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I. INTRODUCTION

Nowadays, flexible electronics offers numerous advantages such as large area production, low cost, and environmental perspectives, and it does not require high temperature processes. Plastics (both linear polymers and resins) are technologically important materials in this field because they have many useful characteristics, such as low specific weight, high strength/weight ratio, and easy processing.1–3 However, many of these synthetic materials have inherently low thermal and electrical conductivities which limit their applications. Although conductive polymers (polyaniline, poly(3,4-ethylenedioxythiophene), etc.) can be synthesized, their low mechanical/chemical performance makes difficult the industrial exploitation.4 Currently, the filling of nonconductive polymers with inert and conductive/semiconductive additives, such as sp2 carbon-based materials5,6 (graphite, carbon nanotube, graphene, etc.), is an effective and inexpensive method to produce conductive composites.7,8 In fact, these materials provide electrical conduction through the π bonding system extending between adjacent carbon atoms in their chemical structure, whereas thermal conduction derives also from the overlapping of sigma-bonds belonging to the same molecular bonding system.9 However, to obtain a conductive composite, it is necessary to reach the percolation threshold that allows continuous pathways of interconnected conductive particles through the dispersing polymeric phase.10

A completely different approach to the fabrication of conductive polymeric materials has been proposed by Huang et al.11 that used graphene multilayers as coatings on the surface of plastic substrates. They deposited an ink of graphene nanoflakes on polyethylene terephthalate and, after drying and compression rolling treatments, obtained a conductive graphene laminate.

A simple and effective micromechanical approach, without any postdeposition treatments, has been recently proposed by Coscia et al.12 They have deposited graphene nanoplatelet (GNP) coating on the surface of a soft polymeric substrate such as low density polyethylene (LDPE) by rubbing some graphite platelet paste between two sheets of this polymer. This procedure produces a combination of opposite tangential mechanical stresses, such as shear and friction forces, that can easily detach weakly bonded GNP from graphite platelets. This micromechanical process could be easily scaled up by adapting

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technologies already existing in industry. Electrically conductive GNP coatings can be very useful to make tracks for printed circuit boards in plastic electronics and optically transparent electrodes for optoelectronics, replacing indium tin oxide and other much more expensive traditional materials.13

In this paper, the morphological, thermal, structural, optical, and electrical properties of the graphene nanoplatelets deposited on the LDPE substrate (GNP/LDPE) using the above micromechanical techniques are presented and compared with those of the pristine LDPE.

II. EXPERIMENT

The pristine LDPE used for the experiments was a commercial film provided by Sabich (99.77% by weight, $M_0 = 280,000$ g mol$^{-1}$, melt flow index $= 7$ g/10 min, and thickness $\sim 42$ μm). Specimens of large area (20 × 30 cm) were prepared by coating LDPE films using the following micromechanical method. First, dry graphite platelets were accurately mixed with pure ethanol (Aldrich, 99.9%) using a sonication bath, and then, this liquid colloidal dispersion was concentrated by solvent evaporation (under sonication) at room temperature to achieve a soft paste. A little amount of this paste was placed on the LDPE surface (firmly fixed to a flat glass) and was accurately spread using a similar LDPE film as counterface, by applying a pressure ranging from 3 to 9 kPa. Soft nonpolar polymers (such as polyethylene, silicon rubbers, amorphous ethylene-propylene copolymers, etc.) can provide enough friction to cause the exfoliation of the graphene platelets. The thickness of the deposited coating can be controlled by varying the amount of paste spread on the surface area. More details were reported in Coscia et al.12

Samples sized 1 × 1 cm were obtained from a large specimen (20 × 30 cm) for the different characterizations. Scanning electron microscopy (SEM) images of the samples were obtained using a FEI Quanta 200 FEG microscope. Transmission electron microscopy (TEM) images were obtained using a Philips CM200 microscope operating at 200 kV and equipped with a LaB6 filament. For TEM observations, samples were prepared in cross-section by using a Leica EM UC6/Fc6 cryo-ultramicrotome.

The thermal gravimetric analysis (TGA) was performed on LDPE, GNP/LDPE, and GNP residues derived from the coating deposition, by using a TA Instruments Q500, operating in nitrogen flow with a constant rate of 10°C/min. The modification of the surface morphology, due to the micromechanical deposition process, is illustrated in the sequence of SEM-micrographs given in Fig. 1. Figure 1(a) shows that the LDPE surface is flat, with very long scratches and few little blisters as defects, probably generated during the film fabrication process (blow molding). In the course of the coating treatment, the surface is progressively covered, as displayed in Fig. 1(b), where the defects are filled but still visible. At the end of the process, the LDPE surface is completely covered [Fig. 1(c)].

In order to investigate the inner structure of the coating deposited on the LDPE, TEM analysis was performed on cross-sectioned samples. In the TEM image in Fig. 2(a), the LDPE substrate and the overlying coating, about 20 nm thick, are clearly visible. In Fig. 2(b), the details of the arrowed region in Fig. 2(a) are presented: the coating is composed of graphene nanoplatelets which are quite parallel to the substrate and are formed by the overlap of 13–14 graphene layers, separated by a distance of $d = (0.35 \pm 0.02)$ nm.

