



## Synthesis and Thermal Stability with Microstructure Study of some Chitosan-Dicarboxylic Acids Grafted Copolymers

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### ABSTRACT

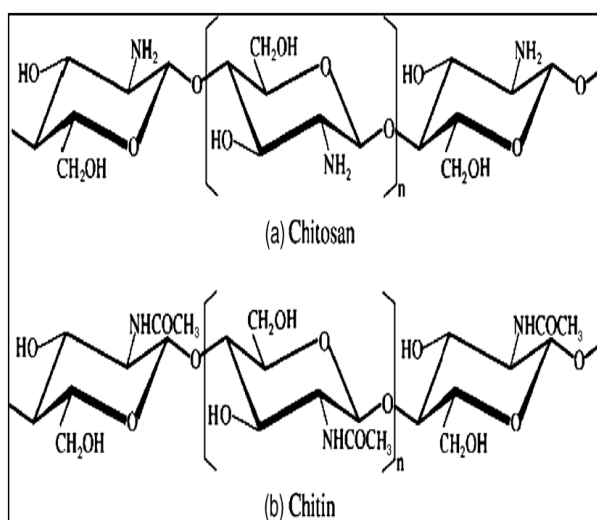
In this study, Chitosan polymer with 93% degree of deacetylation was obtained by the chemical deacetylation process of chitin. Six Chitosan acids, i.e. oxalic, succinic, glutaric, adipic, pimelic, and sebacic acid derivatives were synthesized by grafting the Chitosan with these dicarboxylic acids. The grafted Chitosan copolymers are characterized by FTIR, which confirmed the compositions of the Chitosan-acid copolymers as well as ungrafted Chitosan. This is also supported by scanning electron microscopy (SEM) technique. The thermal stability of the prepared Chitosan and Chitosan-grafted acid copolymers was studied by thermal gravimetric analysis (TGA). The results showed that the Chitosan-grafted acid polymers have higher thermal stability and higher decomposition temperatures than those of ungrafted Chitosan.

**Keywords:** Thermal stability, microstructure, grafted Chitosan, dicarboxylic acids, thermogravimetric analysis

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## Introduction

Chitosan is a natural bio-based characteristic polymer which is a deacetylation product of the chitin. Chitosan has three types of reactive functional groups, an amino group on its backbone as well as both primary and secondary free hydroxyl groups at the C-2, C-3, and C-6 positions respectively as shown in Figure (1) [1]. Chitosan with abundant amine and hydroxyl groups can be easily modified to enhance efficiency for different applications [2], for instance, in water treatment [3], paper making [4], dispersant for ceramic powders [5], and for drug and tissue engineering system delivery [6].



**Figure (1):** Structure of (a) Chitosan and (b) chitin [1].

Thermogravimetric analysis (TGA) is a tool used in investigations of the pyrolysis and combustion behavior of chemical materials, both natural and synthetic solid materials and such studies are of great practical importance in the use of materials [7]. It is possible to use the obtained data to estimate the energy of activation involved in the process. Therefore,

this method is more advantageous than the conventional method, because it is more precise and sensitive; and requires a smaller sample mass and results are obtained more rapidly.

Thermal analysis of Chitosan-based networks was studied by Neto et al. [8]. They thermally analyzed three different materials: pure Chitosan, Chitosan cross-linked with glutaraldehyde and Chitosan blended with a PEO. From the thermogravimetric analysis, it was concluded that the three samples presented some differences in the strength of water-polymer interaction. For pure Chitosan, at low moisture content, water was predominantly bound to the amine groups of Chitosan while for cross-linked Chitosan the peak related to water bound to the polymer hydroxyl groups was also evident. The Chitosan/PEO blend presented the most symmetric peak, indicating that one interaction is preferred in this case.

Ziegler-Borowska et al. [9] also, thermally analyzed three different novel Chitosan derivatives for medical or biotechnological applications have been successfully obtained by chemical modification of reactive amino and hydroxyl groups in the Chitosan chain. The modification has led to the incorporation of different amount (one to three) of long-distanced amino and imine groups into each repeating unit. The thermal stability of all obtained Chitosan materials has been determined using thermogravimetric analysis in an oxidative and inert atmosphere. Chitosan containing two side substituents behaves differently from the other two, which is caused by the significant water uptake.

Herein, we are focused on the synthesis of six acids grafted-Chitosan copolymers, i.e. oxalic, succinic, glutaric, adipic, pimelic, and sebacic derivatives were synthesized by grafting



the Chitosan with these dicarboxylic acids and to study their thermal characterization and behavior using Thermal Gravimetric Analysis (TGA). The various kinetic parameters evaluated included the energy of activation, chare content, temperature and rate of decomposition, and to investigate their microstructure effect on their thermal stability behavior.

## Experimental

### 1. Materials

Materials used in this work are obtained from different sources. Chitosan was extracted from shrimp shells and purified as described in the literature [10]. The acids were purchased from different companies; oxalic acid from Merck, succinic acid from RDH, glutaric, adipic and pimelic acids from Aldrich, and sebacic acid from BDH. Ethyl acetate and tetrahydrofuran were supplied by GCC and Aldrich respectively.

