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Modification on Antibacterial Activity of PVC/PVDF Blend Filled by Silver Nanoparticles Utilizing Laser Ablation Method

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Abstract: A polymeric thin mixture of polyvinyl chloride (PVC)/ polyvinylidene fluoride (PVDF) (30%:70% wt) blend dopant with gradient concentrations of synthesized silver nanoparticles was prepared. Silver nanoparticles were gained from the laser ablation process. Nanocomposite blends were investigated versus gram-positive (*Staphylococcus aureus, Bacillus subtilis*) in addition to negative grams *(Escherichia coli, Pseudomonas aeruginosa)*. Bacterial cells were handled with the nanocomposite blend, and the growth rates were investigated beneath varying the concentrations of Ag-NPs, incubation times, incubation temperatures plus ph. It was obvious that the increase in the nanoparticle content was combined with an increase in the activity index of the corresponding prepared composite samples. The manufactured PVC/PVDF/Ag-NPs blend could be proposed for improving the biological properties, wound healing, and dressing applications.

keywords: Polyvinyl chloride (PVC); Polyvinylidene fluoride (PVDF); Nanocomposite; Silver Nanoparticles; Antibacterial Activity.

1. Introduction:

Nanotechnology has come out as a rapidly growing field with numerous biomedical science applications. Noble metal nanoparticles have unique properties represented in chemical, mechanical, optical, electronic plus magnetic properties which make them differ from those of bulk materials, thus it becomes recently the subject of researches [1]. Nanoparticles are developed with unique properties that make them desirable in material science and biology [2].

Through the variety of metal Nanosized particles, the Ag-NPs were presumably the most extensively studied. Silver nanoparticles are progressively employed in numerous fields, as well as, health care, medical, food plus industrial purposes owing to their physical and chemical properties [3], besides optical, thermal, electrical, and high electrical conductivity in addition to biological properties [4-5]. There are numerous uses of Ag-NPs represented in health care products, optical sensors, pharmaceutical industry, enhancing the tumor-killing effect of anticancer drugs [6]. Ag-NPs are also used in the biochemical device and wound healing [7]. Ag-NPs have been utilized widely in biological applications because of their unique properties.

Along the different methods used for the preparation of silver nanoparticles, the pulsed laser ablation in liquid is one of the simplest routes applied for acquired Ag-NPs. PLAL is one of the favorable methods utilized for the production of Ag-NPs, it’s a simple method with no chemistry involved in these processes, and the gained nanoparticles are free from counter ions or surface-active substances. Laser ablation in liquid focused on the preparation of Nano-size particles. Laser ablation of polymeric materials has attracted considerable research interest and well known for a number of polymers [8].

Polymers are subsisting in our life; this is owing to their unique properties. The polymer is defined as the repeating of small simple units (monomers) into large molecules (polymer). The molecular weight of the polymer is obtained by measuring the degree of polymerization. A combination of two or more diverse polymers is defined as a polymer blend [9]. Lately, the polymer blend caused a great rampage in the polymer industry. The obtained blend improves the characters of the polymers. Natural and synthetic polymers are blended with diverse mass fractions to derive materials for certain applications [9].

Polyvinyl chloride (PVC) is the major thermoplastic material that can be assessed as the third most widely generated polymeric material in the world that is created by free radical polymerization of vinyl chloride [10]. PVC is a relatively low-cost polymer; it has enormous attraction owing to its ability to arrive at the basic raw materials and its superior properties [11].

Due to the presence of fluorine atoms (C-F bond) in polyvinylidene fluoride and their physical and electrical properties, the PVDF has different advantages represented in chemical and thermal stability and mechanical resistant strength [12]. The object of these articles is a synthesis of PVC/PVDF composite embedded with silver nanoparticles produced from PLAL, the obtained nanocomposite blend utilized to improve the antibacterial properties of Ag-NPs.

