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Proceeding Paper

Structural and Electrical Properties of Graphite Platelet Films Deposited on Low-Density Polyethylene Substrate †

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Abstract: Uniform conductive films composed of graphite platelets (GPs) were obtained by spraying a commercial graphite lacquer on low-density polyethylene (LDPE) substrates. According to the scanning electron microscopy investigation and X-ray diffraction analysis, the deposited films are composed of crystalline graphite platelets with an average size of 13.6 nm. The thermoresistive behavior of the GP film on LDPE samples was investigated from 20 to 120 °C. The resistance of the samples increases considerably in the 20–100 °C range and decreases sharply for temperatures above 100 °C. This behavior could be ascribed to the thermal properties of the polymer substrate. Results show that promising materials for thermoresistive applications in flexible electronics can be obtained by combining dielectric polymeric substrates with coatings based on graphite platelets.

Keywords: low-density polyethylene; graphite platelets; spray technique; coating; electrical properties

1. Introduction

The unique physicochemical characteristics of graphene, such as its light weight, optical transparency, flexibility, high electrical conductivity, and biocompatibility, make this material of fundamental importance in many applications [1]. Graphene has become very attractive in flexible and wearable electronics for the fabrication of sensors, actuators, and other types of electronic devices [2,3]. Nowadays, the production of large-surface graphene sheets is difficult and quite expensive, and this aspect represents an obstacle for using this material for mass productions. Graphite platelet (GP) materials are low-cost alternatives to graphene, capable of assuring moderately good mechanical, electrical, and thermal properties. Despite the small dimensions, GPs can be deposited on suitable substrates to form large-area conductive surfaces [4]. However, a uniform deposition with adequate mechanical resistance is not a simple task. It strongly depends on the chemical and physical properties of the substrate [5–9]. Polymer films can be advantageously selected as substrates for both graphene and graphite layers [10–14].

Here, GP films were deposited by spraying a graphite lacquer on low-density polyethylene (LDPE) substrates. Morphological and structural characterizations of the deposited films were carried out by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Electrical resistance measurements of GP films on LDPE substrates were performed as a function of temperature in the 20–120 °C range.

2. Materials and Methods

Large-area coatings of graphite-based materials were deposited on LDPE substrates (20 × 30 cm^2) by spray coating technology, using a commercial lacquer, Graphit 33 (from Kontakt Chemie, Zele, Belgium), which is commonly used for optical and electrical applications. During spraying, the full cone jet spot was horizontally directed on the film, taking a distance of 20 cm. After spraying, the coated substrates were dried in air at room temperature, for 4 h. In order to investigate the morphological and structural properties of the samples, scanning electron microscopy (SEM) was performed using an FEI Quanta 200 FEG microscope and X-ray diffraction (XRD) measurements were carried out by a Panalytical, X'PERT PRO diffractometer with a Cu-Kα radiation source (λ = 1.5406 Å). Electrical properties were studied by means of measurements under vacuum (about 2 mbar) in a coplanar configuration by silver paint contacts (1 cm long and 1 mm spaced) spread on the top sample surfaces. Vacuum was applied to prevent possible effects of moisture or other adsorbates. Current–voltage (I–V) characteristics were taken in a Janis Research ST-500 probe station, equipped with 4 micromanipulators connected to a source-measurement unit (SMU), Keithley 4200-SCS (Tektronix, Inc., Beaverton, OR, USA). The electrical resistance, R, of the samples at different temperatures, T, was measured during heating runs from 20 to 120 °C at a rate of about 5 °C/min. The mean values of resistance were estimated by monitoring R on a period of 60 s.

3. Results and Discussion

SEM micrographs in Figure 1 show that the coating obtained by spraying the Graphit 33 lacquer on the LDPE substrate is quite rough, porous, and made of small platelets well connected together.

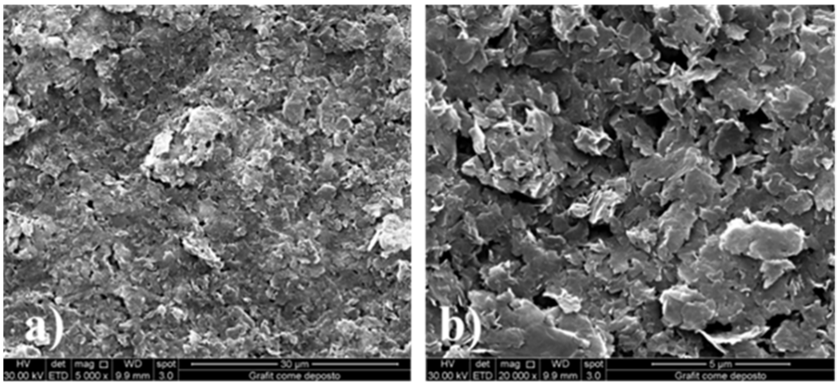

Figure 1. SEM micrographs of the "as-deposited" coating after spraying Graphit33 lacquer on low-density polyethylene (LDPE).

