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The Impact of UnCalcined & Calcined Eggshell Powder as BioFiller for Polylacticacid

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ABSTRACT

The present study includes preparation of eggshell powder from the waste eggshell by milling followed by calcination at 500°C under ambient atmosphere. Composites of uncalcined and calcined eggshell / PLA with contents of 10, 20 and 30 wt% prepared by casting method. The effect of uncalcined and calcined egg shell on structural and tensile properties of polylactic acid (PLA) were studied. The prepared composites were antibacterial tested against Escherichia coli and Staphylococcus aureus (S. aureus) bacteria. Results showed the crystallinity of the synthesized films induced by egg shell. Ultimate tensile strength increased gradually with increment of the filler content and the highest ultimate strength at 30 wt. % this may be attributed to good compatibility between the egg shell and the PLA. The results of bactericidal against Escherichia coli bacteria were lower for PLA and its composites as compared with staph aureus.

1. Introduction

Even though plastics considered an ideal material for many applications because of their durability properties, there is problems of waste disposal because they are not readily biodegradable and may accumulate in the environment. These facts encourage have interest in biodegradable polymers and particular biodegradable biopolymers [1-3].

Biodegradable type of polymers resulted from renewable resources, such as polylactic acid (PLA), polycaprolactone (PCL), Polyglycolic acid (PGA), and polyhydroxy butyrate (PHB), which considered remarkable for their maintained biodegradability of the final products [4]. They included a wide types of biomedical purposes, packaging, production of fiber, and recently, as composite materials for specialized applications [5].

Polylactide or Polylactic acid, a thermoplastic aliphatic polyester usually obtained from L-lactic acid mer by condensation of or lactide ring-opening polymerization [6]. PLA considered a hydrophobic polymer as a result to the presence of side groups (–CH3) [7]. PLA is endowed with many excellent properties, such as good resistance to solubility, excellent biocompatibility, and biodegradability. However, PLA has its limitations in terms of poor thermal stability, slow crystallization rate, and low crystallinity, which greatly restrict its applications [8, 9]. As a consequence, PLA was designed in different ways to improve materials with appropriate properties, such as by impact modification,

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plasticization, and the reinforcement by different fillers [9–13].

Chicken eggshell powder (ESP) is a poultry industrial by-product considered a significant renewable polymer filler that attracts attention due to its low price and availability. The eggshell of Chickens has been classified enviromantly as one of the excessively bad problems over the world, particularly in those cities where the egg output is well developed [14].

Eggshell is considered a natural bio-ceramic composite with an individual chemical composition mainly included of calcium carbonate (CaCO3) (94%), as well as calcium phosphate Ca3(PO4)2 (1%), magnesium carbonate (MgCO3) (1%), organic substances (4%) and trace ions such as Na+, Mg+2 and Sr+2 [15,16]. Even though there was a few attempts to use the substances of the eggshell for various applications, since they considered a potential source for minimizing the environmental impact and gain higher profits [17, 18]

Many researchers have studied the impact of different types of materials on the properties of polylactic acid, Nidhi Pal et.al, studied the effect of both cellulose and reduced graphene oxide in PLA, results showed that it has potential to be used in food packaging applications because of their antibacterial activity of against gam positive and negative pathogens [19]. Gai-Hong Wu et.al, studied the effect of multi-walled carbon nanotube on PLA using the casting/solvent evaporation process [20]. On the other hand, Zhidan Lin prepared composite by adding eggshell to polypropylene through the melt blending method to have high mechanical properties [21], while A. G. Supri made another composite by incorporating the eggshell powder to low-density polyethylene using the same method [22] both of them have a problem with interfacial bonding between the filler and the matrix so that Zhidan Lin used pimelic acid and A. G. Supri used Grafted Maleic Anhydride (PE-g-MAH) as a compatibilizer. S. Murugan et.al studied the effects of Eggshell particle size on poly (vinyl chloride) polymer, composites prepared by Rheomix internal mixer, and results showed good interfacial bonding as the filler particle size ≥0.2 μm [23]. B. Ashok et.al incorporated Eggshell into PLA by casting method and studied the mechanical and thermal properties of the composite. Results indicated improvement of both the tensile strength and modulus of elasticity nearly 4 wt.% then decreased, while elongation recorded a reverse result. [24]. Based upon above the researches foucsed on the effect different types of fillers on PLA also, incorporation of small ratio (less than 4%) of eggshell powder on the mechanical properties only.