2. Experimental Work:

2.1. Materials:

Polyvinyl Chloride (PVC) with (Mw ≈ 500k Da) and Polyvinylidene Fluoride (PVDF) with (Mw ≈ 543k Da) were bought from Sigma Aldrich. A high pure (99.999 %) silver plate was purchased from BDH chemical Ltd pool, England. Tetrahydrofuran (THF) has been employed to provide PVC/PVDF solutions.

2.2. Sample preparation:

First, the base sample of PVC/PVDF was obtained by dissolving pre-calculated amount of each polymer with Tetrahydrofuran (THF), following the solubility of the two polymers, the two polymer solutions were added to each other and stirred for 2 hours, and thus the PVC/PVDF solution was obtained. Second, the silver nanoparticles Ag-NPs were synthesized using pulsed laser ablation in liquid media. Silver nanoparticles target exposed to Nd:YAG nanosecond pulsed laser at 1064nm with width 6 nm and at 4watt power beside 10Hz of pulse frequency. The various concentrations of Ag-NPs were obtained by exposing the silver target to the laser source for different laser ablation times. The various concentration of Ag-NPs obtained was embedded with the composite blend, each concentrations embedded separately with the PVC/PVDF as shown in **Table (1)**. The synthesized nanocomposite blend of PVC/PVDF/Ag-NPs was poured into glass Petri dishes and left to dry at 50^{o}c for two days.

Table (1): Sample nomination and composition

Sample	Composition		
	PVDF	PVC	Ag-NPs×380 ppm
Blend	70	30	-
Ag1	70	30	1
Ag2	70	30	2
Ag3	70	30	3
Ag4	70	30	4
Ag5	70	30	5

2.3. The antibacterial activity:

The Ag-NPs obtained from using the pulsed laser ablation technique in THF has a dynamic effect versus a broad-spectrum bacteria including the two Gram-negative (*Pseudomonas aeruginosa and Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus and Bacillus subtilis*). This process takes place by pouring nanocomposite in Petri dishes full of agar; the dishes were incubated at 36^{o} C for approximately 5 hours. The antibacterial activity was announced after 24 hours of incubation by measuring the inhibition zone and by calculating the activity index at room temperature. THF was also performed against bacteria.

3. Discussion:

3.1. Antibacterial mechanism:

Ag-NPs are an alternative antibacterial agent to antibiotics; it exhibits a wide spectrum of two gram-positive and gram-negative bacteria. The antibacterial behavior of varying concentration of Ag-NPs with pre-calculated amount of the polymer blend was checked versus *Pseudomonas aeruginosa*, *Escherichia coli*, *Staphylococcus aureus plus Bacillus subtilis*. Agar nutrient medium has been used to estimate the antimicrobial activities of the prepared samples. Firstly agar medium was decanted into glass Petri dishes with a diameter of (10cm), and the bacterial microbes were placed on agar nutrient medium. The samples were prepared separately. This process takes place by pouring the nanocomposite into Petri dishes accommodated nutrient agar media with test microbes against cefotax antibiotics, the dishes were incubated at thirty-six degrees Celsius. The antibacterial activity was announced after one day of incubation as shown in **Figure (1)**, cefotax antibiotic is a wide spectrum antibiotic used to determine the activity index for the prepared samples.

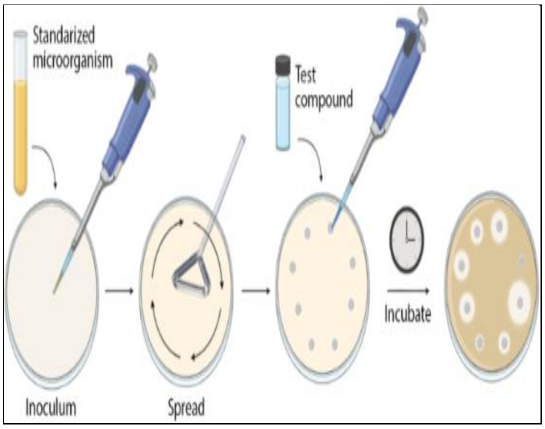

Fig (1): General antibacterial mechanism (13).