A detailed analysis of different regions of the large area sample showed that the coating thickness ranged from 5 to 90 nm and that nanoplatelets were typically thicker near the LDPE substrate (13–30 graphene layers) and thinner at the top of the coating.

Thermogravimetric analysis was carried out to characterize the thermal properties of the GNP/LDPE sample. For comparison, TGA tests were also performed on pristine LDPE and residues of GNP derived from the coating deposition. The samples were heated in a TGA instrument up to 800°C with a heating rate of 10°C min$^{-1}$ under nitrogen. As shown in Fig. 3, the GNP/LDPE sample was thermally stable up to a temperature of $\sim 250$°C, and then, it decreased in weight by 8% at 400°C. In the 400–500°C range, although the weight of GNP decreased slightly, the thermal behavior of the GNP/LDPE sample was the same as that of the pristine LDPE and the weight decreased from $\sim 92\%$ to $\sim 1\%$ because of the complete decomposition of the substrate. The percentage by weight of GNP in the GNP/LDPE system was estimated to be $0.41\%$ by the difference between the GNP/
LDPE and pure LDPE residual weights. Clearly, the amount of deposited coating is extremely low as compared to that of LDPE substrate, and this is the reason for the thermal behavior of the polymer is dominant and the TGA curves of LDPE and GNP/LDPE almost overlap in the full temperature range.

It is worth noting that the weight of the GNP residues continued to decrease slowly even in the 500–800 °C range, reaching 91%, demonstrating the good thermal properties of the deposited GNP. Therefore, the GNP thermal stability is comparable with that of other types of graphene coatings, produced by different techniques.5

The structural properties of LDPE, GNP/LDPE, and GNP samples were investigated by Raman spectroscopy. Figure 4(a) shows the spectrum displaying the typical bands of LDPE (Refs. 8 and 14) centered at 1299 and 1454 cm⁻¹ assigned to all-trans -(CH₂)- groups and to the anisotropic parts of the polymer, respectively. Further, two more bands at 2842 and 2879 cm⁻¹ can be attributed to C-H (methyl) stretching vibrations. The positions of the band assignments are marked by dashed lines as guides to the eye. In Fig. 4(b), it can be seen that the GNP/LDPE Raman spectrum is affected by a higher level of noise. In addition to the above described LDPE bands, three more bands can be observed at around 1358, 1580, and 2680 cm⁻¹, due to D, G, and 2D bands of the GNP coating, respectively.15–17 The D-band can be attributed to the amount of disorder/defects in the structure, while the G band originates from in-plane bond stretching of
sp²-C atoms that can be assigned to doubly degenerate phonon mode $E_{2g}$ symmetry. Finally, the 2D band is the overtone of the D band, and it reflects the number of graphene layers.¹⁸,¹⁹

In order to get more information on the structure of GNP coating, the LDPE substrate was removed from the sample by dissolving it with boiling xylene. The Raman spectrum of the achieved GNP coating residues is shown in Fig. 4(c). The D, G, and 2D bands appear clearly defined, and their intensities can be better evaluated. Indeed, the ratio of the D peak intensity to that of the G peak is about 0.17, revealing a low degree of disorder in the deposited coating, while the ratio of the 2D peak intensity to that of the G peak is about 0.44, indicating a structure based on graphene multilayers,¹⁹ according to TEM analysis.

Figure 5 shows the diffuse reflectance, $R_d$, spectra of LDPE and GNP/LDPE samples, in the UV-Vis-near-infrared (NIR) spectral range (200–2500 nm). The two spectra are very different in the UV region; indeed, $R_d$ decreases for the LDPE substrate, while, in the case of the GNP/LDPE sample, it shows an intense and narrow peak, centered at ~250 nm, due to the surface plasmon resonance of graphene nanoplatelets.²⁰,²¹ In the 500–2000 nm range, $R_d$ is constant for both samples at around 5% and 15%, respectively, and then, it slightly decreases in the 2000–2500 nm range.

The total reflectance, $R_T$, spectra of the above samples, in the UV-Vis-NIR range, are shown in Fig. 6. $R_T$ of the LDPE substrate decreases in the UV region and exhibits a constant value of about 7% in the Vis-NIR region, while $R_T$ of the GNP/LDPE sample increases in the Vis-NIR region and shows a peak centered at ~250 nm in the UV region, as in the case of $R_d$ spectra. From the different behavior of $R_T$ and $R_d$ of the GNP/LDPE sample in the Vis-NIR region, it can be argued that the specular reflectance increases with the wavelength.

In fact, in Fig. 7, it can be seen that the specular reflectance, obtained by subtracting the diffuse to the total reflectance, linearly increases from 6.4% to 14% for GNP/LDPE, while it is almost constant at ~2.5% for the pristine LDPE.

