

**MODIFICATION OF EMULSION PAINT USING CHITOSAN-GRAFTED-
ACRYLIC ACID**

By

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DECLARATION

I declare that the work in this dissertation entitled “**MODIFICATION OF EMULSION PAINT USING CHITOSAN-GRAFTED-ACRYLIC ACID**” has been carried out by me in the Department of Textile Science and Technology. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other Institution.

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CERTIFICATION

This dissertation entitled “MODIFICATION OF EMULSION PAINT USING CHITOSAN-GRAFTED-ACRYLIC ACID” by ISAAC OLUWATOBI ABOLUDE meets the regulations governing the award of the degree of Master of Science in Colour Chemistry and Technology of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research work is dedicated to the Almighty God, my Dad, my Mum and my siblings.

ACKNOWLEDGEMENTS

I am grateful to the Almighty God the Alpha and the Omega of my life for the successful completion of my master's research project and my award of M.Sc degree honours despite all challenges. I will bless the Lord at all times: His praise shall continually be in my mouth.

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ABSTRACT

In this research, the extraction, characterization of chitin and chitosan from desert locust (*Schistocerca gregaria*) were carried out, followed by grafting of acrylic acid to chitosan which was then used as modifying additive to emulsion paint. Chemical demineralization, deproteinization and decolourization were carried out to obtain the chitin followed by deacetylation to obtain the chitosan. Acrylic acid was then grafted onto the chitosan to obtain chitosan-grafted-acrylic acid which was then used as additive to produce modified emulsion paint. The following analyses were carried out; density, solubility test, ash content, moisture content, degree of deacetylation, Fourier transformed-Infrared spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Scanning electron microscopy (SEM), viscosity, drying time, alkalinity test, crosscut test and bend test. The results obtained showed 90.06 % degree of deacetylation of the chitosan, 6.00 % moisture content of the chitosan, 2.24 % ash content of the chitosan, 81.75 % grafting percentage, 72.69 % grafting efficiency, 2360.60 cm^{-1} and 2344.61 cm^{-1} peaks are attributed to the carboxylic acid functional group which indicate the point of grafting of the acrylic acid unto the chitosan, the glass transition temperatures obtained from differential scanning calorimetry were 152.88 $^{\circ}\text{C}$, 229.63 $^{\circ}\text{C}$ and 98.53 $^{\circ}\text{C}$ for chitin, chitosan and chitosan-grafted-acrylic acid respectively. Surface morphology of the chitin shows prominent microfibrils and porous structures while erosion of some of the microfibrils and porous structure on the chitosan was observed which could be attributed to successful deacetylation of the chitin to chitosan whereas the chitosan-grafted-acrylic acid shows the coverage of the little microfibrils and porous structure. Also the overall performance of the modified paint shows increase in density, viscosity, bendability, resistance of the paint coatings to separation from substrates when the right angle lattice patterns were cut into it and decrease in the drying time,

alkalinity and the filler content. The chitosan-grafted-acrylic acid obtained was incorporated into emulsion paint; this was assessed with respect to another emulsion paint produced without chitosan-grafted-acrylic acid and a commercial paint. Tests such as drying time, density, viscosity, bend test, ash test, acidity or alkalinity test and cross-cut test were carried out and it was discovered that the paint with chitosan-grafted-acrylic acid had remarkable improvements in its properties.

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ABBREVIATIONS

ASTM	American Society for Testing and Materials
ISO	International Standard Organization
FTIR	Fourier-transformed Infrared Spectroscopy
SEM	Scanning Electron Microscopy
DSC	Differential Scanning Calorimetry

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Paint is any liquid, liquefiable, or mastic composition that, after application to a substrate in a thin layer, converts to a solid film (Obi, 2013; Ghamande *et al.*, 2016). It is most commonly used to protect, colour, or provide texture to objects. Paint can be made or purchased in many colours and in many different types, such as watercolour, synthetic, etc. Paint is typically stored, sold, and applied as a liquid, but dries into a solid (Lambourne and Strivens, 1999). In formulating paint for a particular purpose it will be essential for the formulator to know the use to which the painted article is to be put, and physical or mechanical requirements they are likely to be called for (Lambourne and Strivens, 1999). Many industrial sectors use organic solvents widely (Ridgwaya *et al.*, 2003). Nervous system damage (central and peripheral), kidney, and liver damage, adverse reproductive effects, skin lesions, and cancer, are the major health impacts associated with organic solvent exposure (*National Institute for Occupational Safety and Health*, 1977). They can also cause death from acute exposure, leading to depression of the brain's respiratory centre and/or cardiac arrhythmias. Solvents share many chemical, physical, and biological properties, which warrant that national attentions need to be directed to them as a group. In addition, many solvent groups or individual substances have special properties that require specific control measures (Jafari *et al.*, 2008).

Solvents are one of the most important components of paint and have the major purpose of reducing (thinning) paints to a suitable handling consistency or viscosity for ease of manufacture and application. After the paint has been applied, the solvent evaporates and leaves the dry paint film on the substrate. In paint production, solvents

vapours are emitted throughout the manufacturing process. If these emissions are left uncontrolled, high concentrations of organic solvents can build up in the work area, compromising workers' health and safety (Williams *et al.*, 2007).

In the living environment, sick-building syndrome is a social health problem which occurs when the quality of indoor air diminishes due to harmful substances contained in it (European Commission Joint Research Center for Environment Institute 1997). Volatile Organic Compounds (VOCs) such as formaldehyde cause sick-building syndrome because VOCs are contained in furniture and building materials (Imai and Motohashi, 2003). To combat this problem, a considerable number of studies have been done to improve indoor air quality (Uedaira *et al.*, 2003; Miyamura, 2003). In interior materials, both the decomposition of formaldehyde using photocatalysts such as titanium oxide, and decomposition using chemical means or the physical adsorption of formaldehyde, have been studied (Miggli *et al.*, 1998; Obee and Brown, 1995; Ching *et al.*, 2004; Gesser and Fu, 1990; Motohashi and Imai, 2003; Santamaria, *et al.*, 2004). Although the means for decomposing formaldehyde are effective, if sufficient ultraviolet radiation cannot be supplied throughout the indoor environment, undecomposed formaldehyde remains. In the case of physical adsorption with porous raw materials such as zeolite, diatomite, and charcoal, there is a problem in that adsorbed formaldehyde is emitted. On the other hand, chemical adsorption by reactions with formaldehyde can be efficiently removed and not re-emitted. Chemical adsorbents, however, are not sufficiently safe (Wada *et al.*, 2005).

Recently, investigations using natural raw materials as adsorbents were carried out. Among the natural raw materials, chitosan is an environmentally friendly material with many superior properties. Chitosan powder was used to inhibit the emission of formaldehyde from plywood (Sato, 1996; Sato *et al.*, 1997). Ishimaru also reported that

chitosan is effective in adsorbing formaldehyde (Ishimaru, 2001). Chitosan is a polysaccharide consisting of 2-amino-2-deoxy-D-glucopyranose as a repeating unit and is obtained by deacetylation of chitin. Chitin exists in crustacean shells, such as crabs and shrimps; in insects, such as beetles and grasshoppers; in cuttlefish bone; and in the cell walls of fungi, such as mushrooms. Compared to synthetic polymers, chitosan has several important advantages, including biocompatibility, biodegradability, and no toxicity. In addition, chitosan has reactive amino groups on pyranose rings and becomes a cationic polymer upon the protonation of its amino groups. However, chitosan simply added to waterborne coatings cannot uniformly disperse. Furthermore, when chitosan-acid solution is added to waterborne coatings using acrylic emulsions, precipitates are formed because chitosan is a cationic polymer (Wada *et al.*, 2005).

1.2 STATEMENT OF THE RESEARCH PROBLEM

Volatile organic compounds (VOCs) such as formaldehyde cause sick-building syndrome because VOCs are contained in furniture and building materials.

To the best of my knowledge, there has been no report on the production of emulsion paint obtained by incorporating a binder synthesized by grafting chitosan obtained from locust with acrylic acid to produce paint with improved properties.

1.3 AIM

The aim of this research is to produce emulsion paint with improved properties by incorporating binder obtained by grafting acrylic acid onto chitosan from desert locust.

OBJECTIVES

The specific objectives of this research include:

- i. Extraction of chitin from desert locust (*Schistocerca gregaria*)

- ii. Conversion of chitin to chitosan
- iii. Grafting of chitosan with acrylic acid through free radical mechanism in order to obtain suitable binder.
- iv. Characterization of the samples using FTIR, SEM and DSC.
- v. Production of emulsion paint with the chitosan-grafted-acrylic acid and without chitosan-grafted-acrylic acid.
- vi. Analyses of modified and unmodified emulsion paints produced and compare with commercial emulsion paint for properties such as drying time, density, viscosity, bend, ash, acidity or alkalinity and cross-cut.

1.4 JUSTIFICATION OF THE STUDY

Desert locust is generally known to be a destroyer of green plants and copolymerization of chitosan obtained from desert locust with acrylic acid for use in emulsion paint will help to create job opportunities.

1.5 SCOPE

The scope of this research is focused on the extraction and characterization of chitin and chitosan from locust, grafting of the chitosan with acrylic acid in order to obtain suitable binder, production of emulsion paint with and without the chitosan-grafted-acrylic acid and evaluation of some properties of the emulsion paints produced and compared with those of commercial emulsion paint.

CHAPTER TWO

LITERATURE REVIEW

Paint is simply a surface coating. The surface of objects left in the open bear the brunt of the sun, rain, fog, dew, ice and snow. Under these conditions iron rusts, wood rots (or shrinks and cracks) and road surfaces crack and disintegrate. Household objects suffer the wear of daily use, scratches, dents and abrasions at their surfaces.

To prevent or to minimize damage, various coatings are applied to the surfaces of these objects to protect them. Coatings can also be used to decorate articles, to add colour and lustre and to smoothen out any roughness or irregularities caused by the manufacturing process (Nkeonye, 2015).

2.1 BASIC COMPONENTS OF PAINT

2.1.1 Binder (or film former)

The binder, commonly called the vehicle, is the film-forming component of paint. The binder imparts adhesion and strongly influences properties such as gloss, durability, flexibility, and toughness.

Binders include synthetic or natural resins such as alkyds, acrylics, vinyl-acrylics, vinyl acetate/ethylene (VAE), polyurethanes, polyesters, melamine resins, epoxy, or oils. Binders can be categorized according to the mechanisms for drying or curing. Although drying may refer to evaporation of the solvent or thinner, it usually refers to oxidative cross-linking of the binders and is indistinguishable from curing. Some paints form by solvent evaporation only, but most rely on cross-linking processes (Berendsen and Berendsen, 1989; Ghamande *et al.*, 2016).

Paints that dry by solvent evaporation and contain the solid binder dissolved in a solvent are known as lacquers. A solid film forms when the solvent evaporates, and

because the film can re-dissolve in solvent, lacquers are unsuitable for applications where chemical resistance is important. The paint type known as Emulsion in the UK and Latex in the USA is a water-borne dispersion of sub-micrometre polymer particles. These terms in their respective countries cover all paints that use synthetic polymers such as acrylic, vinyl acrylic (PVA), styrene acrylic, etc., as binders (Obi, 2013).

The term “latex” in the context of paint in the USA simply means an aqueous dispersion; latex rubber from the rubber tree is not an ingredient. These dispersions are prepared by emulsion polymerization. Such paints cure by a process called coalescence where first the water, and then the trace, or coalescing, solvent, evaporate and draw together and soften the binder particles and fuse them together into irreversibly bound networked structures, so that the paint cannot redissolve in the solvent/water that originally carried it. Paints that cure by oxidative crosslinking are generally single package coatings. When applied, the exposure to oxygen in the air starts a process that crosslinks and polymerizes the binder component. Classic alkyd enamels would fall into this category. Oxidative cure coatings are catalyzed by metal complex driers such as cobalt naphthenate (Obi, 2013; Ghamande et al., 2016).

Paints that cure by polymerization are generally one or two package coatings that polymerize by way of a chemical reaction, and cure into a crosslinked film. Depending on composition they may need to dry first, by evaporation of solvent. Classic two package epoxies or polyurethanes would fall into this category (Berendsen and Berendsen, 1989).

There are paints called plastisols/organosols, which are made by blending PVC granules with a plasticiser. These are stove and the mix coalesces. Other films are formed by cooling of the binder. For example, encaustic or wax paints are liquid when warm, and harden upon cooling. In many cases, they resoften or liquify if reheated.

Recent environmental requirements restrict the use of volatile organic compounds (VOCs), and alternative means of curing have been developed, particularly for industrial purposes. In UV curing paints, the solvent is evaporated first, and hardening is then initiated by ultraviolet light. In powder coatings there is little or no solvent, and flow and cure are produced by heating of the substrate after electrostatic application of the dry powder (Obi, 2013; Ghamande *et al.*, 2016).

2.1.2 Diluent or Solvent

The main purposes of the diluents are to dissolve the polymer and adjust the viscosity of the paint. It is volatile and does not become part of the paint film. It also controls flow and application properties, and in some cases can affect the stability of the paint while in liquid state. Its main function is as the carrier for the non volatile components. To spread heavier oils (for example, linseed) as in oil-based interior house paint, a thinner oil is required. These volatile substances impart their properties temporarily - once the solvent has evaporated, the remaining paint is fixed to the surface. This component is optional: some paints have no diluent. Water is the main diluent for water-borne paints, even the co-solvent types. Solvent-borne, also called oil-based, paints can have various combinations of organic solvents as the diluent, including aliphatics, aromatics, ketones, alcohols and white spirit. Specific examples are organic solvents such as petroleum distillate, esters, glycol ethers, and the likes. Sometimes volatile low-molecular weight synthetic resins also serve as diluents (Lambourne and Strivens, 1999; Ghamande *et al.*, 2016).

2.1.3 Pigment and Filler

Pigments are granular solids incorporated in the paint to contribute colour. Fillers are granular solids incorporated to impart toughness, texture, give the paint special

properties, or to reduce the cost of the paint. Alternatively, some paints contain dyes instead of or in combination with pigments.

Pigments can be classified as either natural or synthetic. Natural pigments include various clays, calcium carbonate, mica, silicas, and talcs. Synthetics would include engineered molecules, calcined clays, blanc fixe, precipitated calcium carbonate, and synthetic pyrogenic silicas.

Hiding pigments are used in making paint opaque, also protect the substrate from the harmful effects of ultraviolet light. Hiding pigments include titanium dioxide, phthalo blue, red iron oxide, and many others.

Fillers are special types of pigments that serve to thicken the film, support its structure and increase the volume of the paint. Fillers are usually cheap and inert materials, such as diatomaceous earth, talc, lime, barytes, clay, etc. Floor paints that must resist abrasion may contain fine quartz sand as a filler. Not all paints include fillers. On the other hand, some paints contain large proportions of pigment/filler and binder.

Some pigments are toxic, such as the lead pigments that are used in lead paint. Paint manufacturers began replacing white lead pigments with titanium white (titanium dioxide), before lead was banned in paint for residential use in 1978 by the US Consumer Product Safety Commission. The titanium dioxide used in most paints today is often coated with silica/alumina/zirconium for various reasons, such as better exterior durability, or better hiding performance (opacity) promoted by more optimal spacing within the paint film (Ghamande *et al.*, 2016).

