

# SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF PVA CYCLIC ACETAL (CU) METAL COMPLEX / CHITOSAN POLYMER BLEND

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**ABSTRACT :** Polyacetal was synthesized from the reaction of PVA with para-methoxy benzaldehyde. Polymer metal complex was prepared by reaction with Cu, polymer blend with Chitosan was prepared through the technique of solution casting method. All prepared compounds have been characterized through FT-IR, DSC, SEM as well as the Biological activity. The FT-IR results indicated the formation of polyacetal. The DSC results indicated the thermal stability regarding prepared polymer, polymer metal complex and Chitosan polymer blends. Antibacterial potential related to synthesized polyacetal, its metal complex and Chitosan blend against four types of bacteria namely, *Staphylococcus aureas*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Escherichia coli* was examined and evaluated. The results reveal that the Polyacetal-Cu complex /polymer blend has the greater potential to kill bacteria than Polyacetal and Polyacetal-Cu complex.

**Key words :** Polycyclic acetal, antimicrobial polymers, polymer blend, chitosan.

## INTRODUCTION

Pharmaceutical industries are continuously facing challenges and expectations of novel technologies and opportunities for development of drug designing due to medical and health care material research. The utilization of excipients in pharmaceutical industries evolves from their traditional auxiliary function in formulations like facilitating flowability and consistency of the product along with their vital role in enhancement of drug performance particularly stability, release and bioavailability. Nowadays biopolymers are considered as key ingredients for the engineered drug delivery systems because of their stability, availability, renewability and low toxicity (García-González *et al*, 2011).

Antimicrobial polymers, therefore are highly demanded as a strategy to avoid hospital acquired infections and they can be prepared either by embedding a biocide agent into the polymer bulk, for instance, during their processing or by applying surface coatings (Kenawy *et al*, 2007). A different approach is the polymerization of monomer-containing biocide groups or the grafting of antimicrobial agents into the polymers (Yuan *et al*, 2004).

Polymer/metal complex emerge as a route to further extend the applications of biocide metals as a large percentage of hospital-acquired infections are spread through surface contacts or catheters mostly made of

plastics. For instance, around 80%–95% of hospital-acquired urinary tract infections originate from urinary catheters (Curtis, 2008).

Polyvinyl alcohol (PVA), which is an essentially made from polyvinyl acetate through hydrolysis, is easily degradable by biological organisms and in water is a solubilized crystalline structure polymer (Razzak, 2001). PVA is an artificial polymer that have been used during the first half of the 20th century worldwide. It has been applied in the industrial, commercial, medical, and food sectors have been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food (DeMerlis and Schoneker, 2003). The poly acetals of poly (vinyl alcohol) (PVA) are obtained by acid catalyzed modification of PVA with various aldehydes (Fernandez, 2006).

Polycyclicacetals of PVA are important industrial products that find various applications in the aviation and automobile industries as well as in biomedical fields (Li, 2006). The physical and chemical properties of poly (vinyl acetal) are highly dependent on the degree of acetalysation, the ratio of the aliphatic and the aromatic acetal moieties, the stereochemistry and the random or block nature of the acetal polymer (AL, 2018).

Polymer blend is a homogenous or a heterogeneous

mixture of at least two or more polymers or copolymers. In some cases, it is also referred as polymer mixture. These polymers can interact chemically or physically depending on their structural properties, and their physical properties obviously differ from their parent components (Jenkins *et al*, 1996). The major objective of polymer blending is to achieve cheap, readily available and commercially viable products with unique properties. Polymer blending is a vast and unlimited subject of interest that requires highest attention theoretically and experimentally. Polymer blend was found that polymer blends have superior properties compared to its component polymers. Blending of different polymers is one of the most important industrial tools to get more efficient and attractive product for various applications. Some characteristics of polymer blending are mentioned below (Khan *et al*, 2019).

## MATERIALS AND METHODS

### Materials

Poly vinyl alcohol M.W 72000 was acquired from Sigma-Aldrich, also all the solvents and reagents have been acquired from BDH and utilized with no additional purifications.

### Preparation of compounds

#### Preparation of PVA cyclic acetal (PA)

PVA (2.5 gm) was dissolved in 25 ml of (DMSO), Also P-Methoxybenzaldehyde (2ml) was dissolved with mixture of solution (20 ml) the solution was mixed in a round bottle (16 ml Benzene), (4 ml Ethanol), (4 drop from Sulphuric acid) after that all the two solutions were mixed, and then magnetically stirred in (40°C) for 12 hours, the resulting mixture was neutralized by adding few drops of NaOH solution until the pH is 7. The crude product was washed with distilled water and recrystallized by

ethanol. Synthetic route related to target compound can be seen in scheme (1) (Delattre *et al*, 2014).

### Preparation of metal complexes

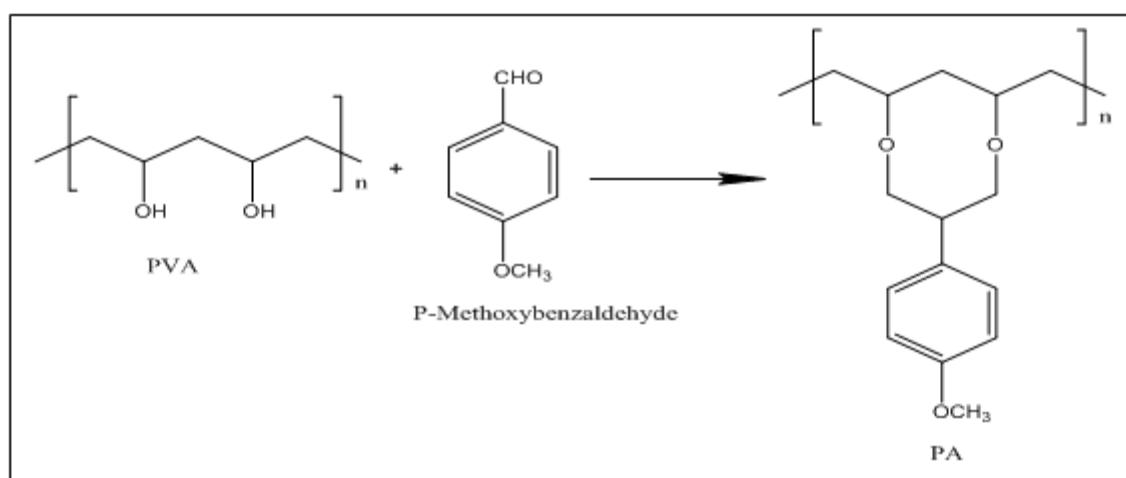
PA (0.6 gm) was dissolved in 10 ml of (DMSO) with heating and stirring dissolving limit, Also  $\text{CuCl}_2 \cdot \text{mH}_2\text{O}$  (0.2 gm) was dissolved in 10 ml of (DMSO) After dissolving them done poured PA on  $\text{CuCl}_2 \cdot \text{mH}_2\text{O}$  once more with heating and stirring for (8-10 hrs) at a temperature (50 -60). After cooling, the complexes were washed with Ethanol and then dried at 60°C in vacuum for 24 hours (Sari, 2006).