### 2. Instruments

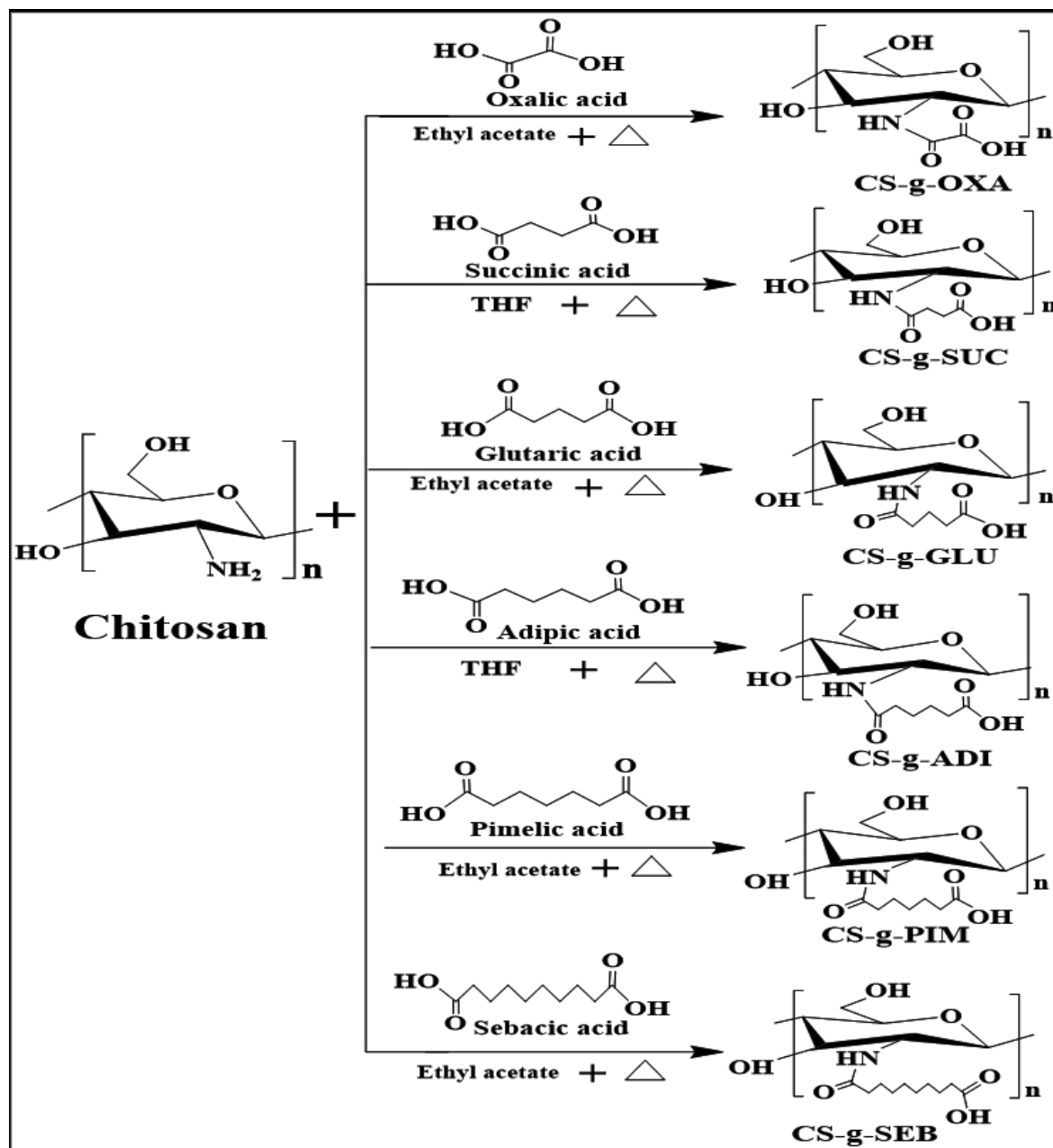
FTIR 8101M Shimadzu spectrometer /Japan was used to record the FTIR spectra. Computer-controlled thermal analysis Instrumentals, TGA-Q50 V20/USA was used to study the thermal stability of the prepared copolymers. The prepared copolymers were examined under Scanning electron microscope type Nova Nano SEM 450/Netherland.

### 3. Preparation of Chitosan Copolymers by Grafting Method

The grafting of oxalic acid (OXA), glutaric acid (GLU), pimelic acid (PIM) and sebacic acid (SEB) onto Chitosan were carried out by the following procedure [10,11]. 3 g of acid was added to the 100 ml of dry ethyl acetate, and the volume reduced to 50 ml by simple distillation to remove the moisture that may present in the acid solutions. Along these lines, 3 g of Chitosan was added to 100 ml of dry ethyl acetate, and then the volume was reduced to 50 ml by simple distillation to remove the moisture from Chitosan. Afterwards, the two solutions are placed in three-neck round bottom flask fitted with a condenser, magnetic stirrer, and a thermometer. The mixture heated and magnetically stirred at a reflux temperature of ethyl acetate solvent for 2 hours, and then it is left shaking and to cool down to ambient temperature. The grafted Chitosan with different acids was filtered and washed with ethyl acetate and acetone several times, respectively, and then the white powder products are dried in the vacuum desiccator. Scheme (1) shows the chemical grafting equations. The same procedure was used to graft succinic acid (SUC) and adipic acid (ADI) onto Chitosan except that dry tetrahydrofuran was used as a grafting medium as exhibits in the scheme (1).

### 4. Thermogravimetric analysis (TGA)

TGA is measured in a temperature range 25-700°C with constant heating rate 50°C/min under N<sub>2</sub> atmosphere.



**Scheme (1):** Chemical grafting equations of Chitosan by different dicarboxylic acids.

## 5. Microstructure Assessment

The microstructures of Chitosan and some samples were examined using a scanning electron microscope by applying approximately 500 Å of gold to eliminate charging effects and to help the elimination of high contrast due to enhanced emission.

