

EFFECTS OF SURFACE TREATMENT ON PROPERTIES OF GRAPHITE NANOPLATELET/EPOXY NANOCOMPOSITES

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SUMMARY: The effects of UV/Ozone treatment on the properties of graphite nanoplatelet (GNP)/epoxy nanocomposites were investigated. Several techniques have been employed to produce useful nanocomposites with uniformly dispersed GNPs, such as high shear mixing, use of dispersant, ultrasonication and UV/Ozone treatment. The UV/Ozone treatment in particular was proven to be a convenient and efficient means to improve the interfacial adhesion between GNPs and epoxy matrix. The UV/Ozone treatment modified the surface chemistry and morphology of GNPs: the insulating organic contaminants and loosely bonded weak materials were removed, and the surface roughness increased while functional groups were created on the graphite surface. All these changes improved significantly the electrical conductivity and mechanical properties of the nanocomposites.

KEYWORDS: nanocomposites, graphite nanoplatelet, UV/Ozone treatment, electrical conductivity, interfacial properties

INTRODUCTION

While many researches have been focused on the use of carbon nanotubes to produce nanocomposites, little work has been devoted towards the advantages of exfoliated graphite nanoplatelets (GNP) in composite manufacturing. Graphite possesses a very high modulus ($E \approx 1060\text{GPa}$) along its graphene plane, and has excellent electrical and thermal conductivities. These useful properties combined with very low cost, especially compared to carbon nanotube, make it a popular filler to produce conducting polymer composites for unique applications in electromagnetic interference shields and thermal conductors [1]. The nanometer-scale layered structure of graphite can be converted into GNPs with very high aspect ratios by exfoliating graphite intercalated compounds (GIC). This allows the formation of an electrical conducting network within a polymer composite with a very low graphite content, compared to many other conventional conductive fillers like carbon black, graphite and metallic particles [2].

Percolation theories are frequently used to describe a sudden transition from one behavior to another. The percolation principle has been applied to the transition between electrical insulator and conductor in polymer composites, where the fillers are the conductor and the polymer matrix is the insulator. If the volume fraction of the conductive filler is lower than a critical value, the composite behaves like an insulator. As the filler volume fraction

approaches a critical value, the composite experiences an insulator-to-conductor phase transition, at which the electrical conductivity of the composite jumps up several orders of magnitude. The critical value is referred to as the percolation threshold.

GNP/polymer nanocomposites possessing unique electrical conductivity along with balanced mechanical properties have been developed for some years. In contrast to many studies on successful fabrication of thermoplastic-based graphite composites [2~7], results on graphite composites containing thermosetting matrices, especially epoxy, have not been encouraging. Percolation threshold values of 2.5 and 1.13 vol%, respectively, for epoxy vinyl ester- [8] and epoxy-based GNP composites [9] were reported. Nevertheless, few studies have been directed towards the optimization of processing conditions and material parameters to produce nanocomposites for useful applications. The success in polymer nanocomposite processing lies in two critical aspects, namely uniform dispersion of nanofillers in the matrix material, and strong interfacial adhesion between the nanofiller and matrix resin.

In this study, several techniques including high shear mixing and ultrasonication were employed to obtain uniform dispersion of nanoparticles in epoxy-based composite fabrication. The GNPs were subjected to UV/Ozone treatment with different exposure duration to improve the interfacial adhesion with epoxy resin [10]. The electrical conductivity and mechanical properties of nanocomposites were characterized in an effort to optimize the above processing conditions.

EXPERIMENTS

Materials

The GIC containing sulfur (2.8wt%) as intercalant was supplied by Asbury Graphite Mills, USA. The epoxy material was Diglycidyl ether bisphenol A (Epon 828, supplied by Shell Chemical), with 1,3-Phenylenediamine (mPDA, supplied by Sigma-Aldrich) as the curing agent.

Preparation of Graphite Nanoplatelet

The as-received GIC was heat treated at 1050°C for 30s to prepare expanded graphite. Upon rapid heating the GIC (shown in Figure 1(a)) were expanded explosively several hundred times along the thickness direction due to the evaporation of the intercalant and the thermal shock. The expanded graphite presents a loosely-bonded, porous and worm-like rod, consisting of numerous thin graphite layers, as shown in Figures 1(b) (with a high magnification image in Figure 1(c)). The expanded graphite was immersed in acetone and sonicated using an ultrasonicator at 70 watts and 42k Hz for 8 hr to be exfoliated into the individual and/or bundles of GNP, as shown in Figure 1(d).

