Synthesis, Characterization and Flocculation Properties of *Acacia tortilis* Grafted with Styrene

A Dissertation Submitted in Partial Fulfillment of the Requirements of the Master Degree in Industrial Chemistry

By:

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2019
Dedication

To the soul of my father, to my mother, husband, sisters and brothers
Acknowledgement

First and foremost I would like to thank Almighty Allah for giving me patience and blessing to complete this work. I express my great appreciation with deep gratitude to my advisor Dr. Essa Esmail Mohammad for his patience, support, enthusiastic encouragement and willingness to give his time so generously, whenever I ran into a trouble spot or had a question about my thesis or writing and steered me to the right direction. I would also like to thank the technicians of the laboratory Awad Allah, Hamza and Waleed for their help in offering me the resources and apparatus. Thanks are also extended to Ustaz Abdulhameed at Sudan University of Science and Technology for providing free access to the laboratory instruments. I am deeply indebted to the soul of my father, to my mother, who have been my source of power and strength, who taught me to work hard for the things that I aspire to achieve, and continually provide her time, her moral, spiritual and emotional support. I express my profound gratitude to my husband, baby, sisters and brothers for backing me with incorporeal, realistic and financial unfailing support and continuous encouragement throughout my years of study and through the process of writing this thesis, this accomplishment would not have been possible without them.
Abstract

The aim of the present study was to prepare and characterize *Acacia* gum grafted polymers as well as their application as flocculating polymers. The grafted gum samples were prepared using varying concentrations of the monomer and gamma radiation doses. The samples were characterized by FTIR, TGA, viscosity, pH measurement and grafting efficiency. The results have shown that the main factor which affects the grafting efficiency is the monomer concentration. It was found that both the radiation dose and the amount of the monomer have considerable effects on the viscosity of the aqueous solutions of the grafted samples. Sample 3c and 1b have shown the highest viscosity values of 49 cp and 44 cp compared to the crude sample for which the viscosity was 10 cp. The thermal analysis has shown three steps of degradation of the crude gum at 199.3, 284.0 and 439.7°C and their accompanying mass loss were 10%, 40% and 60%. Moreover, all the grafted copolymers were thermally stable than the crude gum. Finally, the synthesized graft copolymer showed improved flocculation characteristics in comparison to the crude gum.
مستخلص البحث

هدفت هذه الدراسة لتحضير وتشخيص صمغ الأكاسيا المدمج ودراسة تطبيقاتها كمواد ذات خصائص تجميعية. خضعت العينات المدمجة باستخدام تراكيز متباينة من المونومر وكذلك من جرعات أشعة جاما، ومركز الأشعة تحت الحمراء، والتحليل الحراري الوزني، واللزوجة، وقياس الأس الهدروجيني، وكذلك كفاءة الدمج. بينت النتائج أن كفاءة الدمج تعتمد بصورة أساسية على تركيز المونومر. بالإضافة إلى ذلك فقد وُجد أن كل من جرعة الأشعة وتركيز المونومر لها آثار كبيرة على لزوجة المحاليل المائية للعينات المدمجة. أظهرت العينتان 3c و 1b أعلى قيم للزوجة وهي 49 و 44 cp. مقارنة بالعينة الخام والتي لها لزوجة تبلغ 10 cp. بينت نتائج التحليل الحراري أن العينة الخام تتلف في ثلاث مراحل عند درجة حرارة 199.3 و 284.0 و 439.0 درجة مئوية. وقد وجد أن العينات المدمجة أكثر استقراراً حرارياً من الصمغ الخام. أخيراً فقد وُجد أن للعينات المدمجة خصائص تجميعية أفضل من الصمغ الخام.
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<th>EXPLANATION</th>
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<tr>
<td>A.</td>
<td>Acacia</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Cs</td>
<td>Cesium</td>
</tr>
<tr>
<td>K</td>
<td>Kilo</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>Na</td>
<td>Sodium</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>FAO</td>
<td>Food and Agriculture Organization</td>
</tr>
<tr>
<td>E.g.</td>
<td>Example</td>
</tr>
<tr>
<td>ml</td>
<td>Millimeter</td>
</tr>
<tr>
<td>G</td>
<td>Gram</td>
</tr>
<tr>
<td>PH</td>
<td>Power of Hydrogen Iron</td>
</tr>
<tr>
<td>Cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>m</td>
<td>Meter</td>
</tr>
<tr>
<td>deg</td>
<td>Degree</td>
</tr>
<tr>
<td>mid</td>
<td>Middle</td>
</tr>
<tr>
<td>mj</td>
<td>Millie joule</td>
</tr>
<tr>
<td>Wt.</td>
<td>Weight</td>
</tr>
<tr>
<td>Mwt</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethyl Formamide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>KGy</td>
<td>Kilo gray</td>
</tr>
<tr>
<td>GE</td>
<td>Grafting efficiency</td>
</tr>
<tr>
<td>Wg.</td>
<td>Weight of pure grafted copolymer</td>
</tr>
<tr>
<td>Wp</td>
<td>Weight of polysaccharide</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>K cal</td>
<td>Kilo calorie</td>
</tr>
<tr>
<td>Kg</td>
<td>Kilo gram</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo gravimetric analysis</td>
</tr>
<tr>
<td>Ac</td>
<td>Acrylamide</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetry</td>
</tr>
<tr>
<td>mg</td>
<td>Milli gram</td>
</tr>
<tr>
<td>cP</td>
<td>Centipoise</td>
</tr>
<tr>
<td>(w/v)</td>
<td>The amount by weight (mass) of a solid substance dissolved in a measured quantity of liquid.</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<table>
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<tr>
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<tr>
<td>β</td>
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</tr>
<tr>
<td>γ</td>
<td>Gamma</td>
</tr>
<tr>
<td>κ</td>
<td>Kappa</td>
</tr>
<tr>
<td>*</td>
<td>Asterisk</td>
</tr>
<tr>
<td>&amp;</td>
<td>And</td>
</tr>
<tr>
<td>°C</td>
<td>Centigrade</td>
</tr>
<tr>
<td>%</td>
<td>Percent</td>
</tr>
<tr>
<td>/</td>
<td>Division slash</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>MeV</td>
<td>Millielectronvolt</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>Centimeter power⁻¹</td>
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</table>
CHAPTER ONE

INTRODUCTION

1.2 Introduction

Polysaccharides are polymeric carbohydrate structures which are formed by repeating units joined together by glycoside linkages and contain various degrees of branching, polysaccharides have been used extensively for their functional properties, such as thickeners, gelling agents, stabilizers, interfacial agents, flocculants and encapsulates, in such applications as food, adhesives, coatings, construction, paper, pharmaceuticals, and personal care (Whistler et al., 1993, Stephen et al., 2006, Cheng et al., 1999). Graft copolymer has a preformed polymer acting as a backbone to which polymeric chains are attached at different sites. Thus, graft copolymer consists of a polymer backbone with lateral covalently linked side chains.