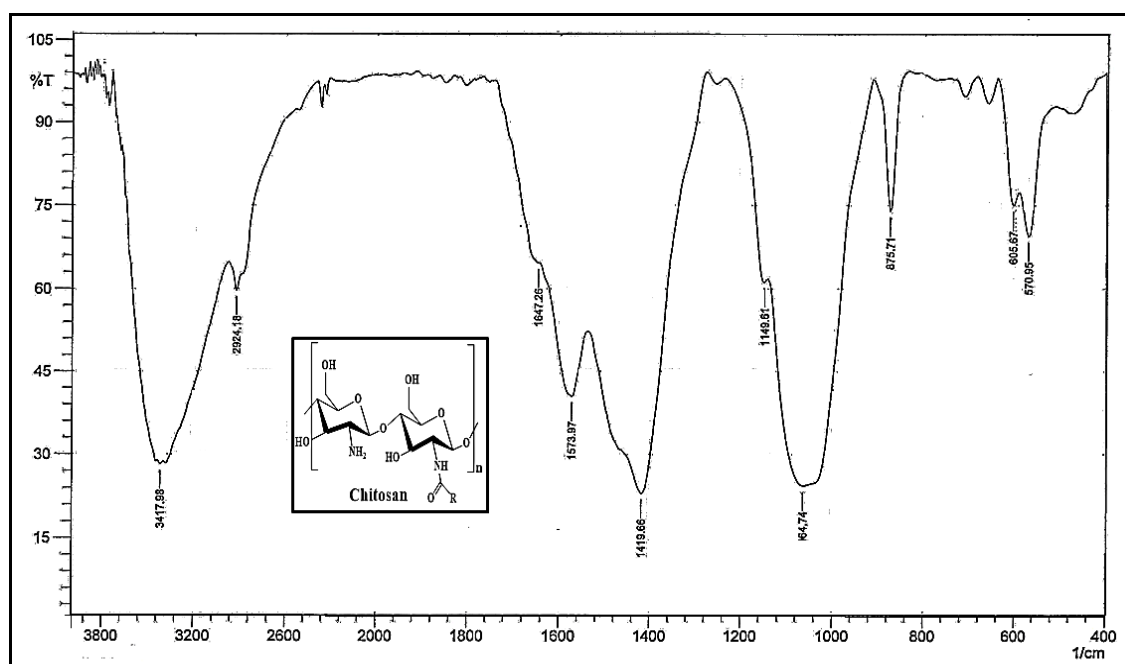
## Results and Discussion

### FTIR Characterization of Chitosan and Its Acid-Grafted Copolymers

FTIR spectrum of pure Chitosan is shown in Figure (2). It exhibits a broadband with a peak at  $3429\text{ cm}^{-1}$  due to (-OH) stretching and a (-NH) stretching, a weak

band with a peak at  $1639\text{ cm}^{-1}$  assigned for amide I which was left from the deacetylation process, verified that Chitosan with a high degree of deacetylation was obtained. Also, the appearance of a strong

band at  $1454\text{ cm}^{-1}$  due to (C-N) stretching bond confirms the deacetylation process [10,11]. Table (1) shows the main Chitosan IR peaks and their assignment.



**Figure (2):** FTIR spectrum of Chitosan.

Grafting Chitosan with different acids revealed the presence of the expected formed a new amide linkage at different wavenumbers

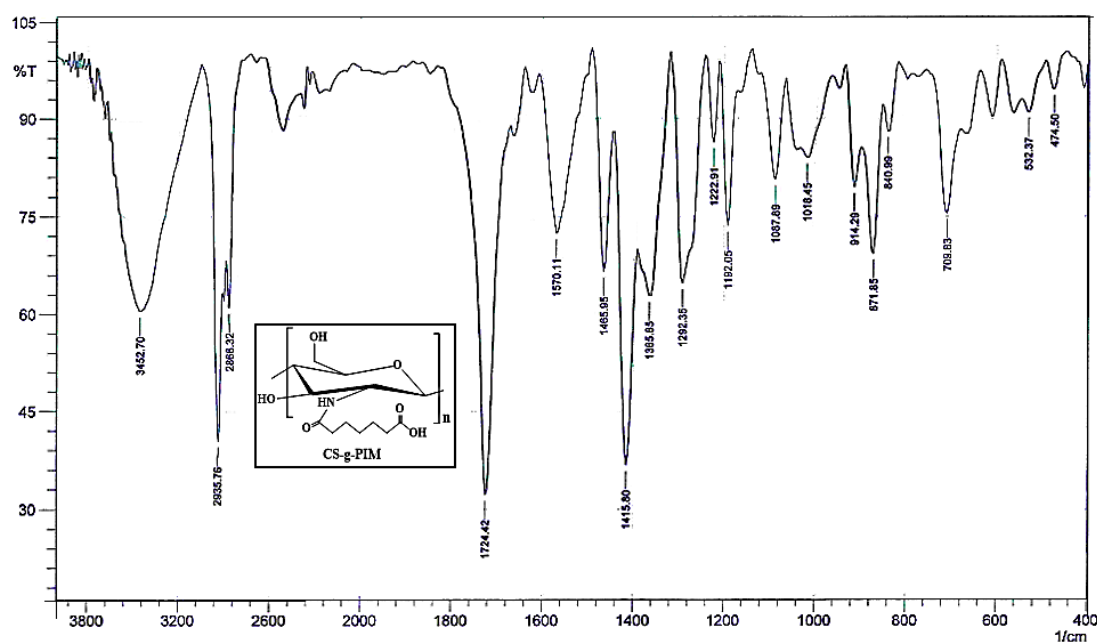
depending on the type of the grafted acid compared to ungrafted Chitosan as shown in Table (2) and at Figure (3).

**Table (1):** The main IR bands of Chitosan.

Functional Group	Assigned Bond	Wave number (cm <sup>-1</sup> )
-CO-OH	O-H	3429
-NH	N-H	3429
-CH <sub>2</sub> -	CH	3000-2900
NH <sub>2</sub> I	N-H	1639
-NH II	N-H	1578
-C-C-N	C-N	1454
C-O-C	C-O	1070

**Table (2):** Main IR bands of Chitosan-acid copolymers.

Chitosan Derivative	Functional Group	Assigned Bond	Wave number (cm <sup>-1</sup> )
CS-g-OXA	-CONH	C=O	1647
	-CO-OH	C=O	1743
CS-g-SUC	-CONH	C=O	1570
	-CO-OH	C=O	1716
CS-g-GLU	-CONH	C=O	1577
	-CO-OH	C=O	1697
CS-g-ADI	-CONH	C=O	1570
	-CO-OH	C=O	1708
CS-g-PIM	-CONH	C=O	1570
	-CO-OH	C=O	1724
CS-g-SEB	-CONH	C=O	1570
	-CO-OH	C=O	1701



**Figure (3):** FTIR spectrum of CS-g-PIM as representative for the grafted copolymers.

### Thermal Gravimetric Studies

The thermal stability of polymers define as the resistance of polymer towards thermal or thermochemical degradation. The thermal stability of any material can be expressed either as a function of temperature or as a temperature-time limit or can be investigated by several techniques such as Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) [12]. In TGA techniques, a considerable loss in weight takes place at a definite temperature, which can be used as a measure for the thermal resistance of the polymers.

