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Comparative Study on Surface Modification of PVC and PTFE using Atmospheric Air Plasma and Low-Pressure Oxygen Plasma Treatments

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Abstract - This study compares atmospheric air plasma and low-pressure oxygen plasma treatments on polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE) to improve surface properties without affecting the bulk. Atmospheric plasma was released at ambient pressure using air, and low-pressure plasma employed pure oxygen in a vacuum chamber for controlled activation. Surface characterization was performed using X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM), contact angle measurements, and Owens–Wendt analysis. XPS revealed the development of polar groups such as C=O and O-C=O, with broader oxidation detected under atmospheric plasma, and a dominating O-C=O peak following low-pressure treatment, especially in PVC, and more selective functionalization under low-pressure plasma, particularly for PTFE. Contact angle dropped from 81° to 23.7° in PVC and from 91° to 86° in PTFE with low-pressure plasma. Surface energy increased significantly, with PVC showing the highest polar component. AFM revealed that atmospheric plasma increased surface roughness due to etching, while low-pressure plasma maintained smoother surfaces, indicating chemical modification. Overall, atmospheric plasma combines chemical and physical effects, while low-pressure plasma enables controlled, cleaner functionalization, guiding treatment choices based on material and application needs.

***Keywords*:** Atmospheric air plasma ,Low pressure oxygen plasma, PVC and PTFE, Surface energy, Wettability, XPS

1. Introduction

Surface engineering improves material performance by modifying surface properties without affecting the bulk. Among various techniques, plasma treatment stands out for being clean, efficient, and precise. Plasma, a partially ionized gas of electrons, ions, and radicals, alters surfaces through chemical activation, etching, and cleaning—enhancing wettability, adhesion, and surface energy[1]-[3].

Polymers like PVC and PTFE are widely used due to their mechanical and chemical stability, but their low surface energy and hydrophobic nature limit adhesion. PTFE is particularly difficult to modify due to strong C–F bonds, while PVC, with polar C–Cl bonds, is slightly more reactive[4], [5].

Traditional methods like chemical etching or flame treatment can be harsh or inconsistent. Plasma treatment offers a dry, non-destructive alternative, enabling the incorporation of polar groups (–OH, –COOH, –C=O) and nanoscale roughening for improved compatibility.

This study examines two plasma methods:

- Atmospheric Air Plasma, a scalable, cost-effective approach that introduces oxygen and nitrogen groups while increasing roughness[6].
- Low-Pressure Oxygen Plasma, a vacuum-based method that delivers controlled surface oxidation, ideal for modifying inert polymers like PTFE.

While various gases like nitrogen and argon have been used, oxygen plasma—especially under low pressure—consistently enhances hydrophilicity. However, comparative studies on both PVC and PTFE are limited.

The novelty of this work lies in its side-by-side comparison of atmospheric and low-pressure plasma treatments on chemically distinct polymers, using XPS (surface chemistry), AFM (topography), contact angle (wettability), and Owens–Wendt method (surface energy). This study also demonstrates, with molecular insight, successful PTFE functionalization under low-pressure plasma. The objective is to analyze surface chemistry via XPS, examine topography using AFM, assess wettability with contact angle, and determine surface energy using the Owens–Wendt method.

2. Materials and Methods

2.1. Materials

PVC (Polyvinyl chloride) and PTFE (Polytetrafluoroethylene), the two commercially available hydrophobic polymer material was considered for the study. These materials were selected due to their widespread application and as well as the challenges associated with these materials regarding their low surface energy and poor wettability.

PVC is a thermoplastic polymer having repeated units of carbon-hydrogen (C–H) and carbon-chlorine (C–Cl) bonds, where chlorine atoms are responsible for the polarity of the material. PVC sheet with a thickness of 2mm were procured and were cut into uniform rectangular samples of 50mm x 50mm for plasma treatment[7].