In the present work, we used PLA as a matrix and loaded with 10, 20, and 30wt.% eggshell powder (ESP) with and without sintering and notice the effect of sintering process and eggshell powder ratios on the properties of the composite films. To our knowledge, there is no direct references that have been suggested to study the antibacterial properties to be used as scaffold for injuries replacement.

2. Exprimental Work

Polylactic acid PLA has molecular weight 60,000 gmol was supplied by Merc Company. firstly, the waste eggshells cleaned and washed by deionized water and left in the open air for 36 h. After that, the cleaned product was ground and milled by ball mill and calcined in a furnace at 500°C for 3 h under air atmosphere. The calcined eggshell was kept in the furnace until the temperature was decreased to room temperature as shown in Figure 1.

Secondly, PLA (1gm) was dissolved in 20 ml of chloroform with high speed stirring at 40°C. The dried eggshell powder was added to this solution at 10, 20, and 30 wt. % and stirred completely by a mechanical stirrer. The mixture poured into a petri dish then kept in a hot air oven at 40 °C for 2 hr in order to remove the remained solvent as shown in Figure 2.

2.1. Preparation of bacterial culture

Escherichia coli and Staph .aureus bacteria were supplied from Nanotechnology and Advanced Materials Research Center (NAMRC) - University of Technology -Iraq. The bacteria were activated by culturing on nutrient agar for 24h at 37°C. A glass test tube contained (10 ml) of normal saline seeded with concentration 107 CFU/ml of bacteria with a piece of PLA and PLA with(10,20,30)% eggshell (1 × 1) cm incubated alone in shaker incubation at 160 rpm in 37°C overnight, then (100 µl) of solution was distributed on petri dish contained Mueller Hiton Agar after serial dilution for three times was occurred and incubated for 24h at 37°C, later numbers of colony bacteria was calculated by :

No. of Colonies [(CFU)/ml] = (No. of colonies for each dilution) × (factor of dilution 103)/ volume of the sample (1)

Fig 1. Schematic illustration of the preparation of (a) Egg shell powder

Also, the percentage of bacteria reductions presented using Bactericidal rate [23].

Bactericidal rate (100%） = (colonies of control group - colonies of test groups/ colonies of control group)×100 (2)

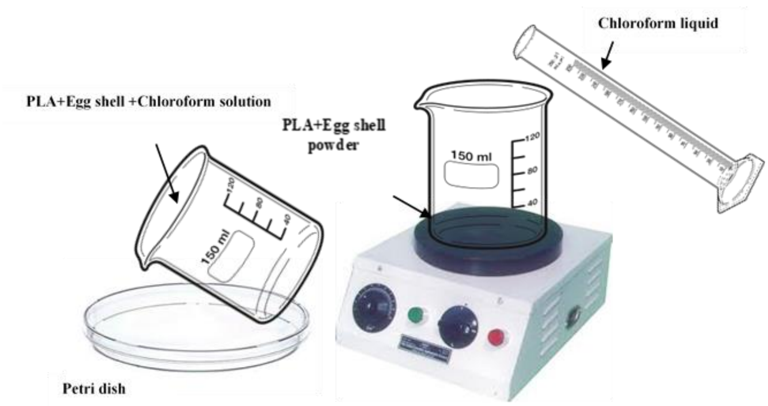

Fig 2. Schematic illustration of the preparation of PLA composite films

3. Result and Discussion

3.1. X-ray diffraction results

Structurally, fresh eggshell composed of three layers; the first layer has foamy cuticle at the surface, brittle similar to ceramic; the middle has a spongy layer and the inner composed of lamellar layers takes nearly 11% of the eggshell weight [25]. The main component in eggshells is

Calcium carbonate (calcite) which is inorganic substance makes up about 94% of the chemical composition of eggshells. Based on the above eggshell may be considered an essential material for the production of the hydroxyapatite [26]. XRD patterns of Eggshell powder, poly, and its composite films are presented in Figures 3 and 4. The pattern of ESP in Figure 3 shows calcite polymorph of calcium carbonate and it is similar to that of calcined ESP in Figure 4 since It was reported that calcium carbonate ($CaCO_3$) can be transformed to calcium oxide by decarbonation process above 800°C [27].