The importance of the thermal stability of Chitosan and its acid derivatives is investigated, their (TGA) thermograms are shown in Figures (4) to (10), and the essential thermal functions are listed in Table (3).

These TGA thermograms reveal that the Chitosan has two decomposition temperatures, first, at 130 °C and the second at 296 °C with

char content at 600 °C equal to  $\approx 73\%$ , while the TGA thermograms of the Chitosan copolymers have higher decomposition temperature than the Chitosan itself, i.e. Chitosan=296°C while Chitosan copolymers = 383.47-325.02°C. That means the introduction of a dicarboxylic acid as grafting moiety to Chitosan polymer chains leads to increase thermal stability due to the formation of the amide linkage, scheme (1). The results, also display that the decomposition temperature of the Chitosan copolymers decreases with the increasing number of methylene groups between carboxylic units, but still, it is higher than Chitosan itself, i.e., CS-g-OXA  $\approx$  CS-g-SUC > CS-g-GLU > CS-g-ADI  $\approx$  CS-g-PIM  $\approx$  CS-g-SEB > Chitosan. On the other hand, these Chitosan copolymers have high char content, and the temperature of 50% weight loss ( $T_s$ ) has reached 343.75°C as a maximum. Table (2) shows the thermal stability parameter of Chitosan and its copolymers. One

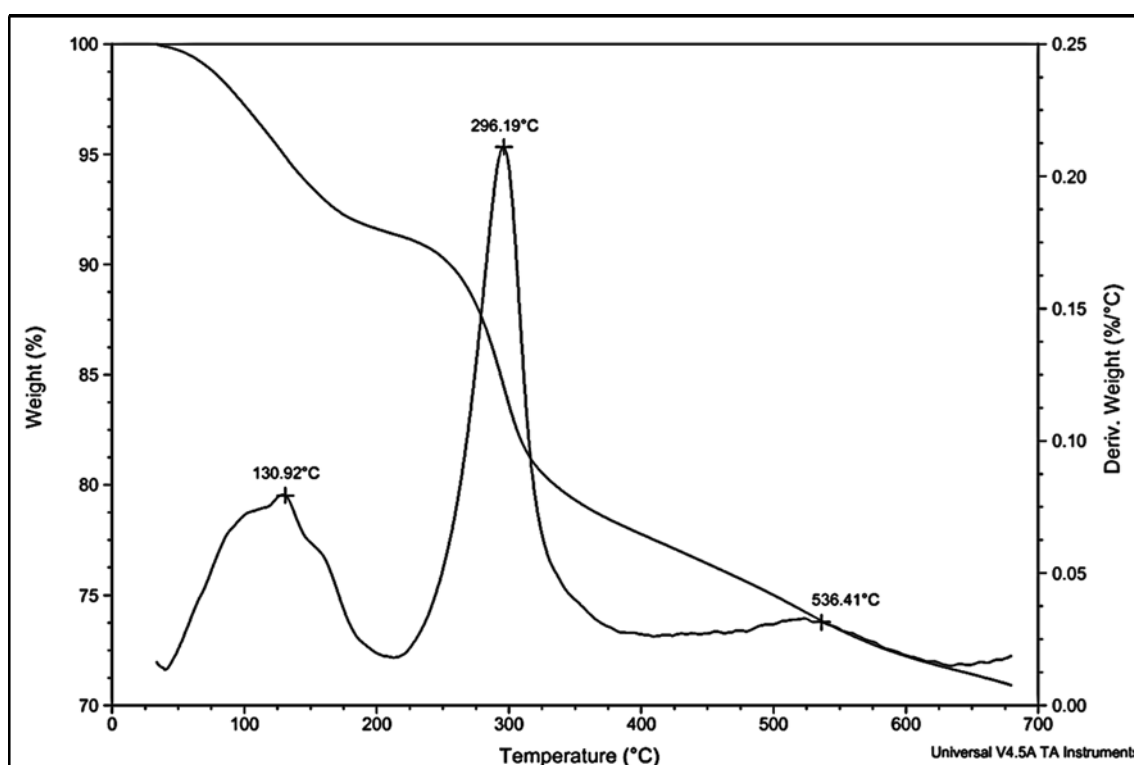
of many advantages of thermal analysis is to study and evaluate some kinetics parameters, and of course activation energy comes as first prime, enthalpy, entropy, and others [13,14]. These parameters are essential to help us in understanding the behavior of the materials in high temperatures [15]. The Broido1969 method is used to calculate the activation energy, according to the following equation [16]:

$$\ln[-\ln Y] = -\frac{Ea}{RT}$$

Where Y is the fraction of several initial weight not yet decomposed; and is given by the following relationship:

$$Y = \frac{W_t - W_\infty}{W^o - W_\infty}$$

Where:  $W_t$  is the weight at any time  $t$ ;  $W_\infty$  weight in total final time and  $W^o$  the initial weight. A plot of  $\ln(-\ln y)$  vs.  $1/T$  gives a straight line, with a slope that represents activation energy  $E_a$  [17], and is shown in Table (3). The activation energy of the thermal decomposition of the Chitosan and its acid grafted copolymers is calculated from the first and second decomposition stages and its average is taken. It appears that Chitosan has higher activation energy among its acid copolymers  $156.22 \text{ kJ.mol}^{-1}$  and this is in a good agreement with literature value  $147\text{-}166 \text{ kJ.mol}^{-1}$  [13, 18].



