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Behavior of Polyethylene-based nanocomposites containing multi-layer graphene filler

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Abstract- In this research, the results regarding the characterization of electrical and mechanical properties of a low-density polyethylene (LDPE) - graphene-like (G) nanocomposite are presented. The processing technique used to fabricate the material was high-energy ball milling. This method was utilized to fabricate samples with a filler loading ranging from 1 wt% up to 7wt%. Low voltage broadband dielectric spectroscopy (BDS), erosion tests and breakdown tests (BD) were the measurements carried out in order to characterize the electrical behavior of the fabricated composites. Then, some of the mechanical properties of the LDPE-G nanocomposites were determined with dynamic mechanical analysis (DMA) and, finally, the crystalline structure of the material was investigated with differential scanning calorimetry (DSC).

I. INTRODUCTION

Graphene is a single layer of carbon atoms organized in a honeycomb lattice, bonded together with atom in a sp^2 configuration. It is the first example of a two-dimensional material and has extremely particular characteristics.

Because of its outstanding mechanical, electrical and thermal properties [1-3], graphene is added as filler into many polymers in order to improve their characteristics. Indeed, with the increasing demand of electric energy is nowadays always more important the development of materials able to guarantee extremely high insulating, mechanical and thermal properties in order to increase the reliability of electric power systems.

Unfortunately, also after several years of researches and efforts, it remains today difficult to transfer graphene's properties into polymeric matrixes. This occurs principally because of the tendency of graphene particles to agglomerate and due to the difficulties in creating strong interactions and binding at the filler-matrix interface. Another issue related to graphene utilization is linked to the difficulties in obtaining high amounts of this material at low-cost with an acceptable grade of defects. In this work, high-energy ball milling was chosen as fabrication technique in order to partially overcome the issues related to the filler inside the polymeric matrix, while, the type of graphene-like additive was selected because of its lower cost and easier fabrication if compared to graphene mono-layers additive.

II. EXPERIMENTAL

A. Materials

LDPE was purchased from Marplex. This material shows a density equal to 0.922 g/cm^3 and a melt flow index equal to

$0.4 \text{ g}/10 \text{ min}$, while, its particle size, is for the $95\% < 500 \mu\text{m}$. The latter is important because particle size is a parameter that influences the ball milling process.

The utilized G was provided by NanoXplore: this multi-layer graphene is a commercial and low-cost graphene nanoplatelet with an average thickness of 20 nm (40 layers) a flake size of $50 \mu\text{m}$ and its surface area, calculated with the BET method, equal to $3 \text{ m}^2/\text{g}$. Finally the carbon content of this filler was $> 95 \text{ wt}\%$ and its oxygen content $< 5\%$.

B. Processing Technique

The fabrication technique utilized in this work was high-energy ball milling. This is a relatively new process for polymer nanoscience and, until now, is utilized especially in a research-laboratory scale. Nevertheless, thanks to this fabrication process, a good graphene dispersion inside LDPE was already achieved by Pironelli et al. [4] and, for this reason, this processing technique was chosen among the others. LDPE and G powders were firstly manually mixed then ball-milled for 40 minutes [5] in a SPEX SamplePrep 8000D Mixer/Mill at room temperature without the utilization of any compatibilizer. After that, the obtained mixture was hot pressed by using a mold to create 0.5 mm thick specimens. This method was used to fabricate samples with a filler loading ranging from $1 \text{ wt}\%$ up to $7 \text{ wt}\%$.

C. Measurements

Broadband Dielectric Spectroscopy - BDS was performed with a Novocontrol Broadband Dielectric Analyzer in a frequency range of 10^6 to 10^{-2} Hz , at a constant temperature of 20°C , with an applied voltage of 3 V root mean square (rms). For each point in the range of 10^6 to 1 Hz , the results were calculated as an average between three different measurements.

Erosion Test - With erosion test the composites' resistance to surface partial discharge (PD) was then evaluated. For these measurements, the samples were cut with a diameter of 40 mm and placed, at a distance of $100 \mu\text{m}$, under an electrode with a spherical titanium tip with a diameter of 4 mm . Then, an AC voltage with 300 Hz frequency and a peak amplitude of 10 kV was applied for 35 hours. The device was protected from short circuit and, if an electrical arc was detected during the erosion process, the latter should be immediately stopped. Finally, the eroded volume was measured with a Veeco Instrument Dektak profilometer. Samples containing 1 , 2 , and $3 \text{ wt}\%$ of G were tested in this way.