2.1.4 Additives

Besides the three main categories of ingredients, paint can have a wide variety of miscellaneous additives, which are usually added in small amounts, yet provide a significant effect on the product. Some examples include additives to modify surface tension, improve flow properties, improve the finished appearance, increase wet edge, improve pigment stability, impart antifreeze properties, control foaming, control skinning, etc. Other types of additives include catalysts, thickeners, stabilizers, emulsifiers, texturizers, adhesion promoters, UV stabilizers, flatteners (de-glossing agents), biocides to fight bacterial growth, and the likes.

Additives normally do not significantly alter the percentages of individual components in a formulation (Obi, 2013).

2.2 QUALITIES OF PAINT

The qualities of paint are determined by the following:

2.2.1 Hiding

This refers to the ability of the paint to cover the substrate so as to prevent light striking the film from reaching the substrate. It is only white paint that possesses this capacity. White hiding is the principal kind of hiding in paint for which reason even coloured paint usually contain much white pigment. The pigment has to possess a high refractive index in order to be considered as good hiding substance. A very efficient substance is titanium dioxide. It has a very high refractive index giving it exceptional ability to bend light incident on the surface so as to prevent it from reaching the substrate more efficiently than most other pigments characterized by low refractive indices (Turner, 1980).

2.2.2 Appearance

A paint must hide the substrate and be applied to produce a uniform film in terms of appearance. Architecturally, pleasing paint appearances is achieved with colour and with uniformity in terms of gloss and shine; i.e. be characterized by low angle of gloss. In general, the lower the gloss of a paint, the easier it is to produce gloss uniformity. It is important to note that gloss changes rapidly with effective pigment volume concentration to critical pigment volume concentration (pvc:cpvc) ratio. The effective pvc:cpvc ratio is affected by the slow wetting action of the vehicle on the pigment. Pigment agglomerates are gradually wetted in their interstices on the vehicle and are gradually dispersed. The primary particles size of pigment particularly the extenders, is important, the smaller the primary particle size, the less the effect on gloss at the same pvc:cpvc ratio (Turner, 1980).

2.3 CLASSIFICATION OF PAINTS

Paints are classified depending on whether they are thinned in an organic solvent or dispersed in water.

2.3.1 Water-thinned Paints

These are based on latex vehicle, which are discrete, small particles of polymer suspended in water. They are formed by emulsion polymerization i.e., introducing a liquor polymer within small droplets. Popular lattices in use in paint formulations include polyvinyl acetate (PVAc), acrylics and vinyl acrylics (Career Projector, 2000).

2.3.1.1 Formulation

There are many latex polymers used where surfactant protective colloids are used to stabilize them. However, they adversely affect the performance of the lattices in a paint formula. The pigment is selected for proper hiding, colour and gloss. They are dispersed in water before the latex is added and surfactants are chosen to plasticize the latex temporarily during film formulation so that the latex particles coalesce. However, since water is not very viscose, the paint may be thickened with additives to promote the suspension of the pigment during storage, proper rheology for application and flow without sagging. An example of formulation that can be used for the paint is as shown below in Table 2.3.1.

Table 2.3.1: A typical emulsion paint

Chemical	Formulation (Kg)
Water	2.60
Titanium dioxide	0.20
Aluminium silicate	0.05
Ammonia liquor	0.02
Kaolin	0.17
Calcium carbonate	3.00
Defoamer	0.02
Kerosene	0.078
PVAc	0.45

2.3.2 Alkyd Paints (Gloss or Oil paints)

There are several requirements for exterior and architectural paints, which are not required for interior paints. The principal ones are that the paints must be more protective of the substrate in a more hostile atmosphere; the film must be more impermeable to moisture and must be resistant to mildew growth, fungal and bacterial

attack. These requirements and others are satisfied by alkyd paints and paints made by the combination of alkyds and latex paints at a given ratio (David, 1967).

Alkyd paints are satisfactory and often are preferred for use on problem free structures. The volume of solids in alkyds paint is greater than in latex paints. This is estimated at 50-60% volume of solids. Normally, alkyd paints are less permeable to moisture, thus offering better protection to the substrate. The higher solid contents of alkyd paints are advantageous against erosion by uv-degradation, wind and room. Alkyd paints are oil-based paints; the oils used are bleached linseed oil, dehydrated castor oil and soya bean oil. Because oil dries too slowly, alkyd paints need a drying agent usually naphthanates of magnesium, Zinc and cobalt with those of calcium as catalyst.

Glossy agents are used in alkyd paints formulation. Anti-freeze agents are not used because oil does not usually freeze. Mineral spirits are the thinners in alkyd paints.

2.3.2.1 Formulation

The principal ingredient of the alkyd paints is the alkyd resin. An alkyd resin is the reaction product of polybasic and a polyhydric alcohol, e.g., glycerol. In paints, alkyd resins usually contain a monobasic fatty acid e.g., Linseed or fatty acids. Polymerization proceeds by way of fatty acids, which are available in numerous molecular weight distributions.

Alkyd paints contain the following components, binder (alkyd resin), thinner (white spirit xylene), vehicles, pigment (various types), thickeners (oils or alkyds, leaded oils, amide-modified alkyds, amine-modified clays), driers (cobalt, calcium zirconium), dispersing agents, anti-skinning agents and stabilizers as shown in Table 2.3.2.

Table 2.3.2: Typical alkyd paint formulation.

Component	Formulation (Kg)
Lwd Lecithin	14.28
50% gloss alkyd	480
Titanium dioxide	165
Calcium carbonate	250
Mineral spirit	243.48
65 Calcium	9.24
Bentone	2.29
75% gloss alkyd	380.00
12% Cobalt	2.25
Zirconium	7.00
Anti-Skin agent (ASA)	1.75
21 butyl acrylate (BA)	220.80
Water	340

2.4 METHODS OF APPLICATION OF PAINTS

There are four main methods of applying paint:

- i. by spreading, e.g. by brush, roller, paint pad, or doctor blade;
- ii. by spraying, e.g. air-fed spray, airless spray, hot spray, and electrostatic spray;
- iii. by flow coating, e.g. dipping, curtain coating, roller coating, and reverse roller coating;
- iv. by electrodeposition.

The methods adopted depend on the market in which the paint is used, each type of paint being formulated to meet the needs of the application method. Spreading by brush or hand-held roller is the main method for applying decorative/architectural paints and the maintenance of structural steelwork and buildings generally. It is also important in marine maintenance, although other methods (e.g. airless spray) may be used during the construction of a ship.

Application by spraying is the most widely method. It is used for painting motor cars in the factory and by refinishers following accident damage; it is used in the wood-finishing industries (e.g. furniture) and in general industrial paints (e.g. domestic appliances). The various forms of spray painting make it a particularly versatile method of application. The flow coating methods are limited essentially to flat stock (e.g. chipboard) and coil coating (aluminium or steel coil) where they are much valued because of the high rates of finishing that can be achieved.

Electrodeposition has become established as the main method of priming the steel body shells of motor cars. The total process which involves degreasing, phosphate treatment, electrodeposition of primer, and then spray application of surfacer and finishing coats has raised the standards of corrosion resistance and general appearance considerably during this period. Electrodeposition may take place with the car body acting as either the anode or the cathode. In recent years it has been claimed that cathodic forms of electropaint give better corrosion protection.

Mainly because of environmental considerations, powder coating has been a major growth area in industrial finishing, particularly in Western Europe, which produced 53% of the total world market for powder coatings in 1993. Powder coatings are normally applied by electrostatic spray, with minimal overspray losses and without the emission of VOCs (Lambourne and Strivens, 1999).

2.5 DRYING OF PAINTS

Drying of paints does not simply involve evaporation of volatile liquid. There are three broad mechanisms, two of which involve chemical reactions while the other is a physical process (Wyszecki and Stiles, 1967).

2.5.1 Drying without Chemical Reaction

The paint here simply dries by evaporation of the liquid. The polymer film is fully formed in the paint container and when free of solvent it becomes relatively hard and sticky during the drying process.

2.5.2 Drying by Chemical Reaction

By chemical reactivity essentially by cross-linking paints dry-up in two types of ways:

2.5.2.1 Reaction between Paint and Air

Water vapour and oxygen are reactive chemicals in paint drying. Oxygen in air reacts with drying oils and other unsaturated compounds to produce free radicals, which brings about polymerization. This reaction gives a cross-linked film. Exterior oils derived from drying oils dry by reaction with the air.

2.5.2.2 Reaction between Ingredients in the Paint

The paints must remain chemically stable and although the reactants must be in the paint, no reaction must occur until the paint has been applied. This is made possible either by separating the reactive ingredients in two or more containers and mixing just before use or by choosing ingredients which only reacts at higher temperature or when exposed to radiation e.g., industrial stoving enamels and polyester wood finishes.

2.6 ACRYLIC POLYMERS

Acrylic polymers are widely used for their excellent properties of clarity, strength, chemical and weather resistance. The term acrylic has come to represent those polymers containing acrylate and methacrylate esters in their structure along with certain other vinyl unsaturated compounds. Both thermoplastic and thermosetting systems are possible, the latter formulated to include monomers possessing additional functional groups that can further react to give crosslinks following the for-

mation of the initial polymer structure. Vinyl/acrylic polymerization is particularly versatile, in that possibilities are far wider than in condensation polymerization, of controlling polymer architecture and in introducing special features; for example, by using modification stages following the initial formation (Lambourne and Strivens, 1999).

2.7 CHITIN

Chitin, found in arthropods (insects, crustaceans, arachnids and myriapods), is the second most abundant biopolymer after cellulose (Rudall and Kenchington, 1973). Chitin is structurally similar to cellulose, but it is an amino polysaccharide having acetamide groups at the C-2 positions in place of hydroxyl groups *i.e.*, β -(1,4)-2-acetamido-2-deoxy-D-glucose. In addition to its unique polysaccharide architecture, the presence of amino groups in chitin is highly advantageous for providing distinctive biological functions and for conducting modification reactions. Chitin is thus expected to have a much higher potential than cellulose in many fields. It is a specialty biopolymer having specific properties including biodegradability, biocompatibility, and bioactivity, and it is therefore interesting not only as an abundant resource but also as a novel type of functional material (Muzzarelli, 1977; Shaofang *et al.*, 2012). Chitin is classified into three types according to the different orientations of its microfibrils: α -chitin (anti-parallel chains), β -chitin (parallel chains), and γ -chitin (the combination of parallel and anti-parallel chains) (Rudall and Kenchington, 1973; Shaofang *et al.*, 2012). The amount of chitin in animal and fungi is specific to species, age and environmental conditions where the organism exists (Ashford *et al.*, 1977). Chitin is insoluble in most solvents because of its compact structure. Therefore, chemical modifications of chitin are performed to obtain more soluble analogs, among which, chitosan, derived by partial N-deacetylation of chitin, is the most common of such

derivatives.

Since they are versatile biopolymers, their potential applications in various industrial fields are being actively investigated. For example, chitin and chitosan have been documented to be useful as antimicrobial, emulsifying, thickening and stabilizing agents in the food industry (Shahidi *et al.*, 1999). They have also shown notable bioactivity in biomedical fields, including wound healing promotion, immune system enhancement, and hemostatic, hypolipidemic and antimicrobial activity (Shahidi *et al.*, 1999; Ong *et al.*, 2008).

Traditionally, chitin is obtained mainly from crab and shrimp shells present as byproducts in the seafood industry. Chitin is also a primary component in insect cuticles. Therefore, insects are an alternative source of chitin and, consequently, of chitosan. Recently, the production of chitin and chitosan from insect sources has drawn increased attention. First, insects possess enormous biodiversity and represent 95 % of the animal kingdom (Labandeira and Sepkowski 1993). Therefore, they offer a tremendous potential as a natural resource for chitin and chitosan production. Furthermore, insect cuticles have lower levels of inorganic material compared to crustacean shells, which makes their demineralization treatment more convenient (Zhang *et al.*, 2000). Chitin in crustacean cuticles is tightly associated with inorganic salts such as calcium carbonate, and also associated with proteins and lipids, including pigments (Kim, 2010). Generally, the shell of selected crustacean consists of 30-40 % protein, 30-50 % calcium carbonate and calcium phosphate, and 20-30 % chitin (Fernandez-Kim, 2004).

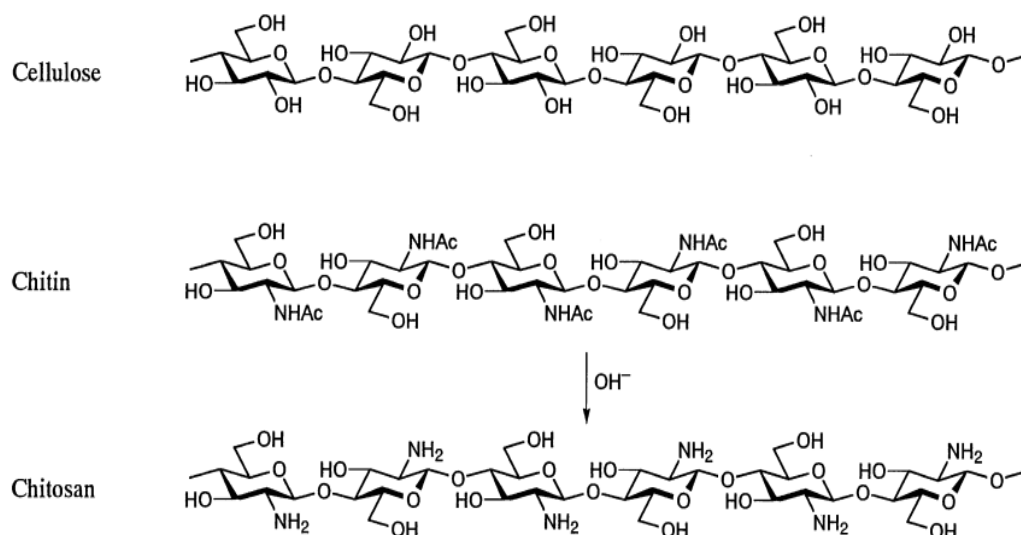


Figure 2.7: Structural differences between Cellulose, Chitin and Chitosan

2.7.1 Chitin Extraction

Chitin is a major component of the insect cuticle, which is always covalently bound to catechol compounds and sclerotin-like proteins (Zhang *et al.*, 2000). The most common method for chitin extraction from insects involves two steps, an acidic step to remove catechols and a basic step to remove the cuticle proteins, as had been mentioned elsewhere for insect chitin isolation (Labandeira *et al.*, 1993; Zhang *et al.*, 2000). Generally, the acidic treatment conditions used for extraction from insects are moderate in comparison to crustacean exoskeletons. The reason for this is that insects have low levels of inorganic material (less than 10 %) as compared to crustacean shells (20-40 %) (Tolaimate *et al.*, 2003; Verkerk *et al.*, 2007)

The ash content of chitin is indicative of the effectiveness of the method used for removal of inorganic materials.

