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Synthesis, Structural Characterization and Biological Evaluation of Functionalized Chitosan Schiff base and its Polymer Blend

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Abstract

Chitosan and p-methylbenzaldehyde reacted to produce chitosan schiff base. The solution casting technique was used to produce a polymer blend with PVA. FT-IR, DSC-TGA, SEM, and biological activity have all been used to characterize all produced compounds. The FT-IR results demonstrated the formation of chitosan schiff base. The thermal stability of produced polymer blends was indicated by the DSC parameters. The synthetic Schiff base and PVA polymer blend's antibacterial ability against four different species of bacteria—Pseudomonas aeruginosa, Bacillus subtilis, Escherichia coli, and Staphylococcus aureas—was investigated and assessed. The produced polymer blends exhibit good antibacterial effects versus all types of bacteria, according to the results.

Keywords: Antimicrobial polymer, Chitosan Schiff base, polymer blend.

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Introduction

Chitosan is getting great attention in the medical and pharmaceutical industries because it possesses unique qualities that make it ideal for biomedical applications, such as biocompatibility, biodegradability, and non-toxicity. Additional properties, such as anticancer, antibacterial, and antioxidant activities, have also been reported(Kumar, 2000; Koide, 1998; Kumar et al., 2004). Additionally, chitosan has many applications in the food industry, such as material recovery from food processing waste, biodegradable film manufacture, and food preservation against microbial destruction. It can also be utilized as a functional food ingredient and a source of dietary fiber(Aranaz et al., 2009).

Schiff bases were frequently utilized, particularly in the realms of medicine and pharmaceuticals. Antifungal, antidiabetic, antitumor, anticancer, herbicidal, and anti-inflammatory actions are only a few of their biological properties(Mohy Eldin et al., 2015). Various studies have synthesized numerous Chitosan schiff bases (Cs) by combining various types of aldehyde with the amine groups of chitosan in the last years, and these (Cs) have been cited as potential antibacterial agents. (Cs) were shown to be efficient antibacterial agents more than chitosan itself (Guo et al., 2007).

PVA (Polyvinyl alcohol) is a nontoxic, biocompatible polymer that was originally made in 1927 from poly(vinyl acetate). PVA is an odorless, soluble in water, film-forming polymer whose characteristics are affected by its degree of hydrolysis and polymerization. PVA and its derivatives have a wide range of uses in a variety of disciplines, including biomedical, cosmetic, textile, paper, and adhesive development (Delattre et al., 2014).

The blending of polymers is a good method to obtain polymeric materials with desirable properties raised from compounds for specific applications (El-Hefian et al., 2014). Natural polymers have recently gained significant attention not only because they are renewable, non-toxic, cost-effective, and produce biodegradable waste (Neto et al., 2005), but also because of their great potential to replace synthetic polymers in a

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variety of applications (Wood, 2001). Among these materials, chitosan has received particular interest owing to its versatility and wide range of applications, especially in the form of polymer blends. Since chitosan's characteristics can be improved by combining it with both naturally occurring and synthetic macromolecules, this research area has received lots of attention lately in a variety of ways(Mucha, 1998; Srinivasa et al., 2003; Shanmugasundaram et al.,2001; Chen et al.,2002; Sionkowska et al.,2004).

2. Experimental

2.1. Preparation of Chitosan schiff base

Before adding the aldehyde, glacial acetic acid 2% was used to dissolve 0.5 g chitosan then stirred for half an hour at room temperature. After that para-methylbenzaldehyde was added to the solution to produce Schiff base. The liquid was heated to 60 degrees Celsius for a 12 hours while being magnetically stirred. After cooling, ethanol was used to wash the crude product. The product was allowed to dry at room temperature for a 24 hours. Equation (2-1) depicts the chitosan Schiff base synthesis pathway (Younus et al., 2024).

