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Synthesis, Characterization and Flocculation Properties of Polystyrene grafted *Acacia nilotica var nilotica* gum

تصنيع وتشخيص والخصائص التجميعية لصمغ السنط (صنف السنط) المدمج معه بوليمر الإستايرن

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

By

Wafaa Hassan Omer

(BSc, Chemistry-Scientific Laboratories, SUST)

Supervisor

Dr. Essa Esmail Mohammad Ahmad

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Dedication

This research work is dedicated to:
My great parents who never stop giving of themselves in countless ways.
My beloved husband who leads me through valley of darkness with light of hope and support.
My beloved sisters, particularly my dearest sister, Safaa who stands by me when things look bleak.
My beloved twin; Ammar & Omer.
All my family, the symbol of love and giving.
My friends who encourage and support me.
All the people in my life who touch my heart.

“

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Abstract

This study was aimed to prepare and characterize *Acacia nilotica var nilotica* gum grafted samples and examine their flocculation characteristics.

The grafted samples were synthesized using varying concentrations of the monomer (2.5, 5, 7.5 and 10g) and different gamma radiation doses (2.5, 5, 7.5 and 10 KGy). Thermogravimetric analysis (TGA) has displayed that the crude gum has two degradation steps at 50-170 ℃ and 260-290 ℃ whereas the grafted samples have shown four degradation steps. In addition, all grafted samples are thermally stable than the crude gum and the stability increases with the increase of grafting percentage. Viscosity and pH measurements both suggest the occurrence of some degradation of the gum molecule as a result of gamma radiation especially at higher doses. Finally all grafted samples have shown better flocculation properties compared to crude gum sample.

مستخلص البحث

هدفت هذه الدراسة إلى تحضير وتشخيص عينات من صمغ السنط المدمج معه المونومر ودراسة خصائصها التجميعية. حُضرت العينات بإستخدام تراكيز مختلفة من المونومر (2.5, 5, 7.5, 10g) وكذلك جرعات مختلفة من أشعة قاما (2.5, 5, 7.5, 10 KGy). أوضحت نتائج التحليل الحراري الوزنى (TGA) أنّ العينة الخام تظهر خطوتين للتفكك عند 50-170 ℃ و 260-290 ℃ بينما أظهرت العينات المدمجة أربع خطوات للتفكك. بالإضافة لذلك فإن كل العينات المدمجة لها ثبات حرارى أعلى من العينة الخام ويزيد الثبات مع الزيادة نسبة الدمج. قياسات اللزوجة والرقم الهيدروجيني تشير إلى وجود تكسّر لجزيئ الصمغ نتيجة لأشعة قاما خصوصاً عند الجرعات العالية. أخيراً فقد وجد أن العينات المدمجة لها خصائص تجميعية أفضل مقارنة بالصمغ الخام.

Table of Contents

CHAPTER FOUR: Results and discussion

List of Tables

List of Figures

List of Abbreviations and Symbols

GP	Grafting percentage
FTIR	Fourier Transform Infrared
TGA	Thermogravimetric analysis
^{1}HNMR	Proton-Nuclear magnetic resonance
DSC	Differential scanning calorimetry
DTA	Differential Thermal Analysis
DMF	Dimethyl formamide
WHO	World Health Organization
FAO	Food and Agriculture Organization
KGy	Kilo Gray
cp	Centipoises
γ	Gamma
℃	Degree Celsius
gm	Gram

CHAPTER ONE

1.1 Introduction

Graft copolymer is a type of copolymer in which one or more blocks of homopolymer are grafted as branches onto a main chain, meaning it is a branched copolymer with one or more side chains of a homopolymer attached to the backbone of the main chain. Graft copolymerization is a unique method among the techniques for modifying natural polymers mostly polysaccharides. Polysaccharide graft co-polymers have been prepared in order to add new properties to the natural polymer with a minimum loss of native properties. Graft co-polymers are prepared by first generating free radicals on polysaccharides and then allowing these free radicals to serve as macro-initiators for the vinyl or acrylic monomer polymerization. In view of the growing interest and research activity in the use of renewable agriculturally derived products as extenders and replacement for synthetic petroleum-based polymers, incorporation of other monomers/ polymers into polysaccharides will not only reduce our dependence on petrochemical derivatives, but also provides improved materials which will biodegrade rapidly in the environment. Since the last three decades, grafting of various monomers onto polysaccharides such as starch has been the most frequently attempted method to impart desirable properties on the polysaccharide without sacrificing its biodegradable nature. Grafted copolymers have found numerous applications in pharmaceutical field, plastics industry, waste water treatment, textile industry and agriculture areas (Ikhuoria, *et al.*, 2010) (Kumar, *et al.*, 2017) (Lele, *et al.*, 2018).

1.2 Objective

The main objective of this study was to prepare *Acacia nilotica var nilotica* grafted samples and examine their applications as flocculent materials.

The specific objective of this study was to:

(i) Investigate the effect of different gamma radiation doses on grafting process.

(ii) Study the varying concentration of the monomer on the graft copolymerization process.

(iii) Inspect the flocculating characteristics of the grafted samples compared to the crude gum.

CHAPTER TWO

Literature review

2.1 Grafting by irradiation

In the past various techniques have been developed for radiation-induced grafting. Radiation-induced grafting method has the advantages such as simplicity, low cost, control over process and adjustment of the materials composition and structure. In addition, this method assures the grafting of monomers that are difficult to polymerize by conventional methods without residues of initiators and catalyst. This method is simply based on the irradiation of a base polymer either in the presence of a monomer (simultaneous radiation grafting) or without a monomer (pre-irradiation grafting) to create active sites. In the pre-irradiation method polymeric matrix is first irradiated in order to generate active sites either in inert atmosphere or in vacuum. The radicals have to be stable at ambient temperature in order to initiate covalent bonds with monomers after irradiation. The procedure results in elimination of homopolymerization, however the yield of grafting is in this case relatively low. Other variation of such a method is an application of air atmosphere during exposure to ionizing radiation. Both techniques are suitable if only formed radicals are stable enough to react with monomers in post-irradiation effect. In such a case grafting, depending on the system, might be performed after long storage time. The most frequent method used for grafting consists in irradiation of monomer solution in contact with the surface of polymer (Przybytniak, *et al.*, 2008) (Işıkel Şanlı, *et al.*, 2011).

2.2 Acacia gum

Gum acacia, also called as gum arabic, is a naturally occurring gum extracted from the hardened exudates of plants *Acacia senegal* and *Acacia seyal*. Commercially available gum acacia is largely sourced from trees in the Sahel region of Africa. It is available in powdered, granular, and spray dried form. It is a complex mixture of sugars and hemicellulose. It is commonly used as an emulsion stabilizer in the food industry. Gum acacia is the oldest and best Known of all the polysaccharide plant exudates (Williams *et al.*, 2006).

Acacia gum is defined by FAO/WHO Joint Expert committee on food Additives (JECFA) as: "Gum arabic is dried exudates obtained from the stems and branches of *Acacia senegal* (L.) Willdenow or *Acacia seyal* (*fam. leguminosae*)". Acacia gum is defined by the European pharmacopoeia 6.8 as: "Air hardened, gummy exudates flowing naturally from or obtained by incision of the trunk and branches of *Acacia senegal* (L.) Willdenow (Idris and Haddad, 2011) (Williams *et al.*, 2006).

United States pharmacopoeia Official Monograph for NF26 (USP 31) defines gum acacia as:"Acacia is the dried gummy exudates from the stems and branches of *Acacia senegal* Willdenow or of other related African species of Acacia". The Japanese Official monograph for part II/ powdered Acacia (JP XIV) defines gum acacia as: "Acacia is the secretions obtained from the stem and branches of *Acacia senegal Willdenow* or other species of the same genus (leguminosae)". Acacia gum is a highly heterogeneous complex polysaccharide consisting of galactose, arabinose, rhamnose, glucuronic acid and 4-O-methylglucuronic acid (Idris and Haddad, 2011) (Williams *et al.*, 2006).

