.9 : Reaction intermediates proposed from the model study of the reaction of 2,4 -xylenol and H

A model study of the reaction of 2, 4-xylenol with HMTA was performed by (Zhang *et al.*, 2007) to investigate the Novolac/HMTA reaction mechanism. Several reaction intermediates including hydroxylbenzylamines, benzoxazines, triazines, diamines and in the presence of trace amounts of water, benzylalcohols and ethers were proposed Figure 2.9. However, curing reactions employing HMTA produce several volatile side products, including ammonia gas. The evolution of volatiles results in voids in the networks, although Novolac/HMTA networks demonstrate this phenomenon to a lesser extent than resole networks (Sheng, 2010).

2.7.1 Synthesis of Phenol (Novolac/Resole) Phenolic Oligomers

The most common precursor to phenolic resins is phenol. Substituted phenols such as cresols, p-tert-butylphenol, p-phenylphenol,resorcinol, and cardinal (derived from cashew nut shells) have also been used as precursors for phenolic resins.The so called “natural” phenol is obtained by the destructive distillation of coal or from wood tar and also from petroleum and organic matter of vegetable origin. Benzene (from petroleum by cracking) is alkylated with propylene through acid catalyst to produce cumene. More than 98% of phenol is produced via the cumene process developed by (Gardziella *etal*.,; Sheng, 2010) Figure.2.10.

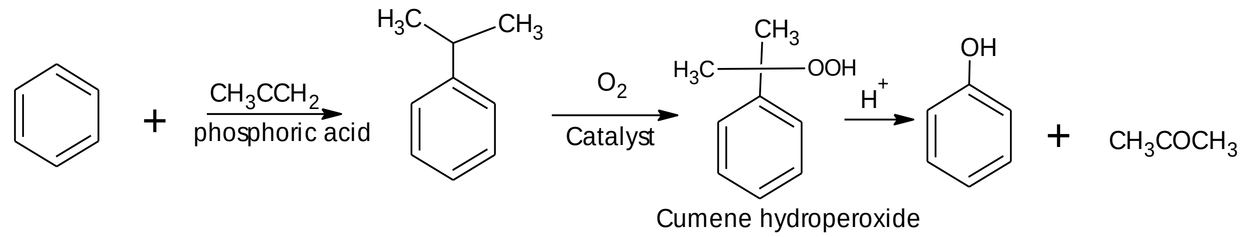


Figure 2.10 : Preparation of phenol monomer

The cumene is then oxidized to cumene hydroperoxide by air in the presence of an alkaline catalyst, and the hydroperoxide is cleared with an acid catalyst to phenol and acetone.Substituted phenol derived from cashew nutshells such as cresols, p-tert-butylphenol, p-phenylphenol, resorcinol, and cardanol have also been used as precursors for phenolic resins which are compatible with many oils, natural resins and rubbers (Sheng, 2010). Such alkylphenolic resins are used as modifying and cross linking agents for the oil varnishes, as coatings and printing inks, and as antioxidants and stabilizers.

2.7.2.0 Analytical Methods for Phenol Determination

Analytical techniques commonly used in the determination of phenols are High-Performance Liquid Chromatography [HPLC] with Reverse Phase [RP] Column technology and Capillary Electrophoresis [CE] in combination with detection [UV] Electrochemical detection or Mass Spectrophometry /Mass spectrometry (MS) (Kwade *et al.*,1994; Bagheri,1993). Liquid chromatography/mass spectrometry [LC – MS] has been widely accepted as the main tool in identification, structural character and quantitative analysis of phenolic compounds. Gas chromatography (CGS) is another technique applied for the separation, identification and quantification of phenolic compounds such as phenolic acids condensed tannins (Shadkami, 2009) and flavonoids (Proestos *et al.,* 2006). The major concerns of GC analysis, not applicable to HPLC techniques, are the derivation and volability of phenolic compounds with GC, quantification of phenolics from food matrices may involve clean-up steps such as liquid removal from the extract, release of phenolics from the glycoside and ester bonds in enzymatic [Liggins, 1998), alkaline (Siess, 1996) and acidic (Wang *et al.,* 2000] media and chemical modification steps, such as transformation to remove volatile derivatives (Liu and Prosek, 2005).

Principally standard methods for qualitative phenol measurement are high performance liquid chromatography [HPLC], electrochemical capillary electrophoresis [CE], gas chromatography [GC] and colorimetric spectrophotometer. Analytical methods for phenolic acids using LC coupled to MS detection is an emerging field. (Giocchim *et al.,* 1989), developed a method for the determination of phenolic acidic in wheat, oat, bran, and cornmeal, using HPLC – MS with an electrospray interface [ESI]. HPLC with the reverse phase [RP] column is the most widespread chromatography technique in the investigation of phenolic acids. Photodiole away allowing for real time UV –V is spectra are the most prevalent detection method. Other technique methods are electrochemical and fluoremetric (Sandner, 2001).

The other versatile chromatography technique used to analyse and identify phenolics is supercritical fluid chromatography [SFC]. Compare to the techniques, SFC has high separation efficiency, high – resolution power, short analysis time, is environmentally friendly and is compatible with different types of detections (Rebecca and Robbins 2003; Lin-Zhang *et al.*, 2005; Ali *et al.,* 2013).

2.7.2.1 Derivatization Methods

Phenolic derivatives are among the most important contaminants present in the environment. These compounds are used in several industrial processes to manufacture chemicals such as pesticides, explosives, drugs and dyes. However, phenolic compounds are not only generated by human activity, but they are formed naturally e .g during the decomposition of leaves or wood. Recently, the determination of such compounds has been paid much attention, and a variety of analytical methods have been reported. The hyphenation of gas chromatophy (GC) and mass spectrometry (MS) has proven powerful for phenolic compounds assay (Kuklenyi, 2004), the cost is generally high. For only GC based analysis the poor polarity and insufficient sensitivity of phenols are troublesome (Tashkov *et al.,* 1991; Khoschsorur and Petek, 2000), so that, chemical derivation, such as silylation (Pyon, 1997) and esterification (Kezic *et al.,* 2000) is necessary, however on the consumption of large amount of sample. Direct detection of these compounds by high – performance liquid chromatography (HPLC) is also difficult because they lack appropriate spectroscopic properties (Asan, 2003) .Therefore, suitable derivatazation is also required (Wada *et al.,* 1999; Tsuruta, 2000).

One chemical characteristic of the hydroxyl group in phenol is the hydrogen bonding capability, which increases the melting group. Analysis in the gas phase requires a chemical modification step, often referred to as derivatization, which is time - consuming, but the derivatives can sometimes be determined at more selective ways. This require sample treatment, clean – up, and preparation. The hydroxyl groups in phenol are converted to esters or ethers. There are a variety of reagents used to modify and generate volatile derivatives. Diazomethane is often used for the generation of methyl esters (Rebecca, 2003). Huset *et al.*, (1997) employed ethyl and methyl chloroformate for the formation of ethyl and methyl esters, respectively.

2.7.2.1.0 Spectrophotometric Methods

2.7.2.1.1 4 – AAP [4 – aminoantypyrine] Spectrometry method

It is the most common optical determination methods for phenols in water. The 4 – AAP methods depends upon the purplish red colour obtained on reacting 4 – AAP with phenols in the presence of potassium ferricyanide (oxidant) in the medium of basic buffer solution ($NH_2.NH_4CI$, pH = 10.0) Figure 2.11.

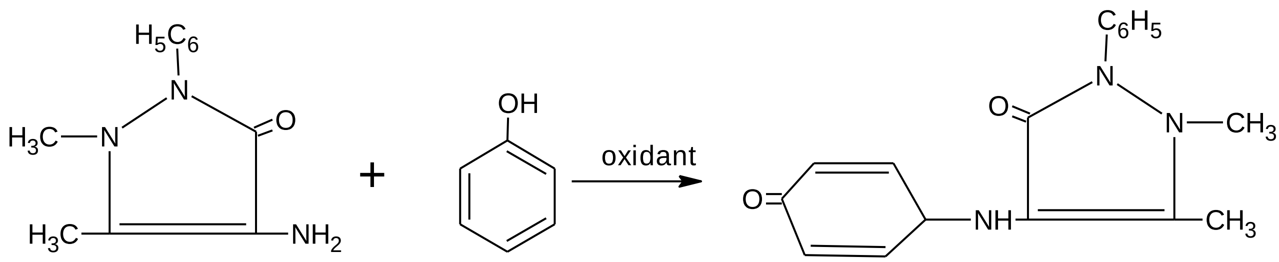


Figure 2.11 : 4 - AAP Spectrophotometry method of determination of phenol

The coupling of aminoantipyrine with phenol takes place in the para position rather than in the ortho position. When the para position is blocked by an alkyl, aryl, ester, nitro, benzoyl, nitrous, or aldehyde groups, no colour reaction take place even though the ortho position is unsubstituted. Chloroform is used to extract the purplish product. The conclusion drawn by (Elsenstsedt, 1943), there must be at least, one free phenolic hydroxyl group in the molecule for a positive test. Phenols in the range of 0.1 to 5.0 mg/l can be determined using this method. The sensitivity of the method is 50 times as many as direct spectrophotometry. Estimation of phenols by the 4-aminoantipyrine method ll products from para-Susttuted Alkylphenols was developed by Peter and Johnson (1973). 4-Aminoantipyrine reacts with p-alkylphenols on oxidation with potassium ferricyanide to give yellow ortho – quinoneimides. These undergo a thermal and based-catalysed rearrangement to benzodihyro oxozepines.

2.7.2.1.2 Berthelot's Reaction Spectrophotometry Tao [1983] Method

In this method ammonia reacts with phenol and hydro chlorite in alkaline medium to produce indophenol which is blue in colour Figure 2.12. The intensity of the blue colour produced is proportional to the amount of ammonia present in the water or effluent sample.

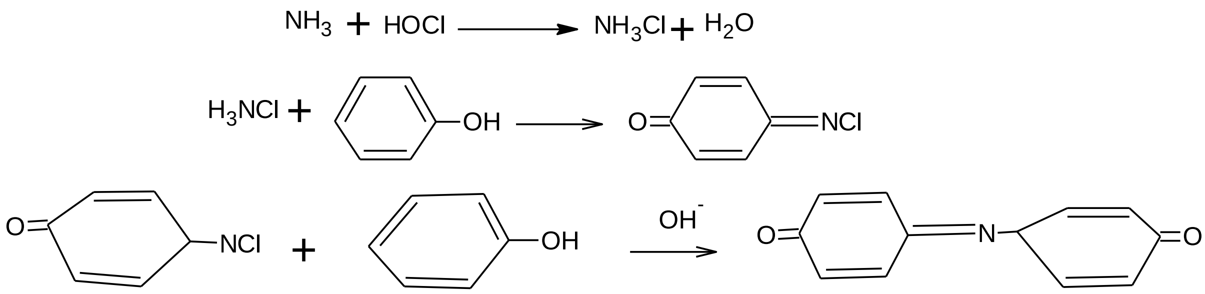


Figure 2.12 : Berthelot's Spectrophotometry method of determination of phenol

The reaction was first used for determining micro ammonia in water . Tao, (1983) used the method to determine micro phenols in water. The procedure involves the use of aminochloride as oxidative reagent for colour developing and sodium nitroprussiate as catalyst. Volatile phenols are also determined by this method. Recently, the Berthelot colour reaction has been applied by measurement of urea nitrogen in urease-treated serum. A blue dye is formed by ammonia in the presence of sodium phenate and sodium nitroprusside. A new approach to indophenol blue spectrophotometry method in determination od ammonia in geothermal waters with high mineral content were modified by (Nikolaos *et al.*, 2010). Spectrophotometric determination of cyanide based on Berthelot reaction was also developed by Deepa and Nagaraja, (2007).

2.7.2.1.3 MBTH [3 – methyl – 2 – benzothiazolylzone] Method

Hunig, 1957 first advanced that phenols were determined by using MBTH (3 – methyl – 2 – benzothiazolylzone) as colour developing reagent Figure 2.13.

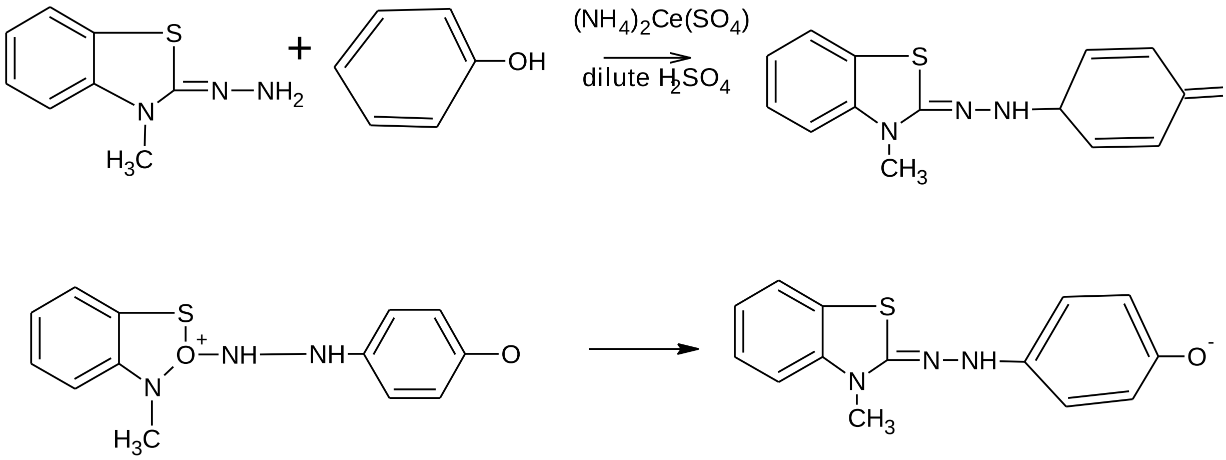


Figure 2.13 : MBTH Spectrophotometry determination of phenol

Kamata, (1966), applied the above – method to determine the phenolic derivatives. The method is also used for determining in phenols in Flow Injection Analysis (FID) . Lei, (1974) studied the method and used it for determining phenol and parachloro phenol. The procedure is: after 5 min when phenols in sewage reaction with MBTH solution in colouring tube, solution of cerium sulfate is added as the oxidant, the content of volatile phenols is determined at the wavelength of 520nm in the medium of neutral buffer solution made up with NaOH, EDTA, and H_3BO_3, while the colour developing time is 15min. the detection limit of the method is 0.01mg/L.

2.7.2.1.4 UV – Derivative Spectrophotometry [UVDS] Method

Talsky, (1983) received an important application of High – Order Derivative Spectrum (HODS) in environmental analysis of phenols and anilines in wastewater can be determined simultaneously by using HODS. Cheng, (1996) studied an experimental method by which micro phenols in waste water can be determined. Wang, (1990) studied the determination of phenolic compounds in oil refining wastewater by UV – 4th order derivative spectrum (4 – ODS) in the medium of 1mol/L HCI solution. (Li, 1994) studied the determination of phenolic compounds in many types of detection were reported by many scientist (Yuan, 1998).

2.8. Determination of Free Phenol in Polymer Composite

Gas chromatography (GC) is the major chromatographic technique employed for the analysis of phenol compounds. The method was typically performed with flame ionization detection [FID] (Young, 2013). The major concerns with this technique is the low volatility of phenol compound s. Free phenol in polymer composite was determined by gas chromatography using a Varian 3400 chromatography with a Flame Ionization Detector [FID] and helium as carrier gas. An HP-INNOWAX (cross linked polyethylene glycol) high performance capillary with certain dimension was used (Ida and Marjor, 2005).and the method of high performance liquid chromatography (HPLC) was determined by (Hui Pan *et al.*, 2003).

Analysis of free phenol in liquefied bark was conducted using HPLC with a UV detector set at a wavelength of 254 nm.(Jung-Uk Lee and Young Sung OH, 2010). The percentage free phenol was determined by (Koppesechaar, 2005) method as described in ATMD 1312. The method is also called bromated-bromide or bromometry method (Ruihang -Lin, 2014). This is to determine free phenol in resins and composite (Sun-Jin, 2014).

2.9.0 Synthesis of Formaldehyde

Since formaldehyde is a colourless pungent irritating gas, it is generally marketed as a mixture of oligomers of polymethylene glycols either in aqueous solutions (formalin) or in more concentrated solid forms (paraformaldehyde). The concentration of formalin ranges between about 37 and 50wt%. And 40% wt aqueous formalin solution at 35^{o}C typically consists of methylene glycols with 1 to 10 repeat units. The molar concentration of methylene glycol with one repeat unit (HO-CH_2-OH) is highest and the concentrations decrease with increasing numbers of repeat units (Dienhm and Hit, 1976). Paraformaldehyde, a white solid, contains mostly polymethylene glycols with 10 to 100 repeat units, it is prepared by distilling aqueous formaldehyde solutions and generally contains 1 to 7wt % water. Formaldehyde is produced on a large scale by catalytic dehydration of methanol. Formaldehyde (methanol) is produced by air-oxidation of methanol in the vapour state over a granulated silver catalysts Fig.2.14.

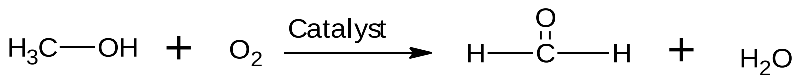


Figure 2.14 : Synthesis of formaldehyde

Other catalyst used for the production of formaldehyde are iron oxide, copper oxide, palladium/cupric chloride and molybdenum oxide. Air is a safe source of oxygen for this oxidation process. Since formaldehyde is a colourless pungent irritating gas, it is generally marketed as a mixture of oligomers of polymethylene glycols either in aqueous solutions (formalin) or in more concentrated solid forms (paraformaldehyde).

Methanol which is the starting reagent for preparing formaldehyde, stabilizes the formalin solution by forming acetal end groups and is usually present in at least small amounts Figure 2.14.

Water is necessary for decomposing paraformaldehyde to formaldehyde. However, water can serve as an ion sink and water-phenol mixtures phase separate as the water concentration increases. Therefore, large amount of water reduce the rate of reaction between phenol and formaldehyde (Dienhm and Hit, 1976 ; Sheng, 2010) .

2.9.1.0 Analytical Methods for Formaldehyde Determination

Several analytical methods have been developed for detecting, measuring and/or monitoring formaldehyde and its metabolites, and further improved to lower the detection units. The most widely used methods for the detection of formaldehyde are Colometry and Spectrophotometry

(Li *et al.*, 2007; Kim *et al.*, 1985; NIOSH, 1994), High-performance liquid chromatography HPLC ISO/TS 17226, 2003; EPA ,1991; ISO16000-4, 2004), Liquid Chromatography (OLiva *et al.*, 2002)), Gas Chromatography-GC (NIOSH, 1994) ; EPA, 8315a ,1996; Sandner *et al.*, 2001), Gas Chromatography/ Mass Spectrometry-GC/MS (NIOSH, 1994; Rivero, 2004), FourierTransform Infrared Spectroscopy-FTIR (EPA, 2004), Flourimetry (Sakai, 2002), Chemiluminesceni (Song *et al.,* 2003), Enzyme Sensors in FIA System (Sakai, 2002), Adsorption Voltammetry (Chan, 1997) (a & b), Thin Layer, Chromatography-TLC and Capillary Electrophoresis (Freige *et al.*,1996).

2.9.1.1 In Situ Methods

For the analysis of formaldehyde (FD) in the outdoor environment, spectroscopic techniques are the most convenient. (Vairavamurthy *et al.*, 1992) have reviewed four in situ monitoring techniques; differential optical absorption spectroscopy (DO AS), Fourier transform infrared absorption (FTIR), laser-induced fluorescence spectroscopy (LIFS), and tunable diode laser spectroscopy (TDLS). Finlayson-Pitts and Pius, (2000) have compared FD detection limits for FITR, TDLS, and matrix isolation. Vairavanmurthy *et al.*, (1965) also pointed out that in situ techniques usually require long optical paths, which makes these methods unsuitable for routine applications. Infrared diode laser spectroscopy was nevertheless used by (Hanoune *et al.*, 2006) for FD measurements at parts per billion (ppb) levels in libraries.

Photoacoustic spectroscopy (PAS) has been used occasionally for the determination of formaldehyde (FD) in door, air (Kniger *et al.*, 1995). However, this method is susceptible to interference and suffers from high detection limits. (Cihelka *et al.*, 2009) used diode lasers in combination with FTIR and photocoustic and achieved detection limits of <100 ppb. Proton-transfer-reaction mass spectrometry (PTR-MS) is based on chemical ionization using H_3O^- as the primary reactant ion. This method has been successfully applied in monitoring FD in outdoor and indoor air, although de (Gouw and Warneke, 2007) state that FD is difficult compound to detect by PTR-MS.

According to Witsthaler *et al.*, (2008) the PTR-MS method is less sensitive to FD than other carbonyl compounds due to the loss of protonated FD resulting from the reaction with water (Hausel, 1997). (Spanell *et al.*, 2008) have applied selected ion flow tube mass spectrometry (SIFT-MS) for the detection of FD in breath gas. (Hak *et al.*, 2005) have made an inter comparison study of four different in situ techniques for ambient FD measurement in urban air. FD concentrations obtained using continuously measuring DO AS, FTIR, and Hantzsch instruments agreed by dinitrophenylhydrazine (DNPH) presented concentrations up to 25% lower.

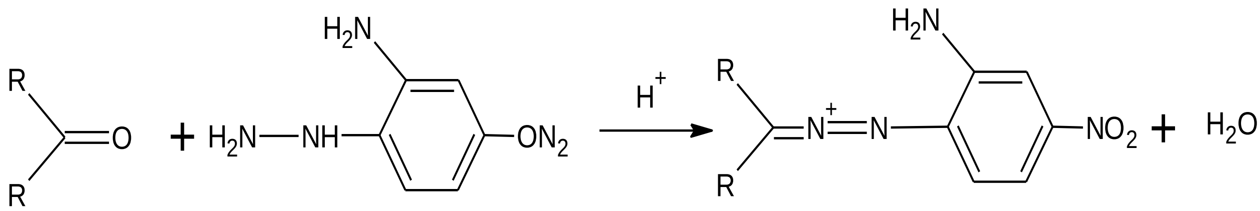
2.9.1.2.0 Derivatization Methods

For indoor applications, batch sampling methods are more convenient. Here, formaldehyde (FD) is trapped in an absorber or on impregnated filters and cartridges. The compound is then reprivatized and the resulting chromophore can be analyzed by chromatography and spectroscopy. However, a common problem is their non-specificity for FD if no chromatographic separation is applied. Different methods for the analysis of aldehydes have been reviewed and discussed by several authors (Vairavamurthy *et al.*, 1992).

For the determination of FD, a number of methods have been proposed so far. In general, in an aqueous environment, most of the proposed methods for the determination of FD require the derivatization with various reagents prior to their measurement, which can form coloured products and can be detected spectrophotometrically.

2.9.1.2.1 [2, 4- DNPH] Method

The (2, 4-DNPH) method by (Sandner e*t al., 2001*) is frequently used for the simultaneous analysis of formaldehyde, other aldehydes, and ketones. In acidic solution, hydrazones are formed from 2, 4-dinitrophenylhydrazine (2, 4- DNPH) by nucleophilic addition to the carbonyl group, followed by elimination of water Figure 2.15.



2,4 -dinitrophenylhydrazine (yellow)

2,4 -dinitrophenylhydrazone (red)

Figure 2.15 : DNPH method of formaldehyde determination

Chromatographic separation of the hydrazones is achieved by means of C_{18} column and water/acetonitrile solvents combinations with binary or tertiary gradients. UV detection is ranging from 340 to 427 nm (Sandner *et al.*, 2001). The method is described in U.S. EPA method TO - 11A, 1999 ; ASTM D 5197, 2003) and accepted as an international by (ISO 1600 – 3, 2001).

2.9.1.2.2 Chromotrophic Acid (CA) Method NIOSH (1994)

Small amounts of formaldehyde and formaldehyde-releasing compounds are commonly analyzed by spectrophotometric methods. Cardoso and Pereira, (1999) and, one of these, the chromotrophic acid (CA) method, especially through its P 4 CAM 125, P 4 CAM 235 (NIOSH, 1977) and 3500 (2) (NIOSH, 1994 ; NIOSH, 1977 and 1994) versions was established as an international reference method for detection of large scale chamber ASTM E 1333, (2002) small scale chamber ASTM D 6007, (2002), and in the desiccator method ASTM D 5582, (2006). Because, it is simple, sensitive, inexpensive and very selective. In the presence of concentrated sulfuric acid, chromotropic acid , (dihydroxynaphthalene- 3, 6- disulfonic acid) reacts with formaldehyde to give a red- violethydiphenylmethane derivative (Pickard.and Clark, 1984), Figure.2.16 .

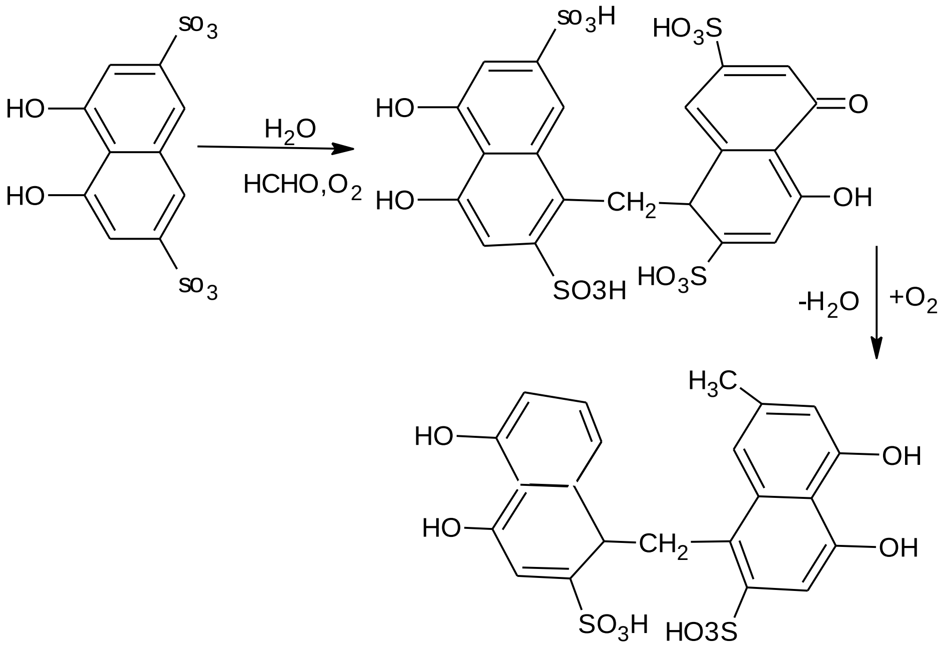


Figure 2.16 : Chromotrophic acid (CA) method of formaldehyde determina

In the second step of the reaction, a violet quinoId oxidation product is formed with atmospheric oxygen. According to (Feigl, 1966), H_2SO_4 participates in both steps as dehydrant and, in the last one also as oxidant, being reduced to sulfurous acid. It is perhaps worth noting that H_2SO_4 rarely acts as an oxidizing agent (Hudlick, 1990). An alternative structure proposed for the chromogen arising from the reaction C.A and formaldehyde is Figure 2.17 (Georghiou, 1989).

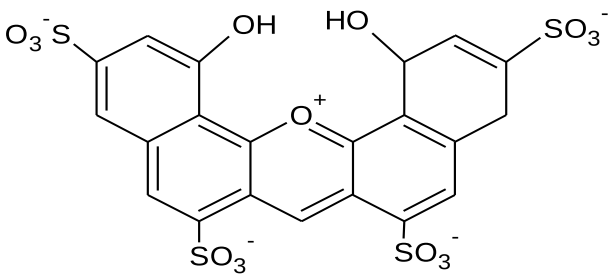


Figure 2.17 : Diaacetylcihydrolatidine chromophore structu

The absoption maximum at 580nm is used for UV/vis detection. The reaction is specific for formaldehyde when the pH value is <1.0. The nature of chromophogen has never been unambiguously proven but evidence has been obtained (Georghiou. 1989), using NMR techniques and calibration line studies to support the hypothesis that the chromogen formed in the analytical procedure has a mono-cationic dibenzoxanthylium structure and not the p-quinoidal one that is commonly cited (Fagnani, 2003).

2.9.1.2.3 The Acetylacetone (acac) (Hantzsch Synthesis) Method Nash (1953)

The method described by (Nash, 1953) is a widely applied standard procedure and recommended in Europe and Japan for the determination of FD emissions from wood-based materials Sumun *et al*, (2010). The Hantzsch synthesis is based on the cyclization of 2, 4-pentanedione (acae), ammonium acetate, and formaldehyde to form a yellow product of 3, 5-diacetyl- 1, 4-dihydrolutidine [DDL] (Julein, 2011). Figure 2.18. It is used for spectrophotometric Li (2007) ($\wedge$= 412 nm) and fluorometric ($\wedge_{ma}$=420$_{nm}$, $\wedge_{m}$=550$_{nm}$) detection of FD (Salthammer *et al*, 1993).

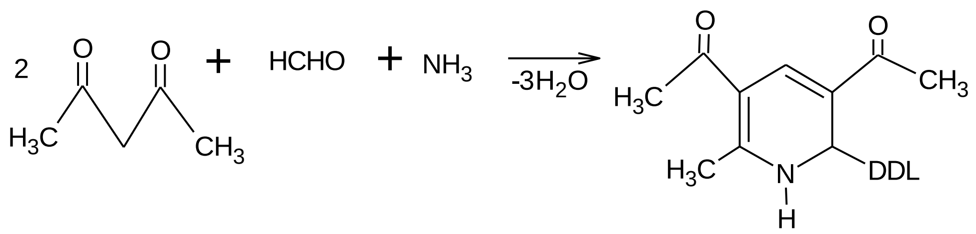


Figure 2.18 : Acetylacetone (acac) method of formaldehyde determination

The DDL molecule is probably polar, both in solution and in the crystals. Aceto acetanilide has been introduced as an alternative to acac for the derivatization of FD based on the Hantzsch reaction (Li. *et al.,* 2007). The reaction is highly specific to formaldehyde. Formaldehyde concentration was determined by reading the colour of the DDL at 412 nm using a spectrophotometer.

2.9.1.2.4 Pararosahiline Method Miksch *et al* (1981) [Malachite Green Method]

The malachite green [4- [4-dimethylanaphenyl] - N- N-dimethylaniline method has been developed for colorimetric determination of very low concentrations of formaldehyde (Miksch *et al.,* 1981). The malachite green chromatic form is a green dye. Under acidic conditions, a nucleophilic addition of HSO_3^{--} occurs, resulting in the form of malachite green, known as Schiff's reagent Figure.2.19.

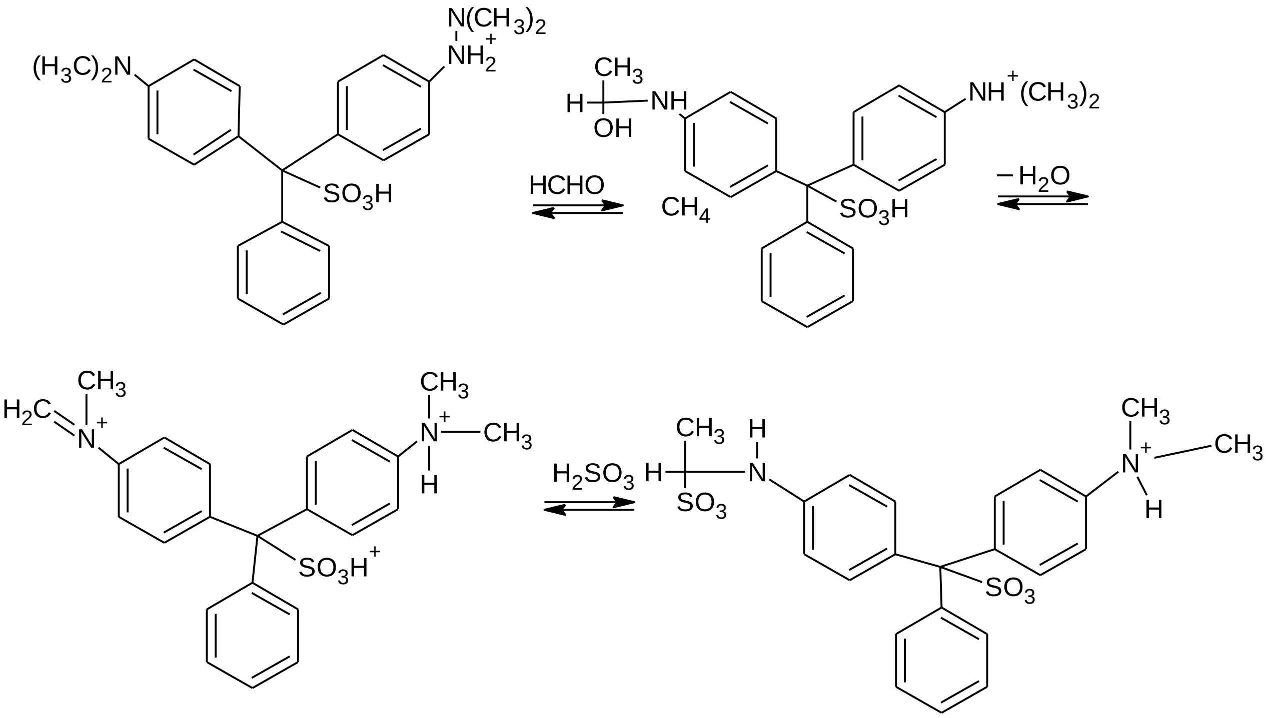


Figure 2.19 : Regeneration of the chromophore system of malachite green

Schiff's reagent reacts with aldehydes, the chromophore system is regenerated via a carbonolamine, from which upon elimination of water imine is formed, which further reacts with sulphurous acid to give rise to a reasonable stabilized coloured cation Figure 2.19. It's absorbance at 570 nm is measured in UV/vis detection. Other aldehydes, such as acetaldehyde, crolein, and propanal, interfere, but at pH≤1.0, the reaction is specific for formaldehyde.

2.9.1.2.5 AHMT (4- amino- 3- hydrazino- 5- mercapto- 4H- 1, 2, 4- triazole)

AHMT (4- amino- 3- hydrazino- 5- mercapto- 4H- 1, 2, 4- triazole) reacts with aldehydes in strong alkaline media to form a colourless intermediate product. This product is oxidized by atmospheric oxygen to form a colourless intermediate product. This product is oxidized by atmospheric oxygen to give a magenta coloured dye, detectable by colorimetry at a wavelength of 550nm Figure 2.20.

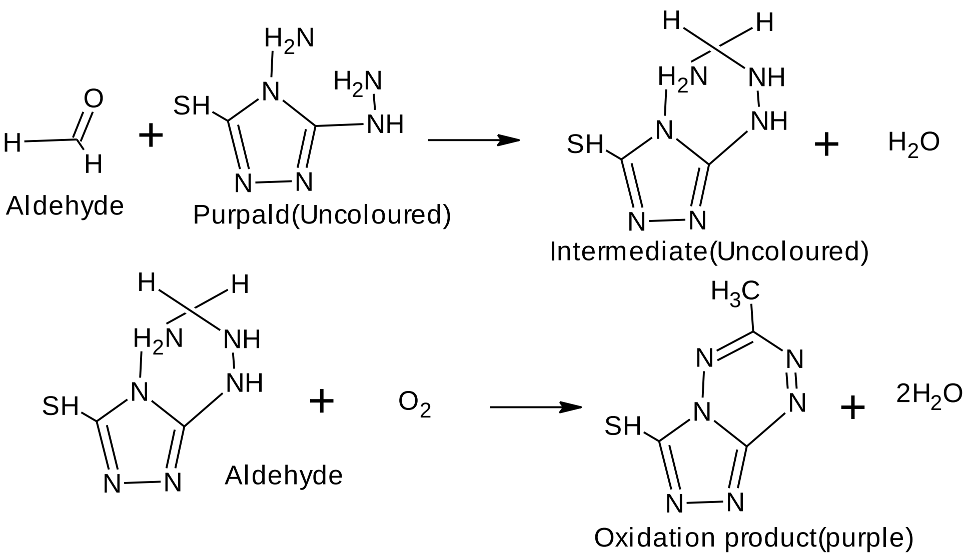


Figure 2.20 : AHMT method of formaldehyde determination

The sensitivity at the AHMT reagent varies, depending on the type or reacting aldehyde (Kawamura *et al.,* 2005) have developed a sensor to measure formaldehyde concentration in the range of 0.04-1 ppm with a sampling time of 3min.

2.9.1.2.6 MBTH Method

MBTH (3- methyl -2- benzothiazolinonehydrazone) is a nonselective colorimetric method for the determination of alphatic aldehydes of low molecular weight. MBTH reacts with aldehydes to give an azide. In parallel with this, a reactive cation is formed by oxidation of MBTH with Fe (lll). In a further step, a blue ionic dye is formed. Absorbance is monitored at 628nm Figure 2.21. Other aldehydes go on analogues reaction, but the yield is generally lower. The MBTH method quantifies total aldehydes in ambient air in terms of their formaldehyde equivalent. This reaction is less sensitive than that of the pararosaniline method. The MBTH method quantifies total aldehyde in ambient air in terms of their formaldehyde equivalent (Sheng, 2010; Salthammer *et al*., 2010)

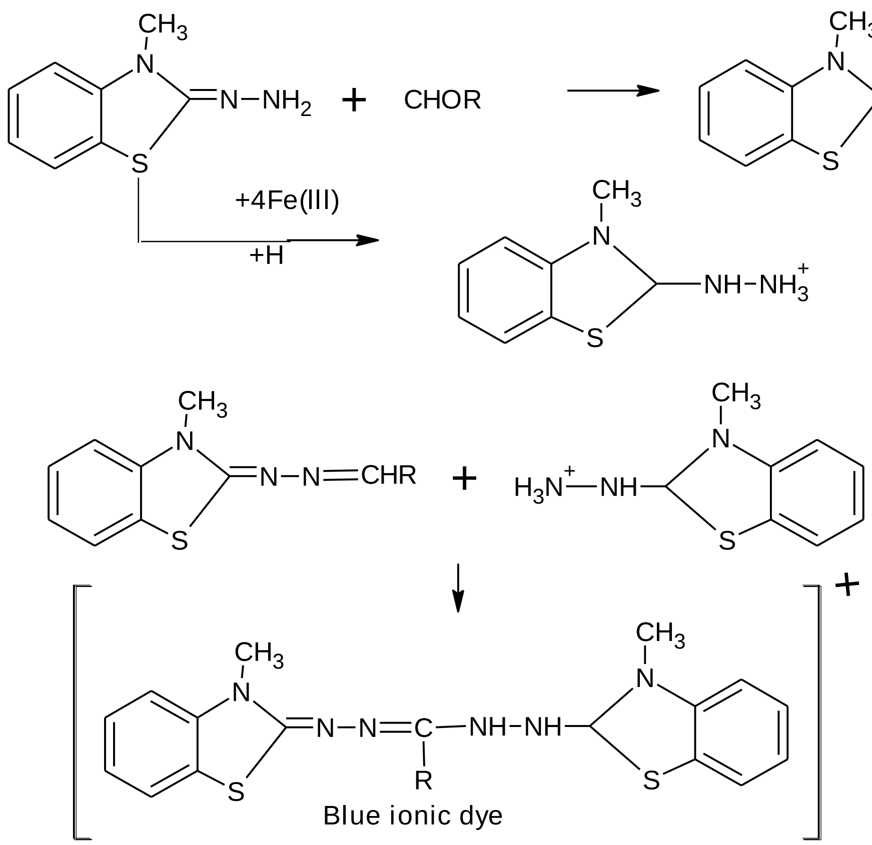


Figure 2.21 : MBTH method of formaldehyde determination

The procedure for formaldehyde analysis recommended by the National Institute for Occupational Safety and Health (NIOSH, 1994) is the chromotropic and spectrophotometric method which is the one that uses concentrated sulphuric acid (Hauser and Cummins, 1964).

2.10.0 Test Methods used for Measuring Formaldehyde Emissions from Composite Product

A variety of methods have been developed to measure formaldehyde emissions from the surfaces of composite products. Basically, the formaldehyde testing material that (FTM**)** fall into two categories: full scale tests, which are designated to give results comparative to the environment encountered in actual use, and laboratory tests ostensibly quality control monitoring, designed to mimic the results obtained using the large scale test protocol.

Formaldehyde test methods were developed along two tracks, large test chambers designed to initiate a room in a home and smaller, quicker tests suitable for lab bench and plant quality control. Formaldehyde testing in chamber and cells is usually time consuming and calls for sophisticated equipment for pretesting and production control. These methods are based on determining the formaldehyde content or formaldehyde release under special testing conditions. A variety of test methods for measuring product emission levels are used. Critical revelers of the methods are provided by many authors by (Roffael, 1993; Risholm-Sundmann *et al*, 2007; EN120: EN717-3; EN717-2; prEN717-1, 1997). Each method measures a slightly produces results in different and non-interchangeable units.

2.10.1 Large/Small Chamber Method

The environmental (large/Small) chamber test method is used for the characterization of formaldehyde analysis and volatile organic compounds (VOCS). American society of testing and materials standard (ASTMD 5116-90/and draft European standard (CENTC 264 WG7) is also specified testing VOC emission and formaldehyde release products (CENTC112 WG5; prEN 717-1; Young.(2004).The real small scale chambers for measuring formaldehyde and VOC emission rates (ERS) from building products are proposed (Kilic, 2008 ; Kim, 2007; Brown, 2007; Kim and Kim, 2005). Recently, small chamber was developed in Japan, and its performance complies with the ASTM D5116-97, (1997); D6007-96 (1996), ECA reports (1991 & 1999) and European preliminary stand ENY 13419-1, (1999).

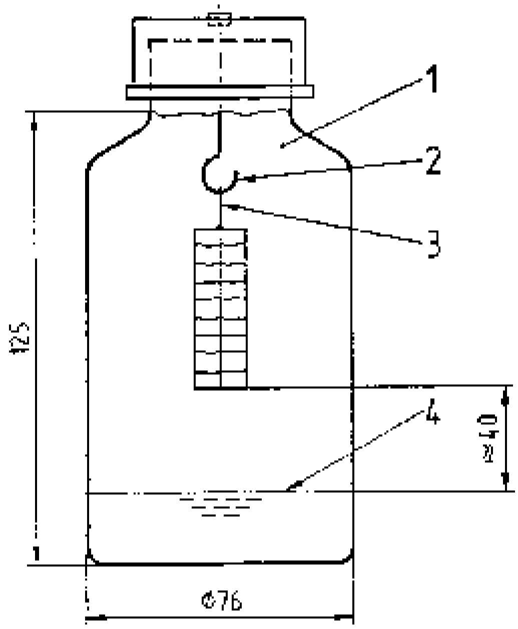
In this method test pieces of products under evaluation are placed in a special chamber simulating the prevailing conditions inside a building. Parameters such as the temperature, humidity, the air exchange ratio, the amount of sample placed are strictly prescribed and the method determines the steady state" formaldehyde emission. The formaldehyde emission in a chamber takes time and requires specialized and expensive equipment (Salthammer *et al.*, 2010).

2.10.2. Perforator Method

In industrial practice, the perforator method is the most widely spread test procedure for measuring formaldehyde content from particle board and medium density fiberboard MDF in European and in also accepted worldwide with the exceptions of North America. In Europe, the perforator method has been used for a long time, for this methods, special apparatus is needed (Roffael and Mehlhom, 1980). The test procedure was originally developed by European particle board association (EPA) in the late 1970s and called it perforator method, which is a simple method that was established in 1984 as European standard EN 120 (1995). The entire procedure allows the determination of formaldehyde content of composite boards suitable for unlamented and unloaded wood based panels (Kim and Kim , 2005). The method measures the total extractable content of formaldehyde present in a sample.

2.10.3 Flask Method

It is another simple test method developed by (Roffael, 1975). The test is based on storing a test sample with a total man close to 20g, in a closed polyethylene bottle with a volume of 400cm^3 of water at 40^{0}C for a period of time, usually 24 hours. The formaldehyde released is absorbed by water the formaldehyde content of the agene solution is determined photometrically at 412nm by the acetyl acetone method (Salthammer *et al*., 2010). A slightly modified version of the method was later standardized as EN 717-3. Variations of the methods have been developed with larger bottles and modified testing times.



1 500 ml polyethylene bottle with bottle top
2 Hook out of stainless steel
3 Elastic rubber band
4 Surface of water

Scheme 2.1: Equipment for determination of formaldehyde emission by the flask method

2.10.4 Desiccator Method

The dessicator test was developed in the middle of the 1970s' in Japan and standalized in the United States in 1983. This method is expensive and smaller to flask method (Roffael, 2006). Test sample are positioned over for 24h at a constant glass. Desiccator with a volume of 9 to132 is used, thus permitting larger quantities of test materials, analysis of formaldehyde is either carried and by the acetylacetone method (Salthammer *et al*., 2010). A number of variations of the dessicator method exist such as ASTM D 5582, 115 A 1460 and JA 5 (2006).

2.10.5 Gas Analysis

Gas analysis method is an eminently formaldehyde test, which determines the accelerated formaldehyde release at an elevated temperature of 60^0C. There are numerous methods for detecting and measuring formaldehyde gas. Analytical approaches include relatively expensive instrumentation EN 717 (1994), such as electrochemical gas chromatographic, optical, chemiluminecent etc. and also inexpensive colorimetric or fluometric methods have been proposed (Nash, 1953). According to (Nakos, 1975), two different methods ie the stationary method which measures the equilibrium creamentic of formaldehyde in the air surrounding the sample but air is not renewed. They gas analysis methods include the gas analysis chamber of klittmann, the TNO gas analysis method, the jar, method the FAIRNI method, the SINTEF method, the micro- diffusion, method, the desiccators method, the modified Roffael method (Nakos, 1975).

In the dynamic methods concentration of formaldehyde is measured in a constants stream of air blown to the sample. The dynamic methods are song and spalt method, the gas analysis method of stronger, and the gas analysis – method of (FESYP, 2003).

2.10.6 DMC (Dynamic Micro Chamber) Method

This method, recently developed in the USA, consists of two different measurements. The measurement of the steady formaldehyde concentration (Cs), in a constant air stream and the measurement of the maximum formaldehyde concentration (Ceg), in the air surrounding the sample when the air stream is turned off. The permeability K of the board (composite) surface can be calculated with the following equation:

$$K = \frac{NC}{L(Ceq - Cs)} \qquad \text{Equation 2.1}$$

The Cs value shows a linear correlation to the large chamber value of the board (composite). For this test samples of 200 by 300 mm approximately are placed in the DMC chamber (after sealing the edges) and measure Cs and Ceq. These values are measured by an electronic sensor. These values are affected by the same parameters as in the large chamber. The software provided with the DMC, however, is supposed to give comparable results for all the cases (Nakos, 1975; Salthammer *et al*., 2010).

2.10.7 Formaldehyde Emission from Composites

Building and furnishing materials and consumer products are important sources of formaldehyde and other volatile organic compounds (VOCs) in the indoor environment. There is a growing concern about the significance of these indoor pollutants for the health and comfort of building occupants. Exposure during time spent indoors can account for most of the total personal exposure of inhabitants to these pollutants. The slow release of VOCs from polymeric materials can affect the performance and durability of products and can adversely affect the indoor air quality (IAQ) and the 'well-being' of occupants.

Indoor air pollutants mainly include nitrogen oxides (NO_x) and VOCs, which can cause adverse health impacts on occupants (Pickrell *et al.*, 1986). VOCs are primarily composed of BTEX (benzene, toluene, ethylbenzene, and o-xylene) and halogenated hydrocarbons (Afshari *et al.*, 2003). Among the numerous VOC compounds, toluene, ethylbenzene, o-xylene and styrene were studied because they are the major VOCs found in indoor environments in different countries (Risholm-Sundman and Wallin, 1999). Wolkoff, (1999) stated that it is necessary to know the nature of the primary and secondary emissions from building products.

The primary emissions are free (non-bound) VOCs and are generally of low molecular weight such as solvent residues, additives and non- reacted raw products, e.g. monomers. Secondary emissions are chemically or physically bound VOCs and several of these are emitted or formed by different processes under special chemical or physical conditions. Many of the building products that are based on natural raw materials, as opposed to synthetic building products, behave as a secondary emission source and generally continue to emit VOCs. These emissions appear to be partly caused by oxidative degradation to lower molecular weight VOCs with low odor thresholds, such as (unsaturated) aldehydes and fatty acids from C_1 to C_{l0}, and alcohols like 2-ethylhexanol (Risholm-Sundman, 1999).

In the past, urea-formaldehyde (UF) and phenol- formaldehyde resin binders have contributed greatly to the progress made by the wood industry. These adhesives are widely used as a major component in the production of building and furniture materials, such as medium density fiberboard (MDF), particle- board (PB), and plywood. However, decreasing the emission levels of formaldehyde fumes from PB manufactured using UF resins has now become one of the major concerns of the timber and wood adhesives industry, particularly in the case of adhesively bonded wood products.

Recently (ECA-IAQ report 13, 1993), attention has turned to other VOCs that may be emitted from wood products. These VOCs include chemicals naturally present in the wood, as well as those added during processing. In new energy-efficient buildings, air exchange rates are low, permitting concentrations of VOCs to accumulate beyond detectable and possibly to harmful levels. The adverse health effects associated with these increased VOC concentrations include eye and respiratory irritation, irritability, inability to concentrate and sleepiness. Moreover, health and the environment constitute two key concerns of the 21st century (Milota and Wilson ,1985; Meyer *et al.*, 1986; Lee and Kim, 2002).

Formaldehyde-based resins also have superb bonding properties and are inexpensive. As a result, they are used extensively as adhesives in the manufacture of a variety of household products. One prominent use of UF resin is in the manufacture of PB, plywood, and chipboard. Several thin sheets of wood are glued together by the UF resin to produce plywood, whereas PB and chipboard are manufactured by mixing wood chips and sawdust with the resin and then pressing the /mixture into its final form at a high temperature (Kim and Kim, 2015).

2.10.8 Mechanism of Formaldehyde Emission from Composites

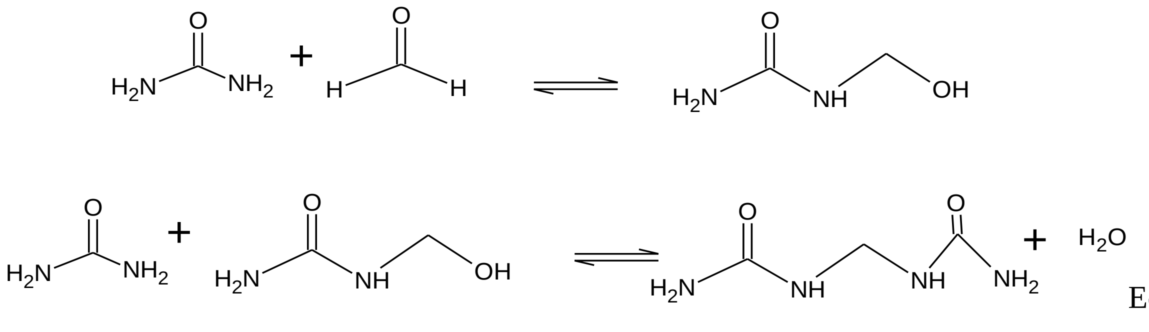
In the past, 1960s and 1970s dwellings in prefabricated houses and mobile homes made from urea- formaldehyde [U/F] bonded particle board, were a major concern, and many occupants complained about bad odours and adverse health effects. Subsequent emissions of formaldehyde were observed and this is due to the presence of small amount of free formaldehyde in the resin and to the reversibility of the UF reaction.

From the available literature (Salthammer *et al*., 2010; Mohamed and Martin, 2013), the main release of formaldehyde comes from the adhesive (resin), urea- formaldehyde and melamine-formaldehyde resins are the main prominent known resins used in composite production. Their usage is always combined with release of formaldehyde during and after the manufacture especially in the production of the material.

The reaction between formaldehyde and urea or melamine is an equilibrium reaction

$$H_2N\text{-}CONH_2 \quad + \quad CH_2O \quad \rightarrow \quad H_2N\text{-}CON\ HCH_2OH \qquad \text{Eq 2.2}$$

$$H_2NCONH_2 + H_2NCONHCH_2OH \rightarrow H_2NCONHCH_2NH\text{-}CONH_2 + H_2O \qquad \text{Eq-2.3}$$



Eq-2.4

Figure 2.22 : (Eq-2.4) Combining of urea and formaldehyde [Mannich reaction]

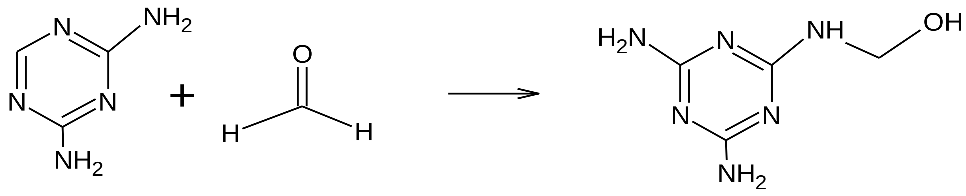


Figure 2.23 : The first step of the melamine-formaldehyde reaction

This means that there will always be some free (unreacted) formaldehyde in a resin, independent of the molar-ratio of this resin. Resin with a formal molar-ratio, the content of reacted formaldehyde will be lower than in a high molar ratio resin. To achieve a good cross linking during the curing of resin a good mechanical properties of the resin must have a large molar ratio of formaldehyde/urea. This means we need formaldehyde in excess. This excessive formaldehyde in the resin is in the form of free (unreacted) formaldehyde and is in the form of end standing methylol groups. A resin contains also other groups which consist of formaldehyde. Other groups found in the resin are methylene-ether [-NH-CH_2-O-CH_2-NH-], and methylene groups [-NH-CH_2-NH-].

