

Impact of ultraviolet radiation on graphene structure and PnBMA-graphene antistatic coating

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Abstract

The influence of prolonged ultraviolet (UV) irradiation on the structural and functional properties of graphene deposited on copper, silicon, and poly(butyl methacrylate) (PnBMA) substrates has been investigated. Using Raman spectroscopy, it was shown that UV exposure induces various types of defects, the nature of which is determined by both the substrate type and the number of graphene layers. It was established that for the transferred PnBMA/Gr1 and PnBMA/Gr2 coatings, a significant increase in specific surface resistance is observed after irradiation, with more pronounced degradation of conductivity being characteristic of the PnBMA/Gr2 sample with fewer graphene layers. It is important to note that despite the increase in resistance, its values for all studied "graphene-PnBMA" coatings remained within the antistatic range (10^4 – 10^{12} Ω /sq) throughout the experiment. The incorporation of commercial graphene nanoparticles into the PnBMA matrix (NP-Gr/PBMA) significantly enhances stability: the composite maintained antistatic properties (resistance of 2–3 k Ω /sq) even after 168 h of irradiation. A critical effect of UV exposure is the transition of the coating surfaces from a hydrophobic to a hydrophilic state due to the photo-oxidation of graphene, which was particularly pronounced in the PnBMA/Gr1 sample. The results demonstrate that the stability of graphene-containing coatings under UV irradiation is determined by the number of graphene layers and the properties of the substrate.

Keywords

graphene, UV radiation, photodegradation, surface resistance, hydrophobicity, polybutyl methacrylate (PnBMA), Raman spectroscopy

1. Introduction

The rapid development of polymer science has revolutionized materials science, leading to the widespread use of polymers in industries ranging from household packaging to the aerospace industry. However, their application under direct sunlight remains limited due to a critical vulnerability: photodegradation under prolonged exposure to ultraviolet (UV) radiation [1]. Processes involving UV-induced chain scission and oxidation reactions compromise mechanical integrity and accel-

erate material failure [2]. To address this problem, the potential of using UV stabilizers [3, 4], protective coatings [5], and reinforcement with nanomaterials [6–8] has been explored. Among the latter, the integration of graphene – a two-dimensional carbon lattice known for its exceptional electrical, thermal, and mechanical properties – into polymer matrices is emerging as a promising approach for enhancing service life [9], as well as for imparting functional characteristics [10]: inducing significant surface conductivity [11] or superhydrophobicity [12].

Graphene-doped composites can exhibit surface resistance values ranging from $10^4 \Omega/\text{sq}$ to $10^{12} \Omega/\text{sq}$, which is a critical threshold for application as anti-static coatings [13]. Such coatings are indispensable in electronics manufacturing, where electrostatic discharge poses a risk to sensitive components [14], and in the automotive industry for reducing dust accumulation on surfaces [15].

Reducing surface dust accumulation by imparting anti-static properties is also used for self-cleaning coatings for solar modules [16]. Superhydrophobic coatings can also be used for such purposes [17]. Despite these advantages, the long-term stability of graphene-polymer composites under UV irradiation remains a limiting factor. Recent studies show that UV radiation can induce structural changes in graphene, such as oxidation or bond scission, due to its high chemical reactivity and large surface area [18]. This can degrade graphene's conductivity, as defective regions reduce electron mobility [19], and alter the surface chemical properties by replacing hydrophobic sp^2 -carbon domains with polar oxygen-containing epoxy or hydroxyl functional groups [20].

Poly(methyl methacrylate) (PMMA) is used for self-cleaning coatings for solar cells [21, 22]; however, like most polymers, it is susceptible to photodegradation [23].

Given the limited availability of methyl methacrylate due to its inclusion in the list of precursors, an interesting alternative is butyl methacrylate, from which poly(n-butyl methacrylate) (PnBMA) can be synthesized.

Our research focuses on studying defect formation in the graphene structure under UV exposure and its effect on surface resistance and hydrophobicity, as well as evaluating the influence of graphene on the degradation of PnBMA.

2. Materials and methods

Graphene was synthesized using the chemical vapor deposition (CVD) method with acetylene as the carbon

precursor on two different copper foil substrates. The resulting graphene films (designated Gr/Cu-1 and Gr/Cu-2) were characterized by Raman spectroscopy to confirm layer uniformity and defect density.