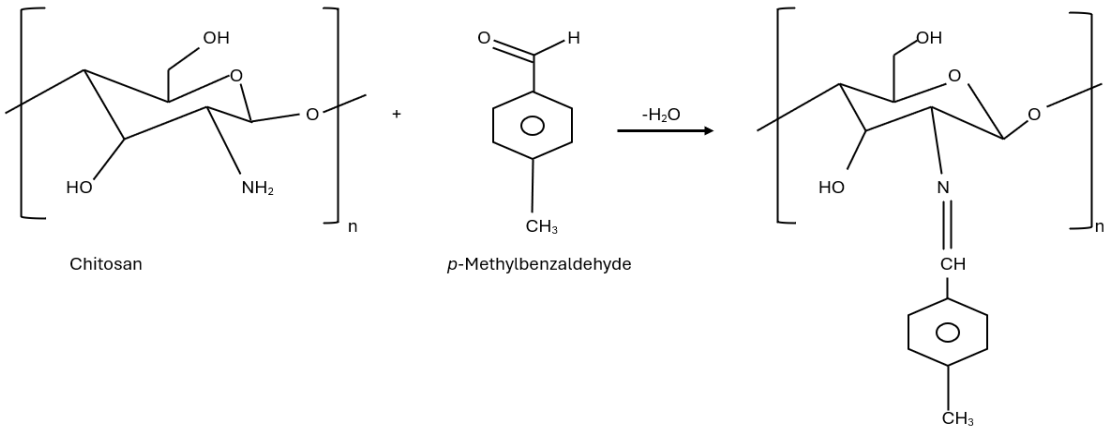

Figure (2-1): The preparation reaction of Chitosan schiff base.

2.2. Preparation of polymer blends

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The solution casting method was used to produce the polymer blends. Schiff base of chitosan solutions were made by dissolving 1 g of chitosan Schiff base into of 2 % aqueous acetic acid solution with stirring at room-temperature. To produce polymer solutions, 5 g of PVA was dissolved in 100 mL hot water to prepare 5% PVA. Cs / PVA mixes were made by combining different Cs: PVA ratios as shown in the table below.

Table (2-1): The weight percentage of the blend of PVA polymer and Chitosan schiff base

Polymer blend	Cs%	PVA%
B1	25	75
B2	50	50
B3	75	25

3. Results and Discussion

3.1. The FT-IR Spectroscopy

Chitosan schiff base was produced from the reaction of Chitosan and paramethylbenzaldehyde. Figure (3–1) presents the FT-IR spectrum of chitosan, with the characteristic bands assigned as follows: the broad absorption at 3465 cm^{-1} coincide to N–H and O–H stretching vibrations, whereas the peak at 2914 cm^{-1} is refer to symmetric C–H stretching. The band at 1645 cm^{-1} represents amide I, whereas the peaks at 1423 cm^{-1} and 1379 cm^{-1} are associated with C–N stretching and NH_2 bending vibrations, respectively. Additionally, the bands observed at 1157 cm^{-1} and 1090 cm^{-1} are attached to C–O–C bending and C–OH stretching vibrations. In Figure (3–2), the FT-IR spectrum of the Chitosan schiff base reveals a newly formed absorption band at 1639 cm^{-1}, which is assigned to the imine group (C=N). The band at 1601 cm^{-1} indicates the presence of C=C stretching in the aromatic aldehyde, while the peak at 814 cm^{-1} corresponds to aromatic C–H deformation. Furthermore, the band at 1167 cm^{-1} is refer to C–O–C stretching vibrations in (1–4) glycosidic linkages. The presence of a secondary amide (–NH) is shown by the band at roughly 1022 cm^{-1} and a hydroxyl group (OH) with polymeric connection(Chen et al., 2002).