### Preparation Chitosan/ PA blend and Chitosan/ PA-M blend

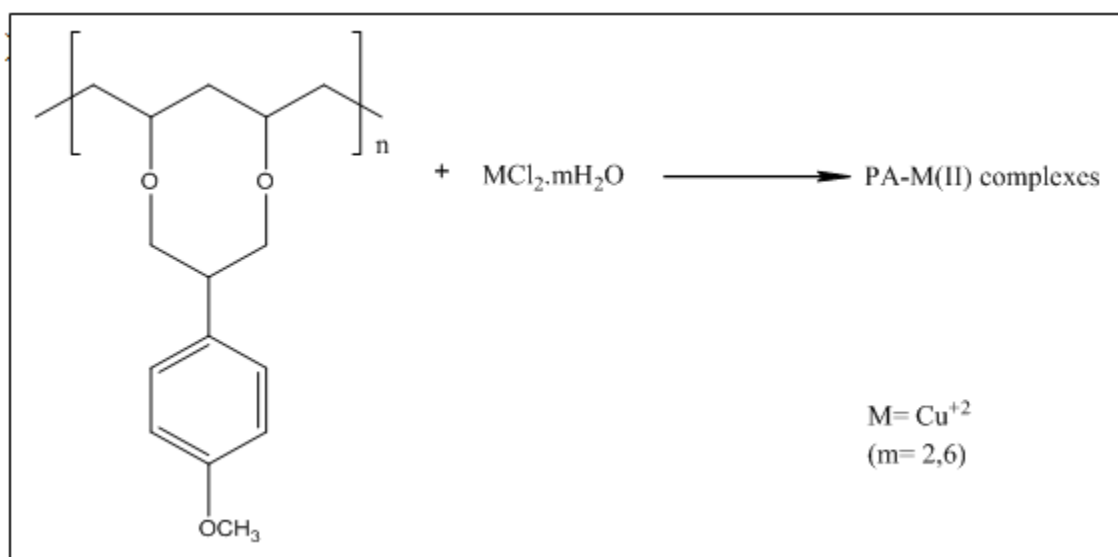
The chitosan solution was prepared by dissolving a different percentage (0.1 g, 0.3 g) (1%, 3%) of chitosan to 25 ml acetic acid (V/V) for three times. Also the PA solution was prepared by dissolving a different percentage (0.1 g) (1%) for twice and (0.3 g) (3%) for once of PA with 25 ml DMSO with heating and stirring dissolving limit. Also the (PA-Cu) solution was prepared by dissolving a different percentage (0.1 g) (1%) for twice and (0.3 g) (3%) for once (PA-Cu) to 25 ml DMSO. After that the chitosan solutions were mixed with different percentage as can see in Table 1 (Ameer, 2016).

Table 1 : Different percentage of mixing.

Polymer blend	% chitosan	% PA
B1	25%	75%
B2	75%	25%
B3	50%	50%
Polymer blend	% chitosan	% PA-Cu
B1-PACu	25%	75%
B2-PACu	75%	25%
B3-PACu	50%	50%



Scheme 1 : Synthetic route related to target compound Polyacetal.



Scheme 2 : Synthetic route related to target compound PA-M.

## RESULTS AND DISCUSSION

### Preparation and characterization of PVA cyclic acetal (PA)

Compound PA was synthesized from the reaction of PVA with P- Methoxybenzaldehyde in mixed from DMSO (16 ml Benzene), (4 ml Ethanol) and (4 drop from Sulphuric acid). The adding few drops of NaOH solution until the pH is 7 and stirred in 40°C for 12 hours (Delattre *et al*, 2014). The FT-IR spectrum of compound PA, Fig. 1 indicated the appearance of bands at (3200-2500 cm<sup>-1</sup>) (2947 cm<sup>-1</sup>) due to (O-H) and (C-H, aliphatic stretching vibration) groups, respectively. Also, the peaks at 1450, 1249 cm<sup>-1</sup>) due to (CH<sub>2</sub>, CH<sub>3</sub> bending vibration) groups respectively and indicated the appearance of bands at (1616 cm<sup>-1</sup>) due to (C=C) group. Also, indicated the appearance of bands at (1118 and 1033) cm<sup>-1</sup> due to (C-O-C stretching vibrations) cyclic acetal group which confirms the occurrence of acetalization reaction between polyvinyl alcohol and P-methoxybenzaldehyde (Qin, 2016).

### Preparation and characterization of metal complexes (PA-Cu)

Polyacetal-Cu (PA-Cu) was synthesized from the reaction of a compound (PA) with CuCl<sub>2</sub>.nH<sub>2</sub>O was dissolved in 10 ml of (DMSO) with heating and stirring for (8 -10 hrs) at a temperature (50 - 60). After cooling, the complexes was washed with ethanol and then dried at 60°C in vacuum for 24 hours (Sari, 2006). The FT-IR spectra of both Fig. (2) the prepared complexes (PA-Cu) exhibited broadband at range (3500 - 3100) cm<sup>-1</sup>. As such exhibited band at range (3500 - 3100) cm<sup>-1</sup> and figures below indicates the appearance of bands at (3078cm<sup>-1</sup>) due to stretching vibration of C-H aromatic.

Also, both figures below indicates the appearance of bands at (2912 - 2947) cm<sup>-1</sup> due to stretching vibration of (C-H) aliphatic and the peak at 1616 cm<sup>-1</sup> due to (C=C) aromatic group. Also, both figures below indicated the appearance of bands at (1118, 1029) cm<sup>-1</sup> due to (C-O-C stretching vibrations) cyclicacetal group(Qin, 2016). At lower frequency the complexes (PA-Cu) appearance new bands (559 cm<sup>-1</sup>), which are due to í(Metal-O) (Gülcan, 2012).

### Preparation and characterization Chitosan/ PA blend and Chitosan/ PA-M blend

Compounds (B1, B2, B3, B1-PA-Cu, B2-PA-Cu, B3-PA-Cu) were synthesized from the reaction of mixed with different percentageas can be seen in Table 1. The presence of OH groups in both polymers leads to hydrogen bond formation, which caused chemical interactions between them. Wherefore, the FTIR spectrum of the blend polymers showed a wide range of combined absorptions ranging from 3600 to 3000cm<sup>-1</sup> assigned for stretching vibrations of primary amine and hydroxyl groups (NH<sub>2</sub> and OH) (Ameer, 2016).

### Thermal analysis

The thermo gravimetric (DSC/TGA) curves of pure PVA, Chitosan, PA, PA-Cu, and (Ch/PA, Ch/PA-Cu) blends were obtained at the heating rate of 0.10°C min<sup>-1</sup> in nitrogen atmosphere, was measured in temperature range from (25-1000 °C). Table 2 shows the thermal decomposition of the pure PVA Chitosan, PA, PA-Cu and (Ch/PA, Ch/PA-Cu). The TGA curves figure (5) of pure PVA showed three main stages of the weight loss, first (80-250°C) devoted to evaporation of the volatile compounds mainly water and weight loss about (-4%) and second stage (250-420°C) decomposition of side

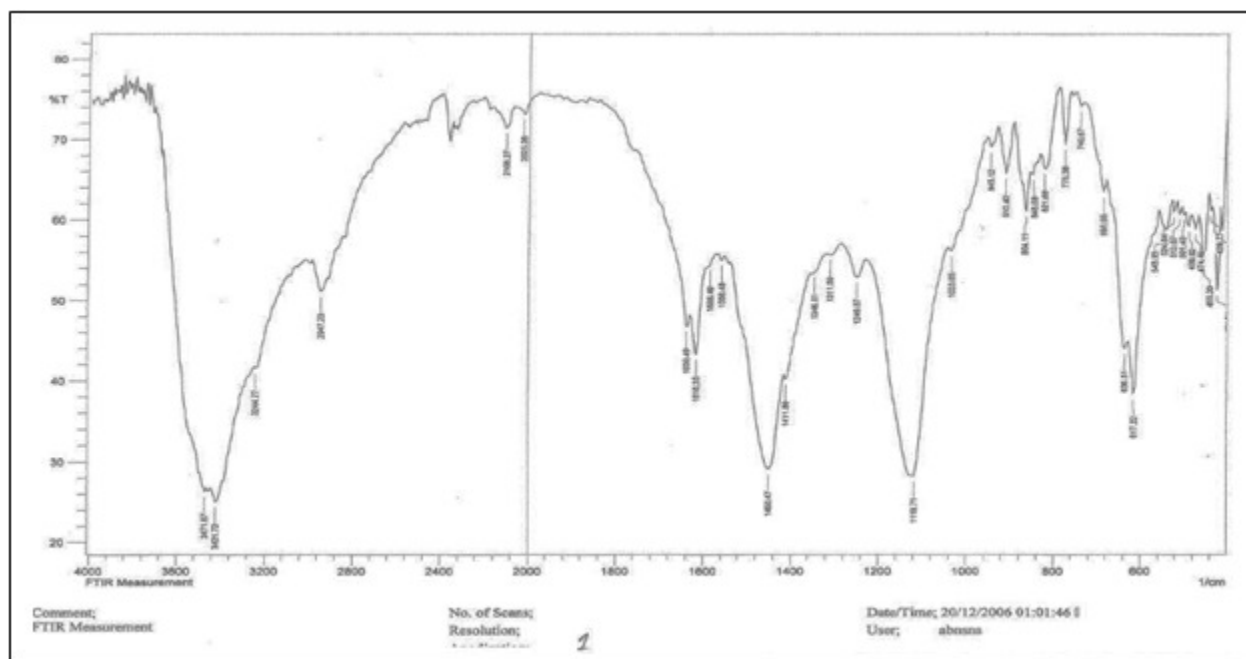


Fig. 1 : FT-IR spectrum PA.