The gum belt agro-ecosystem refers to a broad band stretching across Sahelian regions of Africa and the Middle East situated between latitude 10° and 14° North. It starts from Mauritania in the West, through Senegal and Mali, Burkina Faso, Niger, Northern Nigeria to Sudan, Eritrea, Ethiopia, Kenya, Somalia and Northern Uganda in the East. It is also found in the Middle East, Yemen, India and Pakistan.

Sudan is the world's biggest producer of gum arabic, and since very little is consumed domestically it is also the main source of gum in international trade. The gum belt falls in central Sudan roughly between latitudes 10° and 14° North, with two areas outside these borders found in the north east (Faw, Gedaref and Kassala) and in the south east along the Blue Nile/Upper Nile border (Abdel Nour, 1999). It spans the traditional rainfed agricultural areas of western and central Sudan that include Kordofan Al Kubra 49.3% (N. Kordofan, W. Kordofan and S. Kordofan), Darfur Al Kubra 24.4 % (W. Darfur, N. Darfur and S. Darfur), Kassala region 23.4% (Kassala and Gedaref) and White and Blue Nile region 2.9% (White Nile, Sennar, Blue Nile).

Outside Africa, India produces small amounts of gum, similar in quality to gum (Talha), but a proportion of its exports of gum arabic consists either of re-exports of African gum or locally produced gum *ghatti* (from *Anogeissus latifolia*) misclassified as gum arabic.

2.2.1 Physical properties of gums

The physical properties and appearance of natural gums are of greatest significance in determining their marketability and end use. This differs with different botanical sources. There is a considerable dissimilarity in gum from the same species collected from plants grown under different climatic conditions or even from the same plant in different season. Physical properties are also affected by the age of the exudate and treatment of the gum after collection by, for example, washing, drying, sun-bleaching and storage temperatures (Williams *et al.*, 2006).

2.2.1.1 Solubility

Acacia gum is soluble in cold water (up to 43–48% v/v) but it is not soluble in ethanol. Acacia gum dissolves easily in cold water at low doses but requires higher shear at higher doses to enable complete dissolution. Solutions made with acacia gum do not require any pre-mixing with sucrose or other powder ingredients to facilitate hydration; however, when making a high dose solution (40%) or when using a granulated product, hydration for some hours may be necessary. Solutions made with standard acacia gum are not completely transparent, although recent advances have meant that clear versions of acacia gum are now available (Williams *et al.*, 2006).

2.2.1.2 Emulsifying properties

Acacia gum from *A. senegal* is a very effective emulsifying and stabilizing agent and has found widespread use in the preparation of varied oil-in-water beverage emulsions (Williams *et al.*, 2006).

2.2.1.3 Viscosity

Most gums form highly viscous solutions at low concentrations (>5%). However, at such relatively low concentrations, gum acacia yields solutions that are essentially Newtonian in behavior and have very low viscosities compared to other polysaccharides of similar molecular mass. The viscosity of gum acacia solutions decreases with the addition of electrolytes and this is explained by a reduction in the effective volume due to the suppression of the electrostatic charge. Solution of gum acacia are slightly acidic (typical pH 4.5) and at this pH, the gum is at its maximum viscosity. Gum acacia is stable over a wide range of pH from 3.0 to 9.0 (Williams *et al.*, 2006).

2.2.2 Chemical properties of gums

Gums are composed of carbon, hydrogen, oxygen, small quantities of mineral matter and sometimes a little nitrogen. The pure gum may also contain small quantities of tannin. The chemical composition of the three main exudate gums is complex and varies to some extent, depending on their source and age. Therefore, it is not possible to provide defined structural formulas for these biopolymers. Gum Arabic is recognized by many researchers that Gum Arabic consists of mainly three fractions (Williams *et al.*, 2006).

(i) The major fraction is a highly branched polysaccharide consisting of galactose backbone with linked branches of arabinose and rhamnose, which terminate in glucuronic acid found in nature as magnesium, potassium and calcium salt.

(ii) A smaller fraction is a higher molecular weight arabinogalactan-protein complex (GAGP-GA glycoprotein) in which arabinogalactan chains are covalently linked to a protein chain through serine and hydroxyproline groups. The attached arabinogalactan in the complex contains glucoronic acid.

(iii) The smallest fraction having the highest protein content is a glycoprotein which differs in its amino acids composition.

2.2.3 Applications

Acacia gum enjoys a remarkable diversity of applications and this is mainly due to its desirable physicochemical properties and functions as reported earlier. The functions of gum acacia include emulsifier, formulation aid, stabilizer, thickener, surface finishing agent, processing aid, firming agent, texturizer, adhesive, plasticizer, soluble fibre and prebiotic source, and many others (Idris and Haddad, 2011) (Williams *et al.*, 2006).

2.3 *Acacia nilotica*: Taxonomy of the tree

Domain:	*Eukaryota*
Kingdom:	*Plantae*
Phylum:	*Spermatophyta*
Subphylum:	*Angiospermae*
Class:	*Dicotyledonae*
Order:	*Fabales*
Family:	*Fabaceae*
Subfamily:	*Mimosoideae*
Genus:	*Acacia*
Species:	*Acacia nilotica*

(https://www.cabi.org/isc/datasheet/2342#totaxonomicTree)

2.3.1 Description and distribution

Small tree, 2.5–14 m tall, quite variable in many aspects; bark of twigs not flaking off, gray to brown; branches spreading, with flat or rounded crown; bark thin, rough, fissured, deep red-brown; branchlets purple-brown, shortly or densely gray-pubescent, with lenticels; spines gray-pubescent, slightly recurved, up to 3 cm long; leaves often with 1–2 petiolar glands and other glands between all or only the uppermost pinnae; plnnae 2–11 (-17) pairs; leaflets 7–25 (-30) pairs, 1.5–7 mm long, 0.5–1.5 mm wide, glabrous or pubescent, apex obtuse; peduncles clustered at nodes of leafy and leafless branchlets; flowers bright yellow, in axillary heads 6–15 mm in diam.; involucel from near the base to about half-way up the peduncle, rarely somewhat higher; calyx 1–2 mm long, subglabrous to pubescent; corolla 2.5–3.5 mm long, glabrous or pubescent outside; pods especially variable, linear, indehiscent, 8–17 (-24) cm long, 1.3–2.2 cm broad, straight or curved, glabrous or gray-velvety, turgid, blackish, about 12-seeded; seeds deep blackish-brown, smooth, subcircular, compressed, areole 6–7 mm long, 4.5–5 mm wide. Fl. Oct.–Dec.; fr. Mar.–June.

Native from Egypt south to Mozambique and Natal; apparently introduced to Zanzibar, Pemba, and India; Arabia. Considered a serious weed in South Africa (http://www.fao.org/docrep/x5327e/x5327e0e.htm) (https://hort.purdue.edu/newcrop/duke_energy/Acacia_nilotica.html) (https://www.aphis.usda.gov/plant_health/plant_pest_info/weeds/downloads/wra/AniloticaWRA.pdf) (http://ecocrop.fao.org/ecocrop/srv/en/cropView?id=2667).