Breakdown Test - To perform this test a Baur DTA Automatic Insulating Oil Tester was utilized.

The composites were tested in alternate current (AC) condition in order to evaluate their breakdown strength: a voltage with 60Hz frequency and an amplitude increasing with a rate equal to 2kV/s, was applied until breakdown occurred. During this process the specimens were placed between two cylindrical rod electrodes (6.4mm in diameter) with edges rounded to 0.8mm that were immersed in Luminol Tri insulating oil. For each sample, ten tests were made in order to later process the data with the Weibull statistical distribution.

Dynamic Mechanical Analysis - Dynamic mechanical analysis tests were performed with a TA Instruments Q800 DMA with a tension film clamp. The frequency was fixed at 1Hz while the temperature was scanned from -105°C to +105°C at a rate of 5°C/min. Finally, the oscillation amplitude was set to 20µm, the preload force to 0.0200N and the force track to 120%.

Differential Scanning Calorimetry - Differential scanning calorimetry measurements were performed with a TA Instruments Q20. Dry nitrogen gas was purged through the cell at a flow rate of 50ml/min, while, the scanning rate, was set to 10°C/min. The measurement cycle was composed by two identical thermal routines from 0 to 170°C and from 170 to 0°C. Purpose of the first test, was to reset the sample's thermal history. After the measurements the degree of crystallinity and lamellar thickness of the nanocomposites were evaluated with equations (1) and (2):

$$\%Crystallinity = \frac{\Delta H_f^{Obs}}{\Delta H_f^0} \cdot 100. \quad (1)$$

$$T_m = T_m^0 - \frac{2\sigma_e T_m^0}{l\Delta H_f^0}. \quad (2)$$

Where ΔH_f^{Obs} is the melting enthalpy of the sample and ΔH_f^0 is the melting enthalpy of the sample if completely crystalline, amount known as 293.6 J/g for LDPE. In equation (1), ΔH_f^{Obs} was corrected in order to consider that the analyzed sample was constituted also by filler which does not take part to the crystallization processes. A scaling factor equal to the percentage in weight of polymer constituting the specimen was considered.

Lamellar thickness was then evaluated in accordance with the Gibbs-Thomson equation as shown in (2). In the latter l indicate the lamellar thickness, T_m^0 is the equilibrium melting temperature and σ_e the fold surface energy, both constant and dependent on the material. Every DSC measurement was made two times and the results shown later were calculated as an average of the two different tests.

II. RESULTS AND DISCUSSION

With BDS real (ϵ') and imaginary part (ϵ'') of dielectric permittivity and conductivity modulus were evaluated. As shown in fig.1 is noticeable how the presented cases are characterized by an increase both in the real and imaginary part of the permittivity with the increase of the percentage in weight

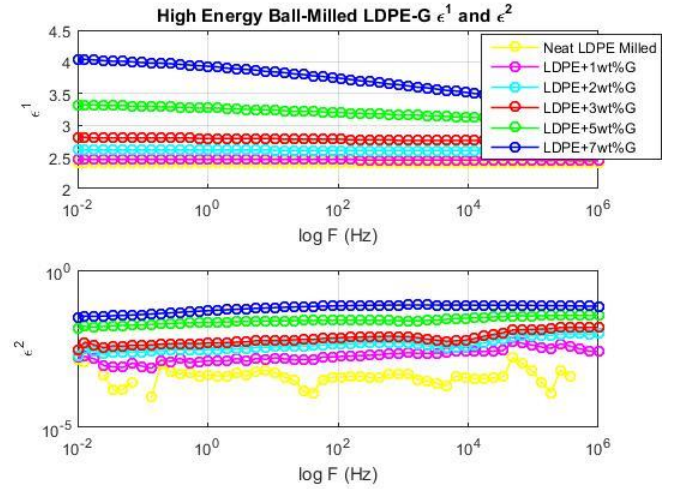


Fig. 1. Real (ϵ') and imaginary (ϵ'') part of dielectric permittivity as a function of frequency

of G inside the composite. The previous observation is in accordance with the physics related to the phenomena. Indeed, the number of free electrical carriers probably increases with the increase of the filler into the nanocomposite. This is reflected in higher losses, linked to the larger ϵ'' , and in an increase of ϵ' , typical of semi-conductors and in accordance with the prediction that could be made with the effective medium theory [6]. In tab.1, then, the values of ϵ' and ϵ'' at 10^{-2} Hz for neat LDPE and for the nanocomposites with the highest filler concentration are reported.

