

## Wettability, Thermal Stability, and Antibacterial Properties of Polycaprolactone /ZnO Nanocomposites in Packaging

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### Abstract

Polycaprolactone is a one of the natural biodegradable polymer mainly used in bioplastics production for packaging. It is usually composed of non-toxic biodegradable compounds. The aim of the work was to examine the role of zinc oxide (ZnO) nanopowder on wettability, thermal stability and anti-bacterial properties against *E.Coli* (gram negative) and against *Staphylococcus aureus bacteria* (gram positive). Pure PCL and PCL-based bio- nanocomposites doped with various ratios (0.5%, 1%, 3% and 5 wt%) of ZnO nanoparticles were prepared by the solving casting method. The results show that wettability properties of PCL were increasingly hydrophobic from 55.77° to 60°.14 because of the added ZnO nanocomposites. The thermal stability for PCL nanocomposites between 300 and 400 °C makes them perfect for the application of food packaging applications. Also, the anti-bacterial screening inhibition against Gram-positive and Gram-negative microorganisms was compared with PCL.

### Key words

Polycaprolactone, ZnO, wettability, thermal, contact angle.

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التبلل والاستقرارية الحرارية والخواص ضد البكتيريا لمترابكات البولبي كابرولاكتون واوكسيد

الزنك في التغليف

علي ناجي عبيد، نادية عباس علي

قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

### الخلاصة

البولبي كابرولاكتون هو أحد البوليمرات الطبيعية القابلة للتحلل والتي تستخدم بشكل رئيسي في إنتاج البلاستيك الحيوي للتعبئة، وتتكون عادة من مركبات غير سامة وقابلة للتحلل. كان الهدف من البحث هو فحص دور المسحوق النانوي أكسيد الزنك (ZnO) في الخواص قابليه التبلل والاستقرارية الحرارية والمضاد للبكتيريا. تم تحضير المركبات الحيوية النانوية بطريقه التطعيم مع نسب مختلفة من جزيئات ZnO النانوية من 0.5%، 1%، 3%، 5% بالوزن بطريقه الصب. أظهرت النتائج أن خصائص قابلية التبلل للبوليمر بولي كابرولاكتون تزداد فيها الخواص الكارهة للماء وتتراوح من 55.77° إلى 60.14° بسبب إضافة مركبات ZnO النانوية، الاستقرار الحراري تراوح بين 300 و 400 درجة مئوية مما يجعلها مثالية في تطبيق تغليف المواد الغذائية. كذلك بينت تثبيط في الفحص المضاد للبكتيريا ضد الكائنات الدقيقة موجبة الجرام وسالبة الجرام، والتي كانت واضحة بالمقارنه مع البوليمر الأصلي PCL.

### Introduction

Due to their properties like air porousness, low temperature marketability, accessibility and low cost, biologically degradable polymers can be used to decrease waste volumes. They restrict emissions of carbon dioxide during production, and

reduce them after removal to fundamental problems [1]. The present pattern in nourishment bundling is the utilization of biopolymers such (PCL) and improving their properties to be suitable in nourishment bundling [2]. PCL is a polymer thermoplastic material and has as of late much consideration on account of its adaptability and biodegradability .It is being applied in nourishment bundling, tissue designing, dressing for wound, and medication conveyance. In any case, a few insufficiency of PCL, for example, significant expense, low dissolving temperature and low glass transition ( $T_g$ ) that utilized as a compatibilizer, and low elasticity of 10-23 MPa, yet a great stretching to break (over 700%) that confines across the board mechanical of PCL [3, 4].

