

Article

Polyimide Reinforced with Graphene/Metal Oxide Nanocomposites: Surface Degradation Study Under Atomic Oxygen

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Abstract

Atomic oxygen in low Earth orbit erodes polyimide, increasing surface roughness and degrading performance. The reactive species scission polymer chains and remove surface material, exposing fresh sites that accelerate further attack and disrupt thermal, electrical, and mechanical functions. In this paper, we evaluate nanoscale reinforcements of polyimide with graphene and metal oxides under controlled atomic oxygen exposure equivalent to 145 days at a 550 km orbit. Graphene with a thickness of few nanometers and particle size less than 2 μm , and metal oxides zirconia, zinc oxide, and titania with particle size less than 100 nm were investigated. Hybrids containing graphene plus metal oxide at a 1:1 ratio and a total loading of 0.75 wt% increased roughness relative to neat polyimide, with graphene-zirconia showing a rise of +121 percent, graphene-zinc oxide +10 percent, and graphene–titania +20 percent. The behavior is consistent with agglomeration, incomplete dispersion, and interfacial mismatch that hinder uniform blocking of atomic oxygen and limit formation of protective oxygenated groups. In contrast, single-filler composites at 0.75 wt% reduced average roughness, with graphene lowering S_a by about 59 percent, zirconia by about 51%, titania by about 47%, and zinc oxide by about 47%. Varying graphene loading from 0.25 to 0.75 wt% diminished erosive features at the higher end, but atomic force microscopy revealed isolated tall peaks at 0.75 wt%, indicating localized restacking or agglomeration. Mechanical testing of graphene-reinforced coatings on fiberglass showed a similar trade-off, with tensile strength around 23 MPa and peak load greater than 50 N at 0.5 wt% compared to about 21 MPa and 40 N at 0.75 wt%, while strain at break remained comparable. These results define practical limits for nanoparticle reinforcement in polyimide, linking filler identity, loading, and dispersion quality to atomic oxygen response and sustained function in LEO.

Keywords: atomic oxygen; LEO; polyimide; composite



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1. Introduction

Erosion resistance is a critical factor in the longevity and reliability of spacecraft materials, as exposure to harsh environmental conditions such as oxygen atmospheres can lead to material degradation over time [1,2]. In the region of low Earth orbit (LEO), through which spacecraft and satellites navigate, atomic oxygen dominates the environmental composition, comprising 80% of the atmosphere, with nitrogen molecules representing only 20% [3]. At altitudes of 300–500 km under ultravacuum conditions of 5×10^{-10} Torr, the short-length (100–200 nm) UV radiation of 10^{-6} W/m² triggers photo-dissociation of O₂ molecules into atomic oxygen (AO) with a flux of 10^{13} – 10^{15} AO/(cm²·s) [4,5], where the mean free path is sufficiently long that the probability of recombination and formation of ozone is insignificant [5]. The kinetic energy from AO collisions with spacecraft surfaces is sufficiently intense to break chemical bonds between atoms, following which the remaining AO atoms bond with free surface atoms and oxidize the surface [6,7]. The collision energy could be up to ~4.5–5 eV/atom or higher because of the velocity of spacecraft travelling through the atmosphere (~8 km/s), also influenced by the angle between the spacecraft and incident AO, the orbital altitude of the satellite and the intensity of solar activity [3]. These interactions negatively impact the material in a number of ways [8]. The scission of chemical bonds [9] results in the development of structural defects and mass loss, contributing to mechanical failure, whereas the evolution of surface morphology rich in standing cones [9] may degrade the performance of optical and thermal control materials.

As a result of these interactions, AO exposure is considered as one of the most important lifetime-limiting factors for materials used in LEOs, especially for flexible materials, thermal blankets, and protective coatings. In addition to mass loss, AO-induced surface roughening and chemical modification significantly affect surface energy, adhesion, and barrier properties. These effects have direct consequences for erosion resistance and functional reliability. As such, limiting AO-related surface effects remains one of the biggest challenges in materials and surface science for space missions [10,11].

Polyimides (PI) such as Kapton® (Wilmington, DE, USA) are recognized for their flexibility, thermal stability, and mechanical strength, and as such are widely used in the aerospace industry to protect spacecraft [12,13]. Since its development by DuPont in the 1960s, Kapton®, which consists of pyromellitic dianhydride and oxydianiline [14], has seen wide applications in advanced engineering due to its ability to retain its mechanical and electrical properties over a very large range of temperatures [15,16], from –269 °C to over 400 °C [17], such as the extreme thermal variations encountered in space. Despite its stability, Kapton® films are susceptible to AO-induced degradation, potentially leaving the space instruments less protected [18,19]. Thus, there is a strong imperative to improve AO resistance of polyimides and other polymers used in space applications [20–22].

Nanoscale fillers have been shown to significantly improve the mechanical properties, heat resistance, flammability, and gas permeability of polymers, with a negligible increase in weight [23–25]. Among promising nanofillers, graphene is recognized for its high strength, flexibility, and electrical conductivity [26,27]. Moreover, its distinctive one-atom-thick carbon lattice structure acts as an effective shield, limiting the penetration of atomic oxygen and thus reducing the oxidation rate [28,29]. Previous studies have shown that both few-layer graphene and graphene oxide were able to improve the resistance to AO degradation in polyvinylalcohol, chosen as a model polymer matrix given the prevalence of its use to investigate the effect of graphene-type materials on the properties of the composite [30]. Flakes with a larger lateral size of 1.3 μm² were found to be more effective than smaller (~0.23 μm²) flakes, reducing the mass loss by 42% at a filler concentration of 1 wt%. A comparable reduction in the AO erosion-induced mass loss of ~60% was also reported for cellulose acetate films reinforced by 1 wt% graphene flakes with a size of ~2 μm² [31].

The reduction was attributed to shielding of the underlying polymer by graphene flakes that were driven during composite preparation to align parallel to the film surface by the combined effects of surface tension of the solution, the two-dimensional structure of the flake itself, and gravitational forces. Furthermore, a ~12% increase in the tensile strength and ~15% increase in Young's modulus was reported, attributed to the interlocking of graphene with polymer chains and increased cross-linking. Films containing 0.25 wt% showed an even higher improvement in the tensile strength of 16% compared to pure polymer, suggesting that agglomeration and restacking of flakes at higher concentrations may impede bonding between the inorganic and organic phases.

Larger graphene flakes were suggested to more effectively consume large quantities of oxygen to form corrosion-resistant epoxy groups, and to be more effective in blocking the diffusion of gases, as, unlike smaller flakes, they have a lower level of wrinkles, lattice defects (e.g., vacancies, grain boundaries) and reactive edges that could allow the passage of or support aggressive chemical reactions with AO [30]. Indeed, the energy calculations based on density-functional theory have shown that while the potential barrier for the O atom with an orthogonal trajectory through the center of an ideal six carbon ring graphene basal plane can reach nearly 22 eV, the barrier value is significantly lower for seven and eight carbon ring, at ~10 and 0.14 eV, respectively, with the latter easily overcome by AO with the average kinetic energy of 5 eV [32]. However, even in graphene with a low level of defects, prolonged AO exposure may lead to graphene fracture through a mechanism known as oxygen-driven graphene unzipping. AO has been modelled to preferentially absorb on the bridge and not the top/hollow sites of the lattice, forming an epoxy group though joining C–C bond of the six-carbon ring. Linearly aligned epoxy groups may induce large strain in the epoxy rings, ultimately breaking the C–C bonds by large stress, with the sheet remaining bridged by oxygen atoms. While the presence of an epoxy line defect reduces the fracture stress of the sheet by only ~16%, the presence of neighboring epoxy pairs lowers the activation energy for the epoxy pair to carbonyl pair from 0.76 eV to 0.45 eV, suggesting its role as an intermediate species to rapidly form carbonyl pairs with a small energy barrier, which ultimately results in the fracture of the graphene sheet [33].

Table 1. Summary of few reported graphene composites with metal or metal oxide for enhanced atomic oxygen resistance.

Sample	Atomic Oxygen Flux (atoms/cm ²)	Impact on Polyimide/Surface Degradation	Reference
Graphene-coated Cu	8×10^{15}	Multilayer graphene coated on Cu have a better anti-oxidation than monolayer graphene	[32]
Graphene flakes/SiO ₂ and Graphene flakes/Al ₂ O ₃ co-doping fillers	10×10^{20}	Decrease in the composite mass loss	[34]
Graphene-wrapped Mg-Al layered double hydroxides nanosheet coating	4.35×10^{20}	Improved resistance to both atomic oxygen and electrostatic discharge	[35]

Table 1. *Cont.*

Sample	Atomic Oxygen Flux (atoms/cm ²)	Impact on Polyimide/Surface Degradation	Reference
Graphene-modified polysiloxane	1.86×10^{20}	Enhances the resistance to AO attack	[36]
Carbon fiber-reinforced cyanate ester composites modified by POSS-graphene-TiO ₂ (PGT)	1.5×10^{21}	The PGT fillers contribute to the improved AO resistance of the prepared composites	[37]

In addition to graphene, embedding nano-sized metal oxides, such as Al₂O₃, SiO₂, ZrO₂, ZnO, TiO₂, etc., (Table 1) into polymer matrices have also been shown as an effective strategy to minimise the AO erosion. These oxides are stable under AO exposure and are non-volatile; thus, they act as passivation barriers, limiting further penetration of AO into the bulk polymer matrix. Nanoscale particles are particularly effective at lower concentrations, where they can disperse uniformly, reduce defect sites, and fill micro voids, thereby lowering the density of AO attack sites. For example, polyimide/ZrO₂ hybrid films have been shown to develop a ZrO₂-rich surface layer after AO exposure, which significantly decreases the erosion rate compared with pristine PI [38].

TiO₂-based coatings on polymer substrates have also been explored as a strategy to mitigate AO erosion. In one example, Al₂O₃-doped TiO₂ films deposited via atomic layer deposition onto polyimide yielded an erosion yield of 2.4×10^{-26} cm³/atom under a fluence of 1.4×10^{22} O atoms/cm², about 100× lower than that in the commercial bare Kapton[®] film [39]. Here, the Al doping improved film continuity by filling defect sites and promoting conformal growth, thus reinforcing the barrier against the AO attack. The dense, non-volatile TiO₂ layer blocks AO penetration and protects the underlying polymer from oxidative degradation. Already used in spacecraft thermal control coatings for its stability under irradiation and optical durability [40], ZnO is another promising AO blocker [41] as it may contribute to passivation and structural reinforcement; however, more targeted AO-erosion testing would be needed to confirm its effectiveness.

In this study, nanoparticles of zirconia (ZrO₂), titania (TiO₂), and zinc oxide (ZnO) were incorporated into the polyimide matrix, with all filler particle sizes below 100 nm. At sub-100 nm dimensions, oxide fillers exhibit high surface-area-to-volume ratios [42], enabling effective interaction with AO-generated reactive species and promoting uniform surface shielding during erosion. Nanoparticles in this size range also disperse more homogeneously within the polyimide films, minimizing agglomeration and preventing the formation of micro-scale defects that can act as preferential erosion sites [43].