Under the cure conditions of moisture, elevated temperature and acid in the resin, all these groups can be hydrolysed and release formaldehyde. The methylol groups are the most unstable ones and the most resistant to hydrolysis are the methylene groups (Sheng, 2010). Wood-based products bounded with phenol formaldehyde (P/F) adhesives show comparatively low formaldehyde emission potentials because the cross linking is more stable (Mohamed and Martin, 2013).

It is obvious the FD released in the environment is hazardous to the health. Therefore, the need of the accurate method to measure the amount of FD released in the environment is neccessary in the air . Many different methods have developed to give a fast, easy and accurate estimation of the test.

2.10.9 Reduction of Formaldehyde Emission from Composites Panel

To reduce formaldehyde emission, the possibility of using replacement materials for urea-formaldehyde (UF) and phenolformaldehyde (PF) adhesives has been studied for a long time. Tannin formaldehyde adhesives are obtained by the hardening of polymeric flavonoids of natural origin, especially of condensed tannin by polycondensation with formaldehyde (Pizzi, 1994). Hardeners, however, cause formaldehyde emission even when tannin-based adhesive is used (Trosa and Pizzi, 1994; Kim *et al.*, 2002).

In the, I^{st} decade, several approaches of producing resins with low emission have been developed. Recently, the finding that hardening of melamine-urea-formaldehyde (MUF) resins occurs mostly due to their melamine reactivity has led to the realization of developing a mechanism or system of hardening to improve the performance of the formaldehyde emission of MF.In Europe, most of the resins currently used have a formaldehyde/urea molar ratio between 1.02 to 1.08 (Chimar , 2002). The reduction of the molar ratio was initially achieved by introducing in the resin production process one or two extra steps of urea addition. The urea reacted with the residual formaldehyde and the free formaldehyde emitted from the board was drastically reduced.

In the meantime, the resin industry has managed to optimize the synthetic route of low molar ratio straight UF resins and together with improved board preparation conditions and the sophisticated equipment employed in board manufacturing plants. However, in order to meet the stringent international standard [EI Specification]. The addition of formaldehyde catchers (or Scavengers) is needed (Dunky, 2004; Marutzky *et al.*, 2004). Various techniques for lowering the concentration of formaldehyde in the indoor environment have been reported by several authors (Salthammer *et al.*, 2010; Jina, 2010), and the followings are the major approach employed to reduce formaldehyde emission.

1. Aminoplastic resins with low molar ratios F/U or F/-(NH_2), respectively.

2. Introduction of substances containing NH_2 groups (formaldehyde catchers), which decreases the molar ratio, F/ $(NH_2)_2$ of the resin mix.

3. Addition of formaldehyde catchers or scavengers during the production of the boards, e.g. to the wet or to the dried chips.

4. Posts manufacture treatment of the boards.

5. Application of a diffusion barrier by coating or lamination or veneering of the board.

The most widely used approach for reducing formaldehyde emission listed above was the regulating the mole ratio of formaldehyde/Urea (F/U). Ratios of about 1P6F that were common 20 to 25 years ago (Mari, 1983) have now long been reduced to values as low as1.0 and. in some cases, lower. Unfortunately, lowing the F/U ratio has as a consequence that these urea-formaldehyde resins cannot be stored for long (shorter shelf-life), require relatively longer pressing times (higher gel time) and produce panels that often have poorer physical and mechanical properties (tendency towards more swelling and low transverse tensile strength) (Myers, 1984 ; Roffael and Dix, 1991). Virtually all related treatments create trade-offs, either in crease expenses or board quality. As a result, the panel manufacturing treatment methods to achieve the necessary reduction in formaldehyde emission levels (Myers, 1986)

2.10.10 Regulations and Testing of Formaldehyde

The European Union, the U.S.A, China, and Japan now have legislation regulating the allowed levels of formaldehyde emission (FE) from wood and composites-based products, and without doubt there will be increased focus and controls placed on products, that are known to release formaldehyde (Salthammer *et al*, 2010). The main source of FE from composite - based products such as medium density fiberboard (MDF), particleboard (PB), and plywood are the resins used, such as urea-formaldehyde (UF), melamine-modified urea formaldehyde (MUT), and phenol-formaldehyde (PF). Solid wood grown in normal forest conditions releases low levels of formaldehyde, particularly during the manufacturing process (Salem *et al.*, 2012).

Furthermore, PF resins, formaldehyde and phenol are often measured together (Horn *et al*, 1998). The emission of formaldehyde from composites is produced during hot-pressing of composite panels, and it is generally accepted that FE from the wood itself is an insignificant contributor to the total measurable level of FE in a composite product (Birkeland *et al.*, 2010).

Most European nations have passed laws that regulate formaldehyde, now known as the EI-emission class, standards such as EN312 (2003) and EN 622 -5 (2003) all require that the 0.1 – mg/m^3h level be met. Testing for this mainly utilizes the EN 13986 (2005) established emission classes E1 and E2 for use in construction. These standards basically require testing to be done on formaldehydes –containing wood products used in construction. In 2006, these same methods with phenol and the associated limits went into effect for panel production.

Because it is very difficult, if not impossible, to eliminate formaldehyde from a building completely, the Japanese standard employs a tiered rating system based on the amount of FE a building material gives off. The system is based on one-star to four-star ratings, with four stars representing the lowest amount of FE. It is shown that for workplace exposure, the allowable FD for concentration for 14 European countries ranges from 0.3 ppm to 2.0 ppm, with the majority of them to range between 0.5 and 1.0ppm. Also, the lowest exposure limit in the living space in most countries is around 0.1 ppm. The acceptable exposure levels in the ambient air are usually 5 to 10 times lower than the exposure limits in the workplace, except for some countries (Salthammer *et al*., 2010).

2.11.0 Chitin/Chitosan

Chitin is the second most abundant polysaccharide in nature after cellulose (Kumar, 2000) Figure 2.24. This polysaccharide is similar to cellulose, both in function, chemical structure and abundance. It is widely distributed in animal and vegetable resource, of the skeletal structures of many classes comprising the group of invertebrates, such as arthropods, mollusks, and annelids. In animals chitin occurs associated with other constituents, such as lipids, calcium carbonate, proteins and pigments.

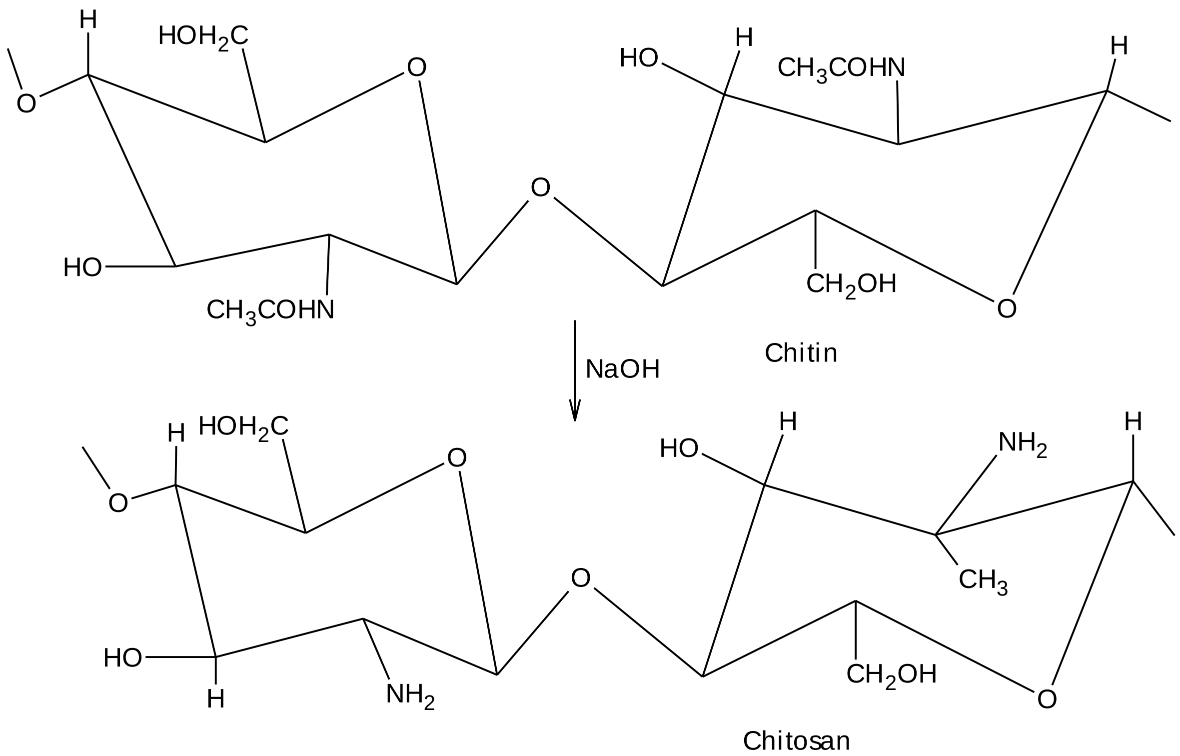


Figure 2.24 : Chemical structure of chitin and chitosan

It has been estimated that the crustacean chitin present in the sea amount to 1560 million tons (Cauchie, 1981). Chitin is also found as a major polymeric constituent of the cell wall of fungi and algae. Fungal chitin exhibits some advantages as compared with animal chitin, such as a greater uniformity in composition, continued availability in time and the absence of inorganic salts in its matrix. It is associated with other polysaccharides, such as cellulose, glucanmannan and polygalactosamine, which makes its isolation difficult (Peter, 2002).

Various procedures have been adopted to obtain high quality chitin (Roberts, 1992). Chitin extraction (isolation) processes are generally performed through the following consecutive steps: raw material conditioning, protein extraction (deprotenization), removal of inorganic components (demineralization, mainly ($CaCO_3$) and decoloration (pigment and lipid).

Chitosan is a linear polysaccharide obtained by extensive deacetylation of chitin Figure 2.24 In general, the major different methods of preparing chitosan from chitin with varying degree of acetylation (DA) are the heterogeneous deacetylation of solid chitin And the homogeneous deacetylation of pre-swollen chitin, under vacuum in an aqueous medium, and enzymatic N-deacetylation (Castelli *et al.*,1996). In both, heterogeneous or homogeneous conditions, the deacetylation reaction involves the use of concentrated alkali (NaOH or KOH) solutions at temperatures above 100°C and long processing times which vary depending on the conditions (Roberts, 1998; Galed *et al.,* 2008). It has been shown that while chitosan obtained by the heterogeneous process are polydispersed in terms of the deacetylation degree of their chains, chitosan obtained under homogeneous conditions do not exhibit chain compositional dispersion (Roberts, 1998).

During chitosan deacetylation, the degradation of the polymeric chain takes place. At the same time, the crystallinity of chitosan can be damaged by using harsh reaction conditions (Rege and Block, 1998). Taking this in account, the reaction conditions must be controlled when preparing chitosan (Sukwattanasinin *et al.,* 1990).

There is evidence that in certain bacteria and fungi, enzymatic deacetylation can take place (Gooday *et al.,* 1991). Deacetylases have been isolated from various types of fungi. However, the activity of these deacetylation is severely limited by the insolubility of the chitin substrate. Because commercial enzymes are costly, one new technology for extraction of chitin that offer an alternative to the more harsh chemicals methods is fermentation by microorganism (Pillai *et al* ., 2009).

Several alternative processing methods have also been developed to reduce the long processing times and large amounts of alkali typically needed to deacetylate chitin to an acid-soluble derivative. Examples of these include the use of successive alkali treatments using thiophenol in DMSO (Domard *et al.*, 1983); thermo-mechanical processes using cascade reactor operated under low alkali concentration (Petletier *et al.*, 1990); flash treatment under saturated steam (Focher *et al.*, 1990); use of microwave dielectric heating (Goycooles *et al.*,1909); and intermittent water washing (Mima *et al.*,1909).

Chitosan displays interesting properties such as biocompatility, biodegradability (Kumar *et al.*, 2004; Sanford *et al.*, 1989) and its degradation products are non-toxic, non-immunogenic, and non-carcinogeni (Muzzanelli, 1995; Bersch and Nies, 1995). Therefore, chitosan has prospective applications in many fields such as biomedicine, waste water treatment, functional membrane and flocculation. However, chitosan is only soluble in few dilute acid solutions which limited its application (Alves and Mano, 2008).

2.11.1 Chemical and Physical Properties of Chitosan

Chitin and chitosan are described as naturally occurring of linear polysaccharides consisting of varying amounts of β (→4) linked units of N-acetyl-2-amino-2-deoxy-D-glucose and 2-amino-2-deoxy-D-glucose units, similar to cellulose as shown in Figure 2.28 (Muzzarelli, 1997). Illustration of possible reaction sites in chitin and chitosan is shown in Figure 2.25. The first systematic study on the solubility of chitin/chitosan was carried out by Austin (1984), who introduced the solubility parameters for chitin in various solvents. The choice of solvent in a particular situation involves many more factors such as presence of sobilizing chemical entities solution viscosity (Du and Hsieh, 2007).

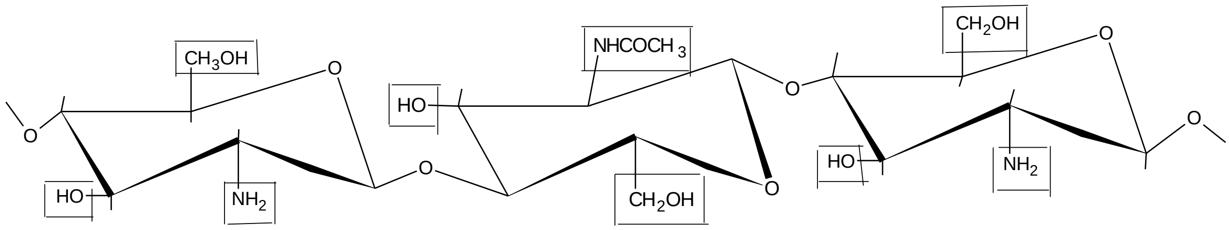


Figure 2.25 : Illustration of the possible reaction sites in chitin and chitosan

Chitin has the same backbone as cellulose, but it has an acetamide group on the C-2 position instead of a hydroxyl group and molecular weight (Mw), purity and crystal morphology are dependent on their source (Hudson and Smith, 1998). Chitin is essentially a homopolymer of 2-acetamide-2-deoxy-β-D-glucopyranose, although some of the glucopyranose units exist as 2-amino-2-deoxy-β-D-glucopyranose, chitin samples have a low amount of 2-amino-2-deoxy-D-glucose units and hence the polymer is insoluble in acidic aqueous media Figure 2.25. On the other hand, the amount of 2-amino-deoxy-D-glucose units in chitosan samples is high enough to allow the polymer to dissolve in acidic aqueous media.

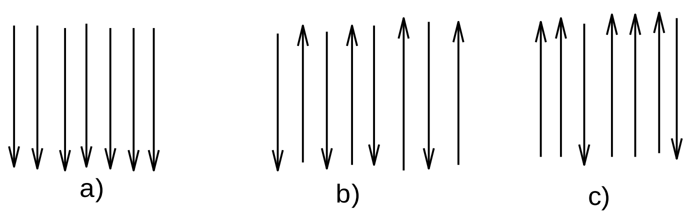
There were several attempts at dissolution of chitin using inorganic bases such as sodium hydroxide and inorganic salts (Kurita, 2001). Hudson and Smith (1998) was reported to have kept chitin in 5% caustic soda at 60^{o}C for 14 days and got a deacetylated product soluble in acetic acid . Weiman (1997) used inorganic salts such as LiCNS,$Ca(CN)_2$, CaI_2, $CaBr_2$, and $CaCI_2$ capable of strong hydration to dissolved chitin/chitosan.

2.11.2. Crystallinity

Three crystalline forms are known for chitin α, β - and γ -chitins. Chitosan is also crystalline and shows polymorphism depending on its physical state. The three forms differ, in the packing of the chains within the crystalline regions (Roberts, 1998).

The- α form (a), is composed of chains arranged in sheets or stacks having the same direction or sense. The sheets are antiparalled polysaccharide strands and are mainly obtained from crab and shrimp.

The β-form (b), is monoclinic chains arranged in a paralled structure. In β-chitin, adjacent sheets along the C axis are paralled strands of polysaccharides found in association with proteins in squid pens (Rudall and Kenchigton, 1973; Rudall, 1969). In contrast with α-chitin, β-chitin can incorporate small molecules into its crystal lattice to form various complexes, in particular anhydrous, monohydrated and dehydrated forms have been identified (Blackwell, 1969). Yet, another key feature of β-chitin is its ability to undergo conversion into, it's α-chitin polymorph by precipitation chitosan from a formic acid solution or by treatment with cold 6M HCI (Saito *et al.*, 1997). The γ-form(c) found in fungi has not been fully classified but an arrangement of two parallel chains and one antiparallel chains has been suggested Scheme 2.2.



Scheme 2.2: Three polymorphic configuration of chitin a) α-chitin b) β-chitin c) γ-chitin

Highly deacetylated chitosan in the solid state can also exhibit a crystalline structure. Two hydrated crystalline forms of chitosan have been identified, namely "L-2 and "Tendon," the latter being the most abundant hydrated polymorph of chitosan (Okuyama, 1997).

2.11.3 Degree of Acetylation (DA)

The degree of acetylation is defined as the fraction or percentage of N-acetylated glucosidic units in chitin or chitosan. It is designated indistinctly as, DA or DA/DD. The degree of deacetylation (DA) is obtained from the formular DA = 100 − % DD.

The process of deacetylation involves the removal of acetyl groups from the molecular chain of chitin in alkaline solution at certain temperature to hydrolyse N- acetyl linkages, leaving behind a complete amino group [$-NH_2$]. Repetition of the process can give deacetylation values up to 98%, but in heterogeneous process can never be achieved without modification (Pillai, 2009). Chitin contains 6-7% nitrogen and in its deacetylated form, chitosan contains 7 to 9% nitrogen. In chitosan between 60-80% of the acetyl groups available in chitin are removed (Sneha Pau, 2014). Chitosan versatility depends mainly on this high degree chemical reactive amino group (Pillai, 2009; Vipin *et al*., 2011). The presence of free amino groups is responsible for its polycationic nature in acidic solutions, and makes the degree of deacetylation important property in chitosan production as it affects the physiochemical properties, hence determines its appropriate applications (Tolaimate *et al.*, 2000).

Various methods have been reported to measure the DD, such as IR Spectroscopy (Muzarelli and Rochetti, 1985; Miya *et al.,* 1990), UV Spectroscopy (Keschen, 1990), ninhydrin test (Curotto and Aros, 1993), hydrogen bromide titrimetry (Baxter *et al.*, 1992; Domszy and Roberts, 1985), H NMR Spectroscopy (Manni *et al.*, 2010), ^{15}N NMR (Yu *et al.*, 1999), Hydrolyte methods (Tanveer, 2002), ^{13}C Solid-state NMR Spectroscopy (Heux *et al.*, 2000), gel permeation chromatography and titration methods (Renata, 2012), residual salicyladehyde analysis (Mima *et al.*, 1983), equilibrium dye absorption (Renata, 2012), Acid degradation followed by HPLC (Davies and Hayes, 1988)), HPLC-Ultraviolet (Pradip Kumar *et al.*, 2004), thermal analysis (Tanveer, 2002), and pyrolysis-mass Spectrometry (Renata, 2012). One of the simplest methods for determining the DD is acid-base titration . In this method, a known amount of chitosan is dissolved in an excess of dilute aqueous acid such as hydrochloric acid and titrated with a standard sodium hydroxide solution. The stoichiometry is determined by pH measurement (Renata, 2012). .

2.11.4 Solubility and Molecular Weight

The relationship between solubility, molecular weight (Mw) and degree of N-acylation has been established by several authors and determination analysis suggested that the distribution of N-acetyl groups in the chitin molecule was more random than those in the regenerated chitin. At 50% N-acetylation, chitosan solubility in water did not show any change with an increase in the Mw (Jae Kweon Park *et al.*, 2011; Sheng (2010) . Generally, the solubility of chitin and chitosan decrease with an increase in Mw (Pradip *et al.*, 2004). Neither chitin nor chitosan is soluble in neutral water. Through functionalization of the chemical structure, the solubility of the almost insoluble biopolymer chitin **(a)** can be enhanced. Quaternized **(c)** and substituted **(d)** derivatives also show much better solubility under alkaline conditions than chitosan **(b)** **(**Jolanta *et al.*, 2011) Figure 2.26.

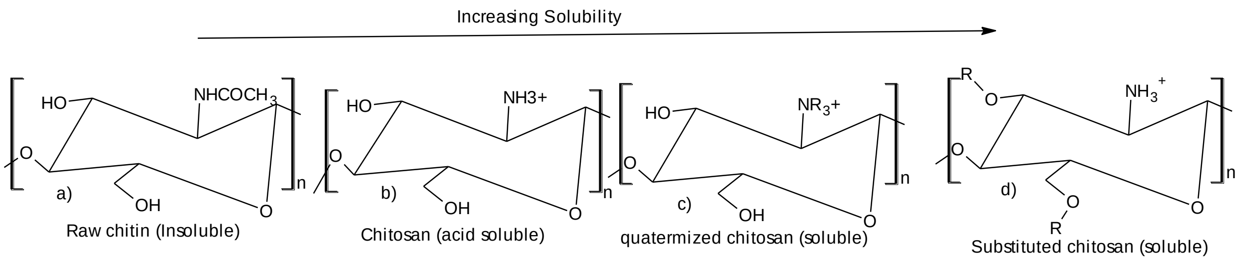


Figure 2.26 : Increasing Solubility through functionalization of the chemical structure

Chitin is a semi crystalline polymer with extensive inter- and intra-molecular hydrogen bonds, which make it difficult to dissolve in dilute acids or organic solvents under mild conditions (Chie *et al.,* 2013).in alkaline or neutral medium, free amino group of chitosan is not protonated and therefore, it is insoluble in water, while in acidic pH, it gets solubilized due to protonation of free amino groups and the resultant soluble polysaccharide is positively cationic polysaccharide. This cationic nature is the basis of a number of application of chitosan. A number of solvents for chitin and chitosan can be found in the literature (Pillai *et al.,* 2009).

2.11.5 Chemical Reactivity

Chitosan has two types of reactive groups that can be crosslinked. First, the free amino groups on the deacetylated units and secondly, the hydroxyl groups on the C - 3 and C - 6 carbons on acetylated or deacetylated units Figure 2.25 and 2.26. Recently, growing interest in the chemical modification of chitosan to improve mechanical and physical properties, and solublilities of chitosan to widen its application are reported in the literature (Kurita *et al.,* 1998; Hevas, 2001). These reactive groups Figure 2.26 of chitosan can undergo many of the reaction, by introducing small functional groups such as alkyl or carboxymethyl groups (Jaya *et al.,* 2006 ; Lu. *et al.,* 2007) which can drastically increase the solubility of chitosan at neutral and alkaline pH values without affecting its cationic character. These reactive groups of chitosan are suitable to impact desired properties in terms of applications of chitosan. The amino functionality gives rise to chemical reaction (Pillai *et al.,* 2009), quaternization (Sheng, 2010), reaction with aldehydes and ketones, alkylation. The hydroxyl functional groups gives reaction such as O-acetylation (Mohamed and Alessandro, 2010), Hydrogen-bonding with polar atoms (Alves and Mano, 2008), crosslinking (Muzzarelli, 1990), and grafting (Sheng, 2010). The chemical properties of chitosan are as follows: Linear polymide, Reactive amino groups, reactive hydroxyl groups available Figure 2.26, and Chelates many transitional metals ions.

2.11.6 Crosslinking

The "Crosslinking" is the association of polymers through a chemical bond. In most cases, the crosslinking is reversible in either intra or intermolecular. The ability of chitosan to dissolve in an acid-aqueous solution is very valuable, many applications for chitosan must have it retain both its mechanical and structural properties, so the crosslinking of chitosan is vital for these applications. A variety of different methods are used to cross-link chitosan. Hexamethylene 1, 6-di (aminocarboxysulfonate) (HDACS) is used to cross link chitosan molecules by bonding between the isocyanate group of HDACS can be activated either by the addition of heat or increase of pH (Weish *et al,* 2002).Glutaraldehyde (GA) is used to cross-link chitosan molecules by bonding between the amines of chitosan and the aldehyde of GA to form an imine bond (Monteiro and Airoldi, 1999).

Other molecules that can be used to crosslink chitosan include genipin, epichlorohydrin (ESH), and ethylene glycol diglycidyl ester (Jin *et al.,* 2004; Wan Ngah *et al.,* 2002).

An important advantage of chitosan is the possibility of agents that perform chemical modification on its structure by binding to amino and hydroxyl groups. Crosslinking with epichlorohydrin maintain the cationic amino function and improves the mechanical properties of the material (Tanveer, 2002). On the other hand, (Muzzarelli, 1995), studied the crosslinking mechanism of chitosan with bifuctional glutaraldehye agent. This crosslinking reaction occurs between primary amino groups and aldehyde groups, resulting in the formation of Schiff bases (Mohamed and Alessandro, 2010).

5.11.7 The Effect of Acetyl Group on Mechanical Properties of Chitin/Chitosan

Chitin fibre is the load-bearing component in a natural chitin-based material. In order to understand how the acetyl group enhances the fracture resistance capability of chitin (Junhe *et al.,* 2016) constructed atomistic models of chitin with varied acetylation degree and analysed the hydrogen bonding pattern, fracture and stress-strain behavour of these models. They noticed that tha acetyl group can contribute to the formation of hydrogen bonds that can stabilize the crystalline structure. In addition, it is found that the specimen with a higher acetylation degree presents a greater resistance agaist fracture.

Because of their outstanding mechanical properties, such as high strength, high toughness and, being light weight , chitin acts as a major load-bearing component in the exoskeleton of a diatom (Brunner *et al.,* 2009; Nakolov *et al.*, 2011; Yang *et al.*, 2014). Apart from the artificial deacetylation process, chitin is naturally partial deacetylated and natural fibre is a composite system with different proportions of chitin and chitosan (No and Meyers, 1995), compared with chitin in terms of chemical structure, chitosan only lacks acetyl group (Palpandi *et al,* 2009). As a results of hydrophobic property of acetyl group, chitin lacks solubility while chitosan is soluble in aquiouse medium (Rinaudo, 2006; Brugnerotto *et al.,* 2001).

Interms of mechanical properties, a lot of studies mainly focus on measuring Youngs modulus by performing experimental tensile test on chitin-based materials (Nishino *et al.,* 1999; Miserez *et al.,* 2008) . Nevertheless, though many parts of cuticle, like insect wings are subjected to high loads which cause cuticle to fail by fracture. Little has been carried out to investigate fracture properties of chitin-based materials up to now (Vincent and Wegst, 2004).

The only chemical difference between chitin/chitosan is the acetyl group. The presence of acetyl group causes more high occupancy H-bonds along the inter-sheet direction of chitin model. In contrast, as there are few acetyl groups within the chitosan model, the H-bond occupancy along two directions is similar. Additionally, van der Waals interaction within chitin crystals is significantly enlarged due to the larger molecular mass of acetyl group. The effect of acetyl group on these non-bonded interactions results in distinct mechanical properties between chitin and chitosan. The H-bond occupancy is correlated to strength according to stoihastic theory of fracture (Ruiz *et al.*, 2013).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

Chitin, from shrimp shells, practical grade, and coarse flake was supplied by Sigma Aldrich. The composite sheet of size 150mm×100mm×5mm were prepared by compression moulding machine Carver Model 3851-D.

3.1.1 Reagents

Acetic acid, formaldehyde, acetyl acetone, sodium hydroxide pellets, ammonium acetate and sodium thiosulphate were reagent grade products from the British Drug House (BDH). Phenol was obtained from P-Park Scientific limited; Northampton, U.K, Oxalic acid was procured by BDH chemicals Ltd, Poole England. Hydroxylamine Hydrochloride was purchased from Titan Biotech Ltd. All the chemicals used were analytical grade. Distilled water was used throughout the investigation.

3.1.2 Equipment/ Instruments

Mettler balance model HR-200 was used for the measurement. The pH of the material (resins) produced was measured using pH meter Jenway model 3505.The Brookfield viscometer or cone-plate rheometer (RVT, Serial 43329) was used for measuring viscosity. Ultra –violet (UV) – Visible Spectroscopy was determined by Jenway Model 6308 Spectrosphometer. A hot plate Jenway 1000 model. Fourier transform infrared (FT-IR) Spectra measurement of all samples were performed in a Shimadzu model spectrum 84005 instrument.

3.2 Methods

The methodology used involved three main stages: preparation of different novolac prepolymer resins with different phenol/formaldehyde (P/F) ratios and the synthesis of chitosan with different degrees of substitution and the production of PF/composites.

3.2.1 Synthesis of Phenol formaldehyde Novolac Resins

In order to determine the optimum product ratio of phenol formaldehyde (novolac) resins, various ratios of phenol-formaldehyde were studied.

The novolac type phenolic formaldehyde resin was synthesized by reacting phenol with formaldehyde in the presence of acid catalyst. Phenol (90%), 37% formaldehyde solution, oxalic acid (4%w/v) were used. Different novolac prepolymers were prepared with different P: F molar ratios: 1P:2F to 1P:8F respectively. First, phenol was melted in a 10ml reactor in a hot water bath. The oxalic acid catalyst was charged into the reactor and kept stirring for 30 min, and then the formaldehyde solution was added drop wise to it. The reaction mixture was refluxed for 2h under stirring at 90^{o}C, and then raised to about 120^{o}C .The sticky resin was first washed with small amount of hot water several times, and later dissolved in water at room temperature to re-precipitate to remove the unreacted phenol and catalyst. Finally, the white-coloured resin after separation from water was dried under vacuum at 50^{o}C for 1h. The final product is transparent and yellowish.

3.2.2.0 Analysis of the Synthesized Novolac Resins

3.2.2.1 pH Measurement

The alkalinity or acidity of the solution of the synthesized resins and chitosan solutions have a major effect on many properties, such as viscosity, molecular weight, reaction time etc. 5.0 cm^3 of the P-F resin was collected into a beaker and toped with 40ml distilled water and the pH value was determined. The pH value from the instrument was recorded. The pH measures the basicity of the resin.

3.2.2.2 Viscometric Measurement

Viscosity is an important factor in the conventional determination of molecular weight and in determining its commercial applications.The viscosity of the resins and chitosan samples was measured using a low-shear, rotating spindle apparatus. The Brookfield viscometer was used to measure the viscosities of the resins (novolac) of P: F ratios 1P:2F to 1P:8F, at room temperature. The machine was run at 50 rpm for spindle 2 and 200rpm for spindle 3. The torque is proportion to the viscosity-resistance experienced in the solution. It provides the viscosity with calculations based upon the amount of torque required to rotate the spindle at a given RPM, while immersed in the sample solution..

3..2.2.3 Water Tolerance Measurement

Water tolerance is an important parameter for resin used in fibre/glass binders and it is also essential for high quality film properties. Water tolerance of resins was measured by adding water from burrete to 5.0ml of resin taken in a conical flask till the appearance of turbidity. The amount of water required in proportion to the amount of resin taken gave the water tolerance of resin (resin: water). It is an important parameter for resin used in fibre/glass binders and also for high quality film properties.

3.2.2.4 Specific Gravity Measurement

The density of a material reflect its chemical structure and its molecular organization. The empty specific gravity bottle was weighed and its weight was recorded. The same specific gravity bottle was filled with phenol- formaldehyde (P: F) samples and weighed. To calculate the relative density of each resin, the following relation is used in equation (3.1).

$$RP = \frac{Wr - W_b}{(W_w - W_b) - (W_{rw} - W_r)} \qquad \text{Equation (3.1)}$$

Where W_r = weight of the composite/Resisn , W_b = weight of the density bottle ,

W_w = weight of bottle with water, and W_{rw} = weight of bottle with water and sample.

3.2.2.5 Resin Solids Content Measurement

The solids content measures the concentration of the phenolic resin which is not evaporable or undissolved materials of the resin. The resin solids contents of the resins was determined by weighing 2g of the resin into a small aluminium dish. The dish was placed in an oven at 100°C for 2 hours and allowed to cool . The dish was then weighed to find the weight of dry resin remaining. The result obtained was used to calculate the total solids content of the resin in equation (3.2).

$$\text{Resin solid level (\%)} = \frac{Sample\ wt\ after\ 2h}{Initial\ samle\ wt}\ x100 \qquad \text{Equation (3.2)}$$

Resin solids content is an important property of phenolic resin in hot processing. Low level of water ejection during hot pressing indicates

3.2.2.6 Gel – time Measurement

Gelation is the point at which resin changes from viscous liquid to elastic soft-solid. The gel-time of all synthesized (novolac) resins were determined by a hot-plate method (Leiber, 1989). An electrically heated plate was maintained at 150°C and 0.5g resin was stoked with a spatula until the sol gel transition was indicated by rapid increase in robberiness or gel character of the resin. A stopwatch was used to record the gel-time each value of gel-time was an average of at least 3 test results. Gelation indicate the point at which resin changes from viscous liquid to elastic soft-solid.

3.2.2.7 Cure – time Measurement

The novolac resin 1P:2F to 1P:8F was cured with hexamethylene tetramine (HMTA). The cured time of the resin was determined (HG 5-1338-80, China). Each resin (1.0g) with 10% HMTA was heated at 150^{o}C on a temperature-controlled hot plate at atmospheric temperature, until the resin solidified into a brittle hard material. The time required for solidification is given as the cure time. Two trials were performed for each type of sample to measure the curing times.

3.2.2.8 Estimation of Synthesized P:F Yield (%)

The weight of P:F produced was measured and the yield was calculated using the expression in equation (3.3).

$$\% \text{ Yield} = \frac{actual\ yield}{theoretical\ yeild} \text{ x } 100 \qquad \text{Equation} \quad (3.3)$$

3.2.2.9 Determination of Free Formaldehyde

Key element for the efforts to evaluate or control the contribution of synthesize or manufactured products on the quality of the indoor air is the means of measuring the actual formaldehyde emissions of a product. Determination of free formaldehyde was determined using a modification of the hydroxylamine hydrochloride method described in (Walker, 1975). A 1.0 to 2.0g sample of resins was weighed into a small beaker, and 10 mL of distilled water was added with stirring. The sample was titrated to pH 4.0 with standardized 0.1 N hydrochloric acid.10 mL of 0.50 N hydroxylamine hydrochloride, previously adjusted to pH 4.0, was added and the solution was stirred for at least 10 min. It was then titrated to pH 4.0 with standardized 0.10 N sodium hydroxide. The percentage of free formaldehyde was calculated from the following equation (3.4).

$$\% \text{ free formaldehyde} = 100(\text{mL} \times \text{N NaOH}) \times 0{:}030/\text{g sample} \qquad \text{Equation } (3.4)$$

3.2.2.10 Determination of Free Phenol

Free formaldehye is undesirable for health reasons and its toxicity level is important.The percentage free phenol was determined by following the Koppeschaar method as described in ASTM-D 1312.The test material 2g was weighed into a 1-L round bottom flask equipped with standard taper joints. A volume of 100 mL of 10% acetic acid solution was added to it. Exactly 500 mL content was steam distilled into a 500 mL volumetric flask. The distillate was allowed to cool slowly and the volume was made up to the mark by double distilled water. A 50 mL aliquot was transferred to a 250 ml stoppered conical flask and treated with 50ml of 0.1N bromide-bromate solution and 10 mL of concentrated hydrochloric acid. The flask was well stoppered and set aside in the dark for 30 min. A volume 10 ml of 20% potassium iodide solution was added to it at a time. The liberated iodine was then immediately titrated against 0.1N sodium thiosulphate solution using starch as indicator which was added towards the end point. Similarly the blank determination was also made at the same time. The concentration of the phenol solution was calculated as follows in equation (3.5).

$$\text{mg/l phenol} = 7.842(AB - C) \qquad \text{Equation (3.5)}$$

Where A = ml $Na_2S_2O_3$ used for the blank. B = ml bromated – bromide solution used for sample divided by 10, and C = ml $Na_2S_2O_3$ used for the sample

3.2.2.11 Infrared Measurement

Infra-red spectra analysis was carried on spectrophotomer by applying samples of resin [phenol-formaldehyde (novolac)], and the chitosan. The test samples were placed in an oven at (150 ±2^{0}C) until a constant weight was obtained. The spectra of the cured resins were recorded in a frequency range of 400 to 4500cm^{-1} using potassium bromide (KBr) disc. The KBr was previously oven - dried at 300^{o}C to reduce the interference of water.

3.3.0 CHITOSAN PREPARATION

3.3.1 Deacetylation (DD) of the Chitosan

The chitosan fibre when deacetylated exerts importance effects on their properties and applications.The commercial chitin (20g) was charged into a 600 ml beaker containing 200ml of 50% (W/W) NaOH and $NaBH_4$ as an antioxidant to prevent yellowing of chitosan under the severe alkaline reaction conditions. The reaction mixture was heated at 110^{o}C for 2hrs while stirring, filtered over a glass funnel with perforated plate, and washed continuously with 50% NaOH solution and filtered in order to retain the solid matter, which is the chitosan. The samples were then left uncovered and air dried. The chitosan obtained were in a creamy white form (Muzzarelli, 1990). This pattern was repeated with an already deacetylated samples to obatain different samples with different degree of deacetylation (DD). The DD is an important parameters affecting physiochemical properties such as solubility, chemical reactivity, biodegradability etc.

3.3.2 Neutralization of the Chitosan with HCl

About 1.6 litres of distilled water and about 20ml of 0.5M HCl (pH 2 to 3) were shaken several times with 60-70g chitosan. Using the funnel the chitosan solution was filtered off. This process was repeated several times, until the chitosan was neutral (pH 7). The obtained neutralized chitosan was creamy white and flake in nature. Then it was grinded into powder, using blender and sieved with 100 micro designation and 60 mesh chitosan was obtained.

3.3.3 Determination of Percentage Degree of Deacetylation (DD %)

Degree of deacetylation (DD%) refers to the removal of acetyl group from the chain and is an important for chitosan. It affects the functional properties.This was determined by potentiometric titration. Chitosan homogenous solution was prepared, 0.5g of chitosan was taken and dissolved in 30ml of 0.5M HCL at room temperature with stirring in a beaker until totally dissolved and then two drops of methyl orange indicator was added. The solution was titrated with 0.1M NaOH solution, until a colour change was obtained. The reading was recorded. To calculate water content, 0.3g chitosan was heated at 100°C to a constant weight. The percentage of free NH_2 groups in chitosan is calculated as follows:

$$\text{Free } NH_2\,(\%) = \frac{[(C1V1 - C2V2) \times 0.016]}{G\,(100 - W)} \text{ x } 100 \qquad \text{Equation (3.6)}$$

$$DD\% = \frac{NH2\%}{9.94} X100 \qquad \text{Equation (3.7)}$$

Chitosan theoretical NH_2 content (%) = 16/161×Neat matrix= 9.94% (Renata, 2012).

3.3.4.0 ANALYSIS OF THE CHITiN

3.3.4.1 Loss on Drying

Loss on drying of the prepared chitosan was determined by gravimetric method. The water mass loss was determined by drying the sample to constant weight and measuring the sample after and before drying. The water mass (or weight) obtained showed the difference between the weights of the wet and oven dried samples (Yong-Hu *et al*, 2002). The percentage loss on drying was calculated according to the following equation (**3.**8).

$$\%\text{ loss on drying} = \frac{(wet\ weight, - Dry\ weight,)}{Dry\ weight} \times 100 \qquad \text{Equation (3.8)}$$

3.3.4.2 pH Value

The pH measurements of the chitosan solutions were carried out using a microprocessor pH meter Jenway model 3505 as in procedure **(3.2.2.1).**

3.3.4.3 Solubility in Chemicals

The miscibility with solvents usually described as solubility. The solubility of chitosan was demonstrated in various solutions such as distilled water, acetone, ethanol, acetic acid and lactic acid solution. Chitosan often have limited miscibility with certain solvents.

3.3.4.4 Solubility Test

The solubility test of the chitosan was performed by dissolving a weighted sample in 2% of the test solvents and stirred at room temperature at the desired time and the sample was filtrated, dried and weighed. The solubility was determined by the following Equation (3.9) (Lim and Hudson, 2001).

$$\text{Solubility} = 1 - \frac{weight\ of\ insoluble\ part}{Total\ weight\ of\ sample}\ \% \qquad \text{Equation (3.9)}$$

3.3.4.5 Ash Content

Ash value indicates the purity and efficiency of the demineralization of that of minerals Chitosan ash content was determined by combustion using a constant weight crucible. The crucible was repeatedly placed into an oven at 550^{o}C ±20^{o}C for 30 minutes and then removed, cooling for 30mins in a dessicator, and then weighed until a constant weight W_o was obtained. Chitosan (2.5g) was combusted in the constant weight crucible in an oven at 550^{o}C ±20^{o}C for 3h. The crucible was removed, cooled in a dessicator for 30mins, and re-weighed (W_1). This heating and cooling process was repeated every 1.5h until a constant weight was established (W_2). The ash percentage was calculated by the equation (3.10).

$$\text{Ash\%} = \frac{W2-Wo}{W1-Wo}\ x100 \qquad \text{Equation (3.10)}$$

Where W_o = ls the constant weight of crucible, W_1 = ls the weight of sample and crucible

W_2 = ls the weight of ash and credible The ash content was determined from samples.

3.3.4.6 Moisture Content

The moisture content is a direct measure of the degree of hydrophilicity, which is believed to influence adhesion to a hydrophobic matrix. Moisture content of the chitosan was determined by the gravimetric method. The water mass was determined by drying the sample to constant weight and measuring the sample after and before drying. The water mass was the difference between the weights of the wet and the oven dry sample at temperature of 50^oC. The percentage of the moisture content was calculated by using the equation (3.10) (Kaith *et al.*, 2003).

Percentage of moisture content = $\frac{(Wet\ weight - Dry\ weight)}{Wet\ samples}$ x Neat matrix Equation (3.11)

3.3.4.7 Density of the Chitosan

The density of the chitosan was determined at room temperature (25.0 + 0.2) using the following expression $e = [\ 0.998\ (M_1\ +A)] \backslash [\ (M_2 + A)]$. Equation (3.12)

Where, M_1 = Weight of the solvent or chitosan solution (g) = Weight of pycnometer and solution or solvent – weight of empty pycrometer. M_2 = Weight of water = Weight of pycrometer, and A = correction factor for the thrust of the air , 0.0012 M_2 , and 0.998 = density (g/cm^3) of water at 20^oC.

3.3.4.8 Viscometric Measurement of Chitin/Chitosan

Chitosan was dried in an oven until a constant weight was observed. Then 5.0g of chitosan was dissolved in 500mL of acetic acid (0.1M) followed by mild stirring and heating at about 55^oC overnight to form 10gL^{-1}chitosan solution (pH 3.99). The solution was then filtered to remove dust and other traces of impurities and was used as a stock solution for determining the viscosity of the chitosan solution.

3.3.4.9 Characterization of Chitin/Chitosan

The prepared chitosan was analysed by FT-IR to determine the functional groups, SEM to determine the morphology of the sample and XRD to determine the crystallinity. This was stated in procedures **(3.2.2.11, 3.8 and 3.7)** respectively.

3.4.0 FABRICATION OF COMPOSITES

Each of the Phenol-formaldehyde resins was thoroughly mixed with different weight percentages of fibres; 10%, 20%, 30%, 40% and 50%, using 5% W/W hexamethylenetetramine(HMTA), (equivalent of the resin) as the hardening agent under atmospheric pressure and temperature. The mixture was degassed at 35^{o}C in a vacuum oven for 10 minutes. The mixture was poured in mould, the surfaces of moulds were coated on the inside with oleic acid to avoid adhesion of the mixture and to allow easy removal of the composite. Composite sheets of size 130mm × 8.5mm × 5mm were prepared by compression moulding technique at a pressure of 400 kg/cm^2 and at a temperature of 120^{o} for 15 minutes. Fibre resin ratio of fibre loading of 40% of 1P:4F and 1P:2F were found to exhibit better mechanical properties. In each case, the number of replications used for the determination of mechanical properties was three. Tests were conducted under ambient laboratory conditions.

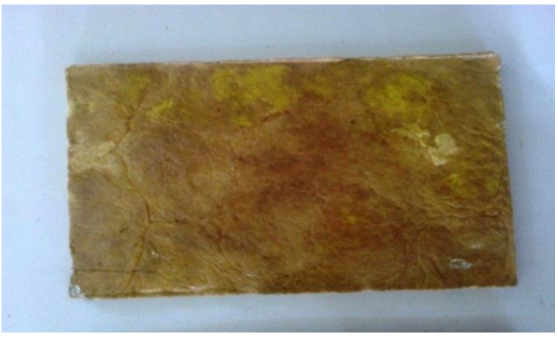


Plate I Prepared composite

3.4.1.0 Analysis of Polymer Composites

The effect of environmental conditions on polymer composite has been the subject of much debate recently. The application of the newly synthesized chitosan reinforced phenol-formaldehyde resins lies in their physical and chemical properties, Keeping in mind the application viability a comprehensive study on the density, swelling behavior in different solvents, moisture absorbance, and chemical resistance behaviors against 1 N HCI and 1 N NaOH were carried out to assess the potential application of this chitosan filler as reinforcing material in a number of engineering applications.

3.4.1.1 Water Absorption

The water uptake of the composites was evaluated according to ASMT D970-81. The composites was preconditioned at 50^{o}C for 24h and weighed (W_i). After immersing in distilled water for 24h, the films were dried with paper towels to remove the excess water on the surface and weighed (W_f). The total weight gain of the composites was used to calculate the absorbed water. The percent moisture absorbance was then calculated in the following manner equation (3.14).

$$\text{Moisture Absorbance } (\%M_{abs}) = \frac{W_f - W_i}{W_i} \text{ X } 100 \qquad \text{Equation (3.14)}$$

3.4.1.2 Density

Density determination of composite materials is an important physical parameter used in assessing the applicability of the fabricated composites materials. The procedure for determining the density of a composite material is the same as that used for any other solid material, and is based on specific gravimetric measurement ASTM specification D792-86.

To calculate the density of the composite, the specimens were weighed on a weighing balance and their weights recorded. Their volumes were calculated from the dimensions. The density were calculated using equation (3.13) .

$$\text{Density} = \frac{mass}{volume} \qquad \text{Equation (3.13)}$$

The masses, m, were determined to nearest 0.001g by using Mettler Electronic top pan balance.

3.4.1.3 Chemical Resistance

For the chemical resistance test, the dried specimens was immersed each in 100 ml of 1 N NaOH and 1 N HCI under ambient temperature and observed for 72 hours. After this the samples were filtered out, dried and weighed. The percent chemical resistance (P_{cr}) was calculated in terms of weight loss in the following manner equation (3.15). This was evaluated according to ASTM D58100.

$$\text{Percent Chemical Resistance } (P_{cr}) = \frac{T_i - W_{aci}}{T_i} \text{ X } 100 \qquad \text{Equation (3.15)}$$

Where T_i is initial weight and W_{aci} is weight after certain interval.

3.4.1.4 Swelling Test

Swelling test was used to observed the effect of polar and non-polar nature of various solvents on the swelling properties of polymer composite so as to assess the properties in various possible applications. Swelling behaviour of the composites were evaluated in solvents such as carbon tetrachloride, ethanol, acetone and water. The swelling property was obtained using the method described in ASTM D -3010 (2010). For the swelling test, the specimens were dried in an oven to contant weights and in a particular temperature and then cooled in a desiccator. A known weight (W_i) of the initial sample immersed in 100 mL volume of the different solvents at room temperature for 15 days the sample was removed and the excess solvents was removed by the help of filter paper, and then the final weight (W_f) was noted. The percent swelling was calculated from the increase in initial weight in the following manner (3.16).

$$\text{Percent swelling (Ps)} = \frac{W_f - W_i}{W_i} \text{ X } 100 \qquad \text{Equation (3.16)}$$

3.5.0 Determination of Optimum Filler Load on P: F Mole Ratio (1P:2F to 1P:8F)

The synthesized 1P:2F to 1P:8F novolac resins, each was taken and reinforced with chitosan at different filler loading of 10% to 50% at 10% intervals.

From the prepared composites at different filler loading of 10% to 50%. Filler loading of 40% with 1P:2F and 1P:4F gave excellent results in terms of mechanical properties. To prove the results, optimization of 1P:2F and 1P:4F were carried out with the 40% filler at different DD% values of 70 %, 81% and 91%. The composites were subjected to physical, chemical and mechanical analysis to optimize the effect of DD % on the composites.

3.5.1.0 Tensile Properties

This is defined as the behaviour of a material under a gradually increasing applied force. Tensile strength testing of a material is generally performed to determine the elastic modulus, yield point, ultimate tensile strength and elongation at break.

3.5.1.1 Tensile Strength Test

The tensile test was performed on the flat specimens. Tensile strength (ultimate) test was carried out as per ASTM standard D 3039. This test was performed using the Hounsfield (Monsanto) Tensometer at a crosshead spread of 5mm/min and gauge length of 40cm. The dimension of the specimen was 80mm x 10mm x 5mm with dog bone geometry made by grinding machine.The stress- strain behavior obtained generated numerous mechanical properties. The test was repeated three times on each composite type and the mean value was reported as the tensile strength of that composite. The tensile strength and tensile modulus were expressed as in equation (3.17 and 3.18) respectively.

Tensile strength (MPA) $= \frac{P}{bh}$ Equation (3.17), Tensile modulus (MPA) $= \frac{\delta}{\varepsilon}$ Equation (3.18)

Where P = Pulling force (N), B = Specimen width (mm), H= Specimen thickness (mm),

$\underline{\delta}$ = Stress (N/mm^2), e= strain.

Plate II Typical Specimens for Tensile Tests

3.5.2 Flexural Test

The flexural strength of a composite is the maximum tensile stress that it can withstand during bending before reaching the breaking point. The three point bend test was conducted on all the composite samples according to ASTM D 790 and 1S0 178 using (universal testing machine 100kN) at a constant rate of 2mm/min and gauge length of 70cm. The dimensions of the specimen was 10mm x 4mm x 80mm. For each test, three replicates samples were tested and the average values are reported.

3.5.3 Impact Strength

The impact strength of a material is the measure of the amount of energy which the material can absorb before its failure. The impact test which is the toughness of a material's ability to resist sudden or impact loads. The impact test was therefore carried out in order to analyze the impact strength of the specimens. The test was conducted in accordance with ASTM D 256 using charpy impact testing machine Cat. Nr412 capacity of 15Jk/25J.

Composite samples made up to dimensions 120mm X 15mm X 5mm and Charpy impact tests were conducted on unnotched samples, low velocity instrumented impact tests were carried out on the composite specimens. Before the test samples were tested, the machine was calibrated. The test sample was mounted horizontally and supported unclamped at both ends. The test samples were then gripped horizontally in a vice and the force required to break the bar was released from the free swinging pendulum. The pendulum was set at certain height and allowed to impact through the specimen to produce a fracture. The value of the angle through which the pendulum has swung before the test sample was broken corresponded with the value of the energy observed in breaking the sample. This was read from the mechanical pointer. The impact strength value was calculated by dividing the energy in KJ recorded on tester by cross sectional area of specimen. $\text{Impact Strength } = \frac{J}{\text{A}}(J/m2)$ Equation (3.19)

Where, J = Energy absorbed (J), A = Area of cross section of the specimen (m^2)

3.5.4 Hardness Testing

Hardness is the property of a material that expresses the degree of resistance to scratching, cutting, puncturing or plastic deformation (usually by indentation). Hardness of the composite sample was tested using a rock well hardness tester . Using the F- scale 60kg as major load and 10kg as minor load with a1/16 inch indenter steel bar and was measured in HRF. HRF is the rock well F- Scale for measurement of hardness (Zwick/Roell Material Testing). A piece was cut from each sample and was placed on the machine, the hardness test was carried out at three different spots on each sample. The test was taken on two different points on each sample. For each test, three replicates samples were tested and the average values are reported.

3..6. Determination of Formaldehyde Released from the Fabricated Composites [formaldehyde Standard Solution]

Formaldehyde emission refers to the quantity of formaldehyde that is freely released by a materials through all its faces and edges in the air of a room under normal or accelerated well determined conditions (Loredana *et al.*, 2013). Freshly prepared formaldehyde stock solution 10ml, was transferred into a conical flask, standard iodine solution 25ml and 10.0ml of sodium hydroxide solution were added.The solution was allowed to stand for 5 minutes. Then the solution was acidified with 11.0ml of hydrochloric acid and titrated for excess iodine by standard sodium thiosulphate solution, 0.1ml of starch solution was added when colour of the solution became pale-straw. After addition of starch solution, immediately the colour was changed to deep blue-black. The titration was continued until the colour changed from deep blue-black to colourless. Similarly, the blank titration was performed. The difference between titration values of blank and sample was used for calculation of formaldehyde contents in stock solution. Hence, the concentration of formaldehyde was determined [appendix B].