2.3.2 *Acacia nilotica*: Chemistry

Babul has been reported to contain l-arabinose, catechol, galactan, galactoaraban, galactose, N-acetyldjenkolic acid, N-acetyldjenkolic acid, sulphoxides pentosan, saponin, tannin. Seeds contain crude protein 18.6%, ether extract 4.4%, fiber 10.1%, nitrogen-free extract 61.2%, ash 5.7%, and silica 0.44%. Phosphorus 0.29% and calcium 0.90% of DM (http://www.fao.org/docrep/x5327e/x5327e0e.htm) (https://hort.purdue.edu/newcrop/duke_energy/Acacia_nilotica.html).

2.3.3 Important uses of *Acacia nilotica*

The Gogo Tribe considers *A. nilotica* to be very important for medicinal purposes and various medicinal uses are reported in the literature. Those mentioned specifically for Tanzania include: juice from phloem strands is used for treating sore throats, leaves are boiled in a tea for chest pain and pneumonia, and boiled roots are used for stomach problems. Other uses mentioned include using powdered roots mixed with water for toothaches, chest and stomach problems and to cure gonorrhoea. The bark and leaves are also used to treat colds, diarrhoea and dysentery. A drink is prepared from the liquid of boiled bark.

The heartwood is especially valued for both firewood and charcoal. It has a calorific value of 4950 kcal per kg. The wood is dense, heavy, termite resistant, and water repellent. It is used for fencing, tool handles, and boat construction.

Pods, leaves, and shoots are important sources of fodder. The leaves are reported to contain up to 12% protein and 21% crude fibre. In some parts of India it is one of the most valuable fodder trees producing up to 80 kg of pods per year (http://www.fao.org/docrep/x5327e/x5327e0e.htm) (https://hort.purdue.edu/newcrop/duke_energy/Acacia_nilotica.html).

2.4 Previous Studies

Several studies have been carried out to synthesized graft copolymers (Apepei, *et al.*, 2012) (Lokhande *et al.*, 1992) (Ikuoria *et al.*, 2010).

Apepei, *et al.*, (2012) were prepared PN– grafted PAN using two initiator (ceric sulphate, ceric ammonium nitrate) in an aqueous medium. Different techniques were used to characterize the product which includes FT-IR, DSC and HNMR. The FT-IR spectroscopy has confirmed the grafting of the AN on starch PS and shows the stretching vibration of –CN at 2244 cm^{-1} for fraction **A**. Fraction **B** which contains amylopectin did not show this characteristic band. Furthermore, the ^{1}H-NMR displayed the characteristic peaks of both PS and PAN for fraction **A** again, which further support the previous results of FT-IR. The results of DSC were further demonstrated the grafting of PAN on PS. The glass transition of PS-g-PAN was appeared at 90 which is in between that of pure polymer of PS and PAN.

In another study, Lokkhand *et al.*, (1992) have studied gamma radiation as an inducer for graft copolymerization of acrylonitrile on guar gum to produced superabsorbent polymers. Various grafting parameters have been studied and the grafted product has been characterized using different techniques IR, TGA, and DTA. Grafting parameters: saponification, molecular weight of grafted side chain, viscosity of saponified product and water absorbency. The IR spectroscopy has confirmed the grafting of acrylonitrile on guar gum and shows characteristics -C≡N absorption band at 2240 cm^{-1} for the purified grafted guar gum and noticed that intensity of the above absorption band increasing with increase in the grafting percentage. The DTA and TGA profiles of raw, unmodified guar gum and purified grafted products were presented. The grafting copolymerization was confirmed by TGA rather than DTA. The exothermic process observed involve formation of new products from the fragmentation products of the polysaccharides and the PAN side chain grafts

Ikuoria *et al.*, (2010) have studied the graft copolymerization of acrylonitrile onto cassava starch by ceric ion induced initiation. Graft copolymerization of cassava starch and acrylonitrile were synthesized in aqueous solution by using ceric ammonium as initiator to the reaction Grafting parameters such as % grafting ratio and % conversion were studied and found that they were increased with increasing in monomer concentration and initiator concentration. Furthermore, the hydrolysis of the grafted polymer were studied which shows that the grafted starch could be used as flocculants. Different techniques were used to characterize the final product which includes IR spectrophotometer, grafted copolymer showed the existence of moderate peak at 2240 cm^{-1} as a strong evidence of grafting.

CHAPTER THREE

Materials and methods

3.1 Materials

An authenticated *Acacia nilotica var nilotica* gum sample was kindly supplied by Professor Mohamed Elmobarak. The sample was ground into a powder form and kept into plastic containers for further steps.

All chemicals used in the study were of an analytical grade and supplied commercially. Styrene (≥99%, Reagent plus, Sigma Aldrich); Acrylonitrile (Assay: 99%, 0.805-0.806 g/ml at 20˚C), Cambrian Chemicals Inc., Canada; N, N-Dimethyl formamide (DMF) (Assay: 99.0 %), Laboratory Rasayan, India.

3.2 Preparation of *Acacia nilotica var nilotica* gum grafted samples

The grafted samples of *Acacia nilotica* gum were prepared using varying concentrations of the monomer as well as varying doses of the gamma radiation. In a typical experiment, 5 grams of the gum were dissolved in 25 ml distilled water which followed by addition of 2.5 gram of the monomer and the content were mixed thoroughly. The sample was exposed to gamma radiation dose of 2.5 KGy. The sample was washed thoroughly by N, N-Dimethyl formamide, dried and weighed. Exactly similar steps were followed to prepare the other samples as illustrated in the following table (Table 3.1):

Table 3.1: Detailed method of preparation of *Acacia nilotica* gum grafted samples

Sample	Weight of gum (gm)	Weight of monomer (gm)	γ-gamma radiation dose (KGy)
1	5	2.5	2.5
2	5	2.5	5
3	5	2.5	7.5
4	5	2.5	10
5	5	5	2.5
6	5	5	5
7	5	5	7.5
8	5	5	10
9	5	7.5	2.5
10	5	7.5	5
11	5	7.5	7.5
12	5	7.5	10
13	5	10	2.5
14	5	10	5
15	5	10	7.5
16	5	10	10

The grafting efficiency in each case was calculated using the following equation:

$G (\%) = (W_1 - W_0/W_0) \times 100$ ……………………………………………… (2.1)

Where, W_0 is the weight of *Acacia* gum and W_1 is the weight of the grafted polymer.

3.3 FT-IR analysis

The infrared spectra of the crude gum and grafted samples were recorded using a Shimadzu-Fourier transform infrared spectrometer (Thermo Nicolet, FTIR-300) in the range between 4000 and 400 cm^{-1}. Few milligrams of each sample were mixed thoroughly with 200 mg of spectroscopic grade KBr, pressed into a pellet and the FTIR spectrum was obtained.

3.4 pH measurement

The pH values of the solutions of the crude gum 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.

3.5 Viscosity measurement

The viscosities of the solutions of crude gum and grafted samples were obtained using Haake Viscotester 6 Plus (Thermo Electron Corporation). In each case 1% (wt/v) solution of the crude and the grafted samples was prepared and the viscosity was recorded in the room temperature.

3.6 Thermogravimetric analysis

The thermal stabilities of the crude gum and grafted samples were performed in Linseis TGA PT 1000-Thermogravimetric analyzer. In a typical experiment, 5 mg of the sample were weighed, transferred into a platinum crucible and heated under a flow of air from 30˚C to 700˚C at a heating rate of 5˚C/minute.