**Figure (4):** TGA thermogram of Chitosan.



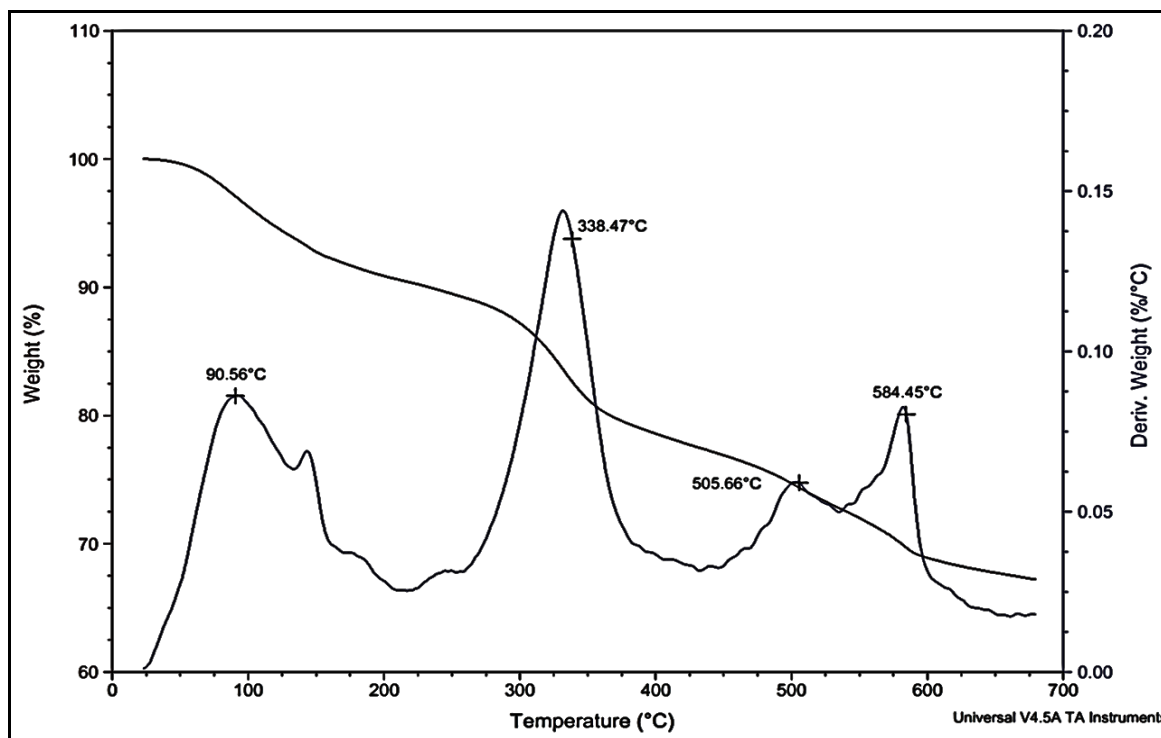


Figure (5): TGA thermogram of CS-g-OXA.

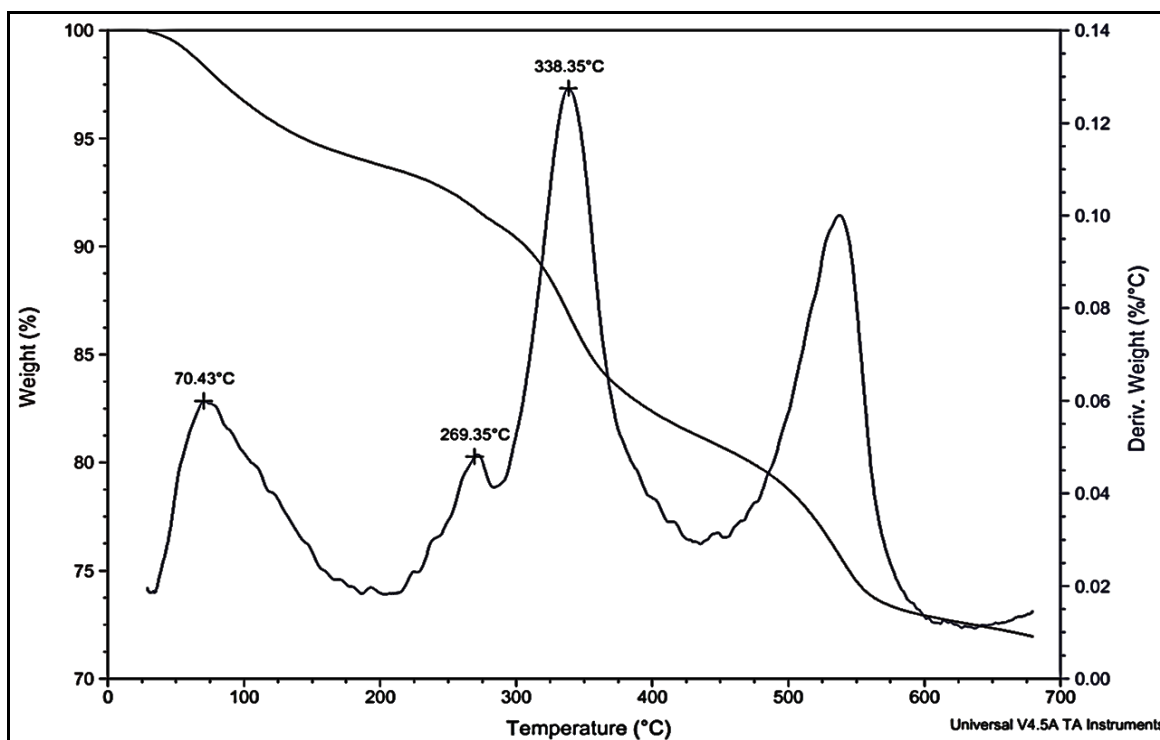


Figure (6): TGA thermogram of CS-g-SUC.