2.7.2 Demineralization

Demineralization is usually accomplished by extraction with dilute hydrochloric acid (up to 10 %) at room temperature with agitation to dissolve calcium carbonate as calcium chloride. A wide variation of the demineralization process has been reported in the literature. The use of HCl at higher concentration and also 90 % formic acid to achieve demineralization has been reported. Optimum demineralization is achieved by constant stirring of the dried ground crawfish shell with 1 N HCl for 30 min at ambient temperature and a solid to solvent ratio of 1: 15 (w/v) (No et al., 1989). The ash content of the demineralized shell is an indicator of the effectiveness of the demineralization process. Elimination of the demineralization resulted in products having 31-36 % ash.

During the demineralization process excessive undesirable foams are produced due to the CO₂ generation ($\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 (\uparrow) + \text{H}_2\text{O}$). To control or reduce the foam, No and Hur, (1998) recommended the use of commercial antifoam comprising of 10 % solution of active silicone polymer without an emulsifier. They also demonstrated that at 1.0 ml of antifoam /L of 1 N HCl, the performance of antifoam is more efficient during demineralization with smaller shell particle size (<0.425 mm and under a slightly faster stirring speed at 300 rpm). Furthermore, they recommended that deproteinization followed by demineralization is a favourable sequence in terms of the amount of antifoam required to control foaming (Fernandez-Kim, 2004).

2.7.3 Deproteinization of Chitin

Chitin occurs naturally in association with protein (Chitinoprotein). Some of this protein can be extracted by mild methods, but other portion is not readily extracted, suggesting strong covalent bonding to chitin (Attwood and Zola, 1967). With regards to chemical structure, protein is bound by covalent bonds to the chitin through aspartyl or

histidyl residues, or both, thus forming stable complexes such as glycoproteins.

Deproteinization breaks the covalent bonds between chitin and protein linkages by using NaOH. A 1 M aqueous solution of NaOH is the common solution for the deproteinization of chitin. NaOH, however, results in partial deacetylation of chitin and hydrolysis of the biopolymer that lowers the molecular weight of chitin (Brine and Austin, 1981).

During the deproteinization process, foam formation can occur, but the foam is not as brisk and intense as that produced during demineralization. Shahidi and Synowiecki (1991) suggested that optimal deproteinization can be achieved using dilute potassium hydroxide solution. Generally, if maximizing protein yield and quality is the objective, then protein extraction before demineralization is recommended (Johnson and Peniston, 1982) or the pH of the aqueous solution must be reduced to the isoelectric point of protein for precipitation (Green and Mattick, 1979).

2.8 CRYSTALLINE STRUCTURE OF CHITIN

Chitin is a linear, high molecular weight, crystalline polysaccharide consisting of β -(1 \rightarrow 4) linked N-acetyl-D-glucosamine, just as cellulose is made up of β -(1 \rightarrow 4) linked D-glucose. Three crystalline forms are known for chitin: α -, β -, and γ -chitins. The most abundant and easily accessible form is α -chitin, where the molecules are aligned in an antiparallel fashion as disclosed by X-ray diffraction studies (Blackwell *et al.*, 1980; Minke and Blackwell, 1978). This molecular arrangement is favourable for the formation of strong intermolecular hydrogen bonding, and α -chitin is the most stable form of the three crystalline variations.

In β -chitin, the molecules are packed in a parallel arrangement, leading to weaker intermolecular forces (Blackwell *et al.*, 1980; Gardner and Blackwell, 1975; Mazeau *et*

al., 1994). β -chitin is thus assumed to be less stable than α -chitin, and its structural characteristics are being studied in detail. On dissolution or extensive swelling, β -chitin converts to α -chitin, but not in the reverse way, suggesting that β -chitin is a metastable entity biosynthesized by a specific mechanism different from the ordinary mechanism leading to α -chitin (Rudall and Kenchington, 1973). Even aqueous hydrochloric acid causes the solid state transformation of β -chitin into α -chitin. Morphological and crystallographic observations revealed that the intercrystalline transformation was dependent on the acid concentration employed (Saito *et al.*, 1997).

Compared to the α - and β -chitins, γ -chitin is found less commonly. It is considered to be a mixture (or an intermediate form) of the α - and β -forms and has both parallel and antiparallel arrangements.

2.9 DEACETYLATION OF CHITIN TO CHITOSAN

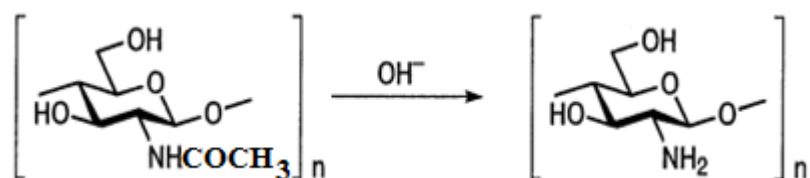


Figure 2.9: Scheme for the deacetylation of Chitin to Chitosan

The N-acetyl groups of chitin can be removed by alkaline hydrolysis under heterogeneous conditions (Fig. 3). Deacetylation is effected by heating a suspension of α -chitin flakes (or powders) in strong aqueous bases such as sodium and potassium hydroxides at 100-160 °C to give chitosan with a degree of deacetylation between 0.70 and 0.95. The extent of deacetylation does not increase much after a few hours. To attain complete deacetylation, it is necessary to isolate chitosan and treat it with alkali in the same manner repeatedly (Mirna *et al.*, 1983). During the deacetylation process,

however, degradation of the main chain occurs as shown by a considerable decrease in the molecular weight. For example, number average molecular weights of the products obtained by the treatment of chitin with 50 % NaOH at 100 °C for 0.5 and 5 hr were 322 and 139 X 10³, respectively (Wu and Bough, 1978).

2.10 CHEMISTRY AND PROPERTIES OF CHITOSAN

2.10.1 Characteristics of Chitosan

Chitosan is a non-toxic, biodegradable polymer of high molecular weight, and is very much similar to cellulose, a plant fibre. One difference between chitosan and cellulose is the amine (-NH₂) group instead of the (-OH) group found in cellulose (Rinaudo, 2006). However, unlike plant fibre, chitosan possesses positive ionic charges, which gives it the ability to chemically bind with negatively charged fats, lipids and cholesterol, metal ions, proteins, and macromolecules. In this respect, chitin and chitosan have attained increasing commercial interest as suitable resource materials due to their excellent properties including biocompatibility, biodegradability, adsorption, and ability to form films, and to chelate metal ions (Fernandez-Kim, 2004). Chitosan can be moulded into different forms. One form is chitosan nanoparticles of size in the range of 200-1000 nm. Many researchers concentrated in the area of chitosan nanoparticle for different applications mainly in the medical field as drug carrier (Sonia and Sharma, 2011). Chitosan nanoparticles can be prepared by different methods like freeze drying, multiple emulsion/solvent evaporation and ionic gelation method. From these methods ionic gelation is the best one for chitosan (Dustgania *et al.*, 2008).

2.10.2 Determination of the Degree of Deacetylation (DD)

Deacetylation simply means the removal of acetyl groups from the molecular chain of chitin, leaving behind a compound (chitosan) with a high degree of chemical reactive amino group (NH₂). This makes the degree of deacetylation (DD) an important property in chitosan production as it affects the physiochemical properties, hence determines its appropriate applications. There is yet to be a difference between chitin and chitosan based on the degree of N-deacetylation. In any case, the degree of deacetylation can be employed to differentiate between chitin and chitosan because it determines the content of free amino groups in the polysaccharides. Evidences have been given suggesting that approximately one in every six to seven residues in the chitosan polymer chain has a proportion of free amino groups that manifests some histochemical properties (Kalut, 2008).

There are two advantages of chitosan over chitin. The first being that in order to dissolve chitin, highly toxic solvents such as lithium chloride and dimethylacetamide are used whereas chitosan is readily dissolved in diluted acetic acid. The second advantage is that chitosan possesses free amine groups which are an active site in many chemical reactions (Fernandez-Kim, 2004).

Many methods have been reported for assessing the degree of deacetylation including elemental analysis, hydrolysis of acetamide groups, titration of free amino groups, dye adsorption, spectroscopic techniques such as IR, UV, and NMR, enzymatic degradation, and pyrolysis. The merits and drawbacks of these methods have been discussed (Kurita, 1997; Davies and Hayes, 1988; Roberts, 1997; Muzzarelli, 1997; Roberts, 1992). For practical use, titration of liberated acetic acid by hydrolysis (Sannan *et al.*, 1976), colloid titration with a polyanion (Terayama, 1952) and conductometric titration (Kurita *et al.*, 1989; Raymond *et al.*, 1993) are relatively reliable and easy.

Compared to the other methods reported, IR spectroscopy is a convenient way for determining the degree of deacetylation quickly, but care should be taken to establish reproducibility. For IR spectroscopic determination, the absorbance ratio of A_{1550}/A_{2878} based on the base line method was first examined (Sannan *et al.*, 1978), but several modifications have also been reported. Other absorbance ratios include A_{1655}/A_{3450} (Moore and Roberts, 1980; Domszy and Roberts, 1985; Domard, 1987; Baxter *et al.*, 1992), $(A_{1655}/A_{3450} + A_{1655}/A_{3450})$ (Shigemasa *et al.*, 1994), and A_{1655}/A_{2867} (Miya *et al.*, 1980; Aiba, 1986). Near IR spectroscopy is also a simple way to determine the degree of deacetylation of chitin and chitosan as well as the monomer sugar ratios in the mixture of N-acetyl-D-glucosamine and D-glucosamine (Rathke and Hudson, 1993). For water-soluble chitin (partially deacetylated chitin) and chitosan, ^1H NMR can be used in D_2O (Varum *et al.*, 1991) and $\text{CD}_3\text{CO}_2\text{D}/\text{D}_2\text{O}$ (Hirai *et al.*, 1991), respectively. Solid state ^{13}C NMR (Pelletier *et al.*, 1990; Li *et al.*, 1997) and ^{15}N NMR (Yu *et al.*, 1999) were recently proposed for the determination of acetyl contents in these materials.

2.10.3 Viscosity

Chitosan has the ability to form viscous solutions in various organic acids. These viscous solutions have been used to make functional films (Park *et al.*, 2002). Viscosity is a very important factor in the determination of molecular weight of chitosan and in determining its commercial applications in complex biological environments such as in the food system (Fernandez-Kim, 2004). Polymers dissolved in solution may have polymer-solvent interactions, and can result in an increase in viscosity. The viscosity of polymers is dependent on molecular weight (MW). The higher the MW of polymer, the more viscous the polymer solution will be (Fung, 2007).

Some factors during processing such as the degree of deacetylation, molecular weight, concentration of solution, ionic strength, pH, and temperature affect the production of chitosan and its properties. Viscosity of chitosan in acetic acid tends to increase with decreasing pH but decrease with decreasing 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. It was found that deproteinization with 3 % NaOH and elimination of the demineralization process in the chitin preparation decreases the viscosity of the final chitosan products. It was also stated that it is not desirable to bleach the material (i.e., bleaching with acetone or sodium hypochlorite) at any stage since bleaching considerably reduces the viscosity of the final chitosan product. Similarly, it was demonstrated that chitosan viscosity is considerably affected by physical (grinding, heating, autoclaving, ultra sonication) and chemical (ozone) treatments, except for freezing, and decreases with an increase in treatment time and temperature. Chitosan solution stored at 4 °C was found to be relatively stable from a viscosity point of view. It was also reported that smaller particle size (1 mm) results in chitosan products of both higher viscosity and molecular weight than those of either 2 or 6.4 mm particle size (Fernandez-Kim, 2004).

It was also reported that when a polymer has a higher MW, it has a bigger hydrodynamic volume, that is, the volume of a polymer coil when it is in solution. The solvent molecules will be bound more strongly to the polymer with increasing hydrodynamic volume, leading to a decrease in the motion of the polymer in the solvent. Hence, the viscosity of a polymer solution is proportional to the MW of the polymer. Therefore, by measuring the viscosity of a polymer solution, the molecular weight of the polymer can be conveniently determined (Fung, 2007).

2.10.4 Solubility

Chitosan contains amino groups with a pKa value of 6.2-7, and it is considered a strong base (Fernandez-Kim, 2004). While chitin is insoluble in most organic solvents, chitosan is readily soluble in dilute acidic solutions below pH 6.0. Organic acids such as acetic, formic, and lactic acids are used for dissolving chitosan. The most commonly used is 1 % acetic acid solution at about pH 4.0 as a reference. Chitosan is also soluble in 1 % hydrochloric acid but insoluble in hydrogen tetraoxosulphate (VI) acid and phosphoric acids. Solubility of chitosan in organic acid is quite limited. Concentrated acetic acid solutions at high temperature can cause depolymerisation of chitosan. Above pH 7.0 the stability of chitosan solubility is poor. At higher pH, precipitation or gelation tends to occur and the chitosan solution forms poly-ion complex with anionic hydrocolloid resulting in the formation (Kurita, 1998). The concentration ratio between chitosan and acid is of great importance to impart desired functionality. At concentrations as high as 50 % organic solvent, chitosan still works as a viscosifier causing the solution to remain smooth. There are several critical factors affecting chitosan solubility including temperature and time of deacetylation, alkali concentration, and prior treatments applied to chitin isolation, ratio of chitin to alkali solution, and particle size.

The solubility, however, is controlled by the degree of deacetylation and it is estimated that deacetylation must be at least 85 % complete in order to achieve the desired solubility. The acid-soluble chitosan with >95 % solubility in 1 % acetic acid at a 0.5 % concentration could be obtained by treatment of the original chitin with 45 - 50 % NaOH for 10-30 min. Chitosan treatment with 45 % NaOH for only 5min, and/or with 40 % NaOH for 30 min, were not deacetylated sufficiently to be soluble in 1 % acetic acid. Insoluble particles were found in both solutions (Fernandez-Kim, 2004).

2.10.5 Emulsification

Even though chitosan alone does not produce emulsions, report has shown that emulsifying capacity of egg yolk increased with the addition of chitosan compared with the control. At 0.5 % chitosan concentration, better emulsifying capacity was observed compared with at 0.1 or 0.3 % chitosan. In general, chitosan emulsions tend to be very stable under temperature changes and ageing. With viscosity, the degree of deacetylation was reported to be a determining factor in the emulsification property of chitosan. The protein solution containing chitosan with intermediate DD produces less effective emulsion compared with that containing chitosan with higher DD. The optimum chitosan DD for sunflower emulsification is 89 (Fernandez-Kim, 2004).

2.10.6 Crystalline Structure of Chitosan

Chitosan is also crystalline and shows polymorphism depending on its physical state. The structures for various forms including an anhydrous form, a hydrated form, and various salts were recently refined by X-ray diffraction analyses (Yui *et al.*, 1994; Okuyama *et al.*, 1997).

2.11 ASH CONTENT

Ash measurement is an indicator of the effectiveness of the demineralization (DM) step for removal of calcium carbonate. Elimination of the demineralization resulted in products having 31 – 36 % ash (Bough *et al.*, 1978). The ash content in chitosan is an important parameter. Some residual ash of chitosans may affect their solubility, consequently contributing to lower viscosity, or can affect other more important characteristics of the final product. A high quality grade of chitosan should have less than 1 % of ash content (No and Meyers, 1995).