A layer of poly(n-butyl methacrylate) was applied via spin-coating (2000 rpm, 60 s) onto the copper substrates with deposited graphene. The copper foil was subsequently etched in a 0.1 M ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) solution, leaving behind graphene/PBMA films (designated Gr/PnBMA).

The Gr1/PnBMA film was transferred onto a silicon substrate (SiO_2/Si). The supporting PnBMA layer was dissolved in an acetone bath (purity 99.8%, 30 min, 50°C), resulting in graphene directly adhering to the silicon surface (designated Gr/Si).

Commercially available graphene nanoparticles (17 wt.%) were incorporated into the PnBMA matrix using solution blending in acetone (stirring for 24 h). The resulting composite (designated NP-Gr/PnBMA) was applied via drop-casting onto glass slides and cured at 80°C for 2 h.

The samples (Gr/Cu-1, Gr1/PnBMA, Gr2/PnBMA, Gr/Si, and NP-Gr/PnBMA) were irradiated in a UV chamber equipped with UV-B lamps (wavelength range: 280–315 nm) at a power of 15 W. This type of investigation allows for accelerated aging assessment of the material under UV exposure and conforms to the ISO 4892-2016 standard. The temperature was maintained at 70°C using a calibrated heating stage. The exposure time was 72 h for Gr/Cu, Gr/PnBMA, and Gr/Si, and 168 h for NP-Gr/PnBMA. Aging of the polymer matrix itself was also conducted in this chamber for 72 h.

All samples were analyzed using a Raman spectrometer ($\lambda = 532 \text{ nm}$, $100\times$ objective, spot size $5 \mu\text{m}$). The intensity ratio of the D and G peaks (I_D/I_G) was calculated to quantify the defect density.

Static water contact angles were measured under standard conditions (ISO 19403-1:2022). Drops of deionized water were deposited on the sample surface using a precision syringe.

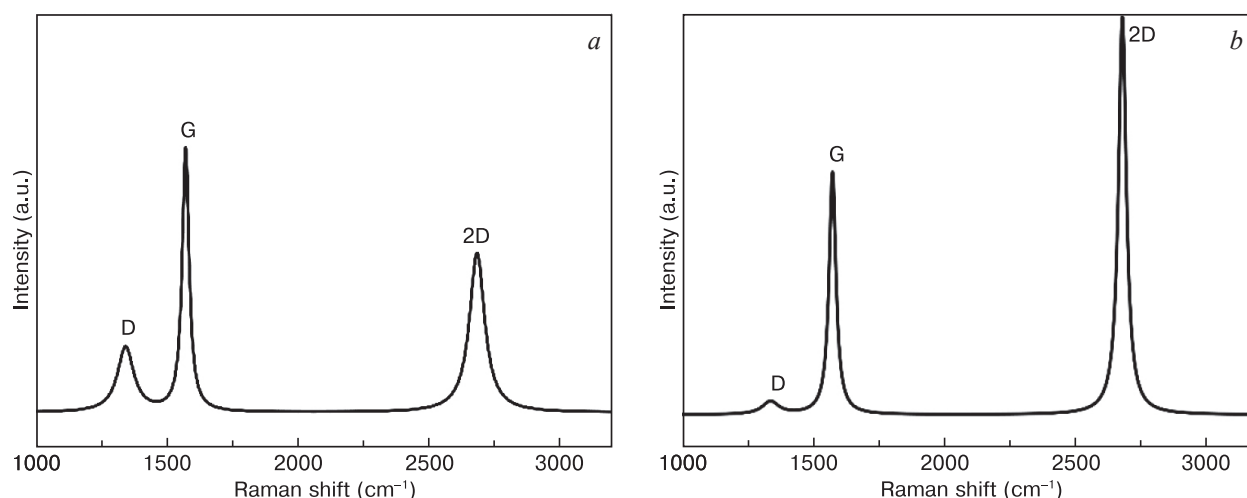


Figure 1. Raman spectrum of graphene on copper substrate Gr/Cu-1(a) and Gr/Cu-2 (b)

The surface conductivity of samples on polymer substrates (Gr1/PnBMA, Gr2/PnBMA, and NP-Gr/PnBMA) was measured using a four-point probe method (Keithley 2450 SourceMeter).