The thickness of the GNP was estimated to be approximately 3nm according to the specific surface area value of 338 m²/g measured by a surface area analyzer (COULTER 3100), suggesting that GNP contain multilayer graphenes even after the exfoliation. The diameter of the GNP was about 46 μm measured by a particle size analyzer (COULTER LS 230), which gave an aspect ratio of 15 x 10³, which is ten times larger than those reported in the literature [9] under the similar conditions.

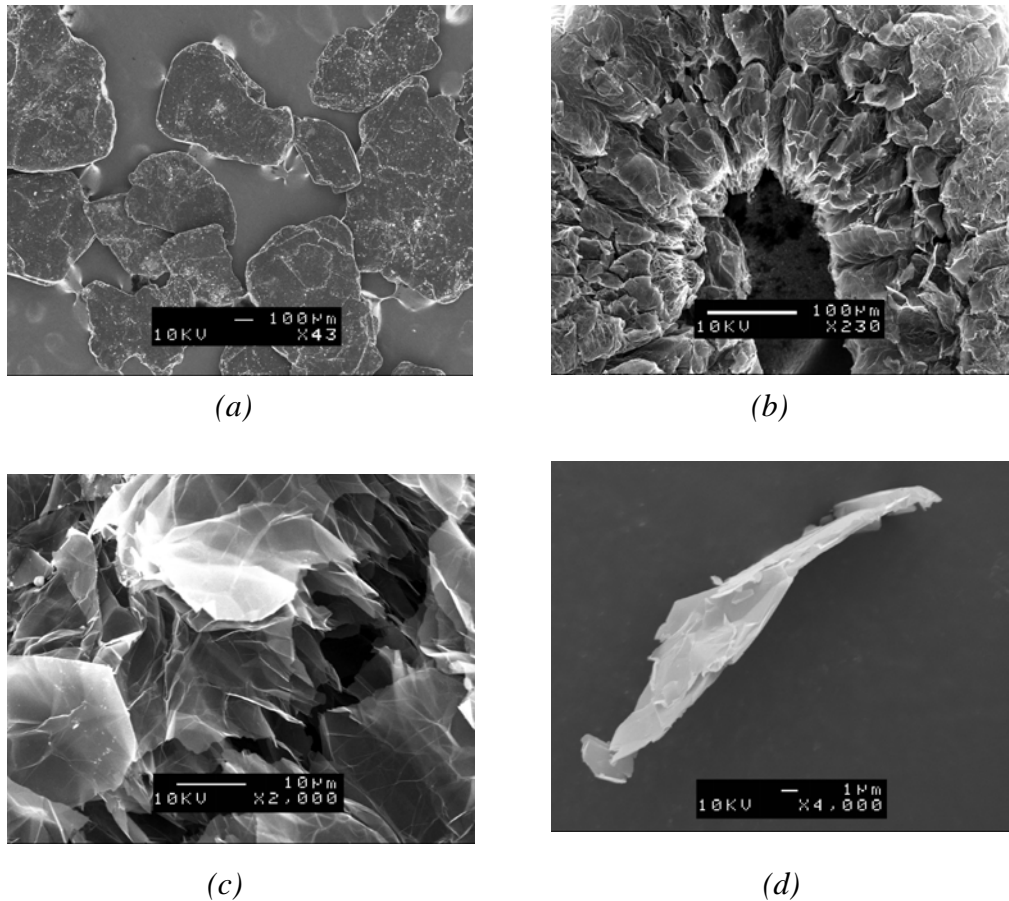


Fig. 1: SEM photographs of (a) graphite intercalated compound; (b) and (c) expanded graphite after heat treatment; (d) individual graphite nanoplatelet after sonication.

Surface Treatment of GNP

The GNPs were treated in an UVO Cleaner model 144AX-220 (Jelight Company, INC.) to improve the surface compatibility with polymer. There were two stages of treatment: UV/Ozone (UV/O) exposure using a 254nm wave length of UV light, followed by ozone exhaust. Different from the low-pressure requirements in plasma treatment, the main advantage of UV/O treatment over a plasma treatment is that the reaction occurs at ambient temperature and pressure, which can be favorably used particularly for the treatment of powder samples.