2.12 APPLICATIONS OF CHITOSAN

The poor solubility of chitin is the major limiting factor in its utilization. Chitosan is considered as a potential polysaccharide because of its free amino groups that contribute polycationic, chelating, and dispersion forming properties along with ready solubility in dilute acetic acid. Chitosan possesses exceptional chemical and biological qualities that can be used in a wide variety of industrial and medical applications. Some of these are listed below (Table 2.13) (Knorr, 1984; Muzzarelli, 1977).

2.12.1 In the Wastewater Treatment

The prime commercial applications for chitosan currently is in industrial wastewater treatment since chitosan carries a partial positive charge and binds to metal ions, thus makes the metal ions removal from waste streams or contamination sites easier (Asano *et al.*, 1978). In terms of utilization, crawfish chitosan as a coagulant for recovery of organic compounds in wastewater was demonstrated to be equivalent or superior to, the commercial chitosans from shrimp and crab waste shell and synthetic polyelectrolytes in turbidity reduction (No and Meyers, 1992).

Table 2.12: Applications of Chitosan

Wastewater Treatment	Removal of metal ions, flocculant/coagulant, protein, dye, amino acids
Food Industry	Removal of dye, suspended solids, preservative, colour stabilization, food stabilizer, thickener and gelling agent, animal feed additive, etc.
Medical	Wound and bone healing, blood cholesterol control, skin burn, contact lens, surgical sutures, dental plaque inhibition, clotting agent, etc.
Agriculture	Seed coating, fertilizer, controlled agrochemical release
Cosmetics	Moisturizer, face, hand, and body creams, bath lotion, etc.
Biotechnology	Enzyme immobilization, protein separation, cell recovery, chromatography

2.13 GRAFTING ONTO CHITOSAN

Graft copolymerizations onto chitosan have also been attempted by various methods, but it is performed typically with 2,2'-azobisisobutyronitrile, Ce(IV), or a redox system. Graft copolymers are synthesized to improve physicochemical properties of synthetic/natural polymers for applications in agriculture, biomedicine and other fields. Different studies have been published on the graft copolymerization of chitosan with various vinyl monomers like acrylonitrile, methyl methacrylate, acrylamide, acrylic acid, using cerium ammonium nitrate as redox initiators (Pati and Nayak, 2011). Also, vinyl monomers such as acrylonitrile, methyl methacrylate, methyl acrylate, and vinyl acetate were graft-copolymerized onto chitosan with 2,2'-azobisisobutyronitrile in aqueous acetic acid solutions or in aqueous suspensions. The grafting percentages were generally low. Grafting vinyl monomers onto chitosan (Jenkins and Hudson, 2011; Don *et al.*, 2002) is one of the most effective methods to improve the performances of chitosan without sacrificing its properties and also is a challenging field of research with unlimited future prospects. Vinyl graft copolymerization can be described as the modification of a preexisting polymer chain (trunk polymer) (Pati and Nayak, 2012). The chitosan-graft-poly(vinyl acetate) was converted into chitosan-graft-poly(vinyl alcohol) by hydrolysis (Blair *et al.*, 1987). Ce(IV) is also a suitable initiator, and polyacrylamide, poly(acrylic acid), and poly(4-vinylpyridine) were introduced into chitosan (Caner *et al.*, 1998). Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) as a redox initiator graft-copolymerized methyl methacrylate. The grafting percentage and grafting efficiency were up to 66 % and 72 % (Lagos and Reyes, 1988). Although chitosan is an effective flocculating agent only in acidic media, the derivatives having side chain carboxyl groups showed zwitterionic characteristics with high flocculation abilities in both acidic and basic media.

2.14 GRAFT COPOLYMERIZATION

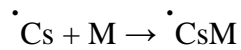
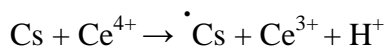
Chemical modifications will open ways to various utilizations of polysaccharides, of possible use is graft copolymerization anticipated to be quite promising for developing sophisticated functions; it would enable a wide variety of molecular designs to afford novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers (Yoshikawa *et al.*, 1998; Retuert and Yazdani, 1993). Graft copolymerization of synthetic polymers onto chitosan can introduce desired properties and enlarge the field of the potential applications by choosing various types of side chains. In recent years, a number of initiator systems such as, ammonium persulfate (APS), potassium persulfate (PPS), ceric ammonium nitrate (CAN), thiocarbonation-potassium bromate (TCPB), potassium diperiodatocuprate (III) (PDC), 2,2'-azobisisobutyronitrile (AIBN) and ferrous ammonium sulfate (FAS) have been developed to initiate graft copolymerization (Caner *et al.*, 1998; Don *et al.*, 2002; Kim *et al.*, 2000; Pedram *et al.*, 2000; Blair *et al.*, 1987). It is also reported that graft copolymerization is initiated by γ -irradiation and enzymes. The grafting parameters such as grafting percentage and grafting efficiency are greatly influenced by type and concentration of initiator, monomer concentration, reaction temperature and time. The properties of the resulting graft copolymers are widely controlled by the characteristics of the side chains, including molecular structure, length, and number. Till today, a number of research works have been done to study the effects of these variables on the grafting parameters and the properties of grafted chitosan polymers (Sun *et al.*, 2003; Xie *et al.*, 2002; Don *et al.*, 2002; Kim *et al.*, 2000; Pedram *et al.*, 2000; Blair *et al.*, 1987).

Graft copolymerization of vinyl monomers onto chitosan is also carried out using redox initiator systems, such as CAN and PPS. These systems have been used to

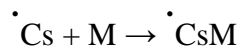
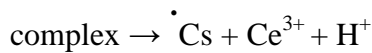
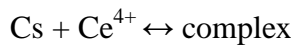
produce free radical sites on many kinds of polymers. Poly(vinyl acetate) (PVAc) is known as a leathery and water-resistant polymer, which may improve the properties of chitosan material and hence the graft polymerization of vinyl acetate onto the chitosan at 60 °C by using CAN as an initiator was reported (Don *et al.*, 2002). The reaction mechanism is following:

1. Initiation

(1) Direct oxidation

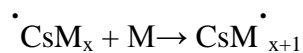
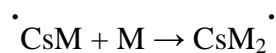


(2) Formation of complex



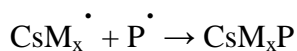
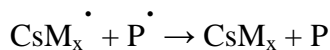
Where Cs is a chitosan chain; Ce^{4+} and Ce^{3+} , ceric and cerous ions, respectively; $\dot{\text{C}}\text{s}$, a chitosan chain radical; and M, the vinyl acetate monomer.

2. Propagation



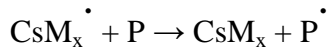
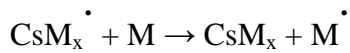
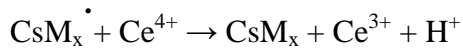
Where $\text{CsM}_x \dot{}$ is a propagating PVAc chain grafted onto the chitosan.

3. Termination



Where $\dot{\text{P}}$ indicates all the propagating polymer chains, $\dot{\text{P}} = \text{CsM}_x \dot{} + \text{M}_x \dot{}$, and $\text{M}_x \dot{}$ is the PVAc chain radical; CsM_x , CsM_xP , and P are all dead polymers.

4. Chain transfer



The monomer conversion was found to be between 70 and 80 % after 2 hr of reaction at 60 °C. The grafting efficiency increased with increasing amount of chitosan. The experimental results indicated that the chitosan molecules not only took part in the graft copolymerization but also used as a surfactant, providing the stability of the dispersed particles. The DSC and TGA results showed that the samples underwent oxidative degradation by the residual CAN at temperatures above 200 °C. The experimental results also showed that the incorporation of PVAc to the chitosan chains increased the toughness and decreased the water absorption of chitosan (Jayakumar *et al.*, 2005).

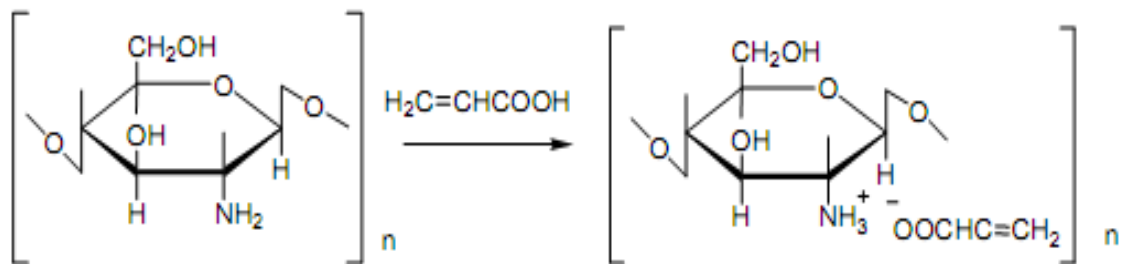


Figure 2.14: Graft copolymerization of chitosan with acrylic acid (Chandur *et al.*, 2011)

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Equipment and Apparatus

- | | | | |
|--------|------------------------------|---------|---------------------|
| i. | Beakers | xxii. | Oven |
| ii. | Weighing balance | xxiii. | 3” hand brush |
| iii. | Conical flask | xxiv. | Stirring rod |
| iv. | Thermometer | xxv. | Cheesecloth |
| v. | Filter paper | xxvi. | Metal aluminum dish |
| vi. | Heating mantle | xxvii. | Plastic slide |
| vii. | Measuring cylinder | xxviii. | Ply wood |
| viii. | Mechanical Stirrer | xxix. | Stop watch |
| ix. | Water bath | | |
| x. | NDJ-8S Digital viscometre | | |
| xi. | Pro phenom X SEM machine | | |
| xii. | Mettler Toledo DSC 1 machine | | |
| xiii. | Nicolet iS10 FTIR machine | | |
| xiv. | Muffle furnace | | |
| xv. | Density bottle | | |
| xvi. | Grinding machine | | |
| xvii. | Three-necked flask | | |
| xviii. | pH metre | | |
| xix. | Dessicator | | |
| xx. | Buchner funnel | | |
| xxi. | Crucibles | | |

3.1.2 Chemical/Reagents

- | | |
|----------------------------------|----------------------------------|
| i. Chitin | xi. Ammonia |
| ii. Chitosan | xii. Natrosol |
| iii. Acrylic acid | xiii. Titanium dioxide |
| iv. Ceric ammonium nitrate (CAN) | xiv. Genoper |
| v. Hydrochloric acid (HCl) | xv. Calcium carbonate |
| vi. Sodium hydroxide (NaOH) | xvi. Calgon |
| vii. Acetic acid | xvii. Distilled water |
| viii. Nitric acid | xviii. Potassium Permanganate |
| ix. Distilled water | xix. N, N- dimethethyl formamide |
| x. Deionized water | |

3.2 LOCUST SAMPLING

The locust sample was purchased from Sabon gari market, Zaria, Kaduna state. This was followed by washing under running tap water to remove impurities and then dried in the sun to constant weight. To obtain a uniform size product, the dried locust was ground followed by sieving.



Plate I: Picture of Desert Locust (*Schistocerca gregaria*)

3.3 EXTRACTION OF CHITIN

3.3.1 Demineralization

The demineralization was achieved by treatment of the dried ground locust powder (450 g) with 1 M HCl solution (1 L) at 100 °C for 30 min to remove minerals and catechols.

The demineralization step was followed by rinsing with distilled water until a neutral pH was obtained.

3.3.2 Deproteinization

Deproteinization was performed by alkaline treatment with 1 M NaOH (1 L) solution at 80 °C for 24 hr, and the product was washed with distilled water until the pH became neutral.

3.3.3 Decolourization

For the purpose of decolourization, the precipitate was further treated with 1 % potassium permanganate solution (400 mL) for 1 hr. The chitin obtained was washed with distilled water and then dried.

3.3.4 Deacetylation of the chitin

Deacetylation of the chitin was carried out in alkaline solution of 50 % NaOH at 100 °C for 5 hrs. After deacetylation, the chitosan was washed with distilled water. The resulting chitosan was then dried to constant weight at 32 °C and prepared for characterization.

3.4 CHARACTERIZATION OF THE CHITIN, CHITOSAN AND GRAFTED CHITOSAN

The chitin, chitosan and grafted chitosan were characterized by FTIR to determine the functional groups present, DSC to determine their glass transition temperature and SEM to observe their surface morphologies.

3.4.1 Fourier transformed infrared spectroscopy

A Nicolet (iS10) FTIR spectrometre in the range of 4000-400 cm^{-1} was used to record the IR spectra for chitin, grafted and ungrafted chitosan in the form of KBr pellets

3.4.2 Differential Scanning Calorimetry

Differential scanning calorimetric analysis was performed on a Mettler Toledo DSC1 machine. 7.7 mg of the samples i.e., chitin, chitosan and chitosan-grafted-acrylic acid were respectively weighed and hermetically sealed in aluminum pans of 40 μL . An empty sample holder was used as reference. Samples were heated from 50-300 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$.

3.4.3 Scanning Electron Microscopy

The surface morphology of the samples were assessed using the Pro X phenom Scanning Electron Microscope at a magnification of 1000.

3.5 DEGREE OF DEACETYLATION

The degree of deacetylation of the chitosan was determined by potentiometric titration. In this method dried chitosan (0.2 g) was dissolved in 20 cm^3 0.1 M hydrochloric acid and 25 cm^3 deionized water (Muzzarelli, 1977). After 30 minutes continuous stirring, next portion of deionized water (25 cm^3) was added and stirring continued for 30

minutes. When chitosan was completely dissolved, solution was titrated with 0.1 M sodium hydroxide solution using automatic burette (0.01 cm³ accuracy).

From the titration of chitosan solution a curve with two inflexion points was obtained. The difference of the volumes of these two points (V_1 and V_2) corresponds to the acid consumed by the amine groups and allows to calculate DD values. Determination of the first derivative helps in precise reading of V_1 and V_2 . Degree of deacetylation (DD) of chitosan was calculated using formula (Şen and Taşkin, 2014):

$$DD (\%) = 100 - \left[2.03 \left(\frac{(V_2 - V_1)}{m + 0.0042 (V_2 - V_1)} \right) \right] \quad \text{--- (1)}$$

where: m is weight of sample. V_1 , V_2 are the volumes of 0.1 M sodium hydroxide solution corresponding to the deflection points. 2.03 is coefficient resulting from the molecular weight of chitin monomer unit. 0.0042 is coefficient resulting from the difference between molecular weights of chitin and chitosan monomer units (Şen and Taşkin, 2014).

3.6 SOLUBILITY

The solubility of the chitosan was tested with acetic acid to see its dissolution in organic acids. 0.2 g of the chitosan was dissolved in 0.5 M acetic acid (25 mL) accompanied with vigorous stirring; the time taken for its dissolution was determined.