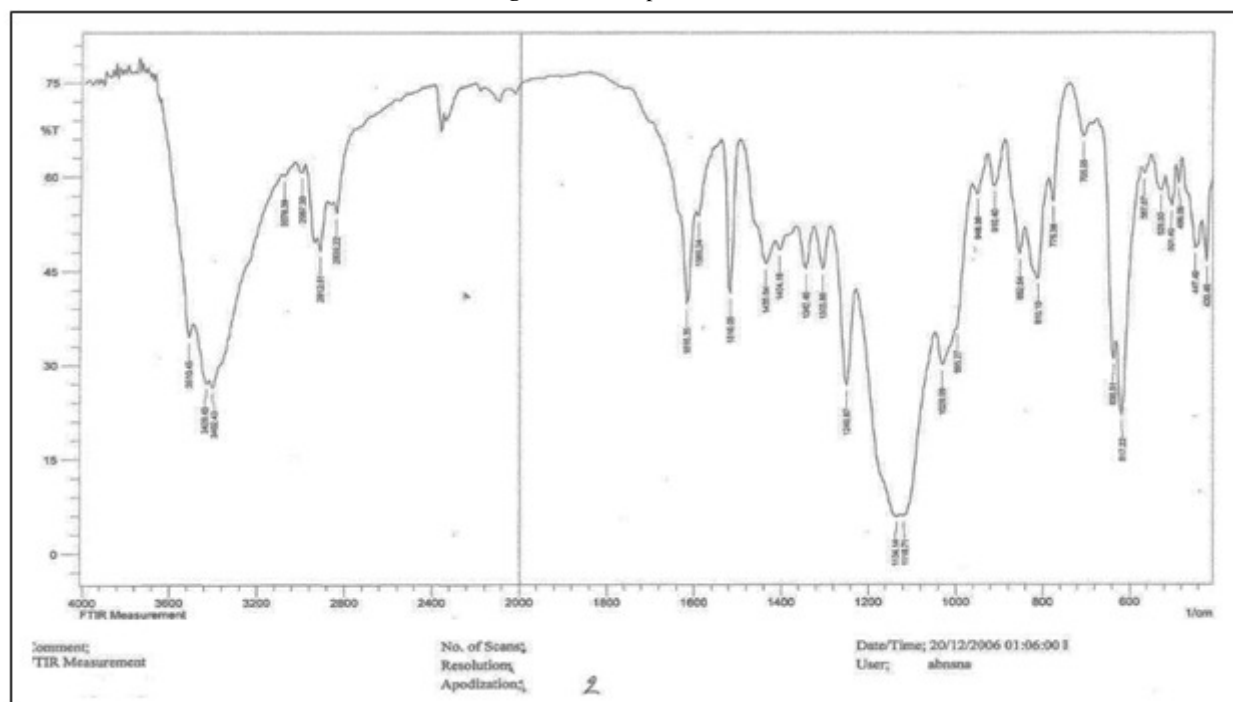


Fig. 2 : FT-IR spectrum of PA-Cu.

chain of pure PVA and weight losses about (-77 %). The last one in from (420–700°C) decomposition of the main chain of PVA, and weight losses about (-11%). The DSC curve in Fig. 5 for PVA film shows a glass transition temperature  $T_g$  of (80°C) exothermic peak at (270°C) represent crystalline temperature  $T_c$ , a broad endothermic peak regard to the polymer melting ( $T_m$ ) at (336°C).

The TGA curves Fig. 6 of PA showed four main stages of the weight loss, first (25–150°C) devoted to evaporation of the volatile compounds mainly water and

weight loss about (-5.702558%) and second stage (150–350°C) decomposition of side chain of pure PA and weight losses about (-38%). Thrid stage (350–660°C) decomposition of side chain of pure PA and weight losses about (-6%). The last one in from (660–800°C) decomposition of the main chain of PA and weight losses about (-10%). The DSC curve in Fig. 6 for PA film shows a glass transition temperature  $T_g$  of 100°C, exothermic peak at (250°C) represent crystalline temperature  $T_c$ , a broad endothermic peak regard to the polymer melting

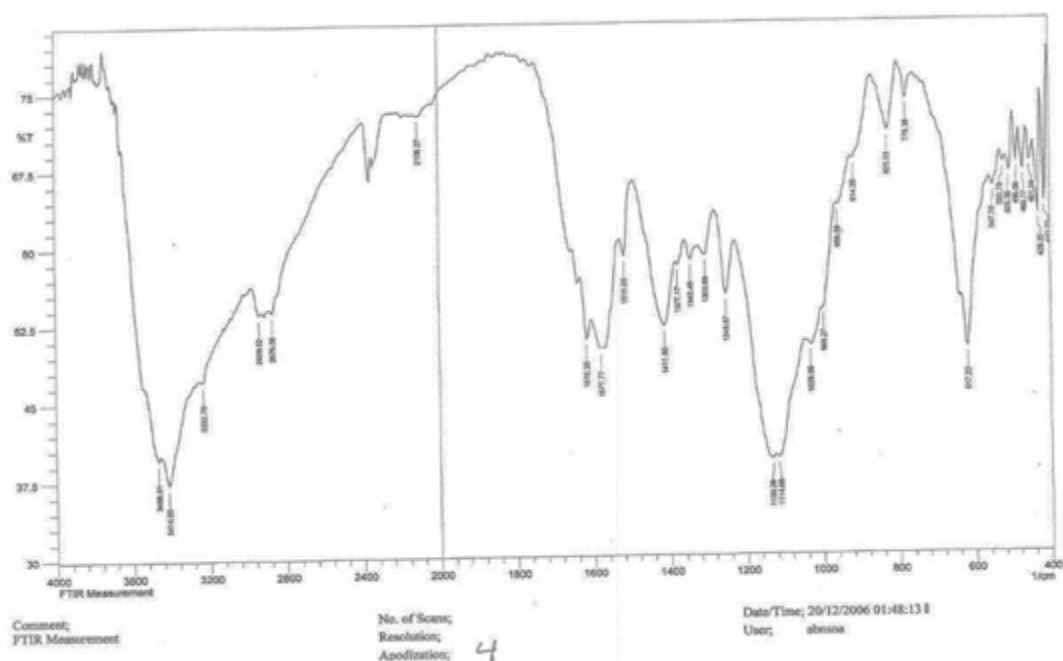


Fig. 3 : FT-IR spectrum of Chitosan/ PA blend [B1].