The XRD diffractogram of a typical film deposited on LDPE is given in Figure 2. This XRD measurement includes four peaks. In particular, the three peaks at 21.78°, 24.05°, and 36.47° belong to the crystalline phase of the LDPE substrate [15] (these peaks are overlapped to a diffuse halo, coming from the amorphous phase in the LDPE substrate) and the (002) diffraction peak located at about 26.74° is due to the crystalline graphite platelets [16].

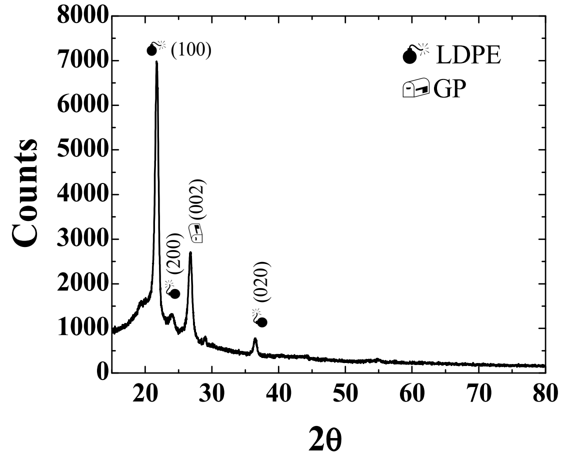

Figure 2. XRD diffractogram of graphite platelet (GP) film on LDPE.

The average size of graphite crystals was determined from the broadening of the (002) graphite diffraction peak by using Scherrer's equation [17]:

$$D = k\frac{\lambda}{FWHM\ \cos\theta}$$

where D is the average size of the ordered (crystalline) domains, k is a dimensionless shape factor, with a value close to unity, λ is the X-ray wavelength (Cu-kα = 1.54 Å), FWHM is the line broadening at half maximum intensity, and θ is the Bragg angle. An average size of 13.6 nm was obtained by using 0.9 as the shape factor.

Electrical measurements of GP samples were carried out under vacuum in a two-probe configuration. In Figure 3, the current, I, of a representative sample is plotted vs. the applied voltage, V, at the temperature of 20 °C. The linearity of the I–V characteristic indicates ohmic contacts. The resistance value, R_0 = (164.00 ± 0.03) ohm, was obtained by the best fit of the experimental data, with a correlation coefficient r = 1.

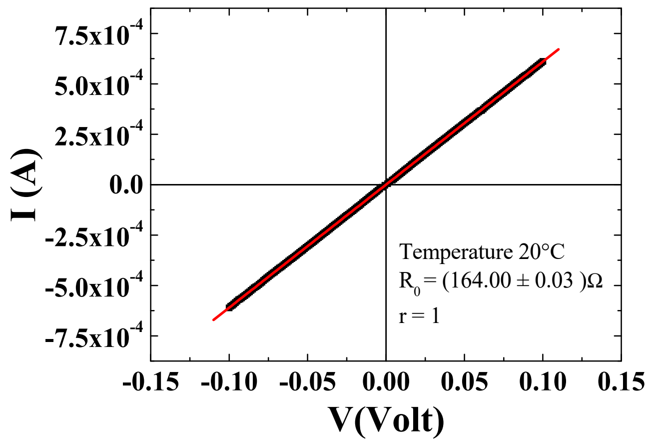

Figure 3. I–V characteristic of a GP film on LDPE substrate. The straight line is a line of best fit of the experimental data.

The thermoresistive properties of GP films were investigated by recording the resistance values, R, during heating runs from 20 to 120 °C. In Figure 4, the resistance change of the sample, shown as the R/R0 ratio, is plotted vs. temperature, T. A large non-linear increase in the resistance can be observed in the 20–100 °C range and this behavior is opposed to that of the graphite material, whose resistance decreases with increasing temperature [18,19]. The resistance increase in GP films on LDPE could be ascribed to the thermal expansion of the polymer substrate [20,21], since the coefficient of linear thermal expansion around room temperature (1–2 × 10^{-4} °C^{-1}) is more than one order of magnitude greater than that of graphite (4–8 × 10^{-6} °C^{-1}) and it increases about one order of magnitude close to 100 °C. The larger thermal expansion of the substrate could induce strains in the deposited graphitic film, leading to the reduction in the contact area of the platelets, with a decrease in the number of conduction paths and the consequent increase in the film resistance.