This study focuses on the effect of introducing a combination of graphene (G) (thickness of a few nm and particle size < 2 µm) and metal oxides (MO) such as zirconia (ZrO₂), zinc oxide (ZnO), and titania (TiO₂) (all with a particle size <100 nm) on AO resistance of PI. In order to further investigate potential synergistic effects, these oxide nanopowders were also combined with graphene at a 1:1 ratio, and the combined additives were added to PI. The rationale for this configuration was that while metal oxides are commonly known to form stable, non-volatile passivation layers upon AO exposure, graphene introduces high thermal conductivity and chemical inertness and as such may enhance barrier uniformity and thermal dissipation. All of the fillers were incorporated at a 0.75 wt% loading,

a concentration chosen from earlier optimization tests that have proved low contents of nanoparticles are sufficient to create composites without severely impairing the mechanical stability of the polymer [44]. It is also at this level that the chances of agglomeration, common at high loadings, are minimized to realize even dispersion and reproducibility in AO exposure tests.

2. Materials and Methods

2.1. Synthesis of Polyimide Composites

The chemicals used in the preparation of the composites included 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) as monomers, dimethylacetamide (DMAc) as solvent, and graphene nanoplatelets (G), zirconium (IV) oxide (ZrO_2), zinc oxide (ZnO) and titanium (IV) oxide (TiO_2) nanopowders as additives. All chemicals were procured from Sigma-Aldrich, Victoria, Australia and zinc oxide was obtained from Fluka Analytical, Victoria, Australia with all reagents used in their original form. A two-step fabrication process was implemented to overcome solubility concerns associated with polyimide (Figure 1). First, individual metal oxides or graphene nanoplatelets, or a mixture (1:1) of metal oxide/graphene were suspended in 15 mL DMC with the view to achieve the final particle concentration of 0.75 wt% (final weight of additives) in the final composite. Separately, 1 g of ODA and 1.08 g of PMDA were dissolved in 15 mL of N,N-dimethylacetamide (DMAc) to produce poly(amicacid). Then, the nanoparticle suspension was mixed with poly(amicacid) using a magnetic mechanical mixer (Thermo Scientific Cimarec S88854100 Stirrer, Marietta, OH, USA) with a heating function. The two-stage mixing was performed to mitigate the high viscosity of the poly(amicacid)/dimethyl carbonate solution, ensuring optimal particle dispersion quality. The mixture was heated to 65 °C, with a rotation speed set at 6rpm, and the mixing duration was 15 min. The mixture was then poured into aluminum molds and kept in an oven at 60 °C for 24 h. Once the composite films formed, the molds were removed from the oven and allowed to cool under ambient conditions, at which point the films (average thickness $\approx$ 1 mm) were stored for further testing inside the mold. Hereafter, the samples are referred to as PI (for pure polyimide control), PI+MO and PI+G (for polyimide impregnated with either metal oxide or graphene particles, respectively), and PI+G+MO (for polyimide with both graphene and metal oxide particles) for all samples where the concentration of additives was kept at 0.75 wt%, and for sample sets where the content of particles was varied, the samples are denoted as, e.g., PI+0.5G to identify polyimide composites containing 0.5 wt% of graphene.

For mechanical testing, rectangular woven glass-fiber cloth pieces (purchased from Trojan Fibreglass, NSW, Australia, featuring a tightly woven construction with an areal density of 200 g·m⁻² and a width of 1000 mm) measuring 12 × 3 cm were dip-coated in the poly(amicacid) solution to ensure uniform coating of the polymer onto the fabric. The coated specimens were left at room temperature for 12 h to allow slow solvent evaporation. Thermal imidization of the polyamic acid into the final composite was carried out by heating the specimens in an oven at 60 °C for 24 h, and then allowing them to cool under ambient conditions. The coated cloth samples were subsequently used for mechanical testing. The thickness of the coatings were approximately 0.5 mm and it was noticed to be uniform across the samples.

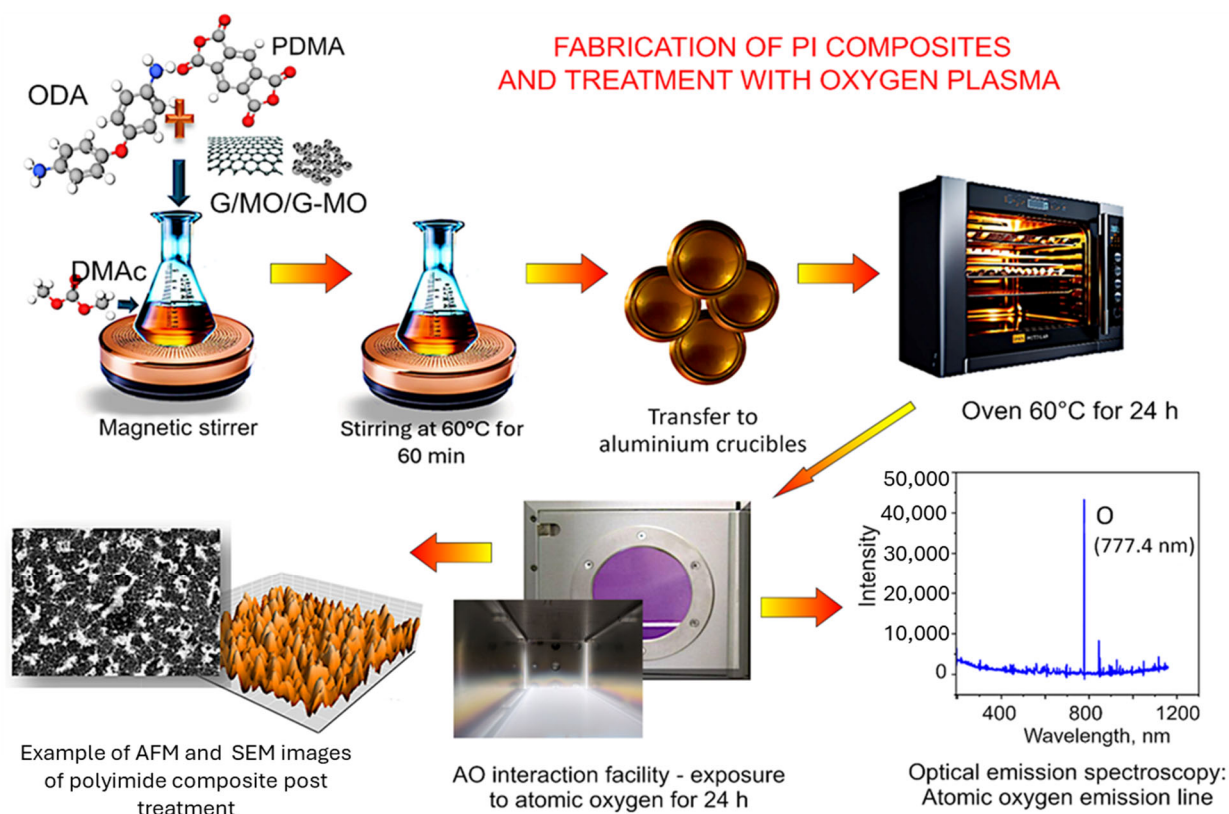


Figure 1. Schematic representation of the fabrication of polyimide (PI) nanocomposite films and their subsequent exposure to simulated atomic oxygen, equivalent to 145 days at a 550 km low Earth orbit altitude. Metal oxides, graphene nanoplatelets, or their combinations were dispersed in dimethylacetamide, blended with a poly(amic acid) precursor, cast, thermally cured, and cooled to obtain free-standing films denoted as PI, PI+MO, PI+G, and PI+G+MO with varying filler loadings and a thickness of 2 mm.

2.2. AO Exposure

To simulate LEO exposure to atomic oxygen, the atomic oxygen interaction facility developed at the National Space Test Facility (NSTF), hosted at the Australian National University, was used. In this study, the samples were exposed to atomic oxygen for a total time of 24 h (6 h per day for 4 days). The effective AO fluence was about 4.72×10^{19} atoms/cm² equivalent to around 145 days of exposure at 550 km orbit [45].

2.3. Characterization

Analysis of surface features and cross-section structures of samples was carried out using the Zeiss UltraPlus FESEM (Oberkochen, Germany). In the case of surface observation, small pieces of samples were cut and affixed to stubs using carbon tape. For cross-section observations, samples were carefully broken into pieces with tweezers in either liquid nitrogen or hydrogen to avoid shear folding typically introduced by conventional cutting methods. To enhance imaging quality, all samples underwent platinum coating using the Emitech K550X Sputter Coater (Montigny le Bretonneux, France), performed in a 0.1 mbar vacuum with a deposition range of 2 mA for 2 min. The FESEM was operated at an acceleration voltage of 1 kV, with the magnification during imaging ranging from 1 k to 100 k.

Atomic force microscopy (AFM) imaging was performed using a NanoSurf AFM instrument (Liestal, Switzerland) equipped with a SICONA cantilever (North Wollongong, NSW, Australia). All measurements were conducted in contact mode, providing

high-resolution topographical maps of the sample surfaces. A Parabola FT 1 μm probe (San Francisco, CA, USA) was used and scanning size for the presented AFM image was $8.3 \mu\text{m} \times 8.3 \mu\text{m}$. Nanosurf core AFM and Gwyddion software were used to calculate different types of roughness.

Identification of functional groups was carried out using Spectrum 3 FT-IR Spectrometer from PerkinElmer (Shelton, CT, USA). The vibrations and their intensity (in terms of reflectance) were plotted against the wavenumber of light with Matlab. Infrared spectra were obtained using ATR-FTIR directly on the polyimide composite films; no KBr pellets or other dilution methods were employed.

For the thermal analysis experiments, thermogravimetric analysis (TGA), differential thermogravimetric (DTG) analysis, and DSC analysis were conducted on STA 449 F3 Jupiter[®] from Netzsch (Selb, Germany). During the experiment, the samples were exposed in an atmosphere of air and heated at constant ramp rate of $10 \text{ }^{\circ}\text{C}/\text{min}$. As the temperature increases, the samples undergo thermal reactions like glass transition, oxidation, and decomposition. The heating process continues until the temperature reaches $800 \text{ }^{\circ}\text{C}$, which is significantly higher than decomposition temperature (above $500 \text{ }^{\circ}\text{C}$) of pristine polyimide. Thermal stability, composition, kinetics and degradation pathways can be investigated with the results.

Nanoindentation tests were conducted using TI-950 Hysitron triboindenter equipped with a 3D Omni-probe. It is comprised of an optical column fitted with either a $10\times$, $20\times$, or $50\times$ objective lens, and an indentation column, which includes the diamond tip and a transducer containing a piezoelectric crystal.

Contact angle measurements were conducted using a KSV CAM200 contact angle goniometer. The contact angle was measured at different positions (up to five) on the samples. To calculate the surface energy of the samples, their contact angles were measured for two solvents: a polar solvent (water) and a non-polar solvent (xylene). The dispersive and polar components of surface energy were then obtained using the Owens, Wendt, Rabel and Kaelble (I) method, as shown in the following equation:

$$\gamma_{lv}(1 + \cos\theta) = 2\left(\sqrt{\gamma_{lv}^D \gamma_{sv}^D} - \sqrt{\gamma_{lv}^P \gamma_{sv}^P}\right), \quad (1)$$

where γ_{lv} , γ_{sv} , and θ represent the surface energy of the liquid, the surface energy of the sample, and the contact angle, respectively. The superscripts P and D refer to the polar and dispersive components, respectively, and the total surface energy of the sample (γ_{sv}) is equal with $\gamma_{sv}^D + \gamma_{sv}^P$. The dispersive and polar energy of water were considered 27.19 and 45.61 mN m^{-1} , while they were assumed 28.9 and 0 mN m^{-1} for xylene.