3. Results and discussion

Figure 1 shows the Raman spectrum of graphene grown by CVD on copper substrates. The spectrum of Gr/Cu-1 (Fig. 1a) exhibits a prominent 2D peak ($\sim 2700\text{ cm}^{-1}$) and a minimal D peak intensity ($\sim 1350\text{ cm}^{-1}$), confirming the presence of multilayer graphene with some initial defect density. The intensity of the 2D peak in Gr/Cu-2 is more pronounced than in Gr/Cu-1, indicating that it has fewer layers than Gr/Cu-1 and a lower defect concentration.

After exposure, the Gr/Cu-1 sample (Fig. 2b) shows the appearance of a D' peak ($\sim 1620\text{ cm}^{-1}$). The intensity ratio $I_D/I_{D'}$ of 2.45, which is below the threshold of 3.5 for vacancy-type defects [19], suggests the formation of wrinkle-like defects during the UV-induced restructuring.

The enhanced intensity of the 2D peak implies a reduction in the number of layers, which is consistent with previous observations of monolayer degradation under UV exposure [18].

Figure 3 analyzes the degradation dynamics of PnBMA. The initial polymer (Fig. 3a) shows characteristic PnBMA bands, while UV irradiation (Fig. 3b) induces a new peak at 1647 cm^{-1} , indicating the formation of carbonyl groups resulting from chain scission via photo-oxidation.

For the Gr1/PnBMA (graphene-PnBMA) sample, the analysis of graphene structure degradation is challenging due to the overlapping signals (Fig. 4a) of the graphene D peak ($\sim 1350\text{ cm}^{-1}$) and 2D peak ($\sim 2700\text{ cm}^{-1}$) with the polymer's spectral bands. Only the G peak at $\sim 1583\text{ cm}^{-1}$ is distinctly visible.

After UV exposure, a new peak appears at $\sim 1647\text{ cm}^{-1}$ in the spectrum of the Gr1/PnBMA sample (Fig. 4b). The decrease in its intensity relative to the polymer peak at $\sim 1726\text{ cm}^{-1}$ suggests a partial shielding effect against UV radiation by the graphene, consistent with its role as a

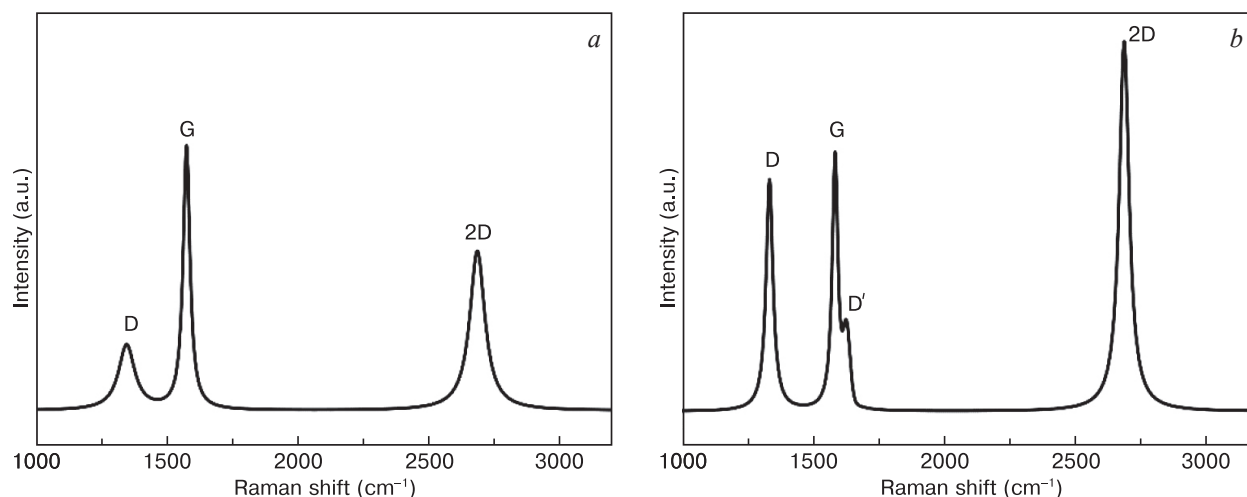


Figure 2. Raman spectra of graphene on a copper substrate before exposure to UV radiation (a) and after exposure to UV radiation for 72 h (b)

