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Research paper

Studying yhe Effect of Nano Silver on Some Properties of Acrylonitrile Butadiene Styrene Copolymer for Medical Devices

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Abstract

Antibacterial polymeric composites were prepared to manufacture medical devices and seats for hospitals. These composites prepared by adding nano silver (Ag NPs) by three ratios (3, 6, and 9 wt %) to Acrylonitrile butadiene styrene (ABS) terpolymer. The antibacterial activity was investigated against *S. aureus* and *Salmoulla* microorganisms using Agar well Diffusion method. Results showed that these composites have antibacterial ability against both *S. aureus* and *Salmoulla* microorganisms. At low Ag NPs concentration, the activity against *Salmoulla* is higher than that against *S. aureus* microorganism. But at higher concentrations, the activity against *Salmoulla* will be less than that against *S. aureus* microorganism. The mechanical properties improved due to the new interactions between nano silver and ABS matrix. Ag NPs addition reduces the surface wettability, enhances self-cleaning tendency, decreases the surface roughness and the groove continuity, enhances the surface bearing index, reduces both the core roughness depth and core fluid retention and shifted the thermal transitions towards low temperatures.

Keywords:

1. Introduction

Bacterial infections have an old history in risking human life. Human beings are usually infected by many microorganisms such as bacteria and viruses. In the 20th century, Infections diseases were the major responsible of death worldwide [1].
Today, hundreds of polymers are used in medical device. This device may be exposed to bacterial infections [2]. Many of studies proved that hospital surface and a lot of used medical equipment become contaminated by assortment of pathogenic and non pathogenic organisms [3].
5-10 % of hospital patients get hospital infection in the United States alone. The most common post surgery infections are urinary tract infection, surgical site infection and Pneumonia. Almost 30% of these infections can be preventable. In the middle of 20th century, the development of new antibiotic and other methods to control infections helped the humans to inhibit many diseases [1].
Control mechanisms usually do not work well, this making microbial Infection the first killer in the world, Treatment of microbial infection has become more complicated because bacteria have the ability to conform themselves against antibiotics over time [4]. So, controlling the growth of bacteria is one of the major issues in material and medicine.
In order to prevent contamination, there are many methods used to achieve this problem, such as used of antibacterial agent [5].
Human have used silver (Ag) as antibacterial agent, which shows a strong resistance towards wide range of microorganisms, thus it has been widely used for biomedical applications and other environmental disinfection procedures for centuries [6].
Silver in a nanometric size involves many catalytically properties compared with those found in the bulk of the noble metal, such as surface Plasmon resonance, scattering, and strong toxicity to a wide range of microorganisms [7].Ag-nanoparticles (Ag NPs) have previously been tested in several fields of biological science, drug delivery and antibacterial compound against both Gram (+) and Gram (-) bacteria by numerous researchers. Ag NPs prevent bacterial growth at very low concentration than antibiotics and till now no side effects are reported [8]. Ag NPs exhibit a wide antibacterial profile toward bacteria, fungi and virus as well. Even bacteria strains which are resistant against antibiotics can be killed by silver [9].
The activity of Ag NPs toward microorganisms is a major reason for produced product with nano silver. It is now day used in an increasing number of consumer goods and medical products. More than 1000 consumer products that have nanomaterials in their composition, almost 25% are contain Ag NPs [10 ,11].
Size, shape, concentration, and dose are the main parameters those affect the bactericidal efficiency of Ag NPs [12]. The antimicrobial activity of Ag NPs with 19–23 nm size mixed with polyamide-hydroxyurethane was investigated against (*E. coli*) and (*S. aureus*) and found that Ag NPs at concentrations 5 µg/ ml were strong bactericidal against (*S. aureus*).

2. Experimental Part

2.1 Materials

Acrylonitrile butadiene styrene (ABS) was purchased from National chemical & plastic industries co. s. a. Zaafaraniya, Baghdad-Iraq, with properties shown in Table (1) and the Ag NPs was purchased from Hongwu International Group Ltd., Guangdong-china with the properties maintain in Table (2)

Table 1: Properties of used ABS

Property	Data
Chemical formula	(C8H8-C4H6-C3H3N)n

Glass transition	105○C
HDT	96○C
Ultimate tensile strength	26.4 MPa
Toughness	3.3 KJ/m2
Density	1.05 g/cm3

Table 2: Physical Properties of Ag NPs

Property	Data
Purity	99.9%
Size	50 nm (spherical)
Crystal	Gray black powder

2.2 Procedure

15g of ABS dissolved in 15ml of THF solvent with continuous stirring for (3hr) at (35℃) to form solution No.1 (S_1). Then different amount of Ag NPs (0.45, 0.9, 1.35g) dispersed in (20ml) THF by Sonication technique to form solution No.2 (S_2). Finally (S_1) and (S_2) solutions were mixed together for (30min) and shaped in suitable mold.