The intrinsic structure and properties of nonionic, anionic, and cationic gums make them found extensive application in various areas, but the raw gum also emerges some drawbacks and cannot meet all application requirements for some special purpose. Thus, the modification of gums with small molecules was conducted because the derivatives can not only bring the favorable properties due to the introduction of functional groups, but also keep the intrinsic advantages of gums to the greatest degree (Dodi et al., 2011), and so the chemical modification always plays a dominant role to improve gums and open prospects for extending the application of raw gums.
1.2 **Objectives of the study**

The objectives of this study were to:

1. To optimize the preparation of *Acacia tortilis* gum grafted with monomers using varying concentrations of the monomer and fixed amount of the gum.

2. To use gamma irradiation as an initiator for grafting because of its successful and wide applicability.

3. To examine the applications of the grafted samples as flocculating materials.
CHAPTER TWO

LITERATURE REVIEW

2.1 Polymers: Natural polymers

The word polymer is derived from Greek words, poly (many) and mers (parts or units) of high molecular mass each molecule of which consist of a very large number of single structural units joined together in a regular manner. In other words polymers are giant molecules of high molecular weight, called macromolecules, which are build up by linking together of a large number of small molecules, called monomers. The reaction by which the monomers combine to form polymer is known as polymerization. The polymerization is a chemical reaction in which two or more substances combine together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight. The product is called polymer and the starting material is called monomer (Gowariker et al., 2005).

The polymers, which occur in nature are called natural polymer also known as biopolymers. Examples of such polymers are natural rubber, natural silk, cellulose, starch, proteins, etc., (Chanda, 2006). Naturally occurring polymers—those derived from plants and animals—have been used for many centuries; these materials include wood, rubber, cotton, wool, leather, and silk. Other natural polymers such as proteins, enzymes, starches, and cellulose are important in biological and physiological processes in plants and animals. Modern Scientific research tools have made possible the determination of the molecular structures of this group of materials, and the
development of numerous polymers, which are synthesized from small organic molecules. These long molecules are composed of structural entities called mer units, which are successively repeated along the chain. ‘‘Mer’’ originates from the Greek word meros, which means part; the term polymer was coined to mean many mers. We sometimes use the term monomer, which refers to a stable molecule from which a polymer is synthesized (William and Callister, 2001).

2.2 Polysaccharides: structure and reactivity

They are linear or branched polymers of up to seven common and uncommon monosaccharide and/or monosaccharaides derivatives that are linked by means of glycosidic bonds. The most prevalent monosaccharide unit in polysaccharides is D-galactose, followed by D-mannose, D-fructose, D-and L-galactose, D-xylose, D-arabinose, D-glucosamine, D-galactosamine, D-glucouronic acid, N-acetyl muran (Dumitrius, 1998). They are formed from both hexose (mainly glucose, mannose, and galactose) and pentose (mainly xylose and arabinose) sugars and, thus, have widely varying structures and properties dependent on the component sugars and mode of linkage. Polysaccharides built from one monomer only are termed homopolysaccharides. Some polysaccharides have a linear structure, whereas others are branched. The branched are attached to a linear main chain of monosaccharides through glycosidic links. Polysaccharides are widely distributed in nature, both in plants and animals, and serve a variety of functions. In general, the can be classified as storage materials structural components, or protective substances. Structural polysaccharides fall into two distinct classes; fibrous
polysaccharides and matrix polysaccharides. The most widely known and pervasive fibrous polysaccharide is cellulose which occurs in higher plants and some algae. Lesser known fibrous polysaccharides include chitin in yeasts and fungi (and chitosan in the shells of arthropods) and (1-3) linked β-D-xylans and (1-4) linked β-D-mannans in algae (Dumitrius, 1998).

Matrix polysaccharides, in contrast, are characterized by their gel-forming capacity which confers flexibility to the structural assembly. Hemicellulose and pectins in higher plants are typical examples of matrix polysaccharides. Polysaccharides have various characteristics which are not found in other natural polymers and biopolymers. Therefore, polysaccharides have been effectively used in every field including food, clothing, and shelter. Recently, effective utilizations of biomass are very important because of the social demands for recourse, energies, and environments and are being positively investigated over a wide variety of fields because polysaccharides are produced by living things, it is advantageous that we can easily obtain them (Dumitrius, 1998).

2.3 Grafting

Reaction in which one or more species of block are connected to the main chain of a macromolecule as side chains having constitutional or configurational features that differ from those in the main chain (ISO, 1986).

2.3.1 Surface grafting

Process in which a polymer surface is chemically modified by grafting or by the generation of active sites that can lead to the initiation of a graft polymerization. Peroxidation, ozonolysis, high-energy irradiation, and plasma etching are methods of generating active sites on a polymer surface (ISO, 1986).
2.3.2 Graft copolymers

The formula of a graft copolymer consisting of a polymeric backbone of monomeric units A to which an unknown number of blocks of monomeric Units B (grafts) are linked at known sites to some of the monomeric units A. A graft polymer is a polymer comprising molecules with one or more species of block connected to the main chain as side chains, these side chains having constitutional or configurational features that differ from those in the main chain. In a graft copolymer the distinguishing feature of the side chains is constitutional, i.e. the side chains comprise units derived from at least one species of monomer different from those which supply the units of the main chain (IUPAC, 1966). A copolymer wherein homopolymer side branches of one mer type are grafted to homopolymer main chains of a different mer (Callister, 2001).

2.3.3 Chemical grafting

Chemical grafting is one of the most effective methods for modifying structure and properties of biopolymers. Graft copolymerization of natural polysaccharides is becoming an important resource for improve the functional properties of these materials (Pal et al., 2012).