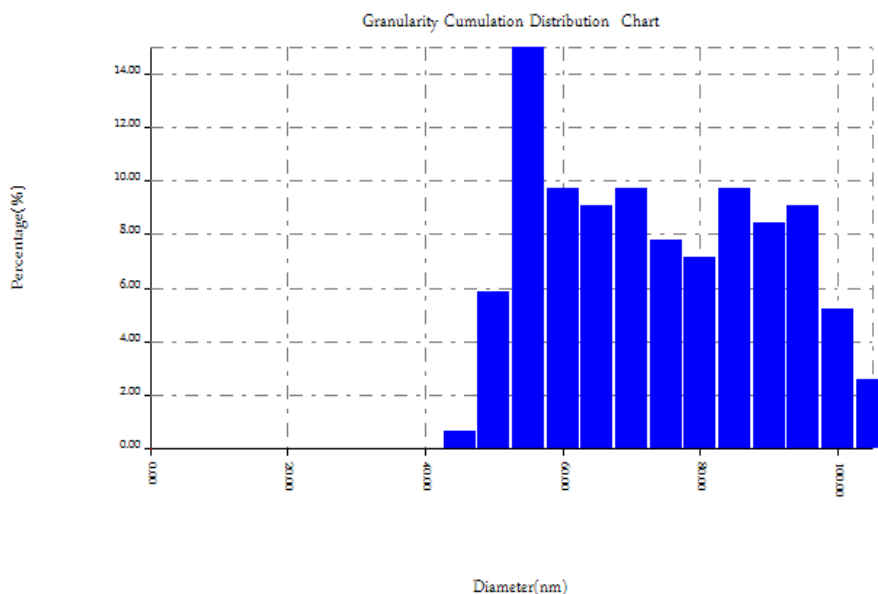
Polycaprolactone is prepared by ring-opening polymerization of  $\epsilon$ -caprolactone in the nearness of tin octoate impetus [5]. Its glass change temperature is low, around -60 °C, and its dissolving point is 60-65°C. PCL is a semi-inflexible material; it could be debased by a hydrolytic component under physiological conditions. Most of the biodegradable polyesters show more slow degeneration rates than common biopolymers [6].

Nanoparticles assume advantageous job in nourishment protection and permit bundling materials to cooperate with nourishment and earth because of their smaller size. Nanoparticles have significantly larger surfacearea than microscale particles [7]. Zinc oxide is known as a bio-safe substance used by the Food and Drug Administration (FDA) in restorative articles. Also, it is very antibacterial, increasing further by a decrease in molecule size [8]. Subsequently, ZnO is an added substance of significant importance in the plastic industry for the anti-bacterial and anti-septicsing, UV-shielding, deodorizing properties. Nourishment bundling polymer materials are dependent on nanotechnology that can give answers for increment the polymers exhibitions applications [9].

## Experimental work

### 1. Materials

PCL was purchased from (Sweden). ZnO supplied by Sigma-Aldrich was with particles size (50 nm) is shown in Fig.1 Measured by (SPM) of nano Zinc Oxide.



**Fig.1: Granularity normal distribution chart for nano Zinc Oxide particl.**

## 2. Method of preparation PCL and PCL/ZnO nano composites

The ZnO have grain size distribution within 50 nm (Fig.1). The preparation of the PCL was from 3 g of pure PCL dissolved in 30 ml of Chloroform ( $\text{CHCl}_3$ ) followed by stirring with a magnetic stirrer at  $60^\circ\text{C}$  for 1 h to obtain a grade solution of PCL. Similarly, PCL/ZnO was prepared from ZnO dissolved in 10 ml of  $\text{CHCl}_3$  and agitated ultrasonically at  $30^\circ\text{C}$  for 10 min. Thereafter mixed with PCL solution and stirred vigorously for 1 h at  $60^\circ\text{C}$ . The final mixture was then thoroughly sonicated until a stable prepared with 0.5, 1, 3 and 5wt% ZnO. They were then cast on the Petri dish and kept at  $60^\circ\text{C}$  in an oven for 24 h to ensure the solvent was completely removed. The images of the prepared PCL/ZnO sheet samples are presented in Fig. 2.