PTFE is a linear chain thermoplastic polymer having repeated units of carbon fluorine (C-F) bond one of the strongest bond in the organic chemistry, making them highly non-polar, chemically inert and resistance to any material modification. A 1mm thickness PTFE sheet was obtained and were cut into similar dimensions as PVC for the treatments[8].

2.2. Plasma treatment:

The plasma treatments were conducted at Facilitation centre for plasma research at Gandhinagar, India

2.2.1. Atmospheric Air Plasma

The plasma treatment was conducted using a dielectric barrier-based plasma system at an ambient condition. The sample was cleaned with acetone before the treatment. The sample was kept between two copper conducting plate, in which one side of the plate was attached to dielectric barrier for ensuring stable and uniform operation To get a breakdown voltage for the gas discharge to become stable and become luminous, a 2mm spacing was given between the plates with an operating voltage of 24kV for 60s. Atmospheric air plasma uses the surrounding air which contains a mixture of oxygen, nitrogen and moisture, leading to generating ions, free radicals and UV radiation.

2.2.2. Low pressure Oxygen Plasma Treatment

The treatment was conducted using a DC Magnetron sputtering as shown in the schematic diagram in figure 1. The dumbbell shaped stainless steel vacuum chamber contains the electrodes with a separation of 15cm. The pressure inside the vacuum chamber was made to be 5.5 x 10^{-2} mbar. Low pressure oxygen gas was introduced into the chamber at a constant flow rate of 8 sccm/min in order to achieve the operation pressure of 6.2 x 10^{-1} mbar. According to Paschen's Law, at low pressure the power supplied to achieve the plasma was 195 W which was the corresponding energy required for the breakdown voltage. This leads to efficient energy transfer of the gas molecules and a dense plasma of reactive oxygen species are formed[9].

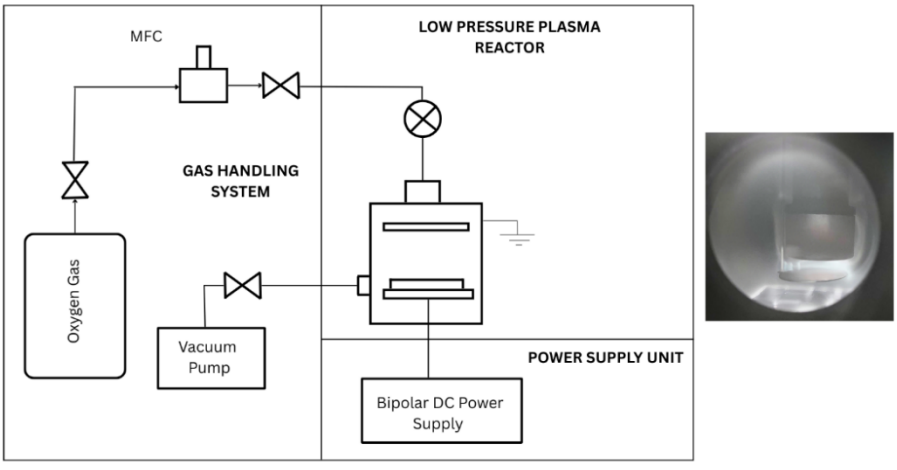

Fig 1. Schematic diagram of DC Magnetron sputtering using low pressure oxygen gas plasma.

2.3. Characterization techniques

2.3.1. Contact Angle Measurement

Contact angle measurement is a typical method for determining the wettability of a solid surface. It is based on Young's equation, which links the contact angle to the balance of interfacial tensions at the solid-liquid-gas interface. In this investigation, the sessile drop method was used, which involved placing a droplet of liquid on the sample surface with a microliter syringe and measuring the angle produced at the three-phase boundary. Deionized water and ethylene glycol were employed as testing liquids. A lower contact angle indicates higher wettability and more surface energy (hydrophilic surface), while a larger angle implies poor wettability and lower surface energy (hydrophobic surface).