3.7. X-ray Diffraction (XRD)

X – ray powder diffraction (XRD) was carried out to investigate the effectiveness of the resin interaction or exfoliation and if any change in the crystalline structure of the composite occurred. Studies were performed on X-ray diffractometer under ambient condition using Cu kα (1.5418Å) radiation, Ni filter and Scintillation counter as detector at 40 kV and 30mA on rotation at 2θ scale and 1s accumulation time and step size of 0.02 degree with 0.5^0 or 1.0mm of divergent and anti-Scattering slit. The continuous scan were taken between 2 to 70.00, at scan speed of 5 degree per minute and present time of 0.24s .Corundum and quartz were used as the reference to verify and calibrate the instrument. The small crystal form of sample was subjected to analysis. The continuous scans were taken and different d – spacing (Å) of each sample run was determined using Bragg's equation (Equation 3.20), taking the highest intense peak as reference (2θ≈20).

$$n\lambda = 2d \sin\theta \qquad \text{Equation (3.20)}$$

The counter reading of the highest peak intensity represents crystalline material and the lowest peak in the halo – pattern corresponds to the amorphous material in the polymer. Degree or percentage of crystallinity (%Cr) and crystallinity index (C.I.) were calculated as per the following method proposed for polymer (Ashish and Balbir, 2013) by using the following equations (3.21 and 3.22).

$$\%Cr = \frac{Ac}{Ac+A\propto} \times 100 \qquad \text{Equation (3.21)}$$

$$\text{C.I.} = \frac{Ac+A\alpha}{Ac} \times 100 \qquad \text{Equation (3.22)}$$

Where: Ac = is the maximum intensity of the reflection at 2θ ≈20 and Aα = is the minimum intensity of diffraction in the amorphous region.

3..8. Scanning Electron Microscopy (SEM)

In order to evaluate changes in the surface morphology of polymer composite, chitosan phenol-formaldehyde resin matrix polymer and composite were analysed by Scanning Electron Microscopy (SEM). SEM micrographs of the samples will show the morphology of the polymer composites prepared. In the SEM study images of the cross-sections of the composites were taken on Quorum Q150RES at an accelerating voltage of 20kV. The samples for SEM characterization were prepared by freezing them in liquid nitrogen before fracturing. Since, phenol formaldehyde matrix had non-conducting behavior, so they were gold plated to have an impact.

3..9. Thermal Analysis

Thermal analysis studies the enthalpy changes associated with heating, annealing, crystallinity or otherwise in thermally treated polymers, and also to study a wide variety of responses of the system to temperature, including polymerization, degradation or other chemical change. Experimental methods involve the use of, thermo gravimetric Analysis (TGA/DTA).This measures the weight change of a sample as a function of temperature. TGA is a technique whereby the mass of a substance is recorded continuously as the temperature is linearly increased from room temperature to a temperature as high as 1200^0C. The information of substance under study can be obtained from thermo gram (a plot of mass (m) verses temperature (T) or derivative thermogram (DTA) (a plot of dm/dT Vs Temperature).

The thermal stability of the prepared P: F alone (resin), reinforced chitosan P: F composite, and DD% composites samples [5mg] were taken for analysis under nitrogen gas from about 20^oC to 600^oC at a heating rate of 10^oC \min . This is in accordance to standard test method for ignition loss of cured reinforced resins ASTM D 2584.

CHAPTER FOUR

4.0 RESULTS

4..1.0 Results Obtained from Synthesized Phenol Formaldehyde (Novolac) Resins

The results of the physiochemical properties of all novolac resins of P: F synthesized from 1P:2F to 1P:8F molar ratios were tabulated and presented in Figures and Tables . The tables were given in Appendix A accordingly as follows pH (Table 4.1), viscosity (4.2) water-tolerance (Table 4.3), density (4.4), , resin solid content (Table 4.5), gel-time and cure-time (Table 4.6), yield yield percentage (%) (Table 4.7), free formaldehyde (Table 4.8), and free phenol content (Table 4.9).

4.2.1 FT-IR Analysis of Synthesized 1P:4F, 1P:5F and 1P:6F Novolac Resins

FT-IR of synthesized novolac resins were given in Figures 4.1, 4.2 and 4.3, and summary of the important IR-characteristic bands were given in appendix A Table 4.10.

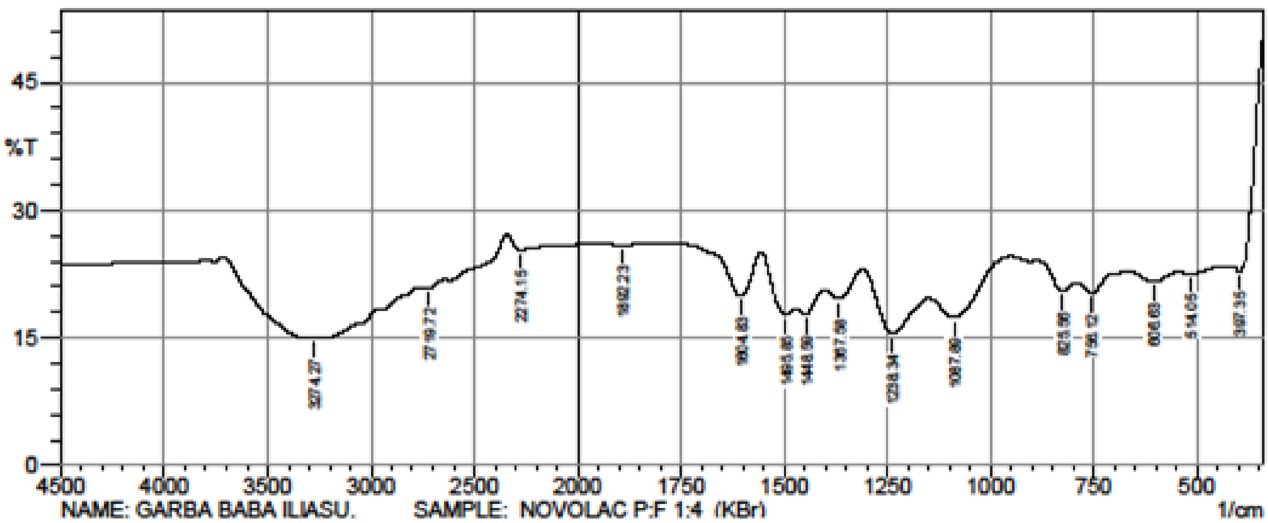


Figure 4.1: FT-IR of novolac 1P:4F resin

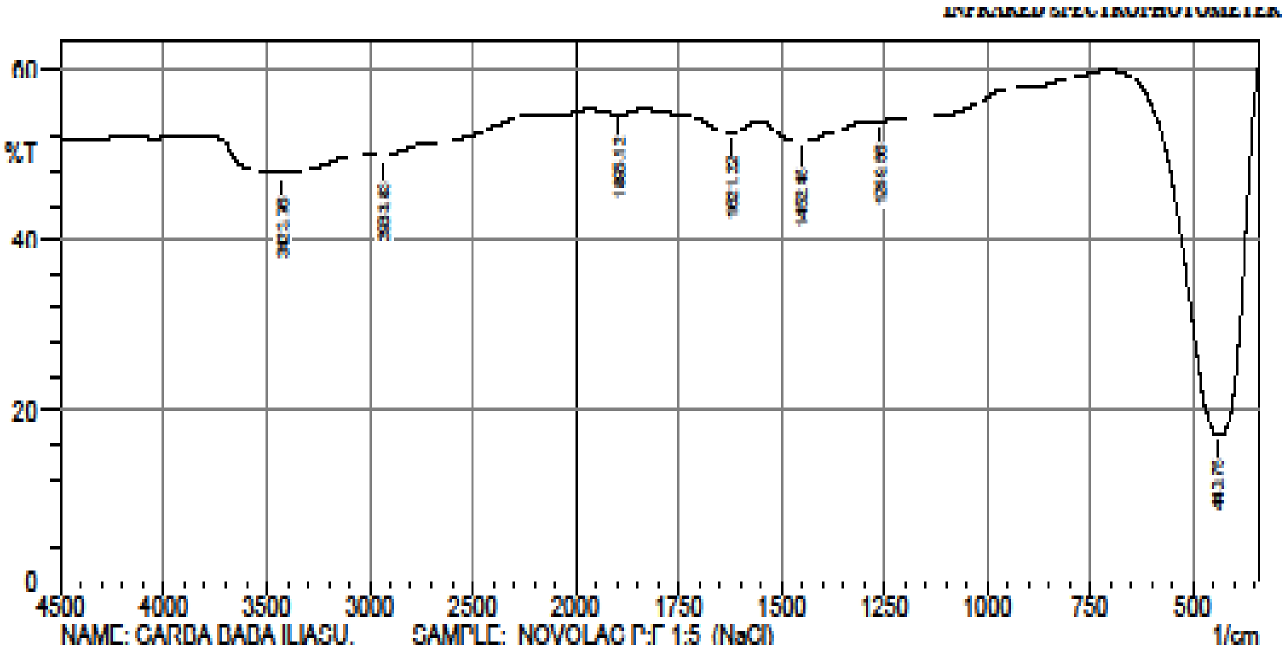


Figure 4.2: FT-IR of novolac 1P:5F resin

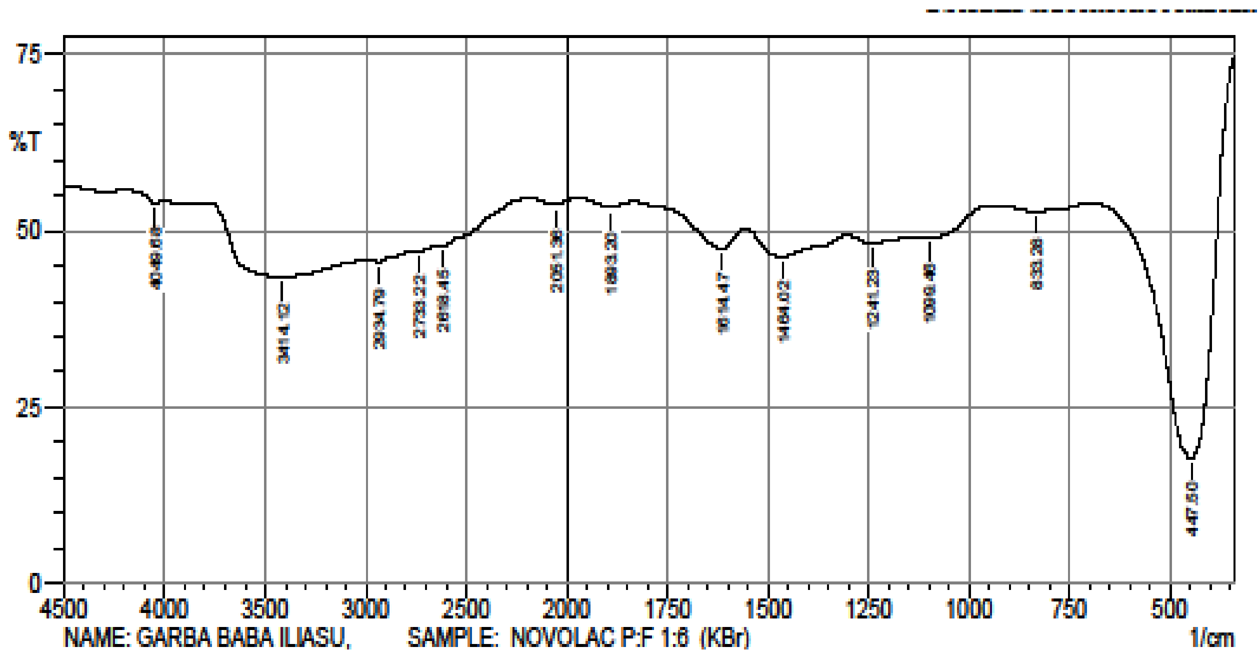


Figure 4.3: FT-IR of novolac 1P:6F resin

4.2.2 Characterization of Synthesized Phenol Formaldehyde Novolac Resins

SEM analysis of neat matrix is given in Figure 4.12 and TGA/DTA in Figure 4.16

4.3.0 Results Obtained from Chitosan Preparation

Results of titration volumes used to calculate values of the degree of deacetylation (DD %) of commercial chitin and deacetylated chitosan, 70%, 81%,and 91% DD are shown in appendix A Table 4.11. Formulars and equations used to calculate values of the degree of deacetylation (DD %) of commercial chitin and deacetylated chitosan, 70%, 81%,and 91% DD are also shown in appendix A. The purchased commercial chitin were treated and subjected to various analysis : Loss on dring, pH, Solubilty test, Ash value, Moisture content, Specific density, Viscosity and colour. The results of the experimental and the theoretical of the various tests were given in appendix A Table 12 . Summary of characteristic FT-IR absorption band of the chitin/chitosan were shown in Table 4.13. The FT-IR Spectra of fresh chitin and the deacetylated chitosan (70 and 81 DD%) were shown in Figures 4.4, 4.5 and 4.6). XRD of the chitin were also given in Figure 4.7 .

4.3.1 Characterizationof Chitin / Chitosan

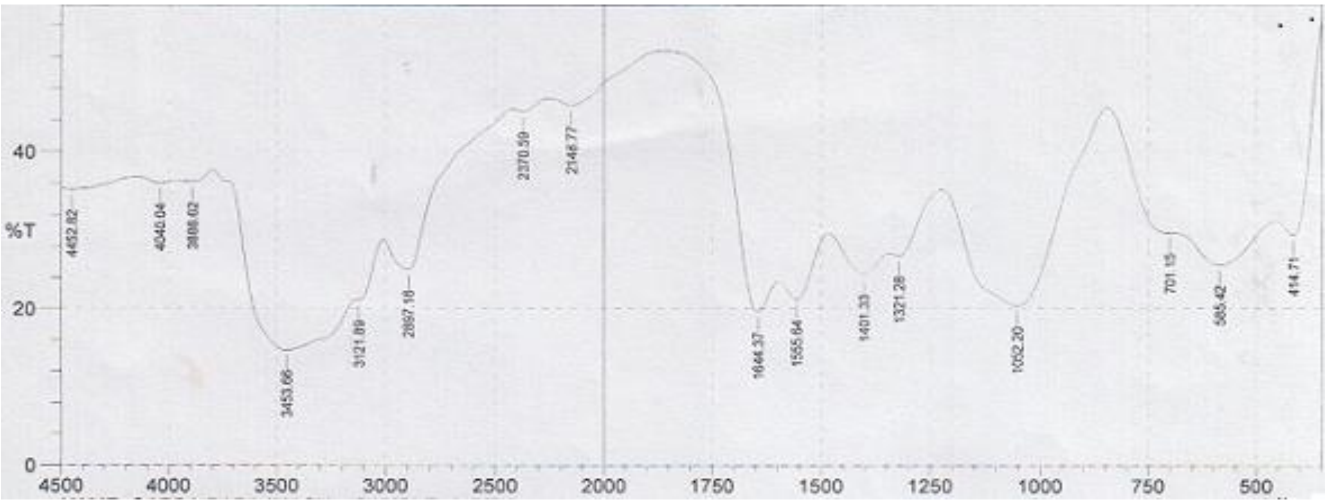


Figure 4.4: FT-IR of fresh chitin

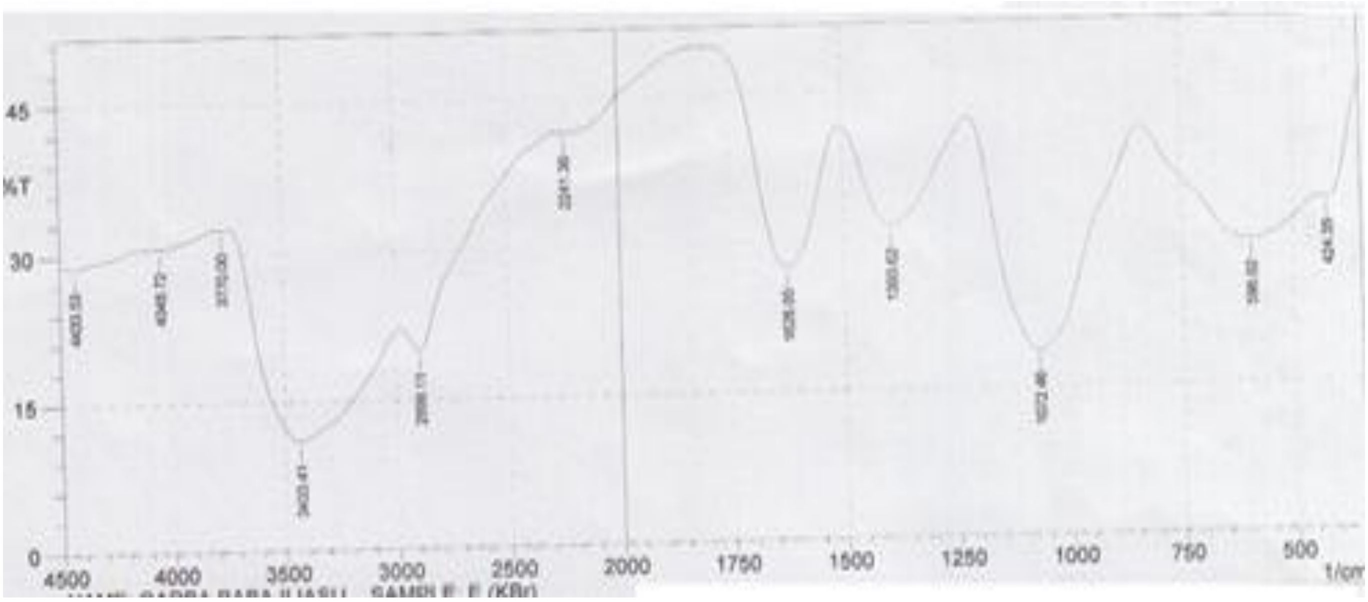


Figure 4.5: FT-IR of 70% DD

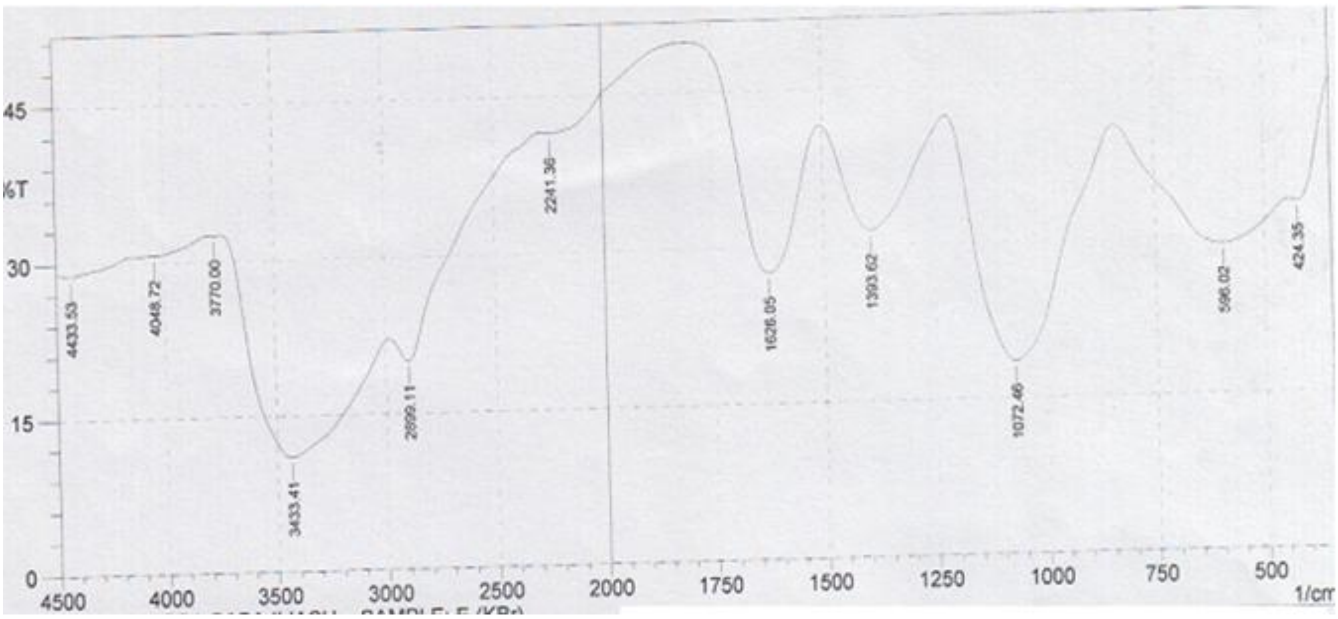


Figure 4.6: FT-IR of 81% DD

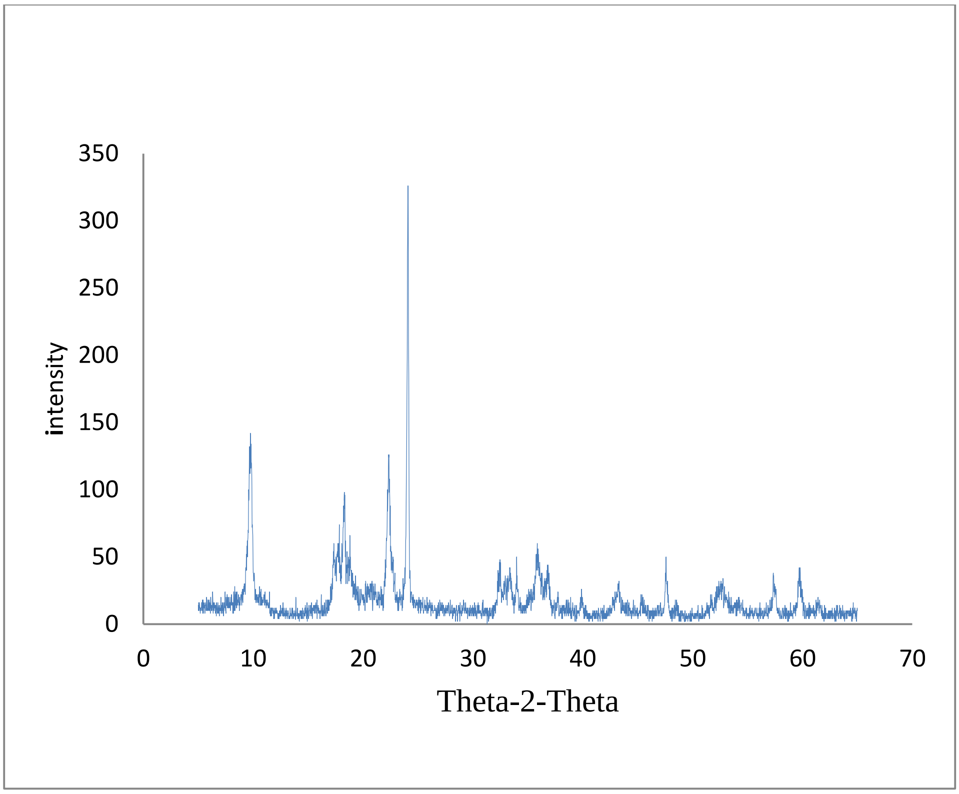


Figure 4.7: XRD of chitin

4.4.0 FABRICATION OF COMPOSITE

4.4.1 Results Obtained from the Synthesized P: F Resins Reinforced With Chitosan at Different Percent Filler Loading (10%, 20% to 50%).

To get the optimum from various P: F mole ratios, all the synthesized resins (1P:2F to 1P:8F) were reinforced with chitosan at different filler loading of 10%, 20% to 50% .and then they were evaluated by physical properties : density and water absorption of the composites at different filler loadings were also calculated and tabulated and given in appendix A Table 4.14 and Table 4.15. Tensile properties of tensile strength/modulus results obtained were given in appendix A Table 4.16 and Table 4.17.

4.4.2 Optimization of Chitosan/Phenol Formaldehyde Composite

All tables in this section were shown in Appendix A. It has been observed that at different filler loading (10%, 20% to 50%) chitosan/phenol formaldehyde composite in the ratio of 1P:4F and 1P:2F exhibited good optimum of physical properties appendix A (Tables 4.14 to 4.15) and mechanical properties from Tables 4.16 and 4.17 in appendix A. Therefore 40% composite of P: F ratio of 1P:4F and 1P:2F were selected for further analyisis. Then composites at different degree of deacetylation (70%, 81% and 91% DD) composites were fabricated for further analysis. Summary results obtained fron the physical properties of composites of 1P:4F and 1P:2F of 40% loading at different DD% were determined : water absorption , density, chemical resistance and given in Table 4.18 (appendix A) and swelling behavior were shown in Table 4.19 (appendix A) .Mechanical test (s) properties were carried out at different DD% as shown in Table 4.20 (appendix A). It was observed that 70% DD with the ratio of 1P:4F gave a maximum tensile strength of 18.40MPa and minimum of 13.20MPa at 91% DD of 1P:4F. A minimum value of tensile modulus of 131.87MPa was observed by 91% DD of 1P:2F and maximum tensile modulus of 70% DD (1P:4F) gave 284.19MPa Table 4.20 appendix A.

Hence further analysis of the prepared composites were proceeded. other mechanical properties at different DD% were determined and results obtained are given in appendix A Table 4.20 and these include, the flexural test of sample ratio 1P:4F could bear a maximum flexural strength of 308.75MPa at 91% DD and minimum flexural strength of 277.66MPa at 70% DD of 1P:2F. High value of flexural modulus of 2,284MPa was given by 91% DD of sample ratio of 1P:4F and a least value of 897.00MPa at 70% DD of 1P:2F Table 4.20 appendix A. Further, the sample of ratio 1P:4F and 1P:2F exhibited impact strength of 924J/N^2 and 666.66J/N^2 and maximum hardness of 46.07HRF and 44.43HRF Table 4.2.0 appendix A. Effect of DD on formaldehyde emission is given in Table 4.21. Characterization of the optimum composites of

1P:4F and 1P:2F such as XRD, SEM, and TGA/DTA of untreated, neat matrix and different DD 70%, 81% and 91% values were carried out on the PF/chitosan composites and are shown in figures in this section below.

4.4.2.1 Results obtained from Characterization of the Optimum Composites of 1P:2F and 1P:4F

Table 4.21 in appendix A gave the results of effects of DD% on the emission of formaldehyde and percentage crystallinity (%Cr) and crystallinity index (C.I) of the untreated, neat matrix and different DD of 70%, 81% and 91% of 40% filler loading of 1P:4F.

4.4.2.2 XRD, SEM, and TGA/DTA of the Optimum Composites of 1P:2F and 1P:4F

Here all the Figures of all characterized samples of the composite samples of the optimized 1P:4F and 1P:2F and their Spectra of XRD, SEM, and TGA/DTA are shown in this section.

4.4.2.2.1 XRD of Neat Matrix and the Deacetylated (DD) 40% of 1P:4F of 70%, 81% and 91%

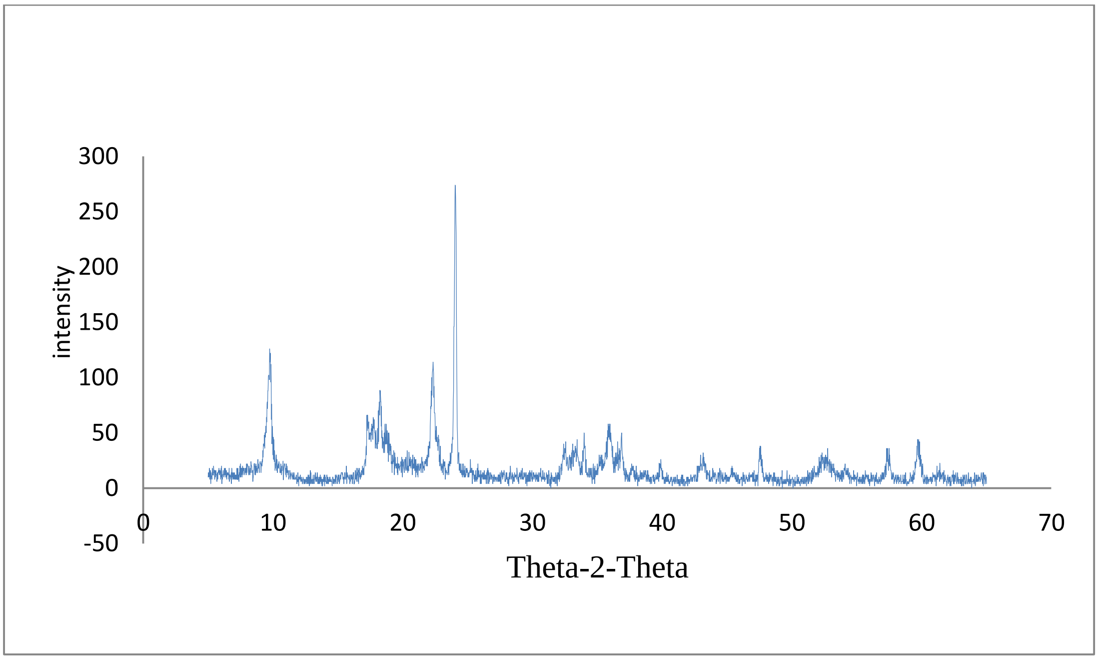


Figure 4.8: XRD of untreated

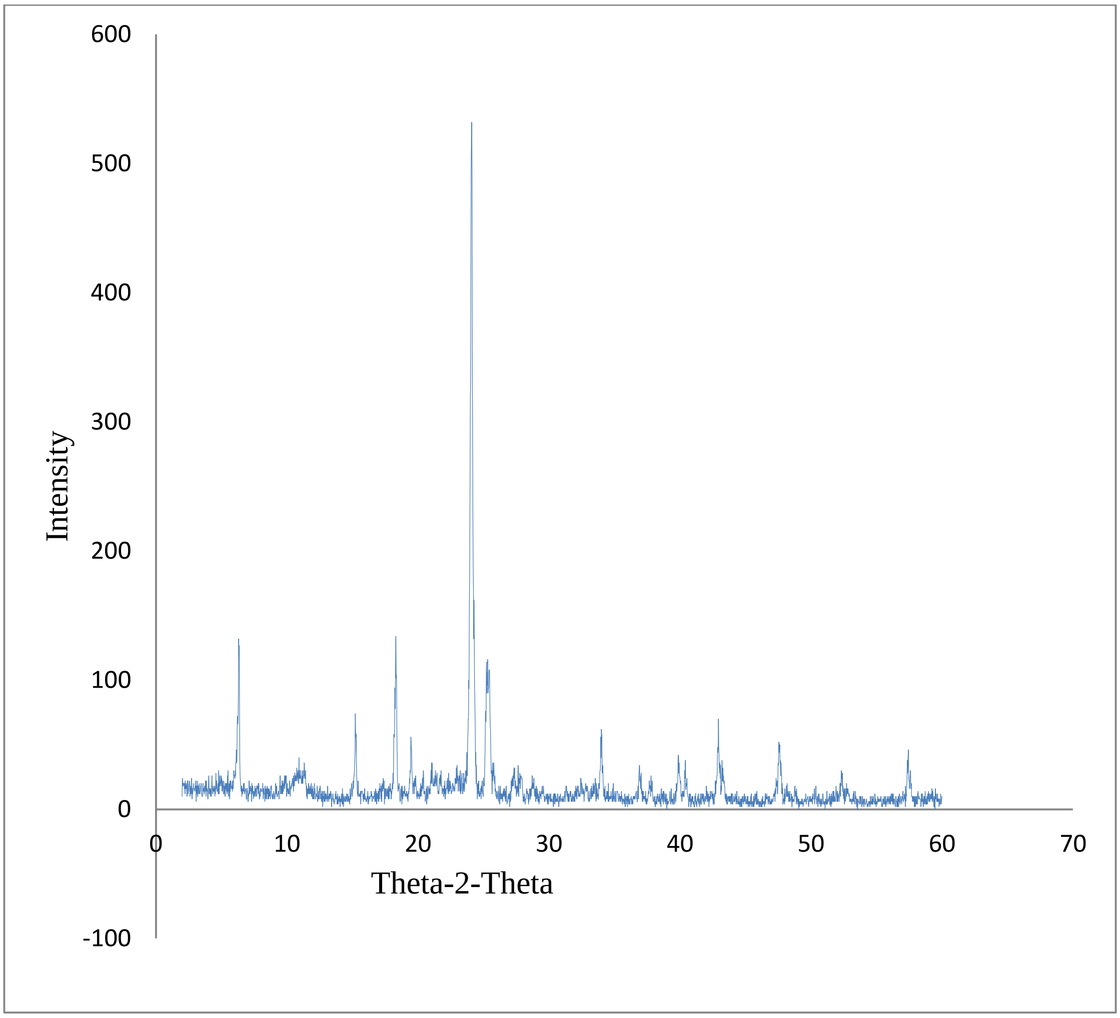


Figure 4.9: XRD of 70% DD of P: F composite

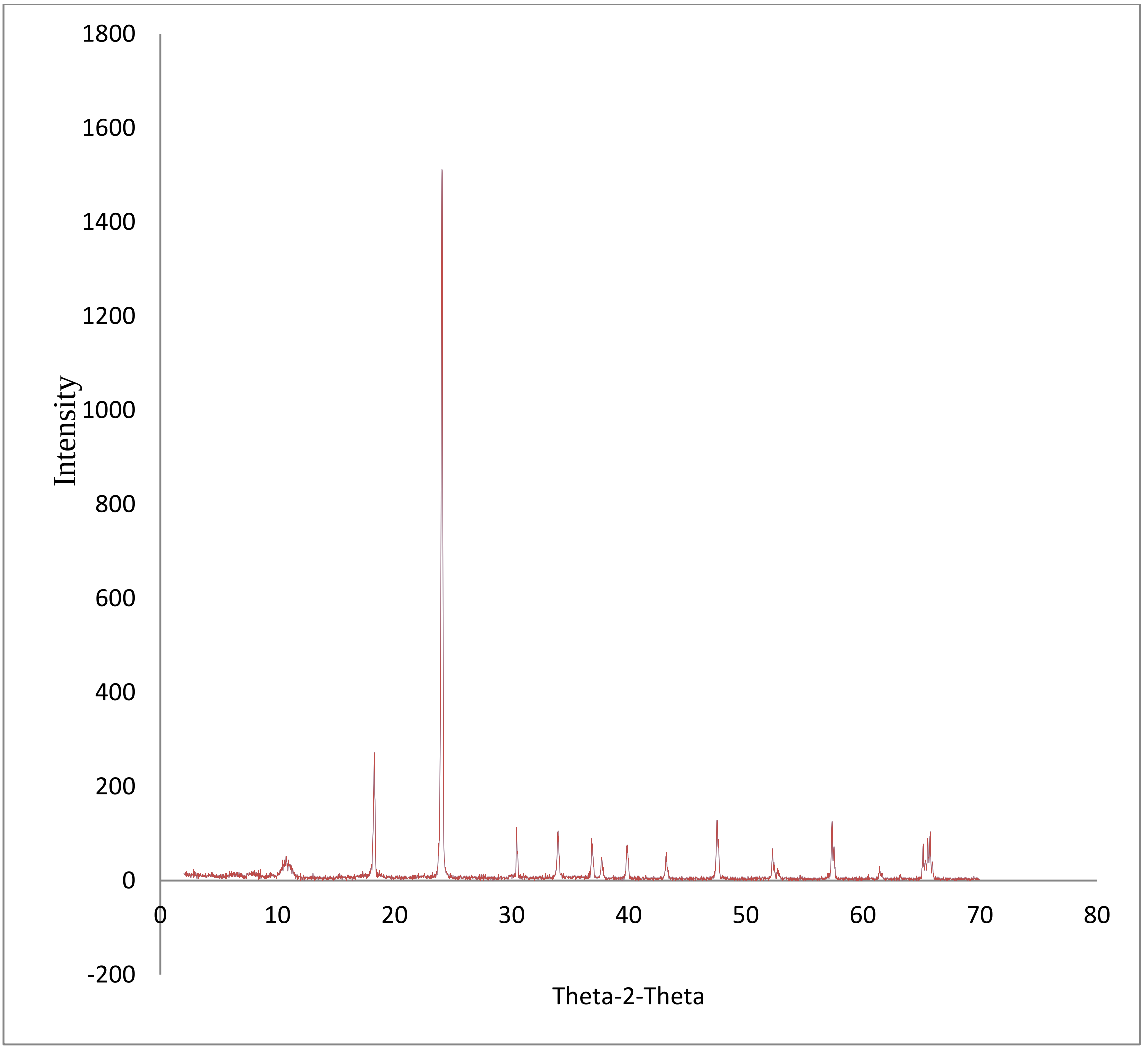


Figure 4.10: XRD of 81% DD of P: F composite

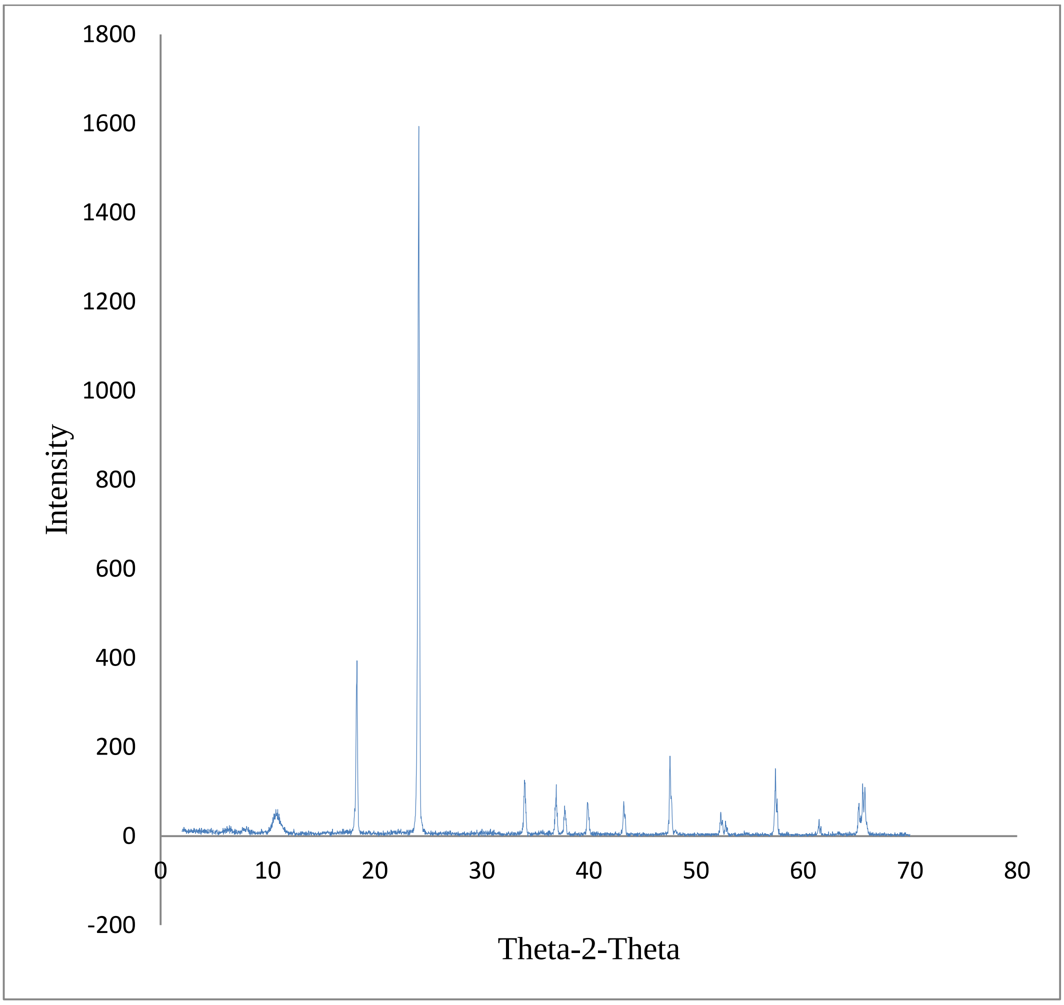


Figure 4.11: XRD of 91% DD of P: F composite

4.4.2.2.2 Scanning Electron Microscopy (SEM) Images of fractured surface of neat matrix , and composites of 40% of 1P:4F 70% and 91% DD.

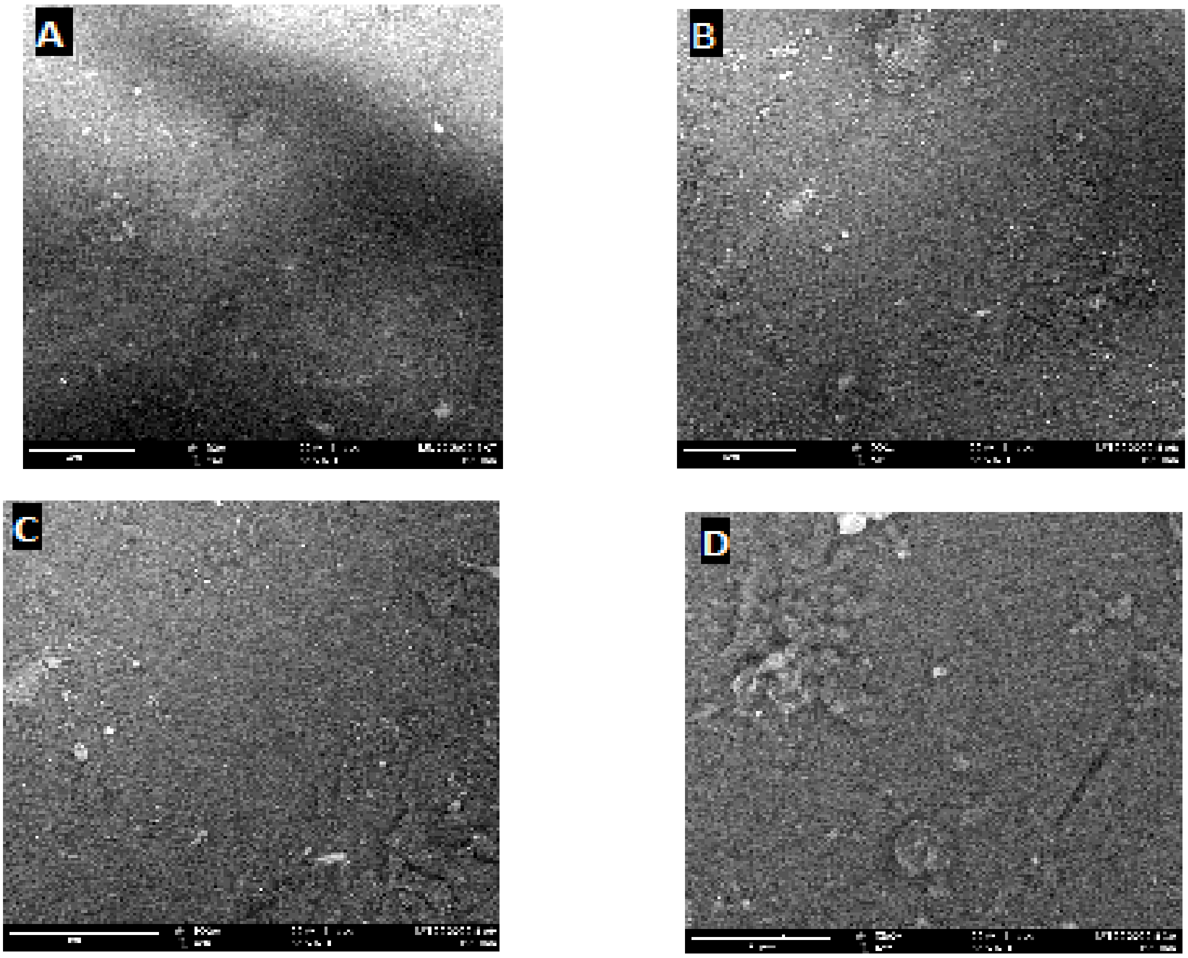


Figure 4.12: A – D SEM images of fractured surface of P: F 100% (neat matrix)