3. Results

3.1. Surface Changes on PI, PI+MO, PI+G, PI+G+MO Composites Post AO Erosion

Changes in surface roughness are considered as one of the most sensitive AO erosion resistance indicators [46], as AO species tend to initiate a multi-polymer-level degradation process with chain scission at surface locations of extreme reactivity, such as at surface protrusions, and at structure defects such as microscopic pinholes or scratches. This site-specific, localized attack stimulates ablation by volatile oxidation products causing a loss of mass and the formation of highly textured morphologies, often presenting like a “carpet” of microscopic needles. This nanoscale-level evolution of surface morphology, quantified by the increase in roughness parameters in the initial phases of exposure, is a more sensitive indicator of AO erosion than bulk mass loss, and therefore is an important index of material lifetime and the degradation and stability of its optical and thermal properties [47]. Materials with poor resistance to AO erosion typically exhibit increased

roughness, pitting, and fibrillation upon exposure to AO bombardment, whereas AO-resistant composites and oxide-modified films form stabilized or smoother morphologies due to the formation of protective passivation layers. Thus, measurement of surface roughness before and after AO exposure represents a quantitative measurement for the evaluation of erosion performance [48].

AFM visualization of composites surfaces after their exposure to AO shown in Figure 2 indicates that the highest AO erosion resistance is for PI+G, as verified by lowest surface roughness, with the addition of graphene into PI reducing the surface roughness by up to 60% compared with pure PI. Graphene is well known for being highly chemically inert, impermeable, and having the highest thermal conductivity, all of which help to protect against AO. Its defect-free, two-dimensional areas are an effective shield against oxygen penetration, and the high thermal conductivity helps to carry off localized AO ion-bombardment-induced heating, avoiding damage to microstructure. The addition of ZrO₂ nanoparticles reduced roughness by ~51% in exposed PI+ZrO₂ composites, showing that oxide fillers can be nearly as effective as graphene. When exposed to AO, ZrO₂ particles form a stable zirconia-rich passivation layer, which shields and prevents further surface degradation [38]. Unexpectedly, in the exposed PI+G+ZrO₂ composite, the surface roughness significantly increased, by 121%, when compared to that of the exposed pure PI samples. Rather than inducing a synergistic effect, the mixing most likely introduced heterogeneities in the form of filler agglomeration, incomplete dispersion, or interfacial incompatibility between graphene and ZrO₂. These defects served as the weak points for AO infiltration to induce cracking and irregular surface morphologies, later supported by SEM visualization [49].

Roughness was reduced by ~47% with the incorporation of ZnO filler, demonstrating a considerable improvement in AO resistance when compared to PI, though slightly less effective than ZrO₂ or G. ZnO, similar to other metal oxides, contributes to AO protection through the formation of a surface passivation layer, which limits direct erosion of the polymer matrix. However, ZnO is known to exhibit photocatalytic activity under UV irradiation, which, when combined with AO exposure, can accelerate surface degradation and reduce the protective effectiveness of the composite. PI+ZnO nanocomposites exhibit dual behavior, providing short-term barrier effects while being less durable in harsh environments compared to more chemically stable fillers such as TiO₂ or ZrO₂ [50,51]. The PI+G+ZnO possessed ~10% higher roughness compared to PI suggesting that rather than forming a homogeneous protection barrier, the mixture of G and ZnO suffered from clustering and incompatibility along the filler–polymer interface. Such agglomeration produces localized stresses and weak points, which can facilitate localized AO erosion (Table 2).

Table 2. Surface roughness parameters for pure PI and PI composites after AO exposure, including areal mean height deviation over the scanned area (S_a), average deviation along a single line (R_a), and root mean square (RMS) roughness (S_q) corresponding to the standard deviation of surface heights across the scanned area. Percentage change is expressed with respect to pure PI as control. Data obtained from AFM image scanning size of $8.3 \times 8.3 \mu\text{m}$.

Sample	Average Roughness, S_a (nm)	Arithmetic Mean Roughness, R_a (nm)	S_a (%) Difference with PI	R_a (%) Difference with PI	Root Mean Square of Height S_q (nm)
PI (control)	154.37	158.62	0	0	208.98
PI+G	62.879	41.25	−59.27	−73.99	92.199
PI+ZrO ₂	75.017	72.985	−51.41	−53.98	94.984
PI+G+ZrO ₂	341.23	293.32	121.05	84.92	493.2
PI+ZnO	81.471	64.563	−47.22	−59.30	101.12
PI+G+ZnO	170.12	282.75	10.20	78.26	235.14
PI+TiO ₂	81.151	79.16	−47.43	−50.09	102.21
PI+G+TiO ₂	185.41	100.85	−20.11	−36.42	267.29

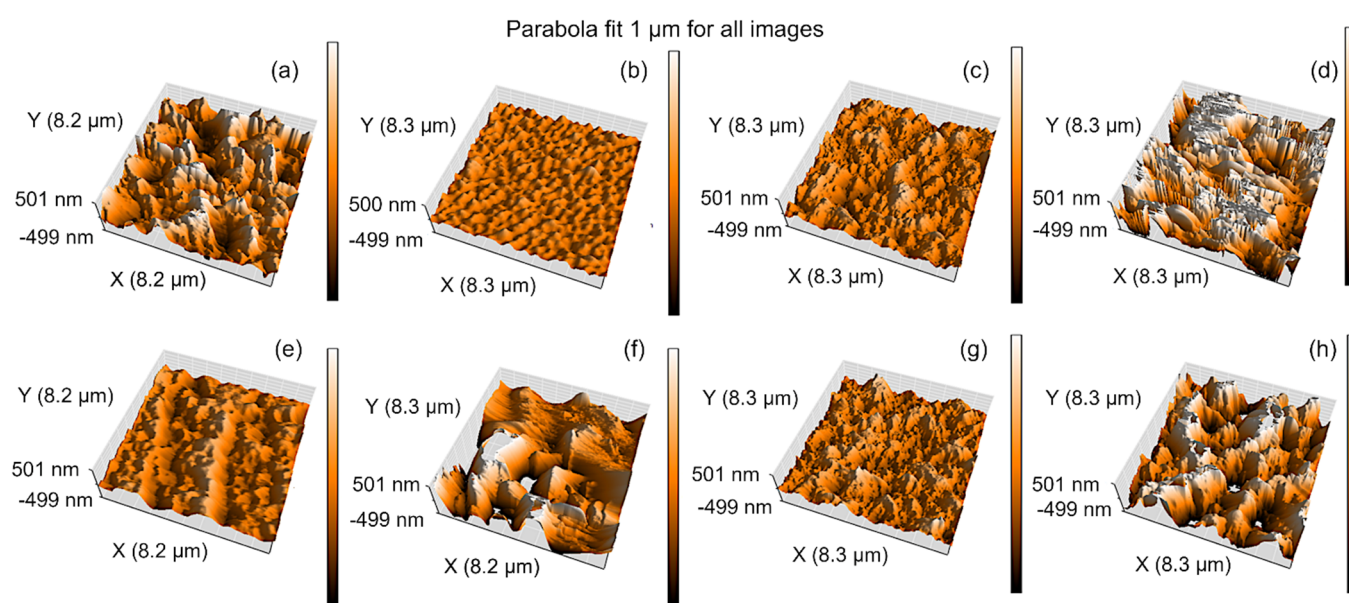


Figure 2. AFM visualization ($8.3 \times 8.3 \mu\text{m}$) and surface roughness of pure PI and composite samples after their exposure to an AO flux of $4.72 \times 10^{19} \text{ atoms/cm}^2$. (a–h) AFM image of (parabola fit $1 \mu\text{m}$): (a) pure PI, (b) PI+G, (c) PI+ZrO₂, (d) PI+G+ZrO₂, (e) PI+ZnO, (f) PI+G+ZnO, (g) PI+TiO₂, (h) PI+G+TiO₂. AFM results after AO exposure indicate that PI+G exhibits the lowest surface roughness, while ZrO₂-filled PI shows a moderate roughness reduction due to passivation. In contrast, PI+G+ZrO₂ displays an increased roughness arising from filler agglomeration and interfacial defects, consistent with SEM observations.

Roughness was also decreased by $\sim 47\%$ in PI+TiO₂ composites, which made them similar to ZnO in terms of AO erosion resistance. Under AO attack, TiO₂ particles preferentially react with incident oxygen atoms, thereby forming a stable, protective oxide surface that shields the underlying PI matrix from further erosion. Earlier NASA reports also emphasize the critical role of oxide passivation layers, noting that oxides such as TiO₂ provide durable protection when continuous and defect-free; however, these are sensitive to coating defects and interfacial instability [39,52]. The PI+G+TiO₂ composites showed an increase in roughness of $\sim 20\%$. Similar to the PI+G+ZrO₂ composites, this adverse effect can be due to filler incompatibility and poor dispersion (Figures S1 and S2). While oxide additives can form effective passivation layers, in composites containing more than one filler, their protective function can be compromised when dispersion is uneven or inter-

facial compatibility is lacking, leading to morphological instability and increased erosion susceptibility [53].

Surface roughness parameters such as maximum peak height (S_p), skewness (R_{sk}), and kurtosis (R_{ku}) are also important while characterizing the topography of material surfaces, especially after exposure to erosive environments like AO (Table 3). S_p measures the tallest vertical protrusion on the surface and is essential for identifying potential defect sites or areas prone to mechanical damage. R_{sk} analyses the asymmetry of the height distribution, distinguishing whether valleys or peaks dominate the surface morphology. Lastly, kurtosis (R_{ku}) indicates the sharpness or flatness of the height distribution, values higher than 3 indicate a surface with many sharp peaks, while values lower than 3 suggest a flatter profile. These parameters provide insight into the surface integrity and erosion behavior of materials and are widely employed in aerospace materials science for surface evaluation [54,55].

Table 3. Surface-profile statistical parameters (S_p , R_{sk} , R_{ku}) demonstrating AO-induced morphology changes in PI and PI-composite films. S_p (maximum peak-to-valley height) quantifies overall surface roughness, R_{sk} (skewness) describes profile asymmetry toward peaks or valleys, and R_{ku} (kurtosis) indicates the sharpness or spikiness of surface features. Values before and after atomic oxygen exposure highlight additive-dependent responses: reductions in S_p and changes in R_{sk}/R_{ku} reflect smoothing or passivation, whereas increases indicate erosion, crack initiation, or development of sharp asperities associated with agglomeration or interfacial failure. A neat 2D FFT indicates a well-ordered, periodic surface in the AFM image: sharp spots or rings reveal the dominant spatial frequencies and their orientations. By contrast, a stochastic noisy FFT describes irregular non-periodic surfaces with spectral power in many frequencies and producing a diffuse, cloudy pattern. These features characterize the sample morphology. Highly ordered surfaces with or regular pore arrays generate distinct FFT features, whereas disordered surfaces with randomly distributed features produce broad spectra. Fractal dimension quantifies the surface complexity change with scale. Higher values mean a more space-filling, irregular surface, while lower values indicate smoother, less complex surface morphology.