3.7 Flocculation properties of the crude and grafted samples

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. 1 gram of each of crude gum 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 percentage

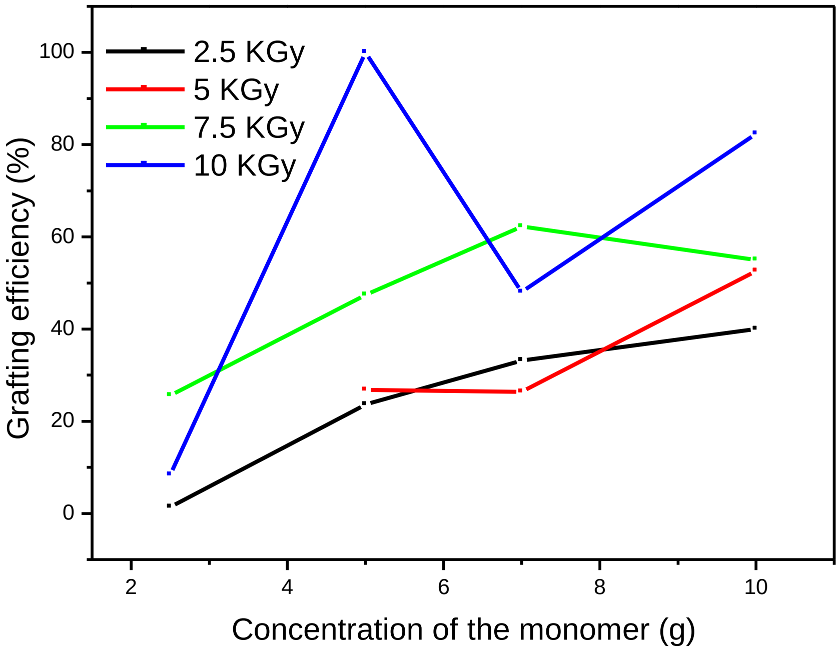

Figure 4.1: Variation of grafting percentage with the concentration of the monomer

Figure 4.1 shows the variation in grafting percentage (GP) with the concentration of the monomer. As it is evident from the figure, the dose of the gamma radiation as well as the monomer concentration both have significant influence in GP. It is clear that GP increases generally with the increase in concentration of the monomer for the same dose although some few exceptions were noticed. On the other hand, GP similarly increases with the increase in gamma radiation dose for the same concentration of the monomer except for 10 KGy which showed the highest GP, sample 8 (Table 3.1), when the concentration of the monomer was only 5 g. Ikuoria *et al.*, (2010) attributed the decrease in grafting parameters to increasing trend of side reaction such as chain transfer to excess molecules in the vicinity of growing ends of grafted chains. Moreover, large amounts of homopolymer deposits may block the way of monomer molecules to the gum macro-radicals resulting in further decrease in percentage monomer conversion and yield.

4.2 FT-IR analyses of crude and grafted *Acacia nilotica* gum Samples

The FTIR analyses were carried out to examine the influence of γ-radiation on the structural features of the crude and grafted *Acacia nilotica* gum samples. Figures 4.2 to 4.7 represent the FTIR spectra of the crude *Acacia nilotica* gum as well as the grafted samples. As it is evident from Figure 4.2, the intense broad band at 3249 $cm^{-1}$is attributed to –OH group stretching vibration, while the sharp peak at 2932 $cm^{-1}$is due to the stretching vibration of –CH group (sp^3 hybridized system). The absorption band located between 1600-1650 cm^{-1} is attributed to –OH bending vibration whereas the bending vibration of –CH and the stretching vibration of C-C and C-O groups were noticed in the region between 1450 to 1000 cm^{-1}. Exactly similar results were reported for acacia gums (Bhushette and Annapure, 2017).

Similar absorption bands were observed for the grafted samples (Figure 4.3 to 4.7) with the presence of some weak and not well-defined absorption band.