2.3.4 Radiation-induced grafting

Grafting by irradiation of polymers in the presence of, or followed by, treatment with monomer has been one of the most successful of all grafting methods and has been applied to an enormous number of polymer-monomer systems. Chemical bonds are ruptured in organic materials when they are irradiated with electromagnetic or particulate radiation of 100 eV or greater. Among the commonly used energy sources are Cobalt-60, electron accelerators, and nuclear reactors. Free radicals have been detected
in irradiated organic systems, and if vinyl monomers are irradiated, polymerizations take place through a free radical mechanism. In the presence of a monomer, graft copolymers as well as homo polymers may be formed. When none of the bonds within a system is ruptured by this low energy radiation, copolymerization can be otherwise promoted by the addition of photosensitizers (Hebeish, 1981).

The gamma (\(\gamma\)) source is the only one which does not require electrical power for activation. Two common \(\gamma\) sources are available Co-60 and Cs-137, though Co-60 is the one used in commercial isotope radiation plants. The reasons for this are not difficult to find. Co-60 is relatively cheap, has a useful half-life of 5.25 years, is unaffected by high energy radiation from external sources, and may be used up to temperatures of 1300 K. The emission of two gamma rays per disintegration provides a total of 2.5 MeV energy per disintegration. Co-60 sources used on a commercial scale lend themselves to ready automation, are reliable and highly penetrating, and provide continuous irradiation during exposure. As stated above, these sources gradually lose strength, though in a controlled manner. This loss of strength means that the sources need replacing at approximately 2-5 year intervals (Hebeish, 1981).

2.3.5 Synthesis of graft copolymers

Graft copolymers, by definition consists of a long sequence of one polymer (backbone polymer) with one or more branches (grafts) of another (chemically different) polymer (Odian, 2002).

The process of graft copolymer synthesis starts with a natural polymer in this case; an external agent is used to create free radical sites on this preformed polymer. The agent should be effective enough to create the required free radical sites, once the free radical sites are formed on the polymer backbone, the monomer (acrylamide compound) can get added up
through the chain propagation step, leading to the formation of grafted chains. The properties of natural polymers can be modified by hybridization with synthetic polymers. The chemical combination of natural and synthetic polymers yields new materials which could have desirable properties (Prieto et al., 2012).

2.4 A. gums

Plant gums are organic substances obtained as exudation from trunks, or “branches of trees, spontaneously or after mechanical injury, of the plant by incision of the bark, or by the removed of branch, or after invasion by bacteria or fungi”. The term gum often describes materials which effect the sense of touch, taste and sight in measure summed up as property of “gummosis” which is difficult to the define but visual and manual examination of the material may cause the observer to call it gum (Mantell, 1947).

Gum refers to any polysaccharide that is dispersible in water to give viscous solution, gels or colloidal dispersions. Generally gums are long chain high molecular weight polymers that dissolve or disperse in water to give thickening or gelling effect and exhibit related secondary functional properties, such as emulsification, stabilization, and encapsulation gum, or hydrocolloids, are mainly long-chain, straight to branched polysaccharides that contain hydroxy groups that can bond water molecules. These chains consist of $2 \times 10^3$ to $10^4$ monosaccharaides units. The sugar monomers can contain linked side units, or substituent groups, such as sulphates, methyl ethers, esters and acetals. Gum composed mainly of $C, H, O$ and $N$ elements, and acidic gums (e.g., gum Arabic) contain mainly $Ca, Mg, Na$, and $Fe$, as cations (Sharma, 1981; Kuntz, 1990, Hirsrt, 1958).
In a wider sense, the name A. gum is also used to denominate gums produced by other A. species, for example A. Karroo, and is sometimes referred to as gum A. (FAO, 1995).

Gums from A. are complex polysaccharides composed of carbohydrate moieties; gum arabic for example is composed of: galactose, arabinopyranose, arabinofuranose, rhamnose, glucuronic acid and 4-o-methylglucuronic acid. The main structural feature is a central chain of β-galactopyranose units with 1, 3 bonds and side chains of 1,6-linked galactopyranose units terminating the glucuronic acid residues. The gum has variable protein content depending on the species. Gums are either hydrophobic or hydrophilic. Hydrophobic gums are insoluble in water and include resins, rubber and others. While hydrophilic gums are soluble in water and can be subdivided into natural, semi synthetic and synthetic gums (Glicksman and Sand, 1973).

The Sudanese major gums of economic importance are in the order of gum Arabic, gum talha and A. polyacantha gum. The source of gum Arabic is A. Senegal var Senegal. A polyacantha exudate is closely related to, and can hardly be distinguished form, the other A. exudates unless recognized by acknowledge gum expert or studying the physicochemical characteristic. The two species A. Senegal and A. polyacantha belong to the same group known as the A. Senegal complex. All gum exudates, from this group of A. species, have a laevorotatory (negative specific rotation) in contrast to the A. seyal complex, which produce gum exudates, which have dextrorotatory (positive specific rotation). Other structure, botanical and immunological characteristic are noticeable even within the same species.
2.4.1 Classification of Acacias

*Acacias* are plants within the subfamily *Mimosoideae* of the family *Leguminosae* (the Pea family), and is the second largest genus in the family *Leguminosae*, with about 1350 species currently recognized. These species are distributed throughout tropical and warm temperate areas of the world, with the largest concentrations occurring in Australia (955 species), with also high numbers in the Americas (about 185 species), Africa (144 species) and Asia (89 species). There has been an accumulation of new data derived from both morphological and molecular genetic studies, and this has led to a better understanding of the classification and phylogeny of *A.* (Maslin, 1990; 2001; Maslin, *et al*., 2003).

Sudan is endowed with more than 30 *A.* species, most of which yield gum (EL Amin, 1990), species with greatest distribution include *A. senegal* (Hashab), *A. seyal* (Talha), *A. polyacantha* (Kakamut), *A. laeta* (Shubahi), *A. mellifera* (Kitir), *A. nilotica* (sunot), *A. sieberiana* (kuk), and *A. Oerfota* (*Nubica*, Laot) (Abdel Nour, 1999).