2.3.2. Surface Free Energy Calculation

The surface free energy was calculated using the contact angle measured for deionized water and ethylene glycol as per the ASTM D7490. Using Owens-Wendt method, the dispersive (γ_s^d) and polar (γ_s^p) components of the both the liquids were calculated using the following equation:

$$\boldsymbol{\gamma_L^T(1+cos\,\theta) = 2\left(\sqrt{\gamma_S^D\gamma_L^D} + \sqrt{\gamma_S^P\gamma_L^p}\right)} \quad \textbf{(1)}$$

$$\boldsymbol{\gamma_s^T = \gamma_s^D + \gamma_s^P} \quad \textbf{(2)}$$

where the superscripts T, D, and P represent the total, dispersive and polar component of the surface energy respectively while the subscript S and L represent solid surface and liquid medium respectively. The surface free energy parameters of the liquids used are given in Table1

Table 1: Surface free energy parameters liquids used.

	Surface free energy parameter (mJ/m^2)		
Testing Liquids	γ_L	γ_L^P	γ_L^D
Water (W)	72.8	51	21.8
Ethylene Glycol (EG)	48	19	29

2.3.3. X-Ray Photoelectron Spectroscopy (XPS)

Photoelectron spectroscopy (XPS) is a surface-sensitive analytical technique in which the elemental composition and chemical states of material surfaces can be determined. The process involves exposing the sample to X-rays, typically Al Kα (1486.6 eV) or Mg Kα (1253.6 eV), in a very high vacuum. In this experiment, an Axis Ultra instrument from Kratos Analytical (UK) was employed. It has an Al Kα source and can scan an area of 700 µm × 300 µm. The data was processed by Shirley background subtraction using specialized vision software following the calibration of the C1s peak at 284.6 eV.

2.3.4. Atomic force Microscope (AFM)

Surface topography and related surface roughness of the materials over a 10 x 10 µm2 region were characterized by AFM using XE-70 Park System. Plotting and bending of the cantilever beam for imaging needs is done. The average roughness (Ra) and root mean square roughness (Rq) values were determined from the images

3. RESULTS AND DISCUSSION

3.1. X-Ray Photoelectron Spectroscopy (XPS)

The C 1s XPS spectra of PVC under various surface conditions—untreated, atmospheric air plasma-treated, and low-pressure oxygen plasma-treated—show significant changes in chemical composition and oxidation. The untreated sample fig 2 (a) shows two primary peaks: one at ~284.8 eV for C-C/C-H bonds from the PVC backbone and another at ~286.3 eV for C-Cl bonds. There is no evidence of oxygen-containing groups, indicating the hydrophobic and inert nature. Atmospheric air plasma treatment fig 2 (b) results in further peaks at ~287.3 eV (C=O) and ~288.7 eV (O-C=O), as well as a tiny peak around ~282.6 eV due to π-π* shake-up, indicating surface oxidation, production of polar functional groups, and structural flaws. This produces a surface that is substantially more hydrophilic and has greater surface energy. The low-pressure oxygen plasma-treated sample fig 2 (c) shows fewer chemical changes, including a maintained C-C/C-H peak and a strong O-C=O peak at ~288.3 eV, indicating selective and controlled oxidation. The absence of π-π* and carbonyl peaks indicates negligible polymer breakdown. Overall, while both plasma treatments increase wettability, atmospheric plasma promotes widespread oxidation, whereas low-pressure oxygen plasma provides cleaner, more tailored functionalization.[10]