3.7 MOISTURE CONTENT

Moisture content of the locust chitosan was determined by the gravimetric method (Black, 1965). The water mass was determined by drying the sample to constant weight and measuring the sample after and before drying. The water mass (or weight) was obtained by calculating the difference between the weights of the wet and oven dry samples. The following procedures was followed: The weight of dish was determined

and recorded, 0.2 g of chitosan sample in triplicates was placed on the metal aluminum dish followed by recording of weight of dish with sample and the sample was then covered with the lid (filter paper to prevent or minimize contamination) in the oven. The oven temperature was adjusted to 60 °C, and the samples dried for 24 hrs. The sample was taken from the oven and placed in a desiccator until it cooled down to room temperature. The sample was weighed, and this weight was recorded as the weight of the dry sample. Moisture content was calculated as:

$$\text{Moisture content (\%)} = \frac{(\text{wet weight, g} - \text{dry weight, g})}{(\text{wet weight, g})} \times 100 \text{ --- (2)}$$

3.8 ASH CONTENT

Ash of the locust chitosan was calculated according to the standard method (#923.03, AOAC, 1990). 0.5 g of chitosan (triplicate) was placed into previously ignited, cooled, and tarred crucible. The samples were heated in a muffle furnace preheated to 500 °C for 4 hrs. The crucibles were allowed to cool in the furnace to less than 200 °C and then placed into desiccators with a vented top. This was allowed to cool and the weight of the crucible and ash were determined.

$$\text{Ash content (\%)} = \frac{(\text{Weight of residue, g})}{(\text{Sample weight, g})} \times 100 \text{ --- (3)}$$

3.9 GRAFT COPOLYMERIZATION

The percentage of grafting and the efficiency of the process were calculated as function of the concentration of initiator and monomer, the reaction time and temperature.

The chitosan powder sample dispersed in a definite volume was dissolved in 2 % acetic acid, in a thermostated reaction flask for 60 min. Ceric ammonium nitrate in 0.5 M

nitric acid solution was then loaded into the reactor under continuous stirring. Then a known weight of acrylic acid was injected into the reactor. The reaction was assumed to have started at the moment the monomer was injected.

Graft copolymerization was carried out at 70 °C under constant stirring in nitrogen atmosphere for 45 minutes. At the end of grafting copolymerization, the reaction mixture was neutralized with a 1 M NaOH solution, and the reaction products (graft copolymer and homopolymer) was filtered and thoroughly washed with distilled water, and then dried to constant weight. The homopolymer was subsequently removed by extraction with N, N- dimethethyl formamide for 6 hrs. The remaining product, after drying to a constant weight was considered to be a graft copolymer.

Grafting percentage (%G) which designates the amount of polymer grafted on the substrate backbone (chitosan) and grafting efficiency (%E), which indicates the efficiency of conversion of the initial acrylic acid to the grafted polyacrylic acid will be calculated from the increase in weight of the chitosan after graft copolymerization in following manner.

$$\% G = \frac{(W_2 - W_1)}{W_1} \times 100 \text{ --- (4)}$$

$$\% E = \frac{(W_2 - W_1)}{W_3} \times 100 \text{ --- (5)}$$

Where:

W_2 = the mass of grafted copolymer

W_1 = the mass of chitosan

W_3 = ((the mass of grafted copolymer - the mass of chitosan) + mass of polyacrylic acid)

3.9.1 Evidence of grafting:

Evidence of grafting was obtained from comparison of SEM, DSC, and FTIR of the grafted and non-grafted chitosan as well as solubility characteristics of the products.

3.10 PREPARATION OF EMULSION PAINT

Table 3.10a: Formulation of Emulsion Paint without Chitosan-Grafted-Acrylic Acid

S/N	Raw materials	Function	Quantity
i.	Water	Solvent	1.1 L
ii.	Calgon	Dispersant	25 g
iii.	Calcium carbonate	Filler	1.6 kg
iv.	Acrylic	Resin (binder)	480 ml
v.	Genoper	Anti foam	25 ml
vi.	Ammonia	pH adjuster	12.5 ml
vii.	Natrosol	Thickener	30 g
viii.	Titanium dioxide	White pigment	62.5 g

Table 3.10b: Formulation of Emulsion Paint with Chitosan-Grafted-Acrylic Acid

S/N	Raw materials	Function	Quantity
i.	Water	Solvent	1.1 L
ii.	Calgon	Dispersant	25 g
iii.	Calcium carbonate	Filler	1.6 kg
iv.	Locust chitosan-grafted-acrylic acid	Resin (binder)	480 ml
v.	Genoper	Anti foam	25 ml
vi.	Ammonia	pH adjuster	12.5 ml
vii.	Natrosol	Thickener	30 g
viii.	Titanium dioxide	White pigment	62.5 g

3.10.1 Procedure (Preparation of Emulsion paint)

After the raw materials have been measured according to the right proportion, water was poured into the reactor followed by the addition of Calcium carbonate with continuous stirring, Titanium dioxide, Calgon, Locust chitosan-grafted-acrylic acid were then added respectively. Natrosol was dissolved in little quantity of water and then added to the recipe, this was followed by the addition of Genoper and Ammonia. This was followed by stirring vigorously for 10 – 15 minutes and then packaged for use.

3.11 ANALYSES OF THE PAINTS

The following paint properties were investigated:-

3.11.1 Density (ASTM 1475)

The density was determined by taking the weight of a known volume of the paint inside a pycnometre by the use of a weighing balance. Three readings were taken and the average value calculated.

3.11.2 Drying Test (ASTM D711)

The different paint samples were each applied on a smooth wall surface; this was checked at different time intervals to determine both the surface drying time and the hard drying time.

3.11.3 Viscosity Test

The viscosities of the different paint samples were each measured with NDJ-8S Digital Viscometre using spindle 4 with a speed of 1.5 rpm at 29 °C. The spindle attached to the machine was dipped into the paint sample in a beaker; the minimum

insertion point on the spindle was taken into consideration which was followed by the running of the experiment.

3.11.4 Cross-cut test of the paints

The resistance of the paint coatings to separation from substrates when the right angle lattice patterns were cut into the coatings was assessed based on ISO 2409 method.

3.11.5 Bend Test

The paints were applied on plastic slides of 10 cm x 4 cm x 1 cm with 3” painting brush and then allowed to dry; this was kept at room temperature for 15 days before testing the bending ability of the different paint samples through an angle of 360⁰.

3.11.6 Acidity or Alkalinity Test

The paints samples were tested for either its acidity or alkalinity with the use of a pH meter.

3.11.7 Ash Test for the Paints (ASTM D2584)

2g of the paint samples were weighed into dried / pre-weighed porcelain crucibles in triplicate; this was heated in a muffle furnace at 700⁰C for 1 hour. The crucibles were weighed after it has been cooled to room temperature in a desiccator. Ash residue remaining in the crucible was considered filler. The percentage ash was calculated using the following expression.

$$\text{Ash (\%)} = \frac{(\text{Weight of residue, g})}{(\text{Sample weight, g})} \times 100 \text{ --- (6)}$$

CHAPTER FOUR

4.0

RESULTS AND DISCUSSION

4.1 DEGREE OF DEACETYLATION (DD)

The degree of deacetylation (DD) of the chitosan from locust by taking the two inflexion points from the linear potentiometric curve (Fig. 4.1) was calculated to be 90.06 %. This result shows that the extract obtained is actually chitosan and not chitin since according to Knaul *et al.*, 1999 chitin with a degree of deacetylation of 75 % or above is generally known as chitosan.

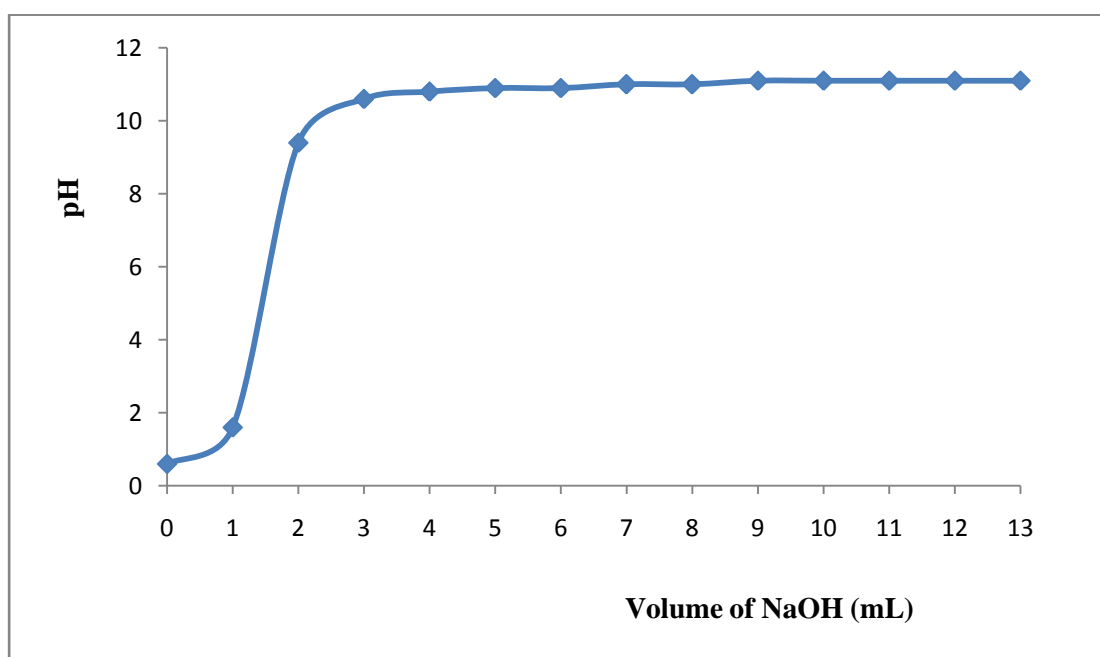


Figure 4.1: Linear potentiometric curve of Chitosan

4.2 SOLUBILITY

The chitosan produced had good solubility in 0.5 M acetic acid. It dissolved in 2 minutes, 40 seconds. The good solubility obtained can be attributed to the high degree

of deacetylation of the chitosan.

4.3 MOISTURE CONTENT

Moisture content of the chitosan was calculated to be 6 %. This result shows that chitosan of a commercial grade can also be obtained from locust which is in line with (Li *et al.*, 1992) who reported that commercial chitosan products may contain <10 % moisture content.

4.4 ASH CONTENT

The percentage ash of the chitosan produced was obtained to be 2.24 %, it shows that the demineralization process for the removal of calcium carbonate was effective; this account for its very good solubility in 0.5 M acetic acid. If the temperature and time for the determination of the ash content is increased, with the result obtained from this research, it also shows that chitosan of a high quality grade could be obtained from locust since according to (No and Meyers 1995), a high quality grade of chitosan should have less than 1 % of ash content.

4.5 GRAFT COPOLYMERIZATION

The grafting percentage (% G) was calculated to be 81.75 % and the grafting efficiency (% E) was calculated to be 72.69 %.

4.6 FTIR ANALYSIS

4.6.1 FTIR of Chitin

The structure of the extracted chitin was analysed by FTIR spectroscopy. The spectrum of chitin showed broad band absorption from 3400.00 cm^{-1} to 3566.46 cm^{-1} which is attributed to -NH and -OH stretching vibration, as well as inter and intra molecular hydrogen bonding in chitin molecules. The band observed at $2,922.74\text{ cm}^{-1}$ and $2,853.23\text{ cm}^{-1}$ corresponds to asymmetric stretching of CH_3 and CH_2 in the extracted chitin (Guo *et al.*, 2005). The peak around 1652.98 cm^{-1} corresponds to bending vibration of carbonyl bonds (C=O) of the amide group CONHR (secondary amide) which is a characteristic feature of chitin polysaccharide and also indicates the occurrence of little deacetylation (Zhang *et al.*, 2011; Marchessault *et al.*, 2006 and Radhakumary *et al.*, 2003). Bending vibrations of CH_3 and CH_2 groups were also visible at 1456.36 cm^{-1} and 1376.55 cm^{-1} respectively (Mano *et al.*, 2003). Absorption in the range from 1154.74 cm^{-1} to 1030.59 cm^{-1} is attributed to vibrations of CO group (Xu *et al.*, 2005). The band located at 1154.74 cm^{-1} is related to asymmetric vibrations of CO in the oxygen bridge resulting from little deacetylation of chitin. The band at 1030.59 cm^{-1} is attributed to ν_{CO} of the ring COH , COC and CH_2OH . The small peak at 892.80 cm^{-1} corresponds to wagging of the saccharide structure of chitin (Darder *et al.*, 2003; Paluszkiwicz *et al.*, 2011; Yuan *et al.*, 2010). The peak at 722.09 cm^{-1} is attributed to N-H wagging (Rumengan *et al.*, 2014).

4.6.2 FTIR of Chitosan

The structure of the extracted chitosan was analysed by FTIR spectroscopy. The spectrum of chitosan showed broad band absorption from 3420.27 cm^{-1} to 3586.76 cm^{-1} which is attributed to -NH and -OH stretching vibration, as well as inter and intra molecular hydrogen bonding in chitosan molecules. The band observed at $2,923.14\text{ cm}^{-1}$

and $2,853.47\text{ cm}^{-1}$ corresponds to asymmetric stretching of CH_3 and CH_2 in the extracted chitosan (Guo *et al.*, 2005). The peak around 1652.75 cm^{-1} corresponds to bending vibration of carbonyl bonds ($\text{C}=\text{O}$) of the amide group CONHR (secondary amide) which is a characteristic feature of chitosan polysaccharide and also indicates the occurrence of deacetylation (Zhang *et al.*, 2011; Marchessault *et al.*, 2006 and Radhakumary *et al.*, 2003). Bending vibrations of CH_3 and CH_2 groups were also visible at 1457.15 cm^{-1} and 1376.03 cm^{-1} respectively (Mano *et al.*, 2003).

Absorption in the range from 1152.49 cm^{-1} to 1031.27 cm^{-1} is attributed to vibrations of CO group (Xu *et al.*, 2005). The band located at 1152.49 cm^{-1} is related to asymmetric vibrations of CO in the oxygen bridge resulting from deacetylation of chitosan. The band at 1031.27 cm^{-1} is attributed to ν_{CO} of the ring COH, COC and CH_2OH . The small peak at 893.50 cm^{-1} corresponds to wagging of the saccharide structure of chitosan (Darder *et al.*, 2003; Paluszkiwicz *et al.*, 2011; Yuan *et al.*, 2010). The peak at 721.67 cm^{-1} is attributed to N-H wagging (Rumengan *et al.*, 2014).

4.6.3 FTIR of Chitosan-grafted-acrylic acid

The structure of the extracted chitosan-grafted-acrylic acid was analysed by FTIR spectroscopy. The peak observed at 2360.60 cm^{-1} and 2344.61 cm^{-1} is attributed to the carboxylic acid functional group and hence indicate the point of grafting of the acrylic acid unto the chitosan obtained from locust. The spectrum of chitosan-grafted-acrylic acid shows a broad absorption band in the region of $3,400.00\text{ cm}^{-1}$ to 3588.01 cm^{-1} that corresponds to OH stretching vibrations of water and hydroxyls and NH stretching vibrations of free amino groups. The band observed at $2,922.55\text{ cm}^{-1}$ corresponds to asymmetric stretching of CH_3 in the extracted chitosan (Guo *et al.*, 2005). The peak around $1,653.88\text{ cm}^{-1}$ corresponds to bending vibration of carbonyl bonds ($\text{C}=\text{O}$) of the amide group CONHR (secondary amide) which is a characteristic

feature of chitosan polysaccharide and also indicates the occurrence of deacetylation (Zhang *et al.*, 2011 and Radhakumary *et al.*, 2003). Bending vibrations of CH₃ and CH₂ groups were also visible at 1457.42 cm⁻¹ and 1374.75 cm⁻¹ respectively (Mano *et al.*, 2003).

