Influence of manufacturing process on electrical properties of LDPE-GnP nanocomposites

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Abstract

In this report electrical properties of the nanocomposite samples, prepared from graphene nanoplatelet (GnP) loaded low density polyethylene (LDPE) by extrusion and compression molding, were examined in order to elucidate the impacts of the nanoplatelets size and material's manufacturing process. It is shown that the extrusion forces a strong anisotropy in material's morphology. The graphene nanoplatelets become aligned along the flow direction. As compared to pure LDPE, a significant reductions of the through-plane low field electric conductivity is found in such samples. On the other hand, the samples produced by press molding exhibit slightly higher level of electric conductivity, which is connected to their less aligned microstructure and filler dispersion. For comparison results of measurements on LDPE-graphene monolayer sandwiches are also presented.

1. Introduction

The high voltage direct current (HVDC) technology is nowadays considered as the most feasible, reliable and economic means for transportation of electric energy across seas and inland. This especially refers to HVDC extruded cable systems, in which terminations and joints are still being under intensive development. The need to precisely control distribution of electric field in these components is today secured by field grading materials made of polymer composites filled with semi-conducting particles such as SiC, ZnO or CB, where the filler loading goes up to 30 - 40 wt.% [1]. Among other foreseen alternatives is to apply nanocomposites loaded with graphene nanoplatelets (GnP), which due to the outstanding electrical, thermal and mechanical properties of this filler can provide numerous interesting features. A possibility for reaching the percolation threshold for nonlinear electrical conduction at low loading contents is one of them.

2. Samples preparation

2.1 Extruded and compressed samples

Graphene nanopowders M5 and M25 (purchased from XG Sciences) were in this study suspended in orto-dichlorobenzene and stirred by means of high shear rotor-stator mixer for 15 min at 10000 RPM and thereafter sonicated for 3 h in a low power sonication bath. This process helps to exfoliate and de-agglomerate the nanofiller before incorporating it into a low density polyethylene (LDPE) powder. The mixture was thereafter dried until evaporation of the used solvent, following the so called dry-coating method [2]. In the next step, this masterbatch was extruded by means of a single-screw extruder (Brabender 19/25D) and pelletized. Then a second extrusion was used for preparing nanocomposite tapes with GnP contents of 1, 5 and 11wt.%. A second batch of samples was produced by means of press molding from the same pellets.

Table 1. Characteristics of the LDPE and GnP.

xGnP *	**M5**	**M25**
SA (m^2/g)	120-160	
d_{ave} (µm)	5	25
thickness (nm)	6-8	
ρ (g cm-3)	2.2	
Electrical conductivity (S/m)	Through plane	In - plane
	10^2	10^7

LDPE	
M_w	91641
M_w/M_n	7.552
T_m (°C)	110.62
T_c (°C)	94.09

Fig. 1 - Sample preparation scheme.

2.2 Graphene monolayers sandwich structures

As a comparison LDPE-graphene monolayer sandwich structures were also studied. Graphene was grown using chemical vapor deposition. A 25-μm thick Cu foil substrate was cleaned to remove native oxide. The reactor was evacuated and then filled to 400 mTorr with $Ar\&H_2$ gasses and the temperature was increased to 1000°C. The Cu foil was annealed for 60 min. The graphene growth was performed by flowing diluted methane by Ar for 120 min. After the growth, the CH_4 flow was turned off and Cu foil was cooled down naturally. The graphene/ LDPE was fabricated using imprint at temperature of 160°C and pressure of 8 bar. First, a LDPE was placed between two graphene films on Cu substrate. Then, they were transferred into an imprint machine and pressed at 160°C under pressure of 8 bar. The Cu-Gr-LDPE-Gr-Cu stack was immersed in a copper etchant overnight. After copper etching, the graphene-LDPE-graphene structure was rinsed in DI water baths. The final structure of the first sample consists of 3 layers of LDPE and 2 layers of Gr-LDPE-Gr which were sandwiched at 160 °C under 8 mbar. In sum produced samples have 2, 4 and 6 layers of graphene sandwiched between 3, 5 and 7 layers of LDPE respectively.