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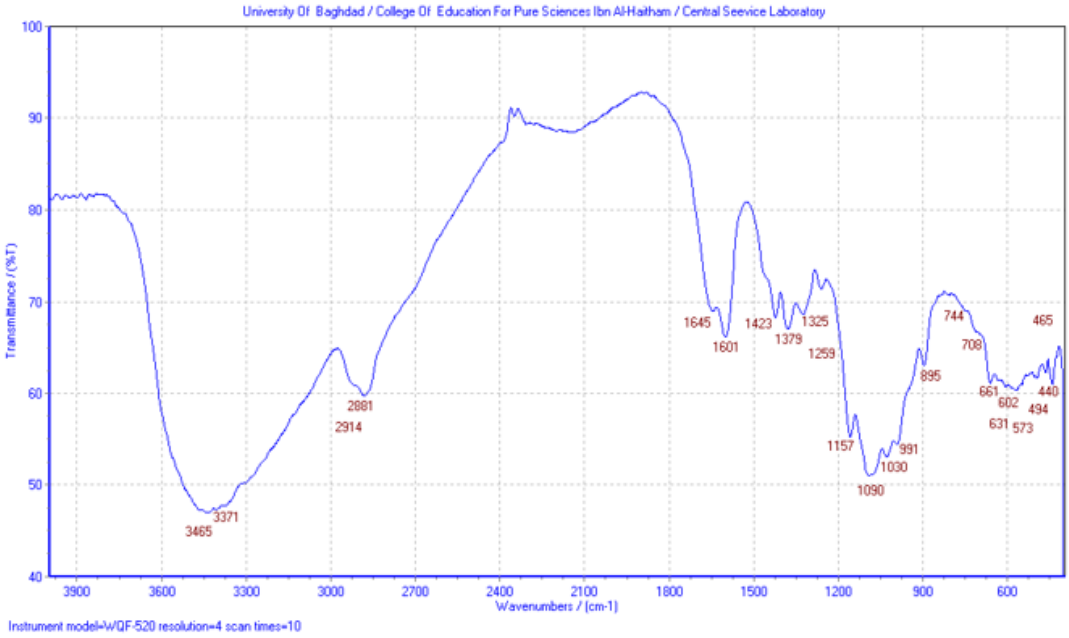
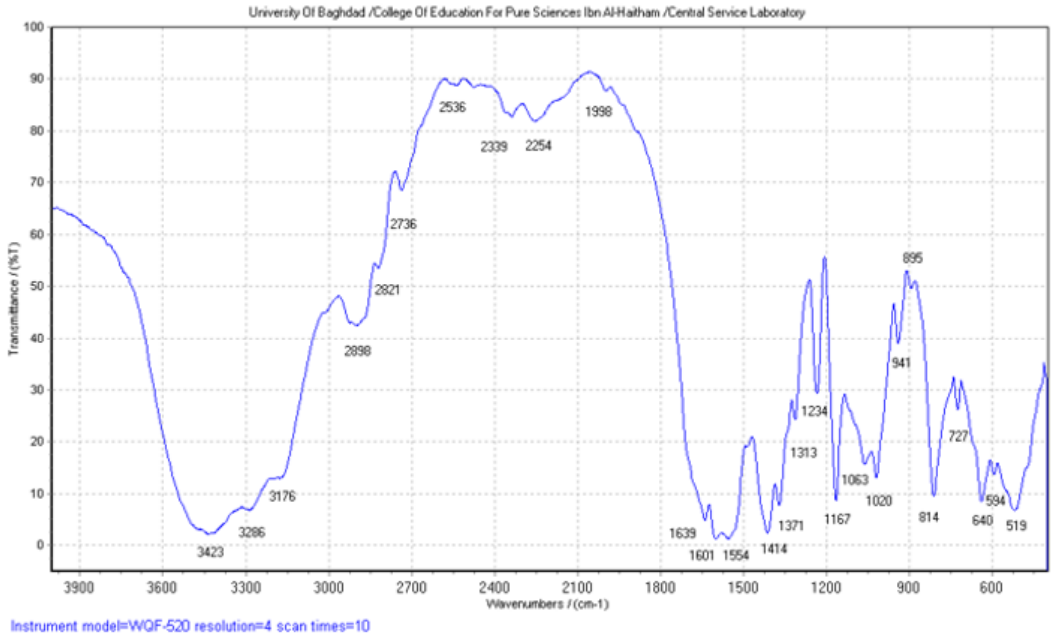


Figure(3-1): The FT-IR spectra of chitosan .