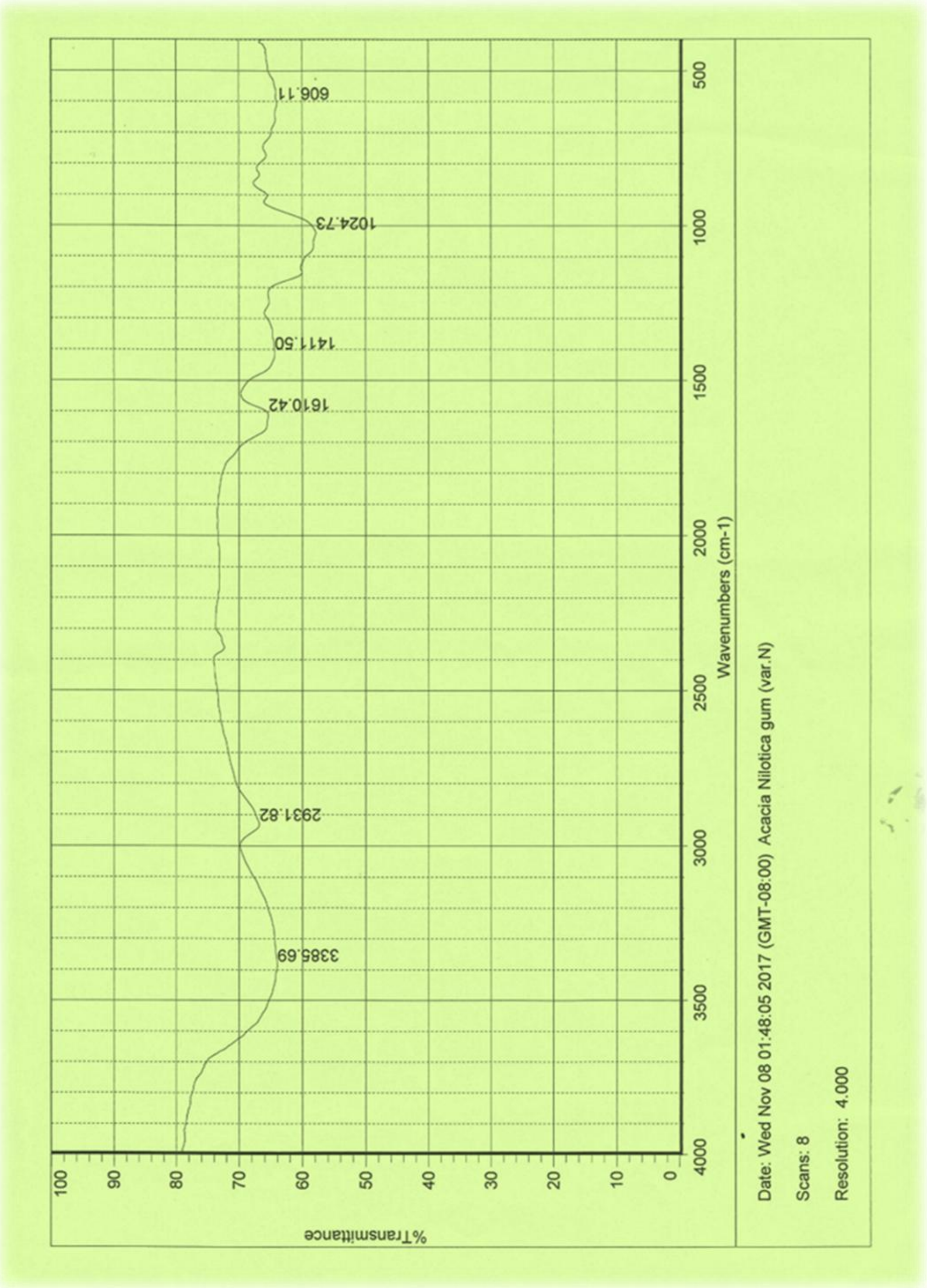

Figure 4.2: FT-IR spectrum of the crude *Acacia nilotica* gum

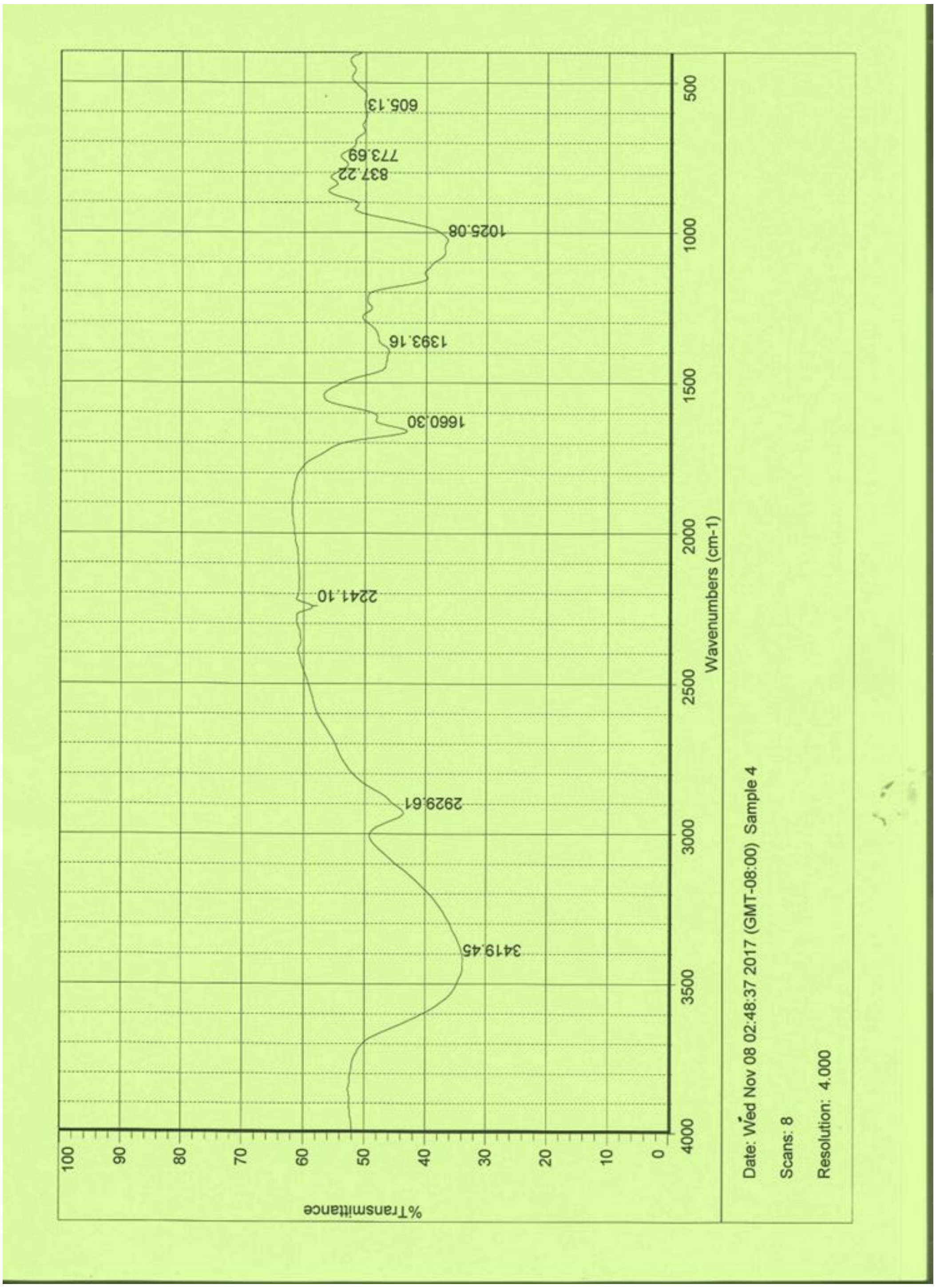

Figure 4.3: FT-IR spectrum of the grafted sample (S4)

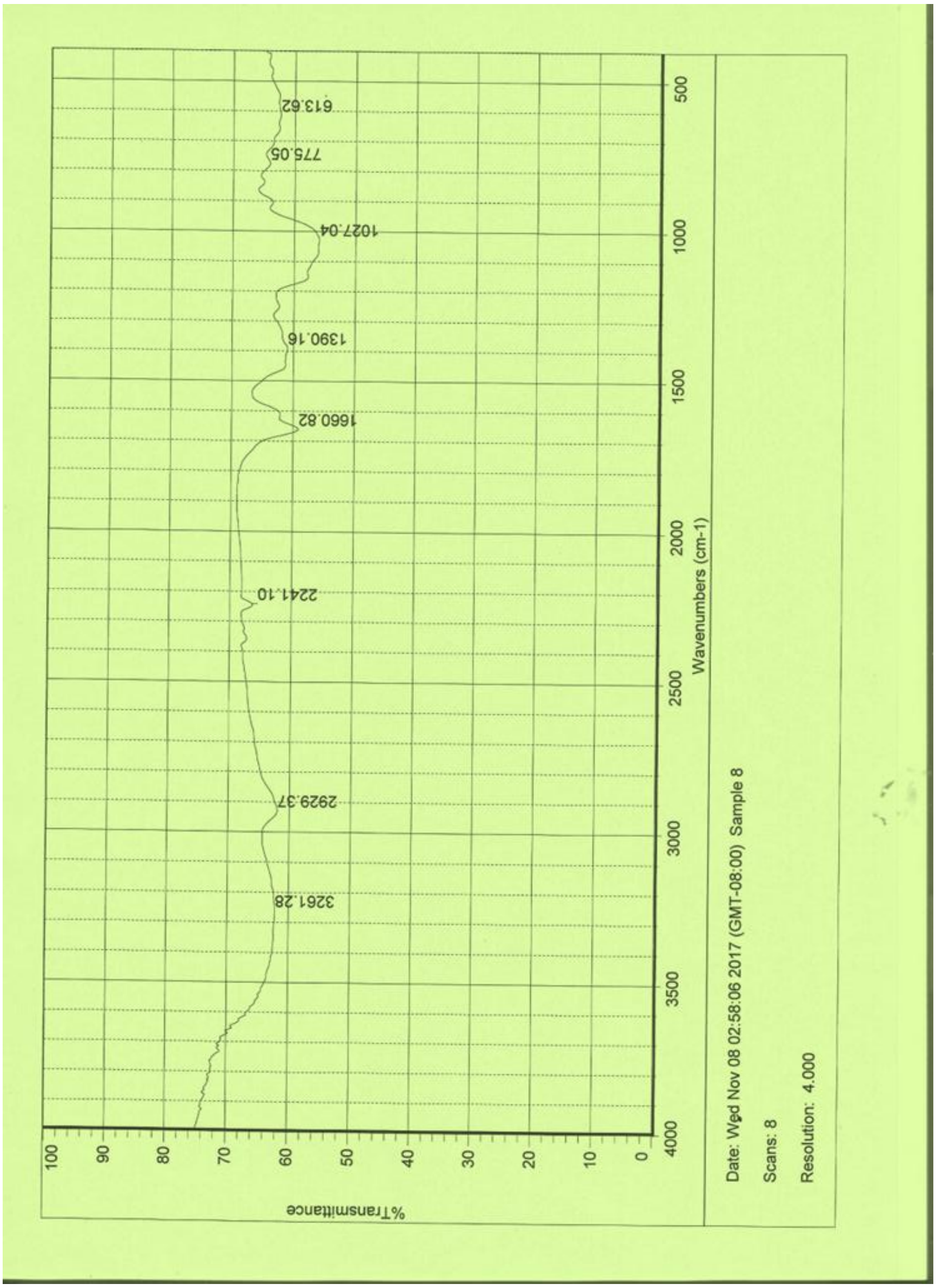

Figure 4.4: FT-IR spectrum of the grafted sample (S8)