TABLE I
REAL (ϵ') AND IMAGINARY (ϵ'') PART OF PERMITTIVITY

| Material | ϵ' | ϵ'' |
|--------------|-------------|----------------------|
| Neat LDPE | 2.41 | $1.44 \cdot 10^{-3}$ |
| LDPE + 7wt%G | 4.04 | $3.25 \cdot 10^{-2}$ |

Finally the ac-conductivity modulus of the different tested composites is reported in Fig.2. It is clearly distinguishable the typical AC-conductivity response of electrical insulating material in all the specimens without noticeable differences. The results provided from erosion tests made possible to evaluate the nanocomposites resistance to surface partial discharges. The LDPE-G system, as shown in fig.3, is more resistant to PD than neat LDPE at low wt% of filler. For a filler concentration equal to 1wt%, indeed, the nanocomposites eroded volume reached a minimum, then, with the increase of filler this value started to increase. Finally, when the G concentration was equal to 3wt%, the test was stopped after 14h36min due to short circuit detection caused by the massive amount of material removed from the PD attack. A possible explanation to this trend could be given by the multicore model [7]. The graphene filler and the interfacial layers next to the filler nanoparticles are characterized by a greater resistance to partial discharge than the LDPE matrix. The erosion process, then, can take part only in the low PD resistant matrix regions between graphene particles becoming, for this reason, slower. When the amount of graphene in the composites becomes too

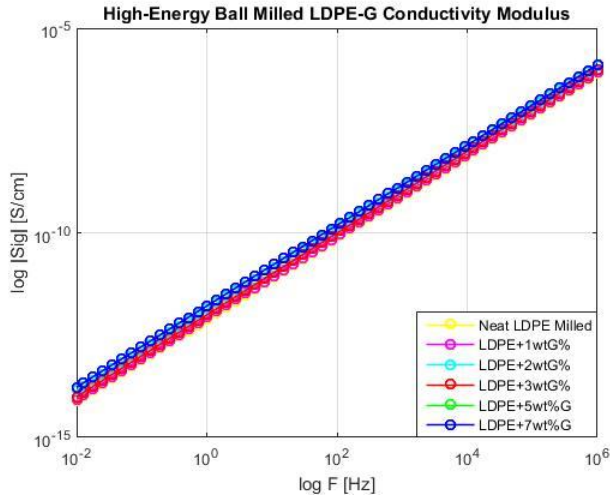


Fig. 2. Real (ϵ') and imaginary (ϵ'') part of dielectric permittivity as a function of frequency

high, however, the conductivity rises reducing thus the PD resistance. The precise values of the eroded volume for the different composites are reported in tab.2.

TABLE II
ERODED VOLUME

| Material | Eroded Volume [μm^3] | % Modification |
|--------------------|-----------------------------------|----------------|
| Neat LDPE Milled | 3.32 | 0% |
| LDPE+1%GV20 Milled | 2.73 | -18% |
| LDPE+2%GV20 Milled | 4.41 | +33% |

Breakdown voltage was the last electrical property in this research studied. After the tests, the values were processed in accordance to the IEC/IEE 62593 standard utilizing the two-parameter Weibull statistical distribution. It has been reported in [4] how low amount of graphene-like additives can improve composites breakdown strength but, as shown in tab.3 for all the studied cases this value decreases if compared to the neat material. This could be addressed to the filler loading, already high enough to introduce a number of charge carriers such that the avalanche process causing the system failure can occur at lower electrical field.

TABLE III
SCALE (α) AND SHAPE (β) PARAMETERS OF THE BREAKDOWN STRENGTH WEIBULL DISTRIBUTION

| Material | α [kV] | β |
|------------|---------------|---------|
| Neat LDPE | 94.00 | 8.984 |
| LDPE+1wt%G | 85.30 | 31.72 |
| LDPE+2wt%G | 75.78 | 9.761 |
| LDPE+3wt%G | 61.59 | 7.049 |
| LDPE+5wt%G | 41.14 | 10.58 |
| LDPE+7wt%G | 26.01 | 6.481 |

Some of the mechanical properties of the composites were than evaluated with DMA. In particular the storage modulus as a function of temperature was measured for all the prepared LDPE-G systems as shown in fig.4. All the presented results