Figure(3-2): The FT-IR spectra of Chitosan Schiff base.

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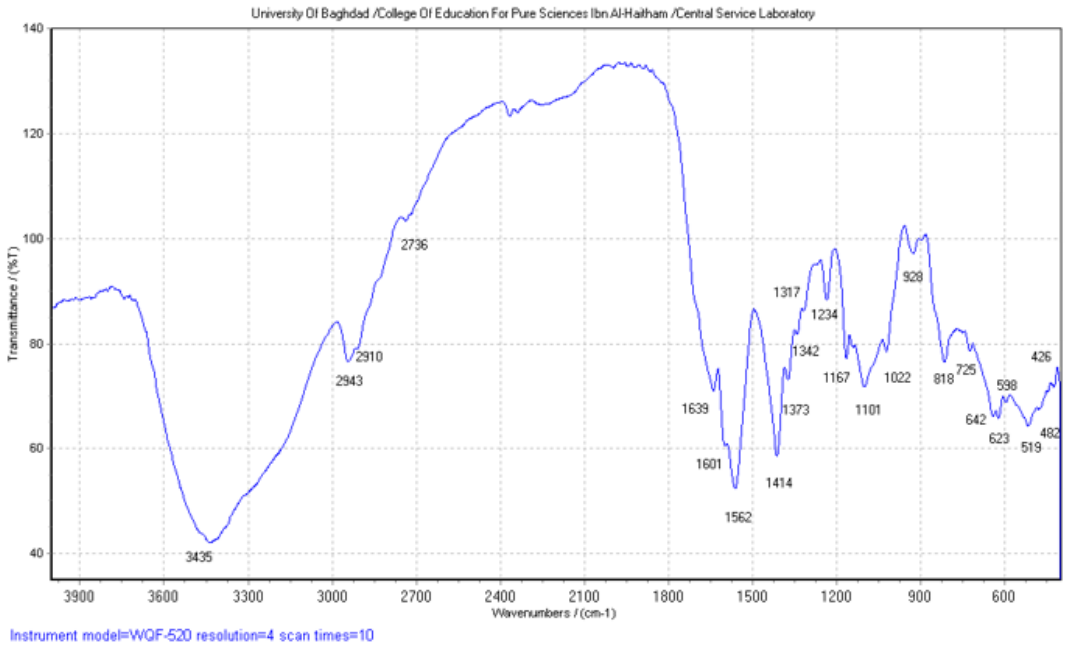

Figure(3-3): The FT-IR spectra of Chitosan Schiff base/ PVA Polymer blend

3.2. Scanning Electron Microscope (SEM)

Chitosan schiff base (Cs) SEM images and polymer blends are represented in the figures below. The (Cs) surface morphology where p-methylbenzaldehyde is added as shown in figure (3-4) shows rough surface appearance this is explained by changing of internal structure of polymer. Immobilization of aldehyde molecules into Chitosan backbone gives the polymer some hydrophobic nature. The SEM for polymer blends B2 and B3in the presence of (Cs) with PVA is homogenously distributed on the matrix surface as illustrated in figures (3-5), (3-6). The SEM for B3 shows increase in surface roughness as increasing the percentage of Cs in the blend (Sionkowska et al., 2004).