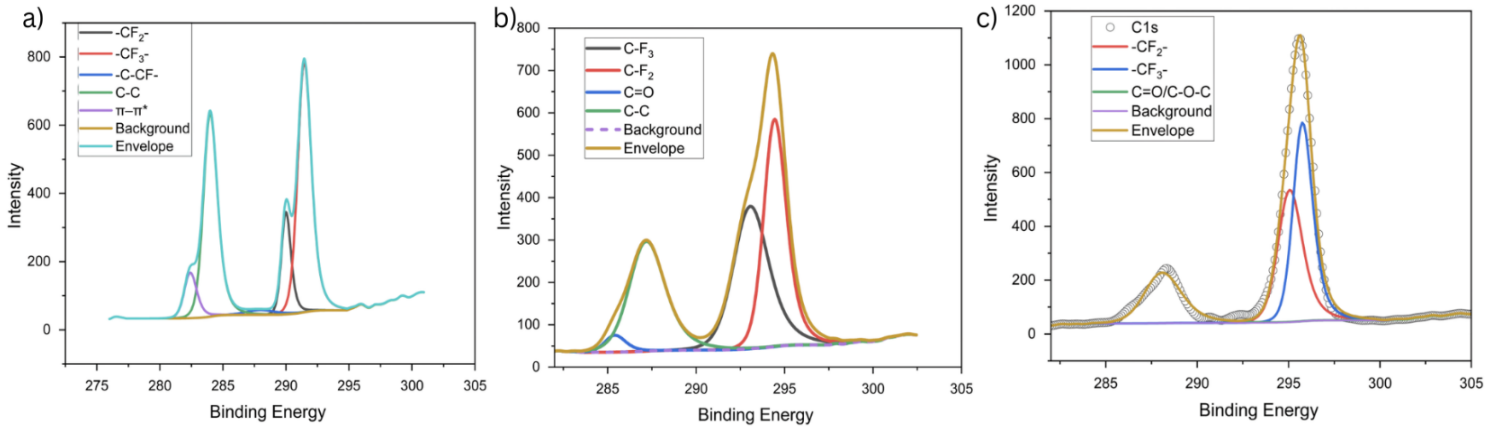

Fig 2. C 1s XPS spectra of PVC sample a) Untreated, b) Atmospheric air plasma treated, c) Low pressure Oxygen plasma treated

The C 1s XPS spectra of PTFE under untreated, atmospheric air plasma, and low-pressure oxygen plasma conditions reveal considerable surface chemical variations. In the untreated sample fig 3 (a), distinct peaks at ~289.9 eV and ~291.4 eV correspond to CF_2 and CF_3 groups, confirming the characteristic fluorinated backbone of PTFE. Minor peaks at lower energies (~282-284 eV) indicate trace levels of C-C and π-π* transitions, likely due to defects or environmental contamination. After atmospheric plasma treatment fig 3 (b), additional peaks arise, including C=O and C-C, coupled with enlarged CF_2 and CF_3 peaks, indicating partial defluorination and integration of oxygen-containing functional groups, boosting surface reactivity. Low-pressure oxygen plasma fig 3 (c) retains the dominant CF_2 and CF_3 peaks but introduces a minor peak around ~288-289 eV, attributed to C=O or C-O-C groups. This indicates more selective oxidation with minimum disruption to the polymer backbone. Overall, both plasma treatments increase surface polarity and reactivity; however, atmospheric plasma causes larger chemical alterations, whereas low-pressure oxygen plasma provides cleaner, more controlled surface modification.