Absorption in the range from 1156.86 cm⁻¹ to 1074.39 cm⁻¹ is attributed to vibrations of CO group (Xu *et al.*, 2005). The band located at 1156.86 cm⁻¹ is related to asymmetric vibrations of CO in the oxygen bridge resulting from deacetylation of chitosan. The band at 1074.39 cm⁻¹ is attributed to ν_{CO} of the ring COH, COC and CH₂OH (Darder *et al.*, 2003; Paluszkiwicz *et al.*, 2011; Yuan *et al.*, 2010).

4.7 SEM ANALYSIS

4.7.1 SEM of Chitin

The surface morphology of the chitin observed using SEM was found to consist of prominent microfibrils and porous structures.

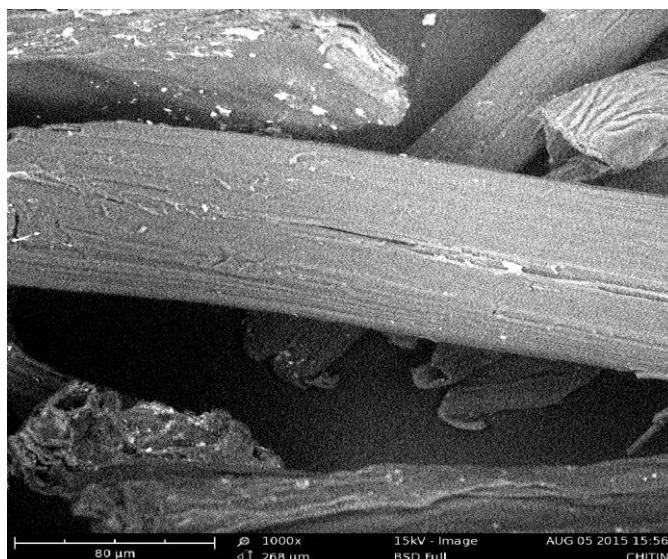


Plate II: SEM image of chitin, magnification X 1000

4.7.2 SEM of Chitosan

The surface morphology of the chitosan observed using SEM however shows the erosion of some of the microfibrils and porous structure which could be attributed to successful deacetylation of the chitin to chitosan.

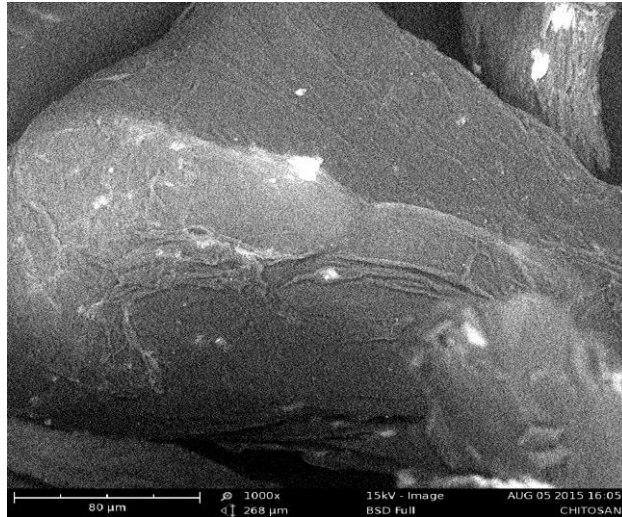


Plate III: SEM image of chitosan, magnification X 1000

4.7.3 SEM of Chitosan-grafted-acrylic acid

In the case of the chitosan-grafted-acrylic acid, the SEM image shows the coverage of the little microfibrils and pores present in the chitosan after grafting of acrylic acid unto the chitosan was done; this shows that the grafting was successful which is in line with (Pati and Nayak, 2011) who found that the fibrillar nature of chitosan was lost after grafting.

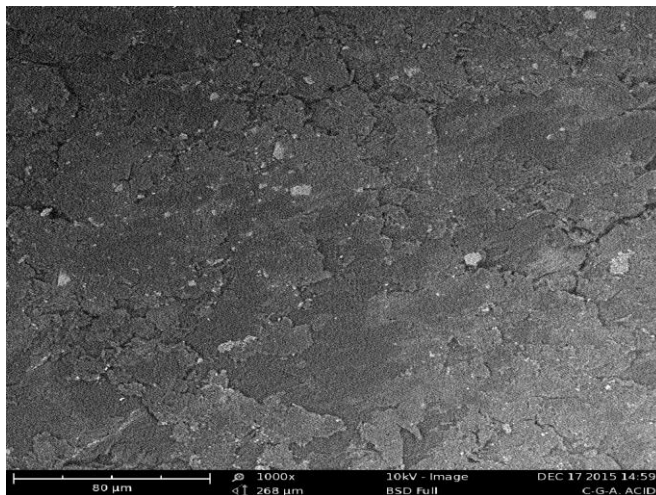


Plate IV: SEM image of chitosan-grafted-acrylic acid, magnification X 1000

4.8 DIFFERENTIAL SCANNING CALORIMETRY

4.8.1 DSC of chitin

The DSC thermograph for chitin (Fig. 4.8.1) shows an endothermic peak at about 55 – 100 °C which corresponded to the evaporation of water; the glass transition temperature of the chitin was obtained to be 152.88 °C and at the temperature of 293.91 °C degradation of the chitin sample sets in (Kittur *et al.*, 2002).

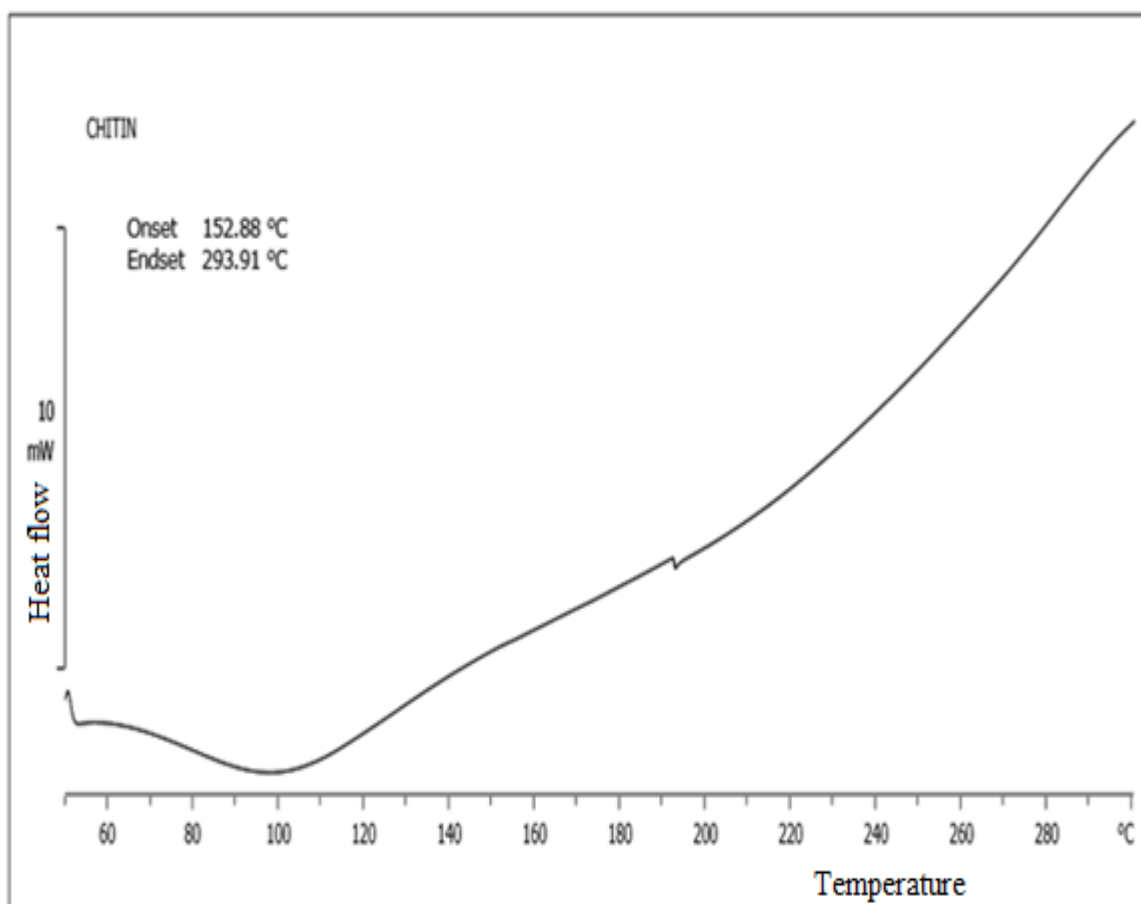


Figure 4.8.1: DSC thermograph of Chitin

4.8.2 DSC of chitosan

The DSC thermograph for chitosan (Fig. 4.8.2) shows an endothermic peak at about 55 – 95 °C which corresponded to the evaporation of water; the glass transition temperature of the chitosan was obtained to be 229.63 °C and at the temperature of 297.73 °C degradation of the chitosan sample sets in (Kittur *et al.*, 2002).

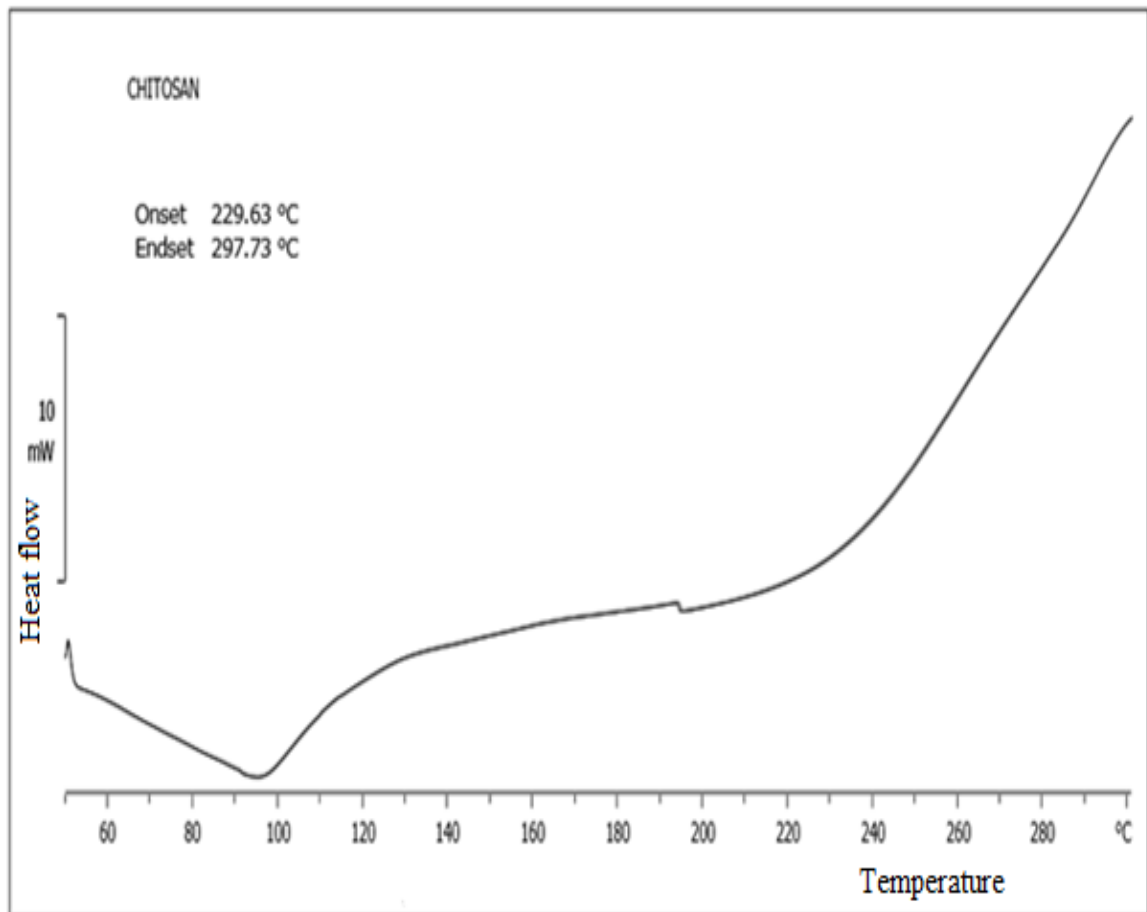


Figure 4.8.2: DSC thermograph of Chitosan

4.8.3 DSC of chitosan-grafted-acrylic acid

The DSC thermograph for chitosan-grafted-acrylic acid shows an endothermic peak at about 55 – 95 °C which corresponded to the evaporation of water; the glass transition temperature of the chitosan-grafted-acrylic acid was obtained to be 229.63 °C and at the temperature of 297.73 °C degradation of the chitosan-grafted-acrylic acid sample sets in (Kittur *et al.*, 2002).