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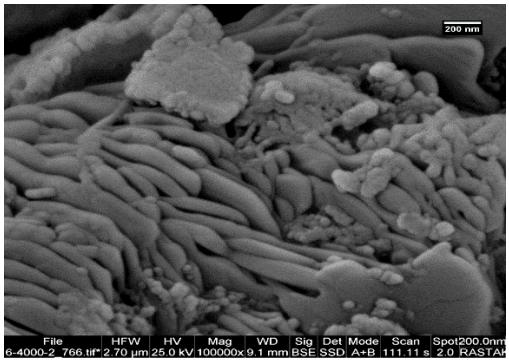
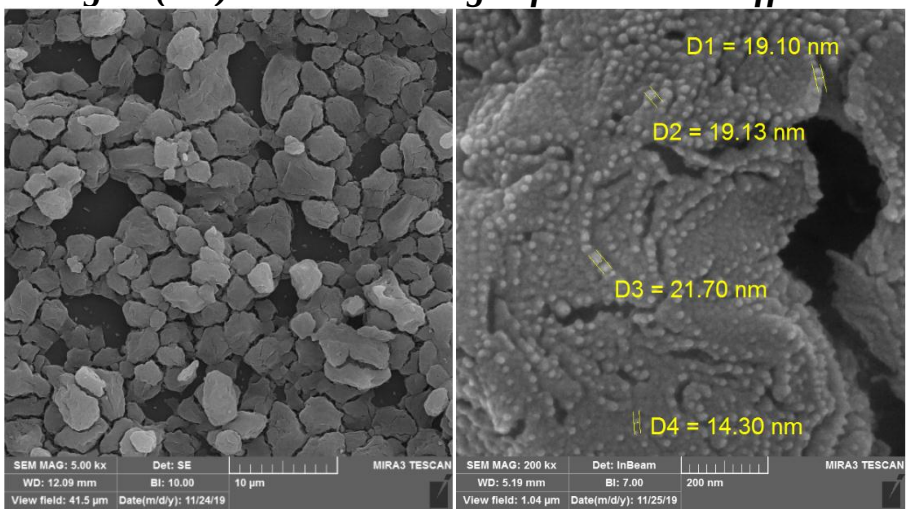
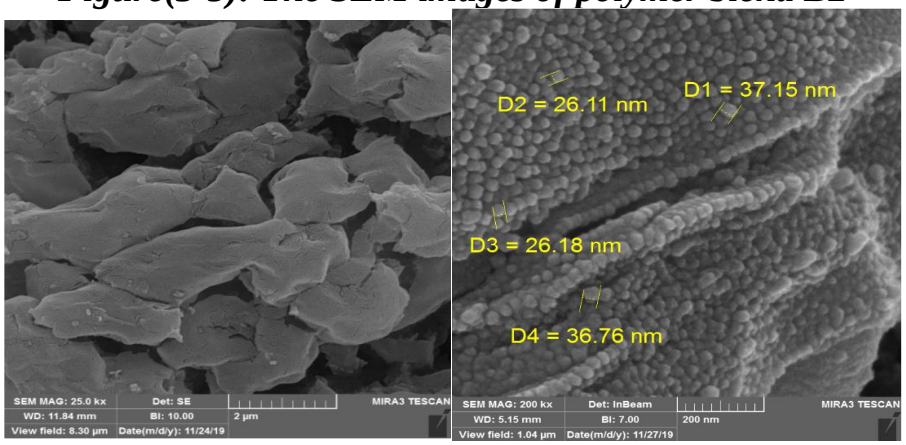


Figure(3-4): The SEM image of chitosan schiff base



Figure(3-5): The SEM images of polymer blend B2



Figure(3-6): The SEM images of polymer blend B3

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3.3 Thermal analysis

The pure chitosan, PVA, and Cs/PVA polymer blend were measured by thermogravimetric analysis (DSC⁄ TGA) at a steady rate of 10°C⁄ min at temperatures between 0 and 600 °C.