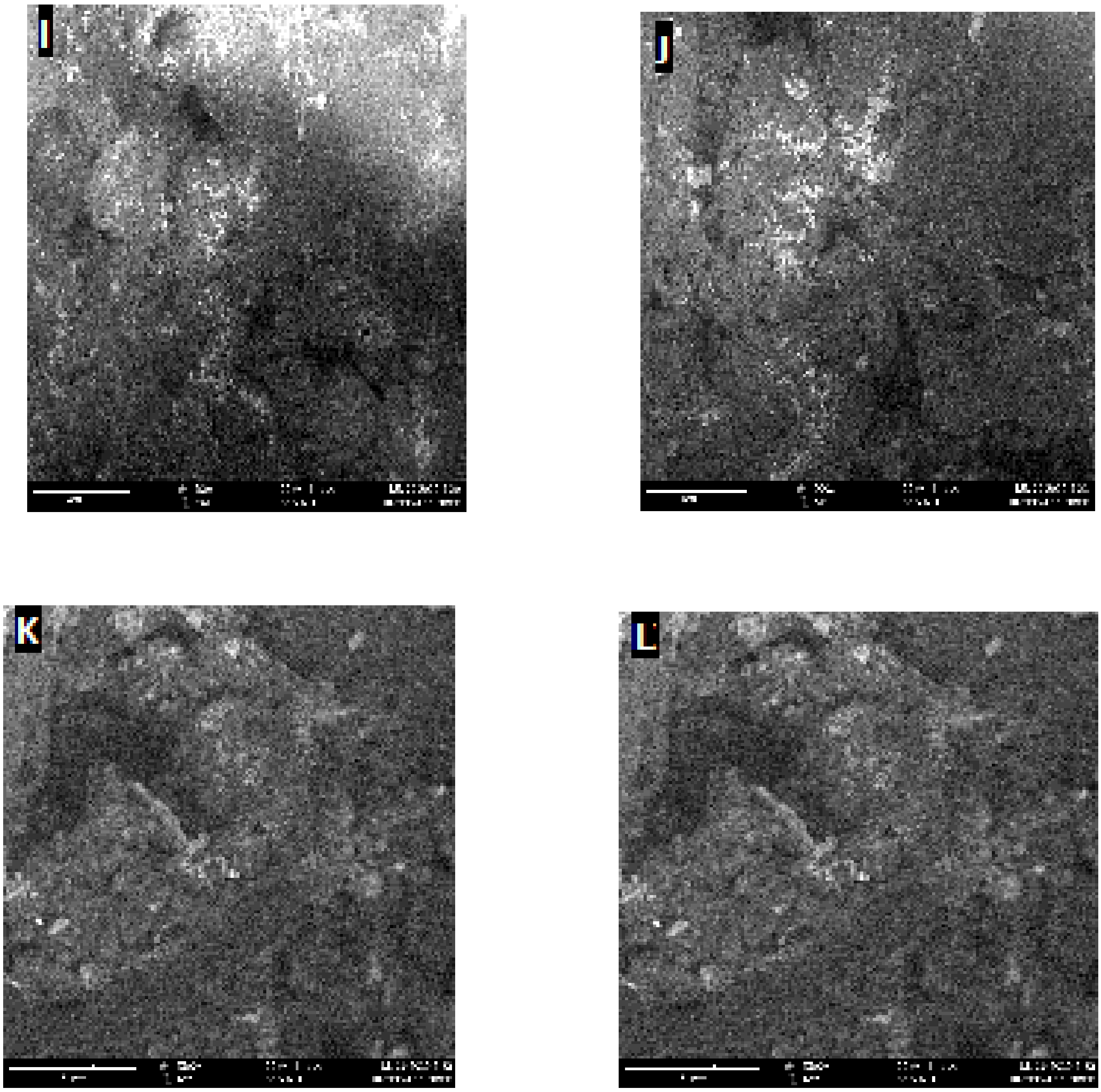


Figure 4.13: I – L SEM images of fractured surface of untreated

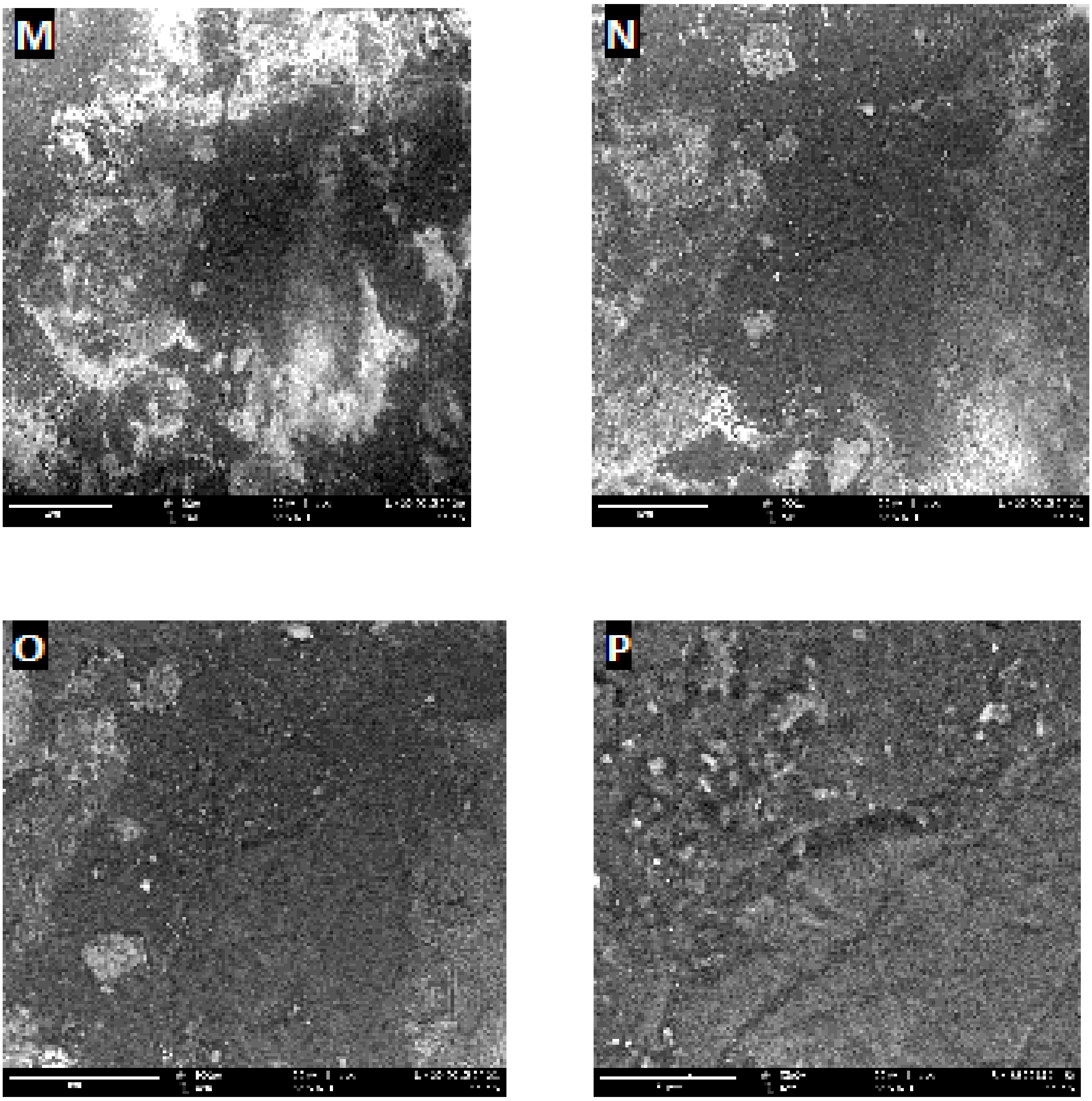


Figure 4.14: M – P SEM images of fractured surface of 70% DD composite

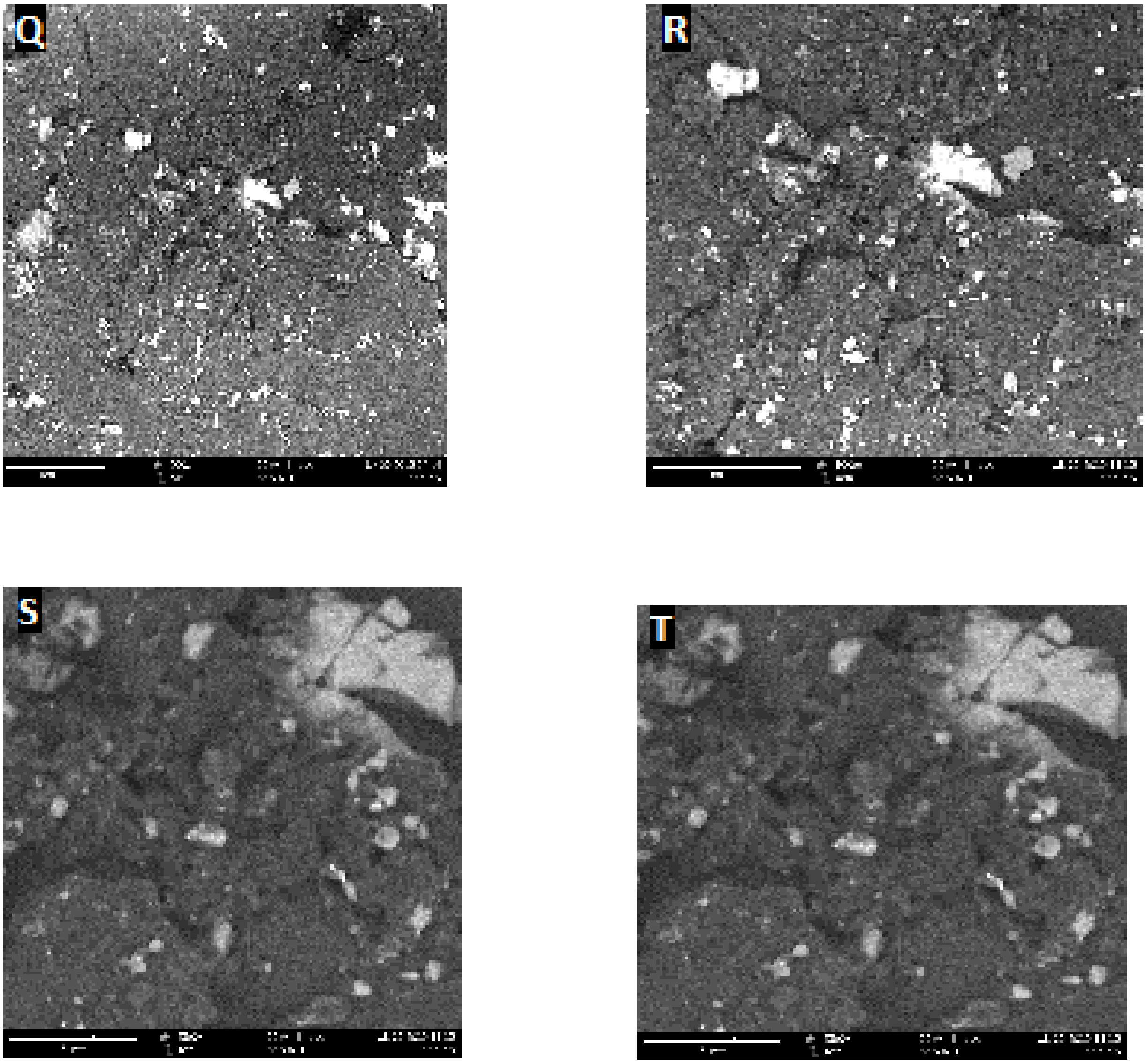


Figure 4.15: Q – T SEM images of fractured surface of 91% DD Composite

4.4.2.2.3 TGA/DTA of neat matrix and the deacetylated (DD) 40% filler loading of 1P:4F of 70%, 81% and 91% composites .

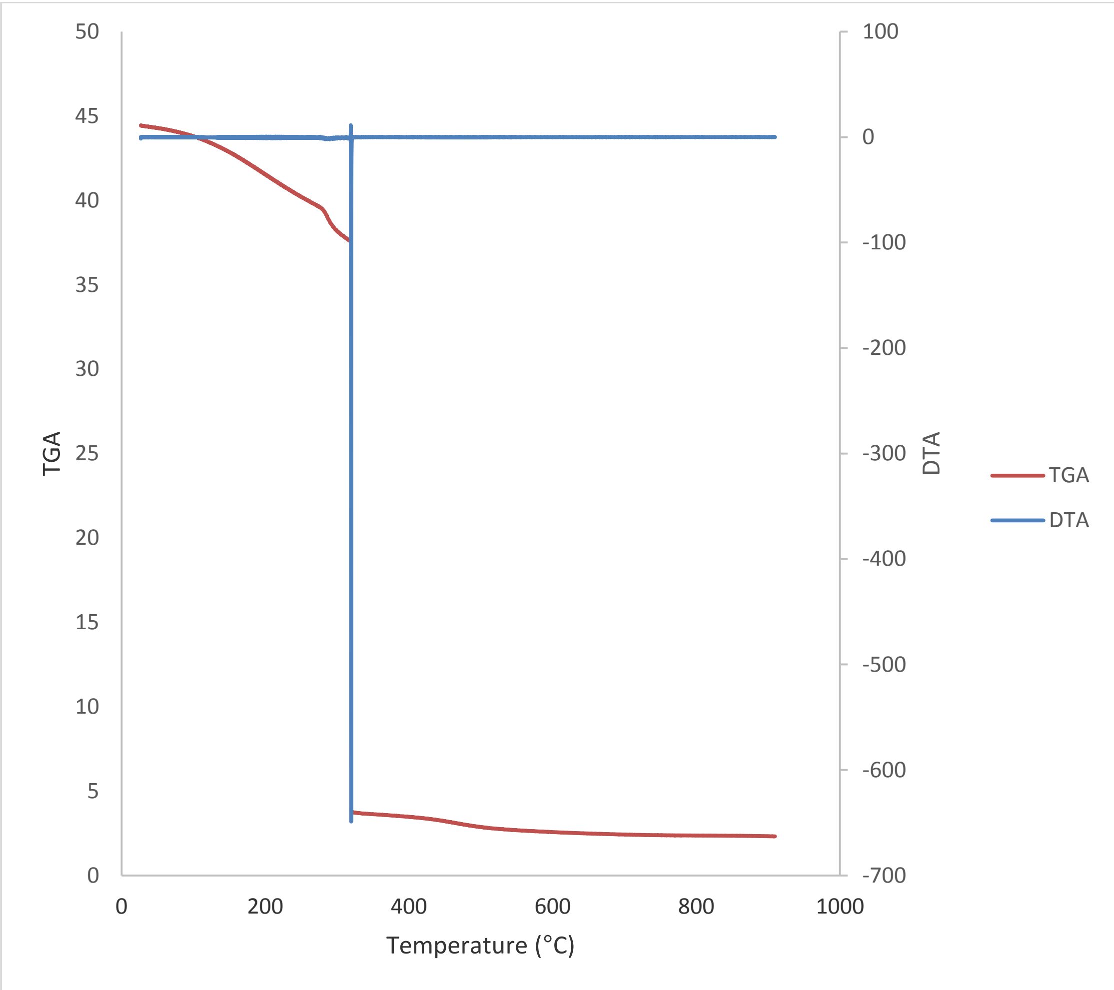


Figure 4.16: TGA/DTA of neat matrix

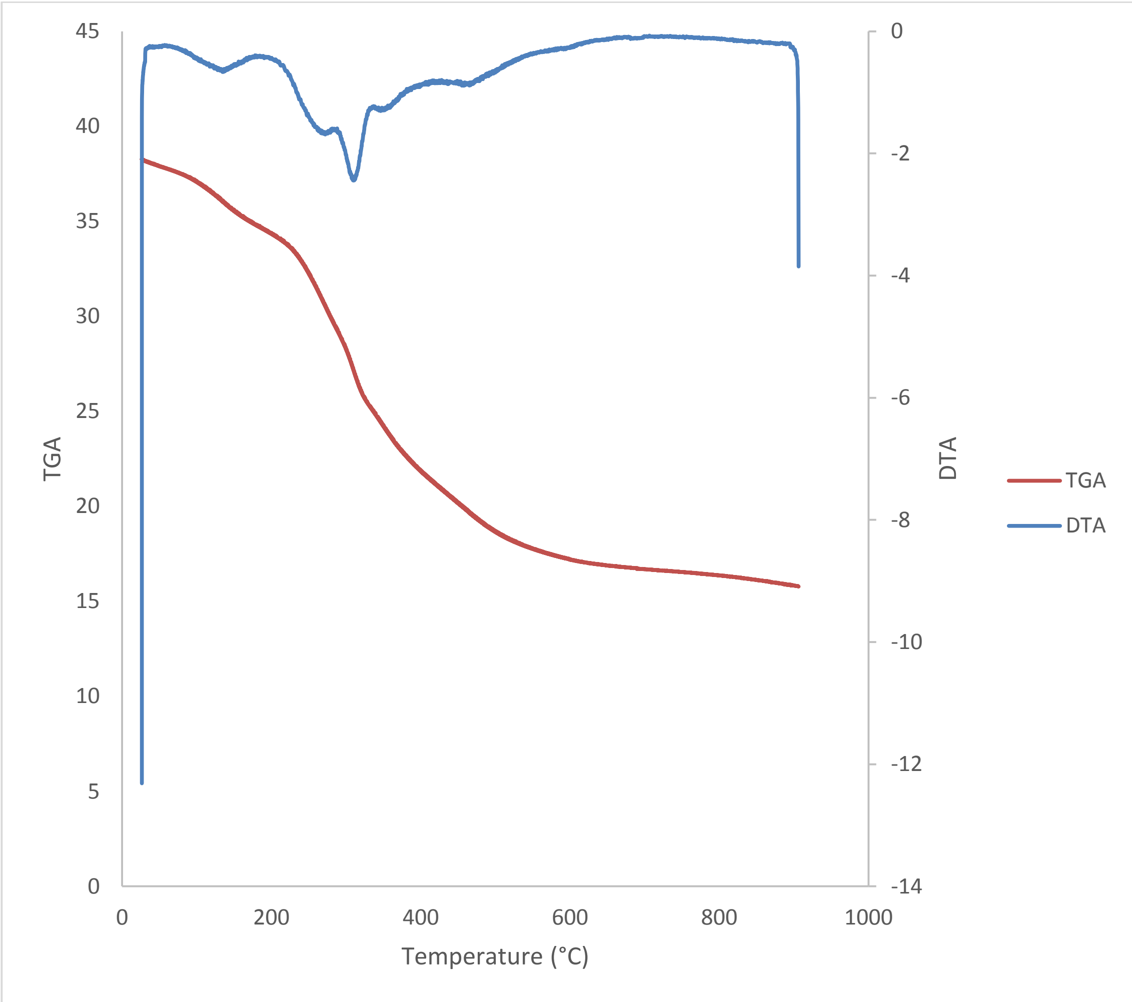


Figure 4.17: TGA/DTA of 70% DD composite

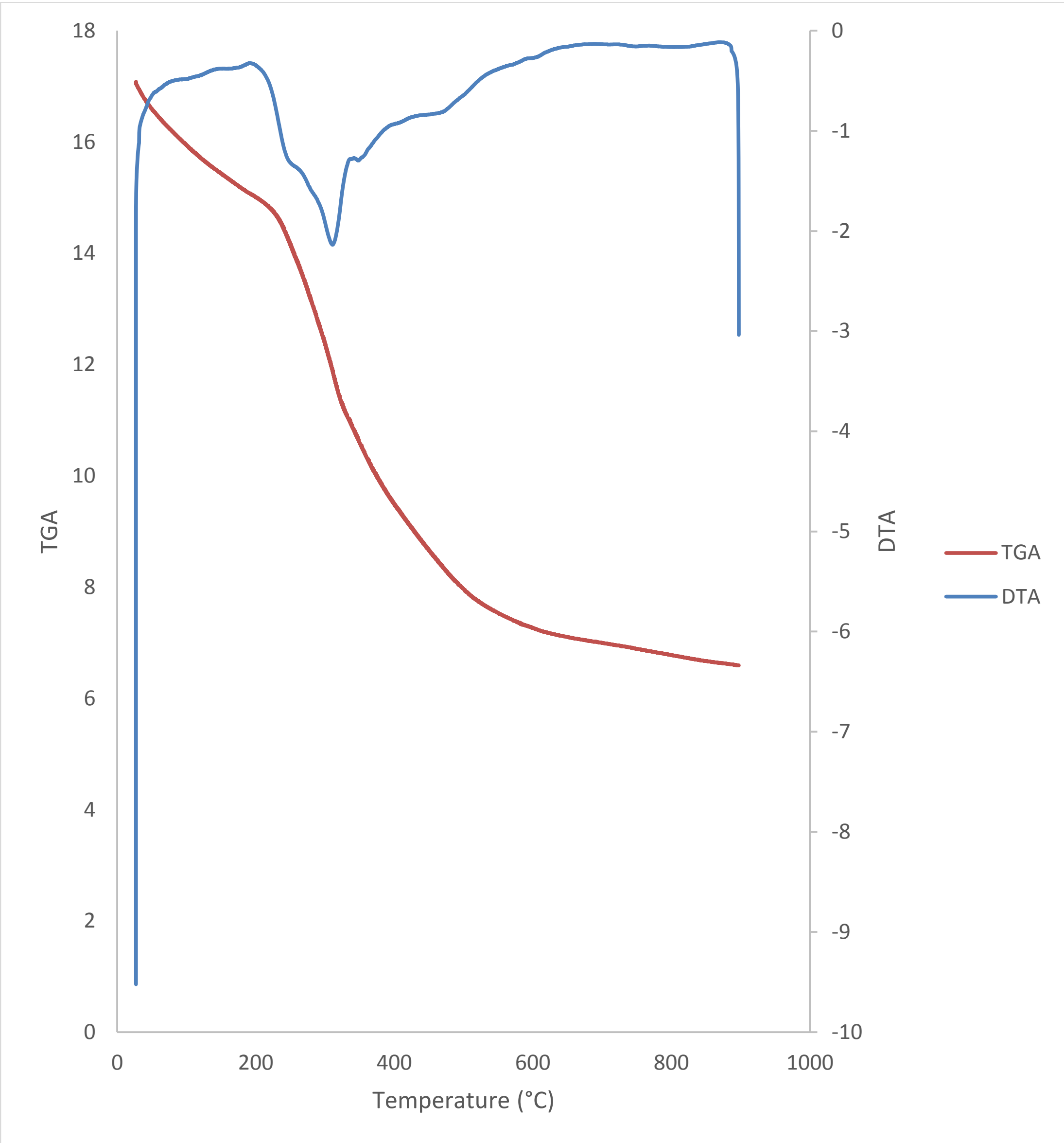


Figure 4.18: TGA/DTA of 81% DD composite

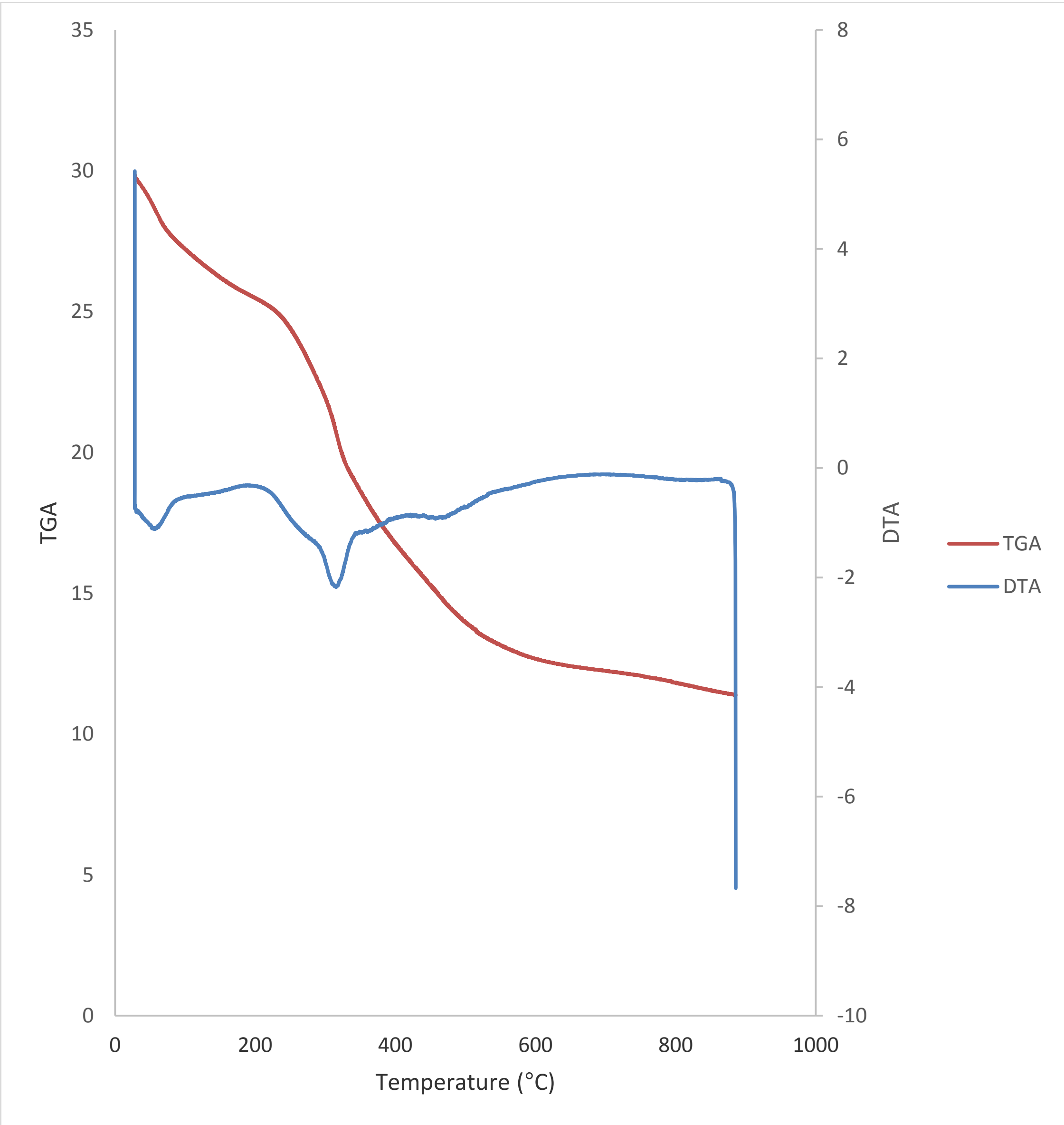


Figure 4.19: TGA/DTA of 91% DD composite

CHAPTER FIVE

5.0 DISCUSSION

5.1.0 Physiochemical Properties of Synthesized 1P: 2F to 1P:8F Novolac Resins.

5.1.1 pH and Viscosity of synthesized novolac resins

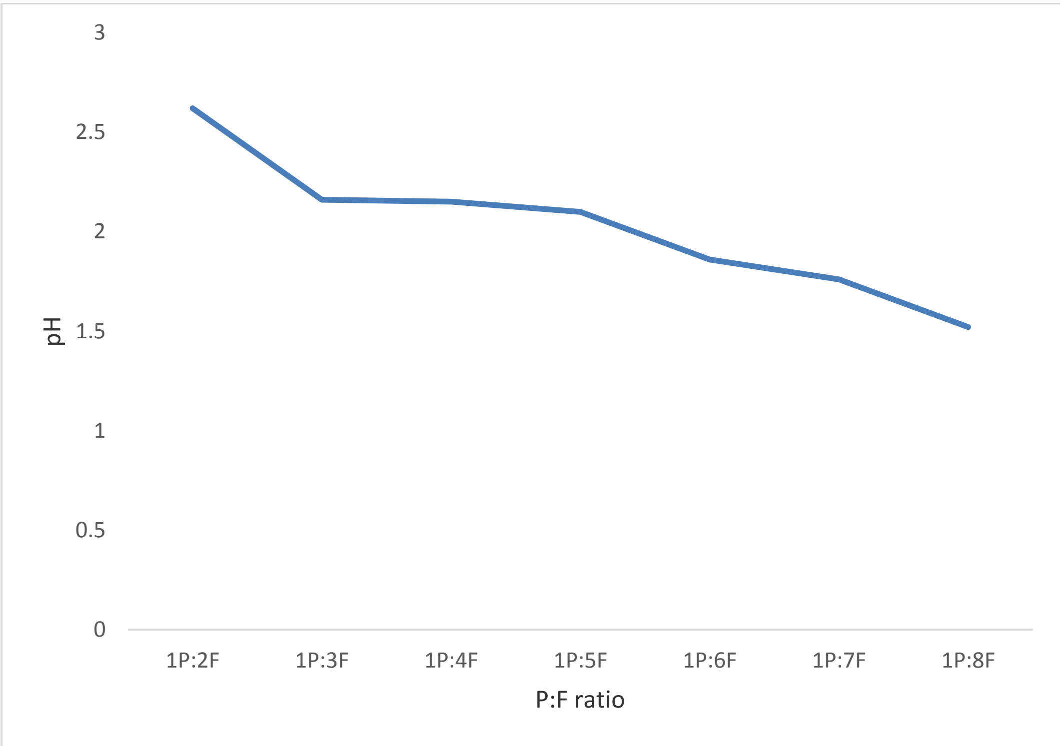


Figure 5.1 : pH Values Vs Synthesized P:F novolac resins

The pH values of the novolac resins (1P:2F to 1P:8F) measured at room temperature are considered reasonable as compared to the values obtained from literature for the standard P:F resin (Pavlos *et al.*, 2000). It ranges from 1.5g/cm^3 to 2.6g/cm^3.Thereby, confirming the influence of composite additives on viscosity variation Figure 5.1.

The viscosity of the chitosan is greatly affected by molecular weight, ionic strength, pH and temperature of the solution Figure 5.2 above. The viscosity of the solution increases with increases in concentration of the chitosan and the degree of deacetylation, but decrease in temperature and pH Figure 5.2 below. It posseses pseudoplastice behavior with the solution viscosity decreasing with an increase in shear rate (Prajakta and Prashant, 2015). Viscosity variations of all the synthesized resins 1P:2F to 1P:8F are shown in Figure 5.2 and Table 4.2 in appendix A. The range of viscosity linearly increases as the amount of formaldehyde added increases.

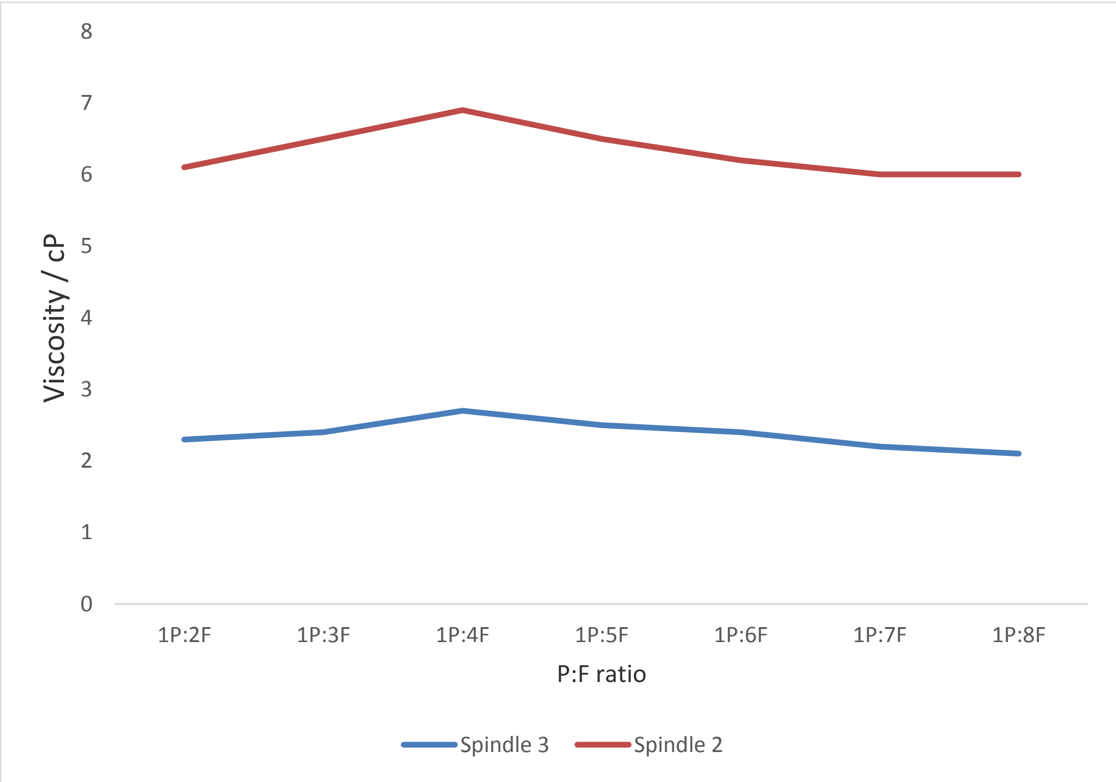


Figure 5.2: Viscosity values Vs Synthesized P:F novolac resins

Table 4.2 in appendix A and Figure 5.2 showed the measured viscosity values of the novolac resins synthesized for various ratio ranged from 2.1 (1P:8F) to 2.7 (1P:4F) (cP) for spindle 3 and 6.0 (1P:8F) to 6.9 (1P:4F) (cP) for spindle 2, which is comparable with the results reported earlier in the case of (Liying *et al.*, 2012). However, it is smaller than the typical viscosity range of (Mo *et al.*, 2015) the low viscosity value 1.3cP to 4.0cP may be attributed to the low molecular weight P:F molecules (Venderbosch and Frins, 2010) as indicated by GC-MS and GPC studies, and to low water content of the P:F. lt is clear from Figure 5.2 that viscosity linearly increases with the increase in formaldehyde solution because in the solution polymer chains tend to orient in the flow direction with an increase in shear rate. This figure also demonstrates a constant strain rate velocity increases with increase in formaldehyde contents because it provides resistance to flow (Mamoor *et al.,* 2009).

The viscosity of crude P:F at various ratios may be taken as an indirect indication of the P: F reactivity as it is generally believed that higher depolymerization of the P: F mass as expected reactivity of the resulting product. Furthermore the viscosity is a critical parameter during pumping and injecting of synthezed P: F during its process handlings. The viscosity of the resin is an important physical properly that affects its movement and flow behavior. Highly viscous resins are more resistant to deformation by stress and flow less easily, while the less viscous resins flow more easily and are less stress-resistant during different physical applications.

5.1.2 Water Tolerance

In principle water tolerance of polymer seems to be excellent candidates as reaction and catalyst supports. Dilute solutions of polymers allow rapid unimpeded access of reactants and reagents to functional groups on the support, and the recovery and separation of the polymer might be achieved by addition of a suitable precipitant, by micro- or ultra- filtration, and in some by thermal recycling (David and Sherinton, 1998). Water tolerance is a viable means of water purification in the 1960s with the development of high performance synthetic membranes (Amjad, 1993).

Generally speaking, lower water tolerance indicates that the system is easier to phase separate when water is introduced. In this case, water tolerance of a system is defined as the volume of water required to bring the system to separate and is determined by titration method (Da-Ming *et al.*, 2000). In a research conducted by Da-Ming Wang in the role of solvents and additives in the formation of cellular surface structure. The results show that systems with spontaneous emulsification have less water tolerance than those systems without spontaneous emulsification.

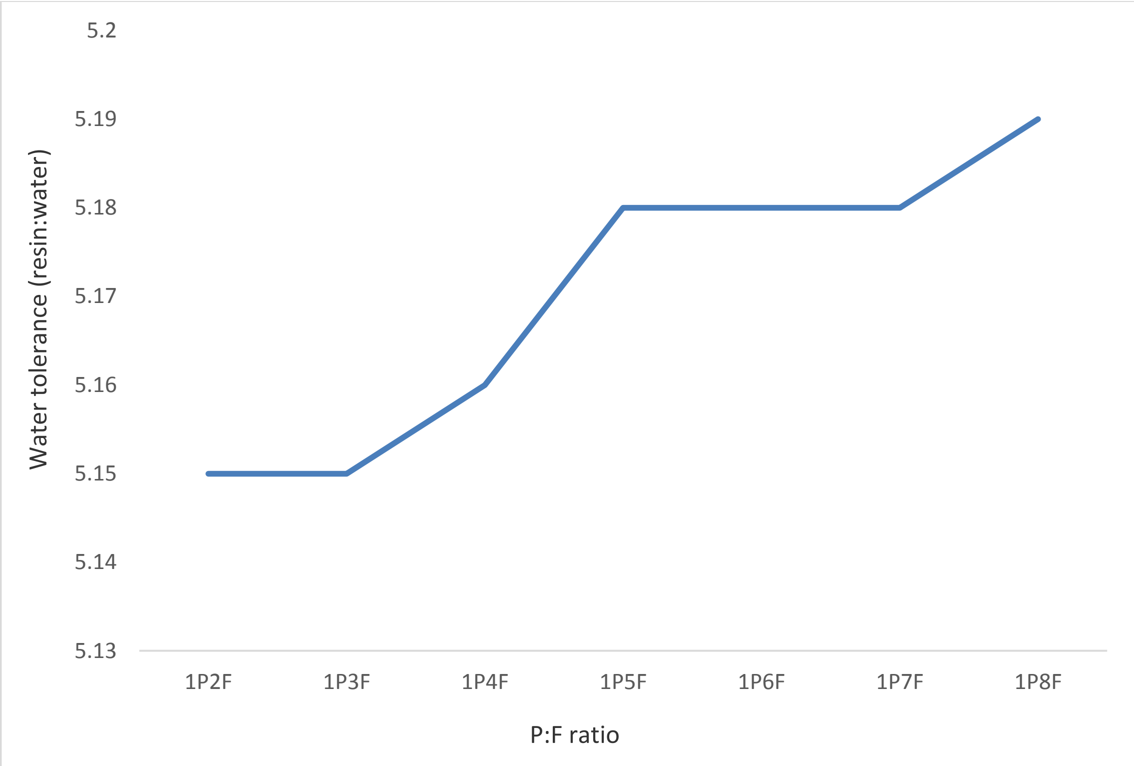


Figure 5.3: Water tolerance Vs Synthesized P:F novolac resins

Table 4.3 in appendix A and Figure 5.3 showed the water tolerance of 1P:2F to 1P:8F of synthesized novolac resins. In all the cases the water tolerance is more than 160%. And it increases from 1P:2F to 1P:8F mole ratio, with a saturation from 1P:5F to 1P:8F. Distilled water at 25^{o}C is gradually added to 10g resin until the resin solution turns hazy. In another words, the term "water tolerance" means the relative amount of water that will cause clouding. The water tolerance of a resin is an indication of the miscibility of the resin with water. To get the water tolerance are to mix a given amount of the resin solution with water and note the number of volumes of water required to cause the first appearance of clouding.

It is an important parameter for resin used in fiber/glass binders since the phenolic resin is normally distilled with water to a concentration as low as 2%. Maintaining a clear solution without phase separation at such dilution is essential for high quality film properties. The higher the water tolerance of the resin is, the lower is the molecular weight of the resin. A low molecular weight resin has more polar end groups than a more condensed resin (Johanneskarl , 2005). Another application of water toterance is in the membrane technology. The most common microporous membranes are phase inversion membrane (Baker, 2004). These are produced by cast film from a solution of polymer and solvent and immersed in the cast film in a nonsolvent for the polymer, which are hydrophilic, so water is the common nonsolvent (Pinnau and Freeman, 2000). Upon contact with the water, the polymer precipitates to form the membrane. The degree of acetylation has a large effect on the resulting membrane properties. A high degree of acetylation gives high salt selection but low permeability (Kesting, 1977). Lower degree of acetylation yield membranes with lower ejection but higher flux.

5.1.3 Density

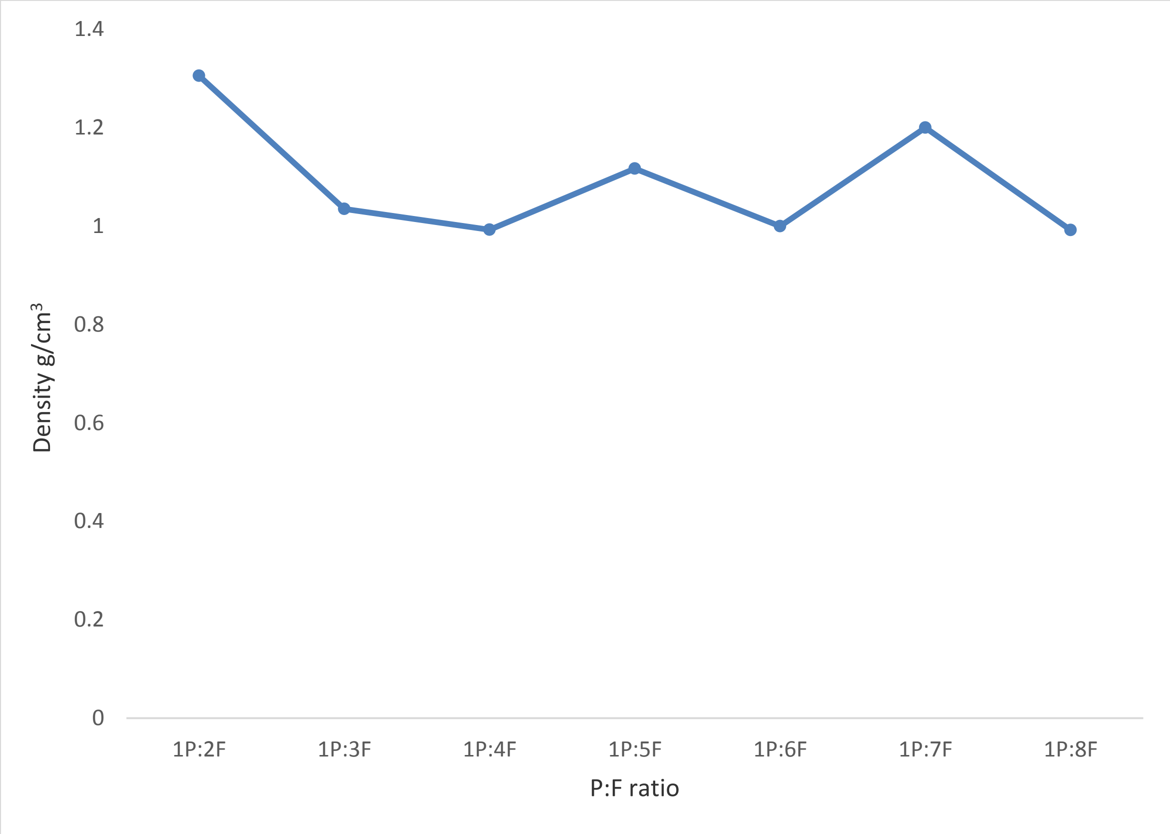


Figure 5.4: Density Vs Synthesized P:F novolac resins

One of the advantages of fibre reinforced polymer composite is its low density and low weight materials can be obtained .The results obtained from density of all resins novolac are shown in Table 4.4 in appendix A and Figure 5.4. The values of the densities are similar and ranged from 0.99 to 1.3g/cm^3, with the least value 0.99g/cm^3 in 1P:4F and highest in 1P:2F with the value of 1.30g/cm^3. It can be seen from Table 4.1 that the density of the chitosan-P/F composites in relation to percentage of chitosan increases with the increase in fraction of filler. This is due to the low density of chitosan (1.0g/cm^3 in relation to the phenolic novolac resin which is between 1.2 to 1.3g/cm^3. It was found 1P:7F (1.3g/cm^3) has the highest value while 1P:4F (0.99g/cm^3) has the least value. In Figure 5.4 it can be seen that the density of the composite are in the order of 15% increase in relation to pure resin matrix. From the literature the specific gravity of P/F novolac is between 1.2 to 1.3g/cm^3 (Knop and Pilato, 1985) and the values of density of the synthesized P:F resin 1P:2F to 1P:8F agreed with this statement. Generally, the density of composites for various fibre types varied between 0.9 and 2.3g/ cm^3, although in most cases it is between 1.2 and 1.8g/cm^3 (Rashed *et al.*, 2006).

5.1.4 Resin Solid Content

Resin solid content is an important property for phenolic resin. Low solid content in phenol formaldehyde will eject out more water during the hot processing, which could reduce the bonding strength with the filler. The solid content of the synthesized P: F ranges from 50.76 % in 1P:2F to 80.38% in 1P:5F which exceeded the minimum requirement of 35% in the phenolic resin adhesive (Jin *et al*, 2010). Table 4.5 in appendix A and Figure 5.5 it shows that with increasing the P: F molar ratio, an increase solid content was observed with highest at 1P:5F mole ratio (80.38%) and then declined and rose again.

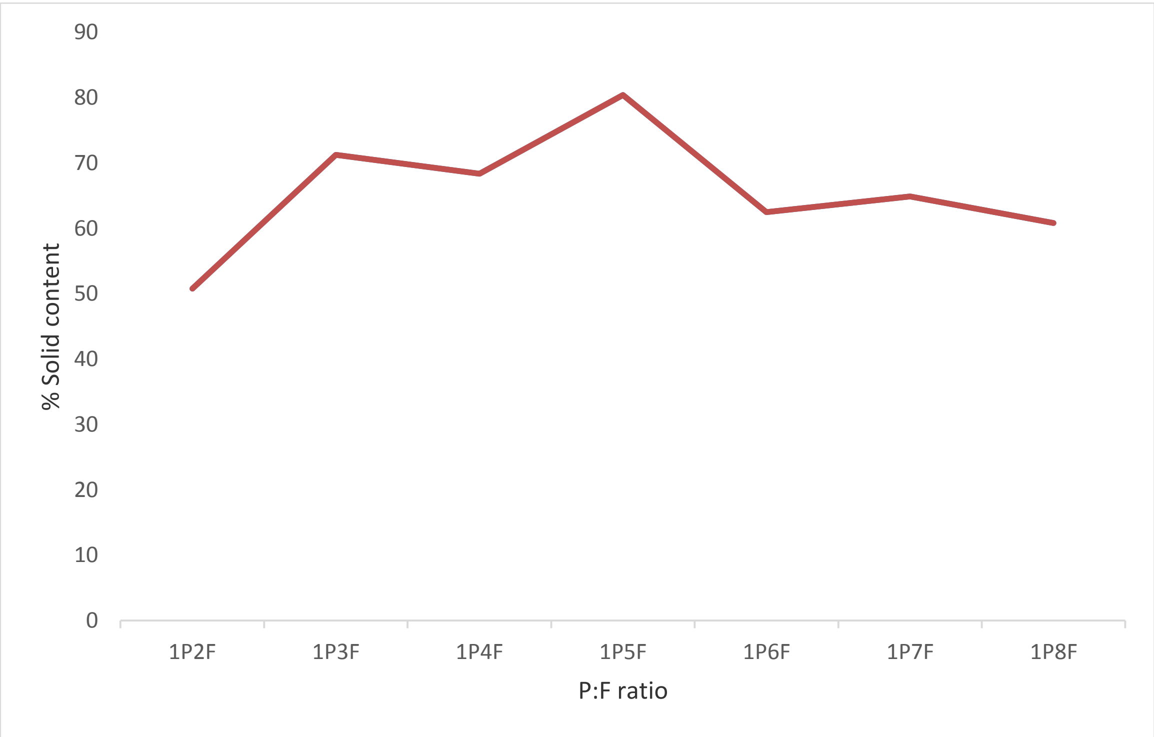


Figure 5.5: Resin Solid Content Vs Synthesized P:F novolac resins

From Table 4.5 in appendix A and Figure 5.5 it is cleared that in a certain range of viscosity, with the decrease of free formaldehyde content and free phenol content from molar ratio (1P:3F to 1P:4F), the apparent solids content tended to decrease, but the change was not great, while from molar ratio 1P:5F it decreased. Resin solid content of some samples such as 1P:5 F (80.38%), 1P:4 F (68.35%), and 1P:3F (71.23%), did not correspond to the literature value of 48% (Young-Sung and Sung-Suk, 2012; Gothwal *et al.,* 2010) The reason, for the higher value of such samples is the addition of the formaldehyde which in turn increase the solid content and decrease the liquid content of the resin. At the same time the pH also increases in this region. The increase in non-volatile solid content may be attributed to relatively unstable structures of the P: F molecules, as explained in (Christy, 2000 ; Sheng (2010). The presence of the hydroxyl methyl group and methylene-ether group of such unstable molecules renders the P: F resins thermally stable, resulting in high yield of non-volatile solid content when heated.

Figure 5.5 also shows that the solid content increases at a low molar ratio linearly with the amount of formaldehyde in the synthesized products. The more the formaldehyde in the resin the higher the solid content of the resin. This means that there are less free formaldehyde, less free phenol and less water content. This appears to indicate that formaldehyde is more reactive than pure phenol.

5.1.5 Gel-time and Cure- time

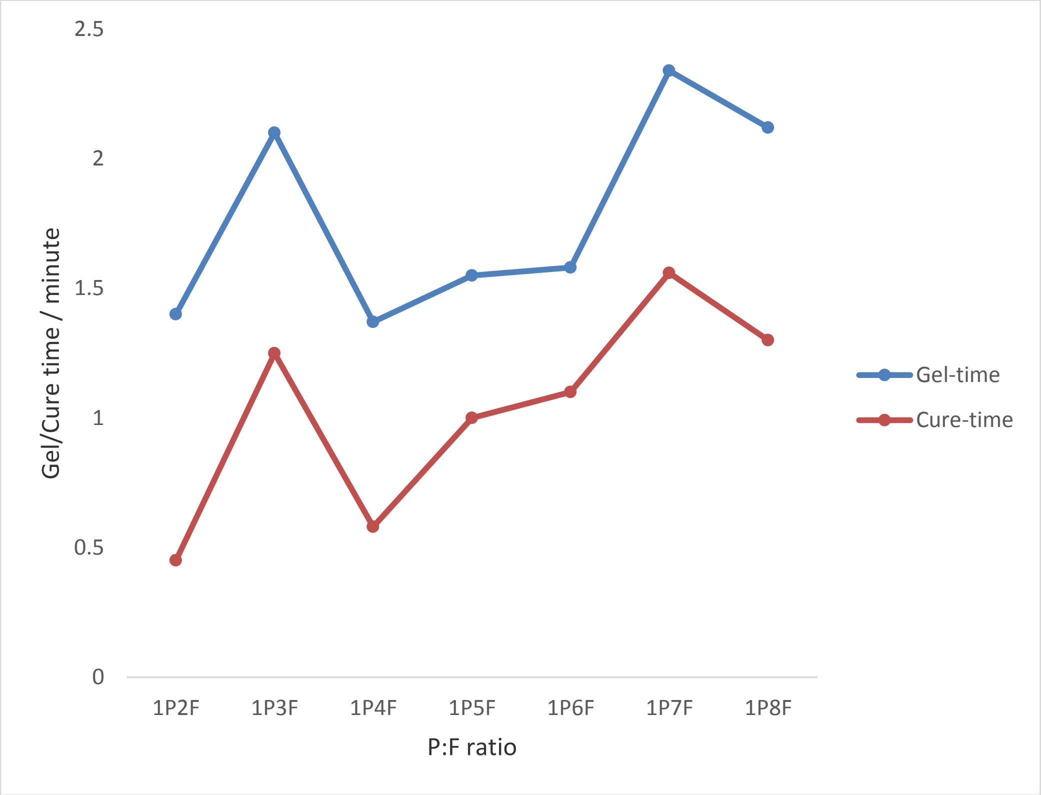


Figure 5.6 : Gel-time and Cure-time Vs Synthesized P:F novolac resins

The measured mean values of the gel and the cure time of all the resins are showed in Figure 5.6 and Table 4.6 in appendix A. The gel time of all resins ranged from least value of 1.37 minute (1P:4F) to highest value of 2.34 minute (1P:7F), while the cure time of all resins ranged from 0.5minute (1P:2F), 1.00 minute (1P:5F) to 1.58 minutes (1P:7F). Figure 5.6 also indicates that both gel and cure time initially increased with the increase of the molar ratio. However, the gel/cure times started increasing up to 1P:3F declined and then rises again up to 1P:7F mole ratio. In both the cases, the gel and cure time showed similar pattern . The initial increase in gel/cure time may be attributed to increase in the molecular weights of the resin, as it is generally believed that lower activation energy is needed for high molecular weight resins to gel/cure (Anwar *et al.*, 2009). The increased in gel/cure time at 1P:6F to 1P:7F, implies low polymerization reactivity indicated by its measured total phenol content, as cited by (Lee *et al.*, 2000). The decrease in gel/cure time at 1P:2F and 1P:6F may also be attributed to catalytic effect and the derivatives present in crude P: F solution. The decrease in gel time also indicates that cross linking rate noticeably increases with the increased mole ratio in P: F due to higher availability of phenol moiety and methylol groups and consequently higher rate of polycondensation (Mo *et al.,* 2014).

Beyond 1P:4F molar ratio become incorporation levels, when P:F became the major substance in the synthesis reaction, the decline in density of polymerization points became significant enough, and thus gel/cure times started increasing due to decrease polymerization reactivity of the syntheses P:F resins. The lower gel time, therefore, shows the lower time of the conversion of reactants into thermoset through crosslink formation. Curing of P: F resin is highly exothermic process. The shape of gel –time curves with the minimum is caused by the decrease of cross linking groups of phenolic components occurring at the same time, which retards the gelling reactions (Khan and Ashraf, 2006). The properties of PF resins prepared with the addition of small amounts of urea appear to be consistent with what is observed in the reactions of the model compounds such as $Mg(OH)_2$, Na_2CO_3, found that their gel times become shorter and viscosity increases with the addition of increasing amounts of urea (Pizzi *et al.,* 1993) .

In another reason, the gel/cure test results expressed by Figure 5.6 suggested that, depending on the molar ratio level, the P: F can play two opposite and effective roles in the process of gelation/curing. At low molar ratio level (1P:4F) the P: F would favour the gelation and curing reactions, while at higher molar ratio (1P:7F) the P: F would exert a retarding effect on gelation/curing reactions. Study of phenol formaldehyde polymer gel system is both scientific and industrial interest. Gels find uses in many engineering applications. Gel formation technology has been implemented widely now for reduction of water produced along with oil from oil wells (Dalrymple *et al.*, 2000 ; Wu, 2002).

5.1.6 Cure-time and Yield %

Table 4.7 in appendix A and Figure 5.7 below shows a yield percentage which ranges from 28.56 (1P:2F) least value to 44.44% (1P:7F) highest value from the synthesized novolac resins using oxalic acid as the catalyst. Oxalic acid is preferred because low colour can be obtained. Oxalic acid also decomposes at high temperature 180^{o}C to CO_2, CO and water, which facilitate the removal of this catalyst thermally. The yield was low compared with other novolacs using other catalysts. The pH value and reaction time are also important parameters for the synthesis of high ortho novolac resins.

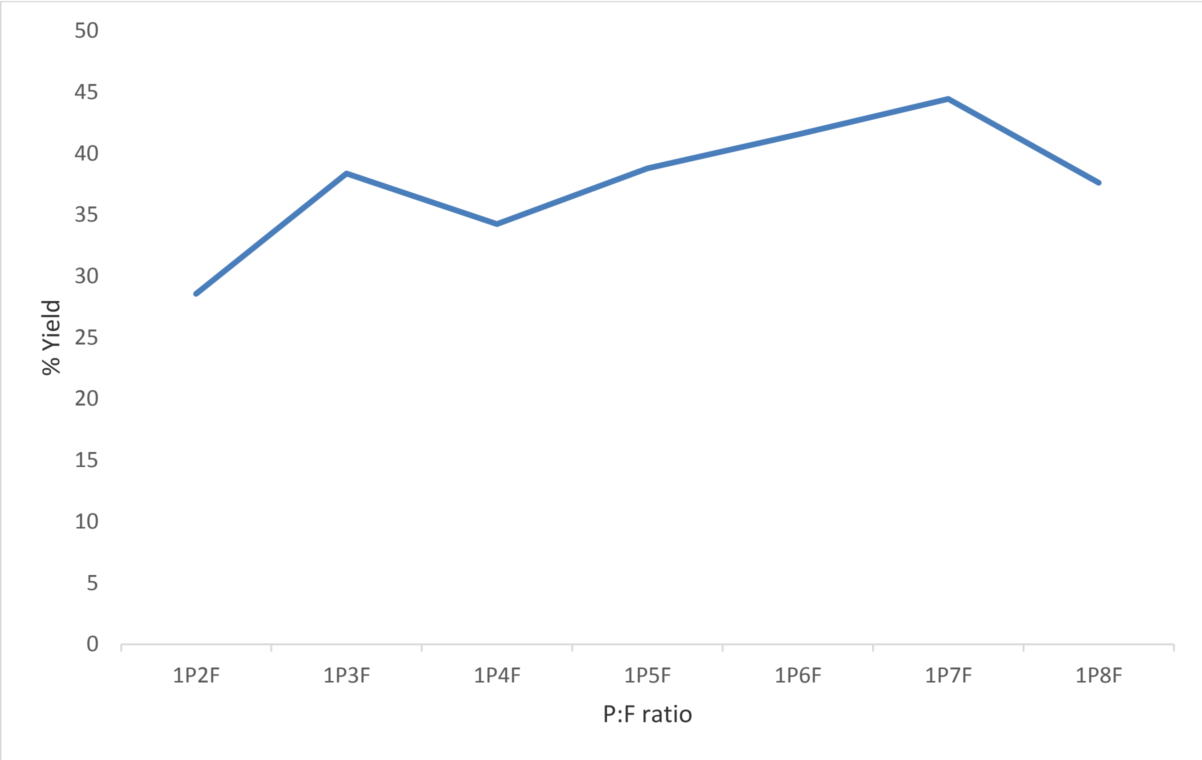


Figure 5.7: Yield % Vs Synthesized P:F novolac resin

From the literature of various catalyst used, $ZnAc_2$ has an outstanding effect on obtaining high ortho novolac resins (Jianying *et al.*, 2005). The yields in phenolic resins have to do with reactive sites for the aromatic substitution available on phenol which have three attacking linkages that is ortho - ortho, ortho - para, and para - para. Ortho-connection and contraconnection in novolac had a great influence on the cure-time because the contra-position of phenol showed higher activity than ortho-position of phenol.

By using $ZnAc_2$ as catalyst, it was possible to obtain high ortho novolac with short cure-time compared with conventional novolacs because $ZnAc_2$ can promote the ortho-position connection in novolacs (Bender *et al.*, 1952). Using $ZnAc_2$ as catalyst novolac obtained gave a poor yield. On the other hand, using HCI as catalyst, the resin obtained was in high concentration. The cure time of the novolac was long. In order to obtain high yield of novolac with short cure-time, a catalyst was used to modify suitable ratio of ortho connection and contraconnection in the resin. A yield up to 90.4% by $HCI/ZnAc_2$ at reaction time (3h) and cure-time 43.6(s) was obtained by (Xu, 2010).

In our case, a yield up to 76% was found by using Oxalic acid and HMTA as the curing agent. Fraser *et al.,* (1957) found that a molar excess of phenol in the original condensation is necessary for high-ortho novolac resins. In the experiment carried out to study the influence of the composition of the reaction medium on the yield, molecular weight characteristics and softening temperature of oligomers formed during polycondensation of formaldehyde by (Miloshev *et al.,* 1990), showed that introduction of solvents such as ethanol leads to a decrease in the viscosity of the reaction mixture and improves its homogeneity. And also, an increase of polycondensation and yield (Jane *et al.,* 2009).

5.1.7 Free Formaldehyde / Free Phenol and pH

Resins is a polymeric material which is used for impregnating and bonding layers of laminate flooring. Amino resins, phenolic resins, and isocyanines are the three most important thermosetting resins systems used by the wood products industry. There has been increasing international attention given to the production and use of adhesives (resins) for the manufacture and production of reconstituted and engineered wood products. This interest in these adhesives has arisen due to a number of drivers, the most important being recent government legislative changes to minimize the health effects relating to product emissions of most notably formaldehyde. A drawback of these materials is the potential release of formaldehyde during and after cure and poor weather ability. So, in developed countries there has been an increased focus on ensuring that any development has a minimal impact on the current and future environment (EPA, 2010).

It is further mentioned that the highest occupational exposure to formaldehyde were measured in varnishing, production of textiles garments, furs, in certain jobs in board mills and foundries. Lower exposure levels have been encountered in formaldehyde production (mean concentration <1ppm). A wide range of exposure levels has been observed in the production of resins in wood productions manufacture, exposure occurs during glue mix preparation, laying of mat, hot pressing and sanding.

Concerns regarding formaldehyde emissions in the past have been mainly in regards to urea-formaldehyde adhesives, which are used in non-structural composite wood products. Urea-formaldehyde form insulation was used in residential construction in the 1970s until concerns regarding emissions led to the discontinuation of use. Formaldehyde-related concerns have most generally been associated with urea formaldehyde adhesives, but not with phenol formaldehyde adhesives (APA, 2008).

Low cost and proven performance have made PF, UF resins the most important wood adhesives for interior applications. However, the formaldehyde emission from PF and UF-bonded wood products has been recognized as a potential source of indoor air pollution leading to inhabitant discomfort and possible health problems. The practical concern over formaldehyde emissions has elicited a great deal of research since 1970s and is well established, potential cause of indoor air contamination (Meyer, 1986). Recent studies indicate these major sources of formaldehyde emission from PF and UF-bonded wood products are unreacted formaldehyde in the UF resins (Ko, 1976; Tomita, 1980) released formaldehyde during the condensation reaction between methylol groups; and emitted formaldehyde from the hydrolytic degradation of the cured resin (McVey, 1982). The WHO, (2002) pointed out that industrial formaldehyde releases can occur at any stage of production, use, storage, transportation, or disposal of the products with the residual formaldehyde.

Tables 4.8, 4.9, and 4.1 in appendix A showed the values of free formaldehyde, free phenol and pH of synthesized P: F novolac resins. Free formaldehyde and free phenol are the components of toxicity in the phenolic or aldehylic synthetic resin. In fact, free formaldehyde in any product is undesirable for health reasons. The main drawback of the phenol formaldehyde resins is its slow release in finished product to the environment, contributing to worsening the indoor air quality, hence there is great desire of producing phenol formaldehyde resins with low free formaldehyde content. In general, low toxic P: F resin follow with poor bond strength, while great bonding strength is often accompanied with high toxicity (Sun-Jin *et al.,* 2014). As can be seen from Table 4.8 to 4..9 in appendix A and Figure 5.8 below, the free formaldehyde for the novolac resins was less than 4% formaldehyde to ppm which is considered to be lower than the standard limit accepted world wide (a value of ≤ 0.1ppm EN13986, Chamber ENV 717-1). Low level of free formaldehyde in P: F type resins indicate that these materials are condensed into other polymeric compounds.