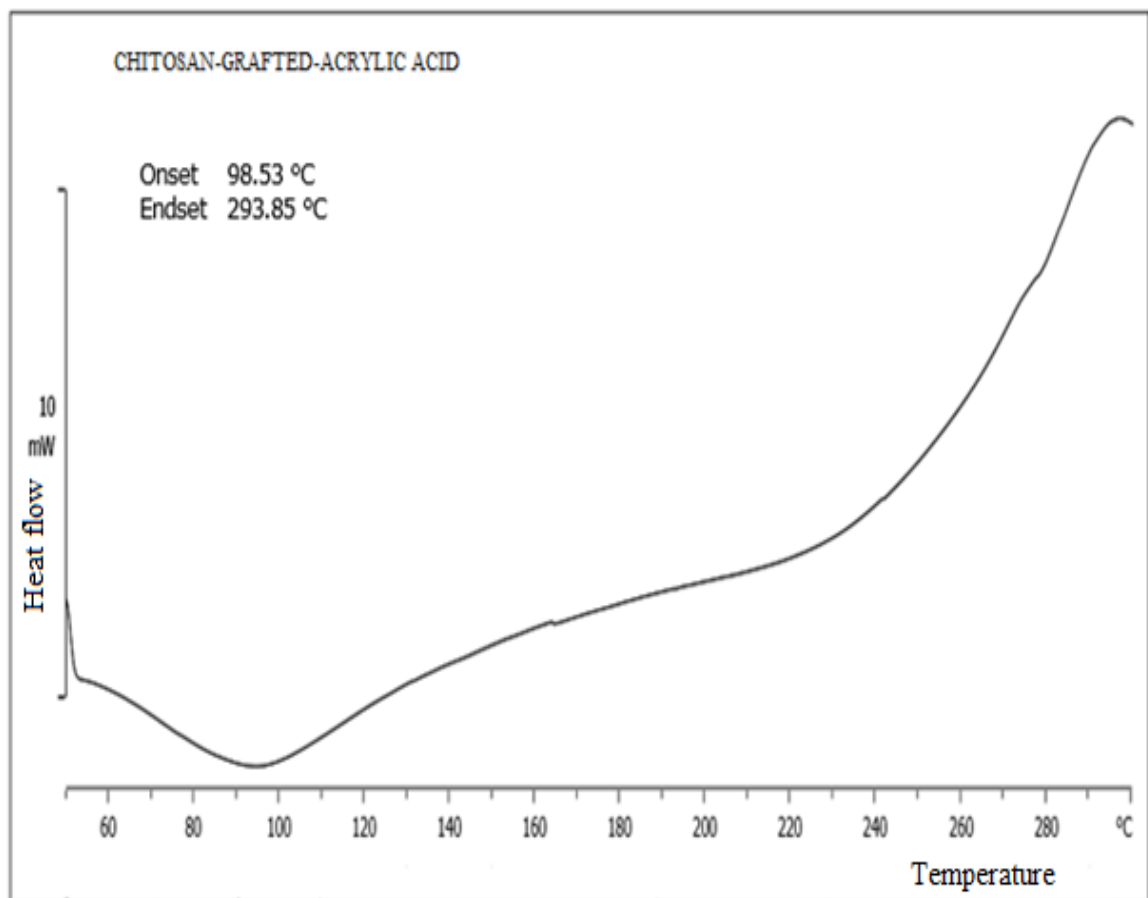


Figure 4.8.3: DSC thermograph of Chitosan-grafted-acrylic acid

4.8.4 Superimposed DSC thermographs of Chitin, Chitosan and Chitosan-grafted-acrylic acid

In general, the glass transition (T_g) temperature will increase somewhat as the crystalline content of the polymer increases (Thass, 2015). It therefore implies from the results obtained that chitosan had the highest crystallinity followed by chitin and then the chitosan-grafted acrylic acid which had glass transition temperature of $229.63\text{ }^{\circ}\text{C}$, $152.88\text{ }^{\circ}\text{C}$ and $98.53\text{ }^{\circ}\text{C}$ respectively as shown on figures 4.8.1, 4.8.2 and 4.8.3 above. It was observed that as the molecular weight of the side chain attached to the polysaccharide chain increases, the glass transition temperature decreases.

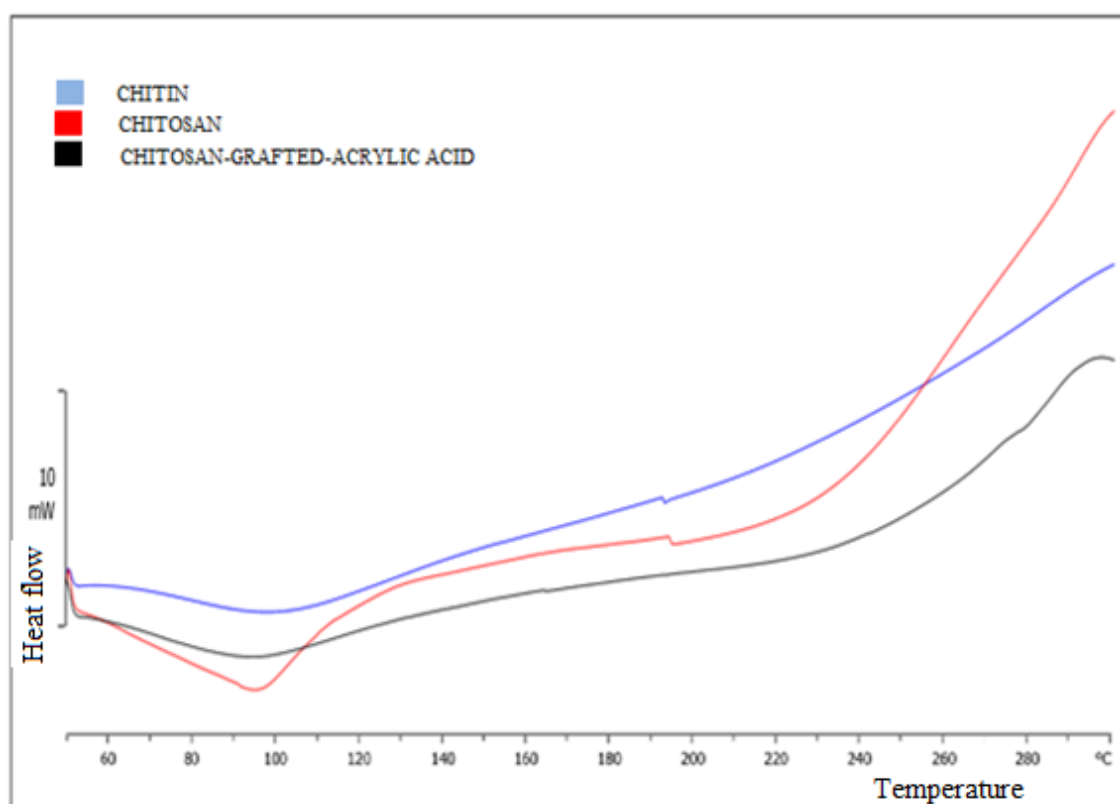


Figure 4.8.4: Superimposed DSC thermographs of Chitin, Chitosan and Chitosan-grafted-acrylic acid respectively

4.9 PAINTS

4.9.1 Densities of the Paints

The densities of the paints were measured by the use of pycnometre and the results obtained shows that paint produced with chitosan-grafted-acrylic acid is denser than the paint produced without chitosan-grafted-acrylic acid and then the finecoat paint.

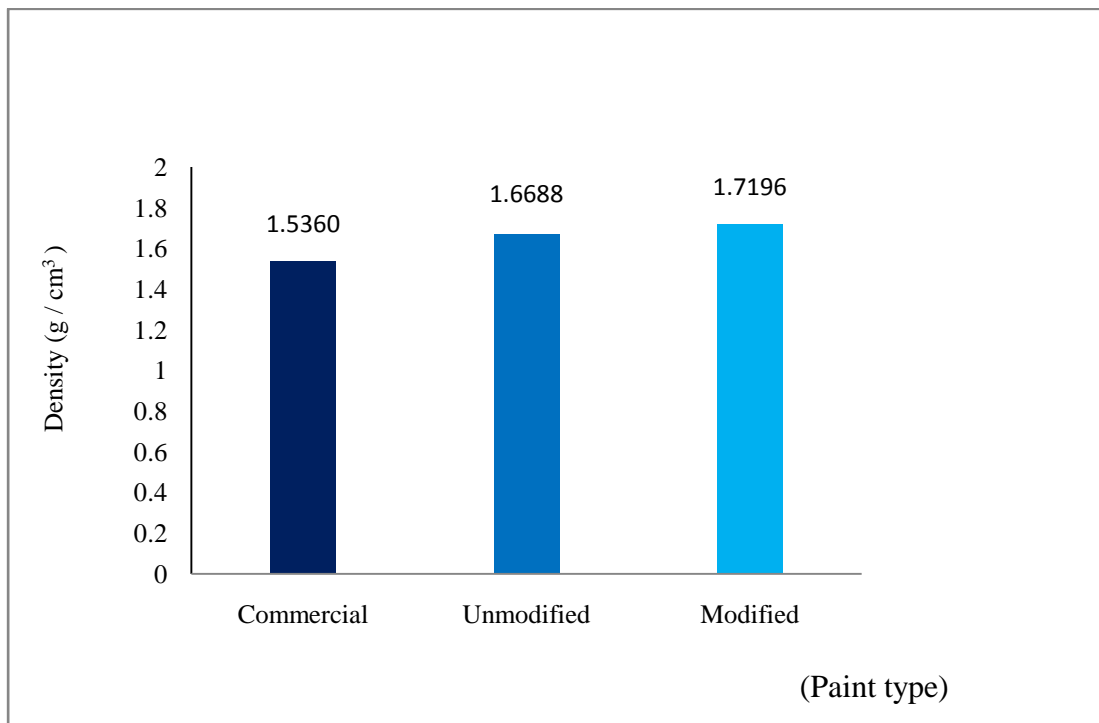


Figure 4.9.1: Densities of the respective paints

4.9.2 Drying Time of the Paint Samples (ASTM D711) .

The No-pick-up times of the paint were determined and the results obtained are shown in Table 4.9.2.

It can be inferred that the presence of chitosan-grafted-acrylic acid in the modified paint made the surface drying time and the hard drying time to be lesser compared to the paint samples without the chitosan-grafted-acrylic acid. The implication of this is that

once paint patterns are made on a substrate it dries in time before any other agents such as man, animals, etc., smear off the patterns on the painted substrate.

4.9.3 Cross-Cut Test

The three (3) test samples (Finecoat paint, paint without chitosan-grafted-acrylic acid and paint with chitosan-grafted-acrylic acid) passed the test. This empirical test showed that paint with chitosan-grafted-acrylic acid had better resistance followed by the paint without chitosan-grafted-acrylic acid and then the finecoat paint, this can be attributed to the nature of the binders used.

4.9.4 Acidity or Alkalinity Test

Finecoat had pH of 8.4, Chitosan-grafted acrylic acid paint had pH of 7.8 while that of the paint without chitosan-grafted acrylic acid had pH of 8.0. This indicated that the three paint samples were alkaline in nature and the values obtained falls within standard value range for paints (Obi, 2013).

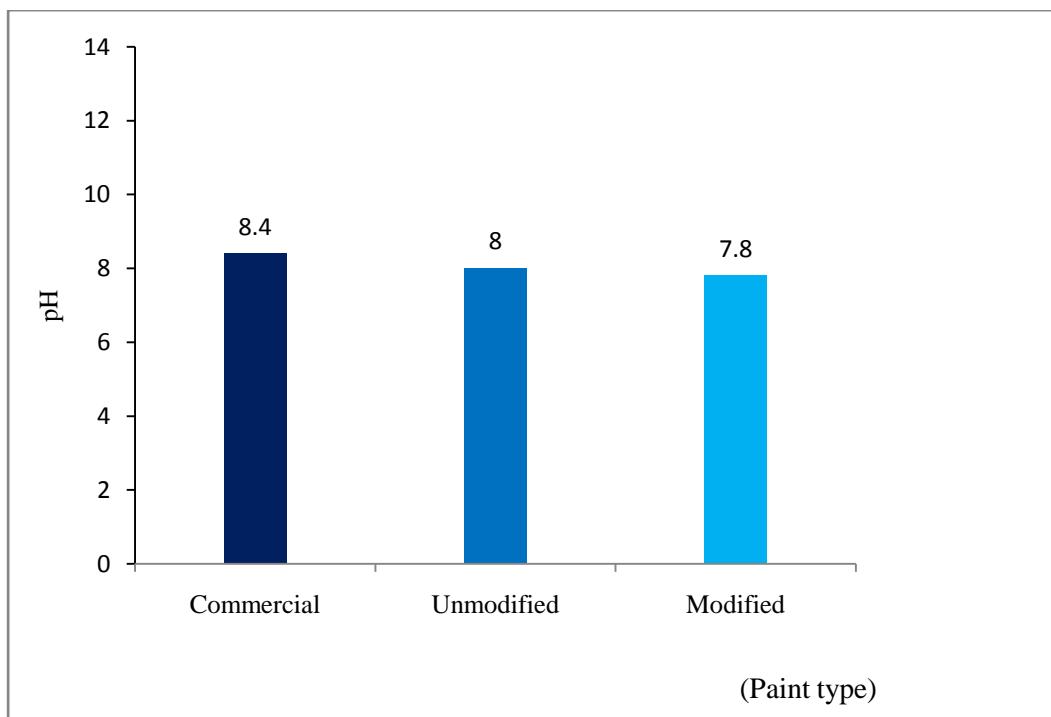


Figure 4.9.4 Degree of alkalinity of the paints

4.9.5 Viscosity Test

From the results obtained Finecoat paint had viscosity of 212724 mPa.s, paint without chitosan-grafted-acrylic acid had viscosity of 257587 mPa.s while that of the paint with chitosan-grafted-acrylic acid had viscosity of 268431 mPa.s. This shows that Finecoat paint has lesser viscosity compared to paint without chitosan-grafted-acrylic acid and then the paint with chitosan-grafted-acrylic acid. It therefore implies that the resistance of the modified emulsion paint to sagging during the application process is higher.

4.9.6 Bend Test

It was observed that the plastic slide coated with Finecoat had more delamination followed by the plastic slide coated with paint sample without chitosan-grafted-acrylic acid and then the one coated with paint containing chitosan-grafted acrylic acid (See Plate XII). It implies that the paint produced with chitosan-grafted-acrylic acid has more ability to withstand the force of bending than the other paint samples tested. This could be attributed to the binder as the binder is known to impart adhesion and strongly influence flexibility property of paints (Lambourne and Strivens, 1999).

4.9.7 Ash Test for the Paints (ASTM D2584)

From the results obtained, it shows that Finecoat paint had filler content of 75.27 %, the paint produced without chitosan-grafted-acrylic acid had 72.44 % filler content while that of the paint with chitosan-grafted-acrylic acid had filler content of 71.09 %. It is usually expected that that the more the filler content the better the toughness of the paint but it is not always true as the nature of the binder or film former also contribute to the toughness property of the paint (Obi, 2013).

