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Research Article

Study the Structural and Morphological Properties of Nano/Micro Polystyrene Treated by Argon Plasma and Apply as the Antibacterial Application

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Abstract:

In this study, plasma parameters in DC glow discharge of argon gas were used for the pure PE film untreated and exposed of argon gas plasma (10, 20 and 25) min samples treatment. X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) were studied for the morphological and structural films. X-ray diffraction patterns of all samples prepared were recorded. The XRD pattern shows the pure PE unexposed that the polycrystalline nature with strong peak around 2θ =21.51° with miller indices (110). After exposed with the argon plasma (10, 20 and 25) min and change the electrode distance (2.5, 3.5 and 4.5) cm, the new peak exhibited and the intensity of the all peaks increased with increasing exposed time, indicating that the orientation of the orthorhombic crystals had changed and also indicate the time exposed of argon plasma was affected. The increase in grain diameter average and particle size for pure PE film and exposed of argon gas plasma (10, 20 and 25) min with an increase in the treatment with dc glow discharge plasma was noted in the FESEM images. The contact angle of untreated pure PE and PE films after exposed of argon gas plasma (10, 20 and 25) min was measured at room temperature with water appeared of the contact angle results decrease with increasing time exposed plasma. The antibacterial activity for the pure PE film untreated and exposed of argon gas plasma (10, 20 and 25) min shows enhanced antibacterial activity against E. coli and S. aureus due to the changes in surface chemistry and physical structure, including increased hydrophilicity, surface roughness, and the generation of reactive species that can damage bacterial cells.

1. Introduction

The plasma activation method has shown great promise in many different processes that allow changing the surface of polymers. Some of these steps are cleaning and etching to get rid of impurities and polymer material, cross-linking and branching to deposit polymer and/or hybrid organic/inorganic multicomponent thin films, and surface treatment to change the polymer's outermost layers by adding certain functional groups chemically [1]. Plasma cutting is often used in microelectronics. These days, plasma treatment of polymers has been shown to be useful for tissue engineering and biomedical uses, like building scaffolding for body implants (like prostheses, catheters, and intraocular lenses), biosensors, and more. Some of these uses are controlled surface modification, layer deposition no matter what the surface geometry is, intrinsic sterility, and the ability to scale up. Plasma treatment also helps cells stick together and multiply, which both improve biocompatibility [2]. Plasmas may be the most common way to change the surface of a polymer. When a polymer is exposed to plasma, radical active sites form right away on its surface, typically only a few nanometres deep. The surface gets rougher, and holes the size of nanoparticles appear [3].

The plasma has a lot of energy that can break the covalent bonds of polymers that touch it. The active sites are different for each gas that was used to

make the plasma, and they can react and/or join to make a lot of different chemical functional groups. This will change the surface properties of the material in a big way. In industry, this is often done to clean parts, activate polymers before painting and sticking, and change the water-repelling or water-attracting properties of surfaces, among other things. Plasma treatment can successfully raise the surface energy of common hydrophobic polymers like polyethylene (PE) and polyethylene terephthalate (PET). This makes them more wettable and better at sticking to metal coatings, adhesives, and inks. [4–8].

Plasma technology surface treatments of polymers offer rapid implementation, ease of integration into existing production protocols, and cost efficiency. The procedures are also environmentally sustainable [9, 10]. The cost-effective alternative for industrial applications involves plasma operations conducted in air or nitrogen environments. However, documentation also indicates the utilisation of noble gases, potentially combined with reactive gases such as O2, steam, and NH3. Plasmas have been utilised for an extended period to enhance the wettability, lubricity, and stickiness of polymers. Recently, however, research has shifted towards employing plasmas in the preparation of polymer-based sensors, flexible electronics, and batteries [11].