*A. trees* are multipurpose; they do not produce only gum, but also prevent desert encroachment, restore soil fertility, and provide fuel and fodder. Almost all commercial gum comes from the so-called gum belt of Africa, a vast area which extends over, Benin, Burkina Faso, Chad, Eritrea, Ethiopia, Kenya, Mauritania, Mali, Niger, Nigeria, Senegal, Somalia, Sudan, and Uganda (FAO, 1995). Sudan is the world's largest producer of gum arabic, followed by Nigeria, Chad, Mali, and Senegal. Gum from the Sudanese Kordofan region is known as the best quality gum and is used as the standard to judge the quality of gums obtained from other areas. Commercial gum arabic is collected from a number of *A.* species, of which *A. Senegal*, *A. Seyal*, and *A. polyacantha* are the most widespread in the gum belt. *A. laeta*, *A. karoo*, and *A. gourmaensis* are some other species with a more limited distribution (Islam *et al*., 1997).
In Sudan, the gums from *A. Senegal* and *A. seyal* are referred to as hashab and talha respectively, the former considered of higher quality (Baldwin *et al.*, 1999).

Most of these species grow scattered in the wild and gum from these untended trees is collected by semi-nomadic people. Cultivation is only practiced for *A. Senegal*. Particularly in Sudan, wild stands of *A.* trees are replaced by monocultures of *A. Senegal* in order to facilitate collection and obtain a more consistent quality. Gum arabic from other African countries may be variable in quality, because it may contain gums obtained from different species which occur jointly in the collection area. After 5 years, trees reach maturity and are tapped. Although the trees can be tapped after 3 years, the quality and yield are consistent only after 5 years, suggesting that gum biosynthesis and tree growth are in competition with each other (Joseleau and Ullmann, 1990).

### 2.5 Physicochemical properties of gums

The physicochemical properties of the natural gum are most important in determining their commercial value and their use. These properties vary with gums different botanical source, and even substantial differences in gum from the same species when collected from plants growing under different climatic conditions or even when collected from the plant at different season of the year (Hirst and Jones, 1958).

The physical properties may also be affected by the age of the tree and treatment of the gum after collection such as washing, drying, sun bleaching and storage temperature. The physical properties of gum arabic, established as quality parameters include moisture, total ash, volatile matter and internal energy.

Gum arabic is a natural product complex mixture of hydrophilic carbohydrate and hydrophobic protein components emulsifier which
adsorbs onto surface of oil droplets while hydrophilic carbohydrate component inhibits flocculation and coalescence of molecules through electrostatic and steric repulsions in food additives (Lelon et al., 2010). Gum Arabic physicochemical responses can be handled depending on the balance of hydrophilic and hydrophobic interactions (Lelon et al., 2010).

2.5.1 Solubility

Gums can be classified into three categories with regard to their solubilities (Omer, 2004):

i) Entirely soluble gums: e.g., A. Senegal, A. seyal.

ii) Partially soluble gums: e.g., Gatti gum.

iii) Insoluble gums: e.g., Tragacanth gum.

2.5.2 Moisture content

The moisture content is weight lost due to the evaporation of water (Person, 1970). It shows the hardness of the gum and hence variability of densities, the amount of densities, and the amount of the air entrapped during formation (Omer, 2004; Anderson and Herbich, 1963). The moisture content of A. Senegal gum was reported to be in the range from 11% to 16.1%. The moisture content of Kordofan A. Senegal was found to be 15.5% (Osman et al., 1993). Recently, (Younes, 2009) reported the mean value of moisture content for A. Senegal gum is 11.01% and the range was 9.91%-14.72%. The hardness of gum would be determined by moisture content. The moisture content of good quality gum does not exceed 15 and 10% for granular and spray dried material respectively. (Siddig, 1996) recently reported that the moisture content of A. polyacanthra gum to be around 8.2%.
2.5.3 Ash

Ash content is a measure of inorganic residue remaining after organic matter has been burnt. The inorganic residues exist as elements (Siddig, 1996; Anderson et al., 1985). The type of the soil (clay or sand) affected the ash content significantly; previously the ash content for A. polyacantha gum was determined as 2.929 ash% (Anderson et al., 1985).

2.5.4 Nitrogen

According to studies of emulsifying behavior of gum arabic, there is strong correlation between the proportion of protein in the gum and it is emulsifying stability. The protein contents of fresh samples were fairly constant (2%) irrespective of the age of the tree. (Idris, 1989 and Siddig, 1996) reported that the average value of nitrogen content of commercial samples of A. Senegal gum and 80% of authenticated samples analyzed were in the range (0.27-0.39%).

2.5.5 Specific rotation

The optical activity of organic molecules (saccharides and carbohydrates) is related to their structure and a characteristic property of the substance (Stevens, et al., 1987). The gum of natural origin, e.g., A. Senegal gum, has the property of rotating the plane of the polarized light. The direction of the rotation, as well as the magnitude is considered as a diagnostic parameter (Biswas, et al., 2000). A. Senegal gum gives a negative optical rotation ranging between -20° to -34°. The optical rotation is used to differentiate between A. Senegal and other botanically related A. gums. (Anderson and Stoddart 1966) reported that the specific rotation for electrodialysed A. Senegal gum was -31.5. Pure gum from A. Senegal has specific optical rotation of -27 to -30 (Tioback, 1922). Certain variation in the degree of the optical rotation (-27 to -32) has been noticed by
They found that the mean of the specific optical rotation of commercial *A. Senegal* gum was -30.54. The optical rotation is not affected by both auto hydrolysis and variation, while mild acidic hydrolysis has a significant effect on optical rotation. (Barron *et al.*, 1991 and Omer, 2004) reported that the mean of specific rotation of authenticated samples of *A. polyacantha* gum was -16.6°.

### 2.5.6 Viscosity

The viscosity of liquid is its resistance to shearing, to stirring or to flow through a capillary tube (Baneraft, 1932). Studies of flow of gum solutions play an important role in identification and characterization of their molecular structure. Since viscosity involves the size and the shape of the macromolecule, it was considered as one of the most important analytical and commercial parameter (Anderson, 1966).