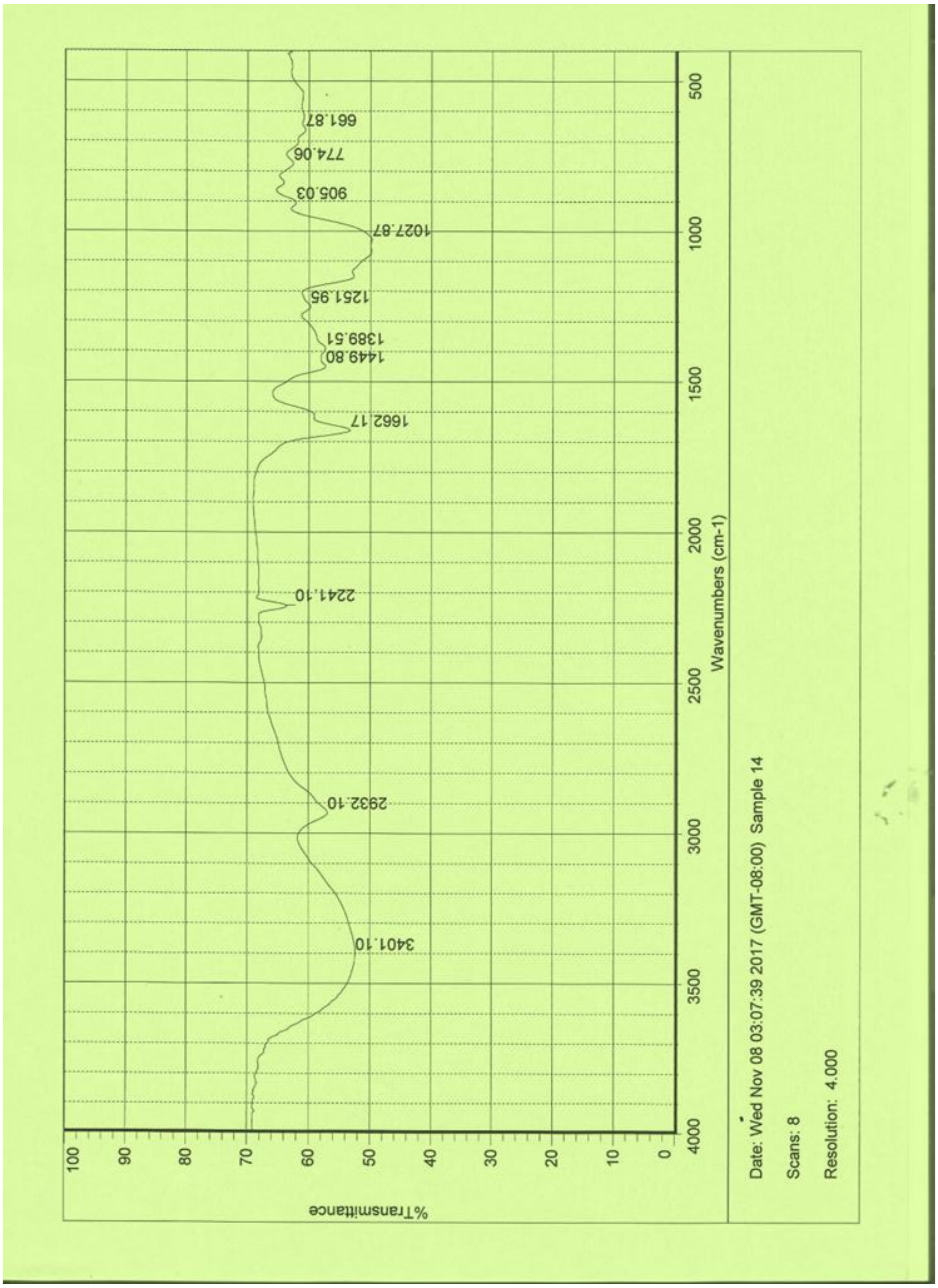

Figure 4.5: FT-IR spectrum of the grafted sample (S14)

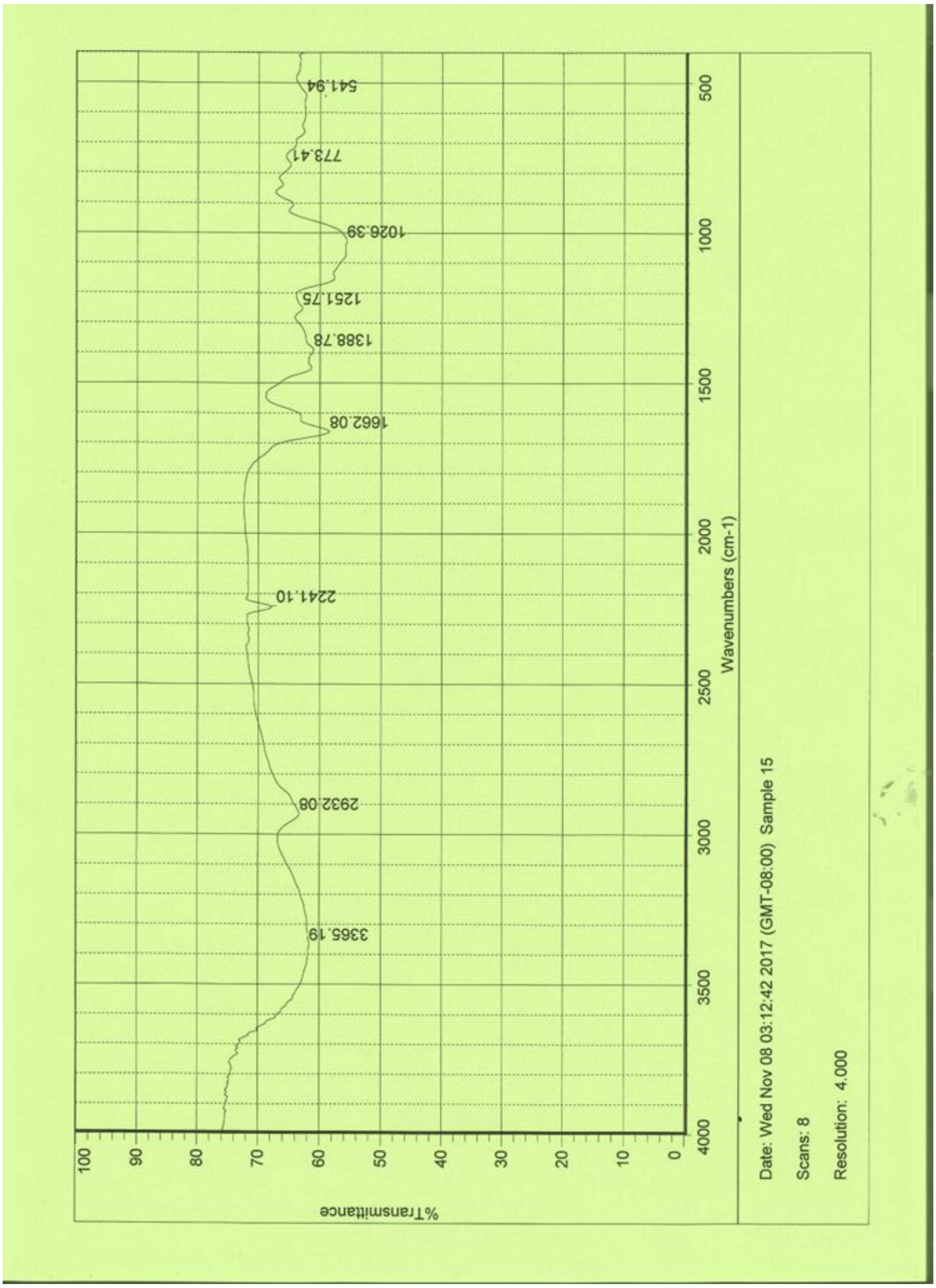

Figure 4.6: FT-IR spectrum of the grafted sample (S15)

4.3 pH measurement

The pH measurements of the aqueous solutions of raw and selected grafted samples of *Acacia nilotica* gum copolymer were examined and the results were reported in Table 4.1. As can be seen from the table the pH value of the crude gum sample has the highest pH value compared to all grafted samples (6.1) and lowest one was for sample S4 (3.5). Examining the conditions of sample preparation reveals that the decrease in pH value has a noticeable correlation to gamma radiation dose. Both, sample 4 and sample 16 were irradiated with 10 KGy whereas sample 9 was irradiated with 2.5 KGy. These results clearly show that the degradation of the gum molecule under the influence of higher gamma radiation doses has taken place. Similar results were observed by Singh *et al.*, (2011) and were attributed to formation of carboxylic acids as a result of degradation of potato starch molecule caused by gamma radiation.