Polyethylene (PE) possesses the chemical structure (C2H4)n and belongs to the polyolefin family. It is mostly produced through the polymerisation of ethene via radical anionic addition, ion coordination, or cationic addition reactions. These technologies produce polyethylene with diverse compositions, molecular weights, branching kinds, branching patterns, and densities [12]. Its straightforward and cost-effective manufacturing methods contribute to its status as a versatile biomaterial with significant clinical implications. Polyethylene (PE) is categorised based on its density and branching, encompassing a range of types from ultra-high molecular weight to medium- and low-density PE, each exhibiting distinct thermal, mechanical, chemical, electrical, and optical properties relevant to biological mimicry. Ultra-high-molecular-weight polyethylene (UHMWPE) was first utilised clinically for joint replacements in 1962, using polyethylene cups articulating with a metal femoral head in total hip arthroplasty [13, 14]. Polyethylene (PE) is a very versatile and adaptable biomaterial extensively utilized in pre-clinical research and clinical applications, surpassing autografts and other biomaterial implants, and establishing itself as the 'gold standard' in numerous therapies [15].

2. Experimental

Surface modification of polyethylene films is achieved through the application of an incandescent direct current (DC) glow discharge plasma, utilising a gas such as argon, as depicted in Figure 1. The PE samples were cut into small slides with dimensions of 2 cm by 1 cm for the purpose of plasma treatment. The samples were positioned within a vacuum chamber, where a vacuum level of 10-2 mbar was sustained through the operation of a vacuum rotary pump. The samples were positioned on a glass stage, maintaining a separation of 2.5 cm from the cathode. The treatment duration with plasma was adjusted to 10, 20, and 25 minutes. The operational parameters are detailed in Table 1.

Table 1. *Typical working parameters for plasma treatment*

Parameters	**Values applied**
Working Pressure	6.5 x 10^{-1} mbar
Electrode separation	5.5 cm
Power Supply	450 Volt
Flow rate of gas	750 cm^3/min
Exposure time	10-25 min
Working gas	Ar

The X-ray Spectra were gotten by utilizing copper filtered Cukα radiation λ=1.54060 (A) worked at 40 (Kv) and 20 (mA) kind (SHIMADZU-6000) made in Japan. The antibacterial was used auger method. The spherical section height (h) and radius (r) were determined and the angle was estimated using the following equation [16].

$$\text{Contact angle } (\theta) = \sin^{-1}\left[\frac{2rh}{r^2 + h^2}\right] \quad \ldots\ldots\ldots\ldots\ldots (1)$$

3. Result and discussion

Figure (1) illustrate results for the XRD pattern of the pure PE film untreated and exposed of argon gas plasma (10, 20 and 25) min respectively. The peaks were indexed and found well-matched with standard data. Furthermore, the crystallite size (D) was calculated using the Scherer formula. Peaks of XRD were recorded between 5° - 100°. From these figures, it seems clear that the pure PE unexposed that the polycrystalline nature with strong peak around 2θ =21.51° with miller indices (110) and small peaks were exhibited at 2θ = 24.093° and 36.49°