As for PLA, the xrd pattern proved its amorphous structure since there is no peaks only hump in the range between 2θ≈ 20° and 30° were observed. Now, the crystalline structure of the egg shell and the amorphous one of the PLA, this overlapping between them may prevent some of peaks from been identified correctly in the XRD patterns of composite films, although the main sharp peak of $CaCO_3$ at 2θ≈29° is cleared in all the composite films as shown in both Figure 3 and Figure 4. Furthermore, the crystallinity of the synthesized films induced by egg shell may also be responsible for the improvement of mechanical properties as shown in following the tensile results. Also the crystallinity of the synthesized films are different at which the films with calcined have somewhat high crystallinity and this will reflected on the mechanical behavior as we will see.

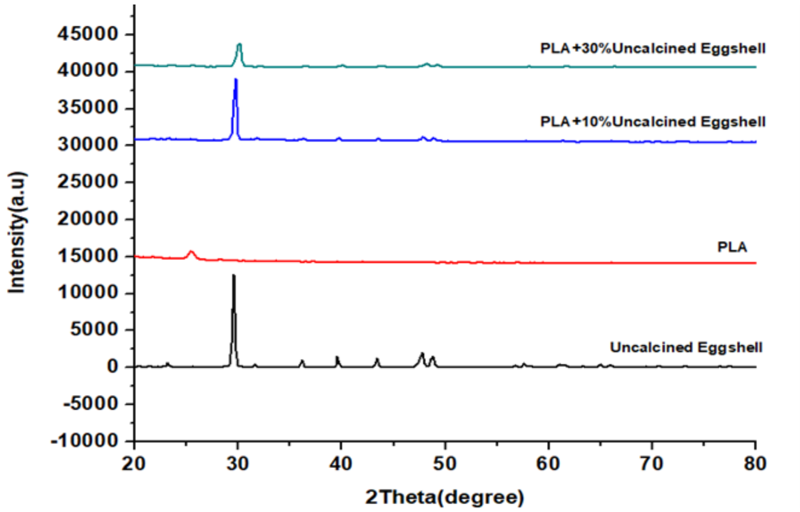

Fig.3.XRD of uncalcined eggshell /PLA composites.

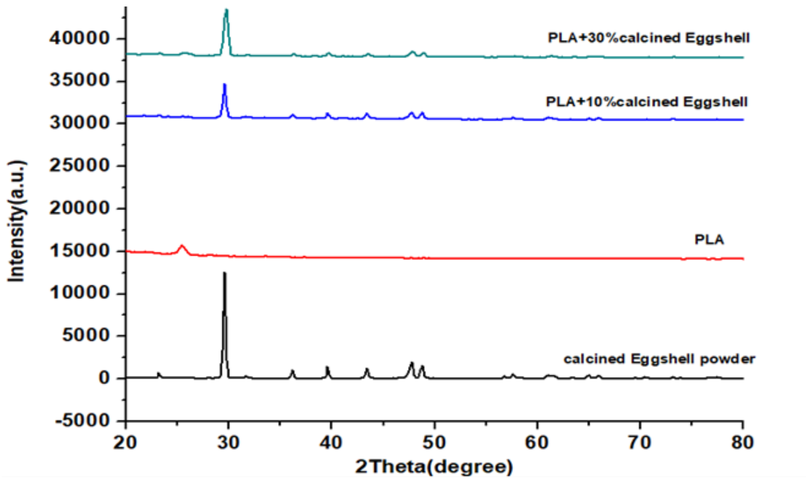

Fig. 4. XRD of calcined eggshell /PLA composites.

3.2. FTIR results

To investigate the interior groups' change and chemical interactions between eggshell and PLA, FTIR spectrum was examined. FTIR spectrum of pure PLA and its composite films prepared by different weight ratios of eggshells were shown in Figure 5 and Figure 6. Results exhibited almost the same characteristic peak as pristine PLA. However, the peak intensity of prepared composite films was less as compared with pure PLA.

The absorption bands in the range of 3500 cm^{-1} assigned to free hydroxyl (-OH) groups. The strong bands at 2997, 2945, and 2847 cm^{-1} were corresponding to the region of CH stretching, νsCH3, νsCH3, and νCH modes. Another strong large peak at 1747 cm^{-1} was set to the mode stretching vibration of (-C=O) carbonyl groups resulted from the repeated units of ester [22]. The absorption band at 1452 cm^{-1} was assigned to the bending–CH vibrations, while the peaks at 1379 cm^{-1} and 1361 cm^{-1} assigned to the deformation and asymmetric –CH bands respectively. At 1182 cm^{-1} the high absorption band attributed to stretching modes of the C–O ester groups in the main -CH-O of the polymer. Also, it is possible to notice the triplet rocking modes at 1134, 1082 and 1047 cm-1 attributed to C-O stretching modes of (–CO-O) group [6]. 1266, 1182, 1134, 1082, 1047 cm-1 were all assigned to the stretching absorption of C–O–C which considered complex because of the different function groups that may adjoining to C–O–C[23].The absorption peaks at both 952cm-1 and 920 cm-1 attributed to stretching mode of the single helical backbone C-C with CH3 rocking modes. While the second high absorption peak at 756 cm-1 belong to the functional –CH3 groups deformation vibration modes. Two last bands related to the crystalline and amorphous phases of PLA were noticed at 879 cm-1 and 756 cm-1 respectively.