Table 4.1: pH of crude and grafted samples

Sample	pH
Crude gum (0 KGy)	6.1
Sample 4 (10 KGy)	3.5
Sample 9 (2.5 KGy)	5.2
Sample 16 (10 KGy)	4.1

4.4 Viscosity measurements

The viscosity measurements of the aqueous solutions of crude and grafted samples of *Acacia nilotica* gum were carried out and the results are shown in Table 4.2. As can be seen from the table, the values of the viscosity of all grafted samples (Table 4.2) are lower than the crude gum sample. In addition, the viscosities of the grafted samples decreases with the increase of irradiation dose which was used during grafting process. This probably due to the degradation of the gum molecule as a result of gamma radiation which was also noticed in the pH measurements. Previous study by Katayama *et al.*, (2006) has revealed that in aqueous solution at low concentration of gum arabic mainly degradation has taken place, but small amount of polymerization could be detected. However, in highly concentrated aqueous solution, polymerization occurred with minimal degradation.

Table 4.2: Viscosities of crude and grafted samples

Sample	Viscosity (cp)
Crude gum	4
Sample 4	3
Sample 9	4
Sample 16	0

4.5 Thermogravimetric (TGA) analysis

Thermal analysis was performed to examine the thermal stability of crude *Acacia nilotica var nilotica* gum and grafted samples. Figures 4.7 to 4.10 shows the thermograms of crude gum, S4, S6 and S1. As can be seen from Figure 4.7, two degradation steps were noticed. The first step which starts at 50˚C and continued up to 170˚C (weight loss of 4% approximately) is attributed to the loss of adsorbed and structural water of the gum (Daoub *et al.*, 2016) The onset of the second degradation starts at 260˚C and reached it is maximum degradation at 290˚C (weight loss of 22%). On the other hand, all the grafted samples have shwon higher thermal stabilities compared to the crude gum.

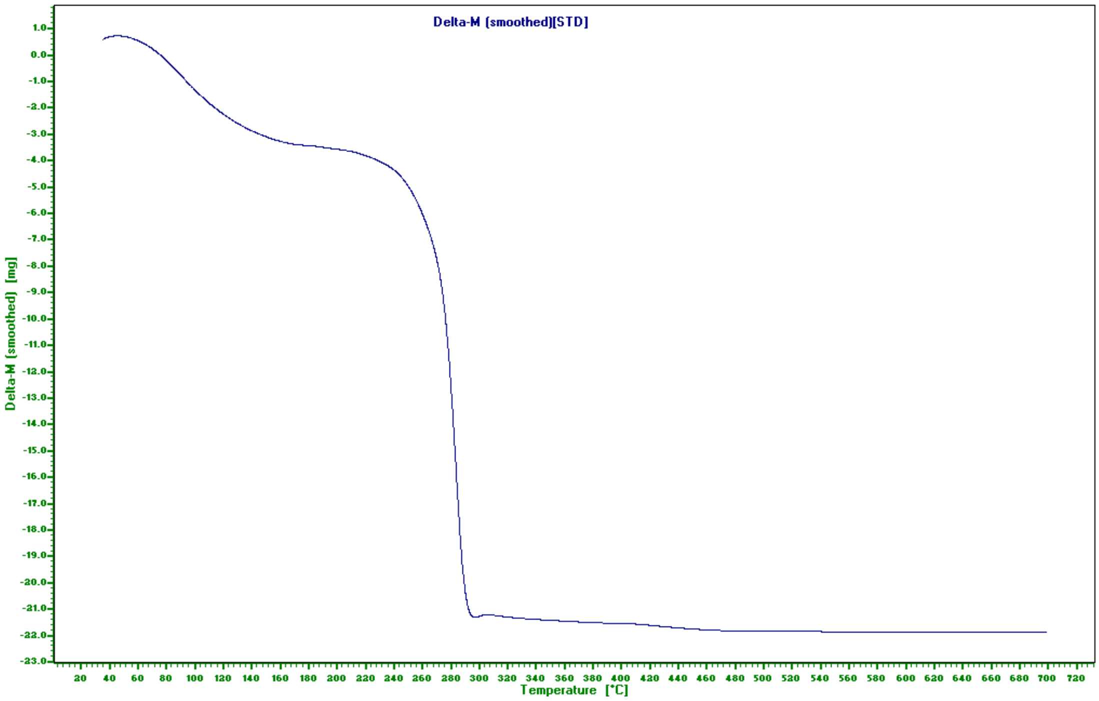

Figure 4.7: TGA curve of crude *Acacia nilotica var nilotica* gum

The thermograms have shown the presence of four degradation temperatures with the disappearance of the first degradation step which was observed in the case of the crude gum at 50 ˚C to 170 ˚C. In addition, the thermal stability increases with the increase in the grafting percentage of the samples (S6 (33.2%)>S4 (8.4%)>S1 (1.4%)>crude). It is worthnoting that all the grafted samples showed relatively small amount of degradation up to 700 ˚C (approximately 12% for samples versus 22% for crude gum).

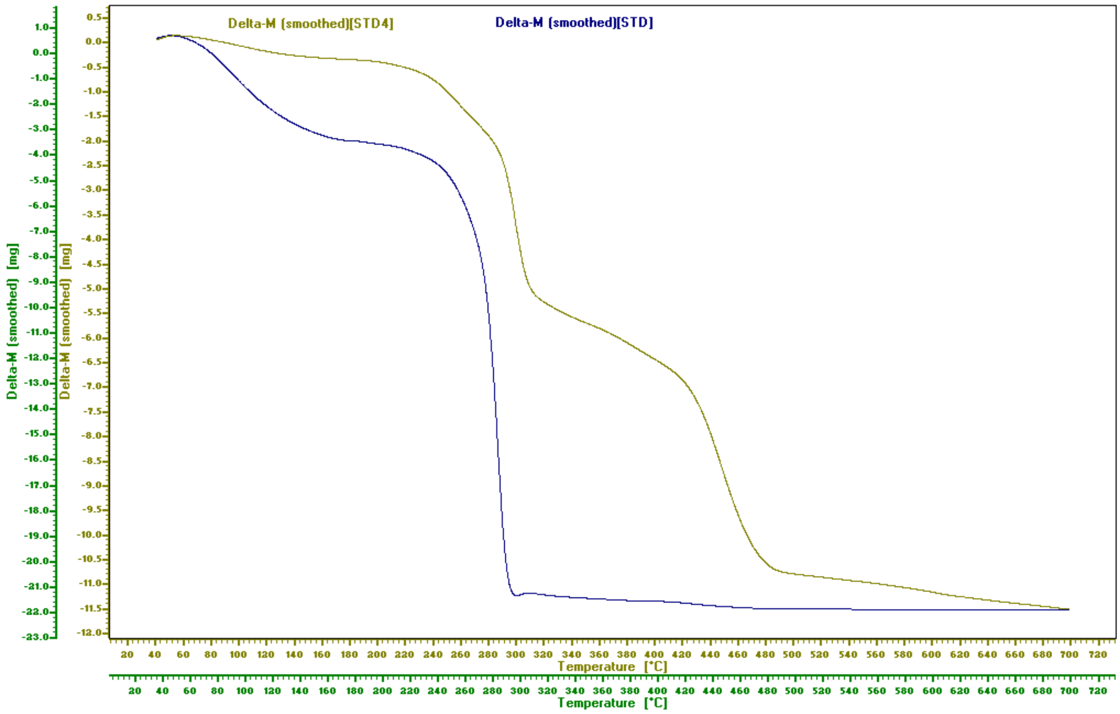

Figure 4.8: TGA curves of crude *Acacia nilotica var nilotica* gum and grafted sample 4 (S4)