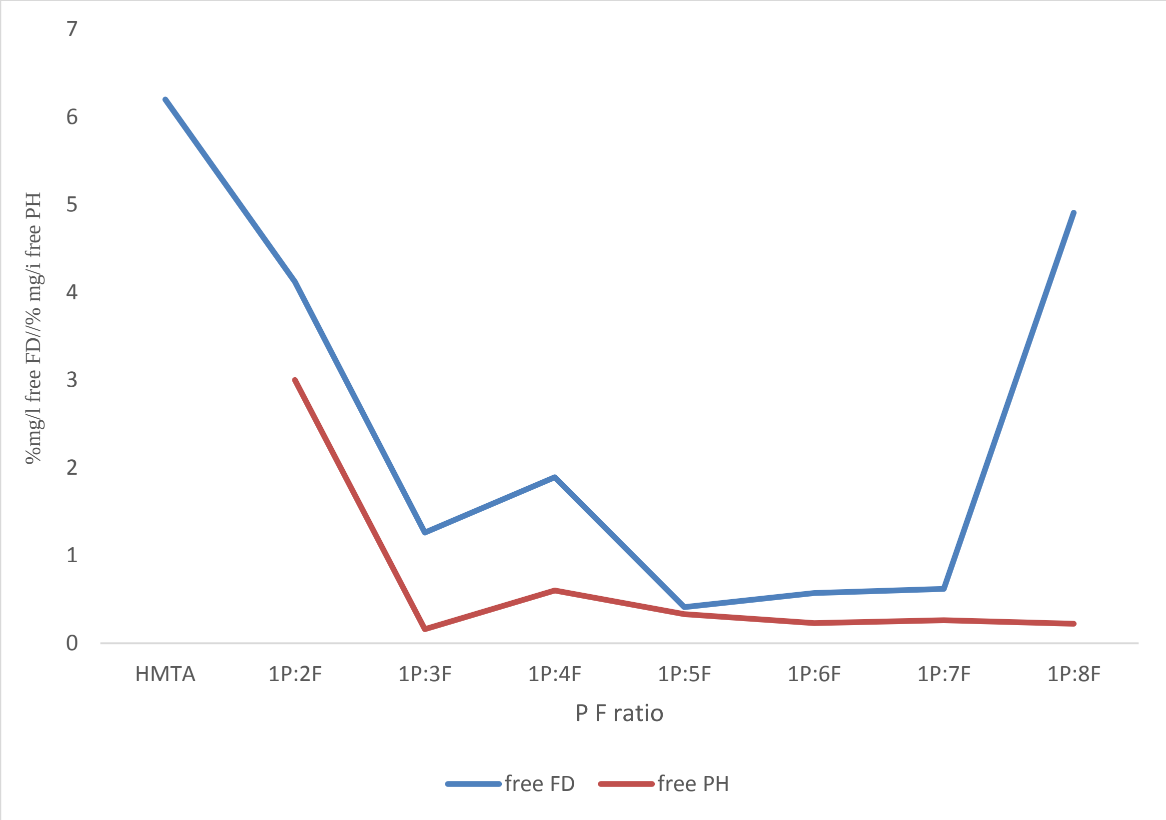


Figure 5.8: Free formaldehyde and Free phenol Vs Synthesized P:F novolac resins

In this synthesis reaction free formaldehyde is the side product. The concentration profiles of methylene bridges in the P: F resins with different molar ratio also influence the formation of the free formaldehyde. As started by (Ida and Krajne, 2005), the reaction rate of hydroxymethylphenols increased with the increasing molar ratio of 1P:2F to 1P.8F and then started to decrease due to the formation of methylene and methylene-ether bridges. For the synthesis of P/F with the molar ratio of 1P:2F and 1P:8F is obvious that the reaction rate of hydroxymethylphenol is actually the same but the reaction temperature may differ during the synthesis, this resulted in the formation of methylene or methylene-ether bridges. The P/F resin under the condition mentioned was soluble in water which corresponds to the PF resins with a high concentration of hydroxymethyl groups. The polymerization of hydroxymethylmphenols was hindered by low pH (1.52 to 2.62) values Table 4.1 in appendix A and Figure 5.1, while the influence of lower starting temperatures was not so significant (Mo *et al.*, 2014).

The lower rate of consumption of formaldehyde in the P: F can be ascribed to the lower pH value of the reaction mixture due to the higher amount of formaldehyde at the start of the reaction and the also the lower starting temperature (Ida and Krajne, 2005). Some studies have been done to investigate the effects of several variables, such as phenol to formaldehyde molar ratio, and catalyst concentration on the physical properties of liquefied wood formaldehyde and mechanical properties of the molded products (Alma *et al.*, 1995). They reported that further condensation reaction of liquefied wood and formaldehyde is an effective method to convert the unreacted phenol (i.e. free phenol) remaining from the liquefaction stage and therefore, greatly improving the thermal flow properties and the mechanical properties of the original wood (Lin *et al.*, 1995).

Shin-ichiro *et al.*, (2000) developed a method for measuring formaldehyde from urea-formaldehyde (UF) resins at high temperature and used to assess the influence of the reaction pH on the formaldehyde emission (FE) and heat stability of the cured resins. In general, as the temperature and reaction pH increased, the amount of emitted formaldehyde increased. The most interested results in the study were the remarkable high-heat stability of the resin prepared at pH 4.0. Even at a postheating temperature at 180^{o}C, the FE was only 0.7mg/g of the resin sample compared to 2.1 and 2.65mg/g with the resins at pH 0.5 and pH 8.0 respectively. The results of this study agreed with the present work, when compare the P: F mole ratios with the pH (Table 4.1 in appendix A), and the FE (Table 4.8). A similarity was observed with a pH of 1P:4F to 1P:3F with a FE of > 1.0 % and 1P:6F to 1P:8F have a FE of < 1.0 % respectively.

But only little information can be found in the literature concerning emission of phenol formaldehyde resins. Most of the information in the literature concerning release of formaldehyde from the resins is from urea and melamine formaldehyde resins. Therefore, information of emission of phenol formaldehyde is scanty and unavailable. This may be due to the strong bond in phenol formaldehyde and hence have less emission of formaldehyde Extensive emission testing has been conducted on PF adhesives within wood products (Emery and John, 2002). Per the U.S. Environmental Protection Agency (EPA, 2010): pressed woods that contain PF resin generally emit formaldehyde at considerably lower rates than those containing UF resin. Some fibres glass insulations use phenol formaldehyde in the binder, which holds the glass fibres together. During the manufacturing process, the binder is cured at very high temperatures, virtually eliminating the formaldehyde content. There is a small amount of free formaldehyde present in today's fibre glass insulation products (EPA., 2010). A novel composite adhesive was synthesized by (Sun-Jin *et al*, 2014), which revealed the new zero-waste and zero-pollution adhesive synthetic by blending of alkaline Chinese fir (Cunninghamia lanceolata) liquid with a small amount of phenol-formaldehyde. The synthesized adhesive showed better physical properties of low free phenol as well as free formaldehyde content.

Particleboards and other wood based panels bonded by aminoplast resins emit formaldehyde during its manufacture as well as during its usage. The formaldehyde release is influenced by exogenous (i.e. air humidity, temperature, air change) and also endogenous factors (wood species, type of resins used, conditions of manufacture). Roffael *et al.,* (1975) found that under the same production conditions, the formaldehyde release from oak particleboards was definitely lower than that from pine particleboards (Roffael, 1993).

Woood-based panels bonded with urea formaldehyde resin emit potentially hazardous formaldehyde fumes (Noisel *et al.*, 2007). A substantial reduction in the indoor formaldehyde concentration can be achieved by source control and the application of a coating as a physical barrier. Goldsh and Rouch, (1984) found that, in a house with a particleboard floor and plywood paneling, formaldehyde levels decreased by 49% and 29% when 75% of the panel board and 59% of the floor, respectively, were removed from the house. However, in other instances, the removal of the urea formaldehyde foam insulation from houses had little effect on indoor formaldehyde levels (Harvey, 2007).

Yong-Sung and Kyung-Hee, (2011) have carried a research on evaluation of melamine-modified urea-formaldehyde (MUF). The MUF resin made in this study showed very low free formaldehyde contents of 0.32 percent. Generally, for industry uses some of the second urea reacted with the residual free formaldehyde present in the reaction mixture, resulting in very low free formaldehyde content in the resin (Sellers , 1985; Lee and OH, 2010).

Some fibres glass insulations use phenol formaldehyde in the binder, which holds the glass fibres together. During the manufacturing process, the binder is cured at very high temperatures, virtually eliminating the formaldehyde content. There is a small amount of free formaldehyde present in today's fibre glass insulation products (EPA, 2010).

Scientific research have shown that some chemically used to make resins emit aldehydes such as formaldehyde and acetaldehyde when the resin is exposed to high temperature such as hot glass. As with phenol-formaldehyde resins, acrylic resins are considered very safe (EPA, 2010). On the other hand, the relationship between the hot-pressing compression schedules and formaldehyde emission levels could be possibly due to the following reasons. The compression during hot-pressing densification determined the amount and pressure of steam released, and the more the free formaldehyde released. The higher the compression, the more the free formaldehyde released. The entrapped free formaldehyde was slowly emitted from the sample after the hot-pressing densification being completed and this make the formaldehyde emission reading during the test become higher.

Wang and Mellissa, (1999) have investigated the effect of pressing variables on volatile organic compound (VOC) emissions, using three adhesives urea-formaldehyde(UF) resin, phenol-formaldehyde (PF) resin, and polymeric methylene bis(phenyl isocyanate) (pMDI). The measurements showed that the effects of press temperature and press time on formaldehyde emissions were significant for all three adhesives. Formaldehyde press emissions with PF resin were lower than with pMDI, due to an additive in the PF resin.

It had been expected that free formaldehyde emission level would have had a correlation with resin load. Rofael, (1993) reported that an increase in the resin quantity leads to an increase in the formaldehyde emission, but the increment does not proportionate. The resin load also plays important role in determining the final properties (Bakar *et al.*, 2005). The amount of resin load may affect the properties of the material, but it does not correlate to the formaldehyde emission level. This statement has tallied with this experiment in terms of resin mole ratios (1P:2F to 1P:8F) were synthesized and their formaldehyde release was determined. The results of formaldehyde release for each mole ratio when compare with the control is different and it so don't correlate to the amount of emission levels of the formaldehyde.

Over the past three decades, great progress has been made (Tomita, 1980; Sundin, 1982) in improving the formaldehyde emission from such wood products as particleboard, hardwood plywood, and medium-density fibreboard. Beneficial steps have included reducing the formaldehyde/urea (F/U) molar ratio,'' synthesizing UF resin with acidic catalysts without first using an alkaline catalyst, impregnating the wood furnish with a formaldehyde scavengers: and treating boards with formaldehyde scavengers or a barrier coating (or both) after manufacture (Myers, 1986).

Shin-Ichiro *et al.*, (2000) developed a method for measuring formaldehyde released during curing and heating at high temperatures. The amount of formaldehyde released during cure was correlated to the content of methylol groups in the UF resin. The cured resin synthesized with a strongly acidic catalyst was more stable toward high temperatures than the resins synthesized under weakly acidic and alkaline conditions. Samarzija-Jovanovic *et al.*, (2011) modified urea formaldehyde resin with nanoSiO_2 particles and heaxamethylenetetramine (HMTA). It was stated that the formaldehyde content of the urea-formaldehyde resin decreased after using nanoSiO_2.

To make resins or adhesives applicable for indoor material, formaldehyde emission from the manufactured resins have to be lower by improving the resin curing state through two approaches, i.e. modifying the hot pressing compression schedule during the process and adopting an extended drying after the process. According to Baker *et al.*, (2005), the wood from the outer part of the oil palm trunk (OPW) can be used as solid wood upon properly treated. Without treatment, OPW has at least four imperfections: Low strength, low dimensional stability, low durability, and poor machining characteristics. Treatment with low-molecular weight PF resin (Lmw-PF) through a modified comppreg method significantly improve its properties, yielded good appearance thus can be used for high-grade furniture and housing materials (Baker *et al.*, 2005). Nevertheless, the treatment leads to another problem. The drawback of this treatment is the emission of considerable amount of free formaldehyde from the resin from the products (Amarullah *et al.*, 2009). It is inherent characteristic of Lmw-PF, in which it has more formaldehyde emission and , to make worse, there is no zero or even less emission Lmw-PF commercial available. The relationship between extended drying periods and formaldehyde emission level was understandable. A formaldehyde emission is free formaldehyde partly release from the resin which is not completely polymerized (Nuess and Price, 2007). Extended drying after hot pressing helped the resin cured better and thus reduced the formaldehyde emission level.

Formaldehyde and phenol dispersed in the atmosphere are carcinogenic to human and harm our common ecological heritage. As a result, health and safety regulations in Europe are tightened.

Wherever formaldehyde is still in use like PF processing of resin media, health and safety as well as environmental protection requirements increase drastically. Formaldehyde and phenol emissions entail the high cost of exhaust air treatments. Meanwhile, high quality standards for production and spares still demand optimal raw materials with excellent physical properties. The avoidance of formaldehyde-containing materials would no doubt constitute the best policy, but most of these materials are inexpensive and have a high performance rating. Because complete elimination of these materials is not a practical solution. Several studies have reported on the usage of coatings, barriers, and chemical treatments. Chemicals such as urea, polyurethane, ammonium sulfite, and sulfur compounds of sodium have been tried as an after treatment of plywood's (Wang *et al.*, 2008).

Much work in emission reduction has focused on the systematic reduction of phenol and formaldehyde. Phenolic resins in Euro typically have resole with specified free phenol of <1.5% and novolac with free phenol of <0.5%, while formaldehyde levels are low enough to remain unspecified. In U.S, for a resole typical levels of free phenol and formaldehyde remain significantly higher, levels of <5.0% free phenol and <1.0% free formaldehyde are specified by all major manufacturers.

The reduction of the free formaldehyde in the resin has actually provided a solution to the problem that severely impaired the use of PF resins. It is well known that free formaldehyde in the resin acts as a cross linker during the polymerization reaction (Gothwal *et al.,* 2010).

5.1.8 FT – IR

Table 4.10 in appendix A showed the summary of the important IR – characteristic bands observed for the resins of 1P:4F, 1P5F, and 1P:6F and their Figures in 4.1, 4.2 and 4.3. Due to the complexity of structure in the polymer the absorption frequencies are broad in case of resin spectra. Broadening may also be observed due to the presence of by products in the resin, such as water and excess formaldehyde which allowed hydrogen bonding with the reactive functional groups such as $–CH_2OH$, NH_2 and –NH present in the resin samples.

However, from Figure 4.1 to 4.3 (1P:4F, 1P:5F and 1P:6F) spectra of cured – resins showed sharper characteristic absorption peaks in this region. In the IR 1P:4F resin a medium absorption peak is observed at around 3375cm^{-1}, which is characteristic absorption of the NH- stretching mode for –NH group. Similarly absorption bands for (1P:5F) and (1P:6F) were recorded in the same region. A medium absorption band in all resin spectra appears in the range of 2970 – 2900cm^{-1} which is ascribed to the symmetrical C-H stretching mode of CH_2 of ether CH_2OH and N-CH_2. A very strong absorption band is observed around 1600cm^{-1} in all the spectra, which may be assigned to the C=O stretching (amide -1) in $–CONH_2$ group. The strong absorption bands around 1550cm^{-1}(1P:4F) may be due to –NH bending mode in 2-amine (amide -11). The 1-amino groups first form methylol derivatives with formaldehyde.

A weak absorption band at 1440 to 1367cm^{-1} for all polymer samples may be ascribed to C-H bending mode in $–CH_2$/ -CH_2OH/ N-CH_2-N. the medium absorption band appearing in the region of 1150 to 1099cm^{-1} may be assigned to asymmetric stretching vibrations of –N-CH_2-N-, the medium bands 1250 to 1259cm^{-1} may be ascribed to C-O stretching and O-H bending modes present in the phenolic moiety. The medium band at -1300cm^{-1} appears mainly due to the –OH deformation in $–CH_2OH$ formed due to the formylation reaction. The strong absorption peaks at ~1024cm^{-1} in the spectra of all polymers are assigned to C-O stretching. The band indicates the presence of ether linkage (CH_2-O-CH_2) due to cross-linking reaction during condensation.

From the Figure 4.1 to 4..3 the infrared spectrum of resin (1P:4F, 1P:5F and 1P:6F) has an absorption peak is sharp and weak at 3650 to 3590cm^{-1} which is related to O – H stretch – free indicating the presence of phenols. The intensity of the absorption at region 2800 to 2700cm^{-1}

is medium and indicates O-H stretching vibration of –CHO (2 bands) confirming the presence of aldehydes (http./www.chem.). At region 3025 to 2800cm^{-1} the intensity of the absorption is medium which an indication of N – H stretching vibration is, hence, primary amine group is confirmed present. The intensity of the absorption at region 2800 to 2700cm^{-1} is medium and indicate C-H stretching vibration of –CHO (2 bands) confirming the presence of aldehydes.

5.2.0 Physicochemical Properties of Chitin / Chitosan

5.2.1 Degree of Deacetylation (DD)

Since the degree of deacetylation DD, depends mainly on the method of purification and reaction conditions, it is essencial to characterize chitosan by determining its DD prior to its utilization.The DD is an important parameter to be noted affecting solubility, chemical reactivity and biodegradabity, DD value of 70%, 81% and 91% was calculated using the equation (**3.6** and **3.7**) in the procedure (**3.3.3**). In this study the results in Table 4.11/4.12 in appendix A revealed that DD of the purchased chitosan is 55.18%, 100% DD is very rarely obtained. Commercial chitin/chitosan have various DD in the range of 52 to 85% is generally found.

The DD of chitosan is important for its application in the industry. From this regard, certain researchers (Li *et al.*, 1992) suggested that the term chitosan should be used when the DD is above 70%. Particle size of chitosan has sparked controversial reports in its effect on its quality and applications. In this case of our study the particle size of our chitosan is 1mm (100 micros sieve designation). Bough *et al.*, (1978), reported that small particle size is better than large particle size, thereby; smaller particle size (1mm) results in a chitosan product of both higher DD and molecular weight (Mw) than of large particle size (2 to 6.4mm). Also the larger particle sizes require longer swelling time resulting in a slower deacetylation rate. From the Table 4.11 in appendix A, it could be noticed that, the DD of chitosan increased significantly ($p \leq 0.5$) by increasing the concentration of NaOH solution used in the deacetylation step, the highest DD%

was obtained by 50% w/v NaOH solution, 81.47 and 90.92% , when compared with our commercial chitin (55.18%). Emilia and Katarzyna, (2015), showed that the higher the DD, the higher the purity grade observed in the polymer sample. Thus, careful selection of chitosan with proper DD should be of great interest,especially with regard to parenteral chitosan-based formulations.

5.2.2 Loss on Drying

The chitin/chitosan obtained fron the above process was reported to have 0.9922 % , which literally concluded that the majority of the linkage was intact instead of splitting up by the influence of the strong alkali Table 4.12 in appendix A. Chitin/chitosan is very sensitive to environmental conditions, hence it is recommended to store in closed container at low temperature (2 to 8^{o}C) (Emilia and Katarzyna, 2015). In the preparation process of chitosan application it is particularly important to establish the shelf-life of the product by conducting stablility studies (Viljoen *et al.*, 2014). The purpose of the stability testing is to provide reliable evidence on how the quality of the chitosan product differs with time under the influence of environmental factors such as loss on drying,humidity and temperature. Type of stability studies (long-term, iintermediate, or accelerated), storage conditions and frequency of testing should be selected with respect to the chitosan formulation properties (Viljoen *et al.*, 2014).

Apart from relarive humidity, temperature is another variable which exerts an effect on the loss on dring in chitosan application. Exposure to elevated temperatures (40 ^{o}C) was found to cause a significant loss of moisture (dehydration of chitosan powder), which resulted in a decrease in hardness and mechanical tablet strength (Emilia and Katarzyna, 2015). In addition, air temperature may affect the chitosan degradation ratio, especially in liquid and semi-solid products. Storage of chitosan solution, both at ambient and elevated temperatuires, resulted in faster degradation of chitosan chains (Nguyen *et al.*, 2009) and the rate of hydrolysis was found to follow first order kinetics. Interestingly, no significant vhain hydrolysis was noticed in the chitosan solution stored at 5^{o}C. Furthermore, long-term stability studies estabilished on chitosan/glucose 1-phosphate thermosensitive solution confirmed the necessity of their storage in a refrigerator (at 2-8^{o}C) (Emilia and Katarzyna, 2015).

Heating is often employed in preparation of chitosan formulation. Exposure to elevated temperature might change a number of polymer properties, including moisture, aqueus solubilty, viscosity and temperature (Howling, 2010). Chitosan/chitin decomposition during heating has been widely established and the rate and degree of the polymer damage was found to accelerate with rising temperature and duration of heating (No *et al.*, 2006).

5.2.3 pH Value

The pH value of chitin is 6.7 in Table 4.12 in appendix A. This showed the basicity of our chitin is lower than that of the literature value 9.86. When the pH of chitin was over 6.5, its solubility is poor, reaction occurred in a non-homogeneous system. To adjust the reaction in the homogeneous condition, pH value has to be adjusted ranging from 4 to 6.5 (Huafei , 2011). At pH>6.5 chitin/chitosan solutions exhibit phase separation, while at pH< 6.5 chitin is soluble, carrying a positeve charge because of the presence of protonated amino group.Above pH 7.0 chitosan does not exhibit a stable solubility. At higher pH, precipitation or gelation tends to occur and the chitosan solution forms poly-ion complex with anionic hydrocolloid resulting in the gel formation The presence of the amino groups indicates that pH substantially alters the charged state and properties (Yi *et al.*, 2005). At low pH, these amines get protonated and become positively charged and that makes chitosan a water-soluble cationic poly-electrolyte. On the other hand, as the pH increases above 6, chitosan's amines become deprotonated and the polymer loses its charge and become insoluble. The soluble-insoluble transition occurs at its pKa value around pH between 6 and 6.5. As the pKa value is highly dependent on the degree of

N-acetylation, the solubility of chitosan is dependent on the DD and the method of deacetylation used. According to the reported results (Yong *et al.*, 2011), the optimum pH of most extracellular chtin deacetylases is neutral or in the alkaline range from 7 to 12, while most intracellular chitin deacetylases have optimal pH values in the 4 to 5 to 6 range.

These pH-dependent properties of chitin/chitosan influence its biomedical activity and potencial applications. The pH values of the medium also determines the stability of chitosan oligomers with the degree of polymerization (DP) < 20, which can be achieved by depolymerization of chitosan (Jolanta, 2011).

5.2.4.0 Solution Properties

5.2.4.1 Solubility in Different Solvents

The solution properties of chitin/chitosan are depends upon distribution pattern of acetyl group along the main chain and molecular weight. The aqueous solubility of chitosan is greatly influence by the addition of electrolyte to the solution. It forms the extended conformation in the solution form of chitosan. It is due to repulsion of positively charge deacetylation unit on the neighbouring glucosamine units. Addition of electrolyte reduces the interchain repulsion and induces a more randomly coil like conformation in the molecule which eventually results in salting out and precipitation of chitosan (Prajakta and Prashant, 2015). Chitosan is insoluble in water, alkali and most organic solvents, but soluble in most aqueous solutions of organic acids such as formic acid, acetic, lactic, citric, etc, when the pH of this solution is lower than 6.3. Moreover, when the pH of an aqueous solution is raised above 6.5, polysaccharide is precipitated from the solution in a form like flock (Burkinshaw and Karim, 1991). Some diluted inorganic acids such as nitric acid, hydrochloric acid, perchloric acid and phosphoric acid can be helpful for preparation of chitosan solutions, but only by prolonged agitation and frequent warming.

The solubility of chitin was tested in six different solvents such as water, acetic acid, chloroform, ethanol, acetone and lactic acid, it was soluble in acetic acid around 97% and acetone, and their solubility were reported. The chitin became soluble in dilute acetic at the DD of 28% or over and soluble in water at the DD of 49%. The solubility of the partial deacetylated chitins had a close relationship with their crystal structure, crystallinity, and crystal imperfection as well as the glucosamine content. The solubility of chitosan occurs through protonation of $–NH_2$ group of D-glusamine derivative which give polycation in acidic medium: chitosan with more than 50% deacetylation is soluble in acidic medium, chitosan with 50% deacetylation soluble in neutral medium and chitosan with less than 50% deacetylation soluble in aqueous medium at pH 9 (Prajakta and Prashant, 2015).

5.2.4.2. Solubility

From literature, the percentage solubility of chitosan demonstrated an excellent solubility at 90%. This result may be due to the reaction time and the concentration of NaOH (30 to 50%) for large particle size (20 mesh) to be sufficiently swollen (Bough *et al.,* 1978). Solubility of the chitin is displaced in Table 4.12 in appendix A. On the other hand, a decrease of the NaOH concentration to 70% required increase in time to obtain a soluble chitosan (No *et al.,* 2000). Solubility of chitosan can be increased by quarternization. Chitosan have amino group, on quarterisation it forms number of derivatives. The increase in solubility is achieved by replacing the primary amino group on the C-2 position of chitosan with quaternary amino groups (Prajakta and Prashant, 2015) .The obtained values of density at 1.0g/cm^3 and loss on drying at 0.99% confirmed with one in the literature (Mahdy *et al.,* 2013 ; Sneha *et al.,* 2014).

The physic-chemical properties of the produced chitosan depend on various factors: Concentration of deacetylation agent, time of deacetylation, ratio of chitin to alkali. Temperature of deacetylation, type of the source, particle size, and type of deacetylation. The solubility of chitin can be enhanced by introducing bulky acyl reisdues into the polymer (as in butyrylchitin and valeroylchitin). However, if modification is carried out with shorter-chain carboxylic acids (as in acetylchitin), the solubility remains poor.

5.2.5. Ash Value

For synthesis purposes ash value is not a critical parameter; however, from combustion perspectives it is an important property (Zhang and Ren, 2007). From Table 4.12 in appendix A chitin has very low ash value, 1.12%, indicated the efficiency of the demineralization and deproteinization steps followed in the preparation of the chitosan sample by removing the minerals and proteins. Althougth chitosan preparation involves basic purification methods like demineralization and deproteination, chitosan material may contain some impurities, such as ash, heavy metals, or proteins. Hence, it shows the purity of the sample. Commercial chitin were reported to have ash value of about 1.18% (Wang, 1976). A high quality grade of chitosan should have less than 1% ash content (No *et al.,* 2002).

The purity level of chitosan is a factor which affects not only the biological properties like immunogenity or biodegradability, but also has a difficulties in chitosan dissolution and impede preparation of chitosan-based drug delivery systems. On the other hand, microbiological contamination of the polymer may enhance chitosan degradation via enzymatic hydrolysis. Therefore, chitosan material should be of high purity and be free of contaminants (including the level of endotoxins where relevant)(Emilia and Katarzyna, 2015) .

5.2.6. Moisture Content

The purchased chitin from shrimp shell supplied by Sigma was analysed and the experimental (physical properties) and the theoretical results for the various test(s) sample of the chitin were presented in Table 4.12 in appendix A. The moisture content of the chitin is around 2.68%

depending upon, the season, relative humidity and sunlight. There is no significant difference in the percentage of moisture content between the report generated by (KFDA, 1995) the moisture content of chitosan powder should be <10%. From the extracted chitin from shrimp shell according to (Wang, 1976) were found to contain moisture in the range 1.0 to 1.3%. The moisture content obtained was found to be 2.68% (Table 4.12 in appendix A).Chitosan is hygroscopic in nature, having a greater capability to form hydrogen bonding (formed with both hydroxyl and amino group) with water compared to chitin (Gocho *et al.*, 2000). The amount of absorbed water depends on the initial moisture content as well as on the storage conditions, especially the environmental temperature and relative humidity.

Rege *et al.*, (1999), found that the moisture level of chitosan powdered ranged from 7% to 11% (w/w) and was independent of polymer DD or Mwt. However, (Mucha *et al.*, 2005), noticed that the water-uptake ability of chitosan decreased on increasing their DD. The presence of absorbed water plays a considerable role especially in solid chitosan-based formulations, affecting the flow properties and compressibility of the powders' or tablets' tensile strength. It was reported that moisture content up to 6%(w/w) may improve particle binding during compression as a result of formulation of hydrogen bonds between the particle (Rege *et al.*, 1999). However, fluctuations in moisture levels of chitosan material upon storage may change the physicochemical and mechanical properties of chitosan-based system. Studies conducted by No and Pringawiwatkul , (2009), revealed that the level of absorbed water in chitosan powder rose during starage, a decline in water binding capacity was observed (Emilia and Katarzyna, 2015).

5.2.7. Density

The obtained density of chitin Table 4.12 in appendix A was found to be 1.0g/cm^3 and the commercial chitin have a value of 1.35 to 1.45g/cm^3 in the literature. From the literature of the study of bulk density chitin from shrimp and crab is normally between 0.06 and 0.17g/ml, respectivelyly (Synowiecki, 2003), indicating the shrimp chitin is more porous than crab chitin. In a study conducted by (Rout, 2001), the bulk density of chitin and chitosan from crawfish shell, is 0.39g/cm^3. This perhaps could be due the porosity of the material before treatment. But once crawfish shell had been demineralized or deproteinized or both there seem to be very minor variations unpacked in bulk densities of the crawfish and commercial chitin and chitosan indicated some variations, which can be attributed to crustacean species or sources of chitosan and the methods of preparation Rout (2001), as also stated earlier by (Brine and Austin, 1975). Rout (2001) reported that increased degree of deacetylation decreased bulk density.

5.2.8 Viscosity

The intrinsic viscosity of chitosan describes the ability to form viscous solution (under specific solvent and temperature conditions) and is directly proportional to the polymer average Mw.the viscosity values of commercial chitin (220 to 1190) and the experimental (7.2) are presented in Table 4.12 in appendix A The Viscosity of chitosan solution is related to many factors such as DD, Mw, concentration, ionic strength, pH, and temperature. The increase in DD with the decrease of Mw strongly reduces the viscosity of the chitosan solution. Viscosity is an important factor in the conventional determination of molecular weight of chitosan and in determining its commercial applications. However, higher molecular weight chitosan often render highly viscous solutions, which may not be desirable for industrial handling. Viscosity of chitosan in acetic acid tends to increase with a decreasing pH but decrease with pH in HCl giving rise to the definition of intrinsic viscosity of chitosan which is a function of the degree of ionization as well as ion strength (Sham *et al.*, 2013). Augmentation of the temperature of chitosan solution usually decreases its viscosity and pH change may yield a different result depending on the type of acid used and solvent. Chitosan is a pseudoplastic material and an excellent viscosityenhancing agent in acidic media. The viscosity of chitosan solution increases with an increase in chitosan concentration and decrease with an increase in temperature (Kurita, 1986).

Bough *et al*., (1978) found that deproteinization with 3% NaOH and elimination of the demineralization step in the chitin preparation decrease the viscosity of the final chitosan products. It is also stated that it is not desirable to bleach the material at any stage since bleaching considerably reuduces the viscosity of the final product. Similarly, No *et al.*, (2000) demonstrated that chitosan viscosity is considerably affected by physical (grinding, heating, autoclaving, ultrasonication) and chemical (ozone) treatments, except for freezing and decrease with an increase in treatment time and temperature.

5.2.9. FT-IR

Summary results of important fuctional groups abserved from FT-IR of fresh chitin and the deacetylated chitin / chitosan are given in Table 4.13 in appendix A and Figures 4.4, 4.5 and 4.6. The major absorption band were observed between 1644cm^3 and 1020cm^3 which reported the free amino group (NH_2) at C_2 position of glucosamine, a major group present in chitosan. Further, the sample showed the absorption bands for the free amino group between 1026 and 1259cm^{-1} when the peak at 1364cm^{-1} represents the –CO stretching of primary alcoholic group ($-CH_2-OH$). The absorbance bands of 3433, 2930, 2899, 1555, and 1401cm^{-1} indicated the N-H stretching. 3433cm-^{1} band is attributed to $-NH_2$ and –OH groups stretching vibration and the band for amide 1 at 1633cm^{-1} is seen in the spectrum of chitosan. Symmetric CH_3 stretching and asymmetric CH_2 stretching, CH stretching, C=O stretching in secondary amide (amide1) and C-N- stretching in secondary amide (amide11), respectively. In the present study also the same absorbance bands were observed at various peaks 2902, 1633, 1555, 1401, 1397, 1072, and 602 cm^{-1}. This confirmed α chitosan type (Juraj *et al.*, 2007; Sneha *et al.*, 2014).

5.2.10 X-ray Diffraction (XRD)

XRD patterns of chitin are illustrated in Figure 4.7. The XRD patterns of chitin exhibits broad diffraction peaks at $2\theta \approx 10^o$ and 21^o which are typical fingerprints of semi-crystalline reflections at 9.7^o and 19.9^o. Prashanth *et al.*, (2002) found that the wide-angle X-ray diffraction patterns of the shrimp chitosan showed two major characteristic peaks at $2\theta \approx 9^o$, $9 – 10^o$ and 19.8, 20.7^o. It is also reported that (i.e. the two characteristic crystallines peaks with slightly fluctuated diffraction angles found in the WAXD patterns indicate that two types of α and γ-chitosans exhibited a comparable degree of crystallinity and had two consistent peaks at $9\text{-}10^o$ and $19\text{-}20^o$ so, in our case chitin showed three consistent peaks at 11.3^o, 19.0^o and 33.0^o.

5.3.0 COMPOSITE FABRICATION

5.3.1 Density

Table 4.14 in appendix A shows the densities of the composites of all novolac resins with the chitosan at different filler loading from 10% to 50% ranges from 0.38 to 1.24 g/cm^3 respectively. Table 4.4 in appendix A shows the densities of the synthesized novolac resins from P: F ratios 1P:2F to 1P:8F ranges from 0.99 to 1.3g/cm^3. Table 4.18 in appendix A gave the density of 1P:2F and 1P:4F at different DD% which ranges a maximum of 1.0g/cm^3 at 91% DD and least value of 0.72g/cm^3 at 70% DD.

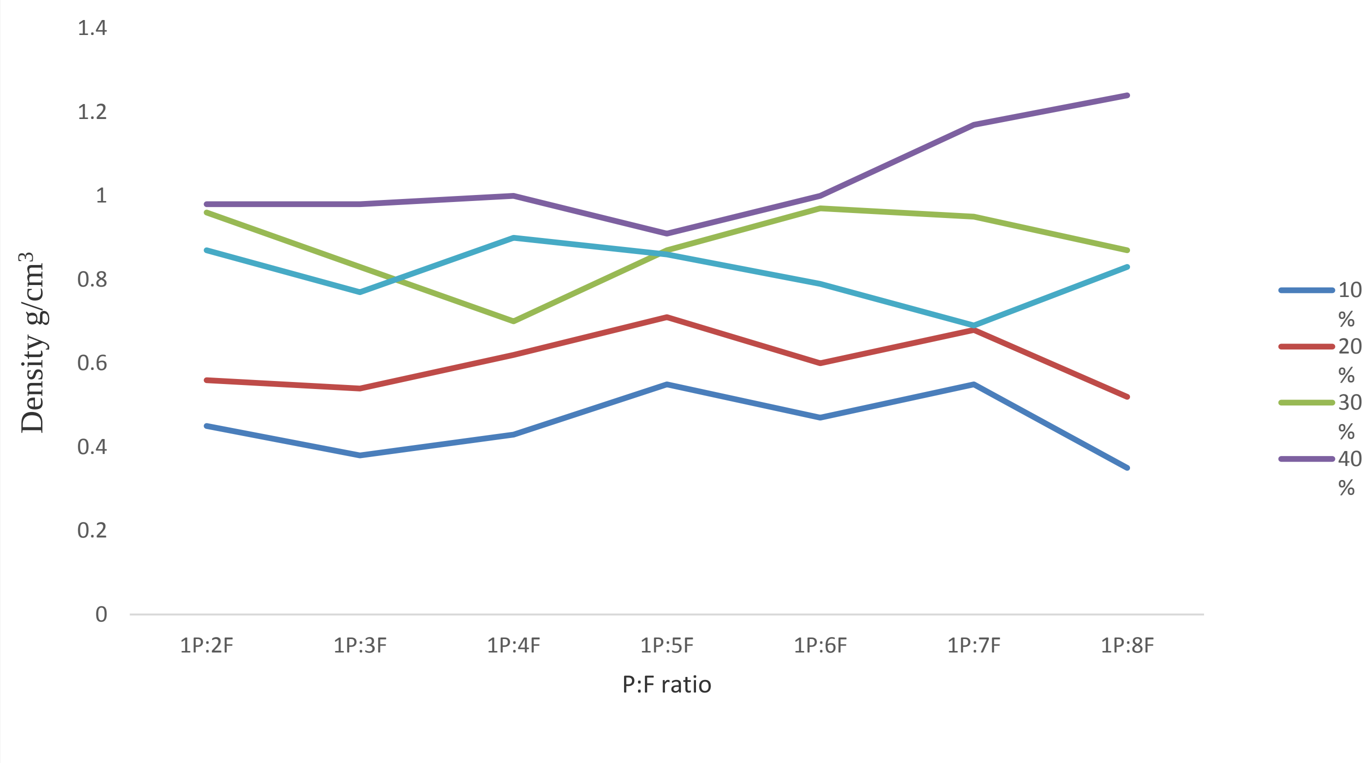


Figure 5.9: Density of synthesized P: F at differenet filler loading 10% to 50%

According to Table 4.14 in appendix A and Figure 5.9 the densities of 1P:4F, 1P:5F and 1P:8F ratios at different filler loading 10 to 50% are similar which have an average percentage increase of 12%. . 1P:3F showed the least with the value of 0.38g/cm^3 at 10% filler loading of 1P:7F and 1P:6F showed the highest value of 1.24g/ cm^3 and 1.17g/cm^3 filler loading and at loading of 40% (1P:6F and 1P:7F) respectively. According to the values stated in Tables 4.14. and 4.4 in appendix A, the densities of chitosan and of the P: F novolac resin are 1.0g/cm^3 and 1.2 - 1.3g/cm^3.· From Table 4.18 in appendix A, it was observed that the density of the resin without the chitosan is 1.20g/cm^3 and density of the untreated chitin was 1.1g/cm^3. A cross the Table 4.14 in appendix A there was 15% of density increased. This clearly showed that the reinforcement of the chitosan into the phenol formaldehyde has significantly reduced the density of the entire material. The increased of density of chitosan-P/F composite of the samples when compared to the density of the chiotsan (1.0g/cm^3) was due to the phenolic novolac resin (which is between 1.2 to 1.3g/cm^3) . After chemical treatment, better interaction between the matrix and the fibre exists, hence had resulted in void minimization in the composites. As filler increases, the number of voids decreases as more chitosan and matrix crosslinked together during the curing step.The higher the density, the lesser the void content of the composte and as is relected in Figure 5.9, the smaller the specific volume. The voids actually allow more water up take into the specimen

This has also showed the real property of the composite. This can be attributed to the high value of water absorption in Table 4.18 in appendix A. In addition high pressure during the pressing process may also result in modification of the chiotsan and subsequently increase the density of the composite. The density values of the composites of different filler loading are given in Table 4.14 in appendix A, it can be concluded that with the increase in filler content there is increase in density for all composite type.

Density of a composite depends on the relative proportion of matrix and reinforcing materials and this is one of the most important factor determining the properties of the composite. This means that although gaining a significant increase in the properties, there is no increase in density of the material. This means extremely light weight materials can be manufactured and so significant weight savings on finished components can be achieved. The obvious advantage of the reinforced polymer composite is its low density, which brings other advantages such as, ease of handling and assembly, ease of transportation of material to construction site, and reducing loads to the elements which are supported, as a result, there is a cost reduction in the above concept (Muhammad *et al.*, 2011).

5.3.2 Water Absorption

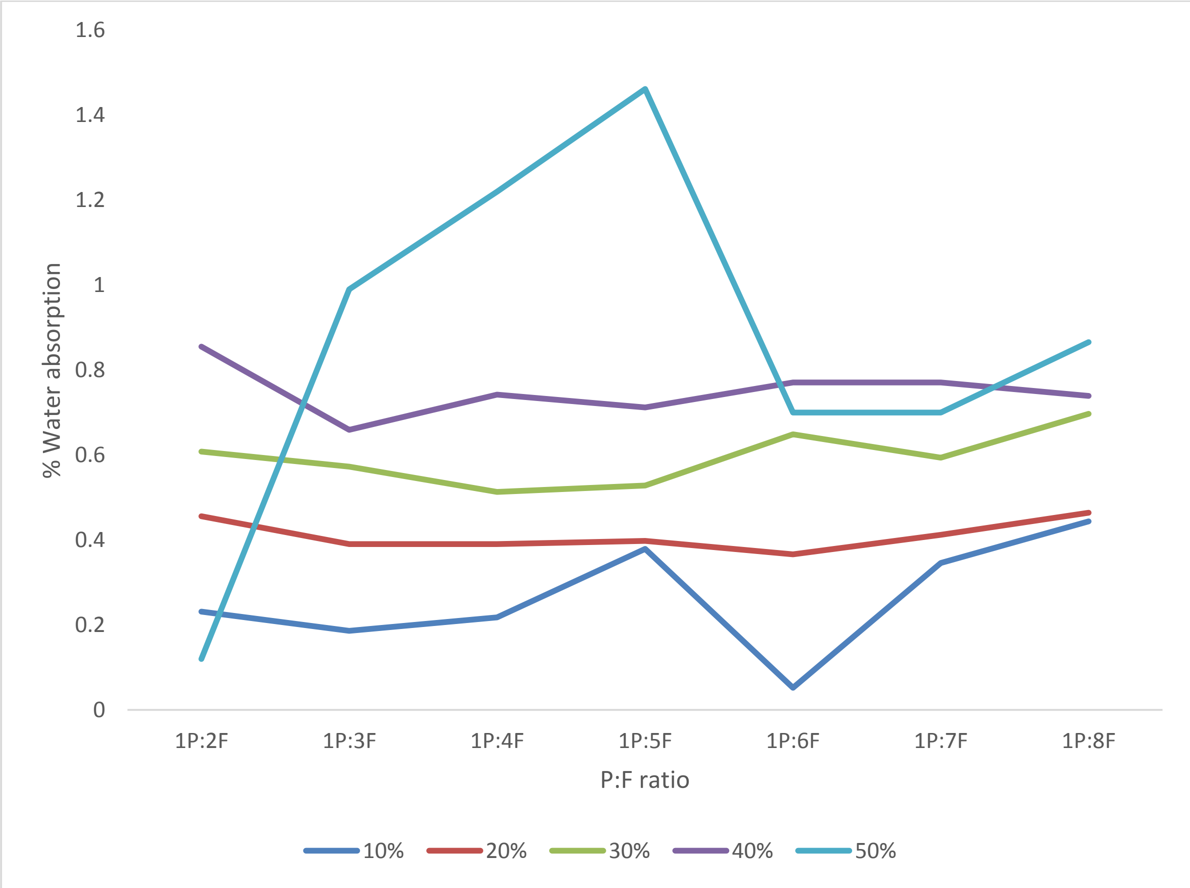


Figure 5.10: Water absorption Vs Synthesized P: F at different filler loading 10% to 50%

Table 4.15 in appendix A and Figure 5.10 shows the water absorption characteristic of composites at different fibre loading (10 to 50%) of 1P:2F to 1P:8F. It was observed that all water absorption of P: F composites (1P:3F, 1P:4F, 1P:5F, 1P:6F, 1P:7F and 1P:8F) increased gradually with increase in loading (Islam *et al.*, 2002 ; Lee *et al.*, 2008 ; Rezaur *et al.*, 2010). It is found that, water increases as the chitosan content in the sample increases.This is due to strong interaction of water molecules with hydroxyl and amino groups in chitosan (Cervera *et al.*, 2004 ; Mali *et al.*, 2005). The water diffusion was strongly affected by chitosan as observed in Figure 5.10. Since chitosan is hydrophilic in nature and porosity of the chitosan-P/F composite will have enhanced the water diffusion process. It has a tendency to attract water molecules. Therefore, the water uptaking tendency increases with the increase in chitosan content. The highest water absorption was observed at 40% filler loading with the value of 0.855% (1P:2F) ratio, and the least was observed at 10% with value of 0.052% (1P:6F) ratio.

When the content of chitosan increases in the composite, the number of free –OH groups inside it responsible for increase of the water absorption increased. These free –OH or hydroxyl groups come in contact with the water and form hydrogen bonding, which result in weight gain in the composites. In contrast, the treated chitosan reinforce composites exhibits the lowest water absorption compared to raw polymer alone Table 4.18 in appendix A. This implies that the chemical treatment had removed some acetyl groups inside the chitosan thus reducing the number of free –OH groups inside the composites which resulted in lowering the hydrophilic groups to absorb water for all the treated composites (Mohammad *et al.,* 2011).

This behavour can be also attributed to the fact that water uptake increases as the chitosan content in the sample increases. From Table 4.15 in appendix A of water absorption at different filler loading , it can be seen that in most cases the absorption of water, on the order of 14% for composites with higher filler loading (50%), increased in relation to pure resin (matrix).

In addition the fewer free hydroxyl groups in deacetylated reinforced chitosan composites attributed to the lower water absorption from 10% to 40% wt filler loading. Composite with high filler contents (40%) wt exhibit lowest water absorption for the deacetylated chitosan composites. Another reason of the less water content of the deacetylated chitosan reinforced composites is good interaction between the matrix and deacetylated chitosan that resulted in void minimization in the resultant composites (Elvy *et al.*, 1995). Conventionally, the moisture absorption increases as the cross-linking increases in the cured polymers from novolac-type resin and phenol novolac Table 4.18 (Ogata *et al.,* 1993).

In another explaination the density of the control polymer alone (neat matrix) was 1.2g/cm^3 in Table 4.4 in appendix A and it increases from (1.2 to 1.3g/cm^3) in some higher filler loading such as 1P:4F, 1P:5F and 1P:6F in Table 4.14, when the filler loading increases to 30 to 40%. This can be attributed to the high density of reinforced chitosan P: F composites. In addition, high pressure during the pressing process may also result in the densification of the filler and subsequently increase the density of the composites (Ogata *et al.*, 1993). The reactivity of novolac to HMTA increases when water content increases and flow distance is reduced in spite of decreasing melt viscosity (Gardziella *et al.*, 2000), the influence of free phenol is similar to water content but is less severe. In addition, curing of novolac is carried out over 100^{o}C, where water forms vapour, and so the final material can present a porous structure with reduced mechanical properties. The synthesized novolac resins cured with the hexamethylenetetramine (HMTA) produces volatile by –products such as water, formaldehyde and ammonia, which lead to voids in the material

5.3.3.0 Mechanical Properties of Phenol Formaldehyde Reinforced with Chitosan at Different Filler Loading .

It has been observed that the performance of natural fibre reinforced polymer composite is controlled by the properties of the fibre-matrix adhesion bonding (Asgekar *et al.*, 2013; Mohan, 2008). A primary requirement for effective use of reinforced properties of natural fibres is good interfacial bonding (or adhesion) between the phenol formaldehyde polymer matrix and chitosan. The interfacial adhesion/bonding characteristics have a significant effect on the strength of fibre reinforced polymer composite (Kumar, 2000). In order to achieved good fibre reinforcement; interfacial bonding between the chitosan and polymer matrix is considered as the most essential factor. Hence an essential understanding of interfacial properties and a quantitative characterization of interfacial adhesion/bonding strength can help in evaluating the mechanical behavior and capabilities of polymer composite materials (Ishaya *et al.,* 2014).

The mechanical properties of polymer composites have been found to depend solely upon extent of fibre matrix bonding (Thirapat *et al.,* 2013), extensive bonding takes place between the hydroxylmethylol groups of polymer matrix and amino groups of chitosan resulting in strong structure which ultimately accounts for better mechanical properties when compared with mechanical properties of the matrix. The bond strength also depends upon surface topology of the filler. The adhesion /bonding between the polymer matrix and the reinforcement is a result of good wetting of the filler the P: F matrix as well as the formation of a chemical bond between the filler surface and the polymer matrix. In addition, there are also secondary forces of interaction between the growing P:F polymers and the non-crystalline amino and the hydroxylgroup molecules of the chitosan (Mohammed *et al.,* 2014).

5.3.3.1 Tensile Strength /Modulus

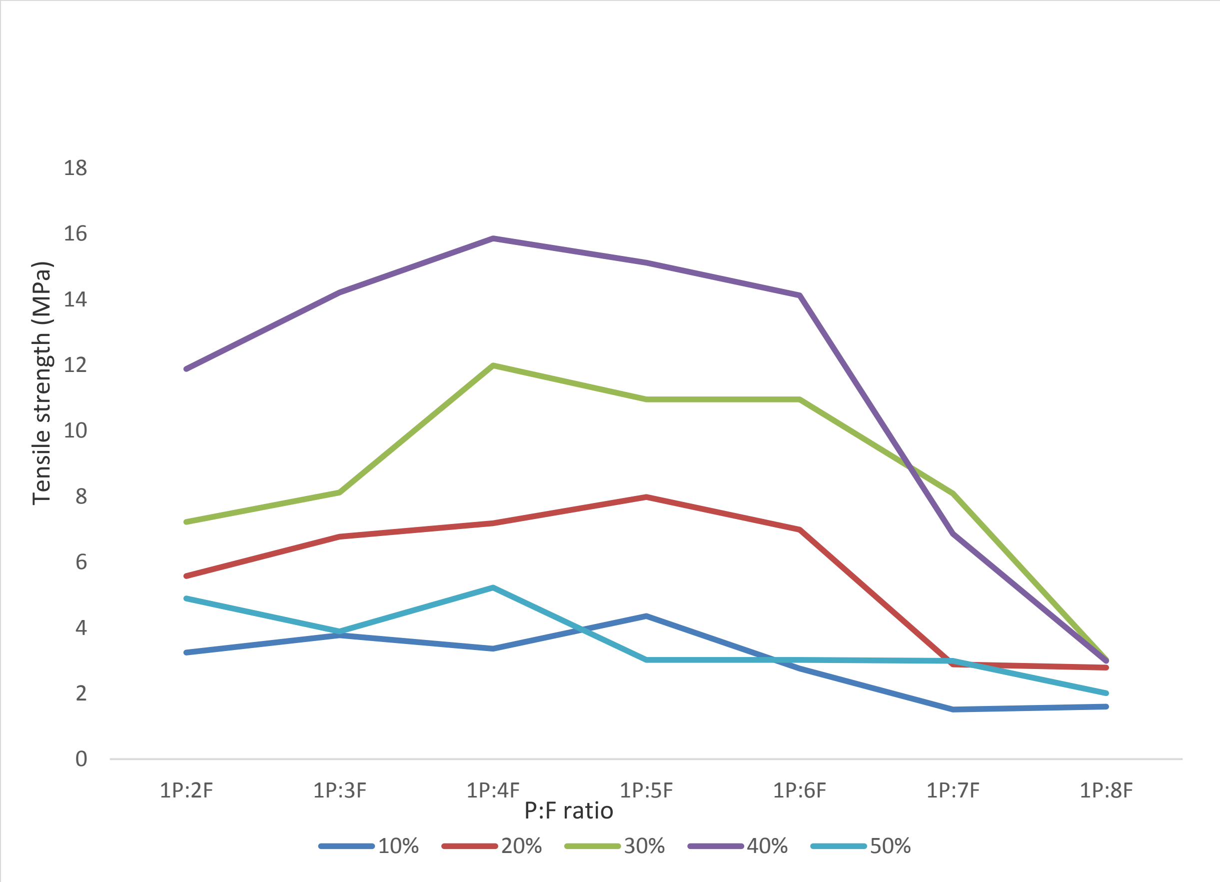


Figure 5.11: Tensile strength Vs Synthesized P: F at different filler Loading (10% to 50%)

Table 4.16 in appendix A and Figure 5.11 show the trend in tensile strength and Table 4.17 in appendix A and Figure 5.12 modulus of the composite samples at different filler loading with synthesized resins at different molar ratio of 1P:2F to 1P:8F. From experimental result of tensile tests, it is observed that the addition of filler with phenolic resin up to 10% and 50 % increases the tensile strength and modulus of the composite as shown in Figure 5.11 and 5.12. When compared to neat polymer (P:F alone) Table 4.16 in appendix A. It was observed that ultimate tensile strength of composites increases on reinforcement with chitosan. Composite at 40% loading bore maximum load 15.86 MPa (1P:4F), followed by 30% 11.98 MPa (1P:4F), 20% 7.98 MPa (1P:5F) and 10% 4.36 MPa (1P:5F) loading respectively. And the least values were observed at 40% filler loading 11.88 MPa (1P:2F), 30% 3.02 MPa (1P:8F), 20% 2.79 MPa

(1P:8F) and 10% 1.51 MPa (1P:7F) respectively. The tensile strength is significantly improved by alkali treatment. But, alkali treatment generally increases the strength of natural fibre composites (Dieu *et al.,* 2004). A strong sodium hydroxide treatment removed the acetyl group to increase the number of reactive hydroxyl and amino groups on the surface of the fibre available for chemical bonding. So, strength should be higher than untreated fibre composites.

The tensile strength/modulus values of the untreated chitin (8.90 MPa/128.89 MPa) and the neat matrix (11.92 MPa/151.19 MPa) in Table 4.20 in appendix A were lower when compared to the treated chitosan (DD) composites. This was due to the lack of curing agent. This was reported that without curing agent, fibre content and fibre length do not have significant effects on composite tensile properties (Sameni *et al.,* 2003). There exist incompatibilities between the surface of the filler and the polymer. To improve affinity and adhesion between filler and polymer, curing agent were used so that tensile strength increases (Khan *et al.,* 2001). Use of curing agent reduces the number of fibre pull-out (Gassan and Bledzki, 2001). Beside presence of amino groups in the chitosan molecule enhanced the mechanical properties because of the strong cohesion between the fibre and the matrix as stated in procedure (**5.5.7.2**).

It is found that at very high 50% filler loading from the Table 4.16 and 4.17 in appendix A, the tensile strength and tensile modulus decrease with the least values of 2.01 MPa (1P:8F) and highest 4.89 MPa (1P:2F). This is because the processing is difficult and dispersion becomes very poor and this may be the reason for the decrease in properties at higher volume fraction of chitosan . Filler layered out at higher loadings due to decreased interminar bonding. Parking defects may occur at higher loading which may reduce effective stress transfer from the matrix to the fibre. Possibility of fibre enstanglement increases and uniformity in fibre dispersion decreases at high loading.