2.3 Characterizations

The antibacterial activity for ABS/Ag NPs composites are measured by Agar Well Diffusion Method. Instron 5556 Universal Testing Machine type (WDW/5E) used to determine the tensile strength according to ASTM D-638-IV, while hardness measured according to ASTM D 2240. FTIR analysis instrument Type (IR Affinity -1) used to investigate the occurrence of any new bonds. SL 200C - Optical Dynamic I Static Interfacial Tensiometer & Contact Angle Meter used to evaluate the Wettability.
The surface morphologies carried by tapping mode SPM model AFM (AA3000) and Scanning Electron Microscope (SEM) model (Tescan VEGA-SB), while thermal transitions monitored according to ASTM D3418-03 using SH1MADZU DSC-60 device.

3. Results and Discussion

3.1 Antibacterial Activity

The antibacterial activity of ABS/Ag NPs composites determined against Staphylococcus aureus (S. aureus) and Salmoulla microorganisms, which are gram-positive and gram-negative, respectively (as shown in figures 1 and 2). It is clear from these figures that Ag NPs causes a significant increase in activity against both the used microorganisms. This is because that Ag NPs damaged the bacterial cell membrane of both microorganisms due to their interactions with the building elements of the cell. This damage can resulted in liberation of silver ion, which penetrates into the bacterial cells. This penetration influences the structures of protein and enzymes which required for the bacterial cell.
That means that the presence of Ag NPs in the medical device surface can help in prevention the bacterial adhesion and subsequent biofilm formation on the medical devices. Biofilm formation can enhances the immune system of microorganisms by acting as a barrier against antimicrobial agents.
This is due to the slow realization of silver from the polymeric composite surface and killing the bacterial population near the surface.
At low Ag NPs concentration; at 3 wt%, the antibacterial activity of ABS/Ag NPs composite against Salmoulla is higher than that against S. aureus microorganism. But at higher Ag NPs concentrations; at 6 and 9 wt%, the antibacterial activity against *Salmoulla* is less than that against *S. aureus* microorganism.

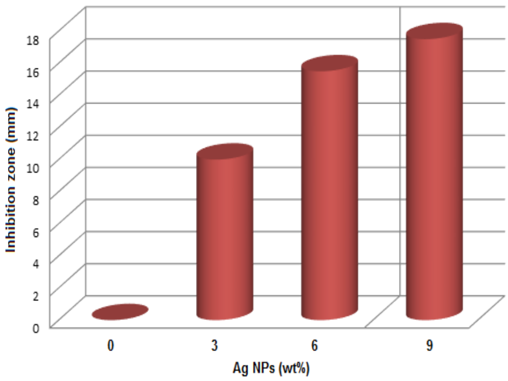

Fig. 1: Antibacterial activity of ABS/Ag NPs against (*S. aureus*)

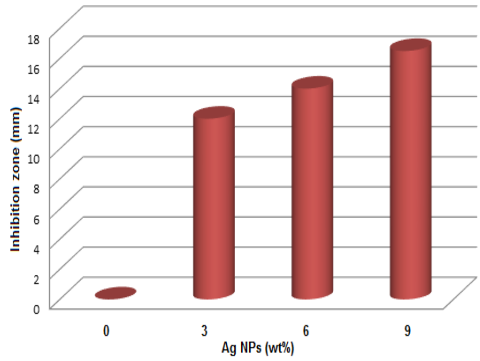

Fig. 2: Antibacterial activity of ABS/Ag NPs against (Salmoulla)

The inhibition efficiency (IE) was calculated according to the following equation.

$$IE = \frac{I\ Zone\ at\ high\ concentration - I\ Zone\ at\ low\ concentration}{I\ Zone\ at\ low\ concentration} * 100\%$$

With *S.aureus*, the inhibition efficiency of 9wt% sample (4) increased by 12.9% compared with 6wt% and by 75% compared with 3wt%. While against *Salmoulla* microorganisms, the inhibition efficiency of 9wt% sample (4) increased by 17.85 compared with 6wt% and by 37.5% compared with 3wt%.
It is clear from the above illation Ag NPs have twice effect against *S.aureus* compared with *Salmoulla* for same concentration (9wt %). This is because the wall thickness of *S.aureus* is thinner from wall thickness of *Salmoulla*.