Regarding continuous mass loss, the TGA curve associated with Chitosan figure (3-7) shows two stages. The initial stage involves a mass loss of -7.6% for the volatile ingredients at 201°C. The second step is at (201-529°**C**) with -60.11% mass lose decomposition regarding polymer's chain. The glass transition temperature Tg at 95.5°C was shown by the DSC curve for the chitosan in figure (3-7). The polymer melting Tm is associated with an exothermic peak at 303.2°C.

In terms of continuous mass loss, the TGA curve related to a PVA figure (3–8) shows three phases. In terms of the volatile materials, The initial stage has a mass loss of (-48.13%) at 340.67°C. The mass loss in the second stage is (-14.07%) at 340.67-435.96°C, while the weight loss in the third stage is approximately (-22.37%) at 435.96-594.67°C (decomposition providing for the polymer's side chain). The DSC curve displayed the glass transition temperature Tg for the PVA at 68.4°C. Td, the degradation temperature, is at 454.9°C, whereas Tm, the polymer melting temperature, is related to an endothermic peak at 214.5°C.

The TGA thermo gram regarding the B(Cs/PVA) figure (3-9) indicates 4 steps, the initial one at a temperature of (173.33°C) with the weight loss approximately (-17.92%), second step is (322.387°C) with weight loss approximately (-17.48%), third step at a temperature of (493.44°C) and weight loss approximately (-20.02%) the fourth stage at a temperature of (595.64°C) with a weight decrease of about -4.76%. Glass transition temperature Tg at 80.4°C is shown by the DSC curve related to B(Cs/PVA). The blend film's thermogram was found to display a single Tg. This suggests that the two polymers have been thoroughly mixed and that hydrogen bonding between the PVA and Cs polymer blend are present (El Hamdaoui et al., 2021).

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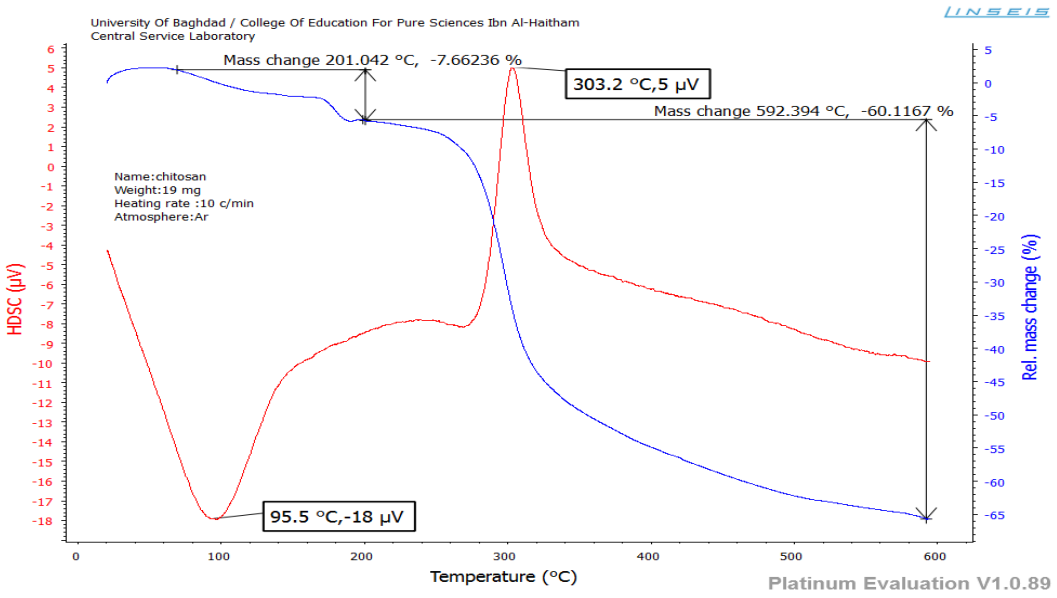