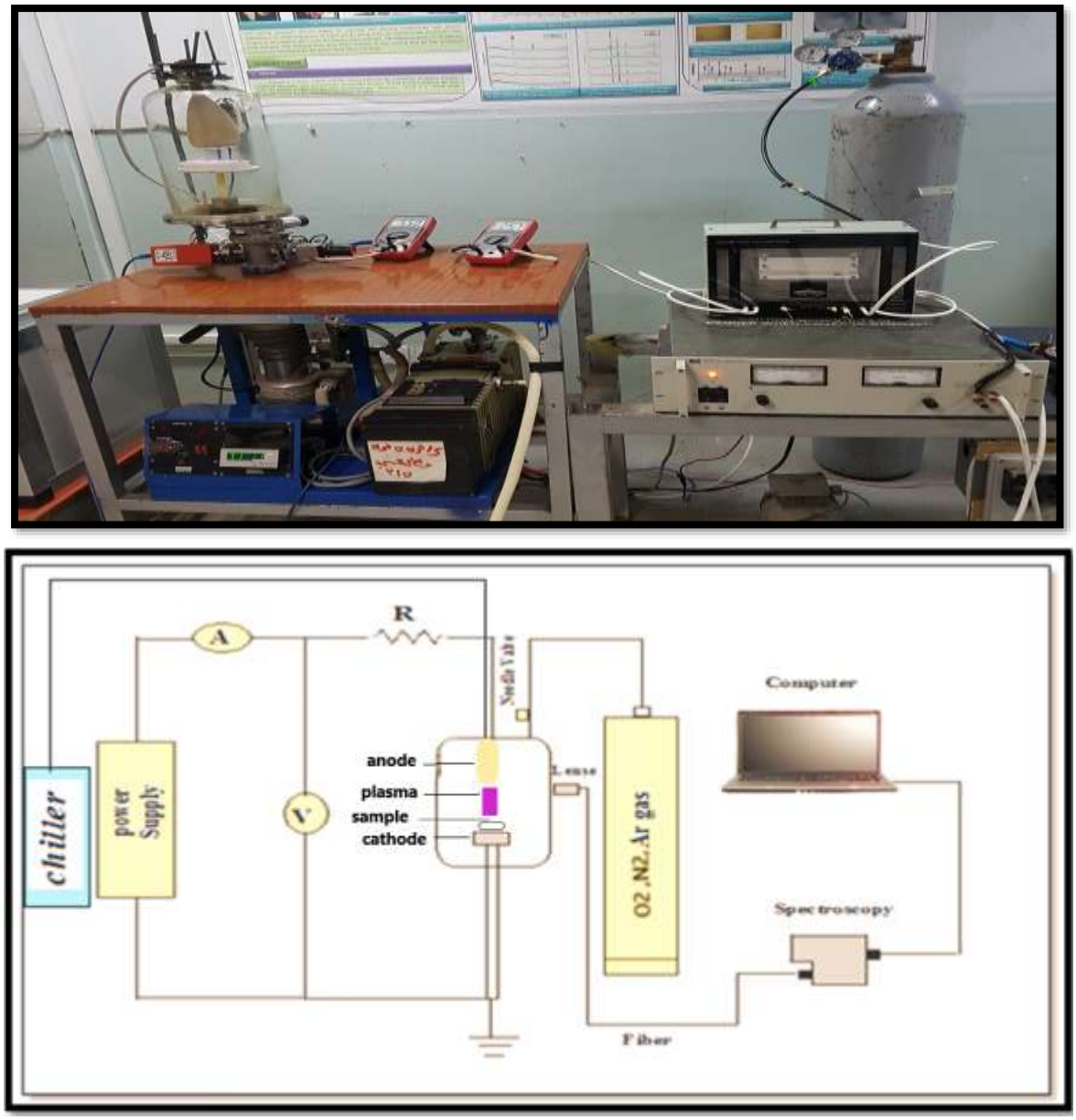

Figure 1. *Experimental Setup of dc glow discharge plasma system*

with miller indices (200) and (020) respectively and indicate that PE used in this investigation shows orthorhombic structure. After exposed with the argon plasma (10, 20 and 25) min, the new peak exhibited at 2θ =10.23° and 29.62° with miller indices (002) and (210) respectively. The intensity of the all peaks increased with increasing exposed time at 25 min and becomes sharper, while that of the (110) diffraction peak decreased and then increased with exposed time and become sharper and shift some peaks toward to the higher and other to the lower degree, indicating that the orientation of the orthorhombic crystals had changed and also indicate the time exposed of argon plasma was affected. This behavior agrees with references [17, 18]. FESEM is employed to analyse structural morphological changes before and after plasma treatment of pure PE films. The surface morphology of the untreated pure-PE films is illustrated in Figures (2) (a) at a magnification of 500 nm, revealing a relatively smooth surface. The surface morphology of the pure-PE films treated by plasma can be examined under optimal conditions for surface adjustment, as illustrated in Figure (2) (b, c, and d) at the same magnification. Clusters of particles can be observed connected to