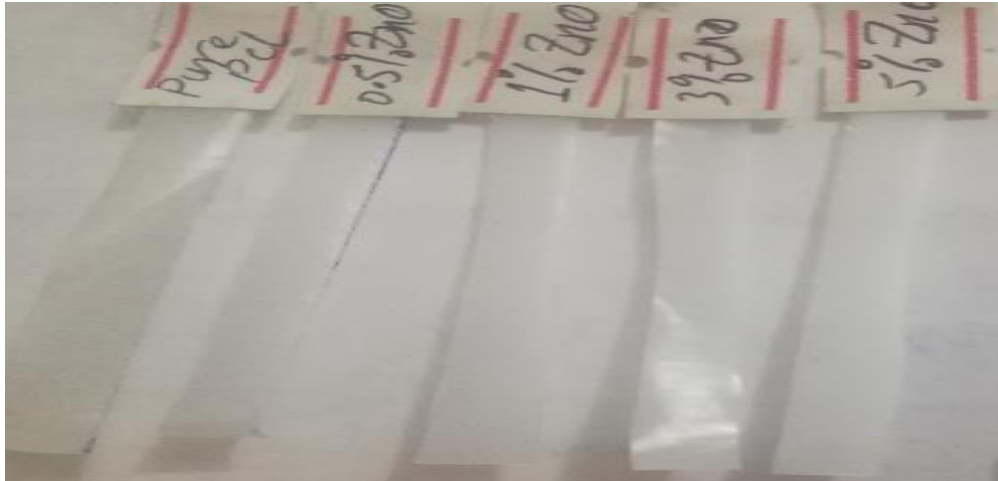


Fig.2: Samples PCL, PCL/ZnO nanocomposites samples test.

## 3. Characterizations

**Fourier transform infrared spectroscopy:** Infrared IR region was obtained in spectrometer that takes a range of  $4000\text{-}400\text{ cm}^{-1}$ .

**Wettability ad contact angles:** measured by the drop water at room temperature on films and measured the right and the left of contact angles on a sample surface at an interval of 60 sec according to French et al. [10].

**Thermal gravimetric analysis (TGA):** This was performed with a Shimadzu TGA 60H unit. Samples of PCL/ZnO, approximately 10-19 mg weight of (1%wt and 5%wt) the lower and upper ratios) were heated in an alumina pan from ambient temperature ( $\sim 23^\circ\text{C}$ ) to  $500^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$ , under Argon flow of 50 ml/min.

**Antibacterial activity:** The antibacterial activity study was done by the agar diffusion technique. Each dish contained 30 ml of Plate Count Agar which were inoculated with 0.1 ml of solution of bacterial (*E. coli* and *S. aureus*) for (1%wt and 5%wt). The inhibition zone was measured in mm after 24 hours at  $37^\circ\text{C}$ .

## Results and discussion

FTIR spectrum of neat PCL membrane is shown in Fig.3. It displays an intensive peak at  $2864$  and  $2930\text{ cm}^{-1}$  which is related to the C–H bond of stretching vibration of hydrocarbon of PCL, a peak at  $3444\text{ cm}^{-1}$  due to the OH stretching vibrations and two peaks at  $1644$  and  $1735\text{ cm}^{-1}$  which are ascribed to the stretching vibration of

carbonyl groups (C=O) of PCL. The characteristic absorption bands in the range of  $1242\text{ cm}^{-1}$  are attributed to the asymmetric COC stretching, bond at  $1174\text{ cm}^{-1}$  in symmetric COC stretching, bond at  $1137\text{ cm}^{-1}$  for C–O and C–C stretching in amorphous. These results agree with the results of Gui et al. [11].

Fig.3 also shows the assimilation tops at around  $3387$  and  $1629\text{ cm}^{-1}$  which are because of the hydroxyl gatherings of chemisorbed as well as physisorbed  $\text{H}_2\text{O}$  atoms on the molecule surface. The peak at  $1103\text{ cm}^{-1}$  is ascribed to CO bond extending of the C–O–H gathering, peaks at PCL related extending modes are spoken to by the peaks at  $2945\text{ cm}^{-1}$  (unbalanced  $\text{CH}_2$  extending),  $2867\text{ cm}^{-1}$  (symmetric  $\text{CH}_2$  extending),  $1722\text{ cm}^{-1}$  (C=O extending),  $1294\text{ cm}^{-1}$  (C–O and C–C extending), and ( $1238\text{ cm}^{-1}$ ,  $1164\text{ cm}^{-1}$ ) comparing to C–O–C symmetric extending vibrations, top at  $541\text{ cm}^{-1}$  can be credited to the twisting vibration at  $478\text{ cm}^{-1}$  and  $490\text{ cm}^{-1}$  can be ascribed to the extending vibration of ZnO in PCL. The band at  $1404\text{ cm}^{-1}$  is because of that bound of C–O extending recurrence and  $1783\text{ cm}^{-1}$  are because of the nearness of C=O extending vibration. The groups at  $3582\text{ cm}^{-1}$  are related to O–H method of vibration, peak around  $3514\text{ cm}^{-1}$  is doled out to the extending vibration and bowing vibration of surface hydroxyl bunches on ZnO. These agree with the results of Xiong et al. [12].