Figure (3-7) Thermal analysis of chitosan

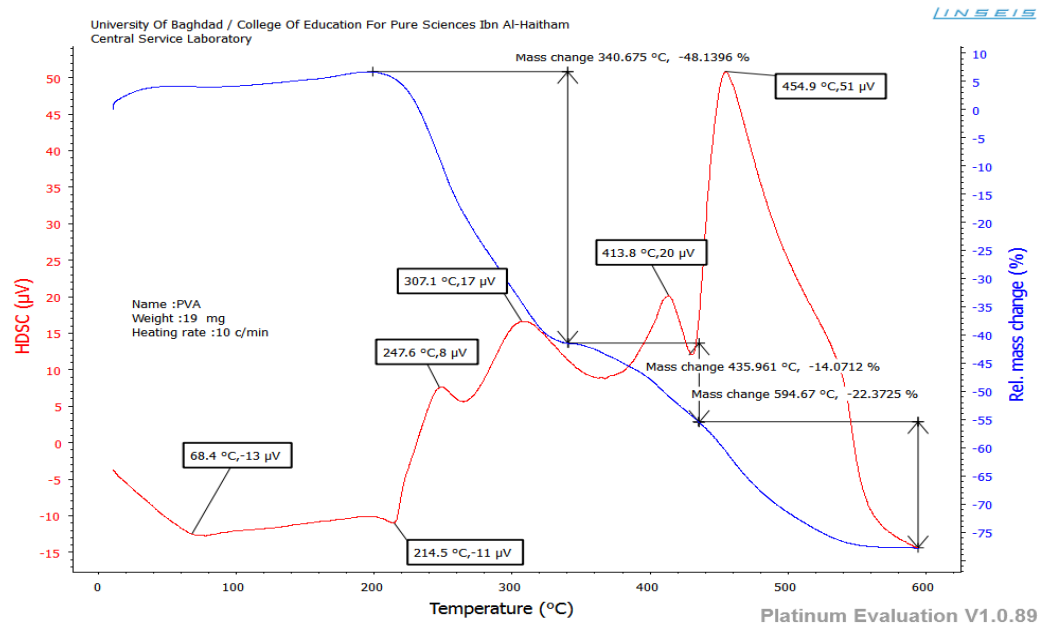

Figure (3-8) Thermal analysis of PVA

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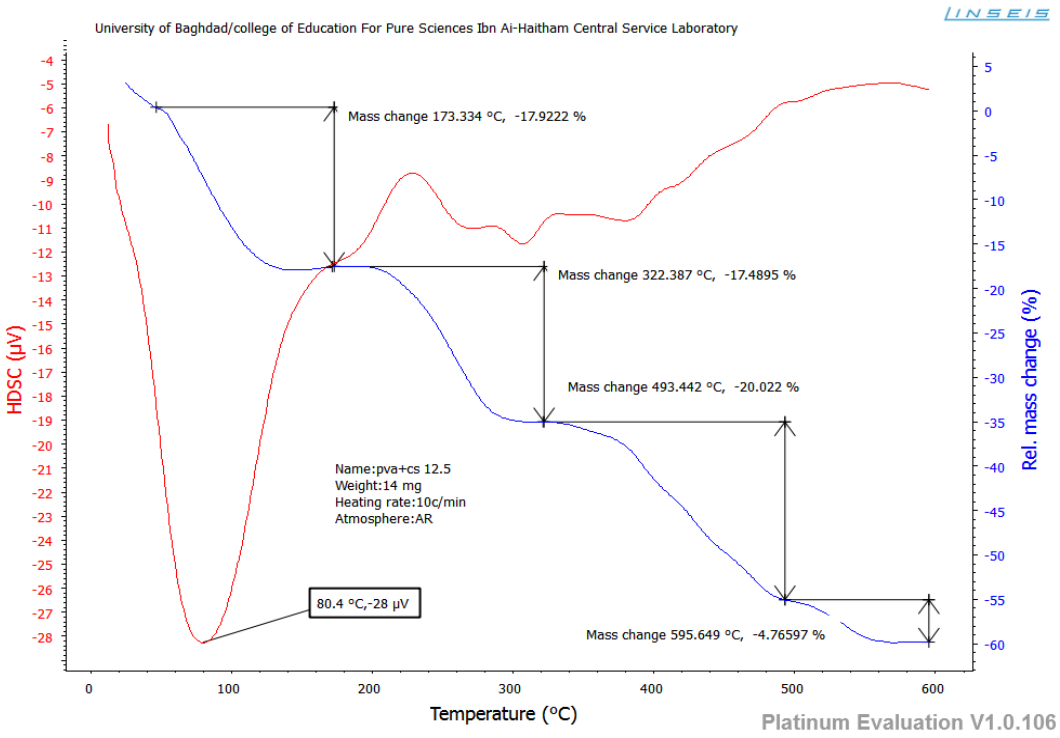