3. Experimental setups

3.1 DC conductivity measurement

DC conductivity measurement setup used in this study is shown in Figure 2. The current flowing through the specimen placed in a shielded electrode system is measured by Keithley Electrometer (6517 series). For making the measurements in a wide range of electric fields, both the electrometer's internal voltage source (up to 1 kV) and a high voltage DC source (Glassman FJ60R2, 60kV) were utilized. A low pass filter was integrated into the setup for limiting the current in case of specimen breakdown and for filtering out high frequency noise.

The used shielded electrode system is similar as the conventional three electrode system with addition of a shielding plate covering the back side of the measuring electrode for avoiding additional capacitive couplings. To control the temperature of the measurement, an oven was used and the specimen were kept in the oven for at least 1 hour before the measurement started.

A LabVIEW based software was adopted for recording and processing the measured data in real-time. An extensive averaging is often required for increasing the signal to noise level when the measured currents go down to sub-pico ampere level. To provide enough data for this averaging, GPIB communication is used, while an algorithm dynamically optimizes the necessary averaging by evaluating the deviation of each incoming data point. This functionality also provides a possiblity to record any fast current dynamics and also serves as an overcurrent protection in the case of specimen breakdown.

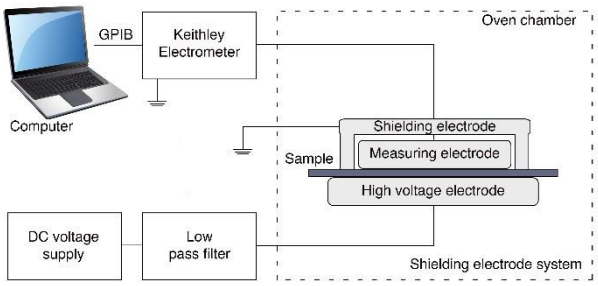

Fig. 2 - Schematic view of dc conductivity measurement setup.

3.2 Scanning Electron Microscopy

A FEI/Philips Field Emission Scanning Electron Microscope was used to investigate the morphology of the LDPE-GnP nanocomposites. The samples were cooled down in liquid nitrogen and then fractured. Thereafter all samples were etched for one hour using solution of 1wt% potassium permanganate in a mixture of sulfuric acid, ortho-phosphoric acid and water [3]. The process was stopped by washing in a mixture of sulfuric acid and water, thereafter in hydrogen peroxide and finally in isopropanol. 5-nm-thick gold layer was deposited onto the observed surfaces by means of a Sputter Coater S150B, BOC Edwards. The observations were carried out for elucidating the influence of the manufacturing process on samples morphology.

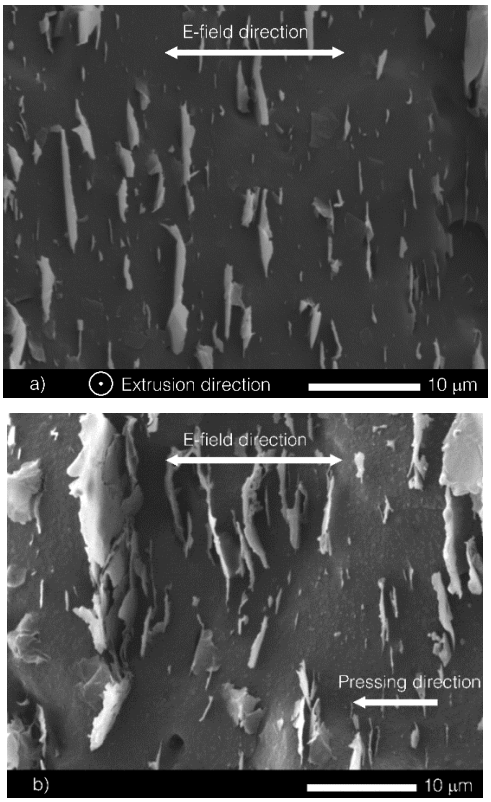

Fig. 3 – Morphology of manufactured samples a) extruded b) compressed with 5% of GnP M25.