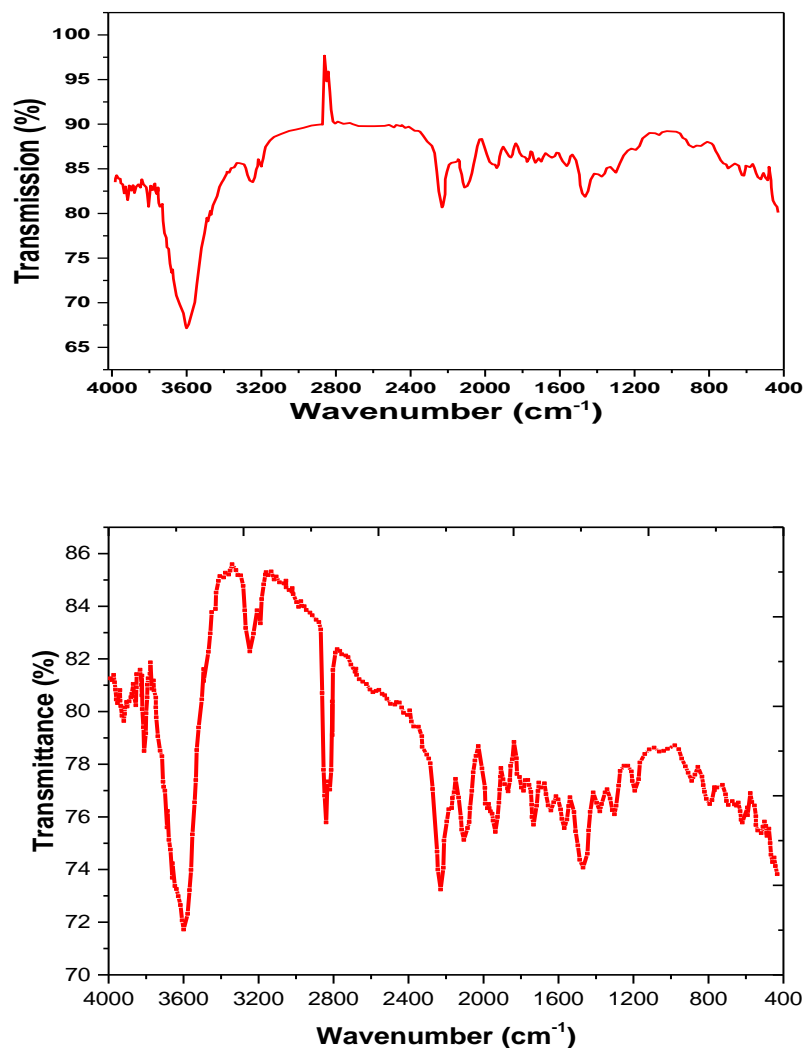
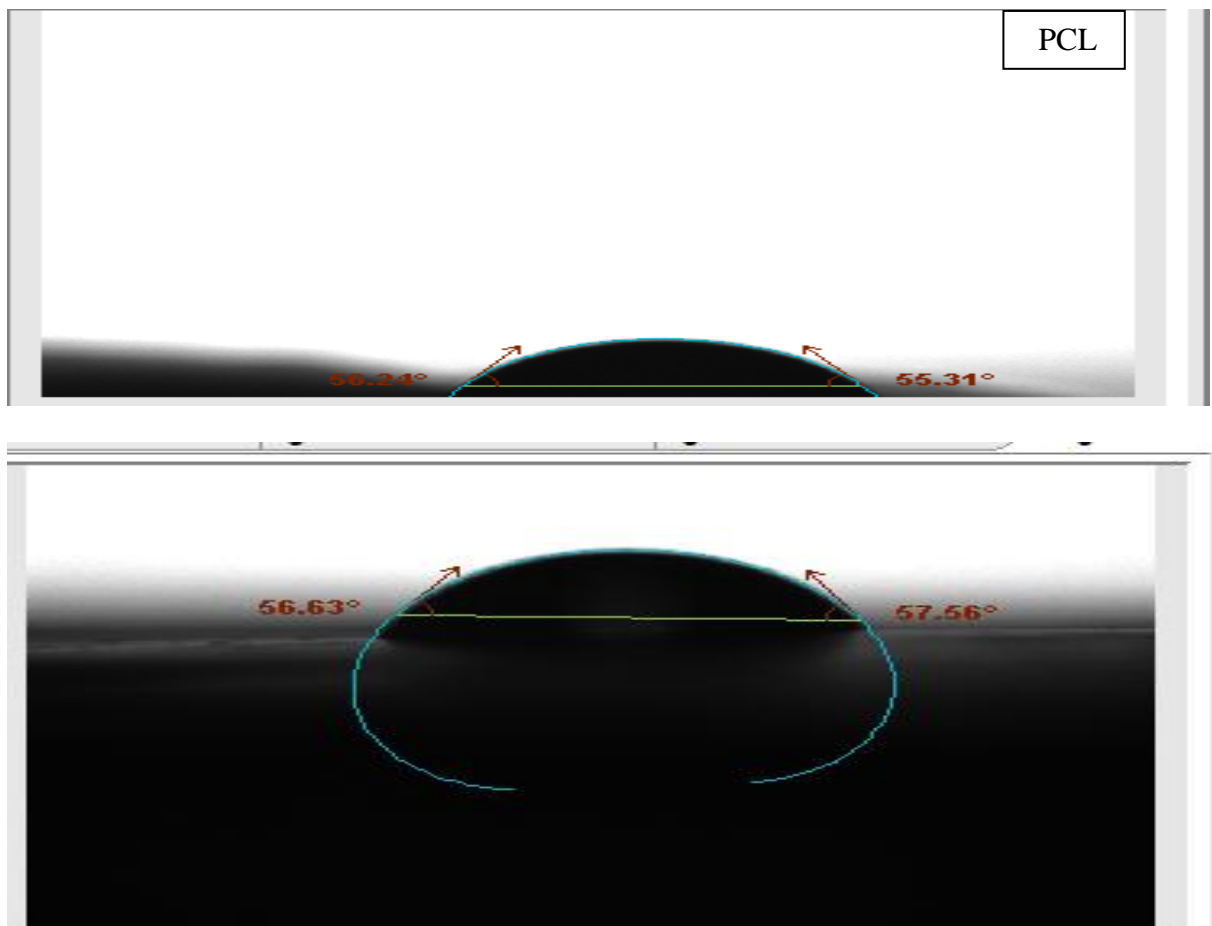