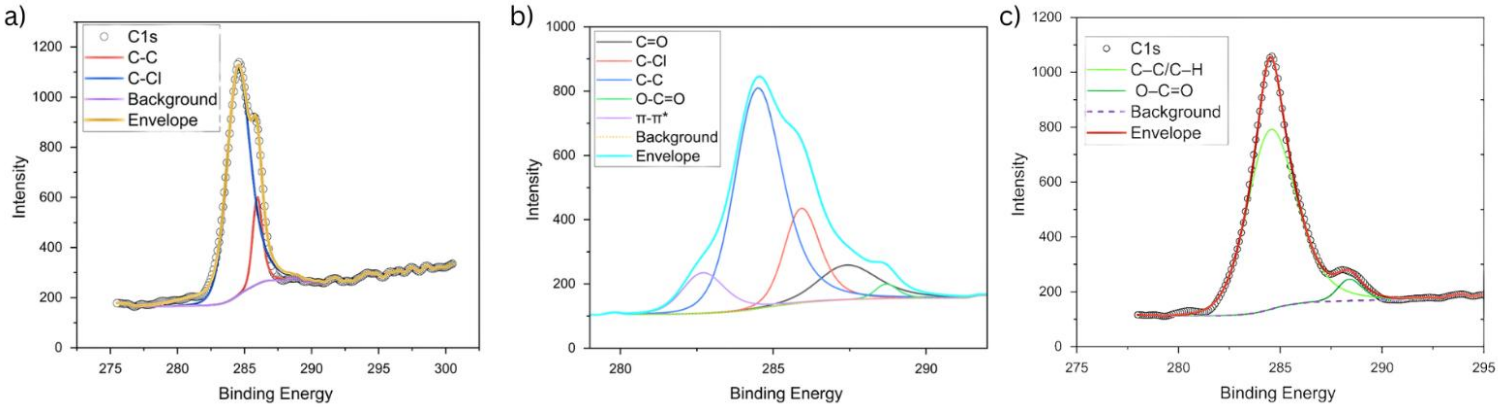

Fig 3. C 1s XPS spectra of PTFE sample a) Untreated, b) Atmospheric air plasma treated, c) Low pressure Oxygen plasma treated

3.2. Contact angle and Surface free energy measurement

The trends in contact angle and surface free energy values are consistent with the chemical changes found in the C 1s XPS spectra of PVC and PTFE following plasma treatments, as shown in tables 2 and 3, respectively. Untreated PVC and PTFE exhibit large contact angles and low polar surface energy components γ_s^P, indicating their chemically inert and non-polar nature, with C-C, C-H, and C-Cl bonds in PVC and CF_2/CF_3 in PTFE. After atmospheric air plasma treatment, XPS indicated the incorporation of oxygen-containing polar groups such as C=O and O-C=O. This resulted in a significant reduction in water contact angle and an increase in total surface energy γ_s^T, particularly the polar component. In PVC, γ_s^P,remained constant (~26.98 mJ/m²), but γ_s^D increased, indicating more physical roughening and minor polar oxidation. In PTFE, an increase in γ_s^D and a minor decrease in γ_s^P suggest partial defluorination and minimal oxygen uptake. Low-pressure oxygen plasma increased γ_s^P in PVC by 114.03 mJ/m² due to substantial oxygen incorporation (confirmed by a dominating O-C=O peak in XPS), resulting in a significant decrease in water contact angle (23.7°). The surface of PTFE remained fluorinated but displayed enhanced polarity (γ_s^P = 0.23 mJ/m²), with minimal oxidation. Overall, plasma treatments improve surface wettability by boosting polar surface functions, with low-pressure plasma providing more targeted chemical activation, particularly for inert polymers such as PTFE, as illustrated in Fig 4. [11]-[13]

Table 2: Contact measurement using sessile drop method.

Samples	Contact Angle (θ)			
	Water		Ethylene Glycol	
	PVC	PTFE	PVC	PTFE
Untreated	82.1(±4.1)	92.9(±6.7)	53.5(±0.4)	80.7(±1.3)
Atmospheric Air Plasma Treatment	56.2(±3.3)	86.1(±4.1)	18.7(±0.3)	71.3(±6.1)
Low pressure Oxygen Plasma Treatment	23.7(±3.3)	91.8(±2.6)	60.3(±3.5)	55.4(±4.6)

Table 3: Surface free energy measured for PVC and PTFE.