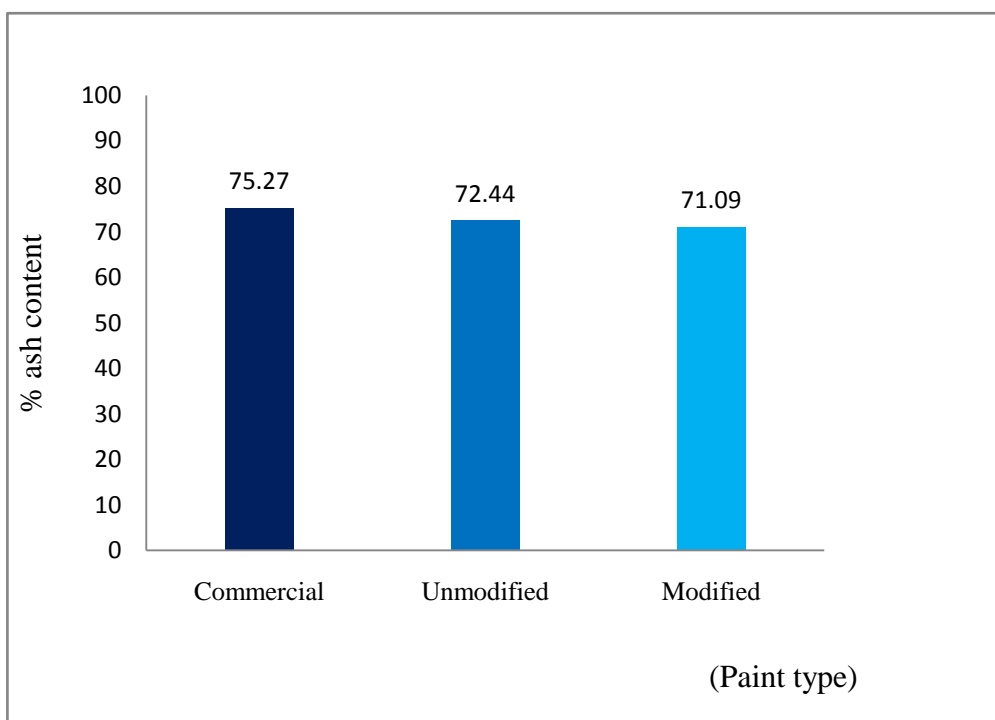


Figure 4.9.7: Percentage ash content of the paint samples

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 SUMMARY

Modification of emulsion paint by incorporating locust chitosan-grafted-acrylic acid as binder and the assessment of some of its Physico-chemical properties shows 90.06 % degree of deacetylation of the chitosan, 6.00 % moisture content and 2.24 % ash content, which revealed that chitosan of a high quality grade was obtained from locust. Acrylic acid was grafted onto the chitosan in an atmosphere of nitrogen and 81.75 % grafting percentage and 72.69 % grafting efficiency were obtained. The characterization of the chitosan-grafted-acrylic acid revealed 2360.60 cm^{-1} and 2344.61 cm^{-1} peaks are attributed to the carboxylic acid functional group which indicate the point of grafting of the acrylic acid unto the chitosan, the glass transition temperatures obtained from differential scanning calorimetry revealed 152.88 $^{\circ}\text{C}$, 229.63 $^{\circ}\text{C}$ and 98.53 $^{\circ}\text{C}$ for chitin, chitosan and chitosan-grafted-acrylic acid respectively, surface morphology observation of the chitin shows prominent microfibrils and porous structures while erosion of some of the microfibrils and porous structure on the chitosan was observed which could be attributed to successful deacetylation of the chitin to chitosan whereas the chitosan-grafted-acrylic acid shows the coverage of the little microfibrils and porous structure. Also the overall performance of the modified paint gave increase in density, viscosity, bendability, resistance of the paint coatings to separation from substrates when the right angle lattice patterns were cut into it and decrease in the drying time, alkalinity and the filler content. Commercial emulsion paint and non chitosan-grafted-acrylic acid emulsion paint assessed gave low performance in terms of density, viscosity, bendability, resistance of the paint coatings to separation from substrates when right angle lattice patterns were cut, decrease in the drying time, alkalinity and filler content

which can be attributed to the nature of the chitosan-grafted-acrylic acid as a binder when compared.

5.2 CONCLUSION

Chitin was successfully extracted from desert locust and subsequently converted to chitosan and there was effective grafting of the chitosan obtained with acrylic acid; the calculated grafting percentage of 81.75 % and grafting efficiency of 72.69 % were obtained respectively. Chitosan with a high degree of deacetylation (90.06 %), good solubility in 0.5 M acetic acid, low moisture content (6.00 %) and ash content (2.24 %) has been obtained from locust. The chitosan-grafted-acrylic acid obtained incorporated into the emulsion paint gave good product when assessed with respect to another emulsion paint produced without chitosan-grafted-acrylic acid and a commercial paint. Tests such as drying time, density, viscosity, bend test, ash test, acidity or alkalinity test and cross-cut test were carried out. Emulsion paint incorporating with locust chitosan-grafted-acrylic acid as binder shows improvement in the properties.

5.3 RECOMMENDATIONS

Generally, chitosan from different sources and different degree of deacetylation have properties that make them distinct; the ratio of the polymer to monomer of the graft copolymer also affects the properties of the binder. Therefore, I strongly recommend that the effect of the use of chitosan with different degree of deacetylation should be investigated in the emulsion paint, the differences and similarities between the use of chitosan from locust and other sources should also be investigated in the emulsion paint and the effect of varying the ratio of chitosan to acrylic acid of the graft copolymer for the emulsion paint should be investigated.

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APPENDICES

Table 4.1: The Volume of NaOH (mL) used and the corresponding pH

Volume of NaOH (mL)	pH
0	0.6
1	1.6
2	9.4
3	10.6
4	10.8
5	10.9
6	10.9
7	11.0
8	11.0
9	11.1
10	11.1
11	11.1
12	11.1
13	11.1

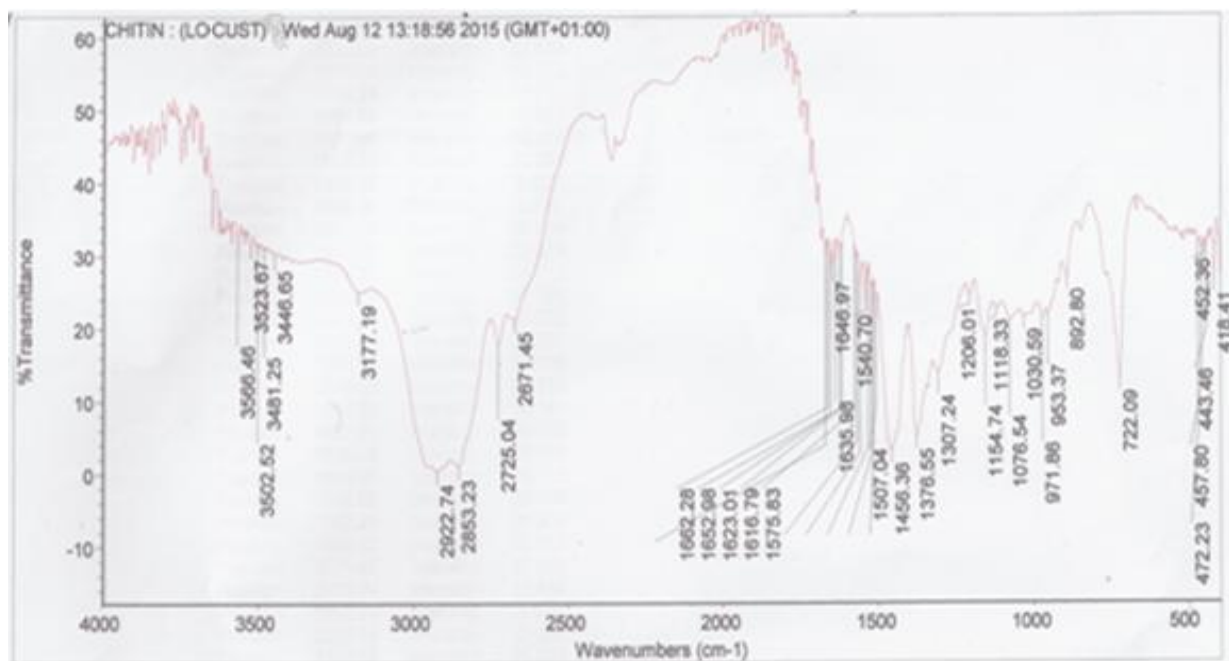


Figure 4.6.1: FTIR spectrum of Chitin

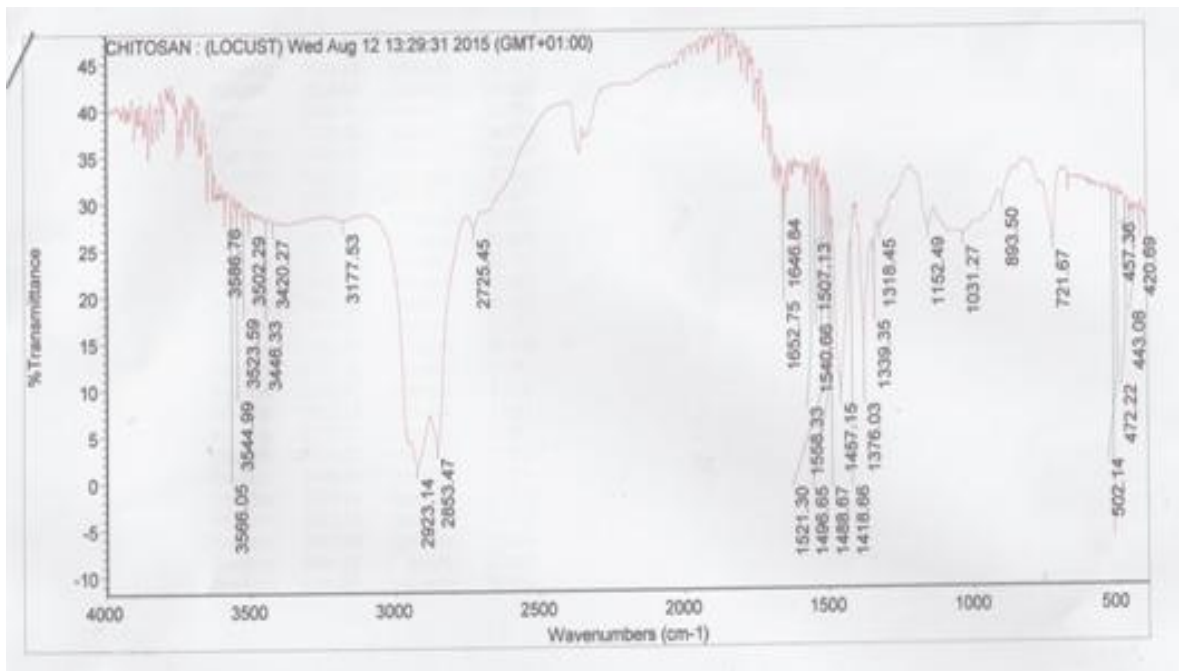


Figure 4.6.2: FTIR spectrum of Chitosan

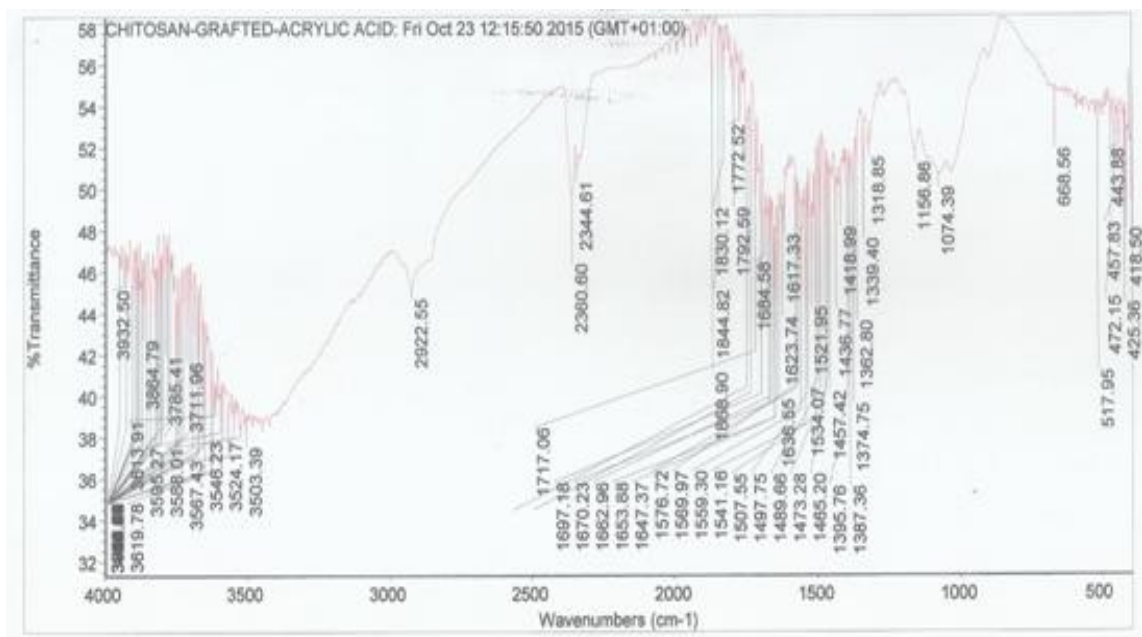


Figure 4.6.3: FTIR spectrum of Chitosan-grafted-acrylic acid

Table 4.9.1 Densities of the paints

Sample (n)	Weight of pycnometre (W ₀)g	Weight of pycnometre + sample (W ₁)g	Weight of sample (W ₂)g	Density (g/cm ³)
1	24.51	62.91	38.40	38.40/25 = 1.5360
2	24.51	66.23	41.72	41.72/25 = 1.6688
3	24.51	67.50	42.99	42.99/25 = 1.7196

Table 4.9.2 The surface and hard drying time for the paint samples

Sample	Surface Drying time (min.:sec.)	Hard Drying time (min.:sec.)
Commercial	4 : 15	24 : 22
Unmodified	2 : 52	18 : 38
Modified	2 : 08	16 : 28

Table 4.9.5 Results of the different paint viscosity

Commercial (mPa.s)	Unmodified (mPa.s)	Modified (mPa.s)
212470	257830	268874
212951	257247	268320
212752	257684	268100
638173/3 = 212724	772761/3 = 257587	805294/3 = 268431

Table 4.9.7 Results of the ash test for the paints

S/N	Original Sample weight (g)	Commercial (g)	Unmodified (g)	Modified (g)
1	2.0000	1.5053	1.4488	1.4219
2	2.0000	1.5053	1.4489	1.4218
3	2.0000	1.5052	1.4487	1.4218
Total	6.0000	4.5158	4.3464	4.2655
	$6.0000/3 = 2.0000$	$4.5158/3 = 1.5053$	$4.3464/3 = 1.4488$	$4.2655/3 = 1.4218$

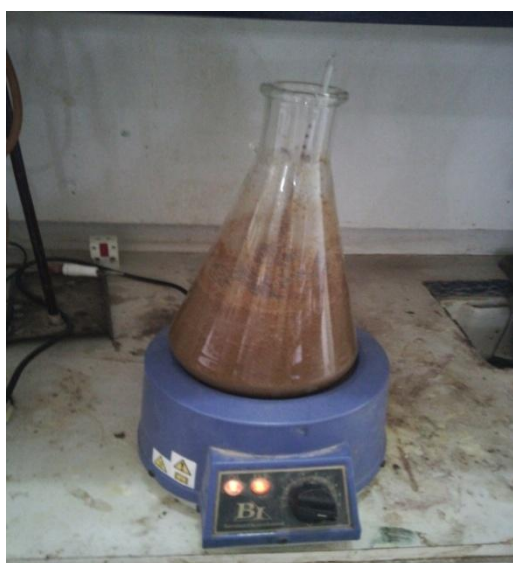


Plate V: The setup for demineralization and the product



Plate VI: The setup for deproteinization and the product



Plate VII: The decolourization process and the dried product (Chitin)



Plate VIII: Dried Chitosan



Plate IX: The setup for the determination of the degree of deacetylation

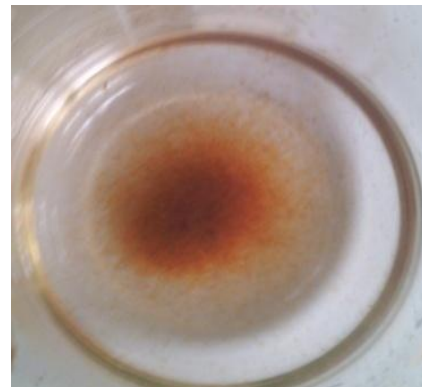


Plate X: Test for the solubility of Chitosan and Chitin in acetic acid respectively



Plate XI: NDJ-8S Digital Viscometre



Plate XII: The test panels for the bend test



Plate XIII: SXL Muffle furnace and some of the crucibles used for the ash test