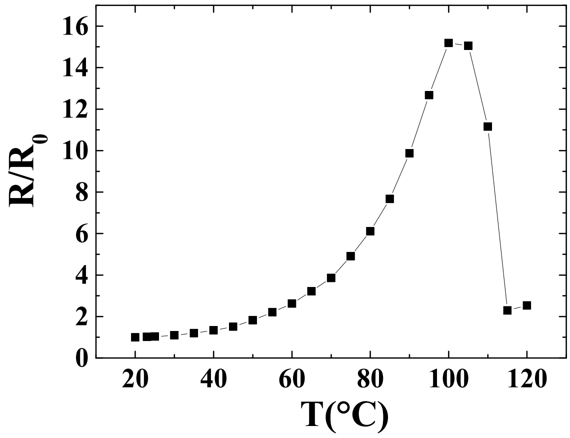

Figure 4. R/R_0 vs. temperature for a GP film on LDPE substrate.

For temperatures higher than 100 °C, the resistance suddenly decreases despite the continuous increase in thermal expansion. Probably, the melting and the resulting sharp decrease in the mechanical modulus of the LDPE could favor the slipping of the graphite platelets with the restoration of the conductive network on the sample surfaces. A similar temperature dependence of the electrical conductivity was observed in the LDPE filled with carbon black and carbon fiber composites [22]. The significant thermoresistive response of the investigated GP films on LDPE makes these systems suitable as temperature sensors and self-switching components in flexible electronics.