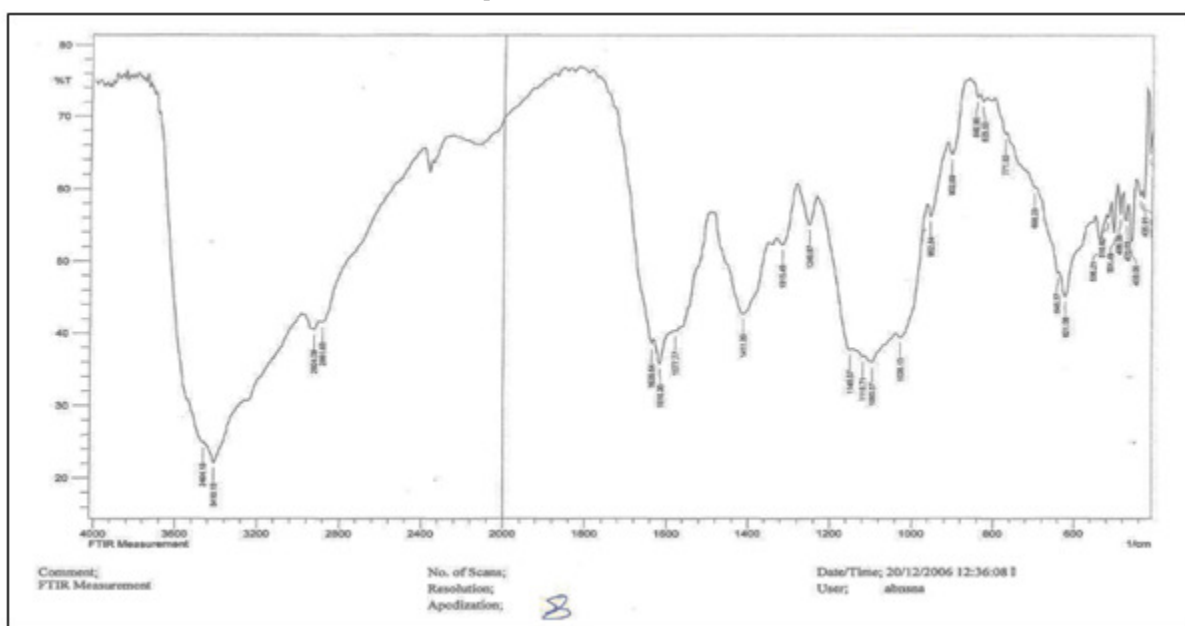


Fig. 4 : FT-IR spectrum of Chitosan/ PA blend [B-PA-Cu].

(T<sub>m</sub>) at (350°C). The degradation of polymer (T<sub>d</sub>) begins in 740°C.

The TGA curves Fig. 7 of PA-Cu showed five main stages of the weight loss, first (40–140°C) devoted to evaporation of the volatile compounds mainly water and weight loss about (-3.389%) and second stage (140 – 350°C) decomposition of side chain of pure PA-Cu and weight losses about (-28%), third stage (350–760°C) decomposition of side chain of pure PA and weight losses about (-12.74567%). fourth stage (760–820°C) decomposition of side chain of pure PA and weight losses about (-16 %). The last one in from (820–1000°C)

decomposition of the main chain of PA and weight losses about (-20.98137%). The DSC curve in Fig. 7 for PA-Cu film shows a glass transition temperature T<sub>g</sub> of (100°C), a broad endothermic peak regard to the polymer melting (T<sub>m</sub>) at (420°C). The degradation of polymer (T<sub>d</sub>) begins in (779°C).

The TGA curves, Fig. 8 of Chitosan showed four main stages of the weight loss. The first step at (40–140°C) devoted to the evaporation of the volatile compounds mainly water and weight loss about (-8 %). The second one in from (140 – 400°C) with weight losses about (-41%), third stage (400–825°C) with weight losses

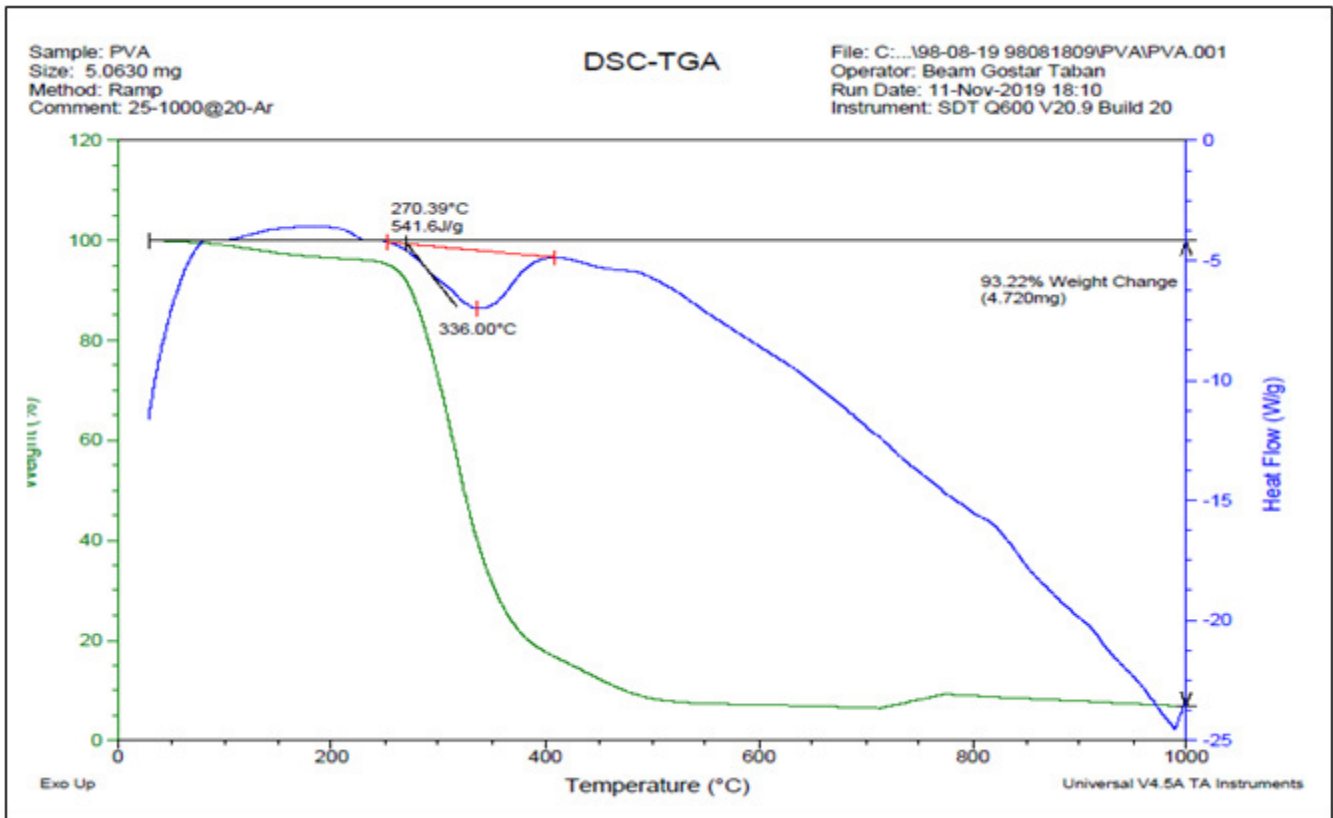


Fig. 5 : Thermal analysis of pure PVA.