3.2 Mechanical Properties

Figures 3 and 4 show the tensile strength and hardness for prepared samples. It is clear that both these two properties increased linearly with Ag NPs addition, which gives a benefit to seats manufactured from these composites in bearing additional weights. The tensile strength increased by 29% and the hardness by only 13.44%, which means that the interactions occur on the whole body, not on the surface alone.
This means that the stiffness of the composite increased with Ag NPs addition. This is due to the extra interactions arise in the composites between the active surface of Ag NPs and the polar matrix of ABS polymer (as shown in figure 5, where a new band appears at wave number 2358 cm^{-1}). This polarity arises from the presence of nitrile group in Acrylonitrile phase. Indeed, ABS is a terpolymer composed from three different phases; Acrylonitrile, styrene and butadiene. Due to its ring group, styrene phase make the surface of the terpolymer an impervious, which reduces its ability to swell by solvents, while due to its rubbery nature, butadiene group gives the toughness character.

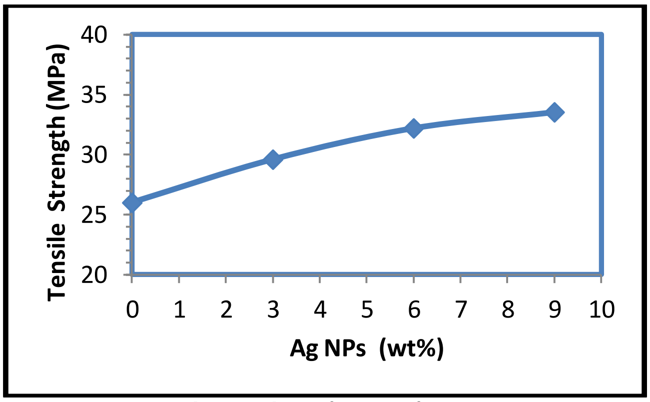

Fig. 3: Tensile strength as a function of Ag NPs content

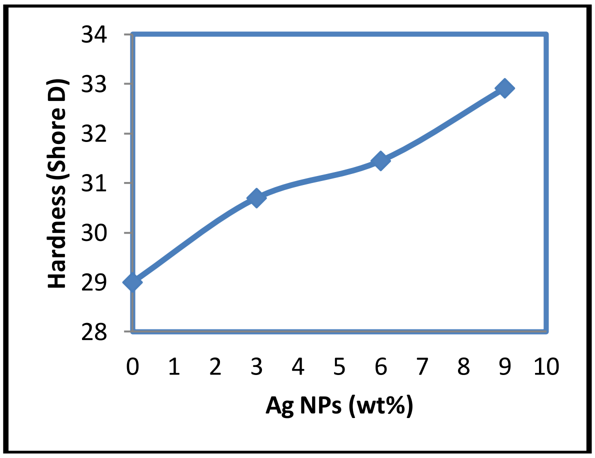

Fig. 4: Hardness as a function of Ag NPs content

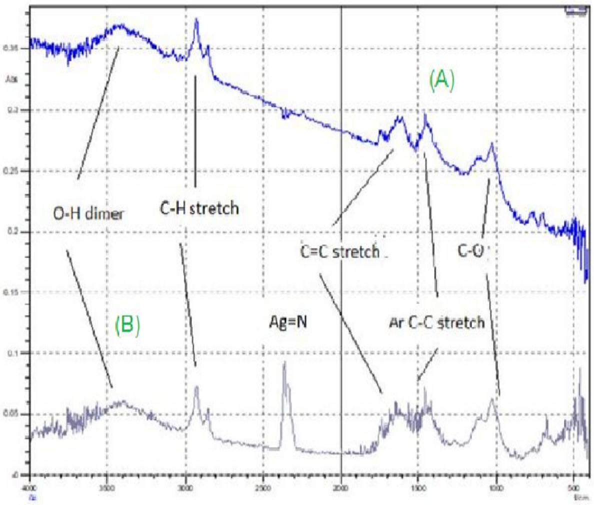

Fig. 5: FTIR spectra for (a) pure ABS (b) composite with 9 wt% Ag NPs

3.3 Surface Wettability

The increments in the hardness property get in good agreement with another surface property, which is the wettability property. Contact angle (Circle fitting mode) used to evaluate the effect of Ag NPs addition on the wettability of composites (as shown in figure 6 and 7). Increasing of contact angle from 39.9^o to 112.2^o means a reduction in the surface wettability and the surface become more hydrophobic. That means the swelling ability decreased and the surface turn towards self-cleaning. This enhances the ability of seats to remove unwanted microorganisms.