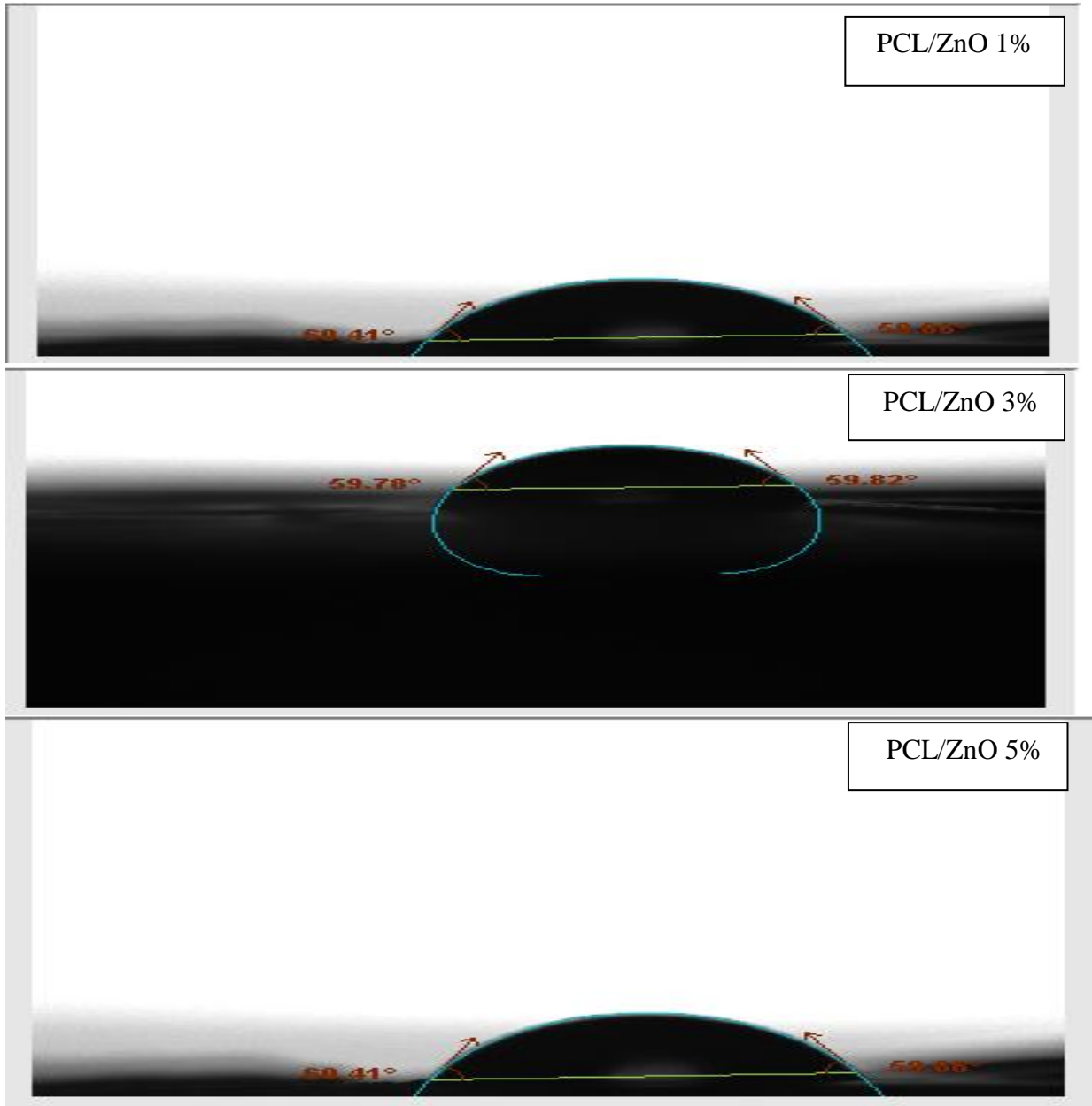
Fig.3: FTIR pattern for pure PCL, and PCL/ZnO nanocomposites at 1%wt.