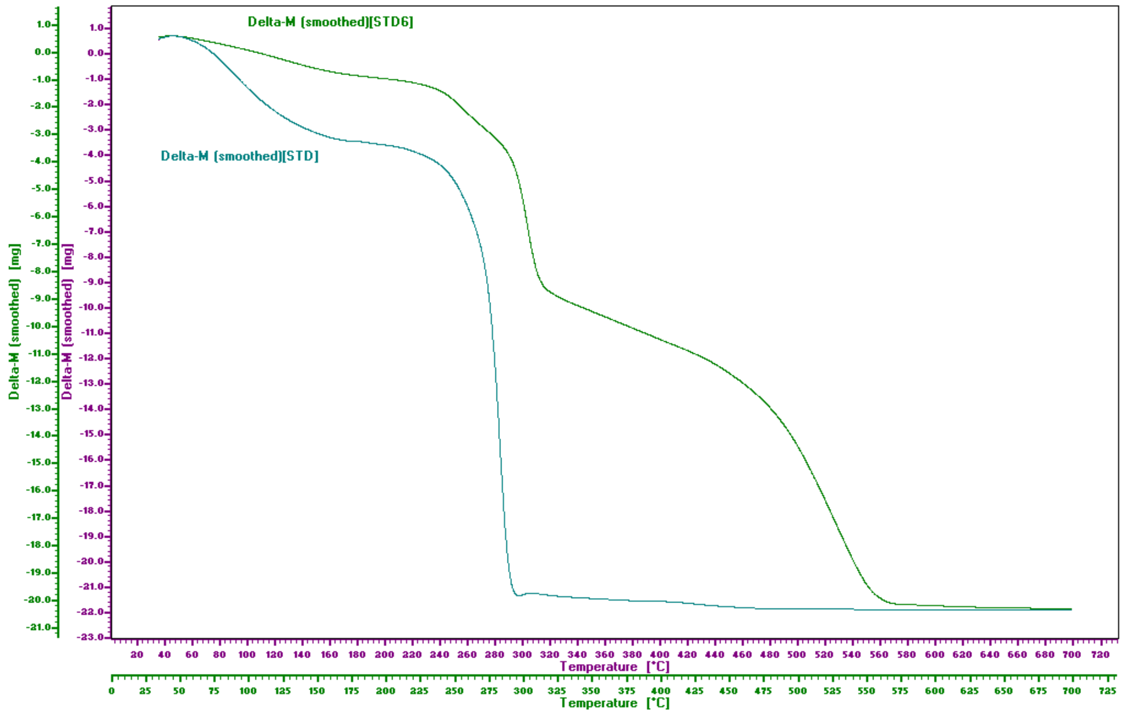

Figure 4.9: TGA curves of crude *Acacia nilotica var nilotica* gum and grafted sample 6 (S6)

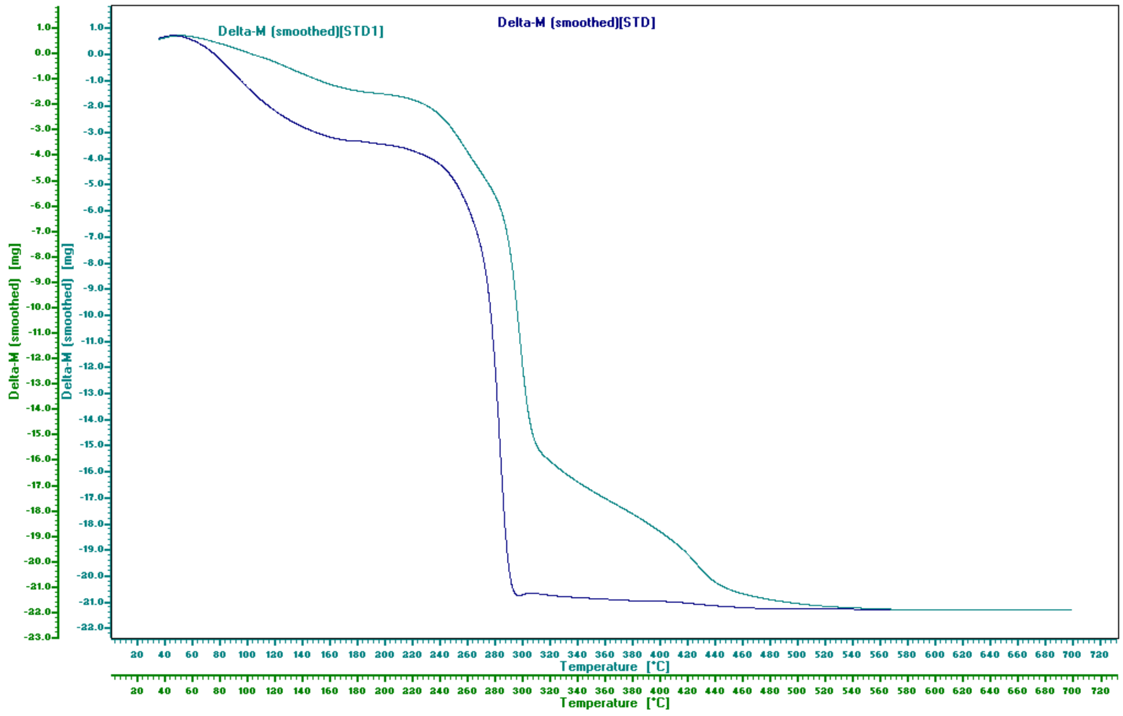

Figure 4.10: TGA curves of crude *Acacia nilotica var nilotica* gum and grafted sample 1 (S1)

4.6 Flocculation properties

Flocculation properties of the crude and grafted samples were investigated using turbid water sample which was obtained from Nile River (Khartoum). The results were shown in Figure 4.11. It is clear from the deposition of the particles in the bottom of the beakers that all the grafted samples have better flocculation capacity of the particles compared to crude gum. The decrease in the turbidity of the water sample is due to the formation of particle-polymer-particle complexes between the particles and the grafted polymer samples. Particles attached to different functional groups present on the polymer chain as soon as they came into contact with the polymer, leading to the formation of extended polymer chains (Mittal *et al.,* 2014).

Figure 4.11: Photo of water sample after addition of 1g of crude, S4, S8, S16 and pure turbid water sample (from left to right)- after passage of 20 minutes

CONCLUSION

Acacia Nilotica var nilotica grafted samples were successfully synthesized and characterized. The grafting efficiency was found to depend mainly on the gamma radiation dose and the concentration of the monomer. Grafted samples were thermally more stable than the crude gum and have better flocculating characteristics.

RECOMMENDATION

(1) Optimization of the grafting process should be conducted in details to examine the effects of all parameters.

(2) Further characterization techniques such as scanning electron microscopy, ^{1}HNMR and differential scanning calorimetry (DSC) are recommended.

(3) Further applications of the grafted samples in treatment of waste water samples from industry are recommended.

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