The major absorption peaks in FTIR spectrum of the prepared composites at (700, 879, and 1415 cm-1) were attributed to (CO3)2- molecules modes, in-plane bending mode, out of plane bending mode, and asymmetric stretching respectively [23, 24].

Furthermore, broadband 3700-3060 cm-1 has low intensity assigned to traces of water molecules along with a very weak intensity near 1650 cm-1 due to OH group (probably belongs to the carboxylic acid group of protein) [23]. It can be seen from Figure 6 the spectrum of composites ESP/ PLA are the same to that of pure PLA explaining mainly physical interactions without production new side groups.

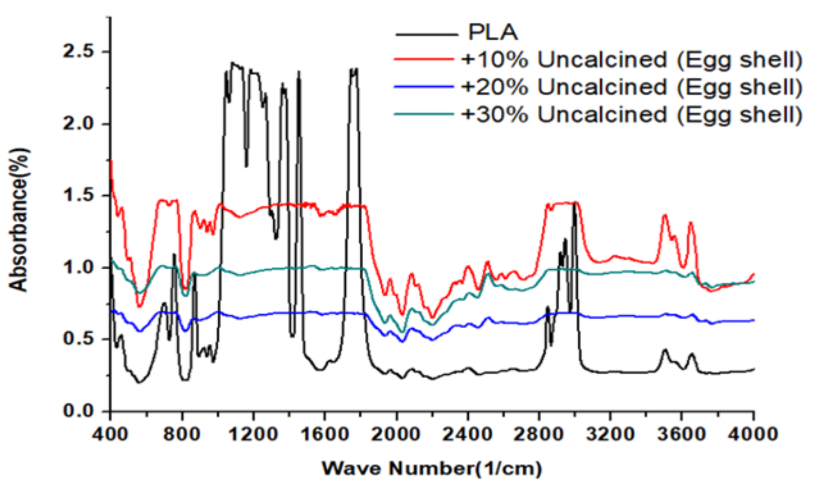

Fig.5. FTIR of uncalcined eggshell /PLA composites.

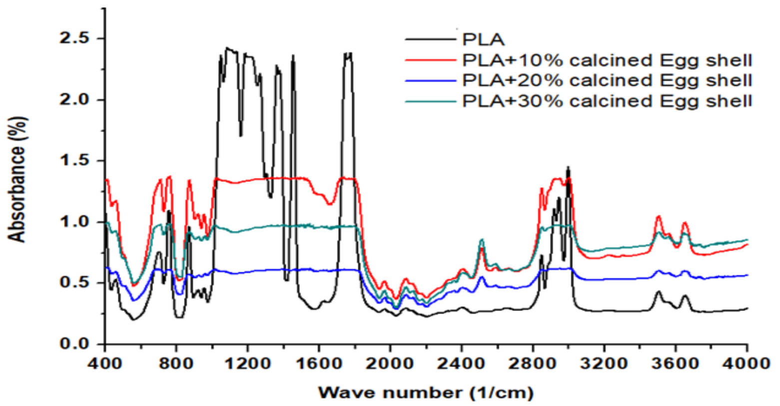

Fig .6. FTIR of calcined eggshell /PLA composites.

Furthermore, the stretching band of C-O in the range 1266-1038 cm^{-1} of composites was slightly higher because of the -H bonds between the C–O of the matrix (i.e PLA) and O–H side groups of eggshell powder.

3.3. Tensile results

To analyze the engineering behavior of the prepared eggshell powder/PLA composites tensile test was performed [28]. Figure 7 and Figure 8 show the stress-strain behavior of PLA and their composites with uncalcined and calcined eggshell respectively. It can be observed that the tensile strength and elastic modulus of the synthesized composite increased as compared with neat polymer because the strength of the bonds between the composite components is higher than the polymer yield strength [29].