Samples	Mean surface free energy (mJ/m^2)					
	γ_s^D		γ_s^P		γ_s^T	
	PVC	PTFE	PVC	PTFE	PVC	PTFE
Untreated	8.84	1.05	26.37	27.36	35.22	28.41
Atmospheric Air Plasma Treatment	20.14	36.89	26.98	2.95	47.12	39.85
Low pressure Oxygen Plasma Treatment	1.51	47.23	114.03	0.23	115.76	47.47

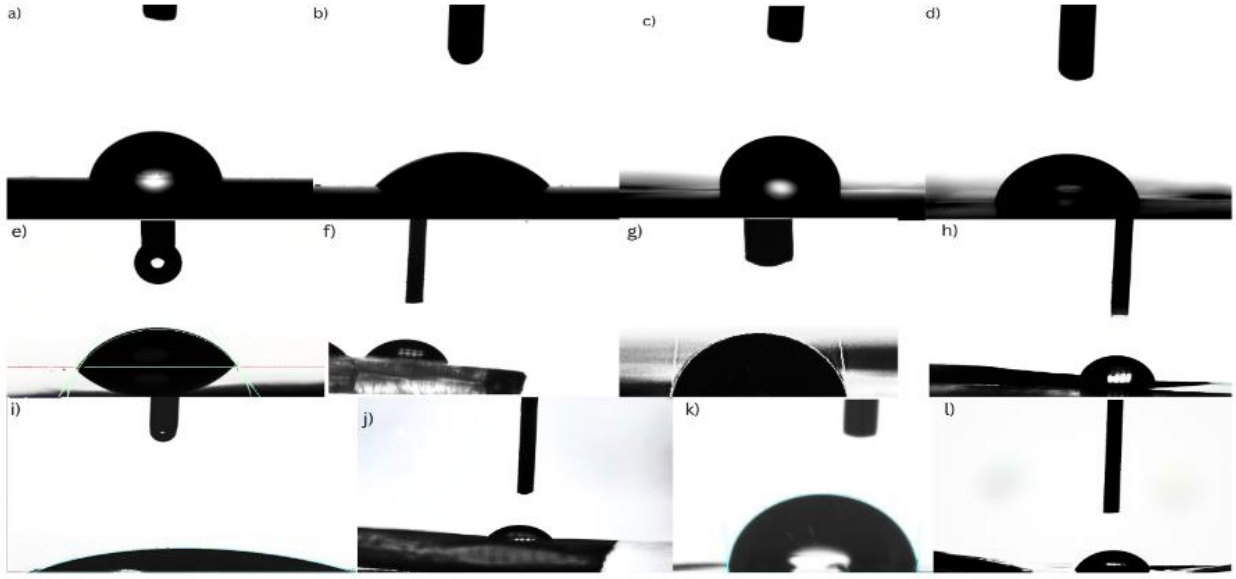

Fig 4: Contact angle of a) PVC Untreated Deionized water ; b) PVC Untreated Ethylene Glycol; c) PTFE Untreated Deionized water; d) PTFE Untreated Ethylene Glycol; e) PVC Atmospheric Air Plasma Treated Deionized water; f) PVC Atmospheric Air Plasma Treated Ethylene Glycol; g) PTFE Atmospheric Air Plasma Treated Deionized water; h) PTFE Atmospheric Air Plasma Treated Ethylene Glycol; i) PVC Oxygen Plasma Treated Deionized water; j) PVC Oxygen Plasma Treated Ethylene Glycol; k) PTFE Oxygen Plasma Treated Deionized water; l) PTFE Oxygen Plasma Treated Ethylene Glycol

3.3. Atomic force Microscope (AFM)

AFM research demonstrates considerable changes in the surface morphology of both PVC and PTFE after plasma treatments as shown in Table 4. Untreated PVC and PTFE have smooth surfaces with low roughness values (Ra = 0.446 nm and 1.214 nm, respectively), which correspond to their high contact angles and low polar surface energy, indicating chemically inert, non-polar surfaces. Both polymers exhibit a significant increase in surface roughness following atmospheric air plasma treatment (PVC Ra = 4.619 nm; PTFE Ra = 4.400 nm), which is attributable to plasma-induced physical etching and oxidation, as evidenced by the presence of oxygen-rich groups (C=O, O-C=O) in the C 1s XPS spectra. Increased roughness improves surface area, resulting in lower contact angles and higher total surface energy (γ_s^T), mostly through better wettability and mechanical interlocking potential. In contrast, low-pressure oxygen plasma treatment results in minimal surface roughness for PTFE (Ra = 0.012 nm) and a moderate increase for PVC (Ra = 0.736 nm), indicating that the treatment primarily changes chemical composition (as confirmed by the dominant O-C=O peak in XPS and high γ_s^P) rather than topography. This implies that surface energy