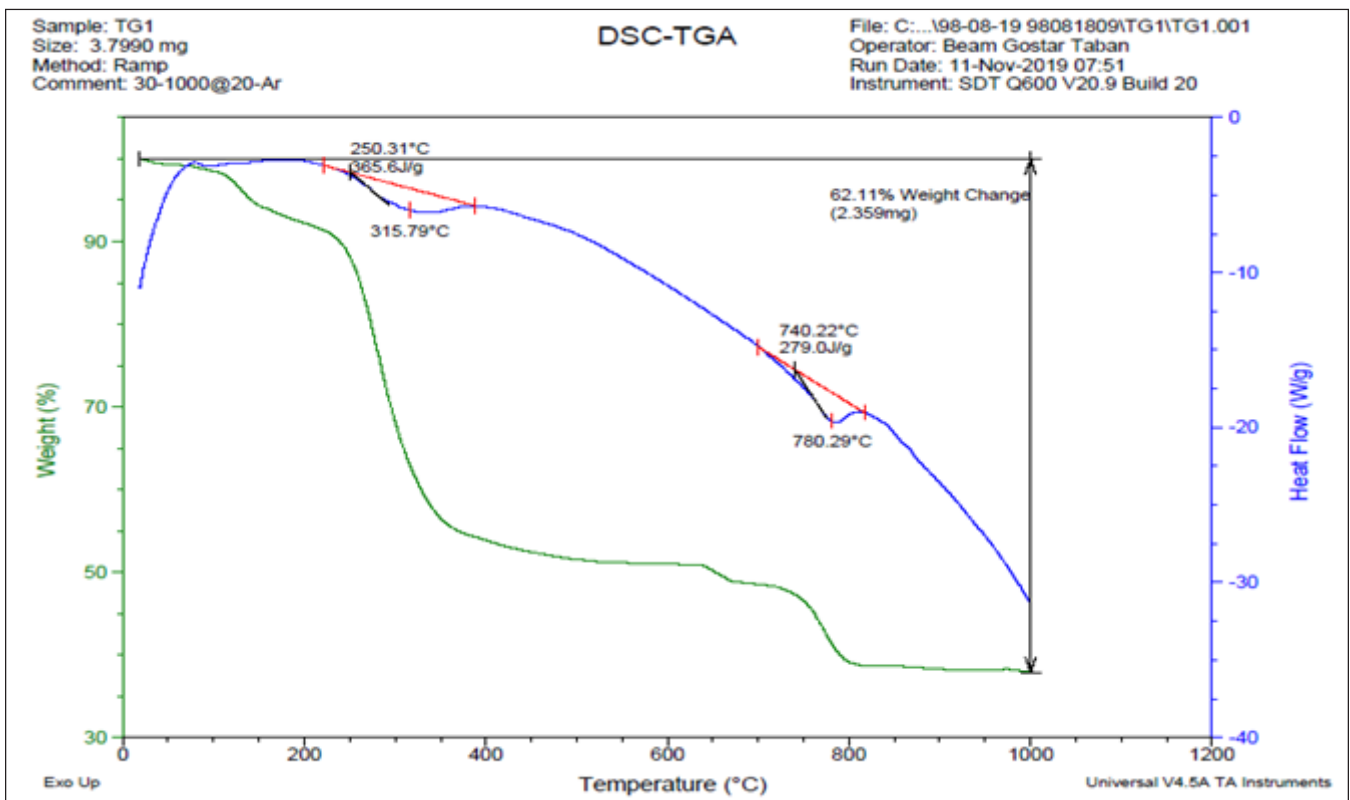


Fig. 6 : Thermal analysis of PA.

about (-12%), fourth stage (825–1000°C) with weight losses about (-4%). The DSC curve, in Fig. 8, for Chitosan shows a glass transition temperature  $T_g$  of 80°C,

endothermic peak at 297°C represent crystalline temperature  $T_c$ , a broad exothermic peak regard to the polymer melting ( $T_m$ ) at 345°C.

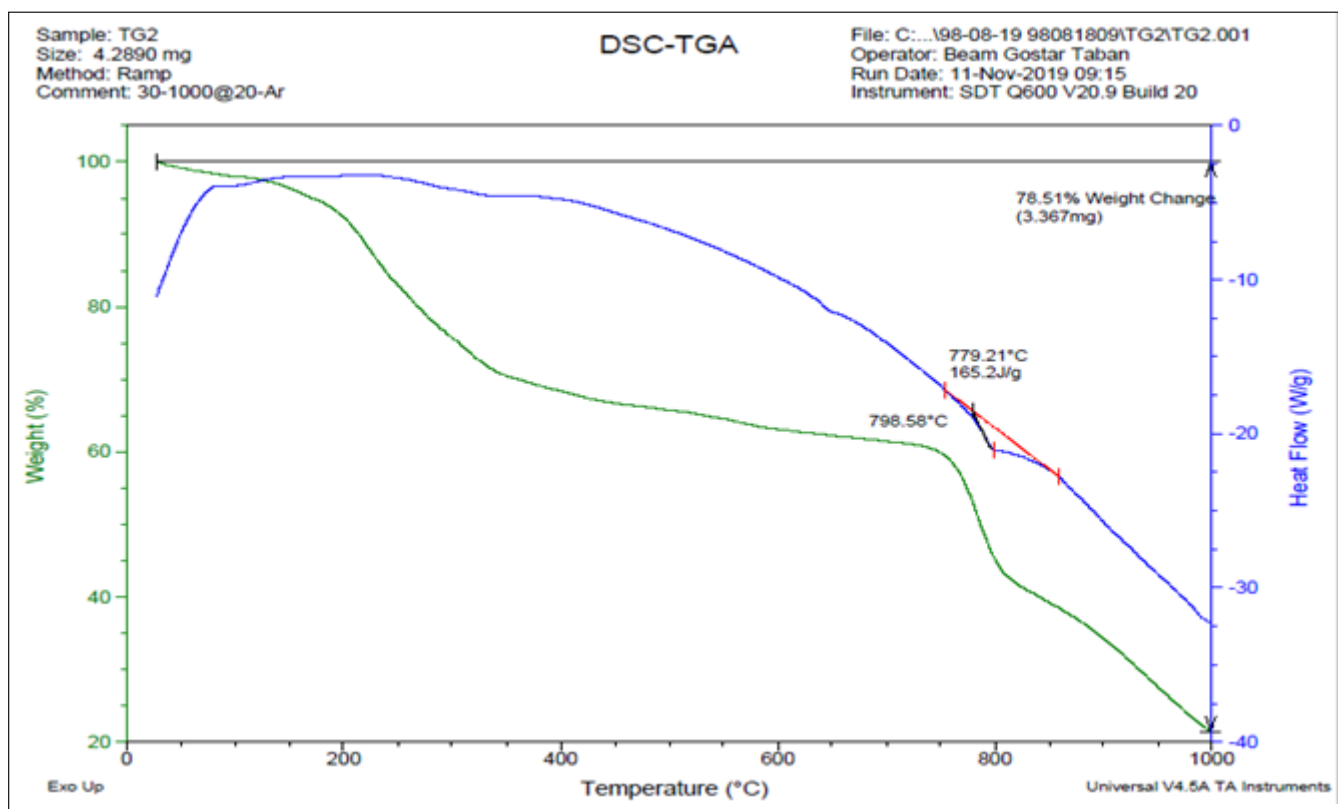


Fig. 7 : Thermal analysis of PA-Cu.