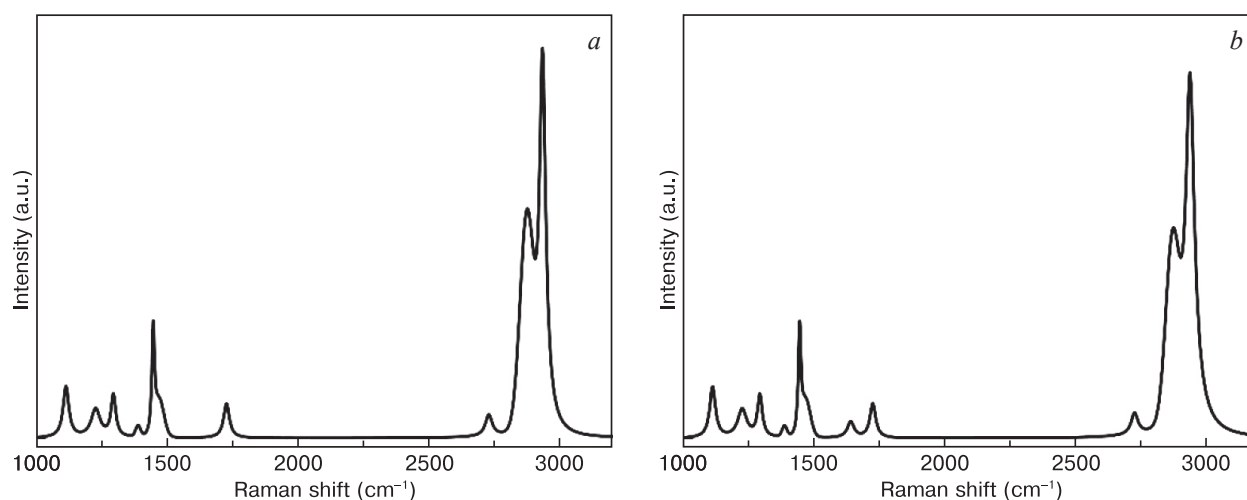


Figure 3. PBMA Raman spectra before exposure to UV radiation (a) and after exposure to UV radiation for 72 h (b)

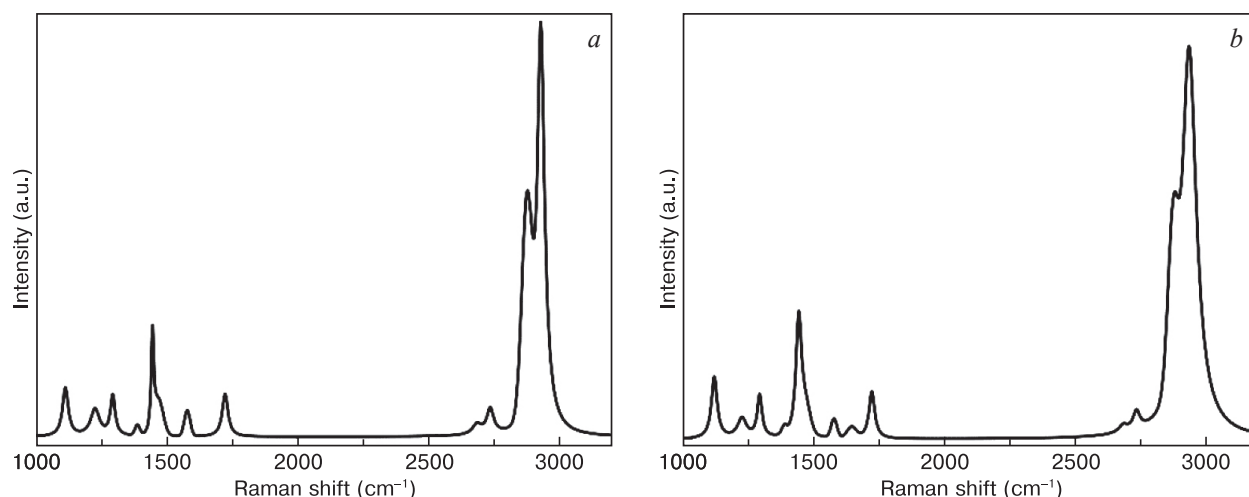


Figure 4. Raman spectra of graphene on a PBMA substrate before exposure to UV radiation (a) and after exposure to UV radiation for 72 h (b)

barrier against oxidative degradation. This observation is supported by the findings of studies [24, 25], which demonstrated that graphene protects the polymer structure from UV-induced damage.