The transmittance spectra, $T$, are shown in Fig. 8. In the UV range, the transmittance of LDPE strongly increases from 13% to 80%, while in the GNP/LDPE spectrum, the typical peak related to the surface plasmon resonance of GNP can be identified at about 250 nm. Furthermore, in the NIR range (2300–2350 nm), the absorption bands, due to the second overtone of the CH₂ bending mode of the LDPE, appear evident in both spectra.²² In the Vis-NIR range (500–2000 nm), the transmittance of LDPE and GNP/LDPE samples is approximately constant at ~87% and ~25%, respectively. Therefore, in this range, the absorptance, A, defined as $A = 100 - R_T - T$, varies in 4%–8% and 45%–58% ranges for LDPE and GNP/LDPE, respectively. This analysis indicates that a thin GNP coating is able to significantly modify the optical properties of the LDPE substrate by increasing both total reflectance and absorptance.

The electrical measurements of pristine LDPE and GNP/LDPE samples were performed in the coplanar configuration. The resistance of the LDPE substrate in dark conditions

Fig. 4. (Color online) Raman spectra of the LDPE substrate (a); GNP/LDPE sample (b); and GNP coating (c). The dashed lines indicate the positions of the typical bands of LDPE.

Fig. 5. (Color online) Diffuse reflectance, $R_d$, spectra of GNP/LDPE and LDPE samples.

Fig. 6. (Color online) Total reflectance, $R_T$, spectra of GNP/LDPE and LDPE samples.
was evaluated to be $\sim 10^{15}\ \Omega$ [see the I-V characteristic in Fig. 9(a)], while, after depositing the graphene nanoplatelet coating, a strong improvement in the surface conductivity properties was found because the resistance of GNP/LDPE was $670\ \Omega$ [see the I-V characteristic in Fig. 9(b)].

In order to determine the electrical response to the white light, the GNP/LDPE sample was illuminated by varying the optical power density, $F$, of a xenon lamp in the 20.9–286.2 mW/cm$^2$ range. The sample was subjected to dark-light cycles at fixed $F$ values with a light exposure time of 300 s. The photoconductivity properties are described, in the following, by means of the photoconductance $G_{ph}$ determined as

$$G_{ph} = \frac{G_{light}}{C_{0}} - G_{dark};$$

where $G_{dark}$ and $G_{light}$ are the conductances in dark conditions (before turning on the light) and under illumination, respectively.

From data analysis, it was found that $G_{ph}$ was independent of the applied voltage in the investigated range (from $-120$ to $120\ mV$). The time-dependent photoconductance at different optical power densities, $F$, is displayed in Fig. 10. Clearly, the sample under white light shows a negative photoconductivity.$^{23,24}$ Also, Shi et al.$^{25}$ and Biswas et al.$^{26}$ found negative photoconductivity in graphene layers under white light and radiation of different wavelengths, respectively. These authors attributed the decrease in conductivity under illumination to the photodesorption of hydroxyl groups and/or molecular $O_2$.

To gain a better insight into this process, the photoconductance recorded after 300 s of illumination, $G_{phf}$, of all the measurements is plotted versus the optical power density in Fig. 11. The trend of $G_{phf}$ as a function of $F$ is well fitted by the linear function
obtained with a correlation coefficient $r = 0.991$

\[
G_{\text{phf}} = kF, \\
\text{where } k = -3.623 \times 10^{-4} \pm 3.4 \times 10^{-6} \text{cm}^2 \Omega^{-1} \text{W}^{-1}
\]

is obtained with a correlation coefficient $r = 0.991$

IV. SUMMARY AND CONCLUSIONS

Coatings of overlapping nanoplatelets composed of 13–30 graphene layers were deposited on the LDPE substrate by a micromechanical technique. This method is based on the application of shear and friction forces to a graphite platelets/ethanol paste on the surface of the polymeric substrate. The TGA shows that the GNP/LDPE structure is thermally stable up to 250°C. It has been demonstrated that a coating of graphene nanoplatelets is able to significantly modify the optical and electrical properties of the polymeric surface. Indeed, in the case of the investigated GNP/LDPE sample, the coating increases both the diffuse and total reflectance, giving rise to a linear increase in the specular reflectance from 6.4% to 14% in the Vis-NIR region, while that of the pristine LDPE remains almost constant at around 2.5%. In the same spectral range, the coating markedly decreases the transmittance from 87% to 25%, leading to an increase in the absorptance from 4%–8% to 45%–58%. On the other hand, the graphene nanoplatelets strongly improve the surface conductivity properties. In fact, the resistance of the LDPE substrate as compared to that of the GNP/LDPE sample decreases by more than 12 orders of magnitude. Electrical measurements of the GNP/LDPE sample, performed under white light cycles, put in evidence a decrease in the conductance and a linear behavior of photoconductance as a function of optical power density. GNP/LDPE for its properties could be advantageously used as a semitransparent/conductive material for large area plastic electronics and optoelectronics.

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