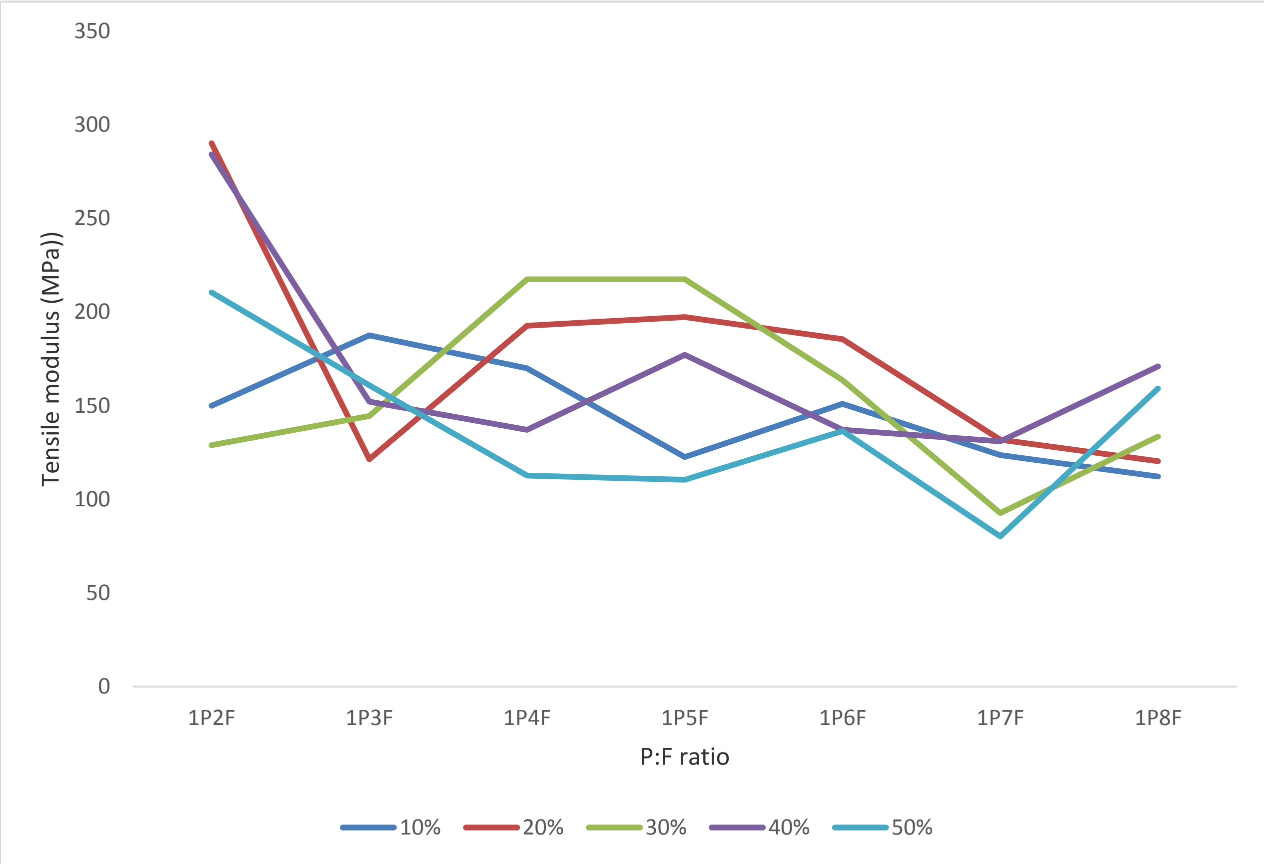


Figure 5.12 : Tensile modulus Vs Synthesized P: F at different filler loading (10% to50%)

Similarly, results of tensile modulus in Table 4.17 in appendix A and Figure 5.12 shows the trend of the tensile modulus of P: F resin with the reinforced fibre weight fraction. The highest values was observed at 40% filler loading (284.19 MPa:1P:2F) 30%, (228.89 MPa:1P:2F) 20%, (185.55 MPa:1P:6F) and 10% (187.62 MPa:1P:3F) and the least values of 40% filler loading (130.92 MPa:1P:7F) 30%, (92.74 MPa:1P:7F) 20%, (120.43 MPa:1P8F), and 10% (112.23 MPa:1P:8F). The increase of fibre content results in a general increase of the initial tensile modulus of the composite. This is expected because the chitosan contributes to the stiffness of the final composite. The composite supposes that the fibre and the matrix present a perfect adhesion and a homogeneous distribution through the matrix. But with incorporation of the chitosan of more than 50% this lead to a non-homogeneuos composite, hence resulted in low tensile strength and low tensile modulus were observed. Hence, 50% filler loading shows a decrease in the tensile modulus with the highest 210.41MPa (1P:2F) and the least 80.12 MPa (1P:7F).

Fibres layered out at higher loading which may reduce effective stress transfer from the matrix to the fibres. Possibility of fibre entanglement increases and uniformity in fibre dispersion increases at higher loading (Kalaprasad *et al.,* 1997; Ku *et al.,* 2008). In compression moulding the squeezing flow causes some transverse fibre orientation in the surface area which is a decisive factor in the mechanical performance of the composite. Possibility for this type of fibre orientation is decreased at higher filler loading (Maron *et al.,* 1978). It can be concluded that the incorporation, filler into the polymer leads to composites having superior performance. Maximum intermingling of the fibres and higher compatibity are achieved at high DD values. The adhesion efficiency between the fibre and the matrix determines the strength property of the composites. This is dependent upon the nature, shape, and surface roughness of the reinforced material (Zweben , 1989).

From the experimental by a two-level factorial design by (Thirapat. *et al.,* 2013) the factors that affect the tensile strength were seven factors as follows, curing time, amount of phenolic resin, curing temperature, interaction between curing temperature and cure time, interaction between curing temperature and amount of phenolic resin, interaction between cure time and amount of phenolic resin, 3-way interaction of amount of phenolic resin, curing temperature and curing time. From the results they concluded that the main effects analysis to determine 75% wt% of phenolic resin, curing time and curing temperature were the best condition to give the tensile strength according to MIL-1-24768.

Numerous different polymers were used in reinforced polymer composites and obviously result in a wide array of different properties ultimately achieved. However, all the reinforced polymer composites offer significant higher properties than the virgin polymer from which they are made.

5.3.4.0 Optimization of Chitosan Phenol Formaldehyde Composite

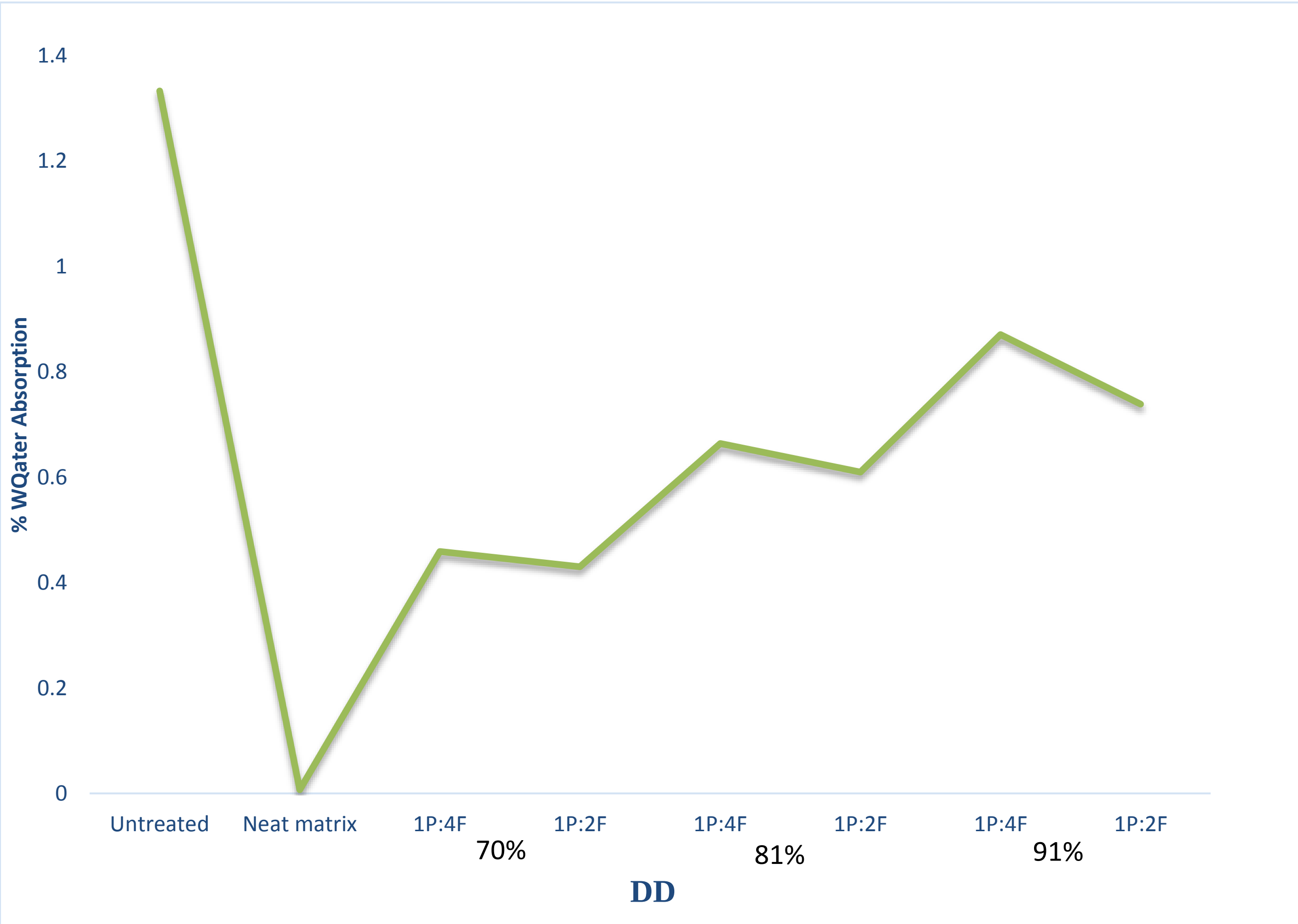
From the discussion of results in (**5.3.3.1 to 5.3.3.2**), determining mechanical properties at different filler loading (10% to 50%) of the chitosan/P: F composites. It was observed from the Table 4.16/4.17 in appendix A and Figure 5.12/5.13 that 40% filler loading exhibited a maximum tensile properties at 1P:4F and 1P:2F mole ratio. A maximum values of 15.86 MPa (1P:4F) and 284.19 MPa (1P:2F) were obtained. Hence, 40% filler loading at 1P:4F and 1P:2F mole ratio were taken for further analysis of : DD%, physicochemical properties, mechanical properties and characterization by (XRD, SEM, and TGA/DTA).

In this case the DD value of the chitosan were increased to determine the optimum value. The DD, which determines the contents of free amino groups in the polysaccharides. Deacetylation which involves the removal of acetyl groups from the molecular chain of chitin, leaving behind amino group (-NH_2) and chitosan versatility depends mainly on the high degree of deacetylation. So, to increase the DD values of chitosan, the temperature and concentration of sodium hydroxide were increased from 100^{o}C to 120^{o}C and 30 to 50%w/v of NaOH. So that a DD values of 70%, 81% and 91% (Table 4.10 in appendix A) were obtained. This had resulted to chitosan molecules with different properties and applications (Baxter *et al.,* 1992); Mima *et al,* 1983). Since the degree of deacetylation depended mainly on the method of purification and reaction conditions (Baxter *et al,* 1992; Tanveer, 2002). It is therefore essential to characterize chitosan by determining the degree of deacetylation prior to its utilization at the development stage (Nguyen, 2009; Inmaculada *et al.*, 2009).

5.3.5.0 Analysis of the Optimum Composites of 1P:2F and 1P:4F

5.3.5.1 Water Absorption

Fluctuations in moisture levels of chitosan material may change the physicochemical and mechanical properties of chitosan based systems. Studies conducted by (No *et al.*, 2009), revealed that although the level of absorbed water in chitosan powder rose during storage, a decline in water binding capacity was observed. Viljoen *et al.*, (2014) showed that six month storage of chitosan tablets caused a dehydration of the polymer, which resulted in a decrease in crushing strength followed by an increase infriability and disintegration time. In addition, the higher the water content in the chitosan structure and the faster is more pronounced was the damage of the polymer (via hydrolysis reactions) (Viljoen *et al.*, 2014).



Figur 5.13: Water absorption of 1P:2F and 1P:4F at different DD %

The practical usage, absorbed moisture was found to plasticize the P: F resins, causing a lowering of the cross-linking agent and in turn affecting mechanical properties (Chauhan, 2009). The water absorption measurement calculated from Equation (3.14) was shown in Table 4.18 in appendix A and Figure 5.13. The untreated chitin and the neat matrix have values of 1.33% and 0.007%. 1P:4F and 1P:2F show a least values of 0.4589% and 0.43% at 70% DD. The highest values were observed for 91% DD with a values of 0.8707% and 0.7300% for 1P:4F and 1P:2F. It showed that all cured P: F resin composite of 1P:4F and 1P:2F ratio had better moisture resistance than that of untreated chitin composite.This means the sample have under goes extensive crosslinking Table 4.18 in appendix A clearly shows that in both 1P:4F and 1P:2F mole ratio at different DD% the increase of the moisture absorption decreases and the hydrophobicity decreased with increase of DD%. This was due to blocking of sites vulnerable for moisture absorbance with hydroxyl group chains thereby, converting the fibre less sensitive to moisture (Kaith, 2003). At high DD% more hydroxyl group are available for bonding to form water.

Conventionally, the moisture absorption decreases as the crosslinking increases in the cured polymers from chitosan novolac-type resin and phenol novoac (Ogata and Kawata, 1993). However, because of the hydrophobic nature of polymer of phenol formaldehyde and amide group from chitosan structure, the cured polymer from the reinforced fibre system exhibited a high crosslinking and relatively low moisture absorption (Chauhan, 2009).

In another reason for the lower water absorption at high DD, can be attributed to the greater adhesion between the fibre and the matrix, the lower water absorption nature of the matrix. It is observed that with increase of DD% from 70 to 91% DD the water absorption intenced. This might be due the poor distribution of fibres in the composite which result in the formation of fibre lumps. These lumps require more force to deform during hot pressing, and as a result more stresses are built in the composites (Krzysik.a *et al.,* 1990). When the composites are tested (water absorption test), a greater proportion of these stresses are released, causing a high water absorption. In addition, chitosan are similar to lignocellulosics and therefore hydrophilic in nature chitosan absorbs readily (Ashish and Baith, 2012).The novolac composite had the lower water absorption Table 4.18 in appendix A and Figure 5.13, confirming the better fibre/matrix interface. In the composites reinforced with natural fibres, the fibres are considered responsible for most of the water absorption. Thus, the better coating of the chitosan by the matrix in the novolac composite prevented the interaction between water molecules and the chitosan, reducing the water absorption in the composite (Ashish and Kaith, 2012 ; Chauhan 2009 ; Ishaya and Josiah, 2014).

5.3.5.2 Density

Table 4.18 in appendix A and Figure 5.14 displayed density of the deacetylated reinforced chitosan P: F composites (1P:2F and 1P:4F) at different DD%, neat matrix and untreated chitin composites. It was observed that density of the deacetylalated reinforced chitosan P: F composites increases as the DD% increases.

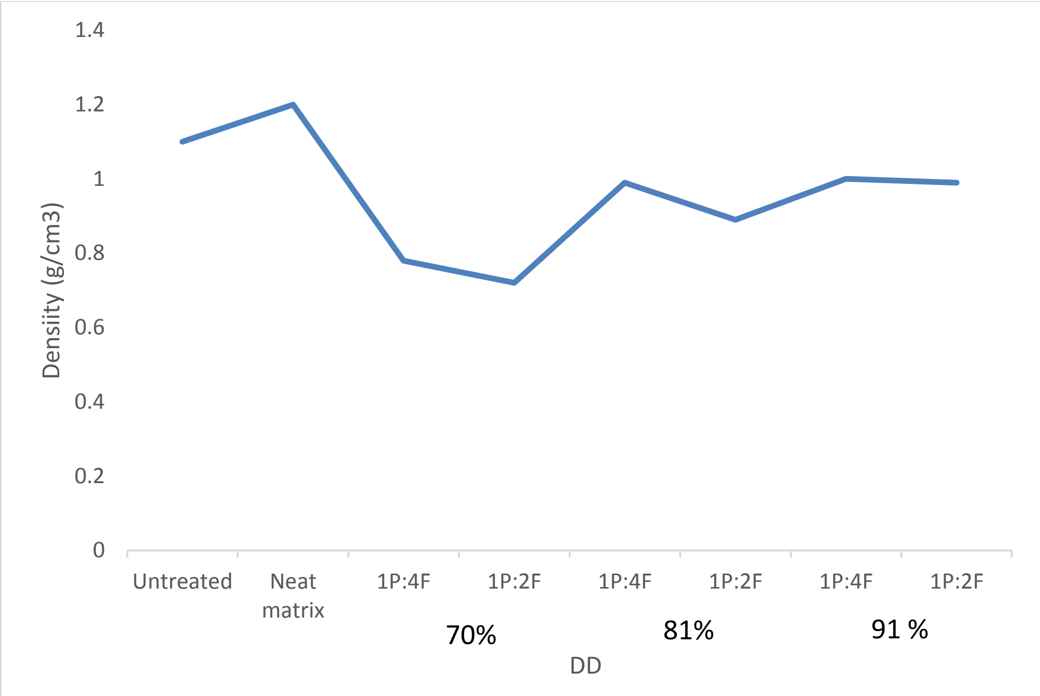


Figure 5.14: Density of 1P:2Fand 1P:4F at different DD %

The highest was observed at 91% DD which is 1.0g/cm^3 and 70% DD gave the least value of 0.78 and 0.72g/cm^3 for 1P:4F and 1P:2F ratio. The neat matrix and the untreated gave values of 1.2g/cm^3 and 1.0g/cm^3.

It was observed that, all the different DD% composites have low density compared to the neat matrix, 1.2g/cm^3 and the uncured composite (1.0g/cm^3) . After chemical treatment of the chitosan and fabricating the composites, better interaction between the matrix and the chitosan exist hence had resulted in a good crystalline structure with increase in DD%. This is due to the strong hydrogen bonding which exist as DD% increases. As the percentage of deacetylation increase, a lot of acetyl groups have been removed and a lot of hydroxyl groups were exposed for bonding .This decreased the molecular weight of the sample, and the crystallility decreases at high DD (91%). This is why the high DD 91% composites have high density (1.0g/cm^3) and the low DD 70% have less density (0.78/0.72g/cm^3) (Kumar, 2000; Ishaya and Josiah, 2014).

5.3.5.3 Chemical Resistance

During hydrolysis, acid acts as a catalyst which split the polymer chains. As a result, a decrease in average Mw, viscosity, and weakness that the rate of hydrolysis followed first-order kinetic. And the main factors affecting this parameter were DD, polymer concentration, type of acid and its concentration, treatment time, and temperature. There are several studies devoted to chitosan hydrolysis using several types of acids, namely acetic (Kani *et al.,* 1999; Nguyen *et al.,* 2008), formic acid (Nguyen *et al.,* 2008), lactic acid (II'ina and Varlar, 2004), and hydrochloric acid (Vairum *et al.*, 2001). Different acetic acid concentration were found not to affect the degradation rate (Nguyen *et al.,* 2008), whereas an accelerated rate of hydrolysis with increased concentration of hydrochloric acid was observed (Vairum *et al.,* 2008). A faster rate chain damage was noticed when chitosan with lower DD was used in the studies (Emilia and Kartar, 2005). Chitosan preparations is differed by the degree of deacetylation. Unlike chitin, chitosan can be dissolved in water and diluted with organic acids for example, in aqueous solution of acetic acid. So, this character causes extensive usage of this polysaccharide in different fields of application.

It has been observed that acid/base resistance of the chitosan increased with increase in percent of chitosan (Chauhan, 2009). This is due to the fact that polymer chains of phenol formaldehyde (hydroxyl group) bonded onto the filler (chitosan amide group) have less reactivity for IN HCI and 1N NaOH as compared to the free hydroxyl group in the polymer. Therefore, the resistance of chitosan towards acid-base was found to increase with the incorporation of the hydroxyl group of the polymer chain and the active site of the fibre that is the amide group.

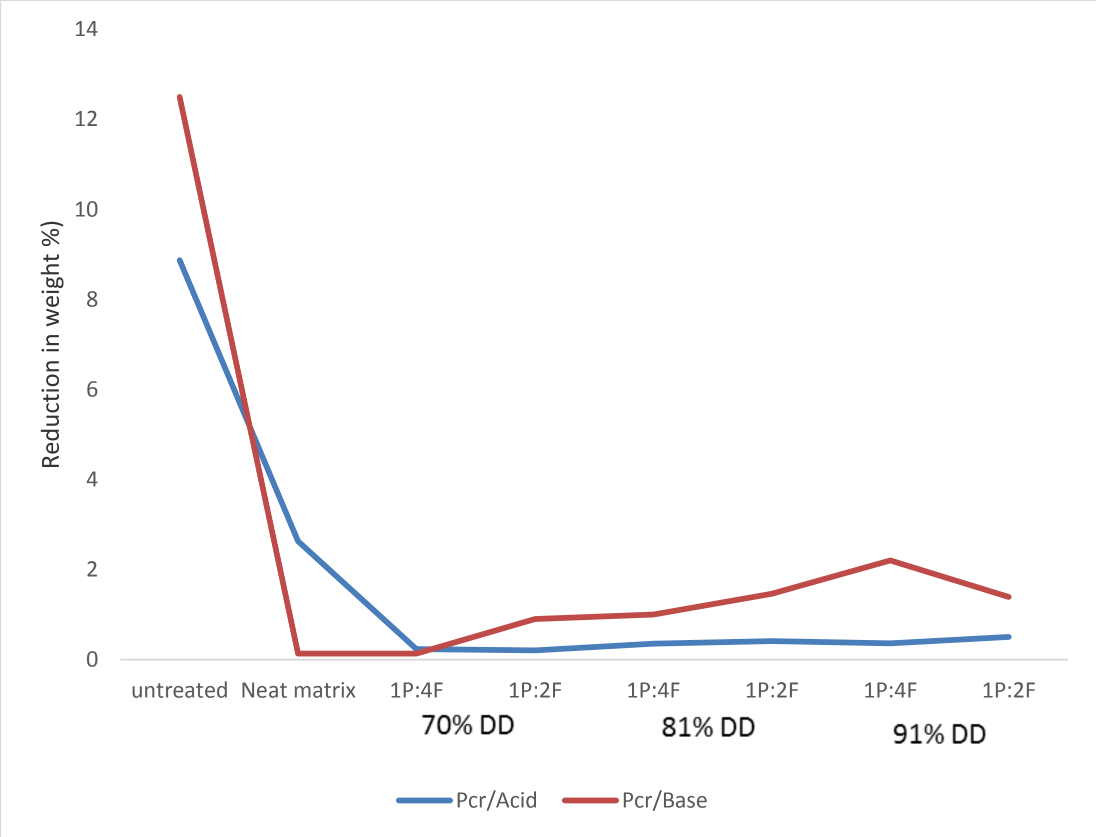


Figure:5.15: Chemical resistance of 1P:2F and 1P:4F at different DD %

This can be seen from the calculated values of chemical resistance in Equation (3.15) and Table 4.18 in appendix A, the neat matrix have a high value of 2.63% 1N HCI and the untreated chitin the highest value of 8.87%. The 91% DD of 1P:4F and 1P:2F gave the highest values of 0.36% ; 0.50% and 70% DD gave the least values of 0.23%/0.2% in the acid media. This confirmed the findings of (Pistin, 2002; Johanneskarl, 2005) that the higher the degree of acetylation, the lower the crystallinity and the higher the rate of biodegradation obtained.When the virgin polymer and the untreated filler were compared to the reinforced composite at different DD, the DD composites (70 to 91%) they all showed a marked chemical resistance due to strong fibre matrix complex formation, in comparison to the resin. . This may be due the hydrogen bonding with the cross-linking ability of chitosan and the matrix. (Chauhan 2009;

Ashish and Kaith, 2012). This test is able to demonstrate that all composites tested can perform creditably well in an acid medium.

Similarly, the 1N NaOH solution showed the same trend. The untreated filler and the neat matrix have a values of 12.5% and 0.13%. Although, the polymer composites gave good result when compared with the untreated and the treated filler. The 91% DD gave a higher value at 1P:2F with 1.39% and 1P:4F gave a value of 2.20%. The least values were observed at 70% DD with a values of 0.13% and 0.90% for 1P:4F and 1P:2F and highest at 91% with values of 2.20% and 1.39% of 1P:4F and 1P:2F. Similarly the non-cured composites gains more weight than the cured Figure 5.24 which can be as a result of non cross-linkage of chitosan with the matrix in the non-cured chitosan composites as this does not agree with (Pistin, 2002).

5.3.5.4 Swelling Behaviors

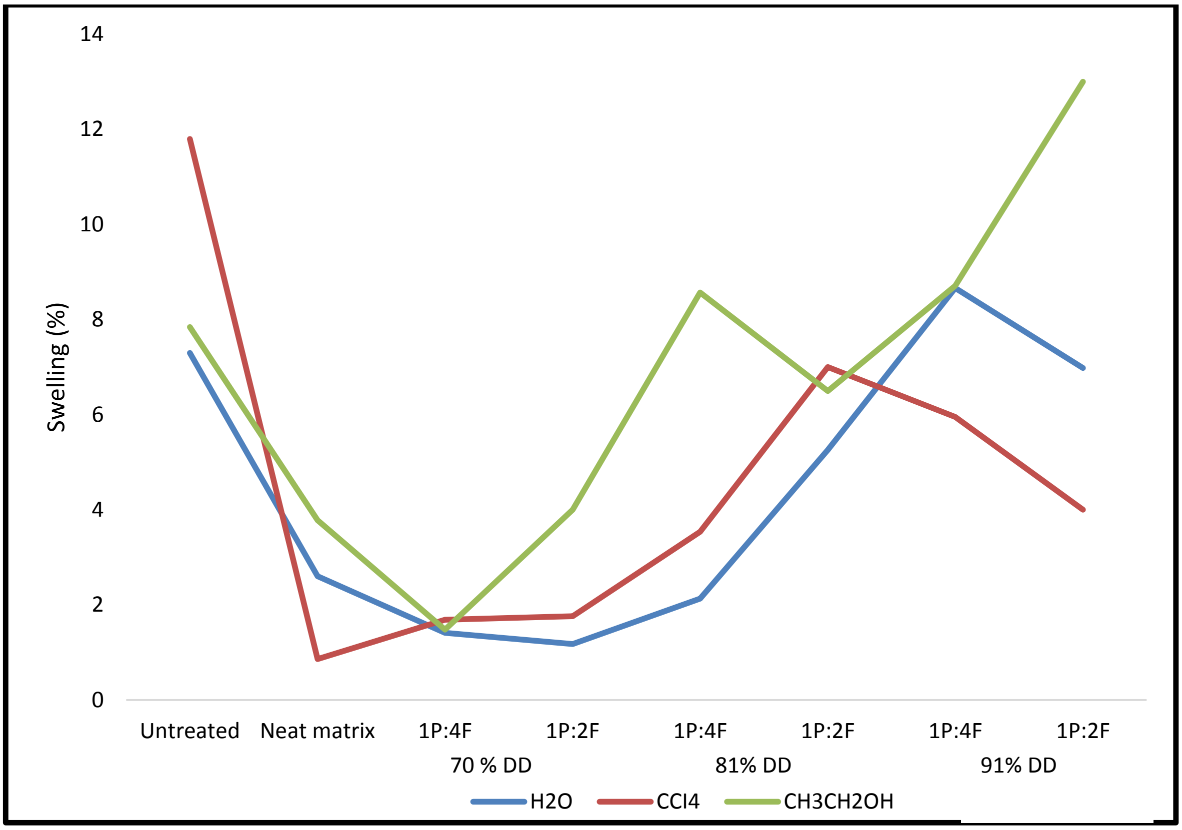


Figure 5.16 : Swelling behavior of 1P:2F and 1P:4F at different DD %

Table 4.19 in appendix A and Figure 5.16 displayed the swelling test result of composite of untreated, neat matrix, 1P:4F and 1P:2F samples. The swelling behaviors were carried out to observe the effect of polar and non-polar solvents on the swelling properties of the chitosan P: F composites, so as to assess the various possible applications. The swelling behavior studies were carried out in different solvents like water (H_2O), tetrachloroethane (CCl_4), ethanol (CH_3CH_2OH), and acetone (CH_3OCH_3). It has been observed that chitosan untreated showed maximum swelling in water (7.30%) followed by ethanol (7.84%) and then CCl_4 (11.80%). The neat matrix have a values of 2.60% in H_2O, 0.86% in CCl_4 , 3.78% in CH_3CH_2OH and 0.4% in acetone. Acetone showed the highest effect on different DD% reinforce composites for both the 1P:4F and 1P:2F, in each case the sample were destroyed (D) in the solvent.

It can be seen that 70% DD of 1P:4F have the following %Sw values in water (1.41%Sw), tetrachloromethene (1.69%Sw), and ethanol (1.48%Sw), and in 1P:2F ratio have a values of 1.18%Sw, 1.76%Sw and 4.0%Sw respectively. The values of %Sw for the 81% DD of 1P:4F in water (2.31%Sw), tetrachloromethene (7.0 %Sw) and ethanol (8.57%Sw), and in 1P:2F ratio have values of 5.26%Sw, 3.54%Sw, and 6.5%Sw respectively. The 91% DD of 1P:F4 have the following values of %Sw in water (8.66%Sw), tetrachloromethane (5.95%Sw) and ethanol (8.71%Sw) and in 1P:2F ratio have a values of 6.98%Sw, 4.0 %Sw and 13.0 %Sw respectively.

The highest %Sw of water is observed at 91% DD (8.66%Sw/1P:4F) and the least is observed 70% DD (1.18%Sw/1P:2F). 91% DD of 1P:4F have the maximum value for tetrachloromethene (5.95 %Sw) and the minimum is observed for 70% DD (1.69 %Sw and 1.76 %Sw) for both 1P:4F and 1P:2F ratios respectively. The highest %Sw of ethanol was observed at 91% DD (8.71 %Sw and 13.0%Sw) for both 1P:4F and 1P:2F ratio. And the least was obtained at 70% DD (1.48%Sw and 4.0%Sw).

It can be seen from the Table 4.19 in appendix A and Figure 5.16 that swelling (%) increases with the increased of DD. The increase of swelling (%) at high DD might be attributed to the presence of free $–NH_2$ groups in the chitosan molecule. The higher the DD, the more was the primary amine groups (Khan *et al.,* 2002). The number of free amide groups was more in the chitosan at high DD. Here, the amount of cross-linking agent might not be able to crosslink all the amine groups. As a result, more and more free amine groups would be available as DD increased. These amine groups increased the hydrophilicity and thereby swelling. This might be responsible for the trend in Figure 5.16 that at high DD, swelling (%) increased.

The untreated filler in all cases showed a moderate values with the highest in CCl_4 (11.8%) and ethanol (7.84%). the neat matrix shows good results with the least value in CCl_4 (0.86%) and highest in ethanol (3.78%) However, from Table 4.19 in appendix A, the swelling behavior of the reinforced composite followed the maximum pattern water > ethanol > CCI_4 > Acetone, and the trend obtained has a direct correlation with the solubility parameters like solvent basicity, the molar ratio, hydrogen bonding formation and percentage deacetylation.

Depending on the chemical nature and property, the pendant groups of the reinforced polymer – and -OH, for water and ethanol, Cl^{--} for tetrachloromethene, >C=O for acetone, have different interaction with such pendent groups that increase with the increase of percent deacetylation. However, a reverse trend has been found in the case of the raw polymer (without filler). Since a crystalline polar polymer is soluble in solvent is capable of hydrogen bond formation therefore, the raw polymer (polymer alone) has more swelling in water, ethanol and CCI_4. Presence of –OH and $–NH_2$ groups in the chitosan fibre supports the deep penetration of the polar solvents into the reinforced chitosan P: F composites, thereby, resulting in higher swelling. Whereas, in the case of >C=O (Acetone) and CI^- of (tetrachloromethene), the affinity of these solvents towards –OH groups is less and ultimately a decreased swelling takes place. In other words, it can be said like terms dissolve and unlike terms does not. Moreover, other factors like the fibre size, steric hindrance and temperature also influence the percentage of swelling (West and Banks 1989 ; Chawala 2002 ; Lee *et al.*, 2005).

5.3.5.5 Tensile Strength and Tensile Modulus

Table 4.20 in appendix A show the tensile behavior of chitosan P: F composites. The untreated and neat matrix P: F (polymer alone) were also presented in the same Table. The brittle nature of the untreated and the virgin polymer had the low values of 8.90MPa and 11.92MPa tensile strength and tensile modulus of 128.89MPa and 150.03MPa respectively.

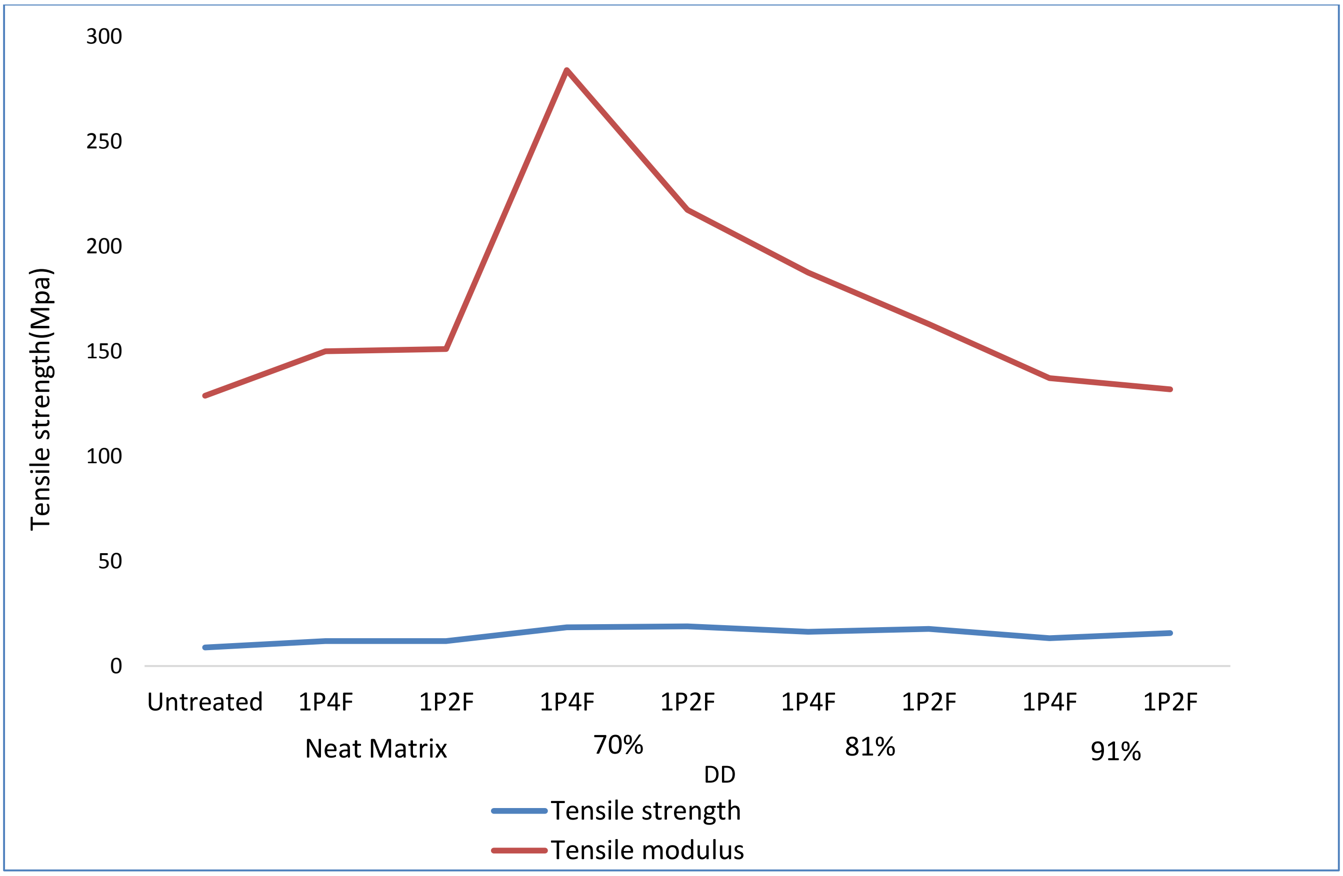


Figure 5.17: Tensile strength/modulus of 1P:2F and 1P:4F at different DD%

Table 4.20 in appendix A and Figure 5.17 shows the variation of tensile strength and tensile modulus of composites 1P:4F and 1P:2F with different chitosan filler loading and DD values. The tensile strength linearly decreases with increase degree of deacetylation DD% and also the tensile modulus decreases with the increase of the DD%. The highest tensile strength was observed at 70% DD with a value of 18.40 MPa in 1P:4F and 18.83 MPa in 1P:2F, while the tensile modulus was 284.19MPa at 1P:4F and 217.53MPa at 1P:2F composites respectively. The least value was observed at 91% DD with a value of 13.20 MPa tensile strength and tensile modulus of 137.31 for 1P:4F composite, and 15.75 tensile strength and 131.87 MPa tensile modulus for 1P:2F composite.

When the values of tensile properties of 1P:4F and 1P:2F were compared with the virgin polymer and the untreated filler, the performance increases with DD% values. Chitosan is primarily characterized by its M.wt, which is responsible for a number of its physicochemical properties such as hydrophility (Pistin, 2002). The higher tha alkali treatment the higher was the DD and lower M.wt. Also, crystallinity decreases with increased of DD and low M.wt of chitosan and it is hydrophilic containing a large number of hydroxyl groups which are easy to combine with another group and formed new bond (Ogawa *et al.*, 1992). It was observed that at very high DD% lower the crystallinity and the higher the rate of degradation obtained.

Alkali treatment is known to deacetylate and degrade chitin. Both this processes are expected to improve solubility. Decetylation reduces crystallinity and degradation reduces the molecular weight. (Liu *et al.*, 2003), showed that hydrogen bonds in chitin were weakened by the alkali treatment and the crystallinity of chitin decreased significantly when soaked in higher concentration alkali solution at room temperature (Hudson and Smith , 1998). The Mw and DD of chitin decreased significantly at treatment temperatures higher than 20% or treatment times longer than 4h. It was found by (Khan *et al.,* 2002; Gupta and Jabrail, 2006) that regenerated chitin obtained by a concentration alkali treatment at low temperature is water-soluble. Kurita and Sannan, (1992) showed that the regenerated chitin with around 50% of deacetylation isolated at low temperature from alkali chitin solution left at 25ºC for 48 to 77hr has very good solublity in water at 0ºC.

The improved solubility of chitin with 50% of deacetylation would be attributed to the partial deacetelylation which brought about the destruction of the secondary structure and also the increase of the hydrophilic property dispersed along the chain to prevent parking of chains resulting from the disruption of the secondary structure in the strong alkali medium. The prolongation of deacetylation increases DD with a reduction in average molecular weight

(Roberts, 1992). .A low concentration of NaOH is correlated with low DD as well as an increase in the viscosity. Gradual deacetylation is preferred to obtain a high-deacetyled product with alow reduction in average M.wt. However, a wide variation between Mw and DD is found for chitosan deacetylated from insects. In addition the reduction in particle size of chitinuos particles decreases the deacetylation time, resulting in a more soluble product distinguished by a higher DD (Keng – Shiang *et al.*, 2014).

5.3.5.6 Flexural Test

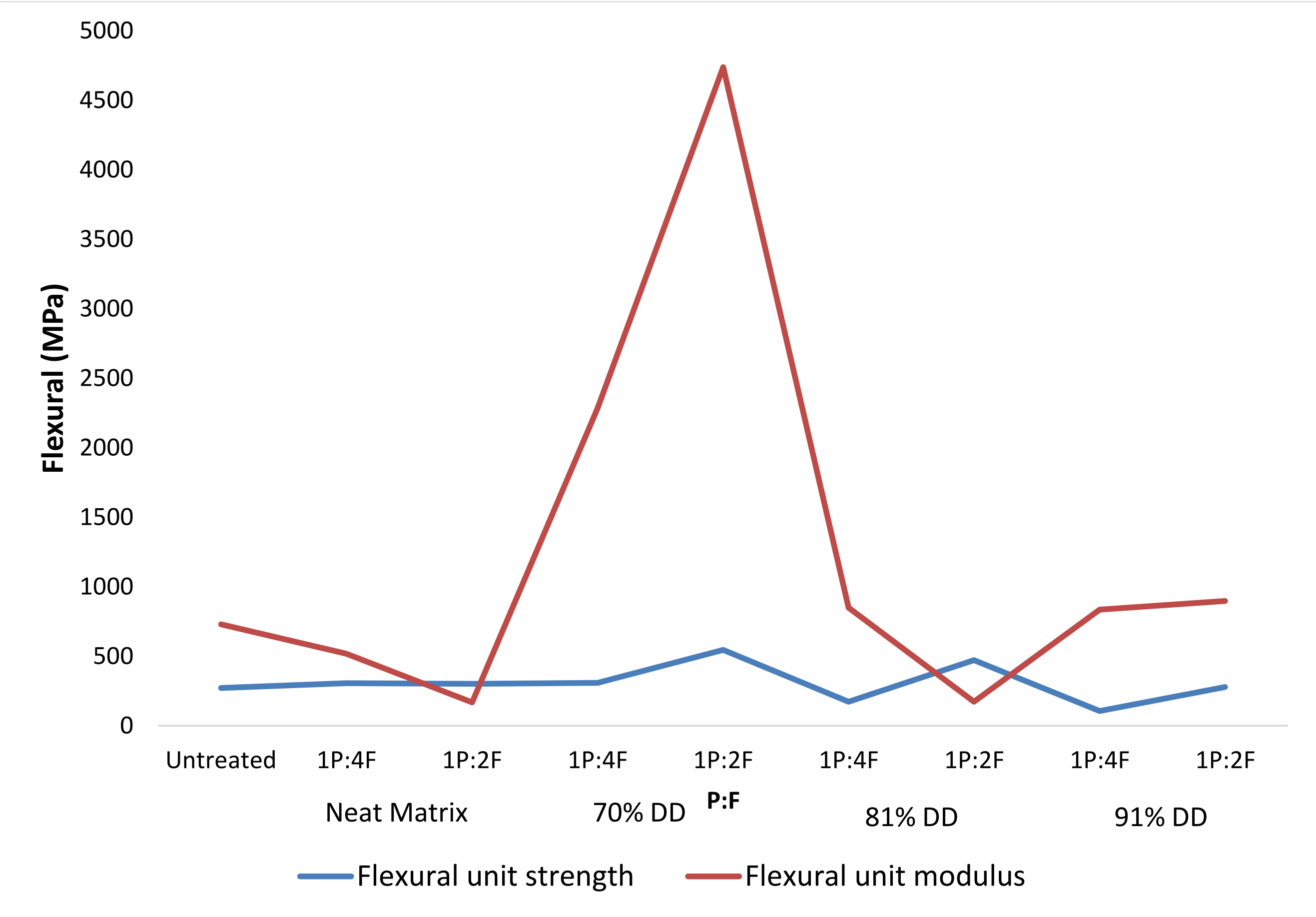


Figure 5.18: Flexural strength and Fluxural modulus of 1P:2F and 1P:4F at different DD%

Flexural modulus is a measure of strength and stiffness of the composite. Flexural test were shown in Table 4.20 in appendix A , as from the calculated value of flexural strength in Equation 16 and flexural modulus in Equation 17, results are tabulated. It can be seen from Figure 5.18

and Table 4.20 in appendix A, flexural strength and flexural modulus of 40% at P: F ratio 1P:4F and 1P:2F composites decreases with the increased in DD. where a peak flexural strength and flexural modulus of 70% DD with values of 1P:4F and 1P:2F were found to be 2,284MPa and 4,738 MPa respectively. And the least flexural strength and modulus was observed at 91% DD with a value of (1P:4F) 105.79 MPa and 835.05 MPa and (1P:2F) 277.66 MPa and 897.00 MPa respectively. The flexural strength and flexural modulus of 70% DD is higher than 81% and 91% DD. The decrease in the values upon modifications is attributed to the weaker interfacial bond formed due to the alkali treatment. The highly deacetylated composite have more amino and hydroxyl groups for bonding. Beside, deacetylation at high level disrupt the structure of the composite from the crystalline material to less crystalline sample.

From the Table 4.20 in appendix A, the values of flexural test of untreated and the unreinforced composite (neat matrix) were given and showed a lower value compared to that of the reinforced composites. The untreated fibre have a value of flexural strength and modulus of 271MPa/730.43MPa and the virgin polymer have 305.37MPa/517.51MPa. It was observed that as the DD% increased there was a decline in the flexural strength and flexural modulus. Therefore, based on the relatively high flexural strength of the 40% at 1P:4F reinforced composite. This is in agreement with many natural fibres as reported by (Bledzki and Gassan, 1999). It shows a strong potential of being used as a suitable material for composite purposes. Decrease in the values upon modifications is attributed to the weaker interfacial bond formed.

5.3.5.7 Impact Strength

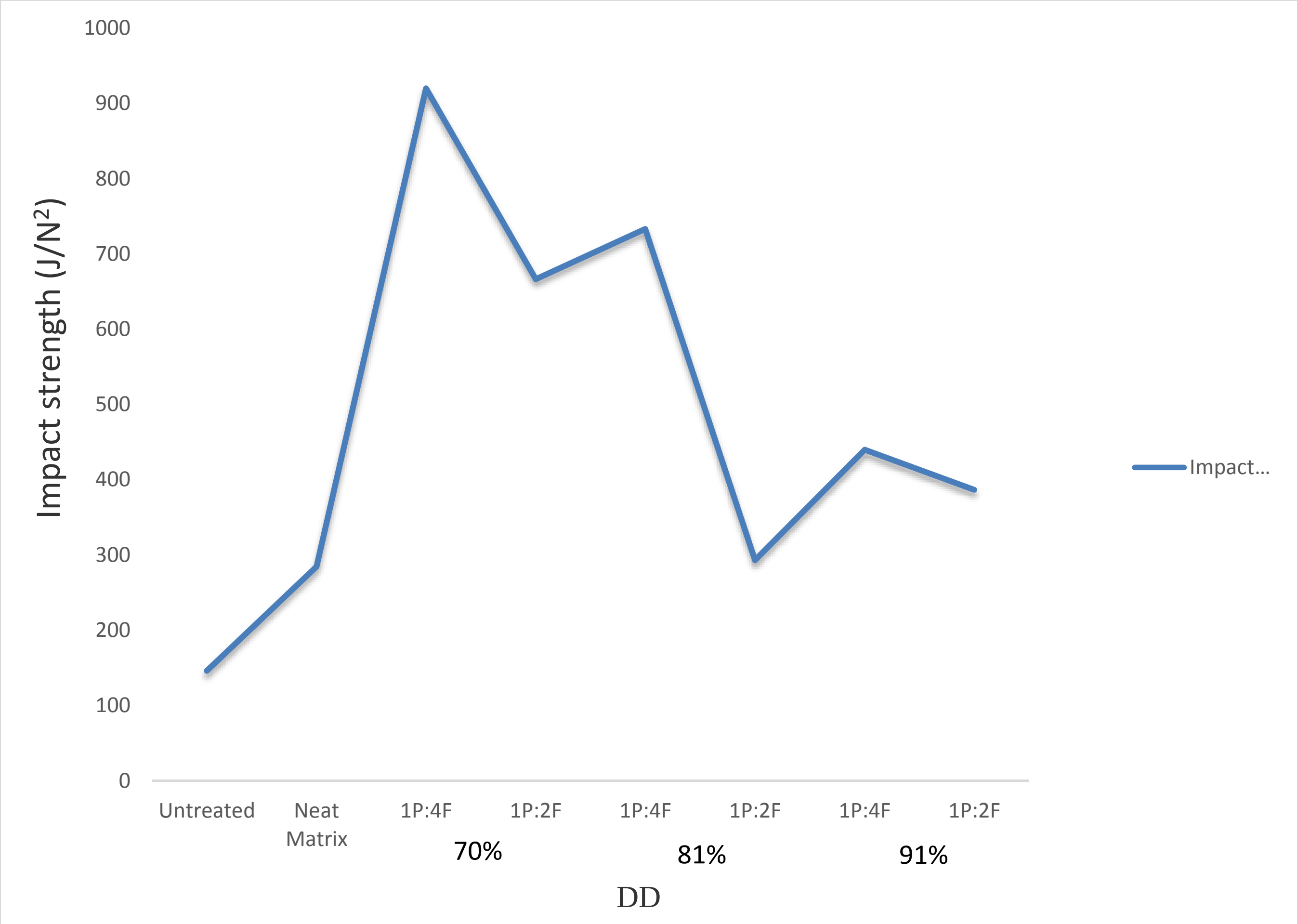


Figure 5.19: Impact strength of 1P:2F and 1P:4F at different DD %

Table 4.20 in appendix A and Figure 5.19 show the variation of values of DD% of chitosan/P: F composites with different filler loading, neat polymer and the untreated. Impact strength shows its highest value at 40 wt% filler loading of 1P:4F and 1P:2F mole ratio. The neat P: F sample shows very low impact strength of 284.44J/N^{2}and the untreated have 146.66JN^2. An enhancement in impact strength was observed by different percentage degree of deacetylation DD% From Table 4.19, the relationship between the average energy and impact strength of the composites was clearly shown. 1P:4F at 91% DD composite has the least impact strength (440.00J/N^2), which was followed by 1P:4F at 81% DD composite with impact of

($733.33 J/N^2$), and highest value of $920.00 J/N^2$ from 70% DD of 1P:4F. Similarly, 1P:2F composite shows similar trend in impact strength with little variation with the values as 666.66, 293.33 and $386.66 J/N^2$ for 70%, 81% and 91% DD. The increased filler content is improving its capability to absorb more energy. Similarly the work of (Elsine *et al.,* 2011) shows an increase in impact strength with an increase in filler content.

The lower DD%, (70 %) with the highest values is an indication and proved to have the highest impact strength. This can be attributed to the presence of strong fibre/matrix interface.

But at higher DD 81% and 91% fibre to fibre contact decreases and fibre breakage will be the predominant failure mechanism. The decrease in impact strength with the increase DD% is attributeed to the poor interfacial adhesion between the hydrophobic (PF) matrix and hydrophilic chitosan filler with void formation in the composite thereby reducing the toughness of the composites as reported by (Raje *et al.,* 2012). The inter filler interaction decreases the effective stress transfer between the fibre and matrix. This contributes to a decreased in impact properties at higher DD% (Ishaya and Josiah, 2014 ; Mohammad, 2012). The higher the alkali treatment, the higher was the DD and reduction of M.wt . ln addition to this, the removal of the acetyl group at high DD, resulted in reduction in polymer chain with more hydroxyl groups , thereby lowering the ability of the system to absorb energy during the fracture. The strength and efficiency were dependent on the degree of deacetylation and crosslinking. And also at high DD%, there is an increase of solubility of the material which is achieved by replacing with the primary amino group and react with carbonyl group of aldehyde (methylene group) from novolac resin and then hydrogenated.

From Table 4.20 in appendix A, the relationship between the average energy and impact strength of the composites was clearly shown. 1P:4F at 91% DD composite has the least impact strength ($440.00 J/N^2$), which was followed by 1P:4F at 81% DD composite with impact of ($733.33 J/N^2$), and highest value of 920.00J/N^2 from 70% DD of 1P:4F. Similarly, 1P:2F composite shows similar trend in impact strength with little variation with the values as 666.66, 293.33 and 386.66J/N^2 for 70%, 81% and 91% DD. The filler is improving its capability to absorb more energy. Similarly the work of (Elsine *et al.,* 2011) shows an increase in impact strength with an increase in filler content.

Therefore it can be concluded from the values in Table 4.20 in appendix A and Figure 5.19 that the relationship between DD percent and impact strength . Generally, increase in the degree of the deacetylation (DD%) of filler content from 70 to 91wt% DD caused the decrease of the impact energy, because of the reduction of cohesion's which exist between the chitosan and the polymer. This is due to the high removal of the acetyl group from the filler which brings strong crosslinking between the filler and the polymer and more hydroxyl group (Elvy *et al.,* 1995). The chemical treatment has reduced the crystallinity through the crosslinking reaction. The hydrogen bond between polymer chains from the two functional groups of $–NH_2$ and -OH was broken due to the mercerization at high level. Then, the amorphous region of the polymer was increased (Li *et al.*, 2007).