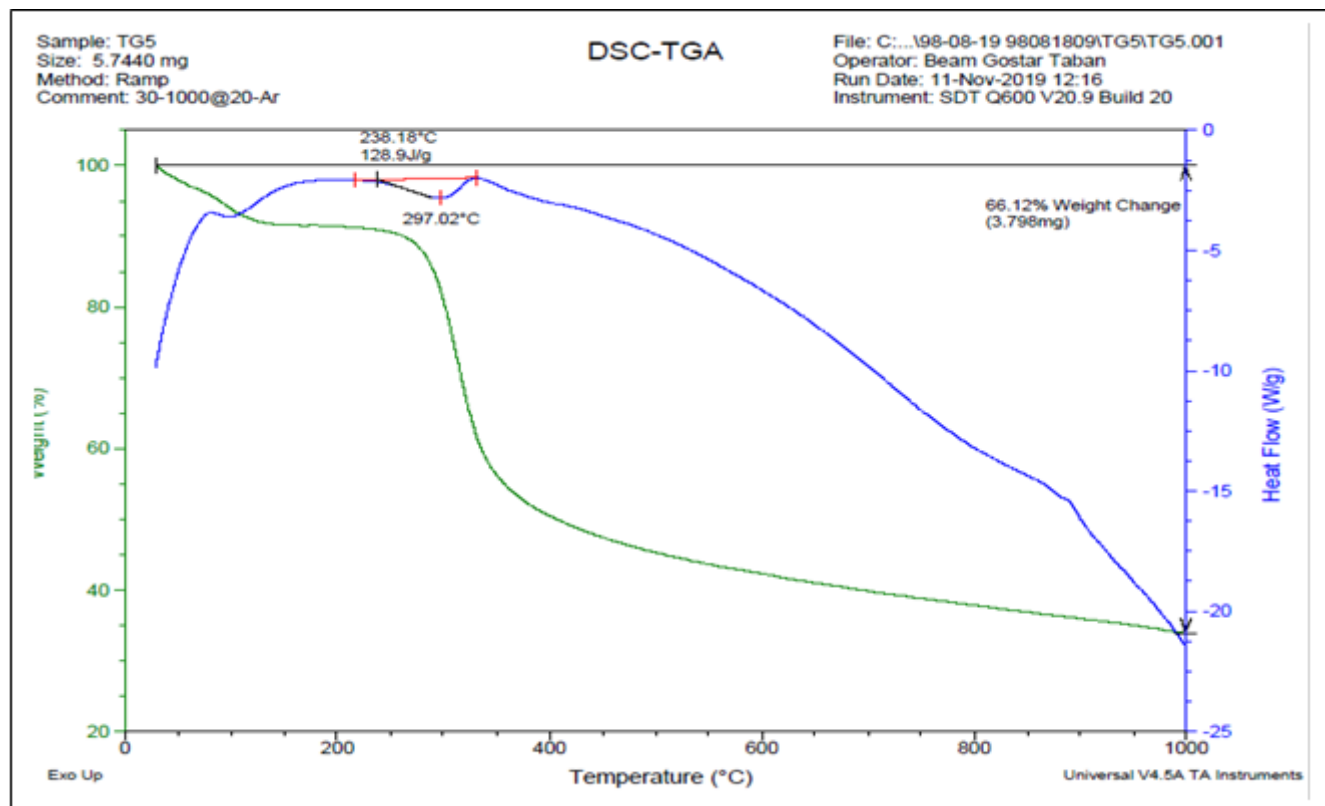


Fig. 8 : Thermal analysis of pure Chitosan.

The TGA curves figure (9) of B-PA showed five main stages of the weight loss, first (25–110°C) devoted to evaporation of the volatile compounds mainly water

and weight loss about (-3.644656%) and second stage (110–250°C) decomposition of side chain of pure PA and weight losses about (-8%). The third in from (250-390°C)

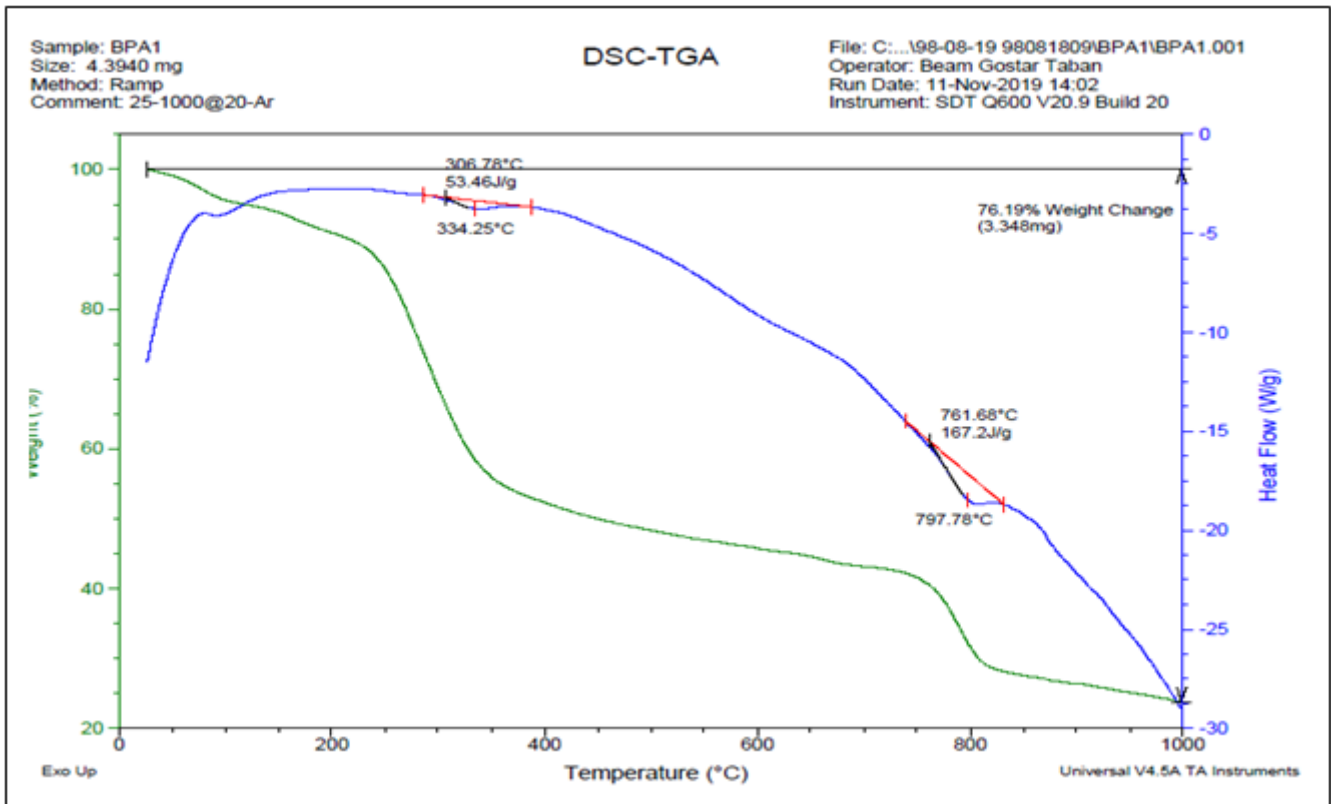


Fig. 9 : Thermal analysis of B-PA.