The changes in graphite surface chemistry after UV/O treatment were analyzed using an X-ray photoelectron spectroscope (XPS, Surface analysis PHI5600) with a monochromated Al-ka (1486.6 eV) X-ray source operating at 350 W (14 kV, 25 mA) in a residual vacuum of 5×10^{-9} Torr. A scanning electron microscope (Jeol-6700F) with high resolution was used to examine the changes in surface morphology after the treatment at the accelerating voltage of 5.0 kV.

Preparation of GNP/Epoxy Nanocomposites

To break the micro-scale GNP agglomerates and thus to improve the overall dispersion of the particles within the epoxy matrix, preliminary tests were conducted using a high shear mixer and a sonicator to determine optimal processing conditions. The Epon 828 monomer epoxy was diluted with acetone before adding GNPs, which was mixed using a high shear mixer for

30 min. Ultrasonication at 70 watts 42k Hz was followed to further break the micro- and submicro-size agglomerates for 30 min. The mixture was then outgassed at 80°C for two hours to eliminate the entrapped bubbles and the remaining acetone. The mPDA hardener was added into the mixture in the ratio of 14.5/100 by weight. The composite was moulded into a flat plate and cured at 80°C for 2 hr, followed by post cure at 150°C for 3hr.

Characterizations

Three-point flexure test was performed to measure the flexural properties of neat epoxy and nanocomposites according to the specification, ASTM standard D790-96. The moulded nanocomposite plates were cut into 12.7mm wide × 70mm long x 3mm thick samples, which were subjected to bending with a support span of 50mm at a constant cross-head speed of 1.3 mm/min on a universal testing machine. Five specimens were tested for each set of conditions. A scanning electron microscope (SEM, JEOL-6300) was used to examine the morphology of the fracture surfaces.

The bulk electrical resistivity of nanocomposites was measured at room temperature based on the four probe method using a Resistivity/Hall Measurement System. As the highest limit of the electrical resistivity measured by Resistivity/Hall Measurement System was $10^8 \Omega \text{ cm}$, the electrical resistivity higher than this limit was measured with a programmable curve tracer (Sony Tektronix 370A). For both cases, the moulded plates were cut into 10 mm square 1 mm thick specimens.

A transmission electron microscope (Philips CM-20) was used to evaluate the local state of dispersion of the GNP in epoxy matrix at an acceleration voltage of 120 kV. Ultra-thin samples were obtained using an ultra-microtome.

RESULTS AND DISCUSSION

Surface Chemistry and morphology of GNP

The atomic concentrations of elements obtained from the XPS analysis of GNPs are shown in Table 1. The oxygen content on the GNP surface increased significantly after 20 min of UV/O exposure. After 20 min, the oxygen content fluctuated, indicating a saturation of oxygen concentration on the GNP surface. Two reasons are considered for the saturation: firstly, the oxygen atoms are selectively reacted with the carbon atoms at the graphene edges and/or lattice defects [11]; and secondly, the chamber temperature increased with increasing UV/O exposure time, which accelerated desorption of the oxygen containing functional groups as CO or CO₂ [12].

Table 1: Atomic concentrations of GNP surface for varying UV/O exposure time (min).

Elements	UV0	UV20	UV30	UV50	UV70
C	98.2	95.1	96.8	95.5	96.9
O	1.7	4.8	3.2	4.5	3.1
Si	0.15	0.15	0	0	0
O/C ratio	1.7%	5.0%	3.3%	4.7%	3.2%

It is also noticed that Si as an impurity on the GNP surface was removed by UV/O treatment, indicating that purification is another function of UV/O treatment of GNP.

Various oxygen containing functional groups on the GNP surface were identified by means of high-resolution deconvolution of the XPS C1s peaks. The changes in chemical structure and the percentage of the corresponding functional groups are summarized in Table 2. The functional groups include hydroxyl/ether, carboxyl and carbonyl groups. UV/O exposure increased mainly hydroxyl and carboxyl groups, which can react with epoxide ring and in turn increase the interface adhesion between epoxy and GNPs [13]. It is also noted that 20 min of UV/O exposure quite sufficient to functionalize the GNP surface.

Table 2: Functional groups of GNP surface for varying UV/O exposure time (min).