### Wettability and contact angle

The surface hydrophobicity can be evaluated by estimating the contact point through the spread of a water bead on surface. After drop water on the surface of samples PCL and PCL/ZnO nanocomposite films with thickness is (100  $\mu\text{m}$ ) that appear in Fig.4 and Table 1 shows the contact of PCL is  $55.31^\circ$  that mean of hydrophobic surface in nature. The contact angle for PCL/ZnO nanocomposites which is range from  $55.77^\circ$  (average left and right) to  $60.14^\circ$  was more hydrophobic surface, that mean the ZnO-joined PCL layers would exhibit on poor wettability, that it is on the basis that the water adsorption surface on ZnO can be explained by water molecule  $\text{H}_2\text{O}$  is not adsorbed on ZnO at all temperatures and contain the roots of OH and  $\text{H}^+$ . The adsorption of  $\text{OH}^-$  radical happens on a  $\text{Zn}^{2+}$  site on ZnO surface. The unpaired electron on  $\text{OH}^-$  radical consolidates with free electron related with  $\text{Zn}^{2+}$  site, which brings about a solid nonpolar bond that prompted high contact edge of the surface, that effect on dry packaging materials (sugar, rice, bread rolls) and avoid development of microorganisms this prevents the growth of bacteria and keeps them away from spoilage that concur with Rešček et al. [13].



*Fig.4: Contact angle test of pure PCL and PCL /ZnO nanocompositesat different concentration.*



**Fig.4: Contact angle test of pure PCL and PCL /ZnO nanocompositesat different concentration.**

**Table 1: Contact angle of pure PCL and PCL /ZnO composites (average value of right and left).**

Samples	Contact angle
PCL	55.77
PCL/ZnO 0.5%	57.09
PCL/ZnO 1%	59.7
PCL/ZnO 3%	59.8
PCL/ZnO 5%	60.14

### Thermal analysis

Figs.5, 6 and Table 2 show the TGA and DSC analysis information in Argon air for the samples PCL and PCL/ZnO nanocomposites. For sample it was PCL found that (T5% temperature for 5% weight reduction) happened at 374.9 °C and the last debasement temperature (Tf) was at 496.9 °C. DSC analysis showed that the melting temperature of pure PCL polymer is 65°C. The melting temperature of PCL decreased for 1%wt and 5% of ZnO to (64 °C, 62 °C) respectively.