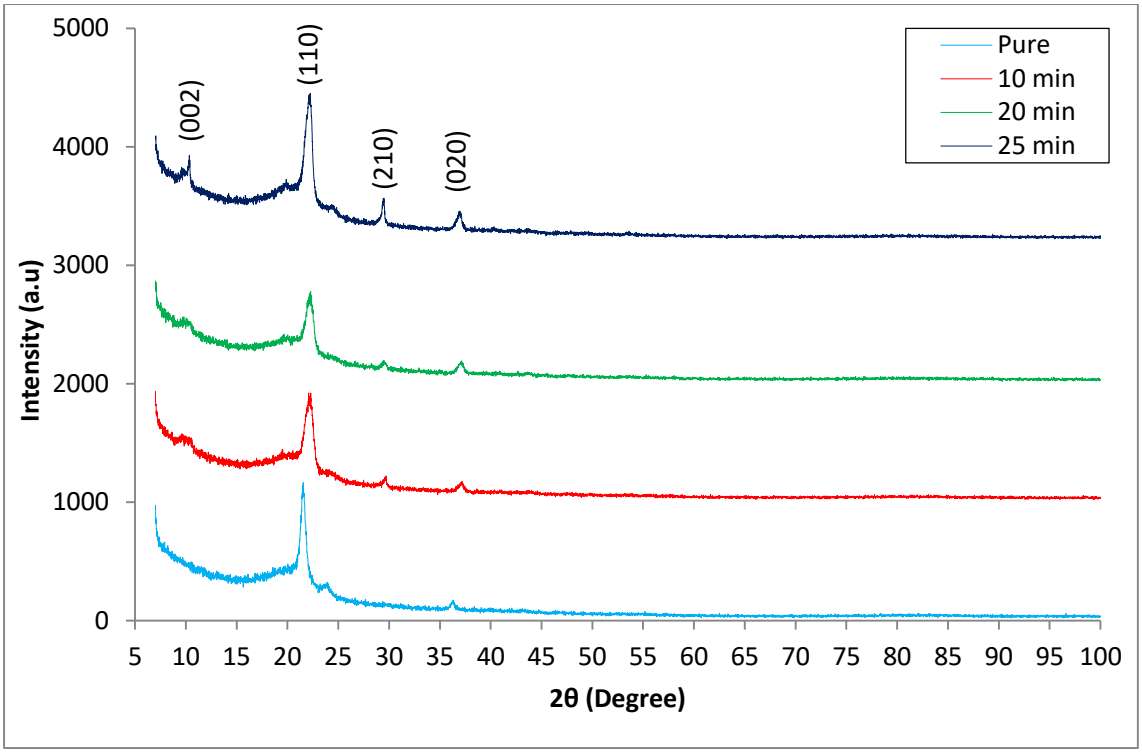

Figure 2. *X-ray diffraction patterns of pure PE and different exposed time*

Table 2. *XRD parameters Comparison between pure PE and different exposed time*

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl}(Å)	C.S(nm)	hkl
Pure PE	21.519	0.451	2.3525	18.74	(110)
	24.093	0.326	2.0387	26.04	(200)
	36.490	0.491	2.0321	17.80	((020)
10 (min)	10.230	0.421	2.3546	19.80	(002)
	22.157	0.641	2.0402	13.20	(110)
	24.193	0.631	1.4422	13.45	(200)
	29.626	0.496	1.2305	17.31	(210)
	37.580	0.541	1.2304	16.21	(020)
20 (min)	10.360	0.368	2.3587	22.65	(002)
	22.320	0.561	2.0356	15.08	(110)
	24.293	0.421	1.4422	20.17	(200)
	29.726	0.511	1.2305	16.81	(210)
	37.580	0.546	1.2311	16.06	(020)
25 (min)	10.440	0.468	2.3587	17.81	(002)
	22.410	0.461	2.0356	18.36	(110)
	24.490	0.321	1.4422	26.46	(200)
	29.810	0.461	1.2305	18.63	(210)
	37.600	0.308	1.2310	28.47	(020)