The viscosity of a solution may have a complicated variation with composition, due to the possibility of hydrogen bonding among the solute and solvent molecules. More hydroxyl groups make high viscosities, because a network of hydrogen bonds is formed between the molecules, this network extends throughout the liquid, thus making the flow difficult. The viscosity of gum solutions is inversely proportional to temperature. They also found that the viscosity of gum arabic solutions changes with pH, but they found a maximum viscosity at pH 6-7. Viscosity can be explained in different terms such as relative viscosity, specific viscosity, reduced viscosity, and inherent viscosity and intrinsic; it is also represented as kinematics or dynamic viscosity. Anderson, 1978 reported that the intrinsic viscosity of *A. polyacantha* gum was 15.8 ml/g. relatively recent (Omer, 2004), reported 10.34 ml/g intrinsic viscosity for *A. polyacantha* gum.
2.5.7 Molecular weight

The molecular weight of the polymers can be determined from physical measurement or by application of chemical methods. The applications of chemical methods require that the structure of the polymer should contain well known number of functional groups per molecule and they invariably occur as end groups. The end group analysis method gives an approximately number of molecules in a given weight of sample; they yield the average number of molecules for polymeric materials. This method becomes insensitive at high molecular weight, as the fraction of end groups becomes too small to be measured with precision (Meyer, 1971). This is due to the fact that fraudulent sources of the end groups not considered in the assumed reaction mechanism steadily become consequential as the molecular weight increases and the number of end groups diminishes to such an extent their quantities determination is not feasible. Those reactions confine frequent application of chemical methods to condensation polymers with average molecular weight seldom exceeding $2.5 \times 10^3$ (Flory, 1953). Physical methods frequently used for establishing polymer molecular weight are osmometry, polymer viscosity, measurement of coefficient of diffusion, ultra-centrifugation and light scattering.

2.6 Uses of gum Arabic

Gum Arabic is being widely used for industrial purposes such as a stabilizer, a thickener, an emulsifier and an encapsulating in the food industry, and to a lesser extent in textiles, ceramics, lithography, cosmetic, and pharmaceutical industry (Verbeken et al., 2003). In the food industry, Gum arabic is primarily used in confectionery, bakery, dairy, beverage, and as a microencapsulating agent.
2.6.1 Paper industry

Gum prevents dilatancy at high shear, helps regular distribution of pulp fibres, increases bursting strength decreases porosity and improves surface properties (FAO, 2007 and Howes, 1949). Gum Arabic is used often as a likable adhesive on postage stamps and cigarette papers.

2.6.2 Textile industry

Gum is used as a thickening agent for pigment in printing fabrics. It prevents migration of dyestuff in pad dying operations, and produces very fine line prints with good definition and excellent washout (Coppen, 1995, FAO, 2007 and Howes, 1949).

2.6.3 Pharmaceutical and cosmetics industries

Gums are principal components in pharmaceutical industries. Gum *Tragacanth* is superior in pharmaceutical applications. Gum is used as suspending agent for insoluble drugs, demulcent agent, emulsification, antiseptic preparations, binder for tablets and tablet coating, jelly lubricants, spermicidal jellies and to mask the unpleasant taste of syrups. It is also used as a medicine for treatment for low blood pressure caused by hemorrhage or surgical shock. It is used topically for healing wounds and has been shown to inhibit the early deposition of periodontal bacteria and the early deposition of plaque (Coppen, 1995, FAO, 2007 and Howes, 1949).

A. Cosmetics

Spreading properties of gums add smoothness to the skin and forms a thin protective coating. They are used for preparation of facial masks, foam stabilizer, production of liquid soaps, lotions, protective creams, face powder, tooth paste, mouth wash and hair cream (Coppen, 1995 and FAO,
Gum arabic serves as an emulsifier and stabilizer in cosmetic products containing oil-water interfaces (Dror et al., 2006).

2.6.4 Food applications

Gum Arabic is a natural dietary fiber which is to human digestive enzymes. It is not digested in the upper intestinal tract digestive enzymes. It is not digested in the upper intestinal tract but is fragmented in the large gut. Its fragmentation leads to stimulation of the endogenous micro-flour (prebiotic effect) and the production of short chain fatty acids. Moreover, it does not exhibit the nutritional side-effects (laxative effect and/or flatulence) generally associated with other bulking agent or low molecular weight fiber. However, properties such as high solubility associated with low viscosity and absence of taste and Oduor made it easy to incorporate. Gum arabic in different food stuffs without disturbing their organo-leptie properties (Kravtchenko, 1998 and Sharma, 1981).

Gum is used in dairy products such as ice creams, packed milk and processed baby foods. It is also used in the backing industry for its comparatively low water absorption properties and its favorable adhesive properties in glazes and toppings. One of the main used of spray dried Gum Arabic is in solution form such as in beverages, beverage emulsion, and flavour emulsions such as orange juice, lemon juice, cherry and cola (Buffo et al., 2001, Phillips et al., 2006 and Prakash et al., 1990). When used as flavour fixative, it is presumed that gum forms a thin film coating around the flavour particle protecting it from oxidation, evaporation and absorption of moisture thus conferring stability, longer shelf life and superior product quality nutritive properties.

A. Confectionery

The gum also emulsifies and evenly distributes the lipid compounds and gives a clear and finer taste. Gum also acts as adhesive, whipping and
stabilizing agents for confections. A large part of gum arabic is used in confectionery products to prevent crystallization (Coppen, 1995, FAO, 2007 and Howes, 1949). Gum arabic prevents sucrose crystallization in gum drops, emulsifies and distributes fatty components in confections; it emulsifies and distributes fat particles in caramel and toffee. It functions as a binder and structure builder in cough drops and lozenges. In panned sugar confections, it serves as a coating agent and film-former (Fennema, 1996).

B. Bakery products
Gums give the good water holding capacity and less flabby appearance for the products. The gum gives softer and better texture and also used as a component in topping, icing bases and flavour release at specific melting temperature (Coppen, 1995 and FAO, 2007). Gum arabic used as a source of soluble dietary fiber in bakery products (Fennema, 1996).

C. Beverages
Gum Arabic is an effective foam stabilizer in beverages and dry mixes, produced by spray dried combinations of vegetable oil and gum Arabic, sold commercially as a clouding agent (Tewari, 2010). Gum arabic used as a source of soluble dietary fiber in beverage (Fennema, 1996). There is “emulsion grade” for gum arabic to be used as emulsifiers in beverages. Significant amounts of gum are needed to stabilize cola emulsions; somewhere between 18 and 22% weight/volume (Mohamed, 2017).