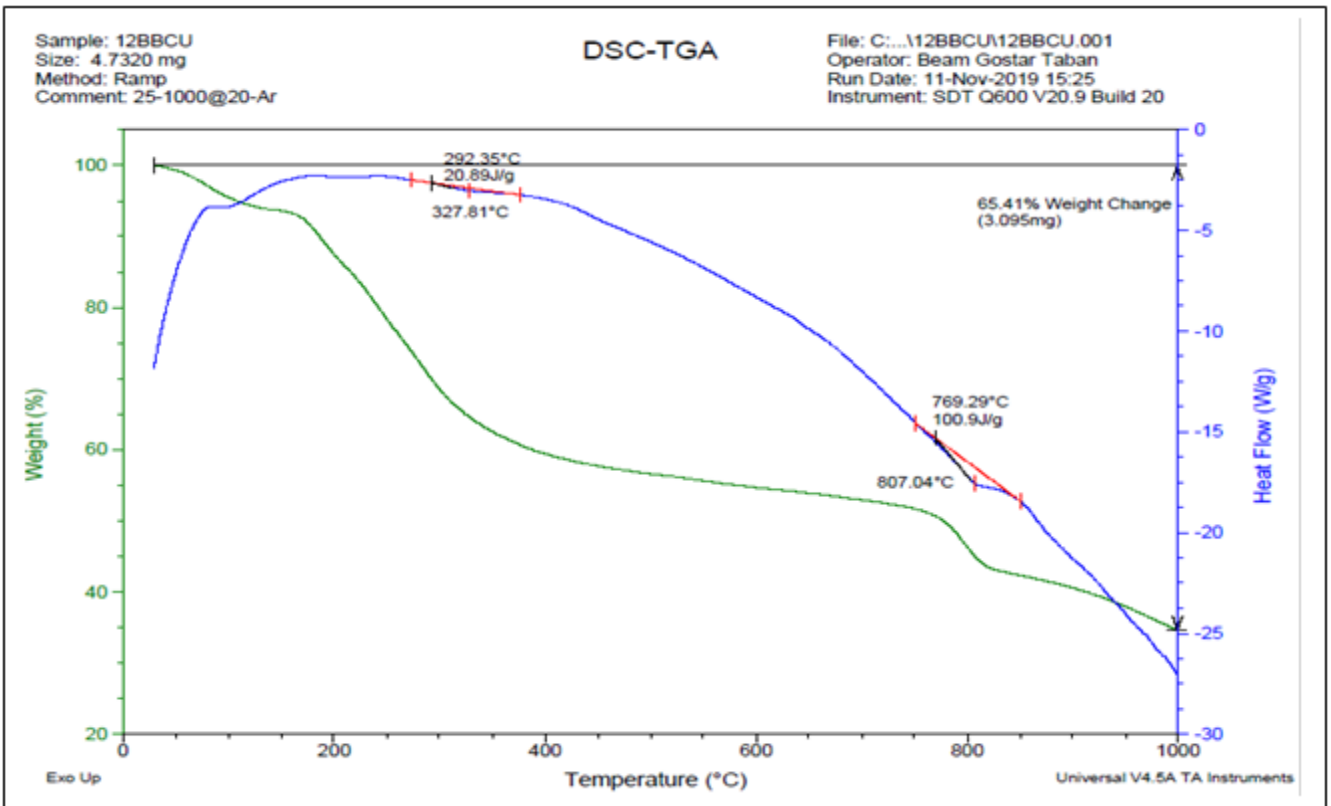


Fig. 10 : Thermal analysis of B-PA-Cu.

decomposition of the main chain of PA, and weight losses about (-36%). The forth one in from (390-820°C) decomposition of the main chain of PA and weight losses

about (-23.0027%), last stage is from (820-1000°C) with weight losses about (-5%). The DSC curve in Fig. 9 for B-PA film shows a glass transition temperature  $T_g$  of



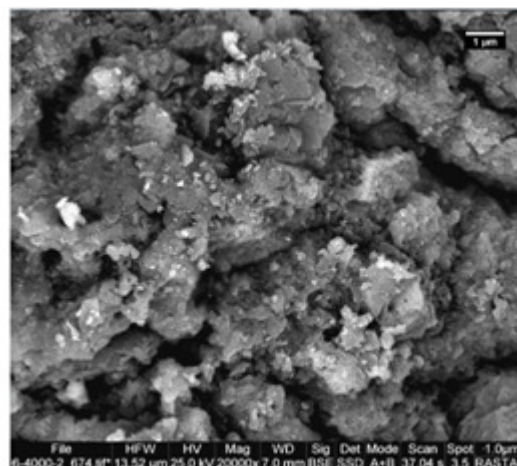
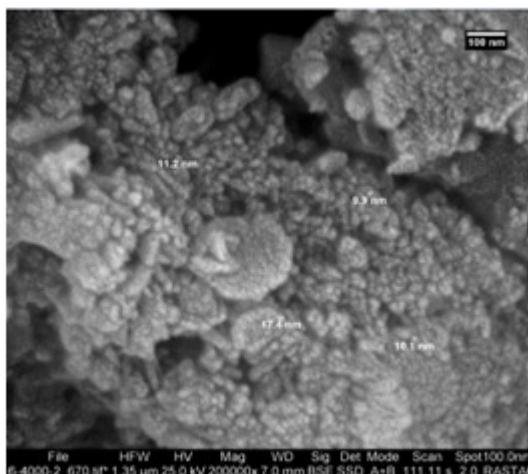


Fig. 11 : SEM images of Polyacetal (PA).

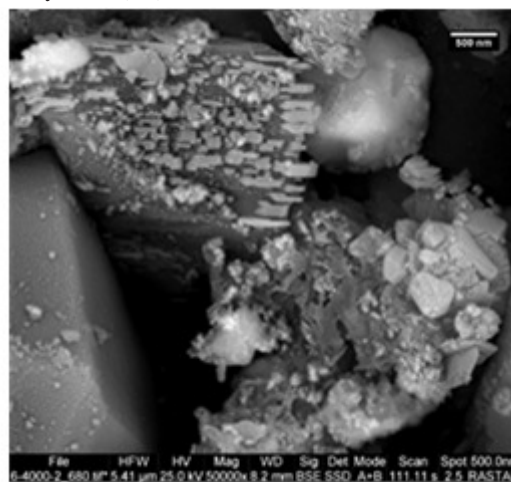
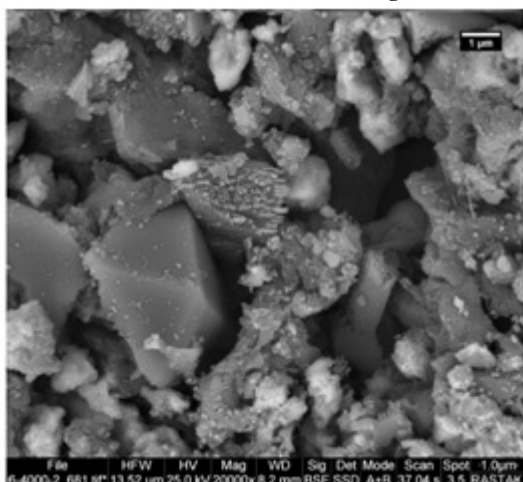


Fig. 12 : SEM images of PA-Cu.

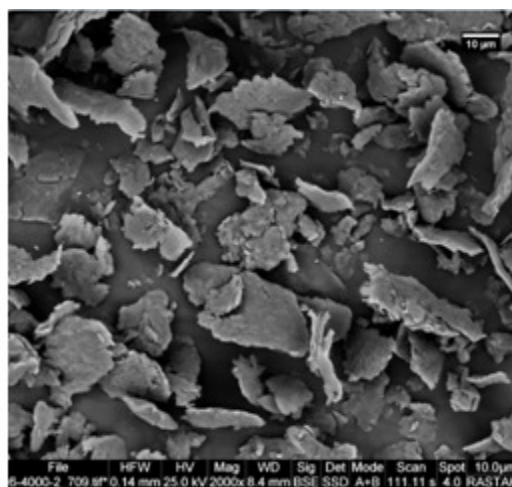
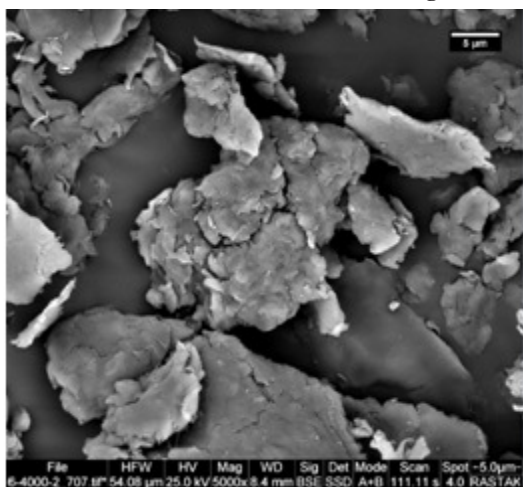


Fig. 13 : SEM images of Chitosan.

(95°C), endothermic peak at 306°C represent crystalline temperature  $T_c$ , a broad endothermic peak regard to the polymer melting ( $T_m$ ) at 390°C. The degradation of polymer ( $T_d$ ) begins in 797°C.