Ultimate tensile strength increased gradually with an increment of the filler content and the highest ultimate strength at 30 wt.% this may be attributed to good compatibility between the eggshell and the PLA and the increased of filler percentage may not leads to weakening the interface region between the matrix and the reinforcement interface due to the agglomeration of filler particles as in A. G. Supri that used copolymer PE-g-MAH to improve The interfacial adhesion between ESP and LDPE[22].

For the second group the ones reinforced by the calcined eggshell, the tensile behavior is different since the maximum tensile strength at the low with ratio 10wt. % and decreased with increasing the powder content. This difference may belong to the crystallinity of the composite reinforced with calcined eggshell is higher than those reinforced with uncalcined eggshell). Moreover, the percentage of elongation at break decreased gradually with increasing filler ratio resulted in stiffening and hardening of the composite films and reducing their ductility.

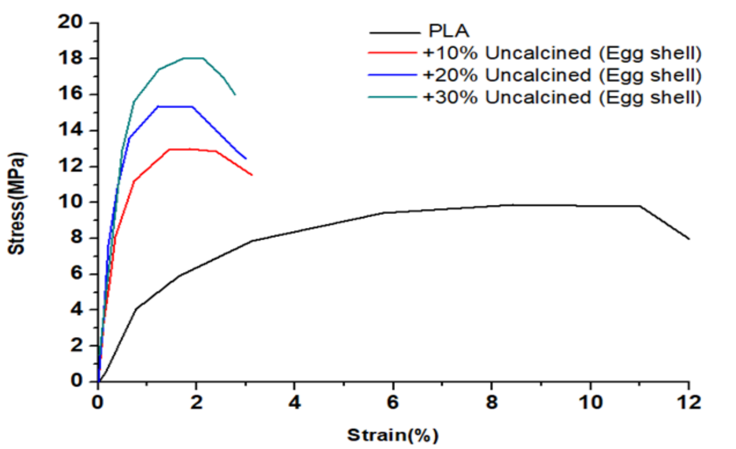

Fig.7. Stress-strain curve uncalcined eggshell /PLA composites.

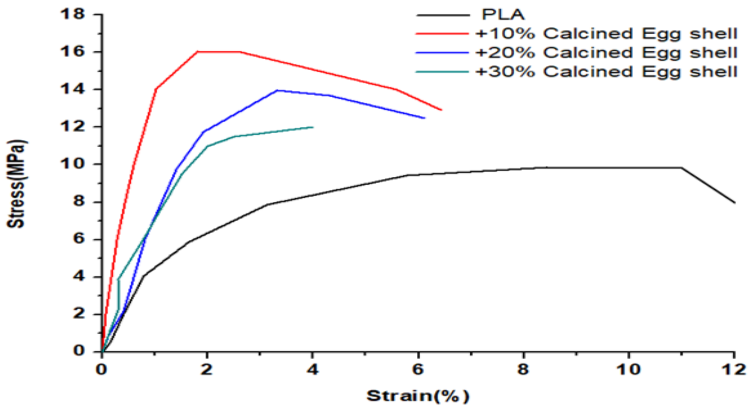

Fig.8. Stress-strain curve calcined eggshell /PLA composites.

3.4. Anti-bacterial results

In this research, the ability of neat PLA and PLA with eggshell in different percentage (10, 20, 30 %) were studied. Two types of bacteria were used E.coli bacteria as an example of gram-negative bacteria and Staph.aureus bacteria as an example of gram-positive bacteria. Figure 9 showed the ability of eggshell to increase the activity of PLA against two types of bacteria. The bactericidal percentages against Staph.aureus bacteria were (56, 64 and 72) % at the content of eggshell (10, 20 and 30) % respectively as compared with 40% for neat PLA. Furthermore, the results of bactericidal against E.coli bacteria were lower for PLA and its composites as compared with staph (34, 45, 52 and 61) % for PLA and its composites. Figures 10 and 11 indicate to photograph picture for the distribution of the colonies of the bacteria.

This results agreed with [30] that explained antibacterial activity of PLA against gram-positive more than gram-negative because of E. coli has proteins, lipopolysaccharides (LPS) and lipidsin the membrane of his cell which supplied effective protection against biocides, while [31] their results in its agreed with our results when explained ability of eggshell to inhibit the growth of gram-positive and negative bacteria and this ability increased when the concentration was increased too. The mechanism action of eggshell belongs to converted CaCO3 to CaO when it's heated and the hydration process of CaO, which produces alkaline solution conditions, is viewed as an essential EDP activity component. One conceivable purpose behind the high cleansing adequacy of Eggshell is that the pH of the thin water layer conformed to the particles is a lot higher than that of the equilibrated solution [32].