2.7 A. tortilis (Umbrella thorn)
2.7.1 Taxonomy and nomenclature (https://www.cabi.org/isc/datasheet/2431)

Degree: Eukaryota
Kingdom: Plantae
Phylum: Spermatophyta
Subphylum: Angiospermae
Class: Dicotyledonae
Order: Fabales
Family: Fabaceae
Subfamily: Mimosoideae
Genus: Acacia
Species: A. tortilis

I. Preferred scientific name: A. tortilis (Forssk.) Hayne

II. Preferred common name: umbrella thorn


IV. Arabic names: samr; sayal; sayyal; seyal; tamat


2.7.2 Description and distribution

A. tortilis, a member of family Mimosoideae is very distinctive and easily recognized with the characteristics mixture of long straight spines and shorter hooked ones combined with spirally twisted or contorted crown has given it the popular name of Umbrella thorn. The name ‘tortilis’ means twisted and refers to the pod structure (Gebrekiros et al., 2016; Orwa et al., 2009).
Is a small to medium sized evergreen tree or shrub that grows up to 21 m tall; well-developed multiple boles support a flat-topped or rounded, spreading crown, bark grey to black or dark brown, rough, fissured or smooth; young branchlets densely pubescent or glabrous to subglabrous and red to brown; spines paired, 2 types-long, straight and white, or short, brownish and hooked; they range from 1.2 to 8 cm in length (Orwa et al., 2009).

*A. tortilis* is drought resistant (Abdallah *et al.*, 2008, Grouzis and Le Floch, 2003) can tolerate strong salinity and seasonal water logging and generally forms open, dry forests in pure stands or mixed with other species. The long taproot and numerous lateral roots enable it to utilize the limited soil moisture available in the arid areas.

*A. tortilis*, widespread throughout the savannah and dry zones of Africa, from Senegal to Somalia and south to South Africa; in Asia in Israel, Jordan and southern Arabia to Iran. In the countries that fringe the Sahara it is often the species that extends furthest into the desert. It is found growing from below sea level and up to 2000 m altitude and tolerates light night frost. It favours alkaline soils and avoids waterlogged sites, but apart from that it will grow on a wide range of sites (Jøker, 2000).


The map below (Figure 2.1) shows countries where the species has been planted. It does neither suggest that the species can be planted in every ecological zone within that country, nor that the species cannot be planted...
in other countries than those depicted. Since some tree species are invasive (Orwa et al., 2009).

Figure 2.1: shows the countries where the species has been planted.

2.7.3 Ecology

A. tortilis is drought resistant, can tolerate strong salinity and seasonal water logging and generally forms open, dry forests in pure stands or mixed with other species. The long taproot and numerous lateral roots enable it to utilize the limited soil moisture available in the arid areas. It tolerates a maximum temperature of 50 deg. C and a minimum temperature close to 0 deg. C. (Orwa et al., 2009).

2.7.4 Biology

A. tortilis is a hermaphrodite. Gravity or propulsion from drying dehiscent pods initiates seed dispersal. In India, trees flower between May and June and fruit by mid-July, and in Nigeria flowers appear in May-June and fruits in July (Orwa et al., 2009).
2.7.5 Uses

A slow-growing species but grows relatively fast on dry soils. It is an important fodder tree in many arid areas. Pods and leaves have a good level of digestible protein (mean = 12%) and energy 6.1 MJ/kg dry matter, as well as being rich in minerals. Seeds are high in crude protein (38%) and phosphorus, an element usually scarce in grasslands (Jøker, 2000). The pods require milling to increase digestion in cattle. Over 90% of the flowers abort and drop from the trees, providing additional important forage. The wood is excellent for fuel wood production and the tree resprouts vigorously when coppiced. Although used for a number of purposes, the timber is neither strong nor durable (Jøker, 2000).

*A. tortilis* starts producing fuelwood at the age of 8-18 years, at the rate of 50 kg/tree. Its fast growth and good coppicing behaviour, coupled with the high calorific value for its wood (4400 kcal/kg), make it suitable for firewood and charcoal. The sapwood and heartwood are white and lustrous, with the heartwood aging to reddish-brown. Growth rings are distinct and separated by brown lines. The wood is moderately soft, not very strong, and is readily attacked by decay-causing fungi and insects. It should be promptly converted after felling and subjected to rapid drying conditions. The timber is not durable in the open but moderately so under cover. It is used for planking, boxes, poles, moisture proof plywood, gun and rifle parts, furniture, house construction and farm implements. It is believed that Noah of the Old Testament made his ark from the wood of *A. tortilis*. The bark is reported to be a rich source of tannin. *A. tortilis* is a powerful molluscicide and algicide; in Sudan, fruits are placed in fish ponds to kill the snail species that carry schistosomiasis, without affecting the fish. The dried, powdered bark is used as a disinfectant in healing wounds; in Senegal it serves as an anthelmintic. In Somalia the stem is used to treat asthma. Seeds are taken to treat diarrhoea (Orwa *et al.*., 2009).
CHAPTER THREE

MATERIALS AND METHODS

3.1 Sample collection and pretreatments

*A. tortilis* gum sample was kindly supplied by Professor Mohamed Elmobarak Osman and was used as received.

3.2 Chemicals

Methanol AR (Mwt = 32.04 g mole\(^{-1}\), minimum assay = 99.5\%), was purchased from SD fine limited; N, N-Dimethyl Formamide (DMF), (Minimum assay = 99.7\%, Mwt = 73.09 g mole\(^{-1}\)), purchased from LOBA Chemie; Styrene (Assay = 99.9\%) was purchased from Merck; Acrylamide, Extra pure (Minimum assay = 99.0\%, Mwt = 71.08 g mole\(^{-1}\)), was purchased from HIMEDIA LABORATORIES, Mumbai, India.

3.3 Synthesis and preparation of *A. tortilis* gum grafted samples

Grafted *A. tortilis* gum samples were prepared based on the detailed method that is shown in Table 3.1. In a typical experiment, 5 g of the gum sample were taken into three separate containers and dissolved in distilled water. 2.5 g (based on the weight of the gum sample) of the monomer were added to each container and mixed thoroughly with a homogenizer at ambient temperature. The first container was irradiated by 2.5 KGy while the second container with 7.5 KGy and the third with 12 KGy. Exactly typical experiments were performed by adding 5 and 10 grams of the monomer to 5 g of the gum sample and irradiated with varying gamma radiation doses as above. The irradiated samples were washed with
methanol and dimethyl formamide to remove unreacted monomer as well as the homopolymer. The product was air-dried at room temperature for 48 hours and further dried at 80 °C in an oven till constant weight was reached. The grafting efficiency (% GE), was calculated according to the following equation:

\[
\% GE = 100 \times \frac{W_g - W_p}{W_p} \quad \text{.......................................................... (3.1)}
\]

Where \( w_g \) and \( w_p \) denote the weights of pure graft copolymer and polysaccharide respectively.