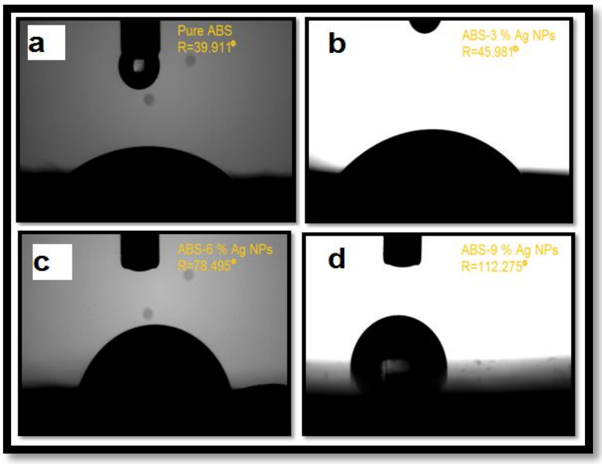

Fig. 6: Contact angle images

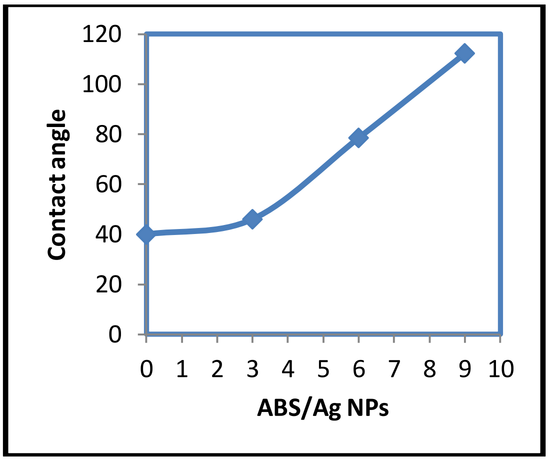

Fig. 7: Contact angle as a function of Ag NPs content

3.4 Morphology Parameters

Also, the previous findings get in good agreement with the average roughness property which obtained from AFM test (Figure 8). The surface roughness decreased linearly with the Ag NPs addition, which means that the surface become smoother and with less cavities and voids.Therefore, the depth of the core roughness depth decreases by 56.2% (from 24.2 to 10.6 nm) and the core fluid retention decreased by 8.7% (from 1.61 to 1.47) as shown in Table 3. These surface changes enhance the surface bearing ability by 17.9% due to increasing of the surface bearing index from 0.324 to 0.382.

These finding coincide with the 2D and 3D images from AFM test (figure 9), where the groove continuity decreased ad Ag NPs content increased.

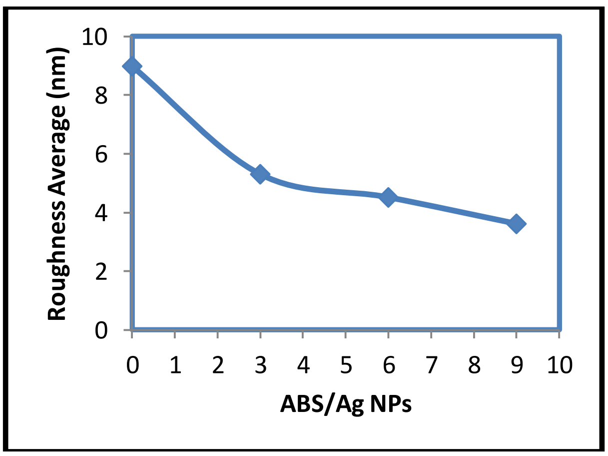

Fig. 8: Roughness average as a function of Ag NPs content

Table 3: Some of surface parameters as a function of Ag NPs content

Ag NPs (wt %)	Surface Bearing index	Core Fluid Retention index	Core Roughness Depth (nm)
0	0.324	1.61	24.2
3	0.351	1.53	16.6
6	0.375	1.54	10.6
9	0.382	1.47	10.6