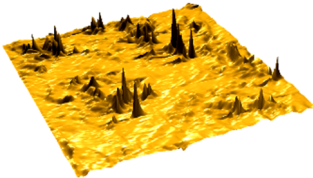
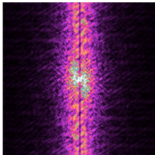
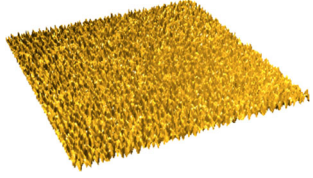
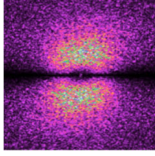
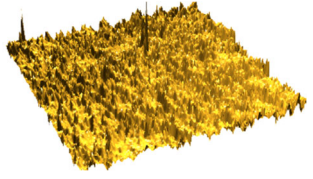
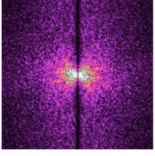
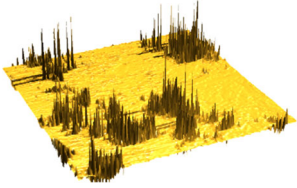
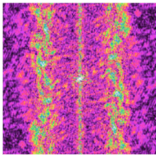
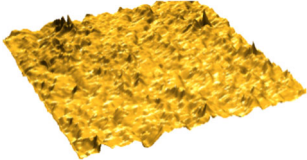
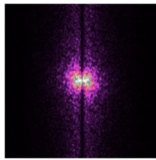
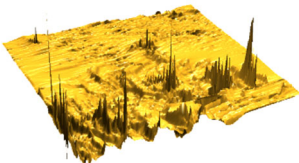
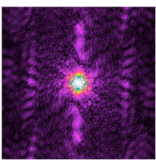
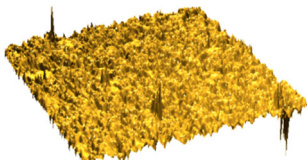
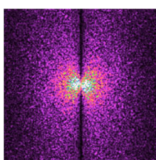
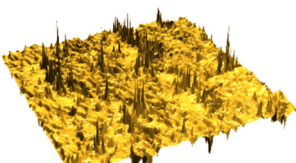
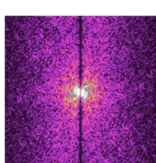
Sample	Maximum Peak Height, S_p (μm)	Skewness, R_{sk}	Kurtosis, R_{ku}	Fractal Dimension, S_f	Representative AFM Images	2D FFT Spectra
PI (control)	1.070	−1.110	11.47	2.26		
PI+G	1.392	−0.2166	−0.8187	2.71		
PI+ZrO ₂	0.491	−0.03439	0.09614	2.49		

Table 3. Cont.

Sample	Maximum Peak Height, S_p (μm)	Skewness, R_{sk}	Kurtosis, R_{ku}	Fractal Dimension, S_f	Representative AFM Images	2D FFT Spectra
PI+G+ZrO ₂	2.710	−1.105	2.217	2.27		
PI+ZnO	0.453	0.1003	0.2262	2.39		
PI+G+ZnO	1.741	−0.4407	−1.074	1.19		
PI+TiO ₂	1.048	0.3603	−0.6976	2.3		
PI+G+TiO ₂	1.295	0.2936	−0.2832	2.36		

When graphene is incorporated into PI (PI+G), there is a suppression of widespread pit formation due to graphene's high barrier properties and chemical stability. This sample showed an increased S_p of 1.39 μm , close to PI's peak height, but a near-zero R_{sk} of -0.22 and a reduced R_{ku} of -0.82 , suggesting that while individual peaks remain tall, likely due to aggregated graphene fillers, the overall surface features fewer valleys and spikes. Graphene would have suppressed widespread erosion, leading to a more balanced surface profile. The values suggest that the overall surface had less pronounced skewness and kurtosis, even though some occasional large protrusions (high S_p) persist, likely due to imperfect filler dispersion.

Samples with oxide fillers like PI+ZrO₂ ($S_p = 0.49$ μm , $R_{sk} = -0.03$, $R_{ku} = 0.10$) and PI+ZnO ($S_p = 0.45$ μm , $R_{sk} = 0.10$, $R_{ku} = 0.23$) showed lowest peak heights and near-zero skewness and kurtosis, reflecting smooth, uniform surfaces with little extreme morphology. This might be due to the formation of stable, protective layers that resist AO-induced surface degradation and prevent pit or spike formation. The presence of a high peak ($S_p = 1.05$ μm) in the PI+TiO₂ sample means that, while titanium dioxide forms a dense, AO-resistant surface lowering the overall roughening and prevents sharp valleys or spikes, some isolated tall features may persist, likely due to localized imperfections or incomplete coverage, though the overall surface is much flatter and more stable than unprotected PI. However, PI+G+MO composites showed the highest S_p at 2.71 μm and a negative R_{sk} of -1.10 ,

indicating morphological instability with deep valleys and large peaks. This suggests that combining different/dissimilar fillers can create heterogeneous microdomains producing uneven protection, thus increasing AO erosion effects locally.

For the control sample PI, AO impacts lead to random breaking of polymer chains and volatile product formation, resulting in pits, deep valleys, and sharp spikes, showing an S_p of $1.07\ \mu\text{m}$, a strongly negative R_{sk} of -1.11 , and a very high R_{ku} of 11.47 . These values collectively indicate predominant valleys and a highly spiked morphology on the surface, signifying extensive AO attack marked by pit formation and undercutting. This rough and irregular surface is typical of polymers exposed to AO erosion [56].

The SEM visualization shown in Figure 3 corresponds to the AFM roughness results, revealing distinct differences in the surface morphologies of PI and its nanocomposites after AO exposure. PI displayed characteristic fibrillation and pits due to chain scission and volatile product release, which explains its moderate roughness values. Incorporation of G, ZrO_2 , or TiO_2 individually into the composites suppressed these erosive features, producing smoother, more compact surfaces consistent with the ~ 47 – 59% reduction in roughness observed by AFM. This is attributed to graphene's impermeable basal planes and thermal conductivity, and to the passivation layers formed by TiO_2 and ZrO_2 . In contrast, PI+G+MO composite systems exhibited irregular, cracked, or agglomerated morphologies, leading to substantially higher roughness values. These findings indicate that while single-component fillers effectively enhance AO resistance, poor dispersion and interfacial incompatibility in composites containing multiple fillers introduce micro-defects that accelerate erosion.

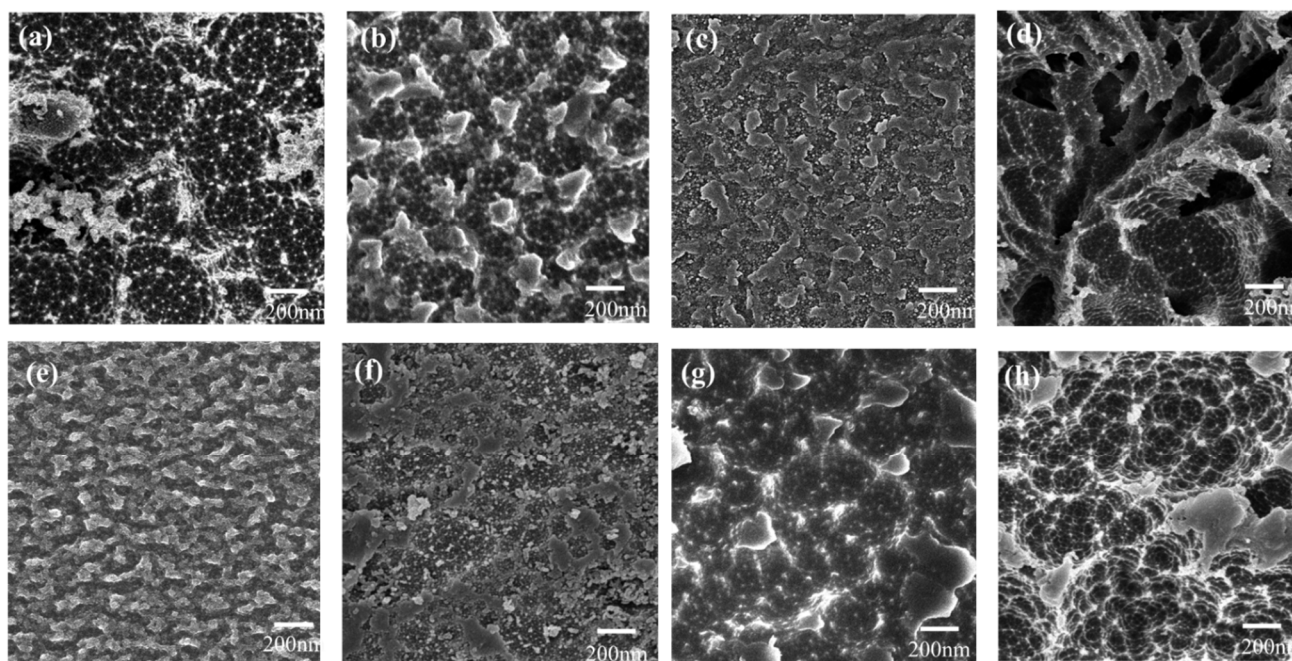


Figure 3. SEM micrographs of pure PI and PI composites after AO exposure. (a) PI, (b) PI+G, (c) PI+ ZrO_2 , (d) PI+G+ ZrO_2 , (e) PI+ ZnO , (f) PI+G+ ZnO , (g) PI+ TiO_2 , and (h) PI+G+ TiO_2 . PI exhibits fibrillation and pits typical of AO erosion, whereas PI+G, PI+ ZrO_2 , and PI+ TiO_2 show morphologies consistent with their lower AFM roughness values. Composites containing two additives exhibit cracked and heterogeneous surfaces, correlating with the increased roughness values, highlighting the detrimental effect of poor filler dispersion and interfacial incompatibility on AO resistance.

As PI+G shows the lowest average surface roughness among all composites, consistent with graphene's ability to suppress broad-scale topographical features and improve AO-erosion resistance, additional tests were conducted by varying the graphene loading from 0.25 – $0.75\ \text{wt}\%$ to evaluate how concentration affects post-AO surface morphology.

Although graphene smooths the overall surface, the maximum peak height remains higher than in control PI, most likely due to agglomerates or poorly dispersed flakes protruding above the matrix. The near-zero skewness and negative kurtosis indicate that these protrusions are isolated outliers rather than representative of the surface as a whole. Comparing the different graphene loadings therefore provides insight into how dispersion quality, flake packing, and aggregation evolve with concentration and how these factors ultimately govern the AO-modified topography.

3.2. Optimization of Graphene Loading: Influence of wt% on AO Erosion Resistance

Since PI with 0.75 wt% graphene exhibited the most significant improvement in AO erosion resistance among all composites tested, subsequent experiments focused exclusively on graphene as the reinforcing filler. This section investigates how varying graphene loading levels influence the surface roughness, morphology, and overall durability of PI under AO exposure. By systematically comparing different graphene wt% concentrations, the aim was to identify the optimal balance between enhanced erosion resistance and preservation of mechanical integrity. The following set of results emphasizes this optimization process and its implications for practical deployment of graphene-reinforced PI in LEO environments.