the surface. Plasma argon was utilised to modify the surfaces of the PE-Pure film. Plasma has been observed to alter the surface in terms of its chemical composition and morphology. The increase in plasma treatment time for PE-pure films from 10 to 25 minutes results in greater damage to the polymer chains, leading to a looser packing of the polymer, which subsequently elevates the etch rate. The alteration of the etch-rate is significant at the outset and diminishes with extended treatment duration [19]. Table (2) presents the maximum and mean grain size for both untreated pure-PE and pure-PE treated with Ar plasma. Contact angle measurements can be utilized to ascertain the surface tension of polymers. Utilizing the sessile drop method [20]. The water contact angle (WCA) is a widely recognized method for assessing surface activation. The angle at the droplet's edge is measured using a goniometer when microliter-sized droplets of distilled water are deposited on the surface [21]. This technique is analogous to the WCA data computed for composites and polymers [22]. The contact angle of the treated PE films in Figure (3) decreased with increasing treatment time. Following an extended exposure period, the values remain constant as a result of plasma

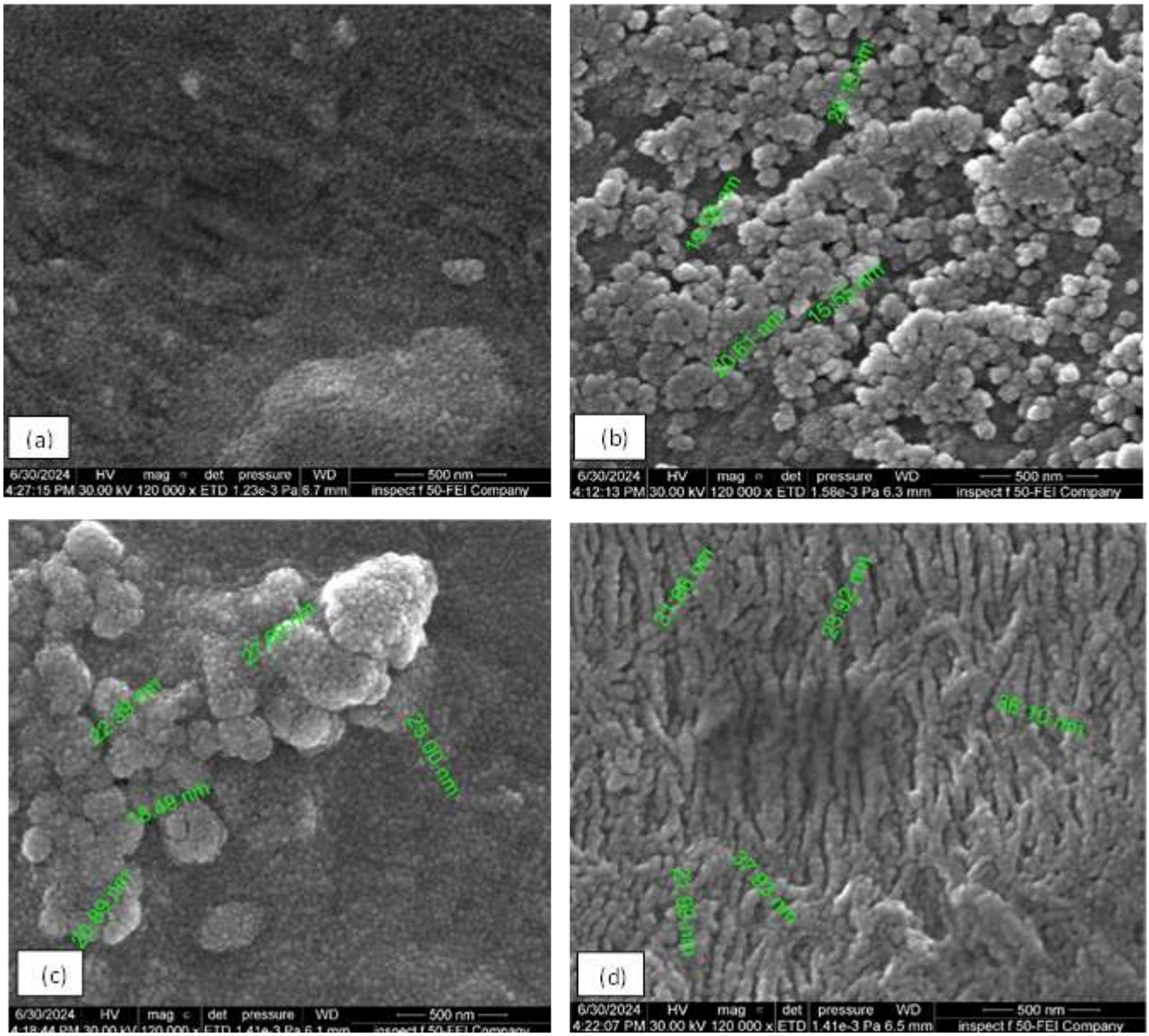

Figure 2. *FESEM images of a: pure PE and different exposed time b: 10 min, c:20 min and d:25 min*

Table 2. *Maximum and Mean Grain size for pure-PE untreated and treated by Ar plasma*