The biological activities of each species were determined by measuring the diameter of inhabitation zones that appeared around the paper disc including the paper itself. The nanocomposite blend interacts with the tested bacteria; we can notice that specific areas were formed around the tested bacteria known as (inhibition zone). If the diameter around the bacteria is wide, this indicates that the nanocomposite blend is susceptible to the bacteria. The nanocomposite blend was resistant to the tested bacteria; if the diameter around the bacterial agent is smaller. Ampicillin and Colitrimazole were considered the common standard antibiotic materials which were used to determine the % activity index for the prepared solutions and Tetrahydrofuran was also performed against bacteria, so we measured the activity index for THF then subtract the value of THF from the samples to obtain an activity index belonging to silver nanoparticles.

The mechanism occurs through the inactivation of cellular protein after treatment with the nanocomposite containing silver nanoparticles. Ag-NPs inactivated the bacterial enzymes and the production of hydrogen peroxide, thus the bacterial cell become dead [14].

3.2. Effect of silver nanoparticles concentration

Recently, the preparation and the production of Ag-NPs take place because these nanoparticles presented an interest in antibacterial activities [15]. Silver nanoparticles are very tiny-sized particles, thus their surface area is very large and give more bactericidal effect than the large particles. The antibacterial activity results of the diffusion over the bacterial cell membrane beside the interaction with the cell protein which leads to bacterial damage as shown in **Figure (2).** At the higher content of Ag-NPs in the nanocomposite, the diffusion become easier through the bacterial cell and this lead to the fast and extra damage to the bacterial cell. The antibacterial activity resulting from PVC/PVDF/Ag-NPs nanocomposite proves that Ag-NPs is an effective growth inhibitor, thus it utilizes in several medical devices. Ag-NPs accumulated on the layers of the cell membrane causing a gap that makes the increase in the permeability of the cell membrane accomplished with the altering in protein nature, deactivation of the enzyme, and destabilization of ribosomes thus the cell dies.

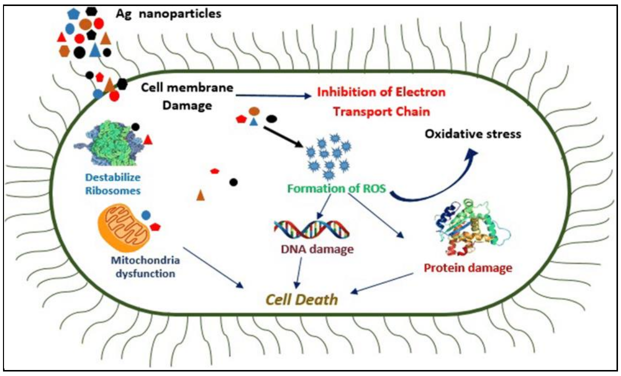

Fig (2): Antibacterial action of silver nanoparticle against bacteria (16).

3.3. Antibacterial analysis:

The bacterial activity was performed versus two gram-negative bacteria (*Escherichia coli* *and Pseudomonas aeruginosa*) in addition to two gram-positive bacteria (*Staphylococcus aureus and Bacillus cereus*) were studied. The appreciated system used in the antimicrobial study is the agar system. All samples were compared with a wide spectrum antibiotic (cefotaxime). The antimicrobial activity percent (%) has been fixed according to the equation [17].

$$\% \text{ Activity Index} = \frac{\text{Zone of inhibition by test compound (diameter)}}{\text{Zone of inhibition by standard (diameter)}} \times 100 \quad (1)$$

The bacterial activity of PVC/PVDF doped by silver nanoparticles has shown high activity index values for both gram-positive and gram-negative bacteria. Increasing nanoparticle content was combined with increases in the activity index of the corresponding samples. The obtained results in **Table 2** show the variation of activity index of the blend without and with adding the different concentrations of Ag-NPs. The activity index for all the samples are nearly the same value or with a small change for higher concentrations. The bactericidal activities at PVDF/PVC/Ag5 show the highest values of activity index of inhibition for all the two gram-negative and also for the two gram-positive bacteria. The activity index values for PVDF/PVC/Ag5 are 14, 13, 13, and 15 for *Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus and Bacillus cereus*, respectively.