The nature of the graphene degradation could not be determined using Raman spectroscopy due to the low intensity of the graphene peaks and the superposition of the polymer and graphene spectral signals. However, structural degradation was confirmed by the change in specific surface resistance (Figs 5 and 6).

The more pronounced decrease in conductivity for PnBMA/Gr-2 compared to PnBMA/Gr-1 suggests a UV-induced degradation mechanism that depends on the number of graphene layers. This is supported by two factors: the increased surface reactivity in thinner graphene films (e.g., monolayers), where greater UV-induced oxidation disrupts the π -conjugated network, and the reduction of percolation pathways in ultra-thin films, where defect formation disproportionately affects charge transport.

These observations are consistent with the higher stability of multilayer graphene nanoparticles, whose 3D structure minimizes UV penetration and utilizes hydroxyl and carboxyl groups to passivate reactive sites.

Figure 7 shows the spectra of commercial graphene nanoparticles (17 wt.%) in a PnBMA matrix. The spectrum before irradiation (Fig. 7a) indicates the presence of thick, highly defective graphene. Notably, 168 hours of UV exposure (Fig. 7b) caused only minor changes in the spectrum. The UV irradiation led to a change in the specific surface resistance from 2 to 3 k Ω /sq. This increased stability is likely related to the presence of defects on the nanoparticle surfaces, which limits the propagation rate of further UV-induced damage.

For all PnBMA-graphene coatings, the specific surface resistance remains within the antistatic range (10^4 – 10^{12} Ω /sq). Consequently, despite the increase in defect density, such coatings retain their antistatic properties.