Functional Groups	Position (eV)	0	20	30	50	70
C	284.6	91.0%	85.8%	85.5%	84.9%	85.5%
C-OH or C-O-C	286.5	4.9%	7.7%	7.3%	8.0%	7.7%
C=O	287.9	2.2%	2.4%	2.9%	2.6%	2.6%
HO-C=O	289.3	2.0%	4.2%	4.3%	4.5%	4.2%

UV/O treatment modified not only the surface chemistry of GNP, but also the surface morphology, as shown in Figure 2. The treated graphite exhibited a rougher surface than the untreated one because of the etching process by the atomic oxygen, which has also been observed in plasma treated graphite surface [12]. The advantage of rougher GNP surface is the facilitation of mechanical interlocking between GNPs and epoxy matrix.

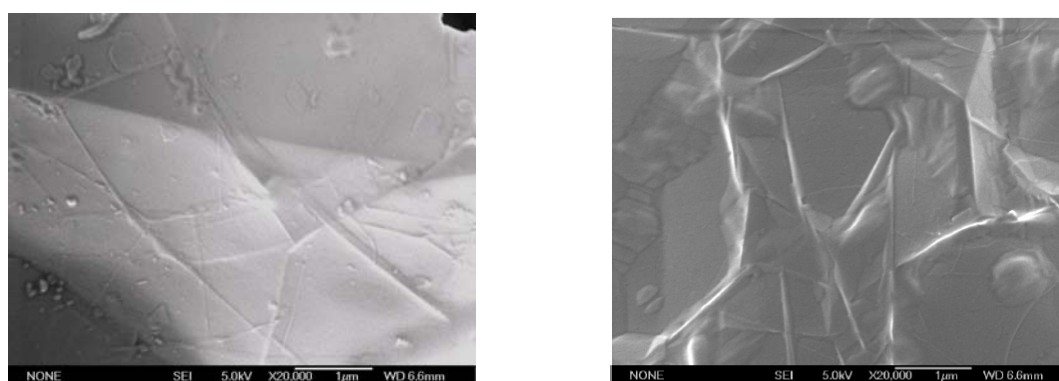


Fig. 2: SEM photographs of GNP surfaces (a) before and (b) after UV/O treatment (Scale bar = 1 μm)

Electrical Properties

The electrical resistivity of the nanocomposites without and with 20min UV/O exposure was plotted as a function of GNP content, as shown in Figure 3(a). To determine the percolation threshold, data points on the Log (resistivity) vs. GNP content curves were defferntiated. The GNP content correspondiong to the highest slope was taken as the percolation threshold, as shown in Figure 3(b). The percolation threshold was found 1wt% (0.5 vol%), which is almost half the value reported for the same composite system previously [9]. Although the UV/O treatment changed little the percolation threshold, it decreased the absolute value of electrical resistivity for a given GNP content, especially when the GNP content was close to the percolation threshold value. The % improvement of electrical conductivity by 20 min UV/O treatment increased from 30% to 95% with increasing the GNP content from 0.2% to 2%. For the nanocomposite with 4% GNP, the electrical resistivity was similar between the samples with and without UV/O treatment. Increasing difficulties involved in uniformly dispersing

higher GNPs contents were mainly responsible for the insensitivity of UV/O treatment on electrical conductivity of nanocomposites.