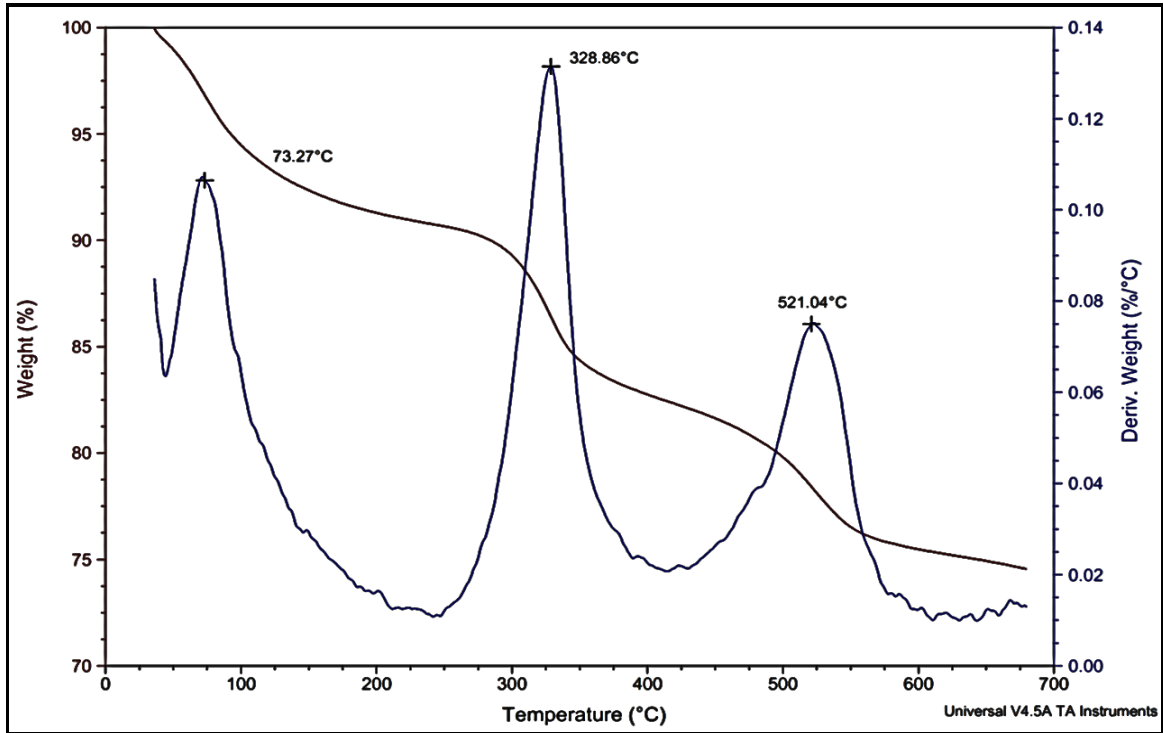


Figure (7): TGA thermogram of CS-g-GLU.

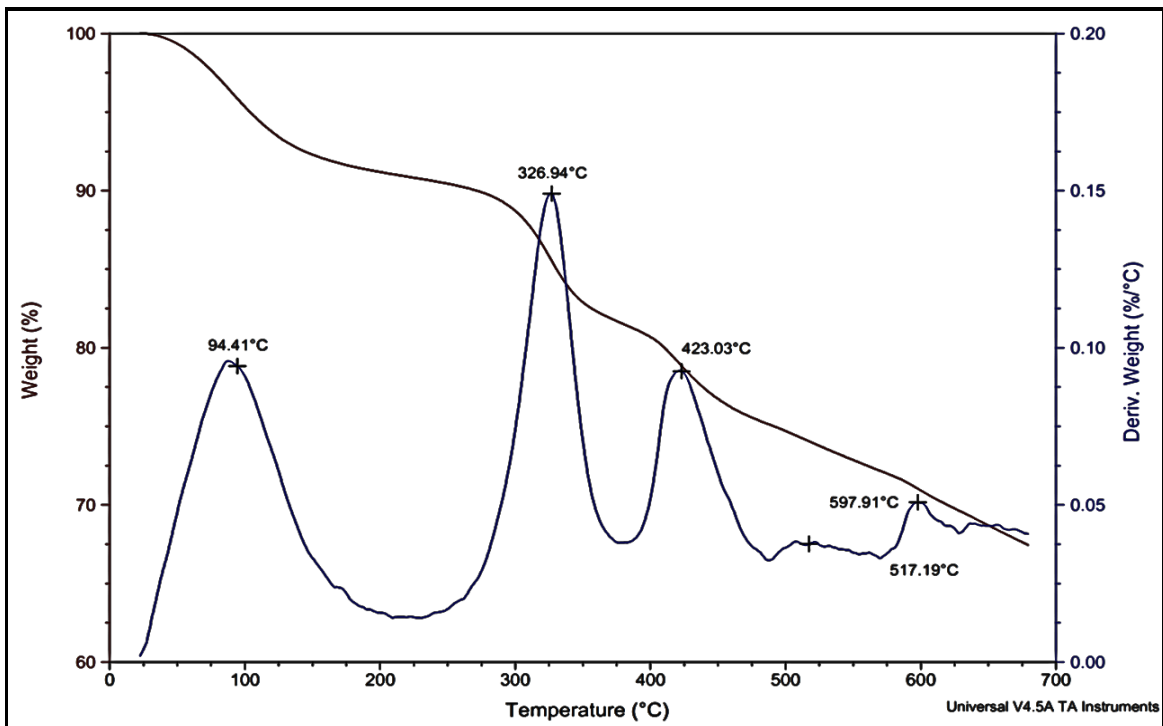


Figure (8): TGA thermogram of CS-g-ADI.