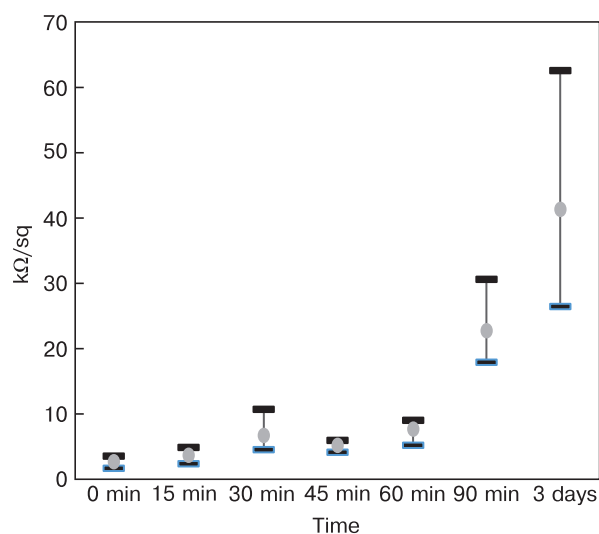


Figure 5. Evolution of sheet resistivity under UV radiation PBMA/Gr-1

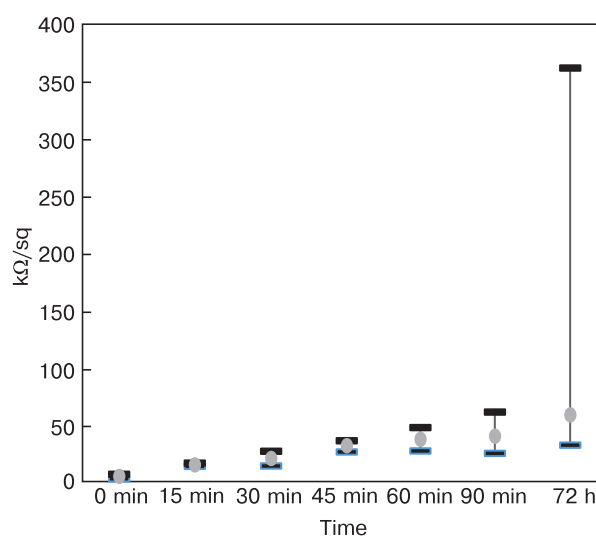


Figure 6. Evolution of sheet resistivity under UV radiation PBMA/Gr-2

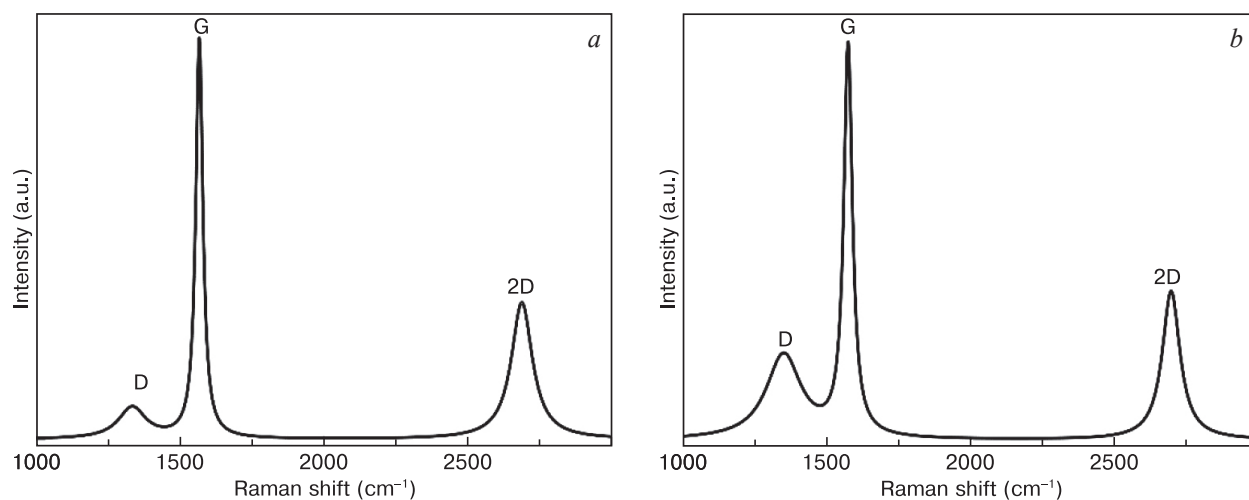


Figure 7. Raman spectra of graphene nanoparticles in a PBMA matrix before exposure to UV radiation (a) and after exposure to UV radiation for 168 h (b)

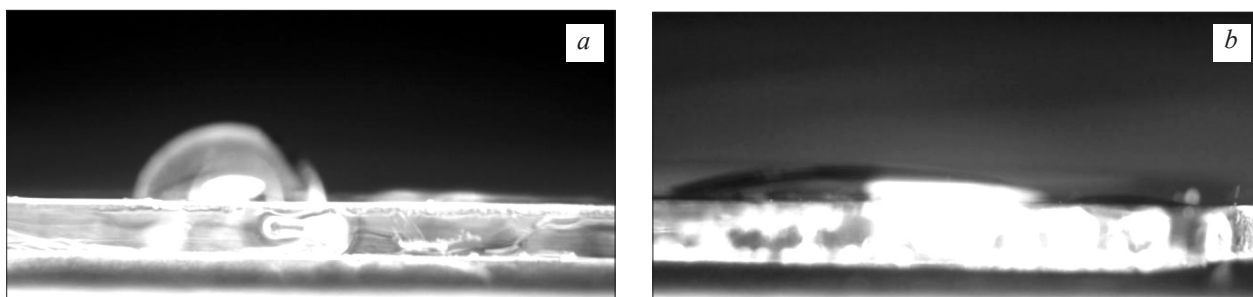


Figure 8. Water droplets on the surface of the PBMA/GR1 coating before exposure (a) and after exposure to UV light for 72 h (b)

Figure 8 shows a critical transition from hydrophobicity to hydrophilicity of the coating after 72 h of UV irradiation, demonstrated by the decreased water contact angle on the PnBMA/Gr1 sample. This transition can be explained by UV-induced functionalization of the graphene, wherein photo-oxidation introduces polar oxygen-containing groups (e.g., hydroxyl, epoxy) onto its basal plane and particle edges. These functional groups disrupt the sp^2 -hybridized carbon network, replacing hydrophobic domains with hydrophilic fragments.