Table 3.1: Represents the detailed preparation conditions of the grafted gum samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Gum (grams)</th>
<th>Monomer (grams)</th>
<th>Gamma dose (KGy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>5</td>
<td>2.5</td>
<td>12</td>
</tr>
<tr>
<td>2a</td>
<td>5</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>3a</td>
<td>5</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>1b</td>
<td>5</td>
<td>2.5</td>
<td>7.5</td>
</tr>
<tr>
<td>2b</td>
<td>5</td>
<td>5</td>
<td>7.5</td>
</tr>
<tr>
<td>3b</td>
<td>5</td>
<td>10</td>
<td>7.5</td>
</tr>
<tr>
<td>1c</td>
<td>5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>2c</td>
<td>5</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>3c</td>
<td>5</td>
<td>10</td>
<td>2.5</td>
</tr>
</tbody>
</table>

3.4 **Fourier Transform Infrared Spectroscopy (FT-IR)**

Infrared spectra of the crude *A. tortilis* gum and grafted samples were obtained using Fourier-transform infrared (FT-IR) spectrometer (8400s, shimadzu), in the range of 400 - 4000 cm\(^{-1}\) with a number of scan of 10 and a resolution of 4 cm\(^{-1}\). Few milligrams of the sample were ground with KBr (1:9), the mixture was pressed to make a disk and the spectra were recorded.
3.5 **Viscosity of the aqueous solutions of crude and the grafted samples**

The viscosities of the aqueous solutions of crude and grafted samples were obtained using Haake Viscotester 6 Plus (Thermo Electron Corporation). In each case 0.5 % (wt/v) solution of the crude and the grafted samples was prepared and the viscosity was recorded in the room temperature.

3.6 **pH measurements**

The pH values of the solutions of the crude and grafted samples were determined by a Jenway pH meter, which was previously calibrated using standard buffer solutions (pH 4, 7 & 10). 1% aqueous solution of each gum sample was prepared and the pH electrode (combination electrode) was immersed in the sample, left for few minutes and the pH value was recorded at room temperature.

3.7 **Thermogravimetric analysis (TGA)**

Thermogravimetric analysis (TGA) was performed to examine the thermal stability of the crude and the grafted samples. 10 mg of each sample was subjected to heating in a platinum crucible in Linseis TGA PT 1000-Thermogravimetric analyzer. The heating rate was 5°C/minute and the temperature range was between 30 to 700 °C under flowing of oxygen gas.

3.8 **Flocculation characteristics of the crude and the grafted A. gum**

Turbid water sample was collected directly from tap water during autumn season in which the water of Nile River turns into deep brown color. 50 ml of the water sample were transferred by a measuring cylinder into four different beakers. 1g of each of crude and grafted samples was dissolved in 20 ml distilled water and added to the above beakers and
photographed at different time intervals to examine the flocculation characteristics of these materials.
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Grafting efficiency

The grafting efficiency of the monomer onto *A. tortilis* gum at different gamma radiation doses as well as varying monomer concentrations were determined and the results are shown in Figure 4.1. As can be seen from the figure the grafting efficiency increased significantly with the increase in monomer. On other hand, slight changes in grafting efficiency with the doses of gamma radiation were observed. The significant increase in grafting efficiency for the same dose with increasing monomer concentration could be attributed to the availability of the monomer molecules for the reaction (Casimiro *et al.*, 2005).

![Graph showing grafting efficiency](Image)

**Figure 4.1:** Grafting efficiency of the monomer onto *A. gum*
4.2 FT-IR analysis

The FTIR spectra of the crude gum and the grafted samples are presented in Figures 4.2, 4.3 and 4.4. As can be seen from Figure 4.2, the intense broad band at 3300 cm\(^{-1}\) is attributed to the stretching vibration of –OH group while the peak at the range 2800 – 2900 cm\(^{-1}\) is due to stretching vibration of –CH (saturated system). The absorption bands at 1636, 1427 and 1371 cm\(^{-1}\) are due to bending vibrations of –OH and –CH groups respectively. In addition, several absorption bands at 1730, 1248, 1150 and 1020 cm\(^{-1}\) are attributed to carbonyl, -C—C-, and -C—O stretching vibrations. Similarly, (Daoub et al., 2016) have reported almost identical FTIR spectrum of A. gum samples. The FTIR spectra of the grafted samples on the other hand, have shown almost identical absorption bands to the crude gum sample with few variations.

Figure 4.2: FTIR spectrum of the crude gum (sample D)
Figure 4.3: FTIR spectrum of the grafted sample (sample 3c)

Figure 4.4: FTIR spectrum of the grafted sample (sample 3b)

4.3 Viscosity

The viscosity of the irradiated samples was measured at room temperature using a viscometer and the results are presented in Table 4.1. The results showed that both the radiation dose and the amount of the monomer have crucial influence on the viscosity of grafted samples. Sample 3c and 1b have displayed the highest viscosity values; 49 and 44 cp respectively. In addition, samples 1a, 2a and 3b have given 20, 13 and 12
It is clear that all the grafted samples have viscosities higher that the crude sample.