3.2.1. Surface Roughness and Morphology

SEM images in Figure S3 show the surface morphology of PI+G composites containing different concentrations of graphene prior to their exposure to AO. It is evident that pure PI has a relatively smooth surface, whereas the introduction of graphene at 0.25% increases the size of protrusions, resulting in the formation of larger, irregularly shaped features on the surface that can be associated with the presence of isolated graphene aggregates. At 0.5% graphene loading, the surface becomes more textured and wavier, with graphene well integrated into the polymer matrix. At 0.75% graphene, the surface becomes more granular and rougher; however, the features reduce in size, suggesting a uniform graphene dispersion, although some aggregation may still occur. Overall, increasing graphene concentration leads to a more prominent surface roughness, which could impact the composite's mechanical and thermal properties.

The SEM images of PI and PI+G composites containing different concentrations of graphene collected after their AO exposure show clear differences in surface morphologies (when compared with the images in Figure S3), with the latter surfaces having distinct cone-like structures and surrounding cavities, differing significantly from the pure PI, as shown in Figure 4. These morphological changes are driven by interactions such as chain scission and the deposition of volatile products during AO exposure [29]. AO targets the bonds in the aromatic backbones and carbon-nitrogen bonds in imide groups of the PI, leading to significant material erosion and the formation of new macromolecules [47]. Chain scissions and the bonding of functional groups (such as carbonyl (C=O), hydroxyl (OH), and carboxyl (COOH) groups) result from these attacks, leading to the formation of new macromolecules on the surface [9,41,57]. The AO attacks also generate free radicals with high energy, propagating chain scission. The interactions between AO and PI are influenced by various factors, including spacecraft operating conditions. The inclusion of different wt% of graphene nanoplatelets influences these interactions by altering the chemical pathways and distribution of reactive sites, which modulates the extent and nature of erosion [34].

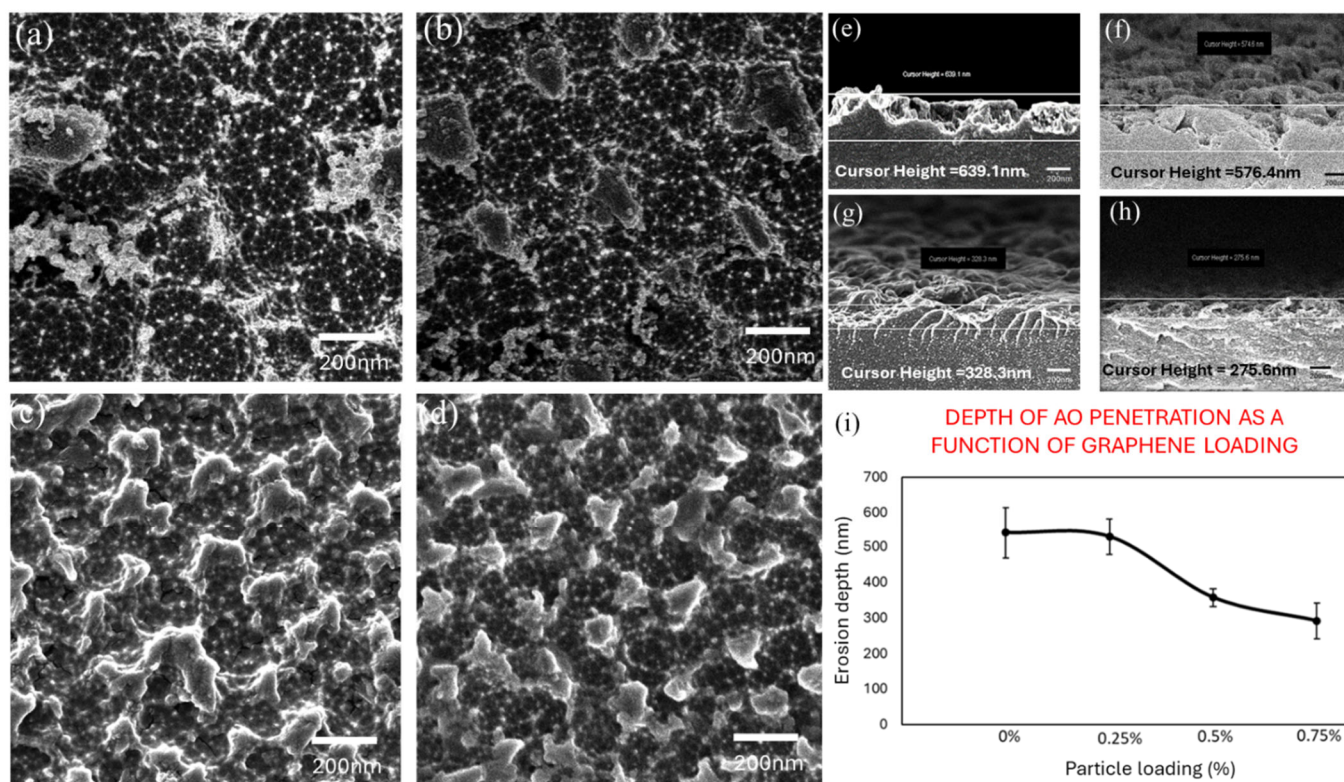


Figure 4. SEM images of PI+G composites after AO exposure. (a–d) Top view and (e–h) cross-sectional SEM images of (a,e) pure PI, (b,f) PI+0.25G, (c,g) PI+0.5G, and (d,h) PI+0.75G. (i) Depth of AO penetration derived from SEM cross-sectional images, and plotted as a function of graphene loading. Atomic oxygen exposure induces chain scission in the polyimide backbone and formation of oxygenated surface groups and volatile byproducts, with high-energy radicals propagating further degradation and driving macromolecular rearrangements at the surface; graphene additions alter reaction pathways and redistribute reactive sites, providing an impermeable, thermally conductive barrier that mitigates erosion, while oxide fillers promote surface passivation through stable oxide layers, but poor filler dispersion or interfacial incompatibility can create heterogeneities that act as initiation sites for AO-induced cracking and accelerated surface roughening.

The analysis of the cross-section of the exposed PI and PI+G composite provides further insights into the effects of graphene addition on AO erosion (Figure 4e–h). In SEM cross-sections, it is observed that the erosion caused by AO exposure resulted in the formation of free-standing cones, representing a fraction of the total erosion depth. The cones and cavities represent the increasing effect of material degradation and molecular reformation, and the length of these cones are meant to increase with increased exposure to AO fluence [47,58,59]. However, it was observed that in the composite material, GNP's presence restrains the AO's impact by distributing the erosion more evenly and possibly decreasing the peak height from 639.1 nm (0% G) to 275.6 nm (0.75% G). This results in a variation in the heights of cones and the depths of valleys, which are reflective of how GNPs alters the surface's response to AO.

The cross-section imaging also shows a notable variation in penetration depths, with PI+0.25G showing similar AO penetration depth to PI samples. In contrast, the penetration depth was notably lower for samples containing a higher fraction of graphene, with PI+0.75G showing the lowest penetration depth, indicating the protective role of higher levels of graphene against AO bombardment by limiting the access of AO species to the bulk of the polymer matrix. As previously noted, graphene flakes enhance the thermal and mechanical properties of the composite, by serving as a network to dissipate local

fluxes of thermal energy from AO bombardment and by increasing polymer cross-linking, respectively, leading to a more controlled degradation process, resulting in the formation of smaller, more uniform cone-like structures upon AO exposure. The cones are likely formed as a result of localized erosion, where graphene helps in maintaining the structural integrity of the surrounding areas. At higher loading of 0.75 wt%, there is a sufficient number of well-distributed graphene flakes to act as a physical barrier to limit AO penetration into deeper layers of the composite [60]. In space environments, AO typically carries an energy of only about 4 to 5 eV, which is considerably lower than the minimum energy barrier posed by graphene (at 5.98 eV) [9]. Thus, AO does not possess sufficient kinetic energy to overcome this barrier and penetrate the graphene layers. As a result, graphene acts as a protective shield, preventing AO from reaching materials beneath it that could be susceptible to oxidative damage. Furthermore, if an AO molecule were to attempt crossing from the top to the bottom side of graphene along a fixed vertical path, it would encounter an even higher energy barrier (up to 16.34 eV). This significantly higher barrier reinforces the protective capability of graphene, essentially acting as a nearly impassable wall against the erosive effects of AO in space [60].

AFM analysis of PI+G composited subjected to AO exposure also confirmed the positive influence of increased graphene loading on the AO erosion resistance of PI+G composite films (Figure 5). Pure PI exhibited the highest roughness values ($S_a = 154.4$ nm, $R_a = 158.6$ nm), and the corresponding SEM images displayed fibrillation and pits, confirming severe AO-induced surface degradation caused by chain scission and volatile product release. With the introduction of 0.25 wt% graphene, the composites showed a notable reduction in surface roughness values after AO exposure when compared to control, at S_a of 67.8 nm and R_a of 65.5 nm, which was consistent with the SEM observations of a denser and more uniform surface. This improvement is due to presence of well-dispersed graphene nanosheets, which act as impermeable barriers to AO and dissipate localized bombardment energy. At 0.5 wt% graphene, the surfaces of exposed composites showed a slightly higher roughness ($S_a = 76.9$ nm, $R_a = 83.2$ nm) when compared to PI+0.25G; however, both parameters were still significantly lower than that of the control PI. This may in part be due to graphene agglomeration, where poorly dispersed regions create interfacial defects that serve as preferential AO attack sites. For PI+G composites containing 0.75 wt% graphene, the roughness values post AO exposure were the lowest when compared to all other samples, at S_a of 62.9 nm and R_a of 41.2 nm. At this concentration, graphene formed an effective shield against AO erosion without significant aggregation. It is possible that at these levels, despite some agglomeration, the presence of a greater number of graphene particles is effectively blocking the penetration of AO species into the polymer matrix. The mechanisms by which graphene may positively contribute to the erosion resistance of PI composites is shown in Figure 6.

These observations show that graphene improved erosion resistance across the loadings tested, with 0.75 wt% giving the lowest surface degradation among the concentrations examined in this study. Higher graphene loadings were not evaluated here, as a previous study [44] reported that increasing graphene content beyond a certain point in polymers typically reduces mechanical strength because dispersion worsens and interfacial load transfer breaks down.