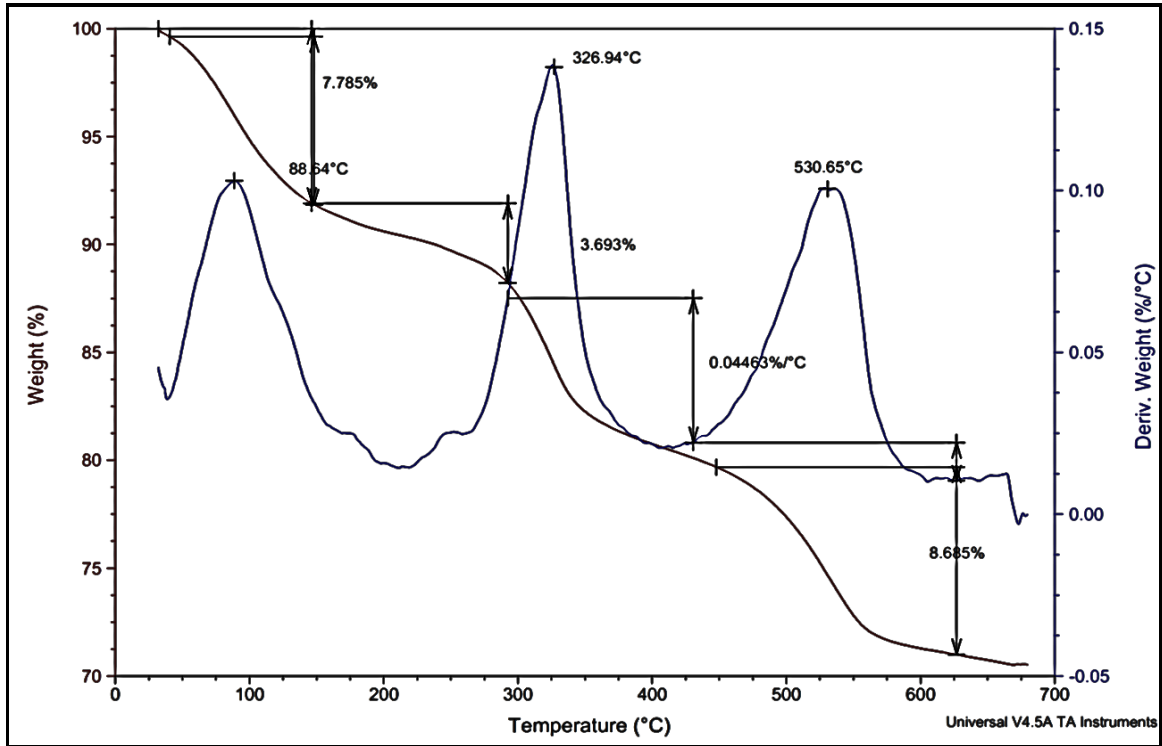


Figure (9): TGA thermogram of CS-g-PIM.

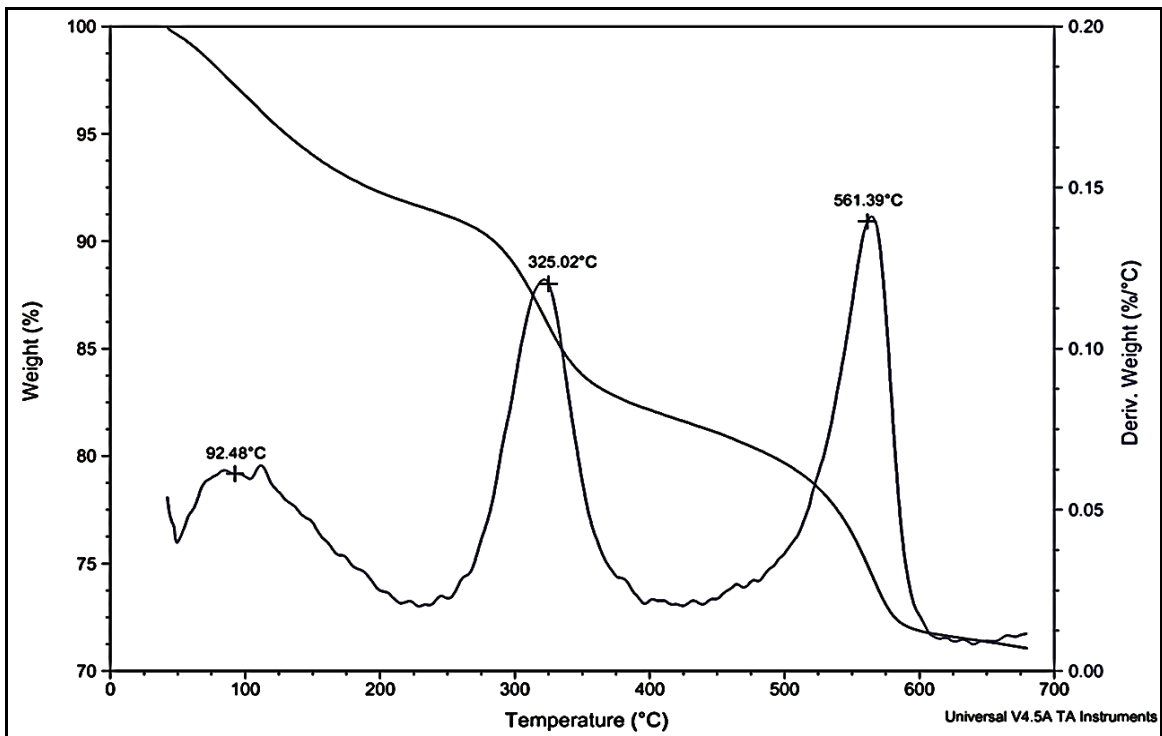


Figure (10): TGA thermogram of CS-g-SEB.