Figure 3 illustrates a bar of the activity index test and shows the inhibition rate result 8 for the pure blend (PVDF/PVC) at all the tested bacteria and also reveals a gradual increase in the activity index with nearly the same value or even with a small change which supports the idea of saturation and clustering of Ag in the high content samples. In the other words, we can say that PVDF/PVC/Ag5 is more valuable than the other samples, as the inhibition efficiency of the bacterial growth was enhanced. Silver nanoparticles make crosslinked with the blend (PVDF/PVC) and then accumulated and stick to the exterior of the bacterial cell membrane and distribute their power function for making a hole through which the bacterial cannot passage. The binding of the nanocomposite stands on the surface area accessible for interaction. The higher concentrations of Ag-NPs having a larger surface area accessible for the communication thus will assign extra bactericidal effect than the lower concentration. According to the findings of the current study, silver nanoparticles may have antibacterial activity against the microorganisms found in PVDF/PVC. The findings point to PVDF/PVC/Ag-NPs composites as potential antibacterial materials for wound healing.

Table (2): The antibacterial activity versus two gram-negative bacteria (*Escherichia coli, Pseudomonas aeruginosa*) and two gram-positive (*Staphylococcus aureus, Bacillus cereus*) of pure PVC/PVDF blend and PVC/PVDF doped by Ag-NPs prepared via laser ablation with different ratios of Ag-NPs.

Sample	E.coliAct. (%)	P.aeruginaAct. (%)	S.aus Act. (%)	B.cereus Act. (%)
PurePVC/PVDF	8	8	8	8
PVC/PF/Ag1	9	9	8	9
PVC/PVDF/Ag2	10	10	10	11
PVC/PVDF/3	12	11	12	12
PVC/PVD/A4	14	13	13	14
PVC/PVDF/5	14	13	13	15
Cefotax	100%			

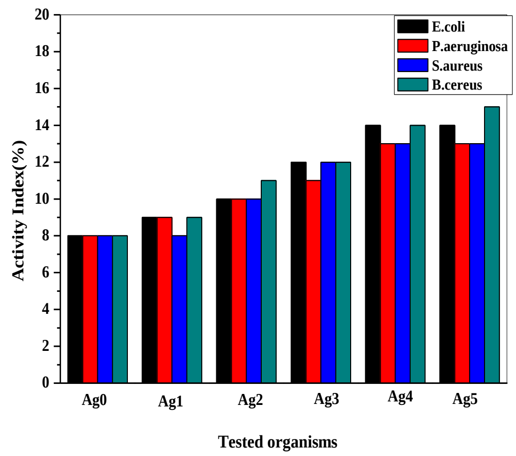

Fig (3): Activity index of pure PVC/PVDF blend and PVC/PVDF doped by Ag-NPs prepared via laser ablation with different ratios of Ag-NPs.

4. Conclusion

Composite polymer blend PVC:PVDF (30%:70%) were successfully formed and then doped with silver nanoparticles obtained from pulsed laser ablation in liquid. Ag target is exposed to different laser ablation times to obtain various concentrations. The nanocomposites blend obtained enhanced and improved antibacterial studies. Antibacterial activity for the nanocomposites blend was tested using grams positive (*Staphylococcus aureus, Bacillus subtilis*) and negative grams bacteria (*Escherichia coli, Pseudomonas aeuroginosa*). The bacterial activity of Ag-NPs shows high activity index values for both types of bacteria. At a higher ratio of Ag-NPs the activity index values are higher (14, 13, 13, 15) for *Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus, and Bacillus cereus* respectively.

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