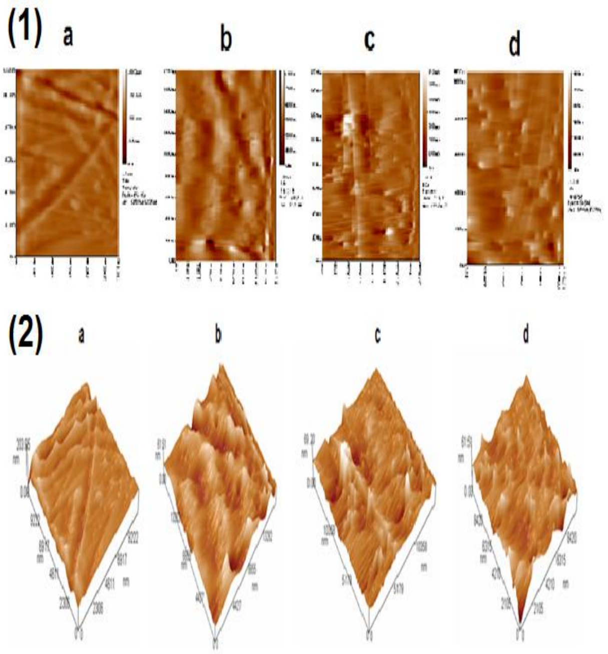

Fig. 9: Surface nature as a function of Ag NPs content (1) 2D images (2) 3D images (a) Pure (b) 3 wt% (c) 6 wt% (d) 9 wt%

3.5 Thermal Transitions

The thermal transitions of these composites generally decreased due Ag NPs addition (Figure 9). This is because that Ag NPs raise the thermal conductivity of the prepared composites and give more mobility to ABS terpolymer chains.

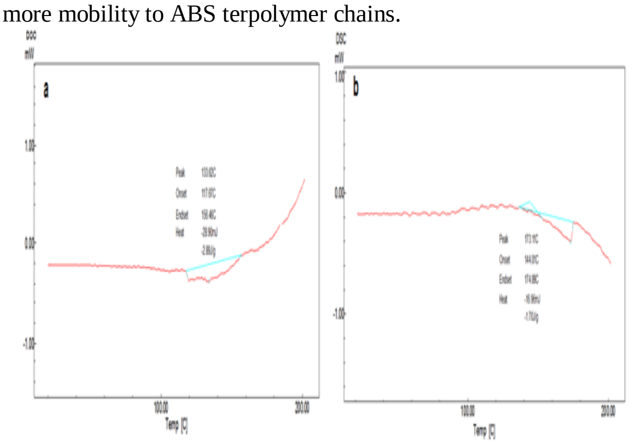

Fig. 9: DSC curves of (a) composite with 9 wt% Ag NPs (b) ABS

3.6 Scanning Electron Microscope (SEM) Test

SEM image for composite (figure 10) shows that Ag NPs were distributed uniformly in the ABS base material and the surface of these composites become smoother and less cavities and voids when the Ag NPs were added. This is due to the new band which appeared (as shown in figure 5). That means that Ag NPs will inhibit the growth of microorganisms on the surface of these composite. This give a clear prevent to previous results which obtained from AFM and FTIR tests.

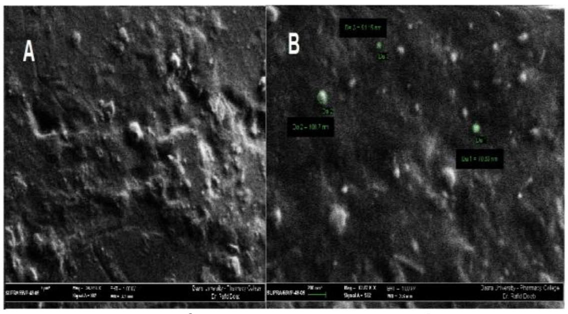

Fig. 10: SEM image of (a) ABS (B) composite with 9 wt% Ag NPs

4. Conclusions

1. ABS/Ag NPs composites have antibacterial ability against both S. aureus and Salmoulla microorganisms.
2. The extent of the antibacterial activity to each microorganism influenced by the Ag NPs concentration.
3. Ag NPs addition arises new interactions, improved the mechanical properties, shifted the thermal transitions towards low temperatures, and enhances self-cleaning tendency and the surface bearing ability.
4. Ag NPs addition decreases the surface wettability, surface roughness, groove continuity, core roughness depth and core fluid retention.
5. The optimum concentration is 9wt% against both S. aureus and Salmoulla microorganisms and its inhibition efficiency against S. aureus is twice that against Salmoulla.

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