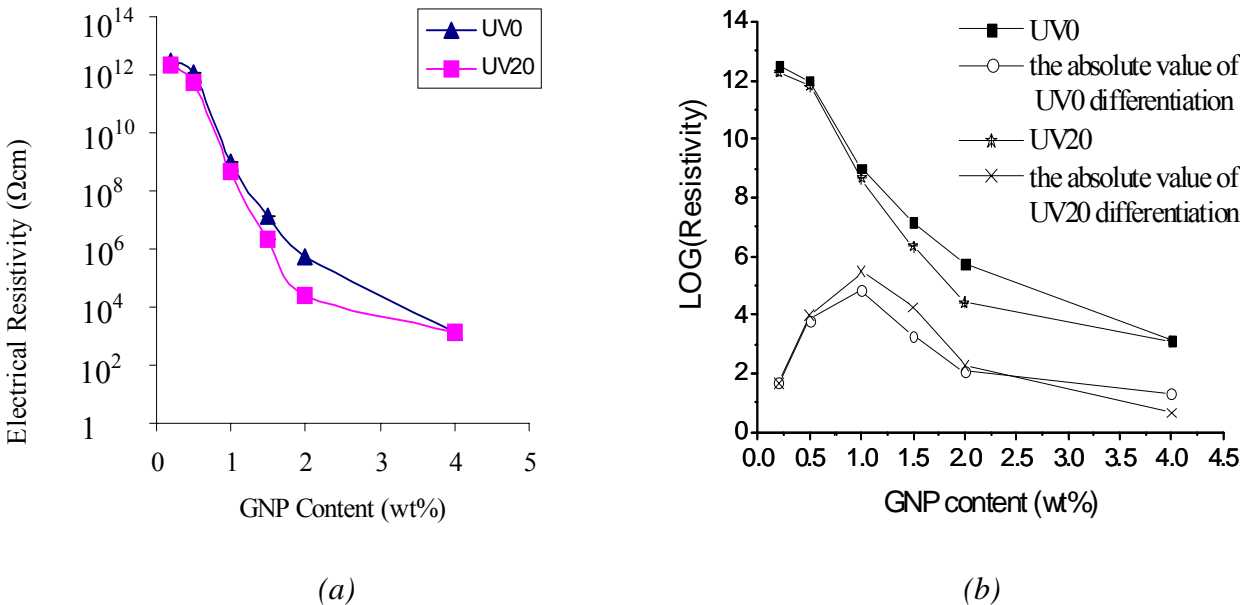


Fig. 3: Electrical properties of the GNP/epoxy nanocomposite: (a) electrical resistivity vs. GNP content; (b) calculation of percolation threshold

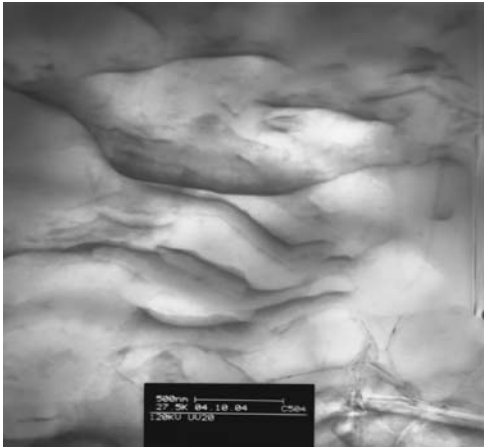


Fig. 4: TEM micrograph of GNP/Epoxy nanocomposite (scale bar=500nm)

One of the most well established conducting mechanisms in graphite nanocomposites is the conductive network formation [2~7]. Important factors determining the successful network formation include conducting filler content, filler aspect ratio and the degree of dispersion of fillers within the matrix. The UV/O treatment improved the dispersion of GNPs because of the steric and electrostatic repulsion of the functional groups on the GNP surface [14], so that the possibility of forming electron pathways increased even with the same GNP content and aspect ratio after UV/O exposure. The state of GNP dispersion in the nanocomposite can be seen from Figure 4. The dark lines represent GNP bundles consisting of a few layers of

individual graphene, indicating that dispersion was quite satisfactory although they were not completely exfoliated. The electrical resistivity value of nanocomposite with 2% treated GNPs was $2 \times 10^4 \Omega \text{ cm}$, which is far below the value $5 \times 10^7 \Omega \text{ cm}$ reported previously [9], for a similar GNP/epoxy nanocomposites with the same 2 wt% GNP content.

Mechanical properties

Flexural properties of GNP/epoxy nanocomposites with and without UV/O treatment are plotted against GNP content in Figure 5. With increasing the GNP content, the flexural modulus increased consistently, while the flexural strength rather decreased. It is well known that a composite modulus is in general more dependent on the moduli and volume fraction of the composite constituents than interfacial properties, such as the interfacial adhesion and the stress transfer efficiency. Nevertheless, there was appreciable improvement in flexural modulus of nanocomposites due to the UV/O exposure of GNPs. The ameliorating effect of UV/O treatment was more pronounced for the flexural strength because the interfacial adhesion between GNPs and epoxy matrix played an important role in determining the composite strength. It is thought that the improved interfacial adhesion resulted from the introduction of oxygen containing functional groups and the increase of surface roughness of GNPs.