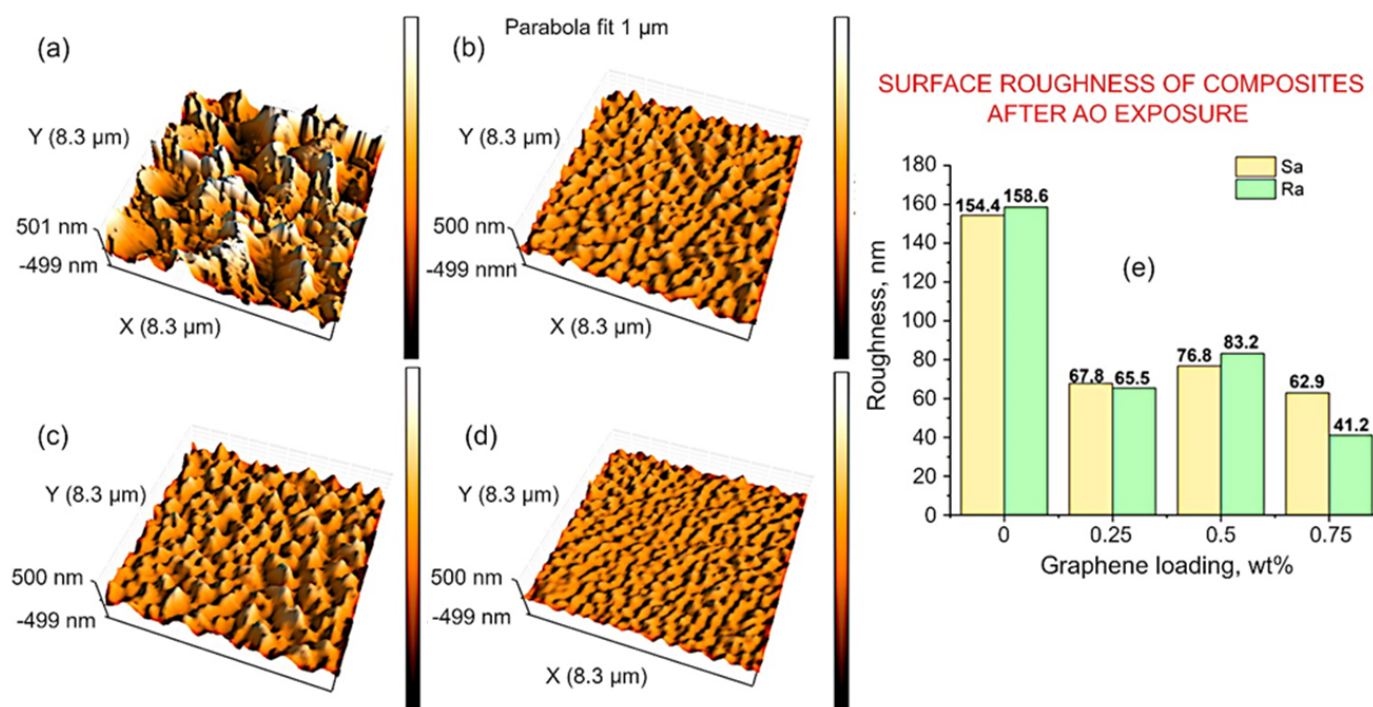


Figure 5. 3D visualization of AFM images (parabola fit 1 μm) of PI+G composites with different concentration of graphene after AO exposure: (a) PI, (b) PI+0.25% G, (c) PI+0.5% G, and (d) PI+0.75% G. (e) Surface roughness S_a and R_a of composites after AO exposure as a function of graphene loading. Atomic oxygen exposure causes chain scission in the polyimide backbone, forming oxygenated surface groups and volatile byproducts while high energy radicals propagate further degradation; graphene reduces erosion by providing an impermeable, thermally conductive barrier and oxide fillers promote passivation via stable surface layers, but poor filler dispersion or interfacial incompatibility can create defects that accelerate AO-induced cracking and roughening.

Table 4 further clarifies that graphene loading produces a non-linear response in surface topography of samples post AO erosion, governed primarily by dispersion quality rather than concentration alone. At 0.25 wt% graphene, the maximum peak height ($S_p = 1.407 \mu\text{m}$) increases and both skewness and kurtosis become strongly negative, indicating that partially dispersed platelets generate isolated peaks and deeper valleys despite the overall reduction in S_a and R_a . At 0.5 wt%, the surface shows lower S_p value ($0.751 \mu\text{m}$), near-symmetric height distribution ($R_{sk} = 0.1261$), and reduced kurtosis, showing decreased AO-driven pit formation. Increasing the loading to 0.75 wt% raises S_p again ($1.392 \mu\text{m}$) and produces slightly negative skewness with low kurtosis, reflecting the re-emergence of isolated tall features arising from agglomeration or partial restacking even though the averaged roughness metrics (S_a , R_a) continue to decrease. These findings show that while graphene increasingly smooths the overall surface with higher loading, its ability to suppress local defect formation lies within a narrow concentration window, with 0.5 wt% providing the most balanced combination of dispersion quality and AO-barrier effectiveness.

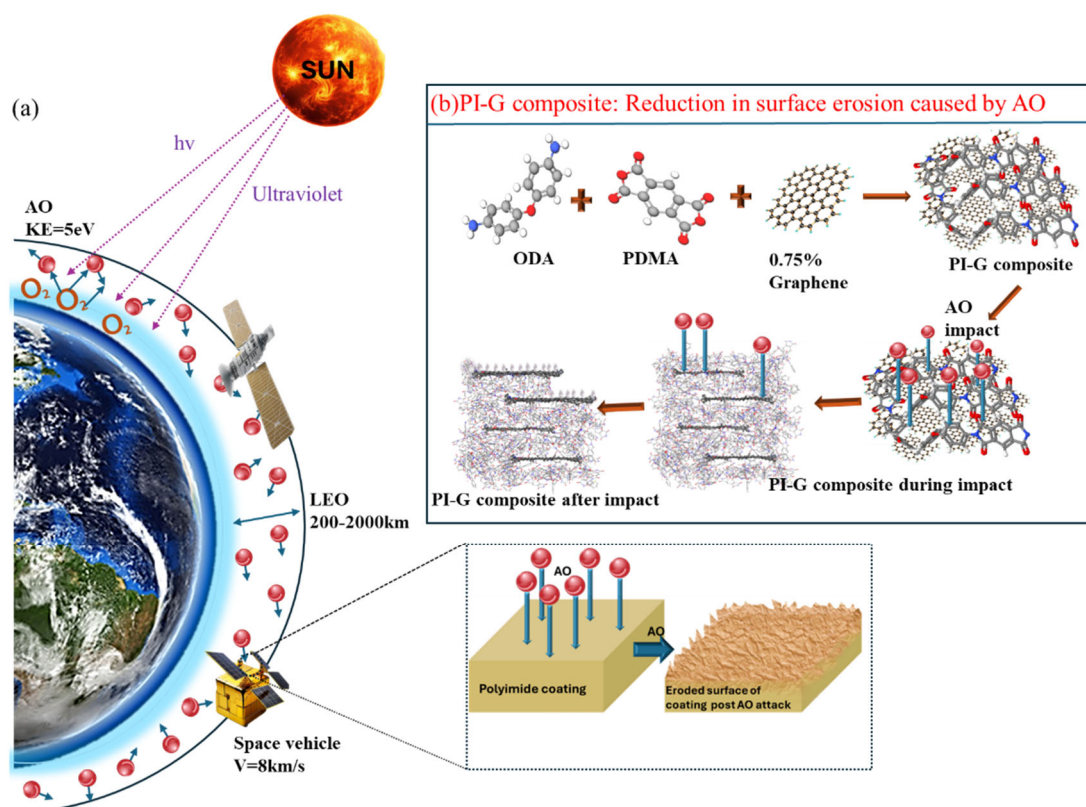


Figure 6. Schematic illustration showing (a) the formation of AO in LEO through photo-dissociation and its erosive impact on polyimide surfaces, and (b) the protective mechanism of graphene in mitigating AO damage. The impermeable basal planes and high thermal conductivity of graphene act as a barrier to AO penetration and dissipate localized heat, thereby reducing surface oxidation, roughness, and mass loss in the composite coating.

Table 4. Surface-profile statistical parameters (S_p , R_{sk} , R_{ku}) demonstrating concentration-dependent changes in surface morphology after AO exposure. These parameters change systematically with AO concentration, reflecting a shift from peak dominated to more symmetric or more extreme height distributions as morphology evolves. These parameters together quantify peak height, asymmetry, and tail weight of the surface profile and therefore provide a compact, concentration-dependent fingerprint of surface morphology.

Sample	Maximum Peak Height S_p , μm	Skewness, R_{sk}	Kurtosis, R_{ku}
0% G	1.070	−1.110	11.47
0.25% G	1.407	−0.2244	−1.089
0.5% G	0.751	0.1261	−0.4452
0.75% G	1.392	−0.2166	−0.8187

3.2.2. Thermal, Chemical, and Mechanical Characterization of PI+G Composites

While AFM and SEM analyses provide critical insight into the surface morphological changes induced by AO erosion, it is important to understand how graphene incorporation influences the thermal stability, chemical structure, and mechanical performance of PI+G composites. Since these properties directly determine the long-term durability and suitability of materials for space applications, further characterization is essential. FTIR captures the chemical and structural changes that occurred in the AO-exposed PI+G composite, while TGA and DSC reflect how different graphene loadings influenced the thermal stability and glass-transition behavior after erosion. Nanoindentation measurements similarly

show how the varying graphene content affected mechanical degradation and residual stiffness in the exposed samples, rather than the unaged polymer.

Figure 7a represents the FTIR spectra of PI+G composites reinforced with different concentration of graphene. The peak at around 724 cm^{-1} is caused by bending vibrations of the carbon-hydrogen bond (C–H) in the aliphatic moiety present in polyimide. A peak at 819 cm^{-1} is related to either linkage vibrations (C–O–C) in the polyimide polymer backbone or modifications to functional groups brought on by AO erosion. A peak at 1114 cm^{-1} indicates the C–N–C transverse stretching. All the samples show strong bands at 1375 cm^{-1} indicating the plane rocking vibrations ($-\text{CH}_3$). The region of about 1497 cm^{-1} is often associated with aromatic ring vibrations, especially with the bending vibrations of aromatic C–C bonds. The peak at 1719 cm^{-1} would suggest the presence of carbonyl groups ($-\text{C}=\text{O}$ stretching) in the material. Upon adding 0.25% graphene, the peaks of the C–O stretching frequency and C–C bonds at 1223 and 1304 cm^{-1} [61], respectively, became less pronounced, indicating that the graphene was effectively incorporated into the composite solution. Even though AO exposure usually leads to the formation of epoxy groups on the graphene lattice; there is no clear, distinct FTIR peak that strongly indicates the presence of epoxy. This is likely because epoxy-related FTIR peaks become diminished or overlapped in a polyimide-containing system by the dominant polyimide vibrations [62]. In particular, the Kapton C–O–C stretch around $\sim 1235\text{ cm}^{-1}$ can overwhelm and mask the symmetric epoxy ring breathing mode, which typically appears in the $1230\text{--}1280\text{ cm}^{-1}$ region.