Figure (3-9) Thermal analysis of Cs/PVA blend

3.4. Biological activity.

Using the diffusion inhibition method, Chitosan schiff base (Cs) and (Cs) /PVA polymer blends biological activities were evaluated against four different kinds of harmful bacteria. The antibacterial activity results are shown in Table (3-5). Gram+ve (B.subtilis and S.aureus) and Gram-ve (E.coli and P.aeruginosa) microorganisms were used to test the materials' antibacterial activity. Each compound under investigation has good bactericidal characteristics, as Table (3-1) clearly shows. The growth of both Gram-positive and Gram-negative bacteria was observed to be inhibited by the synthesized (Cs) and PVA blend, resulting in an inhibitory zone with a diameter of 27 mm.

Because of the chemical structure of PVA and Cs, the produced polymer blends show excellent antibacterial activity against the studied pathogens. The Schiff-base imine group (C=N) with its π-electrons is proposed to increase the lipophilicity of the molecule which facilitates the

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(Cs) molecule's penetration of the microbe's cell membrane. It may be followed by a disruption in the microbial cell's respiration mechanism. Finally, protein synthesis is inhibited, preventing bacteria from growing further (Webster et al., 2007).

Table (3-1): Antibacterial activity of Chitosan Schiff base/PVA polymer blend

Compound	***Esherichia Coli***	***Staphylococcus aureus***	***Bacillus cerues***	***Pseudomonas aeruginosa***
B1	24	21	19	20
B2	25	23	22	24
B3	24	23	24	27

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تحضير،تشخيص والفعالية الحيوية لقاعدة شيف للكيتوسان ومزيجها البوليمري

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مستخلص البحث:

تم تفاعل الكيتوسان مع بارا-ميثيل بنزالديهايد لإنتاج قاعدة شيف للكيتوسان. استُخدمت تقنية خلط المحاليل لتحضير مزيج بوليمري مع بولي فينيل الكحول .تم تشخيص جميع المركبات المحضّرة بواسطة مطيافية الاشعة تحت الحمراء والتحاليل الحرارية والمجهر الالكتروني الماسح إضافةً إلى تقييم الفعالية الحيوية. أظهرت نتائج مطيافية الاشعة تحت الحمراء تكوّن قاعدة شيف للكيتوسان. كما اثبتت التحاليل الحرارية الاستقرارية الحرارية للمزائج البوليمرية المحضّرة. وتمت دراسة وتقييم الفعالية المضادة للبكتيريا لقاعدة شيف المحضّرة والمزيج البوليمري مع PVAضد أربعة أنواع مختلفة من البكتيريا وهي: (Pseudomonas aeruginosa)، (Bacillus subtilis)، (Escherichia coli)، (Staphylococcus aureus) وأظهرت النتائج أن المزائج البوليمرية المحضّرة تمتلك فعالية جيدة مضادة للبكتيريا ضد جميع انواع البكتريا.

الكلمات المفتاحية: البوليمرات المضادة للميكروبات، قاعدة شيف للكيتوسان، المزيج البوليمري.