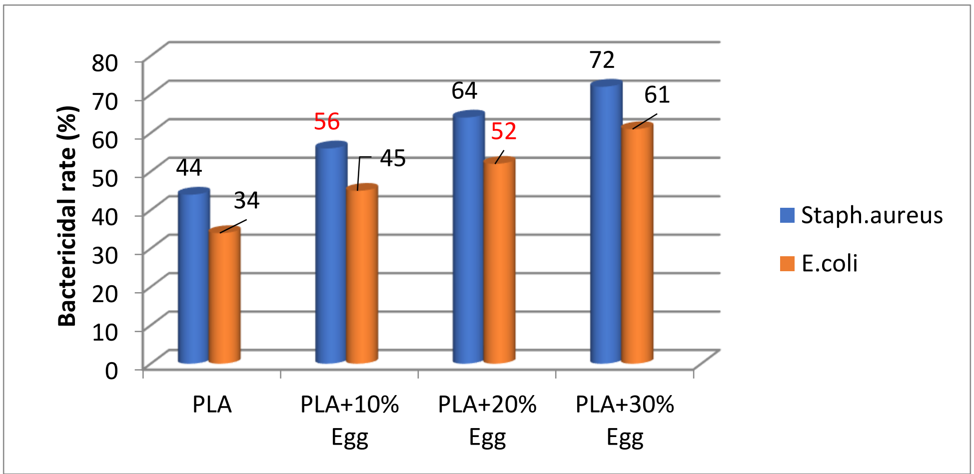

Fig 9. Bactericidal percentage of PLA and PLA with different percentage of eggshell (10, 20, and 30) % against *Ecoli* bacteria and *Staph.aureus* bacteria

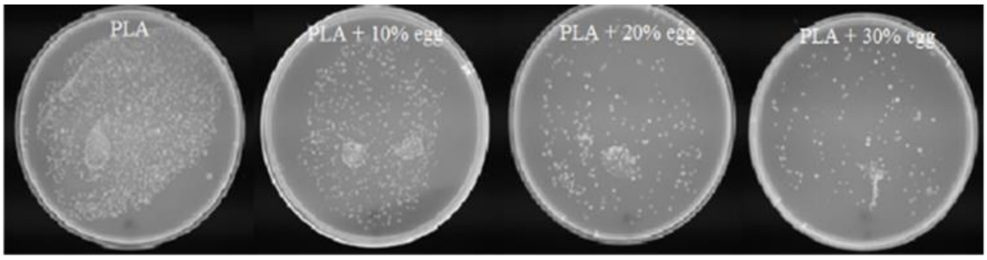

Fig.10. Bactericidal percentage of PLA and PLA with different percentage of eggshell (10, 20 and 30) % against *Staph.aureus* bacteria.

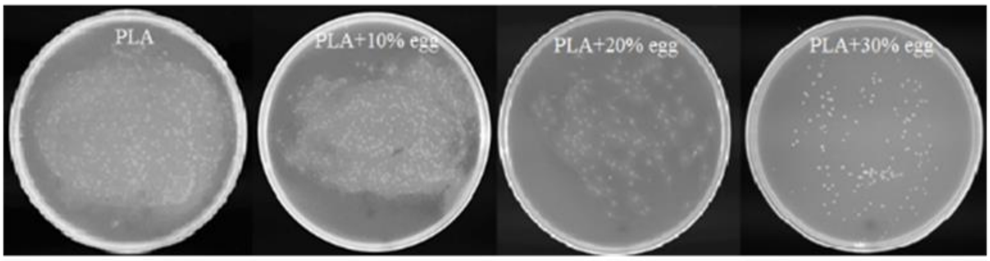

Fig.11. Bactericidal percentage of PLA and PLA with different percentage of eggshell (10, 20 and 30) % against *E.coli* bacteria.

4. Conclusion

- The results showed that the eggshell powder prepared from the waste can be used as a functional filler for PLA. The structural characteristics of the prepared samples have crystalline nature as a result of the inclusion of the eggshell
- The stress-strain curve indicates that the ultimate strength and young modulus of PLA composites were influenced by the inclusion of both calcined and uncalcined eggshells.
- The compatibilization of the composites with PLA was good as the content is lower because of the brittle behavior as the wt. of eggshell increased. Eggshell/PLA has a good bactericidal effect against gram-positive (i.e. Staph.aureus).

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