At the add ZnO (1%wt and 5%wt) to PCL the last temperature (Tf) became 493.6°C and 379.3°C for respectively. The Melting temperature decreased of the PCL/ZnO composite due to the decreased crystallization of composites that agree with Paula et al. [14].

### Anti-bacterial activity

*S. aureus* and *E. coli* bacteria are the most common microorganisms associated with food poisoning. Fig.7 shows the anti-bacterial effect of Zinc oxide against (*S.aureus*) is more than that of (*E. coli*) bacteria. This can be attributed to the morphological variation in the bacterial cells. The porous and charged peptidoglycan surface of (*E. coli*) bacteria make them more vulnerable to ZnO nanoparticles [15].

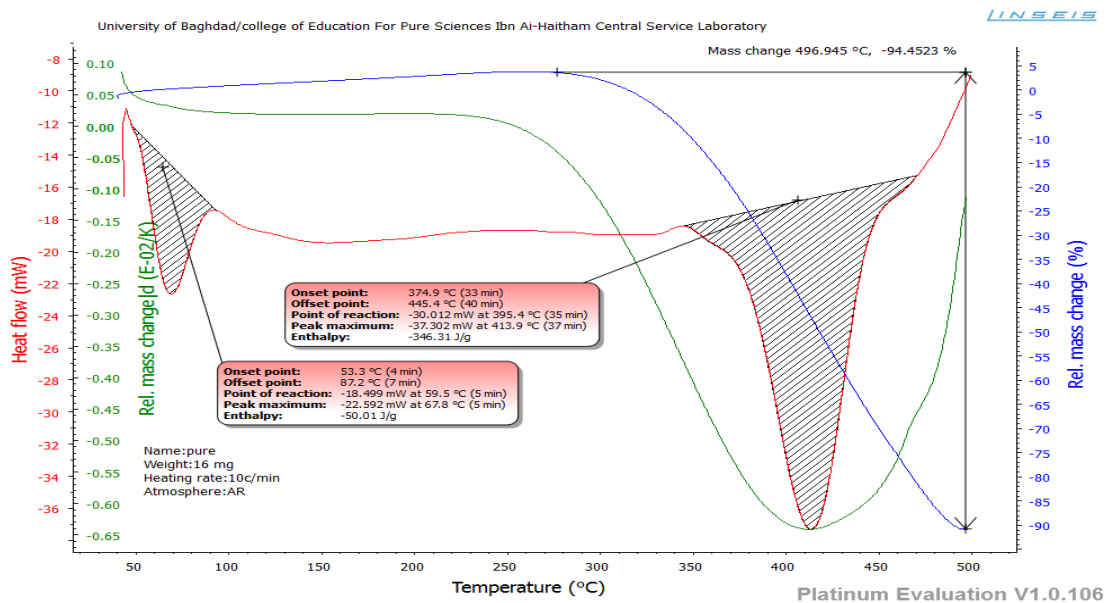


Fig.5: Thermal Gravimetric Analysis of pure PCL.