5.3.5.8 Hardness Testing

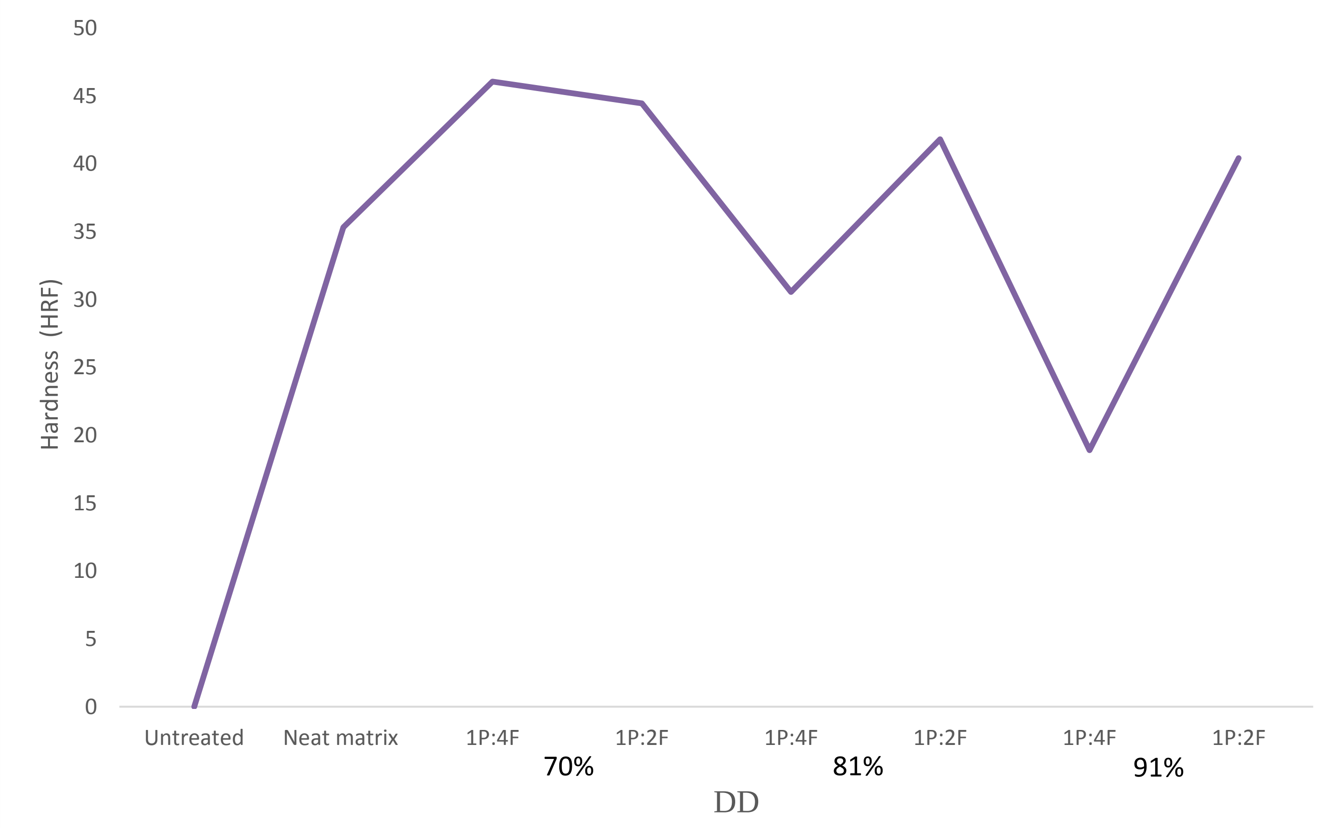


Figure 5.20: Hardness of 1P:2F and 1P:4F at different DD%

Hardness testing values were given in Table 4.20 in appendix A, it shows an average value and phenol formaldehyde itself is hard with a value 35.34 HRF scale and the untreated show brittleness. From the same Table 4.20 shows the average values of hardness of the composites of 40% filler loading of 1P:4F and 1P:2F ratios are shown. The hardness of 1P:4F and 1P:2F were found to be 46.07HRF/44.47HRF as the highest value at 70% DD, and 18.90HRF/40.43HRF as the least values at 91% DD. The hardness of the untreated is brittle. It was observed that hardness of the treated reinforced composite at different DD values decreases with the increase of DD percent. It was observed that the treated chitosan at different DD 70% to 91% values exhibited better hardness compared to the raw polymer (neat matrix) from 70% to 91% DD (Rahman *et al*, 2008). Furthermore, there was considerable improvement in the hardness for the treated P: F composites. This phenomenon could be attributed to the better adhesion of the polymer to the chitosan brought about by the chemical treatment (Elvy *et al.*, 1995).

The highest was observed at 70% DD 40% filler loading and raw polymer (neat matrix) with the values of 35.34HRF and 46.07HRF. This could be attributed of the good dispersion formed between the matrix and the filler besides the reducing of voids and stronger interfacial bonding between the fibre and matrix. The decreased in flexibility and increase of stiffness of the respective composites enhance the hardness properties as reported by other researcher (Rezaur *et al.,* 2010) Thus it is evident from the results that chitosan filler as reinforcement has improved the mechanical properties of the P-F composites. The better mechanical behavior could be accounted due to compatible filler-matrix interaction and orientation of the filler .However, some deviations in the results could be justified by other governing factors for overall mechanical performance like nature and amount of matrix and filler, orientation ,distribution of the filler with respect to the matrix axis, form of reinforcement used, strength of the interfacial bond between the filler and matrix, length of the fibre (continuous or discontinuous), aspect ratio that on mere imbalance may lead to debonding and cracking (Shashi 2002; Mishra *et al.,* 2003; Chauhan, 2009).

5.3.5.9 Effects of Degree of Deacetylation (DD) on the Emission of Formaldehyde

Results of emissions of formaldehyde with different DD% chitosan phenol formaldehyde composites is shown in Figure 5.21 and Table 4.21 in appendix A.To determine the effects of DD on formaldehyde emissions (FE) and the chemical performance of chitosan, three samples of chitosan composites at different DD% (70, 81,and 91) was conducted for the emissions tests. The measurements showed that the effects of DD were significant for all the three deacetylated derivatives. The results showed that emission was between 0.48mg/cm^3, 0.46 mg/cm^3, and 0.28

mg/cm^3 for 70, 81, and 91 DD%. This values are below limit values of formaldehyde emission standard for wood-based panels in Europe, Australia, U.S.A and the Japan (Europe EN 717-1, ≤ 0.1ppm chamber method; EN 120, ≤ 8mg/100g perforator method, EN 717-2 >3. 5 ≤ 8.0mg/h*m2 Gas analysis: Australia AS/NZS 4266 16, ≤ 0.5mg/L,≤ 1.5mg/L, ≤1.0mg/L,≤4.5mg/L Desiccator: U.S.A. ASTM E 1333 ≤ 0.3ppm, and ≤ 0.2ppm Large chamber : Japan JIS A 1480 F** ≤ 1.5 mg/L, F*** E0 ≤ 0.5 mg/L, F**** SE0 ≤ 0.3mg/L Desiccator). The results of the FE was also less than 4%, formaldehyde to ppm which is considered to be acceptable in industry (WHO, 2002) (a value of ≤0.1ppm EN13986, Chamber ENV 717-1).

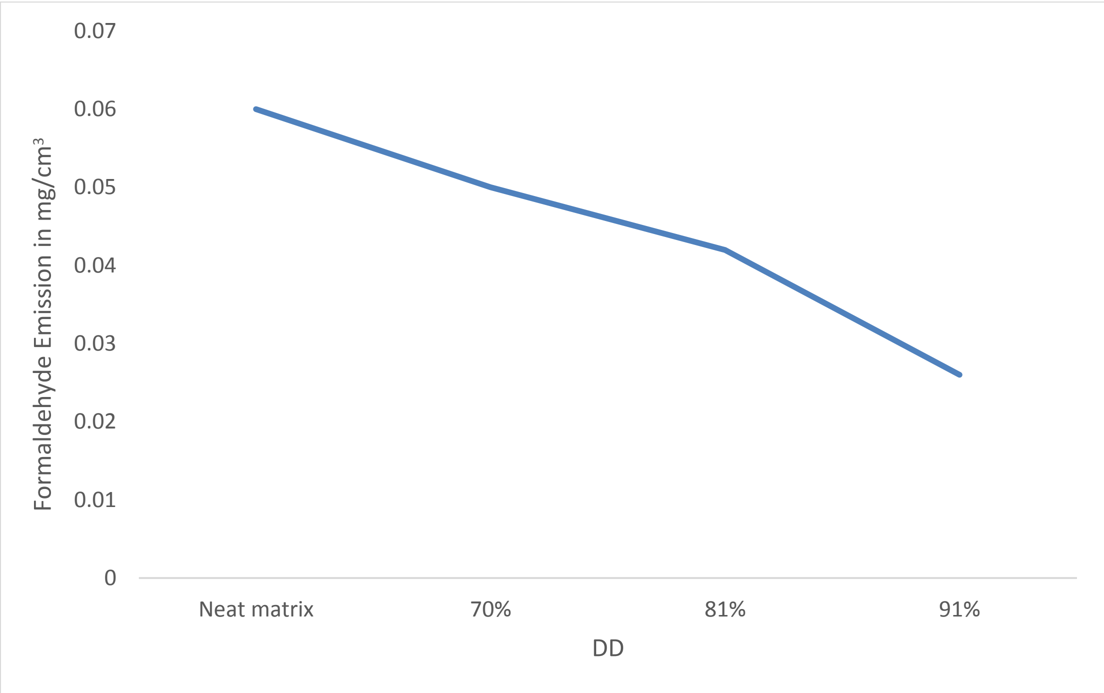


Figure 5.21: Effect of DD on Formaldehyde Emission

When compared to the standard the measurements of formaldehyde emission (FE) also showed that the effects of DD were significant for all the three deacetylated derivatives. Formaldehyde emissions from the three deacetylated chitosan phenol formaldehyde composites 70, 81 and 91% DD are well below acceptable exposure limits specified by WHO, IARC and do not constitute a health risk. At this extremely low level of emission of the deacetylated chitosan composites of 70, 81, and 91% DD of 0.48 mg/cm^3, 0.46 mg/cm^3 , and 0.28 mg/cm^3 of the formaldehyde measured has been emitted by the composites itself. This emission levels is 5 times less than naturally occurring background concentration of 0.003ppm and well below the most stringent Japanese regulation of 0.03ppm.

The degree of deacetylation (DD) is the ratio of glucosamine to N-acetylglucosamine units. The degree of deacetylation of commercial chitosan is controlled by modifying the time and temperature of the N-acetylation process. The lowest DD corresponding to chitosan varies in literature and ranges from 40% to 60% (Li *et al.*, 1997). Chitosan of the higher DD (>90) may be prepared via further deacetylation steps (Talaimatea *et al.*, 2003). DD of chitosan is generally controlled by processing of the native polymer with alkali, and with increasing time and temperature to obtain the highest DD (>90) materials (Kumar, 2000; Harish Prashanth *et al.*, 2002; Khor and Lim, 2003).

Chitin when deacetylated, the acetyl group are removed and more amino groups are exposed. Most applications of chitosan are based on the amino group of the micromolecule and its solubility. Different DD, result in different amounts of amino groups presented at the surface .Generally, after deacetylation, the content of free amino groups in chitosan molecules will increase, but chitosan molecules will be degraded at certain high temperatures. Therefore, the fraction of the amine groups is a key parameter to understand the mechanism and even the emission of formaldehyde and control the processing of the materials. Actually, it would be better to consider the number of accessible-free amine groups rather than the fraction or number of free amine groups available for these applications. The parameter responsible for these amine groups are the DD, Mw, and environmental parameters (ionic strength, pH, temperature, solvent etc). Dormards, (1987) studied on the chitosan different Mw and DD and proposed that the ionisable groups was dependent on the DD.

However, the present study showed the effect of DD on the Emissions of formaldehyde from the composite of chitosan phenol formaldehyde. Molecular weight (Mw) is a crucial factor in determining the physicochemical properties of chitosan. Mw has been shown to be an important factor in chitosan properties.The M w of chitosan is dependent on the initial source material (shrimp, crab, fungi, etc.) and can decrease with processing to increase DD (Tsaih and Chen, 2003).

Moreover, much of the previous published data had been reported on the DD or Mw of chitosan (Dormands, 1987; Talaimatea *et al.*, 2003; Khor and Kim 2003). But no available report for the effect of DD on Formaldehyde Emission. In turn, these properties effect the chitosan behavior and are important for the physicochemical tests. Therefore, this research aimed to evaluate the effect of DD on emission of formaldehyde from the chitosan phenol formaldehyde composites.

While chitosan materials are generally regarded as promising for composite applications, there are inconsistent and conflicting report regarding their emission performance in composites. Uncertainty in understanding their emission performance may be due to poor characterization of chitosan materials. The potential implementation of chitosan in composite can only be explore, if its utilized form is properly developed and prepared. It is very important for composite companies, which have to control different parameters influencing the physical properties of the manufacture materials offered for composite applications, and will help to accelerate their future applications. So, far only their influence or effect of the most important factors, such as the molecular weight, crystallinity, mechanical properties (tensile strength, modulus of elasticity, chain flexibility, etc.), and bonding properties, solubility and degradation are related to degree of deacetylation (DD). And they have been investigated in detail and summarized in some papers (Ogawa and Yui, 2003: Martino *et al*, 2005). No available literature information of the chemical activity of chitosan and phenol formaldehyde products. However, the present study showed the effect of DD on the Emissions of formaldehyde from the composite of chitosan phenol formaldehyde.

How DD of chitosan effects the properties of chitosan phenol formaldehyde composite, the formaldehyde emissions (FE) was measured at different DD% as shown in Table 4.21 in appendix A and Figure 5.21. As per expectation by varying the DD loading 70%, 81% and 91% composites the formaldehyde emission tests was found to vary. As Chitosan DD increased with increasing concentration of NaOH solutions and temperature and formaldehyde emissions of all the samples showed an decreasing trend. This might be attributed to the presence of free amine groups in the chitosan to cross-link with all the abundant hydroxyl groups on phenolic resins to form strong intra- and intermolecular hydrogen bonds with amino groups. This resulted in the formation of the compactness of the composite samples as the DD increased hence the emission of formaldehyde decrease from 70% to 91% DD. .

Again the miscibility and compatibility of chitosan and phenol formaldehyde resin are dependent on the ability of the mixing polymer to form a hydrogen bonding interaction (Flory, 1953; Boyd and Philips, 1993). It is expected that the intensity of the hydrogen bonding and steric effect of acetyl group would be the determinant for compatibility and miscibility between chitosan and polyamides. Chitin can form different types of hydrogen bonds with other chitin molecules (Gonzalez *et al.*, 2000). Firstly, interaction can occur between two hydroxyl groups (OH---OH): secondly, some interactions may happen between hydrogen in the amide group with oxygen in the hydroxyl group (NH—OH): and lastly, a strong interaction between the heteroatoms and the carbonyl of the amide (C=O---HO and C=O---HN) can be formed. The ability of two chitosan polymers to interact between carbonyl groups within chitosan molecules themselves is quite low.

This may be due to the deacetylation process, which removes the carbonyl group (C=O). Blending chitosan with the polymers results in negligible probability of formation of hydrogen bonds of chitosan with other chitosan molecules. In this work, the emission of formaldehyde with different Mw and DD% were demonstrated by the WKI flask method (E 717-3). The formaldehyde emission of the chitosan phenol formaldehyde composites decreasing from 0.48 mg/cm^3 to 0.28 mg/cm^3, when the Mw and DD changing from 70 DD% to 91 DD%. The DD influenced the balance of hydrophilic interactions and hydrogen bonding on chitosan. Because at high DD chitosan has more $-NH_2$ groups to react with formaldehyde in the same molar ratio hence have less emission. This statement agreed with the (Sumin Kim *et al.*, 2007) in comparison of urea with melamine on the NH_2 group to react with formaldehyde that MF has less emission than UF resin. There is a mass reduction in all the three samples when compare with the standard. Although the formaldehyde emission varied slightly across the three DD species, the tendency for reduced formaldehyde emission was similar for all the DD samples.

Jaworska *et al.*, (2003) reported that chitin was much more crystalline than deacetylated materials. The degree of crystallinity depends on the deacetylated degree of the chitosan. The higher the DD, the higher the degree of crystallinity (Dunn, *et al.*, 1997). This may be attributed to the fact that chains of chitosan with the high DD are more flexible and have fewer large acetyl side groups. These are consistent with the results of the present study. It was reported from the (Youling Yuan *et al*, 2011) that processing conditions used to alter DD effects many physiochemical properties of chitosan. Changing the DD of chitosan also change other important properties such as Mw and crystallinity and solubility. Tsaih and Chen, (2003) used a 50% NaOH solution to deacetylate chitin at 90°C or 140°C for 1 to 9 h. their results showed that the DD of the resulting chitosan increased along with reaction time and /or reaction temperature while Mw decreased. Mw of those chitosan reacted at 140^{o}C were smaller than those at 99^{o}C. Cao *et al.*, (2005) also reported the Mw of those chitosan decreased 48.8% after one hour reaction with 40% NaOH at 100^{o}C. In this work DD samples showed increase of crystallinity from 91% to 70% DD, the tensile strength and elastic modulus increased with the increase in DD. And , hence the emission reduced as stated by (Youling -Yuan *et al.*, 2011) that highly crystalline material with much compactness emit less and less crystalline material and less compact material emit high emissions.

The characteristics of DD, molecular weight, hydrophilicity, residual ash and solubility also influence formaldehyde emission responses. The crystallinity of the starting chitosan powders ranged from 66 to 78%, but did not correlate with the DD or molecular weight of the materials (Khor, 2011). This was expected, since crystallinity is generally reported to increase with DD. This is because removal of acetyl side groups to increase DD allows for tighter packing of biopolymer chains than chains with high fractions of acetyl side groups and low DD (Nunthanid *et al*, 2001). Additionally, molecular weight of chitosan is generally reported to decrease with increasing DD, due to increased processing times and removal of the acetyl group from the chain of chitin (Khor, 2011). However, both of these relationships may be may be more typical for chitosan material prepared from the same initial batch.

Emittable potential is evaluated by the flask method (E 717-3), whereas actually emitted formaldehyde are evaluated by several methods: chamber method (717-1, ASM E 1333 or ASTM D 6007), gas analysis (EN 717-2) and desiccator method (JIS A 1460).

Many authors have tried to compare the FE or establish correlations between methods (Que and Furuno 2007; Risholm-Sundmann *et al.,* 2007; Salem *et al.,* (2011; Park *et al.,* 2011), but the relations are influenced by other variables, such as resin type, type of wood-base composites, thickness or manufacturing conditions. Salem *et al.*, (2011) and Kim and Kim (2005) studied formaldehyde emission from different types of formaldehyde-based resins. Salem *et al.*, (2011) showed that the manufacturing variable interfere significantly with formaldehyde emissions, and correlations between methods to assess different products were not possible. Sundin *et al*, (1987) compared four different methods of testing the FE of particleboards, and found good relationships between the methods with correlation coefficients greater than 0.9. Risholm-Sundman *et al.*, (2007) reported that the variations between the measured results were due to the specific differences in test conditions. Bulian *et al.*, (2003) also reported that the lack certified reference material made it difficult to establish an inter-calibration between test methods.

In the past, there was a link between the two terms "formaldehyde emission" and "wood-based products". Formaldehyde emission are from particle board and other wood-based materials have decreased as a consequence of government and voluntary guidelines and regulations. Wood-based bonded with P: F adhesives show comparatively low formaldehyde emission potentials because the cross-linking is more stable. Furthermore, environmentally friendly adhesives using tanning have been developed to reduce the dependence on formaldehyde-based adhesives (Pizzi 1994; Roffael, 2000; Kim *et al.*, 2009).

Most of the research conducted on the emission of formaldehyde in the composite materials is from the wood-based composites, particularly of UF, and MF. Formaldehyde release from incompletely cure, urea-formaldehyde resin bonded, wood-based panels, such as particleboard (PB) and medium density fibreboard (MDB), is well established, potential cause of indoor air contamination Meyer (1986). Emission of formaldehyde from wood-based panels into the air of buildings constructed with these products has been a concern of industry and environmental scientists for several years Brown, (1999). Sumin Kim *et al.*, (2006), studied the effect of formaldehyde emission and bonding properties of melamine-formaldehyde (MF) resins. MF resin gives excellent adhesive performance good moisture resistance, and tends to give lower formaldehyde emission than UF resin (Graldine *et al.*, 2000).

The test conditions and properties of wood composite used to measure the formaldehyde emission with various test methods were studied by (Salem and Bohm, 2013). Salem *et al.*, (2011) reported that by increasing the temperature from 25.2 to 50.6 ^{o}C, the initial emittable formaldehyde from the building materials was increased significantly, by about 50.7%. This means that most of the formaldehyde in building materials cannot be emitted at room temperature; the EN 120 uses temperature around 110^{o}C, and the EN 717-2 method uses temperatures of 60^{o}C (Salem *et al.*, 2012), a high initial concentration of formaldehyde emission (FE) was found and it decreased with time. The referenced chambers (EN 717-1, and ASTM D 6007-02) use conditions common to an indoor environment (Salem *et al.*, 2011). Wood itself generates a significant amount of formaldehyde when expose to certain conditions common to the composite panel manufacturing process that is caused by the thermal degradation of polysaccharides in the wood.

Mohsen Saffari *et al.*, (2010) have reported the study of effects of hardener type and particles size on physical and mechanical properties and formaldehyde emission of UF bonded particleboard. Formaldehyde emission was measured by WKI method (flask method), using acetyl acetone and photometric method (according revised standard EN120). According the results, formaldehyde emission of particleboards made of Ammonium Chloride was less than particleboards made of Magnesium Chloride significantly, but formaldehyde emission of particleboards made of Ammonium Sulfate had no difference with formaldehyde emission of particleboards made of Ammonium Chloride. Particle size had no effect on formaldehyde emission of boards.

Young *et al.,* (2005) studied a comparison of formaldehyde emission of wood-based panels with different adhesives-hardener using a desiccator and perforator methods (JIS A 1460) and the EN 120. The formaldehyde emission behavior of the MF and UF resin showed a desiccator value of 7.1mg/L and a perforator value of 12.1 mg/100 g panel but the MF resin exhibited a desiccator value of 0.6mg/L and a perforator value of 2.9 mg/100 g panel. The formaldehyde emission level of the medium density fibreboards made with the UF resin came under E_2 grade. The formaldehyde emission behavior was drastically reduced by the addition of MF resin.

The effects of edge sealing treatment applied to wood-based composites on formaldehyde emission by desiccator test method by was studied by (Sumin-Kim *et al.,* 2006). Formaldehyde emissions were measured using (JIS A 1469) method for particleboard (PB) and medium density fibreboard (MDF) as a furniture materials. They found that the reduction rate of formaldehyde emission from PB than in MDB was 50-80% for flooring materials and about 30% for furniture materials. The greater core porosity in PB than in MDB may have caused large reduction of formaldehyde emission from the edge seal samples. The amount of formaldehyde emitted from the edge was significantly higher in PB than in MDB.

As stated by APA (2004), the engineered wood association that structural plywood and oriented strand board panel manufactured in accordance with Voluntary Product Standards PS 1 and PS 2 easily meet or are exempted from the world's most stringent formaldehyde emissions standards. This formaldehyde regulation for wood panels is widely considered the most stringent in the world.

Some confusion was cast on the question of formaldehyde and batt insulation by a study done conducted by the California Department of Health Services (DHS) for the California Integrated Waste Management Board in 2003, which while not identifying individual products, appeared to indicate that formaldehyde free insulation products may also emit formaldehyde in excess of section 01350, (2006) limits. DHS has since indicate that the study should not be used to identify individual products for selection and the state continues to recommend the avoidance of products with added formaldehyde CARB, (2004). Subsequently testing of batt products with no added formaldehyde has repeatedly shown passage of the 01350 test (John , 2008) and have shown no detectable emissions of formaldehyde.

Currently, North America consumes approximately 3 billion pounds of UF-based resin annually. There is not enough existing resin manufacturing especially among the preferred no added –formaldehyde [NAF] sources, to replace this volume. Even converting existing UF manufacture the performance-equivalent replacement amount of PF production would be highly unlikely in the timeframe allowed under the proposed regulation order.

A U.S. federal law, the formaldehyde standards for composite wood product, Act, mirrors the CARB standard in 2013. Again, composite wood products regulated by this law do not include structural wood products. Phenol-formaldehyde is classified as ‘’ ultra-low formaldehyde emitting resins’’ within this law. U.S. Government agencies have generally concluded that phenolic resin-bonded wood products do not cause significant formaldehyde-related problems. Moreover, in a recent joint publication by the U.S. Consumer Product Safety Commission and the U.S. Environmental Protection Agency, (1995), it is stated, “ Even if you do not experience such [adverse] reaction to formaldehyde, you may wish to reduce your exposure as much as possible by purchasing exterior grade products, which emit less formaldehyde.” Thus, these governmental agencies endorse the use of phenolic resin-bonded wood products in buildings where low levels of formaldehyde are desired.

World health Organization, (2004) advisory body—International Agency for Research on Cancer—IARC proposes to reclassify formaldehyde. IARC proposal contains serious contradictions but initiates worldwide discussions about formaldehyde. The formaldehyde reclassification remains open. Pressure on politics, authorities and industry will trigger reevaluation of exposure levels and emission classes. The methodology for estimating emissions is continually reviewed and is subject to change to revision. Discussions on a new emission class are currently under way in Europe.

Modern technology also opens up possibilities for new measurement techniques, especially sensors. At present time, detection limits are inadequate, but it is foreseeable that the next generation of sensors may be suitable for many applications in active and passive formaldehyde measurement. Nanoscience and nanotechnology have numerous advantages for composite materials. The use of nanotechnology in the manufacture of composite materials is of great importance to overcome the formaldehyde emission issue (Ciraci 2005; Candan 2012).

Free phenol is not available in the composites, but their widespread application is found as phenolic compounds. Phenolic compounds are present in the environment as a result of their uses and the processes in which are implemented. They are gaining great popularity due to their widespread application to produce polymeric materials, dyes, paper, pesticides and petrochemical products etc. Due to its toxicity, they could have significant detrimental effects on water quality or animals as well as some plants even at low level. The European Community (EC) specifies a legal tolerance level of 0.5µg/L for each phenol in water intended for human consumption and Japan’s Ministry of Health, Labour, and Welfare specifies a maximum contaminant level of 5µg/L for phenols in drinking water (Ljompart, 2002).

Our commercial chitin/chitosan materials exhibit a wide range of properties, such as DD, molecular weight, crystallinity, and solubility and there is not necessarily any correlation between these characteristics and with the properties of the chitosan composites prepared in this work. All chitosan composites used in this study were prepared at the same laboratory conditions and procedures. There was no relationship found between the normal chitin (commercial chitin) characteristics and the properties of the chitosan composites. The lack of correlation may have been limited to the fact that when chitosan is deacetylated its physio-chemical property changed entirely. Data do indicate that there is much variability in the effect of FE on DD and that this variation may make to understand the principal behind it. Hence, detailed and systematic characterization of chitosan composites is needed to understand and optimize their emission performance for consistency and reproducible outcomes.

5.3.5.10 Effect of Chitosan in the Reduction of Formaldehyde Release in the Production of Chitosan /Phenol formaldehyde Composites.

WHO, (2002) pointed out that industrial formaldehyde releases can occur at any stage of the production, use, storage, transportion, or disposal of products . Emissions have been detected from chemical manufacturing plants, pulp and papers, coating processing plant, automobile manufacturing plant and metal product industry. The avoidance of formadehyde-containing materials would no doubt constitute the best polycys but most of these materials are inexpensive and have a high performance rating. Because complete elimination of these materials is not a practical solution, several studies have reported on the coating, barriers, and chemical treatments. Chemicals such as urea, polyurethane, ammonium sulfite, and sulfur compounds of sodium have been tried as an after treatment of plywood comosites. It is difficult to determine the global emission of formaldehyde completely (Wang *et al.*, 2008).

Efforts have been made to modify the chemical formular of resins to reduce formaldehyde emissions. Many manufacturers of wood product composites are working in this area. Thus much research attention has focused on reducing or controlling the formaldehyde emission from composites. In this research work using chitosan a natural polysacharide with abundant amino and hydroxyl functional groups in making chitosan/phenolformaldehyde composites it tried to solve this problem of formaldehyde emission. The prepared composite led to drastic reduction in the emission level.

5.3.5.10.1 Mechanism Reaction of Chitosan and Novolac Resin

Chitosan undergoes the reaction typically of amines, of which N-acylation and Schiff reactions are the most important. The presence of readily functionalized hydroxyl and amino groups on the chitosan and insolubilty in organic solvents make it very attractive in the application (Rout, 2001). These groups can introduce new moieties that can effectively interlock with matrix-surface characteristies such as wetting, adhesion, surface tension, porosity etc. In this work, the interaction of chitosan with P/F novolac resin is excellent due to the hydrophobic nature polyamide group chitosan and the methylol of PF resin. Thi is shown schemitacally in steps (a), (b) and (c) Figure 5.22.

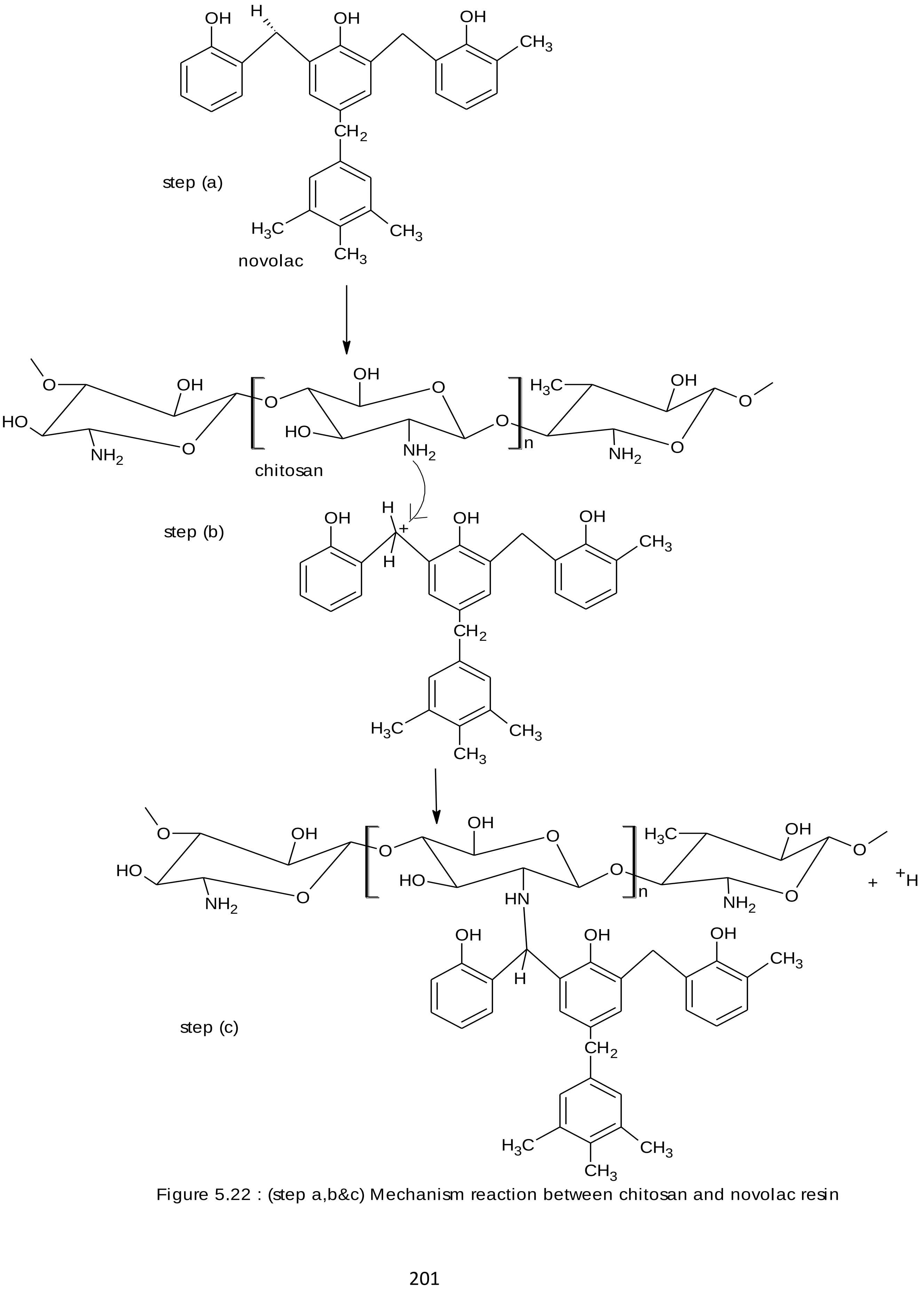
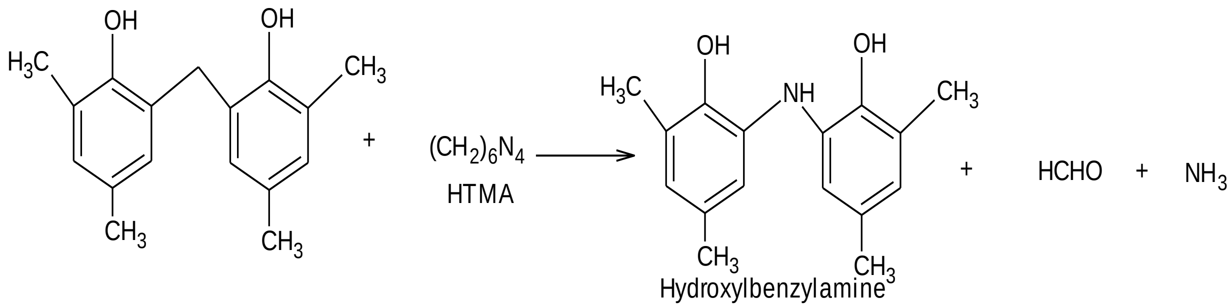


Figure 5.22 : (step a,b&c) Mechanism reaction between chitosan and novolac resin

In Figure 5.22 active methylene group from novolac resin (a) is hydrogenated by the reaction in step (b), have a hydrogen atom covalently bonded to a saturated carbon atom. This saturated carbon atom is further covalently bonded to two electron-withdrawing molecule amide group ($-NH_2$) of the chitosan in step (c) . It forms carbonium ion which is used in the reaction and are continuously formed to cap the free formaldehyde generated (Sharp and Dimano 1998 ; Prajakta and Prashant 2015).

Novolac are mixtures of isomeric polynuclear phenols of various chain length, which promote condensation reactions of methylol groups.Thus, the prepolymers produced contain no methylol groups and are unable to crosslink. And consequently cross-link and harden to form infusible and insoluble resins only when mixed with the compound such as HMTA or hexa that can release formaldehye methylene bridges (Young and Lovell 1991; Pizzi 2003). It was stated that high content of methylol groups in PF resins gives favourable conditions for reaction (Simer *et al.*, 2007). The incorporation of HMTA as curing agent was employed to facilitate crosslinking reaction and to enhance mechanical strength and toughness. However, curing reactions employing HMTA produced several volatile side-products including ammonia gas Figure 2.23.

In the production of these composites the curing agent used is heaxamethalenetetriammine (HMTA). Curing under normal temperature, this agent has such advantages as quick curing preparation of stable curing structure, absence of water discharge during curing and good electrical performance of workplaces. Fast-reacting phenolic novolacs have been found to harden with HMTA via the formation of majority of stable benzylamine bridges Figure 2.9 rather than methylene bridges.



Hydroxylbenzylamine

(Majority)

Figure 5.23: Reaction of Novolac and HMTA decomposition above 100oC

This process entails the minimal decomposition of HMTA to formaldehyde and hence much reduced formaldehyde emission from the hardened resin and products bonded with it (Pizzi 1994; Pizzi and Tekely 1994; Pizzi *et al.*, 1996; Kim *et al.*, 2003). As reported by Liu Weili, (2015) HMTA decomposes into dimethyl carbinol and formaldehyde once its temperature exceeds100^{o}C, whch enables a crosslinking reaction with phenolic resin as shown in Figure 5.23.

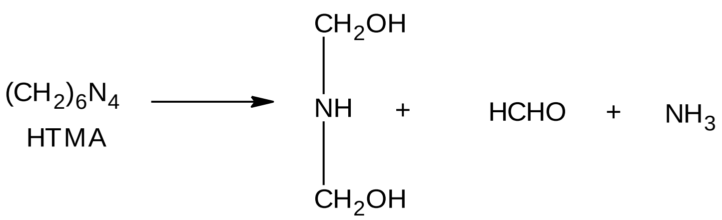


Figure 5.24: HMTA decomposition above 100oC

Because this fast reactivity leads to a poor reaction occurrence, resin and hardener are not able to be cross-linked, which leads to auto condensation taking place in the system. Consequently, unreacted formaldehyde is emitted, thus giving rise to formaldehyde release for the cured composite. Although the pure chitosan/phenolformaldehyde composite with hexamine as hardener showed a low formaldehyde emission 70% and 91% DD with a values of 0.48mg/cm^3 and 0.21mg/cm^3. The least emission was observed at high DD 91% due to large number of amino groups.The reason would be due to the curing mechanism of the hardener and reactivity of chitosan molecule toward formaldehyde as shown below in Figure 5.24. Chemical crosslinking of chitosan is the most straight forwad approach to fabricate, due to the formation of covalent bonds between micromolecular chains.

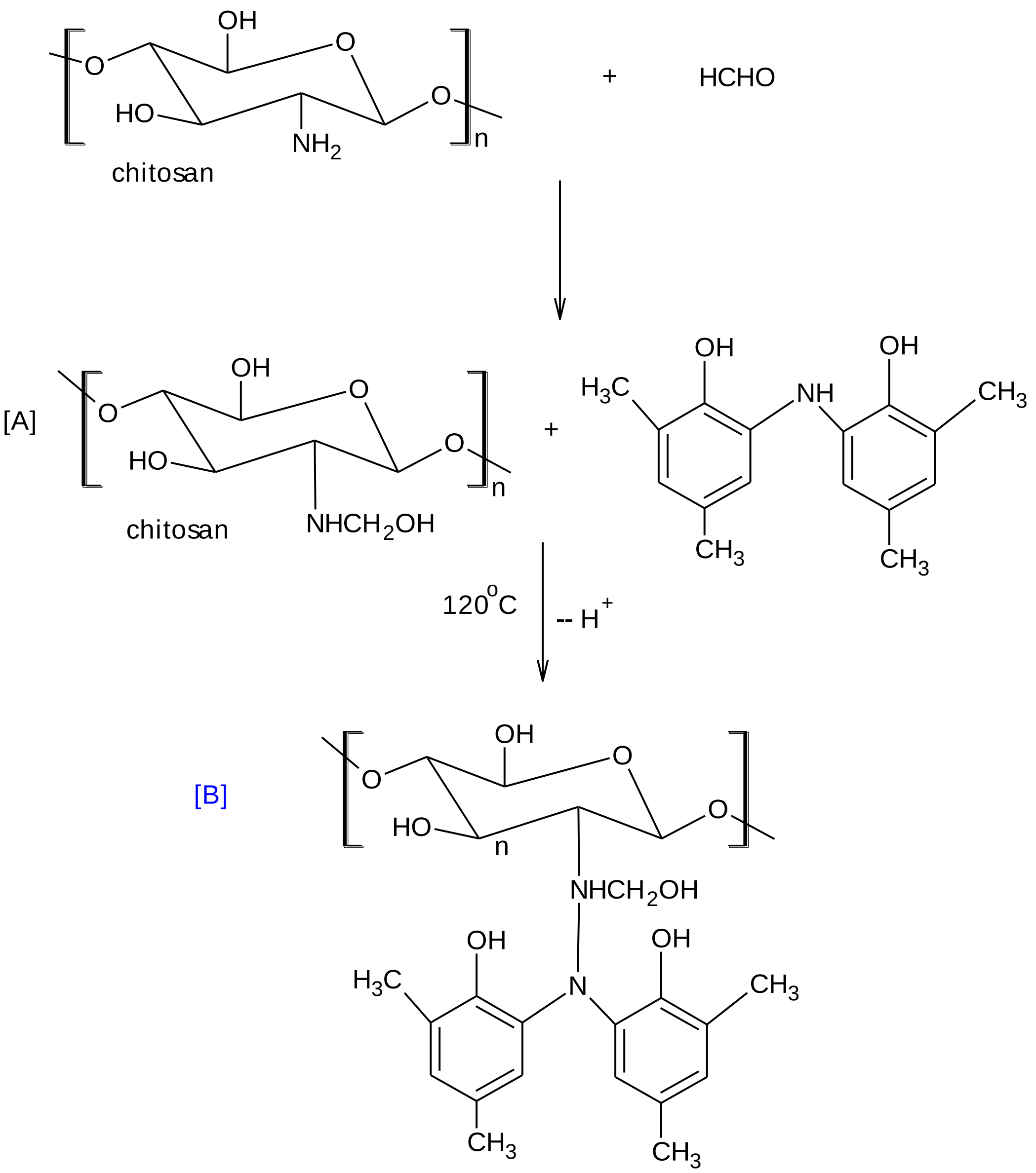


Figure 5.25: Reaction of amino group of chitosan with residual formaldehyde

Chitosan/phenolformaldehyde composite were prepared by a two-stage reaction (A & B) Figure 5.25. The first stage (A) involves the reaction of amino group of the chitosan and with the residual formaldehyde and the free formaldehyde emitted from the compound to form methylol chitosan. In the final stage curing process transforms intermediate to the desired P/Fchitosan composite through, the reaction of acid conditions at elevated temperature, where condensation or crossliking takes place with each other by the reaction between methylol chitosan (-$NHCH_2OH$) and the hydroxylbenzylamine (novolac) resin Figure 5.25. As used herein, the amino group from the chitosan was used as formaldehyde scarvengers or acceptors. The amino group from the chitosan served as capping to the pendant methylol groups and preventing the formation of free formadehyde (Smith, 1992). Another recent approach which is similar to this one, is the addition of acetyls and acetylization reactions. It is based on the addition to the resin of certain additives capable of decreasing the percentage of any PF resin needed for bonding while still conserving the same adhesive and joint performance. These additives are acetyls (Pizzi, 2003), methylal and ethylal being the two most suitable due their cost to performance ratio. These do not release formaldehyde at pHs higher than one (pH > 1), (Liu , 2015).

The chitosan scarvengers are capable of reducing the formadehyde concentration of the composition or preventing formaldehyde formation in a composition as used in Figure 5.25. Further attempts have been made to reduce formaldehyde and ammonia emissions in addition to the use of nitrogeneous formaldehyde scarvengers. This agreed with U.S Patent No 5,340,868 where the traditional P/F binders are replaced in a whole by a binder containing a polycarboxy polymer, a β – hydroxyalkylamide, and a trifunctional monomeric carboxylic acid. The most common nitrogenous scarvengers are melamine, dicyandiamide, and urea. However, such conventional formaldehyde scarvengers containing ammonium compound donot always provide suffient formadehyde scarvenging performance U.S Patent 2011. Unless methods may be found to sharply cutail both formaldehyde and ammonia emissions, continued commercial visibility of P/F base binders is questionable. Moreover, wholesale substitution of other resin systems, thus far, proved to be too costly, or to produce a cured binder with inadequate properties.

It was reported by (Bough, 1978), the scarvenging abilities of different extracted chitosan samples on 1.1-dephenyl-2-pic-crylhyrazyl DPPH radicals were increased with their concentration increased. The scarvenging abilities of chitosan at particle size 20 and 60 mesh increased with increasing concentration of NaOH solution used in N-acetylation, as the values were in the range of 52.81 to 74.08% and 53.79 to 90.48 % at 10mg/ml, respectively. It seems that scavenging abilities of chitosan increased with increasing the degree of deacetyalation DD. These results (statement) agreed with (Yen *et al.*, 2008). On the contrary, about the scarvenging ability of chitosan samples at particles size 40 mesh, it could be noticed that its values were higher for samples deacetylated wih NaOH solution at concentration of 30%, where it was 80.69% at concentration of 10mg chitosan/ml. These results may be due to its higher solubility at high DD and had more amino groups on C_2.scarvengers can reduce formaldehyde emissions by 2 to 10 times, but cannot eliminate it completely. Significant quality control is required in manufacturing to maintain these reductions in mass production of the finished product.

5.3.6.0 X-ray Diffraction (XRD)

The crystal structure of polyamide results from the conformation of the macromolecules and their lateral packing. Generally, the packing of polymer chains will be such that the occupied volume is at a minimum, thereby minimizing the potential energy of the structure, but maintaining appropriate distances for intermocular forces between adjacent chain segments. In polyamides, these intermocular forces are both Van der Waal's bonds and hydrogen arrangements between adjacent chains. The stacking of these hydrogen-bonded sheets controls the size and shape of the polyamide molecules (Li *et al.*, 2007).

5.3.6.1 Degree of deacetylation (DD) and X-ray diffraction (XRD)

It is well known that the crystalline structure of chitin influences its properties including its susceptibility to hydrolysis and deacetylation yield. The occurance of crystallinity improvement for the prolonged deacetylation of biopolymer was also confirmed in the literature (Kurita and Sannan 1992; Roberts, 1992).

Chitin from Shrimp have the low DD, high crystallinity index (C I), and prolonged process of deacetylation for obtaining the soluble chitosan. Chitosan samples with DD lower than 75% have a more-ordered structure, however C I decreased gradually with further increase in DD. Long deacetylation time, giving chitosan with DD higher than 92%, resulted again in higher C I, though the lattice angle $2\theta \approx 9.8^o$ and 19.4^o (chitin Mw). This fact suggests that crystallinity diffraction pattern of these chitosan increase for the chain segments that already exist in more ordered region of chitin, which are therefore susceptible to deacetylation only at longer reaction times (Roberts, 1992).

5.3.6.2 Effect of DD on Crystallinity (Cr)

Wide angle x-ray analysis (XRD) was carried out to investigate the effectiveness of the resin interaction or exfoliation and if any change in the crystalline structure of the composite has occurred (Res, 2000).

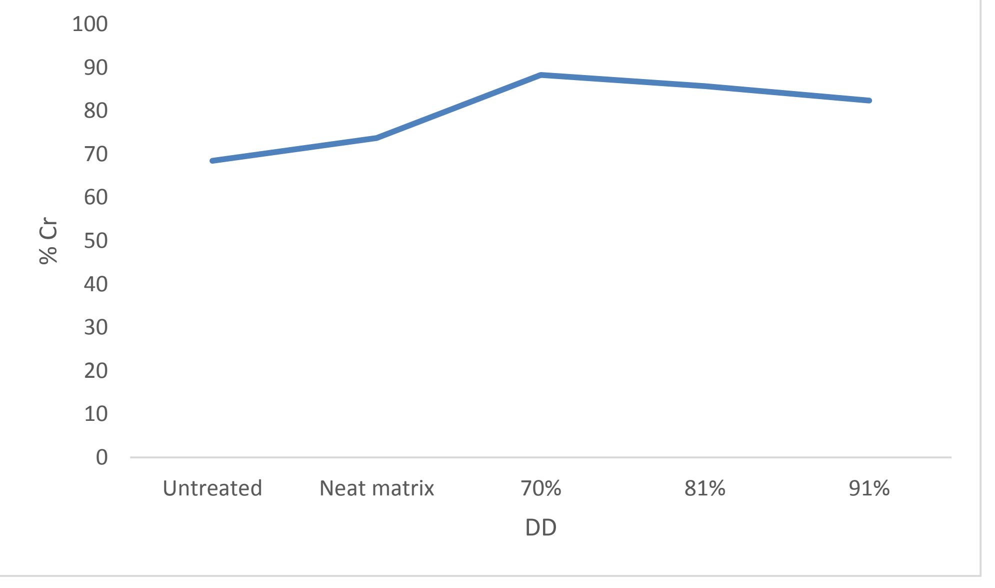


Figure 5.26: Effect of DD on percentage crystallinity (%Cr)

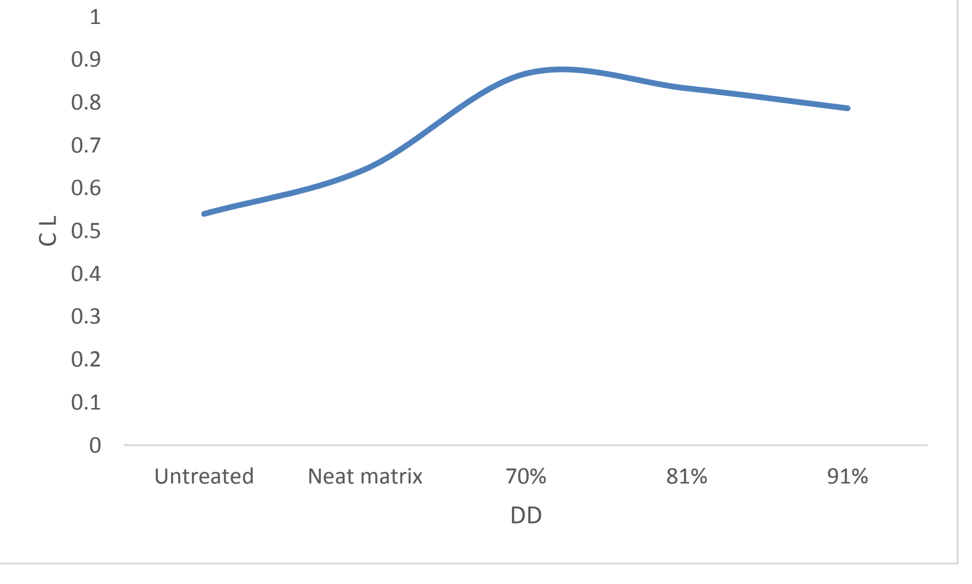


Figure 5.27: Effect of DD on crystallinity index (C I)

Figure 4.7 and Figure 4.8 had shown the X- ray of chitin alone and untreated samples, while Figure 4.9 to 4.11 displayed the X-ray diffraction of 70%, 81% and 91% DD samples. And Table 4.20 gave the values of %Cr and C I. To understand clearly the crystallinity and crystallinity index of our samples Figure 5.26 and 5.27 also displayed the %Cr and C I. It was evident from Figure 4.7, 4.8 to Figure 4.11 and Table 4.21 in appendix A that the curing process for all the deacetylated composites (70 to 91% DD) decreases the degree of crystallinity (%Cr) and crystallinity index (C.I.) parameters when compared with the polymer alone (neat mstrix) and untreated chitin. In case of the neat matrix and the untreated the one without alkali treatment the %Cr and C.I. are lower with the values of 73.76% Cr and 0.6442 C.I.

And with the incorporation of the filler into the polymer the crystallinity increases with the decrease in DD%. The least values of 82.42% Cr and 0.7867 C.I was observed for 1P:4F at 91% DD. At 81% DD the %Cr and C.I have increased to 85.71 and 0.8333. The highest values waas observed for 70% DD with values of 88.31% Cr and 0.8676 C I. The higher the DD, the lower the %Cr and C I. Crystallinity of polymer describes the arrangement of polymer chains in a neat orderly manner, while if there is no order, and the polymer chains just form a big tangled mess, we say the polymer is amorphous. So XRD analysis will help to investigate the differences. The crystallinity index gives a quantitative measure of the orientation of the polymer in the filler. A lower crystallinity index in case of untreated (0.5401) composite means poor order of the arrangement of polymer crystals in the filler, which is due to dis – orientation of the polymer crystalline lattice to the filler cross – linking.

In Figure 4.4, matrix (alone) showed highly crystalline behavior at an angle of 10 - 24^0. From Figure 4.11 to 4.13 (91%, 81% and 70% DD), it can be seen that the polymer peak was sharpened with the increase of the degree of deacetylation (DD%). It was observed that the increase of DD of the fibre at high concentration, caused positive effect on crystallization and especially at the higher ratio of DD. Different crystalline structures emerged such as derivatives of DD values of 91%, 81%, 70%. The Figures 4.11 to 4.9 also depict that abroad doublelet peaks which occurs in Figure 4.7 fibre alone and Figure 4.8 untreated have disappeared. When the resin is almost completely dispersed, the peak didn't appear in Figure 4.11 to 4.9.

In the higher DD values such as 91%, 81%, 70% the intensity of polymer peak increase and smaller peaks disappears as parallel to the decrease of the deacetylated group in the chitosan material. This increase in the signal intensity is probably due to the formation of the crystal structure of chitosan material interactions between chitosan and the polymer matrix (Rivero, 2005). As observed in the Figures 4.11 to 4.9 for 91%. 81%, 70% DD composites showed crystalline structures. While P: F resin alone and the untreated fibre composite crystalline structure showed amorphous structures. After adding chitosan to the resins, their crystalline structures deformed due to the formation of exfoliated – interacted structures in the polymeric matrix (Ashish and Balbir, 2012).

From the literature, the XRD pattern of chitosan exhibits broad diffraction peaks at $2\theta \approx 10^o$ and 21^o which are typical fingerprints of semi-crystalline chitosan (Banyekan and Srikulkit, 2006). Yen and Mau, (2007) found that fungal chitosan showed two crystalline reflections at 9.7^o and 19.9^o. Prashanth *et al*, 2002 found that the WAXD patterns of the shrimp chitosan showed two major peaks at $2\theta \approx 9$, 9 to 10.7^o and 19.8 to 20.7^o.this value had tallied with what we got from our XDR. In Figure 4.9, and the peaks at, 9 to 10.7^o and 19.8 to 20.7^o respectively. It is also reported by (Ming. *et al.*, 2009), the two characteristic crystalline peaks with slightly fluctuated diffraction angles found in the WAXD paterns indicated that two types of α- and γ-chitosans exhibited comparable degree of crystallinity and had two consistent peaks of 9 to 10^o and 19 to 20^o.

5.3.7.0 Scanning Elecron Microscopy (SEM)

Figure 4.12 to 4.15 (A – T). This indicates that semicryetalline polyamide become encapsulated in amorphous chitosan and insected in the continuous phase of chitosan amorphous polyamide. By using the scanning electron microscopy (SEM) technique, the morpholpogy exhibited phase segregation at high acetyl group contents. SEM micrographs of the samples show the morphology of the polymer composites prepared.

5.3.7.1 Changes in Morphology during Deacetylation

It is noted Kurita and Sannan, (1992) that deacetylation, process carried out under heterogeneous conditions favourably degraded the lesser ordered area of chitosan with deacetylation not higher than 70%, keeping the crystallinity structure characteristic of chitin. For the range of chitosan DD from 70% to 90%, the crystallinity structure is not detected. However, relatively low number of N-acetylaglucosamine units (G/cNAc) in chitosan with the DD higher than 90% caused the higher chitosan crystallinity.