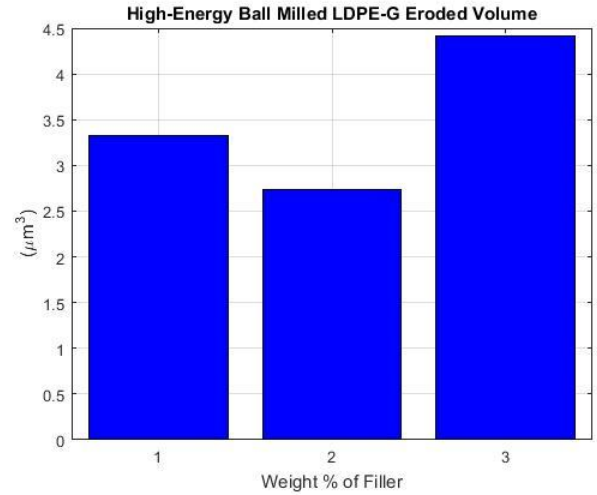


Fig. 3. Eroded volume in different LDPE-G composites as a function of Gwt%

show a storage modulus that remains almost unchanged up to the specimen containing the 2% in weight of filler, increasing then, remarkably, especially at low temperatures. This occurs because G cause a reduction in the chain mobility of LDPE, acting, for this reason, as a reinforcing filler [8,9]. Finally, it has been reported [10] that graphene nanocomposites could show a worse mechanical behavior once reached a filler threshold but, the previous graphs, show that this critical filler loading has not been reached up to 7 wt%.

The last characterization carried out in this work was DSC. Results of the calculated crystallinity and lamellar thickness are shown in tab.4.

TABLE IV
DEGREE OF CRISTALLINITY AND LAMELLAR THICKNESS

| Material | Cristallinity % | Lamellar Thickness [nm] |
|--------------------|-----------------|-------------------------|
| Neat LDPE Extruded | 44.85 | 7.72 |
| LDPE+1%GV20 Milled | 43.80 | 7.71 |
| LDPE+2%GV20 Milled | 42.87 | 7.76 |
| LDPE+3%GV20 Milled | 42.66 | 7.72 |
| LDPE+5%GV20 Milled | 42.41 | 7.73 |
| LDPE+7%GV20 Milled | 41.79 | 7.80 |

It is worth noting that crystallinity does not drastically change with the increase of filler, indicating that the internal material structure was not strongly influenced by the presence of the graphene. Nevertheless it is possible to recognize a slight decreasing trend with the increase of G wt%. When filler particles are properly dispersed in a polymer, indeed, they penetrate through its chains and, acting as physical barrier, cause the interruption of the crystallization process [11,12]. On the other hand, lamellar thickness remains almost equal to 7.8nm for all the filler concentrations.

III. CONCLUSIONS

This research showed as high-energy ball milling is a viable way to produce LDPE-G nanocomposites with a good filler dispersion as confirmed from the slight reduction in the

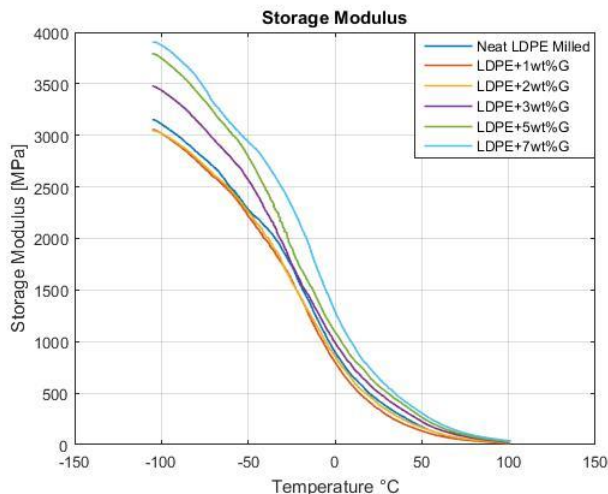


Fig. 4. Storage modulus at 1Hz as a function of temperature for different G wt% loadings.

composites crystallinity. Results highlighted also that an enhanced PD surface resistance, storage modulus and real part of the dielectric permittivity are obtainable with the use of this nanocomposite instead of neat LDPE. On the other hand, an increase in dielectric losses as well as a reduction of the breakdown strength with the increase of G concentration inside the composites were found. Nevertheless these materials could have a possible application in field grading devices where higher permittivity and conductivity as a function of field are required, but this will be presented in another paper.

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