augmentation in low-pressure treatment is predominantly chemical, whereas in air plasma, both chemical and physical changes contribute to improved surface wettability as shown in fig 5.[14]

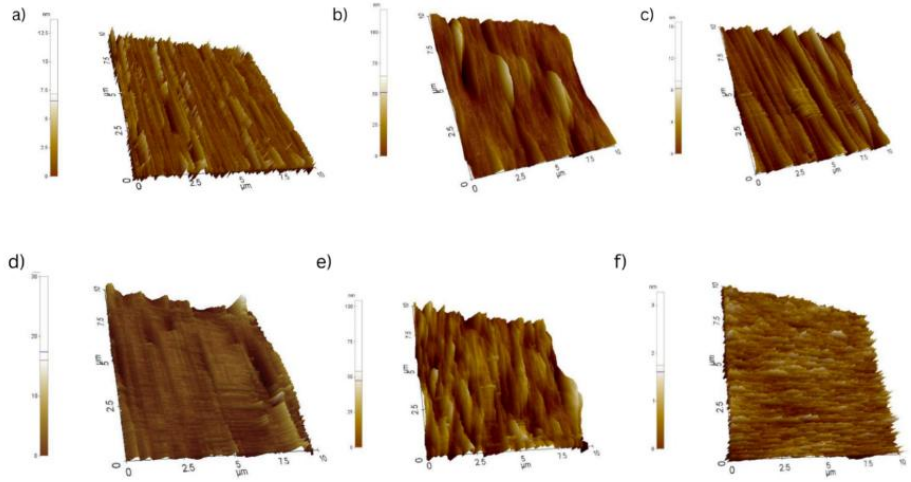

Fig 5 : Surface topology of PVC a) untreated, b) atmospheric air plasma treated, c) low pressure oxygen plasma and PTFE d) untreated, e) atmospheric air plasma treated, f) low pressure oxygen plasma

Table 4: Surface free energy measured for PVC and PTFE.

	Surface roughness parameter (nm)			
Samples	R_a		R_q	
	PVC	PTFE	PVC	PTFE
Untreated	0.446	1.214	0.611	1.745
Atmospheric Air plasma treatment	4.619	4.400	6.623	5.417
Low pressure Oxygen plasma treatment	0.736	0.012	0.919	0.015

4. Conclusion

This paper presents a novel comparative evaluation of atmospheric air plasma and low-pressure oxygen plasma treatments on two chemically different polymers—PVC and PTFE—using a wide range of surface characterization techniques. The methodology included XPS for surface chemistry, AFM for surface morphology, contact angle measurements for wettability, and an Owens-Wendt analysis for surface energy. XPS results validated the successful integration of polar functional groups such as C=O and O-C=O, with atmospheric plasma producing broader oxidation and low-pressure plasma allowing for more selective functionalization, especially in inert PTFE. Contact angle data revealed increased wettability in both materials, with the most significant improvement in PVC treated with low-pressure plasma, which also had the highest polar surface energy. AFM research revealed that atmospheric plasma-treated samples had higher surface roughness due to physical etching, but low-pressure plasma had smoother surfaces, indicating chemically driven surface activation. Overall, the results show that atmospheric plasma undergoes both chemical and physical changes, but low-pressure plasma provides a more controlled and clean chemical treatment. These findings are useful for choosing optimal surface activation procedures based on polymer type and application requirements.

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