The treatment by sodium hydroxide of first affected the destruction of amorphous regions and then proceeded from the surface to the centre of the crystallinity region, thereby resulting in an increase in bloc-type copolymers of GlcNAc and GlcN segments. This fact suggest that the crystallinity of chitosan deacetylated long time arise from those chain segments originally present in the crystalline region of the chain and which are only deacetylated in the later stages of treatment. SEM migroghs gave evidence that, by increasing the DD of chitosan/phenol formaldehyde composites (70% to 91%DD) higher compability of the compound was achieved. This may be due to strong hydrogen bonding between molecules and acetyl contents in the chitosan polymers. According to (Gonzallez *et al.*, 2000) acetyl contents influences the degree of compatibility and miscibility due to steric impediment presented by the acetyl group, affecting the formation of hydrogen bonding. They also reported that increasing DD causes less hindrance to acetyl (group by interacting polymer with chitosan) via hydrogen bonding. This shows high DD polymers are more compatible because of hydrogen bonds as compared with low DD chitosan.

5.3.7..2 Morphological Study

The SEM images of 1P:4F composites were displayed as follows neat matrix Figure 4.12 (A-D), untreated in Figure 4.13 (I – L), Figure 4.14 (M – P) for 70% DD and Figure 4.15 (Q – T) for 91% DD. Figure A-D and l - L indicate images of pure polymer (neat matrix) and the untreated . The micrographs shows fracture surface which contains large number of voids and poor and non-uniform dispersion were observed Figure A-D and Figure I - L lt was cleared from the SEM micrographs that chemical treatment changes the surface Figure 4.14 (M-P) and 4.15 (Q-T) (70% and 91% DD), a smooth surface topography with uniform dispersion structure were obtained for the neat matrix Figure 4.12. Morphological results clearly show that when polymer resin matrix was deacetylated at different degrees DD% of chitosan with the resin (P: F), surface modifications took place, depending upon the bonding between the varying loading of reinforcement and the polymer resin matrix. The presence of amino groups in chitosan at low DD have enhanced the bonding and surface integrity. The SEM of the chitin (untreated) Figure 4.13 I-- L and the chitosan (DD% of 70 and 91%) Figures 4.14 and 4.15 revealed that chitin (untreated) has a smoother surface than chitosan (deacetylated) as can be seen from the Figures. The rough surface of the chitin composite (DD) is attributed to the low degree of deacetylation (Abdel-Fattah *et al.*, 2007). The chitosan phenol formaldehyde (70 and 91% DD) showed prominent sheath-like layers than the chitin (untreated), this could probably be as result of deacetylation of the chitin which removes some bonding agents and explosing more sheaths in the chitosan.

In the case of untreated composite with low DD and there was weak bonding between the matrix and the reinforcement Figures 4.14 (M – P) and hence lower mechanical properties as compared to high DD (91%) of 40%. In case of 91% loading there was intimate mixing of the reinforcement with the resin matrix Figure Q-T, which resulted in a polymer composite with higher chitosan content (beyond 30%) agglomeration of particles took place, which resulted in decreased mechanical properties. In Monarul Islam *et al*, (2011) in the preparation of chitosan from shrimp and investigation of its properties found that the SEM morphologies examination of chitosan showed non homogeneous and non-smooth surface with straps and shrinkage. Esam Hefian *et al.*, (2010) reported that chitosan exhibits, some strips in the surface. In this case the morphology after the reinforcement of the filler there was no such character.

Figure 4.12 (A – D), shows SEM images of neat matrix surface base composite. It was seen that the cross – section of the surface is clean, and with the introduction of filler Figure 4.13 to 4.15 (I-T), the cross – section has changed. In the case of 40% loading of 70% DD value Figure M-P the formation of the chitosan has been noticed (showed by cracking) as shown in the Figure 4.14. These P: F /chitosan acted a bridge for improving the interfacial adhesion between the matrix and the fillers. Here the composite surface exhibits resin rich with less voids and debris. The presence of the resin layer improved the bonding and surface integrity with high fibre-marix adhesion.

In another reason, it can be said that Figure 4.13 (I – L, untreated) shows the SEM image of surface of the resin bonded without addition of the curing agent i.e HMTA. It is seen that the surface is relatively smooth with many cracks on it. It is obvious that compared with the surface pattern without curing agent the pattern bridge is changed dramatically after addition of the active agents. The curing agent are believed to play an important role in cross-linking of resin and have great potential to increase the strength. The SEM analysis, also collaborates that the filler dispersion is homogeneous until reach the 40% weight (Alamri and low, 2012).

5.3.8.0 THERMAL ANALYSIS

5.4.8.1 Thermal (TGA/DTA)

Thermo-gravimetric technique were employed to measure the decomposition of the phenolic chitosan composites as a function of weight loss. The TGA graphs of the P: F (neat matrix) resin Figure 4.16, and the reinforced chitosan phenol formaldehyde composites (40% filler loading) at different DD% were presented in Figures 4.17 to 4.19, while the derivatives of the mass loss towards temperature (DTA) were also cited in the same Figures. The TGA graphs of reinforced chitosan phenol formaldehyde composites at 70%, 81% and 91% DD shows clearly that the mass loss exhibits two distinct slope breaks in the mass loss curves Figures 4.17, 4.18 and 4.19.

The first significant mass loss were noticed at a low temperature between 100^{o}C and 230^{o}C, where about 4 to 5% of the initial mass was lost with a slight plateau thereafter to 800^{o}C.At low temperature stage, the phenolic composite with and without chitosan, were stable relatively in nitrogen atmosphere. However, a small amount of weight loss (4 to 5%) happened because of the evolution of gaseous trapped in the matrix material during curing process. The gaseous components such as carbon dioxide, water vapour, methane, and at a minor extent to the emission of the formaldehyde that remained unbounded in the resin were release in this stage (Knop and Pilato, 1985). This degradation may correspond to a loss of adsorbed and bound/water. The chitosan has a greater capability to form hydrogen bonding as compared to chitin and chitosan will be more hygroscopic when crosslinked with the other materials (Gonzallez *et al.,* 2000; Yeh *et al,* 2006). This means that the intial decomposition around 100^{o}C can be attributed to the strong water-adsorptive nature of chitosan. This was supported by the relative DTA graphs in the Figures 4.17, 4.18 and 4.19.

The presences of chitosan in the polymer as a reinforcement in Figures 4.17, 4.18 and 4.19 significantly shifted the weight loss curve down when compared to the neat polymer alone without fibre in Figure 4.16. This loss was expressed by a curve with a peak temperature at 87^{o}C (91%DD) the DTA (T_{max}) appears between 95^{o}C and 350^{o}C for all reinforced chitosan samples analysed, as can be seen in Figures 4.17, 4.18, and 4.19. Pyrolytic degradation in this region involves fragmentation of inter-unit linkages, releasing monomeric phenols into the vapour phase, while above 500^{o}C for 91% DD the process is related to the decomposition of some aromatic rings and the non-volatiles (El-Saied and Nada 1993; Sun *eta al*, 2000).

The secondary significant mass loss occurred from temperature of 315^{o}C to 580^{o}C (T_{max}), with the highest mass loss of 25% for 81% DD, 20% for 91% DD, and 18% for 70% DD and no appreciable mass loss were observed up to 800^{o}C. The utmost thermal decomposition were observed in the temperature range of 390^{o}C to 615^{o}C owing to the polymer pyrolysis chain scission of the phenol formaldehyde chitosan composite specimens. The second mass loss were attributed to the breakdown of methylene linkages to yield aldehydes and phenols (Khan. *et al*, 2004). The relative DTA graphs also signifies these mass reductions by two endothermic curves with peaks at the temperatures of 110^{o}C and 333^{o}C/310^{o}C for 70% DD, 30^{o}C and 330^{o}C for 81% DD, and 87^{o}C and 333^{o}C for 91% DD accordingly.

The above findings were consistent with the literature references where TGA measurements show phenol formaldehyde in crude cashew nut Papadopoulou and Chrissafis, (2011) to perform two degradation peaks temperatures at 335^{o}C and 522^{o}C accordingly. At the high temperature stage, TGA curve for all studied materials were almost flat. At 800^{o}C, the residual mass of neat polymer was 75%, and the residual mass of composite of 40% filler loading with 70%, 81% and 91% DD were 78%, 70% and 75% respectively. The TGA graph of the polymer alone in Figure 4.14 shows only one pattern of mass loss with only 4% and mass loss curve shifted up high in the graph when compared to the reinforced chitosan phenol formaldehyde composites. From the Figures 4.17 to 4.19, it can be noticed that the DD had a little influence on the thermal degradation: the composites with the highest DD degraded at a higher temperature (the temperature of the excessive thermal degradation occurred at around 600^{o}C, compared to 580^{o}C for the composite with lower DD.

In another evidence, the second stage was due to degradation of chitosan/phenol formaldehyde composite and the temperature at which maximum degradation occurred (T_{max}) above 300^{o}C. Similar results were observed by Liu *et al*., (2003) and Gonzallez *et al.*, (2000) . Mishra *et al* (2009) reported that a sharp endothermic peak in the thermogram curve of chitosan at 310^{o}C is due the decomposition. Therefore, by increasing DD of chitosan sample, chitosan/phenolformaldehyde composites (70% to 91%DD) become less thermally stable Figure 4.17 to 4.19.

Considering together all Figures 4.16 to 4.19, we can say that both the resin alone and the reinforced chitosan composites perform the same first mass loss at relative temperatures. The second mass loss that is attributed to the degradation of the polymer, starts earlier in the reinforced chitosan phenol formaldehyde composites (395^{o}C). this shift to lower temperature were explained by the participation of the filler within the polymer to the phenomenon that also performs a mass loss at this temperature area (394^{o}C to 542^{o}C) Hence, this show that thermal stability of the fabricated composite specimens is elevated with increasing DD% in the polymer matrix due to the excellent thermal endurance and even dispersion of the incorporated fibre in the polymer matrix. The results of the thermal analysis of the composites show that they meet the criteria necessary for high temperature application.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

6.1 Summary

In this work, chitosan was produced from commercial Shrimp Chitin with particle size 60 mesh by deacetylating with different concentrations of NaOH solution (30%, 40% and 50%) under oxalic acid condition for 2hrs. The degree of the deacetylation (DD %) were determined and was found to increase with the increasing concentration of deacetylation of alkali solution. A DD% of 70% , 81% and 91% was achieved based on titration and were reproducibly obtained. The process describes a successful procedure in comparison to other conventional methods. The experimental results of various tests indicate a significant values of pH (6.7), Ash value (1.12), Solubility (01.95%), Viscosity (7.2 cP), Loss on drying (0.99%), Specific gravity (1.00g/cm^3) and moisture content (2.68 %). Characterization of chitosasn was carried out using FT-IR spectroscopy analysis, which shows some important functional groups of standard and observed wave length of fresh chitin and the deacetylated chitosan of 70 and 81% DD. The values agreed with the ones of the available literature. It is clearly from the SEM and XRD studies that the crosslinking reaction between the filler and the polymer had formed.

The P: F resins (novolac) were successfully synthesized from phenol formaldehyde, at different molar ratios of 1P:2F to 1P:8F. A summary of the physicochemical properties of all P: F resins are shown in Table 4.1 to Table 4.8 in appendix A. The experimental results of the various analytical tests performed revealed that a significant percentage level was obtained and tallied with standard results. From Table 4.1 the P:F resins exhibited acceptable levels of values made in the present study are in the range of pH (1.52 to 2.615), Viscosity (2.2 to 2.7cP spindle 2, and 6.1 to 6.9cP spindle 3), yield% (28.56 to 44.44), Gel-time (1.41 to 2.34 min), Cure-time

(0.45 to 1.58min) Resin Solid Content (50.76 to 80.38%), Density (0.9 to 1.1g/cm^3), and Water-tolerance (5:15 to 5:19) . The free phenol obtained in this work has also reached the normal human levels (<10mg/L in urine of persons not exposed to phenol or benzene), according to Agency for Toxic Substances and Disease Registry. Synthesized P/F resins exhibit excellent improvements for free formaldehyde content and free phenol content. Hence, the values (< 4.0mg/L (%) Formaldehyde and < 3.0mg/L (%) phenol) of the synthesized P/F novolac resins are in range with specifications that have been established for use of commercial novolac resins. The values of %free formaldehyde and %free phenol values meet the world standard. European countries ranges from 0.3ppm to 2.0ppm with the majority of them to range between 0.5 to 1.0ppm. Also the lowest exposure limit in the living space in most countries are around 0.1ppm.

FT-IR analysis was carried out to ascertain the functional groups of the compounds. Some important functional groups of standard and observed wave length for resins (phenol-characterized and found to tally with the literature value. The FT-IR of 1P:4F and 1P:5F indicate the presence of phenol in an absorption peak at 3650 to 3590cm^{-1}. And absorption at region 2800 to 2700cm^{-1} confirmed the presence of aldehydes. And also other major absoptions band at 1072, 1633, and 3453 of FT-IR band indicate that simultaneously with the formation of the novolac methylene group of the novolac have been consumed, most likely by intermolecular crosslinking reactions.

To determine the optimization of P/F molar ratio, composites were prepared using phenol-formaldehyde resins (novolac) at different molar ratios of 1P:2F to 1P:8F. Using 5%w/w HMTA as curing agent under atmospheric pressure and temperature. Mechanical characterization of thirty five chitosan phenol formaldehyde polymer composites were carried out. The maximum value observed are 15.86 MPa at 40% fibre loading. The tensile modulus at different % filler loading with maximum of 284.19MPa for 1P:2F, 10% loading. Tensile strength and tensile modulus increase with the incorporation of chitosan into the matrix due to the transfer of stress from the matrix to the filler. Some physical properties of the prepared composites of 10% to 50% fibre loading such as density and water absorption were also determined for the samples.

The optimums in the resins ratio and percentage filler loading were selected from the experiments. Filler loading of 40% at 1P:4F and 1P:2F gave optimum results and hence were selected for further analysis. A series of analysis were carried out. In the case of mechanical behavior chitosan phenol formaldehyde resin matrix based polymer composite showed a slight increase with the increase in the deacetylation degree (DD%) of chitosan when reinforced and excellent results obtained when the chitosan were reinforced in making the composites. An optimum results of mechanical properties such as tensile strength 18.83MPa, tensile modulus 284.19MPa, flexural strength 546.00MPa, flexural modulus 4,738MPa, Impact strength 920.00 J/N^2, and Hardness 46.07HRF of reinforced chitosan phenol formaldehyde composite were found of excellent results at high DD of 90%.

The results of swelling, moisture absorbance, density, chemical resistance behavior of composites were reported and these could be used as determining parameters for the end applications of these composites. Physico-chemical studies of polymer composites carried out show that these composites are sensitive to swelling in water, ethanol, and tetra chloromethane and poor in acetone. The water absorption and the density are excellent and are within the range of 0.82 to 1.33 in all. Chemical resistance of the composites due to the hydrophilic nature of the chitosan also gave a good results in both acid 0.20% to 8.87% (1N HCI) and base 0.13% to 2.20% (1N NaOH).

From the foregoing study the novolac resin prepared contains some amount of free formaldehyde, as determined by the titration method procedure (hydroxylamine hydrochloride method). The possible harmful effect of formaldehyde emission in indoor air must be addressed. A comparative analysis of formaldehyde emission from the chitosan phenolformaldehyde composites were carried at different DD%. In this formaldehyde emission test using flask method were carried out on the composite procedure (**3.6**). More importantly the results of the analysis revealed a good properties of synthesis P/F which meet the requirement of JIS K6806 – 2004 standard, BS EN120 British Standard and B EN 717 – 3 European Standard in exterior application and the formaldehyde emission. They stated that the range of emission should be between 0.48 to 1.26% which is much less than that of the E_o (European Union, EU) specified in the JIS A1460 – 2003 standard (the value is less than 0.5mg/L). Our results of formaldehyde emission was only around 0.2mg/L, when compared with standard of values of <0.5m/L.

A reaction between chitosan and novolac resin are proposed by mechanism reaction showing in three steps a,b and c. An explanatory equations of reaction of novolac and HMTA decomposition and reaction of amino group of chitosan with the residual formaldehyde were given and highlighted their importance. This is to show the effect of chitosan in the reduction of formaldehyde release in the production of chitosan phenol formaldehyde composites. And also the effect of degree of deacetylation (DD) on the emission of formaldehyde from the chitosan phenol formaldehyde composites were stated and showed the importance of DD on fromaldehyde emission. It was shown in the work that tha chiotosan are used as a scavengers or formaldehyde/catcher and is capable of reducing the formaldehyde emission in the production of chitosan phenol formaldehyde composites. The scavenging abilities of chitosan increased with the increasing the DD.

SEM studies, on comparison with morphology of polymer alone (neat matrix) and morphology of reinforced chitosan phenol formaldehyde composite, morphological results clearly show surface modification took place .lt was obvious when compared with the surface pattern without curing agent the pattern bridge was changed dramatically after addition of the curing agents.The curing agent (HMTA) are believed to play an important role in the cross-linking of resin and have great potential to increase the strength of the polymer composites.

XRD analysis, X-ray diffractograms results of the polymer alone (neat matrix) and untreated (without alkali treatment) have shown a low percentage of crystallinity and percentage of crystallinity index. But with the incorporation of the deacetylated chitosan into the polymer increased the crystallinity. And this crystallinity decreased with the increase of the degree of deacetylation (DD%).

Thermal properties of the reinforced chitosan phenol formaldehyde composites as compared to the neat polymer had improved. The temperature at which degradation took place was improved from 330 to 615^{o}C in the presence of chitosan, indicating a significant improvement in the thermal stability. Improved stability was manifested throughout the whole range of temperature studied. The residual weight obtained at 615^{o}C was found to be almost in the same range for all the different degree of deacetylations DD%.

6.2 Conclusion

The synthesis of phenol formaldehyde reinforced chitosan composites with different degrees of deacetylation were found to have undergone tremendous physiochemical-thermal and morphological changes. The higher optimum composites obtained (40% of 1P:2F/1P:4F) could be accounted by the efficient physic-chemical behavior and interaction between the monomers. The increase in DD% P: F chitosan composites increases the performance in terms of moisture absorbance, solubility, swelling behavior, chemical resistance, and hydrophylicity.And percentage crystallinity (%Cr) and crystallinity index (C.I) decreased at higher DD %. But incorporation of phenol formaldehyde chains into the chitosan increased the physic-chemico-thermal resistance and improved the mechanical performance of the composites. The synthesis of such novel P: F (resins) novolac is judicious, economic, fruitful means to utilize the natural fibre of chitosan for various scientific applications and the development of technology. The alkali treatment of chitosan at different DD value was aimed to remove some acetyl group from the chitosan and explore it more to susceptibility for bonding. The results of SEM studied reveals that alkali treatment of the chitosan by deacetylation altered morphology of the composite when compared with the untreated. Generally, good filler-matrix interaction which results from chemical modification improved the properties of the composite.

The following conclusions are drawn.

1. Phenol Formaldehyde

1 The resins (novolac) synthesized has low molecular weight and useful in many applications. They offer a versatile chemistry with a wide range of properties. The experimental results of various analytical and statistical tests revealed that the resins synthesized exhibited acceptable levels of viscosity, yield%, water tolerance, resin solid

content, gel/cure times, density, and bonding performance. Hence, we can predicate that P: F resin synthesis will not only help reduce polymer industry independence in petro-chemical industry but also be applied for industrial production of composites.

2 In this work HMTA were used as curing agents and found to increase the degree of curing and hence reduced the free formaldehyde of the composites. Therefore, there is a need to try other catalysts and curing agents to further determine their efficiency.

2. Chitosan

1. Chitosan is a good filler for toughening the phenolic resin. There is an increasing interest in application of chitosan and chitin in a wide range of the technologies taking advantage of their special properties such as low density, biocompatibility, biodegrability, reactivity, non-toxicity, adsorption properties, etc. Production cost of chitin and its derivatives continue to be the prime factor limiting more widespread application of these substances.
2. Chitin and chitosan can be derivatized by utilizing the reactivity of the primary amino group and secondary hydroxyl groups to find applications in diversified areas. In this research work, an attempt has been made to understand the importance and characteristics of chitosan/phenol formaldehyde composites by describing the various aspects, including the physical and cheimical properties, processing, and applications. In view of this, this research work will attract the attention of intrepreneurs, industrialists, academicians, and environmentalists.
3. The quality of our environment over the years has declined as a result of various human activities. Nigeria as a developing country are plague with poverty and also gave little attention to environmental issues. One of the challenges is the management of the municipal waste. The waste of these natural polymer (chitin) is a major source of surface pollutant in the coastal area of Nigeria. Chitosan is no longer considered as just a waste

product from sea food industries. The production of Chitosan from crustacean shells as a food industry and composite industry, waste is economically feasible. The proper utilization of those water resources (aquaculture) in terms of research in chitin and chitosan can bring the economic and academic prosperity of the nation.

4. This research has to a reasonable extent demonstrated the use of phenol formaldehyde resins as a sources of material for composites production especially: Polymer industries cannot absolutely rely on synthetic fibres for finishing: But can compliment the available synthetic fibres with natural fibre such as chitosan:Also life can easily be affected by substances that are toxic. This work extended to cover the toxicity assessment and the results obtained confirmed the composite to be toxic free.

3. Chitosan/PhenolFormaldehyde Composite

1. The synthesis of such novel P: F (resins) novolac and the Chitosan P: F composites is judicious, economic, fruitful means to consider the natural fibre such as chitosan composites applications. Where high impact and other mechanical properties are requirements such as in some parts of automobile, aircrafts, ships, insulators, electrical appliances etc. The resins synthesized could be used as reinforcement in phenoplast matrix based composite, improved the physic-chemico-thermo-mechanical competence, caused the degradation, sustained availability and alternate to other filler as reinforcement. These novel phenol – formaldehyde chitosan composites has immerse applications in the development of the latest technologies and one of the best uses to prepare the composite.
2. It was observed that as the chitosan content increased, there was an increase in the mechanical properties. An optimum results of 40% of 1P:4F were found as tensile strength 18.83 MPa, tensile modulus 284.19 MPa, flexural strength 546.00N/m^2 and

flexural modulus 4,738 N/m^2 at 90% DD. Impact strength of chitosan filler loading of 40% composite was quite high with impact strength of 920J/m^2 (representing 65%) improvement over that of the neat P: F when compared with the other composites. It was found that reinforced chitosan composite at 40% loading had the highest hardness (46.07 HRV representing 28% improvement on the hardness of the P: F (neat matrix) . Hardness of the sample was influenced by a considerable increase in filler content in the composite and the DD value of the chiotsan. Composite of (1P:4F) at 40% loading of filler show shorter gel time/cure time, which indicates higher rate of polycondensation and crosslinking formation in these novolac resins.

3. In the composites made by the chitosan phenol formaldehyde, the formation of void is reduced in the presence of HMTA as the curing agent. The voids formed have little effect on the composite properties. In this research, the use of chitosan as a filler had tremendously reduced the emission of formaldehyde, in the process the chitosan act as a formadehyde acceptor or scavenger due to the presence of amino groups in the chitosan. Hence, the emission has reduced.
4. There is also seen that decrease in density of the composites which is also greatly depended on the content of filler. Composites are dependent on the filler matrix interphase, and interface and the resins used, for the effective performance of the composites. The utilization of composites should be encouraged because of their excellent properties. The water absorption of composite at higher DD and filler loading (40%) of 1P:2F (0.4300 %) and 1P:4F (0.4589 %) was higher than that of P: F (neat matrix) with a value of (0.0070%). However, the density of chitosan composite (an average of 1.0g/cm^3) was more than that of the pure P: F (neat matrix) with a value of (0.84g/cm^3).

5. The release of free formaldehyde content was solved by the use of chitosan as the matrix, had greatly reduced the released during the polymerization reaction.This is due to the presence of amino groups in chitosan which act as scavenging or formaldehyde acceptor. Formaldehyde emission from the composite has been shown to be impermanent, and its level is below that set by the EN 717-1 and EN 717-2 standards.
6. Currently, it have shown that it is possible to meet the new demands for F-zero formaldehyde emission from composite panel's products with the use of properly formulated aminoplasttic resins systems, without any deterioration in panel performance. Resins formulators should produce a product that does not raise some environmental health concerns. Taking into account any potential added costs associated with the product.
7. This research is an example of the usefulness and solution of a materials-science based approach to the diagnosis of emissions of formaldehyde and phenol of indoor air quality as well as the measurement procedures, were critical to arriving at the study's conclusion. Further progress analysis in many areas related to indoor air quality are possible using similar approaches of this study.
8. The use of chitosan reinforced on phenol formaldehyde as composite have bee developed by this method of composite production and found to be environmental friendly. It can be concluded that the objectives of this research had been achieved with the production of the non toxic composites and this would offer industry an importance opportunities.

The overall results of the study work of the deacetylated chitosan, the synthesized P:F resins (novolac), and the reinforced chitosan phenol formaldehyde composites show that, composites which were deacetylated, reinforced and cured with the hardener (HMTA) the 70%, 81% and

91% DD have given excellent mechanical properties enhancement and better physical properties than those without deacetylation and curing agent. The use of chitosan in the production of composite of chitosan phenolformaldehyde have tremendiously reduced the formaldehyde emission to 5 times less than the limit standard. This is due to the abundant amino groups ($-NH_2$) on the chitosan, which when introduce into the resins (P/F), acts as a formaldehyde catchers, which decreases the molar ratio, $F/(NH_2)_2$ of the resin mix. The relevance of chitosan resides in its chemical acitivities of biodegradability, biocompatibility, non-toxicity and physicochemical properties of degree of deacetylation and molecular mass. There is no doubt that chitosan remains one of the most important biopolymer.

6.3 Recommendations

Despite the obvious important physio-mechanical tests and characterizations carried out on the reinforced chitosan phenol formaldehyde composites, the following recommendations are still being made:

1. Further work can be done to improve on the degree of deacetylation especially through size reduction of the chitin particles in different sizes (20, 30, 40, 50 and 60 mesh), increase in concentrations of the reagent, reaction time and increase in temperature of deacetylation as suggested by literature.
2. Novolac resin is one of the intermediate materials got from condensation reaction of formaldehyde and phenol under acidic condition, while resole is the other intermediate produced by alkali solution. Therefore it is very important to carry out a research on the resole part (the opposite part of novolac). A comparison of tests properties, analysis of the composite should be made to find out which one will demonstrate a suitable and reliable method.

3. The resin solid content of the synthesis P: F resins gave some high values in some molar ratios, therefore, there is need to investigate and find the reason.

4. Scienties or formulators need to to have a knowledge of the chemistry of the resins synthesized in this work, since this is the key for their compatibility in adhesive formulators. It is essential to know the softening point, molecular weight and aliphatic/aromatic balance, as well as the polarity of the resin. In this way resins provide formulors the ability to optimize their adhesives.

5. Chitosan reinforced phenolformaldehyde developed in the study is environmentally friendly. Moreso, the handlay-up technique utilized in the study is economically suitable though labour intensive. In general, it can be said that more studies about processing of the composite materials are needed to increase the scientific knowledge concerning these materials and their commercial potential. The different fabrication techniques in order to expand and enhance their performance in use.

CONTRIBUTIONS TO KNOWLEDGE

1. In the synthesized novolac resin a yield up to 76% was obtained by using oxalic acid as a catalyst.
2. A green composite is produced with greater mechanical properties. An optimum results of 40% filler loading gave the following: 38% improvement in tensile strength/modulus
   27% improvement in flexural strength/modulus
   65% improvement in Impact strength and
   25% improvement in hardness
3 The use of chitosan as the matrix, had greatly reduced the released of formaldehyde during the polymerization reaction, 5% times less than the standard. This is due to the presence of amino groups in chitosan which act as scavenging or formaldehyde acceptor. Formaldehyde emission from the composite has been shown to be impermanent, and its level is below that set by the EN 717-1 and EN717-2 standards.

4 In this research work, an attempt has been made to understand the importance and characteristics of chitosan phenol formaldehyde composites by describing the various aspects, including the physical and chemical properties, processing, and applications. In view of this, this research work will attract the attention of entrepreneurs, industrialists, academicians, and environmentalists.

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APPENDEX A

Results Obtained from the Synthesized Phenol Formaldehyde (Novolac) Resins

Table 4.1 pH Values of 1P: 2F-1P:8F Novolac Resins

	pH values			
Sample P: F	1st reading	2nd reading	average	pH
1P:2F	2.43	2.80	2.615	2.62
1P:3F	2.18	2.13	2.155	2.16
1P:4F	2.17	2.12	2.145	2.15
1P:5F	2.09	2.11	2.10	2.10
1P:6F	1.88	1.83	1.855	1.86
1P:7F	1.69	1.51	1.76	1.76
1P:8F	1.72	1.31	1.515	1.52

Table 4.2 Results of Viscosity (cP) Values Obtained from Novolac Resins of 1P:2F-1P:8F

Sample (P: F)	Spindle (3) Dial Reading (Viscosity/cPa)	Spindle (2) Dial Reading (Viscosity/cPa)
1P:2F	2.3	6.1
1P:3F	2.4	6.5
1P:4F	2.7	6.9
1P:5F	2.5	6.5
1P:6F	2.4	6.2
1P:7F	2.2	6.0
1P:8F	2.1	6.0

Table 4.3 Water Tolerance Measurement of 1P:2F – 1P:8F Novolac Resins

	Measurement			**Water Tolerance**
Sample (ml)	Trial-1	Trial-2	Trial-3	Mean Value
1P:2F	5:14	5:12	5:19	5: 15
1P:3F	5:18	5:20	5:17	5:15.5
1P:4F	5:14	5:13	5:19	5:18.5
1P:5F	5:14	5:18	5:20	5:18.5
1P:6F	5:14	5:17	5:22	5:18.0
1P:7F	5:13	5:17	5:21	5:18.5
1P:8F	5:13	5:19	5:21	5:19.0

Table 4.4 Calculated Values of Density of 1P:2F – 1P:8F Novolac Resins

Sample	Wr	Wb	Ww	Wrw	Density
P: F (1:2)	2.4573	28.5324	79.1120	79.5715	1.0053
P: F (1:3)	0.7314	24.8845	75.9900	76.1730	1.0350
P: F (1:4)	1.0581	28.5324	79.1120	79.3085	0.9925
P: F (1:5)	1.3270	28.5324	79.1120	76.2415	1.1170
P: F (1:6)	0.5091	28.5324	79.1120	79.2600	1.0000
P: F (1:7)	1.5461	28.7099	79.1120	79.2700	1.0000
P: F (1:8)	0.2455	28.7099	79.2045	79.4500	0.9917

Table 4.5 Resin Solid Content of 1P:2 F-1P:8F Novolac Resins

Sample	Sample weight after 2hr	Initial weight	resin solid level %
1P:2F	0.5459	1.0758	50.76
1P:3F	0.7586	1.0650	71.23
1P:4F	0.7355	1.0760	68.35
1P:5F	0.8900	1.1073	80.38
1P:6F	0.6747	1.0800	62.48
1P:7F	0.7221	1.1130	64.87
1P:8F	0.6914	1.1373	60.80

Table 4.6 Gel-time and Cure-time of 1P:2 F-1P:8F Novolac Resins

	Gel-time/min			Cure-time/min		
Sample	1st reading	2nd reading	Mean value (min)	1st reading	2nd reading	Mean value (min)
1P:2F	1.58	1.32	1.41	1.20	0.25	0.45
1P:3F	2.12	1.58	2.11	1.30	1.55	1.25
1P:4F	1.39	1.36	1.37	1.02	1.54	0.58
1P:5F	1.59	1.54	1.55	1.02	0.58	1.00
1P:6F	1.49	2.41	1.58	1.08	1.02	1.10
1P:7F	2.39	2.29	2.34	1.06	1.52	1.58
1P:8F	2.01	2.21	2.12	1.10	1.51	1.30

Table 4.7 Yield Percent (%) of 1P:2 F-1P:8F Novolac Resins

Sample P: F	Total Vol P/F (ml)	Oxalic acid (g)	Total mass (P/F) (g)	Yield -1	Yield-2	Yield -3	Mean Yield	Yield (%)
1P:2F	67.04	2.63	69.67	19.60	21.34	18.76	19.90	28.56
1P:3F	63.58	2.54	66.12	24.94	24.94	26.24	25.37	38.37
1P:4F	60.61	2.42	63.03	19.48	21.78	23.49	21.58	34.24
1P:5F	58.00	2.32	60.32	21.92	23.34	24.89	23.38	38.77
1P:6F	55.78	2.23	58.01	23.76	24.56	23.95	24.09	41.53
1P:7F	53.80	2.15	55.95	24.72	24.98	24.89	24.86	44.44
1P:8F	50.03	2.00	52.03	19.33	20.23	19.12	19.56	37.59

Table 4.8 Free Formaldehyde;The percentage of free formaldehyde was determined from the following.

%free formaldehyde = 100 (ml × N NaOH) ×0.030/g sample: Where ml = Volume of 0.50 N ,Hydroxylamine hydrochloride solution NaOH = Volume of NaOH used (ml),g sample = Mass of the resin used (mg).

Sample	ml(ml)	N NaOH (ml)	g Sample (mg)	% free formaldehyde
1P:2F	32.70	4.20	1.0000	4.1200
1P:3F	35.30	11.90	1.0000	1.2600
1P:4F	35.10	18.00	1.0000	1.8954
1P:5F	32.70	4.20	1.0000	1.8954
1P:6F	39.80	4.80	1.0000	0.4120
1P:7F	31.30	6.60	1.0000	0.6197
1P:8F	34.10	48.0	1.0000	4.9100

Table 4.9 Values of Concentration of the Free Phenol Solution

The percentage of free phenol was determined from the following:

mg/l phenol = 7.842 (AB − C)**:** Where A = ml $Na_2S_2O_3$ used for the blank, B = ml bromated – bromide solution used for sample divided by 10, C= ml $Na_2S_2O_3$ used for the sample.

Sample	A (ml)	B (ml)	C (ml)	mg/l (%)
1P:2F	30.2	20.0	60.00	3.00000
1P:3F	32.0	25.0	60.10	0.15684
1P:4F	32.0	27.0	15.00	0.15684
1P:5F	32.0	15.0	5.80	0.33093
1P:6F	32.0	14.2	16.0	0.23086
1P:7F	32.0	16.0	18.0	0.26035
1P:8F	32.0	17.0	18.0	0.28545

Table 4.10 Important Functional Groups of Standard and Observed Wave numbers for Resins (Phenol formaldehyde) Novolac of 1P:4F, 1P:5F and 1P:6F Mole ratios

Standard (cm^{-1})	1P:4F (cm^{-1})	1P:5F (cm^{-1})	1P:6F (cm^{-1})	Functional group
3400	3274	3423	3414	OH stretch general
	2719	2933	2934	
2724	2274	_____	2733	OH bend overtone
	____	_____	2051	
	1892	1895	1893	
1605	1604	1621	1614	C=C aromatic
1510	1495	1452	1404	C-H bbend
1390	1367			
		1259	1241	C-C-O asymmetric
1020	1087		1099	stretch, -COH
960	825		833	-C-H

Table 4.11 Calculated Values of the Degree of Deacetylation (DD %)

Sample	V_2 (ml)	W (%)	%DD
	Commercial		
Chitin (55.18%)	40.1	0.2800	55.18
Chitosan (70%)	16.5	0.0350	70
Chitosan (81%)	16.8	0.0300	81.47
Chitosan (91%)	13.0	0.2725	90.92

Table 4.12 Experimental and Theoretical Results for the Various Test(s) Sample of Chitin

Test	Commercial Chitin	Chitin value
DD (%)	55.18	
pH	9.86	6.7
Ash value (%)	<0.5 – 1.8	1.12
Solubility (%)	0.71	1.95
Viscosity (cPa)	220 – 1190	7.2
Loss on drying (%)	<10	0.9922
Specific density (g/cm^3)	1.35 - 1.45	1.002
Moisture content (%)	<10	2.68
Colour	white	white

Table 4.13 Important IR-Characteristic Bands (Functional groups) Observed Wave numbers for fresh Chitin and the Deacetylated Chitosan (70% and 81% DD)

Standard	Fresh chitin	Chitosan 70% DD	Chitosan 81% DD	Functional group
752	791		586	NH out-of-plane
1026	1052	1072	1072	bending
	1401			
	1321	1397	1362	-C-O stretching
1563	1565			
1661	1644	1633	1626	Amide 11
	2148	2218	2241	
	2370			
2930	2807	2932	2895	Amide 1
		2902		
3268	3453	3441	3433	Symmetric CH_3
			3770	Stretching
				NH stretching

Table 4.14 Results of Density of Composites at Different Filler loading

Filler Loading (%)	P: F ratio						
	Density g/cm^3						
	1P:2F	1P:3F	1P:4F	1P:5F	1P:6F	1P:7F	1P:8F
10	0.45	0.38	0.43	0.55	0.47	0.55	0.35
20	0.56	0.54	0.62	0.71	0.60	0.68	0.52
30	0.96	0.83	0.70	0.87	0.97	0.95	0.87
40	0.98	0.98	1.00	0.91	1.00	1.17	1.24
50	1.24	1.00	1.27	1.20	1.33	1.37	1.09

Table 4.15 Water Absorption Measurement of Composites at Different Filler loading

	Water Absorption (%Mabs)						
Filler	P: F ratio						
Load (%)	1P:2F	1P:3F	1P:4F	1P:5F	1P:6F	1P:7F	1P:8F
10	0.231	0.186	0.218	0.379	0.052	0.346	0.440
20	0.456	0.387	0.390	0.398	0.366	0.222	0.464
30	0.608	0.573	0.513	0.528	0.649	0.649	0.497
40	0.855	0.659	0.742	0.712	0.771	0.771	0.739
50	1.12	0.99	1.22	1.462	0.700	0.600	0.816

Table 4.16 Tensile Strength of Composites at Different (%) Filler Loading

Filler Loading (%)	P: F ratio						
	1P:2F	1P:3F	1P:4F	1P:5F	1P:6F	1P:7F	1P:8F
			Tensile strength (MPa)				
10%	3.25	3.77	3.36	4.36	2.76	1.51	1.60
20%	5.58	6.78	7.18	7.98	6.99	2.89	2.79
30%	7.22	8.12	11.98	10.96	10.96	3.09	3.02
40%	11.88	14.21	15.86	15.12	14.12	13.86	12.32
50%	4.89	3.89	5.23	3.02	3.02	2.99	2.01

Table 4.17 Tensile Modulus of Composites at Different (%) Filler Loading

Filler Loading (%)	P: F ratio						
	1P:2F	1P:3F	1P:4F	1P:5F	1P:6F	1P:7F	1P:8F
				Tensile Modulus (MPa)			
10%	150.0	187.62	170.1	122.53	150.99	123.59	112.23
20%	190.12	1 21.41	1 92.67	1 97.30	185.55	131.87	120.43
30%	228.89	1 44.41	217.53	217.53	163.56	92.74	133.51
40%	284.19	1 52.10	137.33	137.18	137.18	130.92	171.04
50%	210.41	1 60.89	112.60	110.54	136.47	80.12	159.23

Table 4.18 Physicochemical Properties Measurement of Optimum Samples of 40% Composites of 1P:4F and 1P:2F at Different DD%

				% Chemical Resistance % wt loss after 72 hour	
		Water Absorption	Density	% wt loss in 1N HCl	% wt loss in 1N NaOH
Sample	Resin	%M	g/cm^3	Pcr	Pcr
Untreated		1.3333	1.1	8.87	12.5
Neat matrix	1P:4F	0.0070	1.2	2.63	0.13
	1P:2F	0.0068	1.2	2.58	0.14
70% DD	1P:4F	0.8707	0.78	0.23	0.13
	1P:2F	0.7390	0.72	0.20	0.20
81% DD	1P:4F	0.6642	0.99	0.35	1.00
	1P:2F	0.6100	0.89	0.41	1.46
91% DD	1P:4F	0.4589	1.0	0.36	2.20
	1P:2F	0.4300	1.0	0.50	1.39

Table 4.19 Swelling behavior of 40% composites of 1P:2F and 1P:4F

		% Swelling			
Sample	P: F	H_2O %Sw	CCl_4 %Sw	CH_3CH_2OH %Sw	CH_3OCH_3 %Sw
Untreated		7.3	11.8	7.84	D
Neat matrix	1P:4F	2.60	0.86	3.78	0.4
	1P:2F	2.67	0.92	3.93	0.4
70% DD	1P:4F	1.41	1.69	1.48	D
	1P:2F	1.18	1.76	4.0	D
81% DD	1P:4F	2.13	3.54	8.57	D
	1P:2F	5.26	7.00	6.5	D
91% DD	1P:4F	8.66	5.95	8.71	D
	1P:2F	6.98	1.761	13	D

Table 4.20 Mean Values of Mechanical Properties of Various Parameters Obtained from Measurement of 40% Composites of 1P:2F and 1P:4F at Different DD%

Sample	Resin P: F	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural Strength (MPa)	Flexural modulus (MPa)	Impact Strength (JN^2)	Hardness HRF
Untreated		8.90	128.89	271	730.43	146.6	Brittle
Neat matrix	1P:4F	11.92	150.03	305.37	517.51	284.44	35.34
	1P:2F	11.83	151.19	301.00	167.31	273.23	33.48
70% DD	1P:4F	18.40	284.19	105.79	835.05	924.00	46.07
	1P:2F	18.83	217.53	277.66	897.00	666.66	44.43
81% DD	1P:4F	16.25	187.62	172.74	848.25	733.33	30.57
	1P:2F	17.75	162.99	471.33	171.96	293.33	41.83
91% DD	1P:4F	13.20	137.31	308.75	2,284	440.00	18.90
	1P:2F	15.75	131.87	546.00	4,738	386..66	40.43

Table 4.21 Effects of (DD) on the Emission of Formaldehyde and % Cr and C.l of Neat matrix, Untreated of 40% Filler Loading at Different DD % of 1P:4F Composite

Emission of Formaldehyde		XRD	
DD%	FD Released mg/cm^3	%Cr	C.l
Untreated	---	68.50	0.5401
Neat matrix	0.58	73.76	0.6442
70	0.48	88.31	0.8676
81	0.46	85.71	0.8333
91	0.21	82.42	0.7867

Calculations of the Degree of Deacetylation (DD %)

The results obtained from the potentiometric titrations to determine the degree of deacetylation (DD %) of the fresh chitin and the alkaline treated chitosan was determined using the below formular in Equations (1 and 2). Various values of the parameter are shown in Table 4.1. The percentage of free NH_2 groups in chitosan is calculated as follows.

$$NH_2(\%) = \frac{[(C1V1 - C2V2) \times 0.016]}{G(100 - W)} X100$$

$$\text{Free } NH_2 = NH_2/9.94 \times 100 \qquad \text{Equation (1)}$$

Chitosan theoretical NH_2 content (%) = 16/161×100%= 9.94% Equation (2)

Where: The degree of deacetylation (DD %) = [NH_2 (%)/9.94(%)] x100%]

C_1: Concentration of HC (M) = (0.5M), C_2: Concentration of NaOH = (0.1M)

V_1: Volume of HCL = (30ml), V_2: Volume of NaOH added by titration (ml)

G = Sample weight g = (0.3 g), W = Sample water content (%)

DD % of 70: Where C1=0.5 ,C2=0.1, V1=30, V2=16.5 , W=0.0350, and G=0.3

$$NH_2(\%) = \frac{[(0.5\times30) - (0.1\times16.5)\times0.016]}{0.3((0.03)/0.3\times100)} X100 = 0.07042\times100$$

DD (%) = 7.042/9.94×100 = 70.84%

APPENDEX B

Determination of free formaldehyde

Preparation of reagents

0.1M HCI Solution

About 2.0ml of pure Conc HCl was poured into a 25ml volumetric flask containing about 100ml of distilled water. The mixture was shaked and top to the mark with distilled water.

0.5M Hydroxylamine hydrochloride [$NH_2OH.HCI$] solution.

34.50g of $NH_2OH.HCI$ was dissolved in 1litre.

0.10M Sodium hydroxide [NaOH] Solution

01.0g of NaOH pellet was dissolved in 250ml of ditilled water.

0.1M Sodium thiosulphate [$Na_2S_2O_3.5H_2O$]

24.80g of Sodium thiosulphate was dissolved in 1litre of distilled water.

APPENDIX C

Determination of Free Phenol Content

Preparation of reagents

10% acetic acid

10ml of acetic acid solution was poured into a 100ml measuring cylinder and top to the mark.

Starch solution

0,5g of starch was dissolved in asmall quantity of water and then make it up with 50.0ml of boiling water. The mixture was heated to a boil for a while until a clear solution was observed.

20% potassium iodide solution

20g of potassium iodide was taken and diluted with distilled water to 100ml mark.

Preparation; stock phenol solution

I. **1**g of phenol was accurately weighed and dissolved in freshly boiled and cool distilled water, and then diluted to litre. This solution gives 1ml=1mg phenol. But for extreme accuracy the solution were standardized as given below.

II. **10ml** of the stock solution ws diluted to 1litre. The solution gives 1ml=10mg phenol.

III. 1ml of the stock solution was diluted to 1litre. The solution gives 1ml=1mg phenol. (fresh preparation).

IV. **Bromated – bromide Solution, 0.1M**

About 2,784g of anhydrous KBrO3 was accurately weighed and dissolved in some distilled water. 10g of KBr was also weighed and dissolved in distilled water. The two solutions was added together and made up to 1litre.

Preparation of 0.125M $Na_2S_2O_3.5H_2O$ Stock Solution

I. About 24.82g of $Na_2S_2O_3.5H_2O$ was dissolved in boiled and then cooled distilled water and diluted to 1iter. 5ml of chloroform was added as a preservative.

II. **To prepare 0.0125M $Na_2S_2O_3.5H_2O$**

250ml of the stock solution was diluted to 1litre. The standard solution was preserved by adding 0.04g NaOH per litre. For exact 0.0125M $Na_2S_2O_3$.5H2O**,** 1ml=200mg (0.2g).

Standardization of phenol solution

100 ml distilled water was placed in a 500 ml Erlenmeyer glass-stoppered, conical flask. 50ml of stock phenolsolution and 10ml, 0.1M 0.1M bromated – bromide solution was added together, and immediately, 5ml Conc HCI was also added. The flask was stopped and swirl gently. Bromine was released as brown colour.when the colour does not persist, 10ml portion of bromated –bromide solution was added until the brown colour persist. The flask was stopped and allowed to stand for 10minutes. 1g Kl or 40ml of bromated – bromide solution was added in 4 equal portion and swirled gently.

A blank was prepared in exactly the same manner; using distilled water and 10 ml, 0.1N bromated – bromide solution. The blank was titrated and sample with 0.0125M $Na_2S_2O_3$ titrant using starch solution as indicator.

APPENDIX D

Formaldehyde Emission Determination

Preparation of Reagents

0.1M HCI Solution

About 2.0 ml of pure Conc HCl was poured into a 25 ml volumetric flask containing about 100 ml of distilled water. The mixture was shaked and top to the mark with distilled water.

0.5M Hydroxylamine hydrochloride [$NH_2OH.HCI$] solution.

34.50g of $NH_2OH.HCI$ was dissolved in 1litre.

0.10M Sodium hydroxide [NaOH] Solution

1.0g of NaOH pellet was dissolved in 250ml of ditilled water.

0.1M Sodium thiosulphate [$Na_2S_2O_3.5H_2O$]

24.80g of Sodium thiosulphate was dissolved in 1litre of distilled water.

Acetyl acetone [Pentane – 2, 4 – dione] solution

15.0g of anhydrous ammonium acetate was dissolved in 0.30ml glacial acetic acid and 0.2ml pentane -2, 4 – dione reagent in 25ml water. This was diluted up to the mark in 100ml volumetric flask with distilled water.

Reagent without pentane – 2, 4 – dione.

15.0 of anhydrous ammonium acetate was dissolved in 0.30ml glacial acetic acid in 25.0ml water and diluted up to the mark in 100ml volumetric flask with water [pH of solution about 6.4].

Formaldehyde dilute standard solution [0.001mg/ml]

2.50ml of formaldehyde stock solution ws transferred to 50ml volumetric flask, mixed well and diluted up to the mark with water. 1.0ml of this solution was further diluted to 100ml with water and mixed well.

Formaldehyde calibration solution

A series of reference solutions were prepared by pipetting suitable volumes of above formaldehyde dilute standard solution into a 50ml conical flask. Formaldehyde dilute standard solution of 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0ml, and blank solution was also prepared.5.0ml of pentane – 2, 4 – dione solution was dissolved in each of the reference solutions and concentration (mg/l) of formaldehyde after mixing 30ml of water was determined.

Absorbance measurement of calibration solutions

Absorbance measurements of calibration reference solutions and blank were done by using water as reference. The calibration curve was constructed by subtracting absorbance value of the blank solution (Absorbance [As – A y]) from each of absorbances obtained from the calibration graph figure 5.11. The absorbance values was plotted against the formaldehyde concentrations between 0.1666 and 0.8333 mg/L. the slope of the graph was determined.

Sample Preparation

A piece sample of composite with surface area of `10cm2 (20g) was taken and transferred to 250ml conical flask, 100ml of water was added to the sample at 40oC and closed. The flask was kept on a magnetic stirrer for unform stirring of the solution for an hour. 5,0ml of aqueous solution was transferred into 50ml conical flask followed by addition of 5.0ml of pentane -2, 4 – dione reagent and 20.0ml of water.

Sample reference solution

5.0ml of aqueous solution was transferred into a 50.0ml conical flask followed by addition of 5.0ml of reagent without pentane – 2, 4 – dione and 20.0ml of water.

These solutions were shaken for about a minute and immersed in a thermostatic water bath at $40^{o}C$ for 10minutes following by cooling for about 5minutes in a bath of ice – block. Absorbance measurements were taken.

Spectrophotometric Analysis (Analyte Conc)

To determine the analyte concentration (formaldehyde), absorbance value of blank solution (A_2) was subtracted from absorbance value of reference solution (A_1).The absorbance of reaction product was measured over the range of 660nm to 450nm. The absorption at 412nm was used for quantitative calculations. Each solution was analysed in duplicate.

Calculation of formaldehyde concentration is as follows:

$C(HCHO) = (V_o - V) \times 15 \times C(Na_2S_20_3) \times 1000/20$

Where C (HCHO) is the formaldehyde concentration, in milligrams per litre

V is the volume of the thiosulphate titration solution, in millilitres

V_o is the volume of thiosulphate for the blank, in millilitres

$C(Na_2S_20_3)$ is the concentration of sodium thiosulphate solution, in moles per litre

APPENDIX E

Photographs of Instruments and Materials of the Analysis

Plate III Experimental set up

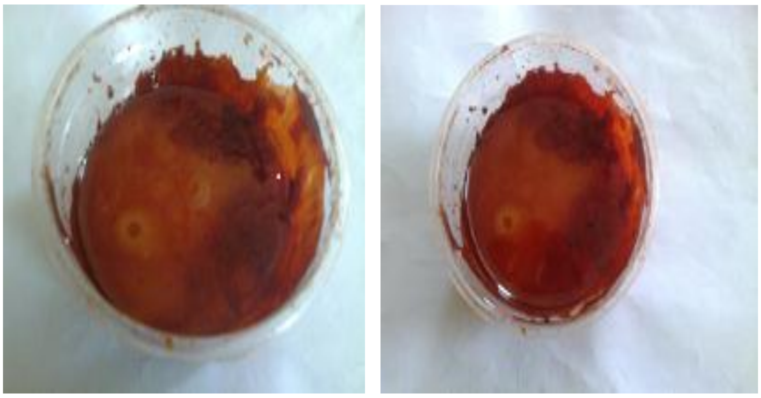

Plate IV Synthesized Novolac Resins

Plate V Fresh chitin

Plate VI Prepared composite before fabrication

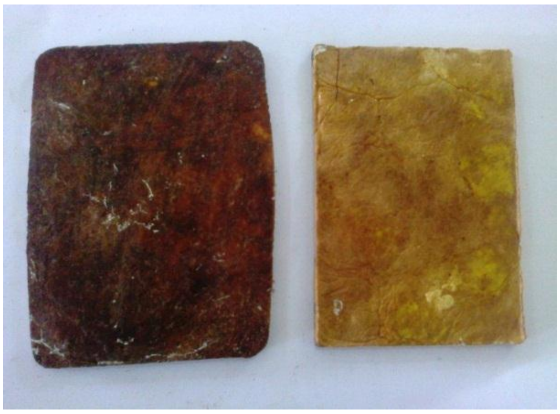

Plate VlI Composite Sheet

Plate VllI Prepared composite before degassing

Plate IX Hounsfield (Monsanto) Universal Tesing Machine

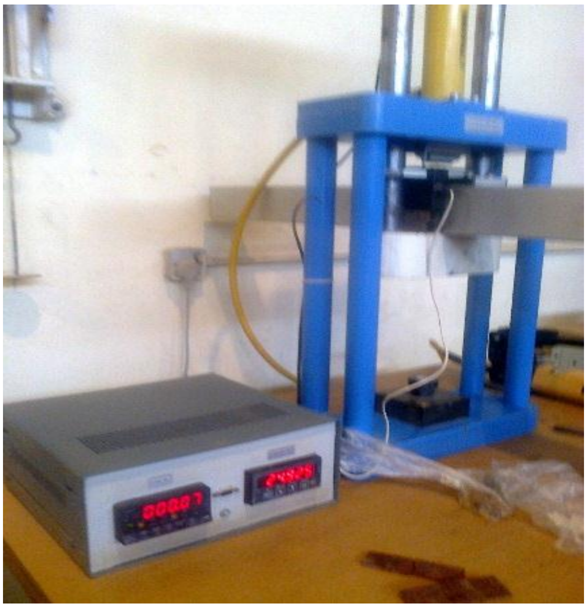

Plate X ZHU187.5 Universal Hardness Tester   **Plate Xl Universal Testing Machine**