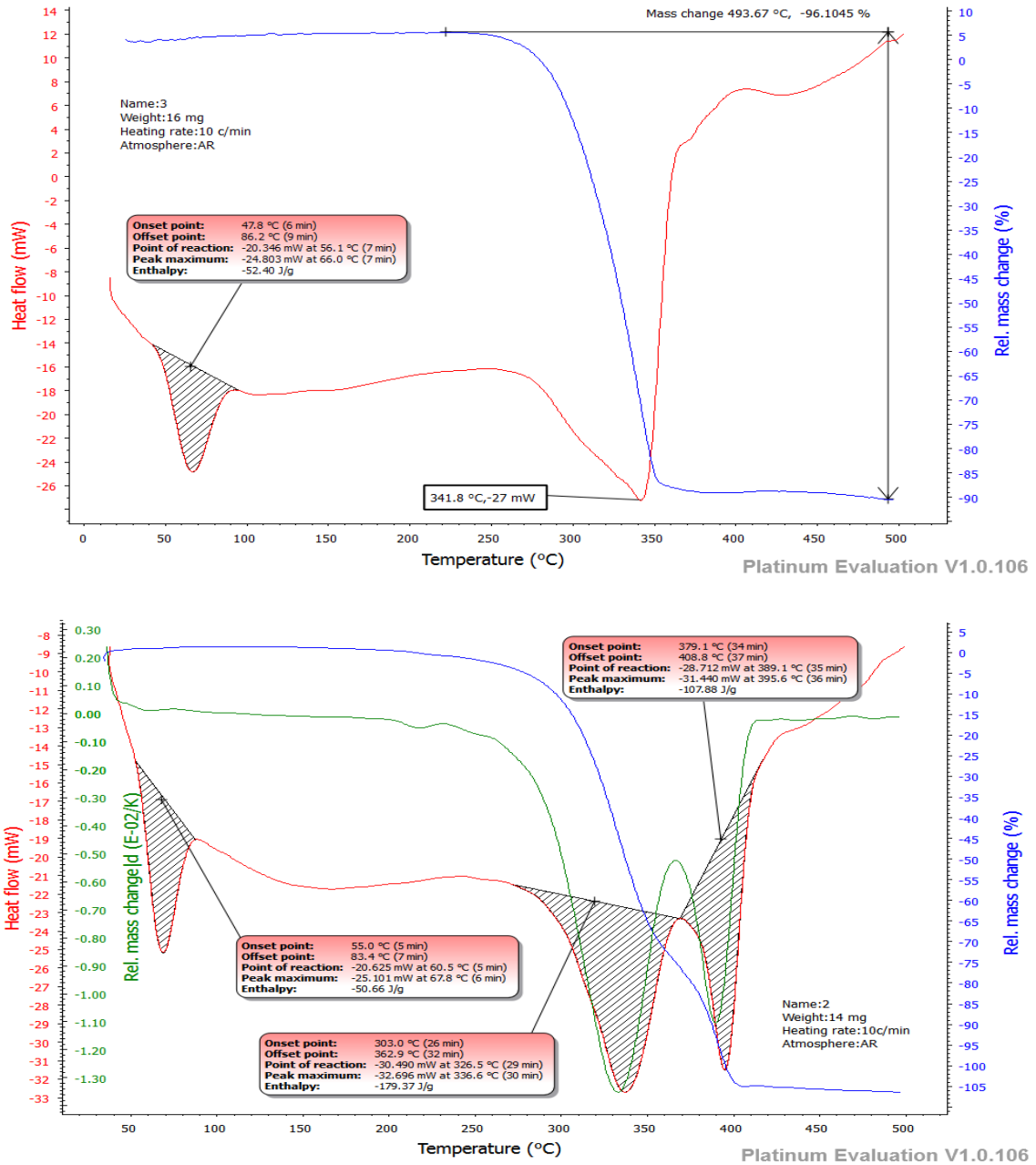


Fig.6: Thermal Gravimetric Analysis of PCL /ZnO nanocomposites at (1%wt and 5% wt).

Table 2: Thermal Gravimetric Analysis of pure PCL and PC /ZnO composites.

Samples	T <sub>5</sub> % (°C)	T <sub>95</sub> % (°C)	T <sub>m</sub> (°C)
PCL	374	496.94	65
PCL/ZnO 1% wt	341.9	493.94	64
PCL/ZnO 5% wt	303.1	379.1	62








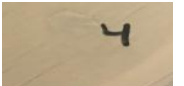
E.coli (Gram -)	S. aureus (Gram +)
 pure PCL	 pure PCL
 5% ZnO	 5% ZnO
 1% ZnO	 1% ZnO

Fig.7: Ant-bacterial activity for pure PCL and PCL/ZnO nanocomposites at 1% wt and 5%wt.

### Conclusions

It is concluded from the present study that FTIR spectroscopy showed all the carboxylate and hydroxyl groups of PCL/ZnO nanocomposites. The improvement of wettability and contact angle point between ( $55.77^{\circ}$ -  $60.14^{\circ}$ ) was ascribed to the expanded hydrophobic surface of composites tests. Thermal Analysis properties showed that PCL and PCL/ZnO nanocomposites between ( $200^{\circ}\text{C}$ -  $500^{\circ}\text{C}$ ) and the melting temperature decreased from  $65^{\circ}\text{C}$  to  $62^{\circ}\text{C}$ . Also, the anti-bacterial action of ZnO-filled biodegradable composites is remarkable against *S. aureus* and *E. coli*.

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