Table 4.1: The viscosity of 0.5% (w/v) aqueous solutions of crude and grafted samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Viscosity (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a (2.5g M and 12 KGY)</td>
<td>20</td>
</tr>
<tr>
<td>2a (5g M and 12 KGY)</td>
<td>13</td>
</tr>
<tr>
<td>3a (10g M and 12 KGY)</td>
<td>11</td>
</tr>
<tr>
<td>1b (2.5g M and 7.5 KGY)</td>
<td>44</td>
</tr>
<tr>
<td>3b (10g M and 7.5 KGY)</td>
<td>12</td>
</tr>
<tr>
<td>3c (10g M and 2.5 KGY)</td>
<td>49</td>
</tr>
<tr>
<td>Crude gum</td>
<td>10</td>
</tr>
</tbody>
</table>

On the other hand, the viscosities of the grafted samples decreased with the increase in radiation dose and to some extent with the increase in the amount of the monomer. This may due to appearance of branched chain which decreases the viscosity, because the viscosity of gum is influenced by its chemical structure, the linear chain shows higher viscosity when it compared to branched one. It could also be due to the larger area and volume required for gyration of linear chain gums than the branched one. Similar results were reported by (Srivastava and Kumar 2013) for k-Carrageenan. the viscosity of acrylic acid-g-(k-Carrageenan) copolymer was lower than the carrageenan, that might be due to the presence of grafted chain, which make the molecule more flexible and reduce the viscosity drastically because a branched polymer`s hydrodynamic volume will be lower than the linear polymer (Srivastava and Kumar 2013). Comparative study by (Bhushette and Annapure 2017) also showed the same result for A. nilotica when it compared to other A. gums (Bhushette and Annapure, 2017). Additional study, Effect of gamma irradiation on rheological
properties of polysaccharides exuded by *A. fluccosus* and *A. gossypinus* by (Alijani *et al.*, 2011) proved that the viscosity of linear polymers is higher than that of the branched polymer. But also the results proved that the viscosity increase with the increase in radiation amount as it was happened in samples (1b, 3b, and 3c), and (crude gum) showed only 10 cp viscosity. Same result obtained by (Katayama *et al.*, 2006) for Radiation-induced Polymerization of gum Arabic (*A. Senegal*) in aqueous solution.

### 4.4 pH measurements

The pH measurements were performed for the crude gum and the grafted samples and the results are presented in Table 3.2. As it is evident from the results, the aqueous solutions of both the crude gum and the grafted samples are acidic. Furthermore, there is a slight decrease in the acidity of the grafted samples with the increase in gamma radiation dose for the samples having the same amount of monomer and gum (samples 3a, 3b and 3c). The acidity of *A.* gums like gum Arabic (*A.*senegal), *A.* sieberiana and *A.* nilotica is expected since they are known to contain salts (Ca, Mg, K, Na and Fe) of acidic polysaccharides, the acidity of which is due to uronic acid in their structures.

**Table 4.2:** The pH of 0.5% (w/v) aqueous solutions of crude and grafted samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude gum</td>
<td>5.193</td>
</tr>
<tr>
<td>1a (2.5g AC and 12 KGy)</td>
<td>5.3264</td>
</tr>
<tr>
<td>2a (5g AC and 12 KGy)</td>
<td>5.413</td>
</tr>
<tr>
<td>3a (10g AC and 12 KGy)</td>
<td>5.661</td>
</tr>
<tr>
<td>1b (2.5g AC and 7.5 KGy)</td>
<td>5.302</td>
</tr>
<tr>
<td>3b (10g AC and 7.5 KGy)</td>
<td>5.517</td>
</tr>
<tr>
<td>3c (10g AC and 2.5 KGy)</td>
<td>5.319</td>
</tr>
</tbody>
</table>
Almost identical results were obtained from characterization and functional properties of some natural A. gums, which showed that the pH of A. gum is slightly acidic due to the presence of free carboxyl groups of D-glucuronic acid and 4-O-methyl D-glucuronic acid residues (Karamalla et al., 1998). Similar results were also obtained by (Abu Baker et al., 2007, Ahmed et al., 2009 and Elnour et al., 2009).

4.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) or thermogravimetry (TG) is a technique where the mass of a sample is measured as a function of temperature or time while the sample is subjected to a controlled temperature program in a controlled atmosphere. Polymers generally exhibit mass loss, although mass gain may be observed prior to degradation at slow heating rates in an oxidizing atmosphere. Mass loss may be categorized as volatile components such as absorbed moisture, residual solvents, or low-molecular-mass additives or oligomers that generally evaporate between ambient and 300°C.

The results of thermogravimetric analysis of the crude gum and the grafted samples are shown in Figures 4.5 to 4.7. It could be noticed that the thermogram of the crude gum has shown three distinct steps of degradation at 199.3, 284.0 and 439.7°C and the accompanying mass losses were 2 (10%), 8 (40%) and 12mg (60%) respectively. It could also notice that there is a gradual decrease in the mass of the crude gum with the increase of heating temperature below 200°C which is attributed to moisture loss. Moreover, the curve displayed that up to 700°C the mass loss has reached 17mg (85%). Similarly, sample 1a showed also three degradation steps with almost the same degradation temperatures and mass loss as well as the loss of the moisture below 200°C. On the other hand, samples 3c has revealed higher thermal stability (higher onset of degradation temperatures) and with
minimum mass loss in all degradation steps compared to the crude gum and sample 1a.

**Figure 4.5:** TG thermogram of the crude gum

**Figure 4.6:** TG thermogram of sample 1a
4.6 Flocculation properties of crude and grafted samples

The flocculation characteristics of the crude and grafted samples are shown in Figures 4.8 and 4.9.

Figure 4.8: Flocculation characteristics of crude gum and grafted samples after 30 minutes of addition (from left: Crude, Sample 2a, Sample 2b and Sample 3c).
It is obvious from the two figures that all the grafted samples have better ability to deposit the suspended particles in the bottom of the beakers compared to crude gum and this increases with the increase in time, from 30 minutes to 60 minutes. The decrease in the turbidity of the water sample could be attributed to the formation of particle-polymer-particle complexes between the particles and the monomer grafted polymer samples.

**Figure 4.9:** Flocculation characteristics of crude gum and grafted samples after 60 minutes of addition (from left: Crude, Sample 2a, Sample 2b and Sample 3c).
CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

*A. tortilis* grafted samples were successfully synthesized, characterized and their flocculation properties were examined. The monomer concentration was found to be the crucial factor that determines the grafting efficiency. The viscosity and the thermal properties of grafted samples were both improved whereas some degradation was also noticed as the dose increases.

5.2 Recommendation

The following are recommended for future work:

1. Optimization of the grafting reaction by varying the different parameters such as the gum, the monomer and the gamma radiation doses.
2. Using other techniques such as scanning electron microscopy and differential scanning calorimetry (DSC) to characterize the grafted samples.
3. Further applications of the grafted samples in industry is of great importance.
REFERENCES