samples	Maximum Grain size(nm)	Mean Grain Size (nm)
Pure PE	20.19 nm	17.92 nm
10 min	27.6 nm	21.21 nm
20 min	29.15 nm	22.87 nm
25 min	37.93 nm	30.32 nm

saturation effects on the PE films. The contact angle of the PE film decreased from 73.33° to 36.17° after a 25-minute treatment with argon plasma. Argon plasma influenced PE films by generating a significant quantity of active species that rapidly interacted with the polymer surface. The contact angle decreases as a result of the consolidation of oxygen-containing polar groups, such as OH, C=O, and O-C=O, on the surface of the treated plasma film [23, 24], as illustrated in Table 3. The reduction in surface activation may decrease the wettability of the surface, potentially leading to a diminished reduction in contact angle [25]. The antibacterial properties of the of the pure PE film untreated and exposed of argon gas plasma (10, 20 and 25) min as shown in Figures (4) in contrast to gram-positive Staphylococcus aureus (*S. aureus*) and gram-negative Escherichia coli (*E. coli*) and the obtained data are presented in Table (4). As shown in the figure, the inhibition zone rises

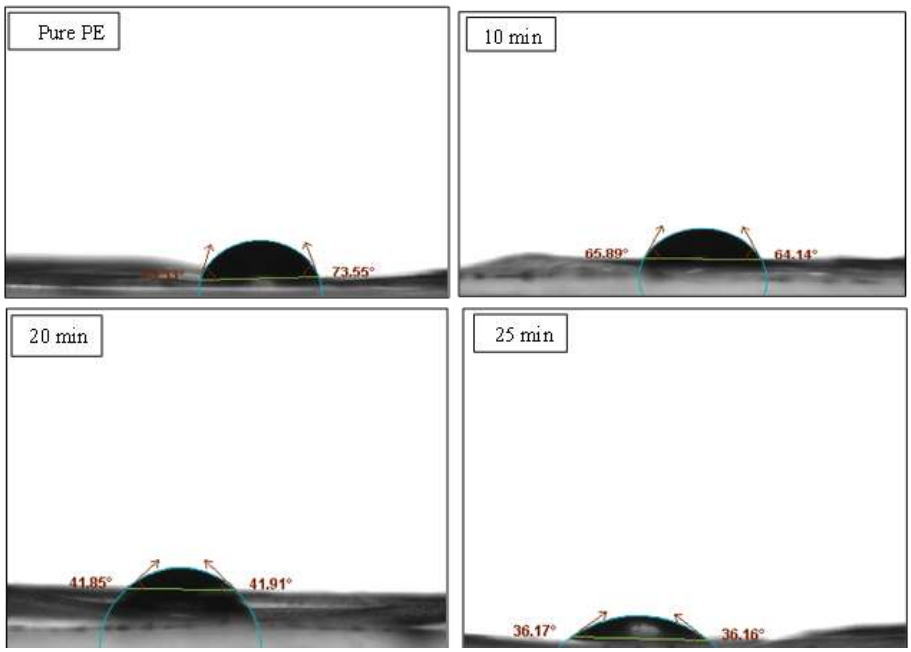

Figure 3. *contact angle measurement of unexposed pure-PE and PE exposed argon with different time (10, 20 and 25) min.*

with increasing with increased exposed time. It's increased from 0 mm for unexposed of pure PE to 26 mm and 24 for exposed 25 min of PE for *E. coli* and *S. aureus* respectively.