Figure 9 shows the Raman spectrum of graphene on a silicon substrate after transfer. The increased intensity of the D peak and the appearance of the D' peak after 72 h of exposure indicate a rise in defect density. The intensity ratio $I_D/I_{D'}$ suggests that the defects are primarily due to the transition from sp^2 to sp^3 carbon ($I_D/I_{D'} = 23.59 > 17$). The decrease in the 2D peak indicates a transformation towards a graphite-like structure.

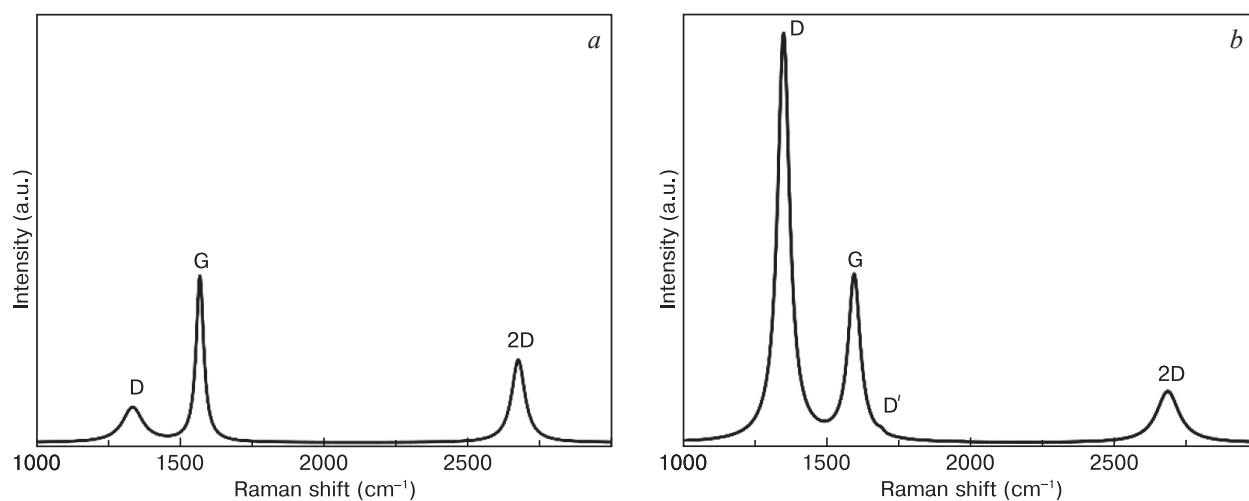


Figure 9. Raman spectra of graphene on silicon substrate before UV exposure (a) and after 72 h UV exposure (b)

Conclusion

This study demonstrates that the stability of graphene under UV irradiation critically depends on the number of its layers and the nature of the substrate, which directly affects the specific surface resistance and wettability of the coatings.

A comparison of the PnBMA/Gr1 and PnBMA/Gr2 coatings revealed a layer-dependent degradation: the PnBMA/Gr2 sample with fewer layers showed a more significant increase in specific surface resistance under UV irradiation compared to PnBMA/Gr1. This confirms the higher vulnerability of thin graphene films, where damage to the π -conjugated network has a stronger impact on conductivity. It is fundamentally important that, despite the observed increase in resistance, its values for all PnBMA-graphene coatings remained within the antistatic range (10^4 – 10^{12} Ω /sq) even after prolonged irradiation.

The most stable antistatic properties were demonstrated by the NP-Gr/PBMA composite, where the specific surface resistance changed only slightly (from 2 to 3 k Ω /sq) even after 168 h of irradiation. This is explained by the protective role of the polymer matrix and the stability of the multilayer nanoparticle structure.

A critical consequence of UV exposure for all coatings is the transition of the surface from a hydrophobic to a hydrophilic state. Using PnBMA/Gr1 as an example, a substantial decrease in the water contact angle was recorded after 72 h of exposure, which is associated with the photo-oxidation of graphene and the formation of polar oxygen-containing groups on the surface.

Thus, for designing durable graphene-polymer coatings resistant to photodegradation, it is necessary to consider both the architecture of the graphene layer (number of layers) and the properties of the substrate, which jointly determine the preservation of the material's antistatic properties and hydrophobicity. The obtained results confirm the promise of using graphene-PnBMA composites for creating antistatic coatings operating under UV load, as their conductivity remains functional even during the structural degradation of graphene. Future research could valuably assess the effect of doping graphene structures on the properties of this coating.

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