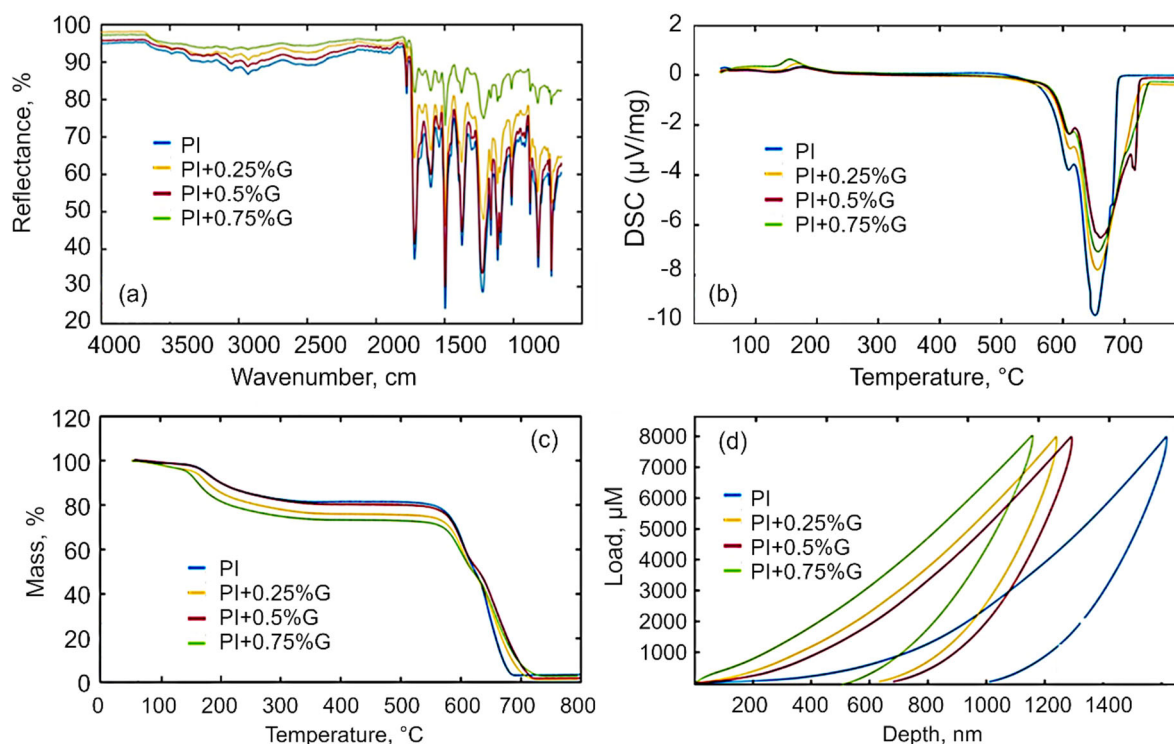


Figure 7. Thermal, chemical, and mechanical characterization of PI+G composites with varying graphene loadings. (a) FTIR spectra highlighting structural changes and polymer–graphene interactions. (b) DSC thermograms illustrating glass transition behavior. (c) TGA curves showing thermal stability and decomposition onset. (d) Loading–unloading curves during nanoindentation.

Graphene interacts weakly with PI chains through physical interactions such as π – π interactions and van der Waals force of attraction [63,64]. The interactions between graphene and polyimide may affect the distribution of oxidative damage or the formation of oxygen-containing functional groups on the surface of the composite material, which

is reflected by the changes in intensity of the FTIR spectrum. At 0.75% graphene, an enhanced intensity is observed compared to the others. This can be due to the π - π stacking or Hydrogen bonding [65] between the graphene filler and the polyimide, polarizing the functional groups of the Kapton. The 0.75% graphene concentration represents the ideal balance between having enough filler to create extensive interfacial area and maintaining good dispersion to prevent the graphene sheets from agglomerating.

Thermal stability is an important factor that must be considered when employing polymer composites in a LEO environment [66]. The thermal properties of PI+G composites after AO exposure were determined using TGA and DSC, with the results shown in Figure 7b,c. All PI+G samples exhibited thermal behavior similar to that of pure PI, including a slow mass loss starting at about 50 °C (Figure 7c). Above 150 °C, mass loss accelerated, and a steady curve is observed from 350 °C to 550 °C. The mass loss observed below 200 °C is attributed to the removal of physically absorbed moisture and trace residual solvent [67]. FTIR and DSC results confirm that the polyimide films are fully imidized prior to thermal analysis. The thermal decomposition starts at approximately 550 °C, resulting in a notable mass loss in the form of volatile products. A steep increase in mass loss is observed around 580 °C. Out of the four samples, the PI+G composite containing 0.75% graphene loses mass more slowly than the other three samples. The breakdown temperature of PI is increased by the addition of graphene, with higher loading of graphene resulting in greater improvements in thermal stability [25]. As graphene content increased, DSC measurements showed a decrease in the glass transition temperatures. A small peak appears at about 170 °C, suggesting that it is an endothermic reaction that could be related to imidization.

The loading–unloading curves during nanoindentation are shown in Figures 7d and S4. From these curves, the hardness of pure PI is estimated to be 0.16 GPa. The hardness of PI+G composites is shown to increase with graphene loading, estimated to be 0.23 GPa, 0.28 GPa and 0.36 GPa for 0.25, 0.5 and 0.75 wt% of graphene, respectively. The increase in hardness with graphene loading is consistent with the literature showing that graphene nanosheets enhance local load-bearing capacity and constrain plastic deformation through efficient stress transfer at the filler–matrix interface. Similar trends have been reported for graphene–polymer systems, where increasing graphene content leads to higher indentation hardness and improved micro-mechanical performance due to the high intrinsic modulus and aspect ratio of graphene [68,69].

3.2.3. Surface Wettability and Free Surface Energy of PI+G Composites Before and After AO Exposure

Contact angle and surface energy measurements were carried out to assess how graphene incorporation influences the wettability and surface chemistry of PI films before and after AO exposure. These parameters are important because AO erosion not only alters the surface morphology but also changes the chemical composition of polymer surfaces, often increasing polarity through the introduction of oxygen-containing groups. Post the AO exposure, the PI+G composite samples show slightly higher (nearly negotiable) contact angle values compared to the non-exposed ones, suggesting that AO exposure has made the surfaces more hydrophobic (less wettable by polar solvents). This increase in the contact angle suggests that the AO exposure altered the chemical nature of the surface, possibly by removing or changing polar functional groups on the surface of the polyimide. This is confirmed by examining the FTIR peak intensity of pure PI and PI+G composites before and after the AO exposure shown in Table 5.

Table 5. Vibrational band assignments for pure PI and PI+G composites before and after the AO exposure. Arrows show changes in the peak intensity with respect to PI control.

Group	Chemical Bond	Wavenumber, cm^{-1}	PI	PI+G	PI Treated	PI+G Treated
Imide rings	C–N–C out-of-plane bending	721	735	735↓	735↑	735↑
	Imide C–N–C transverse stretching	1112	1147	1150↓	1147↑	1143↑
	C–N–C axial stretching	1371	1334	1332↓	1329↑	1326↑
	C=O out-of-phase vibration	1712	1686	1686↓	1685↑	1682↑
	C=O in-phase vibration	1774	1761	1761↓	1756↑	1757↑
Aromatic rings	C=C stretching	1494	1520	1521↓	1521↑	1523↑
Non-cyclic	C–O–C	1234	1279	1280↓	1278↑	1276↑

↑: intensity increase compared to spectrum of PI. ↓: intensity increase compared to spectrum of PI.

PI primarily evidenced by consistent changes in absorption intensity rather than large wavenumber shifts. Specifically, nearly all characteristic bands associated with the imide rings (such as C=O stretching at 1774 cm^{-1} and C–N–C bending at 721 cm^{-1}) and the aromatic stretching at 1494 cm^{-1} exhibit a significant increase in intensity throughout the modified samples, among which the PI+G treated composite shows the highest enhancement. A general increase in intensity is indicative of strong molecular interactions, most likely π – π stacking between the aromatic rings of polyimide and the graphene sheets, which caused a more ordered structure or an alteration in the dipole moment of the functional groups and enhanced their infrared activity. Most imide and aromatic peaks, such as those assigned to C–N–C and C=C vibrations, respectively, appear with decreased intensities (↓) in PI treated with AO, reflecting oxidative degradation of the imide structure and partial ring opening. After exposure of PI+G to AO, however, most intensities increase once more (↑), indicating that graphene protects the underlying polymer chains from AO-induced erosion and preserves the structural vibrations of imide carbonyls, aromatic rings, and C–O–C linkages. From all the above spectral trends, it can be concluded that graphene increases the chemical stability of Kapton and significantly reduces AO-related chemical attack.

This hydrophobic effect seems more noticeable at high graphene concentrations (Figure 8a). With increased graphene concentrations, it is possible that a higher amount of graphene got exposed on the surface after AO treatment. Since the concentration of graphene in the composites is low, the difference between the AO-exposed and non-exposed samples is not large enough. In contrast, contact angle measurements with non-polar solvents revealed relatively minor changes upon the treatment, which evidenced only minor changes of the surface affinity towards non-polar solvents (Figure 8b).

Surface energy calculations revealed that polyimide surfaces are mostly of a dispersive nature both before and after the treatment with AO (Figure 8c). However, there was a slight increase in the polar energy post AO exposure, probably due to the presence of graphene which slightly changes surface roughness. Regardless, all samples showed the dominance of the dispersive component, which implies that the overall surface energy is more influenced by non-polar interactions, probably increased upon the addition of graphene fillers. The result indicates that AO treatment had significantly altered the surface properties of polyimide with graphene fillers, especially in terms of surface hydrophobicity and slight modification of surface energy, which are important in the application of aerospace material in harsh oxidative environments, as AO first attacks and removes the outermost low-energy functional groups, so loss of hydrophobicity is therefore an early indicator of surface oxidation and degradation [70].

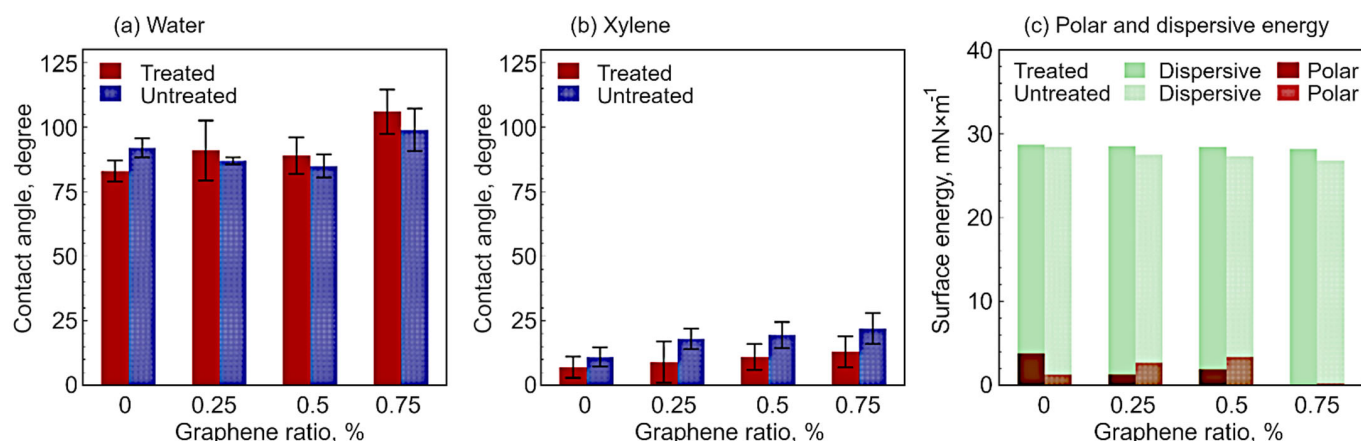


Figure 8. Contact angle measurements on PI+G composite with different percentages of graphene before and after atomic oxygen exposure: (a) water as a polar solvent, (b) xylene as a non-polar solvent. (c) Free surface energy calculated using Owens, Wendt, Rabel, and Kaelble (OWRK) method.