4. Conclusions

Large-area GP films were deposited on LDPE substrates by a spray coating technology, using a graphite lacquer. SEM images and XRD analysis show that the films consist of overlapped graphite platelets composed of crystallites with an average size of 13.6 nm in the (002) direction. The electrical characterization of the samples, as a function of temperature, suggests that the thermal properties of the LDPE substrate (thermal expansion and phase transition) strongly affect the thermoresistive properties of GP films. The resistance of the GP film on LDPE considerably increases in the 20–100 °C range but sharply decreases above the temperature of 100 °C. The investigated material could be used as a temperature sensor in the thermal ranges where the polymeric substrate still remains solid.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Warner, J.H.; Schaffel, F.; Rummeli, M.; Bachmatiuk. A. *Graphene: Fundamentals and Emergent Applications*; Elsevier: Oxford, UK, 2013.
2. Stoppa, M.; Chiolerio, A. Wearable electronics and smart textiles: A critical review. *Sensors* **2014**, *14*, 11957–11992.
3. Singh, T.B.; Sariciftci, N.S. Progress in plastic electronic devices. *Annu. Rev. Mater. Res.* **2006**, *36*, 199–230.
4. Cataldi, P.; Athanassiou, A.; Bayer, I.S. Graphene Nanoplatelets-Based Advanced Materials and Recent Progress in Sustainable Applications. *Appl. Sci.* **2018**, *8*, 1438.
5. Kondratov, A.P.; Zueva, A.M.; Varakin, R.S.; I.P.; Taranec, I.A. Savenkova, Polymer film strain gauges for measuring large elongations. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *312*, 012013.
6. Huang, X.; Leng, T.; Zhang, X.; Chen, J.C.; Chang, K.H.; Geim, A.K.; Novoselov, K.S.; Hu, Z. Binder-free highly conductive graphene laminate for low cost printed radio frequency applications. *Appl. Phys. Lett.* **2015**, *106*, 203105.
7. Longo, A.; Verucchi, R.; Aversa, L.; Tatti, R.; Ambrosio, A.; Orabona, E.; Coscia, U.; Carotenuto, G.; Maddalena, P. Graphene oxide prepared by graphene nanoplatelets and reduced by laser treatment. *Nanotechnology* **2017**, *28*, 224002.
8. Bonavolontà, C.; Camerlingo, C.; Carotenuto, G.; De Nicola, S.; Longo, A.; Meola, C.; Boccardi, S.; Palomba, M.; Pepe, G.P.; Valentino, M. Characterization of piezoresistive properties of graphene-supported polymer coating for strain sensor applications. *Sens. Actuators A Phys.* **2016**, *252*, 26–34.
9. De Castro, R.K.; Araujo, J.R.; Valaski, R.; Costa, L.O.O.; Archanjo, B.S.; Fragneaud, B.; Cremona, M.; Achete, C. New transfer method of CVD-grown graphene using a flexible, transparent and conductive polyaniline-rubber thin film for organic electronic applications. *Chem. Eng. J.* **2015**, *273*, 509–518.
10. Palomba, M.; Longo, A.; Carotenuto, G.; Coscia, U.; Ambrosone, G.; Rusciano, G.; Nenna, G.; Barucca, G.; Longobardo, L. Optical and electrical characterizations of graphene nanoplatelet coatings on low density polyethylene. *J. Vac. Sci. Technol. B* **2018**, *36*, 01A104.
11. Coscia, U.; Palomba, M.; Ambrosone, G.; Barucca, G.; Cabibbo, M.; Mengucci, P.; de Asmundis, R.; Carotenuto, G. A new micromechanical approach for the preparation of graphene nanoplatelets deposited on polyethylene. *Nanotechnology* **2017**, *28*, 194001.
12. Fechine, G.J.M.; Martin-Fernandez, I.; Yiapanis, G.; Bentini, R.; Kulkarni, E.S.; De Oliveira, R.V.B.; Hu, X.; Yarovsky, I.; Neto, A.H.C.; Ozyilmaz, B. Direct dry transfer of chemical vapor deposition graphene to polymeric substrates. *Carbon* **2015**, *83*, 224–231.
13. Martins, L.G.P.; Song, Y.; Zeng, T.; Dresselhaus, M.S.; Kong, J.; Araujo, P.T. Direct transfer of graphene onto flexible substrates *PNAS* **2013**, *110*, 17762–17767.
14. Tian, M.; Huang, Y.; Wang, W.; Li, R.; Liu, P.; Liu, C.; Zhang, Y. Temperature-dependent electrical properties of graphene nanoplatelets film dropped on flexible substrates. *J. Mater. Res.* **2014**, *29*, 1288–1294.
15. Murray, K.A.; Kennedy, J.E.; McEvoy, B.; Vrain, O.; Ryan, D.; Cowman, R.; Higginbothama, C.L. Characterisation of the Surface and Structural Properties of Gamma Ray and Electron Beam Irradiated Low Density Polyethylene. *Int. J. Mat. Sci.* **2013**, *3*, 1–8.
16. Johra, F.T.; Lee, J.-W.; Jung, W-G. Facile and safe graphene preparation on solution-based platform. *J. Ind. Eng. Chem.* **2014**, *20*, 2883–2887.
17. Klug, H.P.; Alexander, L.E. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed.; Wiley: New York, NY, USA, 1974.
18. Dinh, T.; Phan, H.-P.; Qamar, A.; Woodfield, P.; Nguyen, N.-T.; Dao, D.V. Thermoresistive effectfor advanced thermal sensor: Fundamentals, design consideration and application. *J. Microelectromech. Syst.* **2017**, *26*, 966–986.
19. Iwashita, N.; Imagawa, H.; Nishiumi, W. Variation of temperature dependence of electrical resistivity with crystal structure of artificial graphite products. *Carbon Am. Carbon Commit.* **2013**, *61*, 602–608.
20. Palomba, M.; Carotenuto, G.; Longo, A.; Sorrentino, A.; Di Bartolomeo, A.; Iemmo, L.; Urban, F.; Giubileo, F.; Barucca, G.; Rovere, M.; et al. Thermoresistive Properties of Graphite Platelet Films Supported by Different Substrates. *Materials* **2019**, *12*, 21.
21. Di Bartolomeo, A.; Iemmo, L.; Urban, F.; Palomba, M.; Carotenuto, G.; Longo, A.; Sorrentino, A.; Giubileo, F.; Barucca, G.; Rovere, M.; et al. Graphite platelet films deposited by spray technique on low density polyethylene substrates. *Mater. Today Proc.* **2020**, *20*, 87–90.
22. Di, W.; Zhang, G.; Xu, J.; Peng, Y.; Wang, X.; Xie, Z. Positive temperature coefficient/negative temperature coefficient effect of Low density polyethylene filled with a mixture of carbon black and carbon filler. *J. Polym. Sci. Part B Polym. Phys.* **2003**, *41*, 3094–3101.