### Scanning Electron Microscopy (SEM) of the Chitosan-g-Acid copolymers

The surface of the graft copolymer was examined by scanning electron microscopy. The scanning electron micrograph of Chitosan, CS-g-OXA and CS-g-SEB copolymers are shown in Figures (11), (12) and (13), respectively.

It is seen from Figure (12) and Figure (13) that the fibrous nature of Chitosan appeared

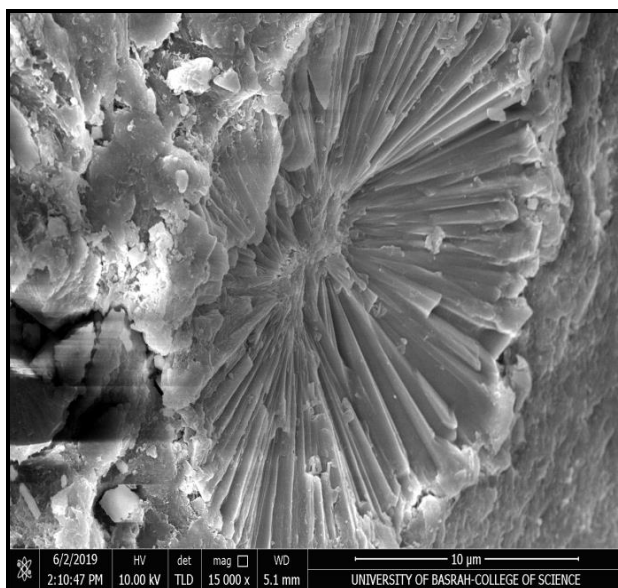
in Figure (11) is modified after the grafting process. Because of strong interactions between Chitosan and grafted acids, SEM image of Chitosan-g-acid copolymers showed spherulites like structure, which may provide a larger surface area for better applications as we mentioned before. All these observations imply that grafting different acids onto Chitosan allows better compatibility between Chitosan and the studied grafted acids.

**Table (3):** Thermal stability functions of all prepared polymers

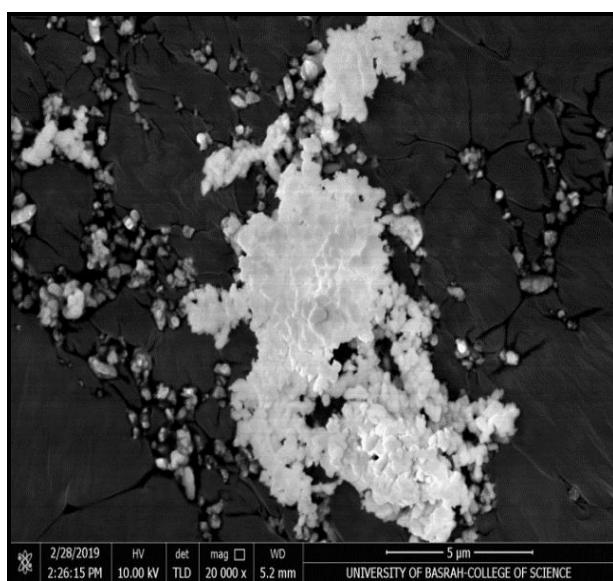
Polymer	*TOP Decomp. (°C)	%Char Residue at 600 °C	Rate of Decomp. (%wt/min)	*Ts (°C)	Activation Energy, Ea (kJ.mol <sup>-1</sup> )
Chitosan	296.19	72.5	2.15	278.5	156.22
CS-g-OXA	338.47	68.9	2.41	325	106.24
CS-g-SUC	338.35	72.9	2.03	337.5	84.02
CS-g-GLU	328.86	75.4	1.85	312.5	126.50
CS-g-ADI	326.94	70.8	2.46	343.75	120.44
CS-g-PIM	326.94	71.3	2.15	312.5	98.36
CS-g-SEB	325.02	71.9	2.11	325	138.98

\* TOP Decomp. = Optimum decomposition temperature

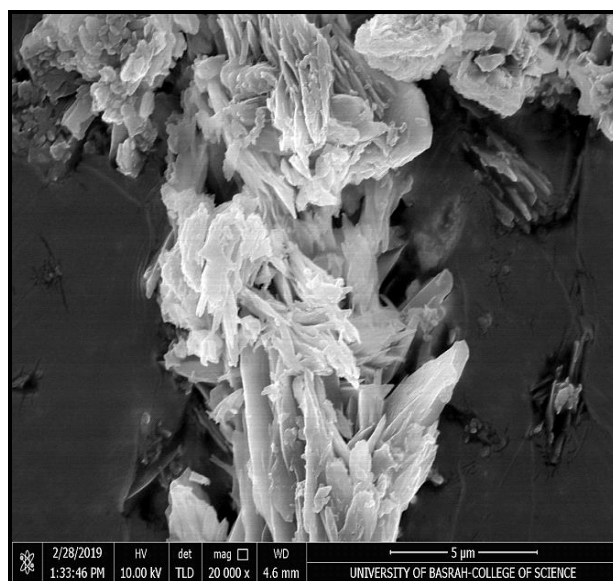
\*Ts = Decomposition Temperature at 50% weight loss from the weight of the material used.



**Figure (11):** SEM micrograph of Chitosan.



**Figure (12):** SEM micrograph of CS-g-OXA.



**Figure (13):** SEM micrograph of CS-g-SEB.

## Conclusions

The following conclusions can be drawn out of the current study:

1. Chitosan is grafted easily with six different dicarboxylic acids, namely; oxalic, succinic, glutaric, adipic, pimelic and sebacic acids by grafting copolymerization.

2. The synthesis and hence the expected copolymer structures of the Chitosan grafted copolymers are confirmed by FTIR spectroscopy.

3. Thermal gravimetric analysis (TGA) thermograms of the Chitosan copolymers show



higher decomposition temperatures than Chitosan itself that means the introduction of a dicarboxylic acid as grafting moiety to Chitosan polymer chains leads to increase thermal stability.

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