The TGA curves Fig. 10 of B-PA-Cu showed four main stages of the weight loss, first (40–140°C) devoted to evaporation of the volatile compounds mainly water

and weight loss about (-6%) and second stage (140 – 390°C) decomposition of side chain of pure PA and weight losses about (-34%). The third is from (390-805°C) decomposition of the main chain of PA, and weight losses about (-15%). The last one in from (805-1000°C) decomposition of the main chain of PA and weight losses about (-10%). The DSC curve in figure (10) for B-PA-

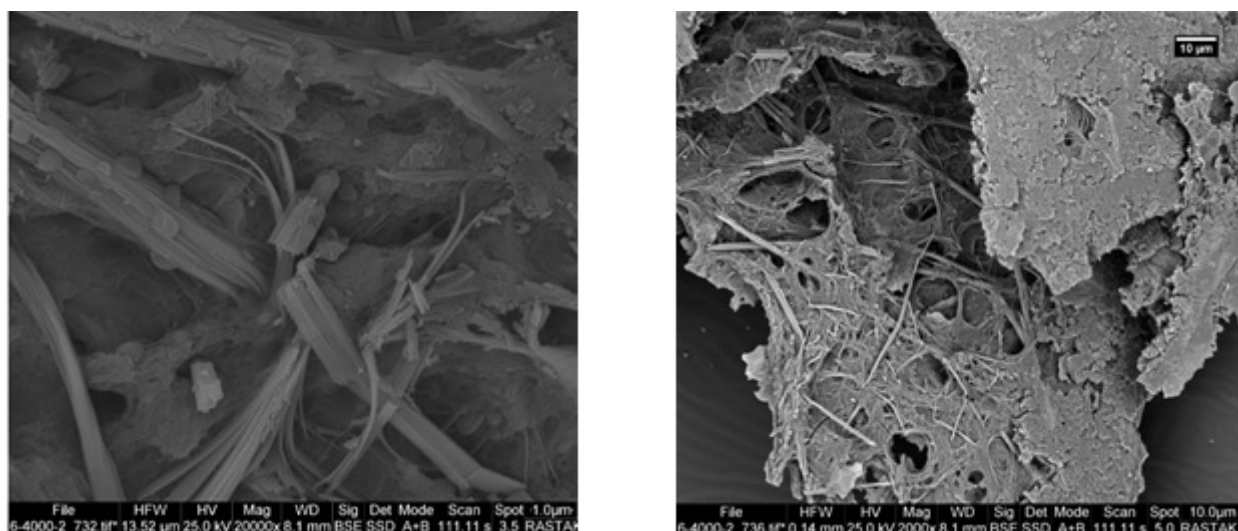


Fig. 14 : SEM images of Ch/PA blend.

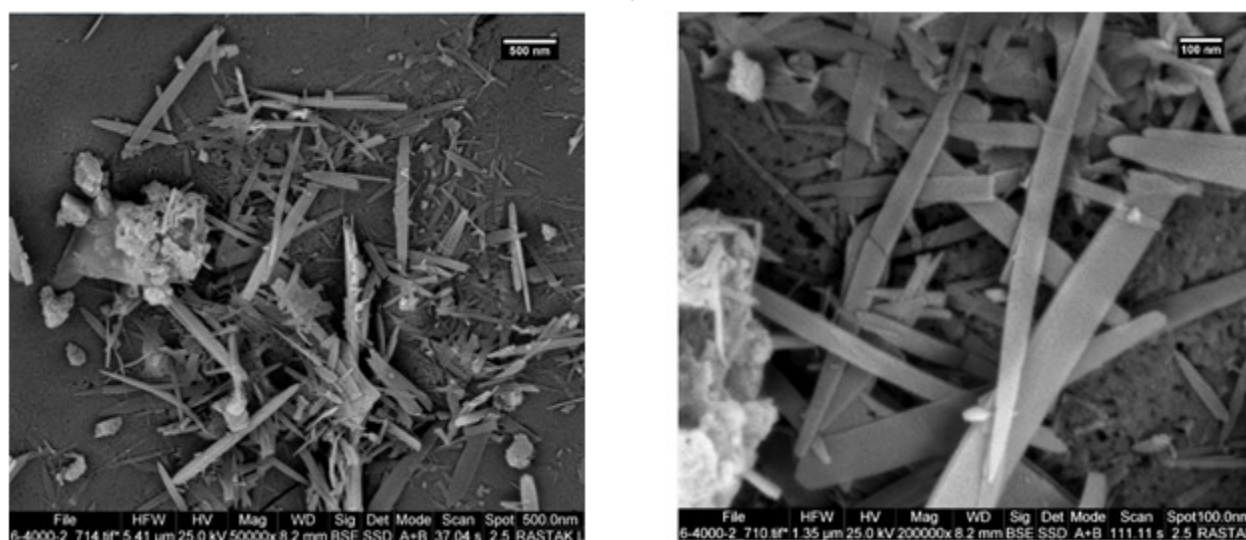


Fig. 15 : SEM images of Ch/PA-Cu blend.

Cu film shows a glass transition temperature  $T_g$  of 90 °C, a broad endothermic peak regard to the polymer melting ( $T_m$ ) at 390°C. The degradation of polymer ( $T_d$ ) begins in 769°C.

### Scanning Electron Microscope (SEM)

The surface morphology changes for the prepared PA, PA-Cu and (Ch/PA, Ch/PA-Cu) blends were studied using SEM technique. SEM micrograph for PVA loaded with particles of p-Methoxybenzaldehyde was depicted in Fig. 11. The surface appears porous with some included certain randomly distributed particles on the surface. Fig. 12 and illustrates the surface morphology of sample has evidence rough the surface synthesized for PA-Cu. The SEM image of pure chitosan exhibited a nonporous, smooth membranous phase consisting of dome shaped orifices, microfibrils and crystallite have been depicted in Fig. 13. The SEM image of Ch/PA blend exhibited, consisting of dome shaped orifices, mi-

crofibrils, crystallite and rods randomly linked with chitosan by hydrogen bonds was depicted in Fig. 14. The SEM images of Ch/PA-Cu blend exhibited, consisting of crystallite and rods randomly linked with chitosan by hydrogen bonds and copper particles are clearly visible been depicted in Fig. 15 (Kumar, 2012).

### Antimicrobial activity

Most of the newly synthesized derivatives were screened for their antibacterial activity against *Escherichia coli* (G-), *Pseudomonas aeruginosa* (G-), *Bacillus cereus* (G+) and *Staphylococcus aureus* (G+) *in vitro* by measuring the zone of inhibition in millimeter (Kachhadia, 2004). The results in Table 2 obtains the variation of diameter zone and calculated activity index with PA sample and CS/PA blend sample by different concentration. It observed that increasing concentration of PA result in increase of the diameter zone and activity index in all cases. According to Table 2 the activity

## Synthesis, characterization and antibacterial activity of PVA cyclic acetal (Cu) metal complex

**Table 2 :** The inhibition zone of some synthesized compounds.

Sample	<i>Pseudomonas aeruginosa</i>	<i>Escherichia coli</i>	<i>Bacillus cereus</i>	<i>Staphylococcus aureus</i>
PA 1 (PA)	–	–	–	–
PA 14 (B1)	17	–	–	16
PA 11 (B2)	21	14	12	15
PA 10 (B3)	22	17	16	16
Cu 2 (PA-Cu)	–	–	25	28
Cu12 (B1-PACu)	24	18	30	26
Cu 7 (B2-PACu)	23	16	28	22
Cu 9 (B3-PACu)	26	21	34	30

increased from PA to B1 with max activity in B3. Such effect can be attributed to the presence of OH group in the PA which may react with free ions released during the interaction between NH<sub>2</sub> group of Chitosan and other constituent. Also according to Table 2 the activity increased from PA-Cu and PA-Cu to B1-PA-Cu with max activity in B3-PA-Cu. Such effect can be attributed to the presence of OH group in the PA-Cu which may react with free ions released during the interaction between NH<sub>2</sub> group of Chitosan and other constituent in addition to the presence of the metal ion (Cu) the antibacterial activities regarding metals complex is because of the impact regarding metal ions on normal cell process. Potential action mode is through the increase in the toxicity could be taken into account.

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