This behavior aligns with studies on PI films exposed to AO in previous studies where it was observed that AO exposure increases surface oxygen concentration and modifies wettability in PI films [71]. Also, in polymer surfaces, changes in the surface chemistry (through the introduction or removal of functional groups) can strongly influence wettability measured via contact angle, independent of morphological changes [72].

3.3. Mechanical Performance of PI+G Composites on Woven Fiberglass Substrates

In the final stage of this study, the investigation was extended from thin films to coated substrates to evaluate the practical performance of PI+G composites in real application scenarios. Since one of the uses of AO-resistant coatings is in astronaut extravehicular mobility units (EMUs) or space suit components during on-orbit repair works in LEO [73], it is important to assess how graphene-reinforced polyimide coatings behave when applied to structural fabrics such as woven fiberglass cloth. Fiberglass is widely used as a reinforcing textile in aerospace due to its high strength-to-weight ratio, thermal stability, and dimensional integrity [74]. However, its surface can be brittle and susceptible to erosion or cracking under harsh environments [75]. By dip-coating rectangular woven fiberglass specimens with poly(amicacid) solutions containing 0%, 0.25%, 0.5%, and 0.75% graphene, followed by solvent evaporation and thermal imidization, a uniform PI+G composite layer was formed that infiltrated the fabric microstructure. These coated substrates were then subjected to mechanical testing to determine whether the improvements in AO erosion resistance observed in free-standing films translate into reinforced composites, and to assess any trade-offs between enhanced AO durability and mechanical strength retention. This step was particularly important since increasing graphene content, while beneficial for AO resistance, can sometimes compromise strength due to filler agglomeration [44] or reduced matrix cohesion. Moreover, the S_p values in Table 3 also showed the formation of tall peaks, for higher concentration of graphene, which may correspond to poor dispersion or particle agglomeration. Therefore, the woven cloth testing provides a critical bridge between laboratory film characterization and potential application in astronaut protective systems or aerospace structural laminates.

The tensile stress–strain behavior of coated and uncoated samples shows the reinforcing effect of graphene on the mechanical performance of the coated cloth (Figure 9a). The uncoated cloth sample exhibited very low tensile strength (<5 MPa) and stepwise failure, indicating its weak load-bearing capacity. In contrast, the samples of cloth coated with pure PI showed a significant increase in tensile strength, reaching ~17 MPa, while the

introduction of graphene into the coating led to further improvements. Where cloth coated with PI+0.25G showed a slightly improved strength over cloth coated with pure PI, cloth coated with PI+0.5G showed the highest tensile strength of all samples tested, at ~23 MPa, attributed to a more effective stress transfer and particle reinforcement of the PI polymer matrix. However, the tensile strength of cloth samples coated with PI+0.75G composite was slightly lower than that for PI+0.5G, at ~21 MPa, probably due to partial agglomeration of graphene at higher loading that hinders uniform stress transfer. Although the cloth samples coated with PI+0.75G showed a lower mechanical strength, it had a slightly higher strain at break (up to ~0.1), indicating improved toughness and ductility.

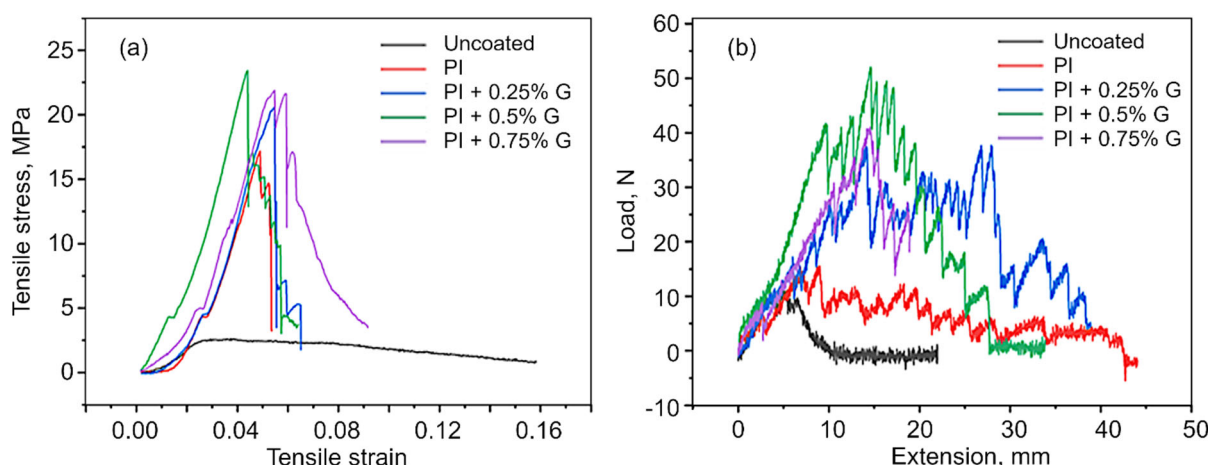


Figure 9. Mechanical characterization of PI+G-coated woven fiberglass cloth with varying concentrations of graphene additive in the PI+G composite, with uncoated cloth and cloth coated with pure PI as controls. (a) Tensile strength. (b) Tear test showing the applied load (N) versus the resulting extension (mm). All samples containing PI+G composite coatings showed an increase in both strength, toughness and tear resistance relative to the uncoated and PI-coated cloth controls.

For the tear test shown in Figure 9b, the uncoated fabric and fabric coated with pure PI both had relatively low peak load values (approximately 10 N) and premature failure. In contrast, fabrics coated with PI+G composite films exhibited increased mechanical strengthening. While the fabric coated with PI+0.5G exhibited the greatest peak load capacity, which exceeded 50 N, fabric coated with PI+0.75G showed a peak load of around 40 N. The difference in mechanical strength between PI+0.5G and PI+0.75G is probably attributed to greater levels of graphene agglomeration in the latter (Figure 10), and consequently the reduction in effective load transfer area. This property was also evident in Table 4.

Although PI+0.75G exhibits a slightly lower tensile strength than PI+0.5G, this reduction is associated with bulk composite mechanics rather than AO resistance. Atomic oxygen erosion is a surface-driven phenomenon controlled by near-surface chemistry and morphology, whereas tensile strength reflects bulk filler dispersion and interfacial load transfer. At higher filler loadings, localized agglomeration can reduce mechanical strength without compromising surface shielding effectiveness. Consequently, variations in tensile strength do not directly correlate with AO protection performance in the present system. Considering the overall performance, specifically better AO erosion resistance along with the symmetric mechanical profile, the PI+0.75G presents the best multifunctional performance of all PI+G samples tested in this study.

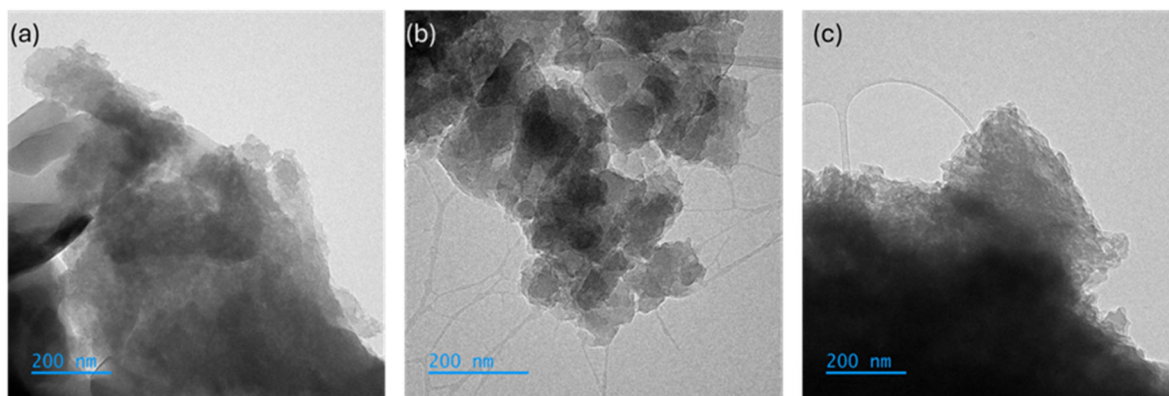


Figure 10. TEM images of PI-G nanocomposites with graphene loadings of (a) 0.25 wt%, (b) 0.5 wt%, and (c) 0.75 wt%. The 0.25 wt% sample shows relatively uniform graphene dispersion with minimal aggregation, the 0.5 wt% sample exhibits partial sheet overlapping and localized graphene-rich domains, and the 0.75 wt% sample displays pronounced restacking and aggregation. Scale bar is 200 nm.

4. Conclusions

This research investigated the AO erosion resistance of PI and its composites with graphene and metal oxides (ZrO_2 , ZnO , TiO_2), and P+G+MO against simulated AO, which is a characteristic feature of LEO environments. AFM surface roughness data, supported by SEM examination, demonstrated that PI is highly susceptible to AO erosion, exhibiting fibrillation, pitting, and great increases in roughness. The composites containing more than one filler exhibited the increases in roughness, when compared to pure PI (control), after AO exposure. This behavior is attributed to agglomeration and non-uniform microstructures, which limited the ability of the fillers to provide consistent surface protection. SEM and AFM analysis confirmed the composites to be highly susceptible to AO attack, showing characteristic pitting, and large increases in surface roughness parameters.

In contrast, composites containing a single filler showed improvements relative to PI. PI+G reduced average roughness by nearly 60%, while ZrO_2 and TiO_2 decreased roughness by approximately 50%. The surface-profile statistics further clarified these differences: PI+ ZrO_2 and PI+ ZnO showed near-zero skewness and low kurtosis indicating symmetric height distributions with minimal sharp features and suggesting uniform nanoparticle dispersion and stable oxide surface formation. PI+G also yielded reduced average roughness; however, the negative kurtosis and isolated high peak values at certain loadings reflect the presence of occasional tall peaks associated with platelet restacking or incomplete dispersion. Nonetheless, the overall height distributions remained less spiked than those of control PI, indicating suppression of widespread pit and cone formation.

The influence of graphene concentration was further examined in PI+G films with loadings from 0.25–0.75 wt%. While average roughness decreased with increasing graphene content, the AFM peak-height parameters demonstrated that isolated tall features reappeared at higher loadings, which might be due to localized agglomeration. Mechanical testing of these composites coated on fiberglass cloth showed that even with lower graphene additions the mechanical strength increased. The coating with 0.5 wt% graphene displayed the highest tensile strength of all concentrations tested, whereas at 0.75 wt% graphene, the tensile strength was lower than the 0.5 wt% composite but still comparable to, the PI control coating. Contact-angle and surface-energy measurements before and after AO exposure indicated only minor wettability shifts.

Overall, the results demonstrate that both graphene and metal oxide fillers enhance the AO-erosion resistance of polyimide relative to PI control, with their distinct surface-

profile signatures governed by dispersion quality, filler geometry, and microstructural uniformity. These findings define the performance limits of the specific compositions examined here and provide guidance for designing PI-based materials intended for LEO-relevant environments.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/polym18040522/s1>; Figure S1: TEM Images of (a) PI+ZrO₂ and PI+G+ZrO₂, Figure S2: Raman Spectra of PI+ZrO₂ and PI+G+ZrO₂ composites, Figure S3: SEM images of pure PI and PI+G composites prior to AO exposure, Figure S4: Displacement vs. load curves for PI+G composites with a different concentration G.

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