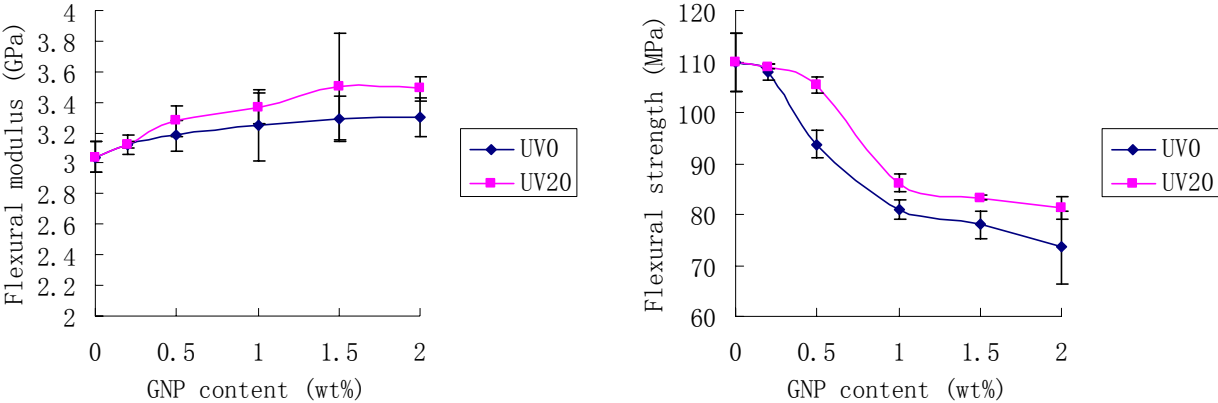


Fig. 5: Flexural properties of GNP/epoxy nanocomposites

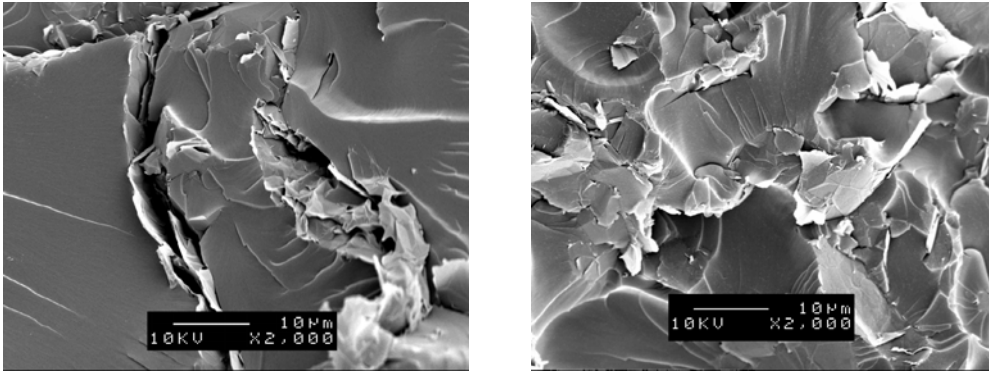


Fig. 6: SEM photographs of fracture surface of nanocomposites with (a) untreated and (b) UV/O treated GNPs

The SEM photographs of fracture surface of the nanocomposites containing 2% GNP were shown in Figure 6. The cracks along the GNP/epoxy interface indicate that the interfacial debonding is predominant between the untreated GNPs and epoxy matrix, whereas a stronger bond with the matrix is evident for the treated GNPs. These photographs further confirm the beneficial effect of UV/O treatment on enhancing the interfacial adhesion.

CONCLUSIONS

The effects of UV/O treatment on the electrical and mechanical properties of graphite nanoplatelet (GNP)/epoxy nanocomposites were studied. Several techniques such as XPS, SEM, TEM were employed to characterize the GNP powder and GNP/epoxy nanocomposites. The following can be highlighted from the study:

1. UV/O treatment introduced hydroxyl and carboxyl groups on the GNP surface, and increased the surface roughness of GNP.
2. UV/O treatment had a more pronounced effect on flexural strength than flexural modulus of nanocomposites, indicating improved interfacial adhesion between GNPs and epoxy matrix.
3. The percolation threshold of GNP/epoxy nanocomposites was about 1 wt% (0.5 vol%), benefited from the high aspect ratio and uniform dispersion of GNP in epoxy matrix, as confirmed from the TEM analysis. .
4. UV/O treatment improved significantly the electrical conductivity of nanocomposites, although it had little effect on percolation threshold. The electrical resistivity of nanocomposite with 2% treated GNPs was $2 \times 10^4 \Omega \text{ cm}$, which is several orders of magnitude lower than the reported value for similar nanocomposites.

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