Table 3. *contact angle measurement for unexposed pure-PE and PE exposed argon with different time (10, 20 and 25) min.*

Samples	Contact angle
Pure-PE	73.33°
10 min	65.89°
20 min	41.85°
25 min	36.17°

This result can be explained for unexposed PE. This is the original, untreated surface of polyethylene. Typically, PE is hydrophobic and chemically inert, which means it doesn't easily interact with other substances, including bacteria. As a result, unexposed PE surfaces may not have significant antibacterial properties. When PE is exposed to argon plasma, its surface undergoes physical and chemical changes. Plasma treatment can introduce functional groups (like oxygen-containing groups) to the PE surface, making it more hydrophilic, increasing its surface energy, and potentially altering its interaction with bacteria [26]. Also, Argon plasma is a type of cold plasma that consists of ionized argon gas. When PE is exposed to argon plasma, the high-energy particles in the plasma can etch the surface of the polymer and introduce reactive species. This process can lead to changes in surface roughness, chemical composition, and wettability, which are all factors that can influence antibacterial activity [27]. The plasma-treated PE surface might exhibit increased antibacterial activity against both *E. coli* and *S. aureus* due to changes in surface properties. The increased hydrophilicity and possible introduction of reactive species can make it harder for bacteria to adhere and survive on the surface. Plasma treatment may increase surface roughness, which can affect bacterial adhesion [28]. For some bacteria, increased roughness might lead to enhanced antibacterial effects due to mechanical disruption of bacterial cells or the creation of microenvironments that are unfavorable for bacterial survival. Plasma treatment can generate reactive oxygen species on the surface, which can directly damage bacterial cell walls, leading to antibacterial effects. These species can be particularly effective against *E. coli* and *S. aureus* by disrupting their cell membranes or walls [29].

Table 4. *Diameter of inhibition zone (mm) for unexposed pure-PE and PE exposed argon with different time (10, 20 and 25) min. on S. aureus and E. coli*

S. Aureus	E. Coli	Sample
0	**0**	**Bo (Pure-PE)**
13	**16**	**B1 (10 min)**
19	**20**	**(20 min) B2**
24	**26**	**(25 min) B3**

4. Conclusion

This work conclude from the XRD pattern shows the pure PE unexposed that the polycrystalline nature with strong peak around 2θ =21.51° with miller indices (110). After exposed with the argon plasma (10, 20 and 25) min and change the

Figure 4. *Image for inhibition zones unexposed pure PE and PE exposed argon with different time (10, 20 and 25) min. on S. aureus and E. coli on S. aureus and E. coli*

electrode distance (2.5, 3.5 and 4.5) cm, the new peak exhibited and the intensity of the all peaks increased with increasing exposed time, indicating that the orientation of the orthorhombic crystals had changed and also indicate the time exposed of argon plasma was affected. The increase in grain diameter average and particle size for pure PE film and exposed of argon gas plasma (10, 20 and 25) min with an increase in the treatment with dc glow discharge plasma was noted in the FESEM images. The contact angle of untreated pure PE and PE films after exposed of argon gas plasma (10, 20 and 25) min was measured at room temperature with water appeared of the contact angle results decrease with increasing time exposed plasma. The antibacterial activity for the pure PE film untreated and exposed of argon gas plasma (10, 20 and 25) min shows enhanced antibacterial activity against *E. coli* and *S. aureus* due to the changes in surface chemistry and physical structure.

Author Statements:

- **Ethical approval:** The conducted research is not related to either human or animal use.
- **Conflict of interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper
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- **Data availability statement:** The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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