4. Results

4.1 Sample morphology

The freeze fractured surfaces of LDPE-GnP with 5wt% filler loading are demonstrated in Figure 3. The surface shown on Figure 3a) is perpendicular to the extrusion direction and exhibits the influence of processing direction on GnP nanoplatelet distribution in the polymer matrix. The nanoplatelets are aligned along the extrusion flow direction. This effect was also observed in our earlier study [4, 5]. Figure 3b) presents the GnP nanoplatelet distribution in the compressed sample. One may notice here a more agglomerated structure with some flakes aligned at an angle to the material flow.

4.2 DC Conductivity measurements

Low field behavior of DC conductivity in extruded and pressed samples was measured at 30°C and 10kV/mm. Figure 4 shows time dependence of the conductivity, for extruded samples, calculated from the measured charging current. For the long charging times, LDPE-GnP extruded composites show lower DC conductivity as compared to the pure extruded LDPE samples, even for 11 wt.% filled nanocomposite. The influence of flake size is not visible at the low field level. One may thus conclude, that morphology of extruded samples has a strong influence on the observed behavior of conductivity.

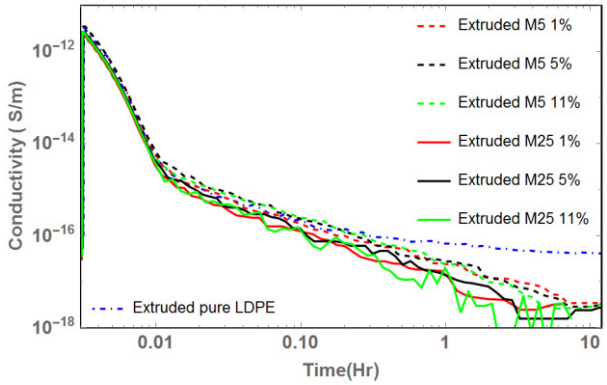

Fig. 4 – DC Conductivity of extruded samples at 10kV/mm.

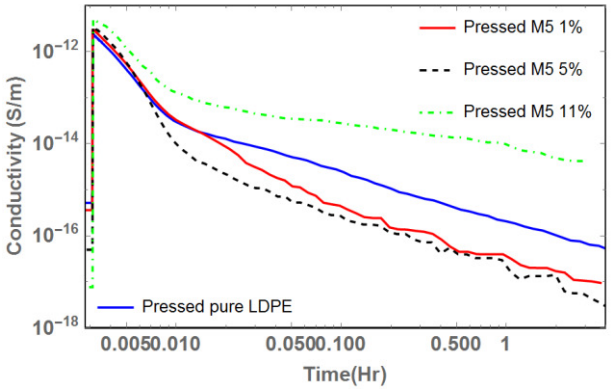

Fig. 5 – DC Conductivity of pressed LDPE-GnP M5 composites at 10kV/mm.

As the extrusion process forces a parallel filler alignment, which in the measurements remains perpendicular to the current flow, a possible explanation of this behavior should be join with influence of the GnP-LDPE interface. The interfaces between LDPE and filler particles may limit charge transport by introducing deep traps into the material. Figure 5 shows, on the other hand, time dependence of the conductivity, for pressed samples with GnP M5 as the filler. The measurements were conducted at the same conditions as for the extruded ones. The samples filled with 1 and 5 wt.% of GnP M5 showed similar behavior as the extruded samples, with the conductivity lower than reference material. However, sample filled with 11wt% of GnP M5 showed higher conductivity than pure LDPE. One may thus conclude that at the high filling level there appear in the pressed samples a higher possibility of creation of percolation paths that yield the increased conductivity. At the same time however, the resulting morphology of the material increases a risk for breakdowns at elevated fields, as often happened in the pressed GnP M25 samples.

Figure 6 presents for comparison time dependence of the conductivity for the laminated sandwich structures of CVD graphene flakes (2, 4 and 6 layers) between 3, 5 and, 7 layers of LDPE. The laminates demonstrate similar behavior as pure layered LDPE, with the conductivity on the level 10^{-16} (S/m). It seems that the presence of graphene monolayers has practically no influence on the effective DC conductivity of such laminates.

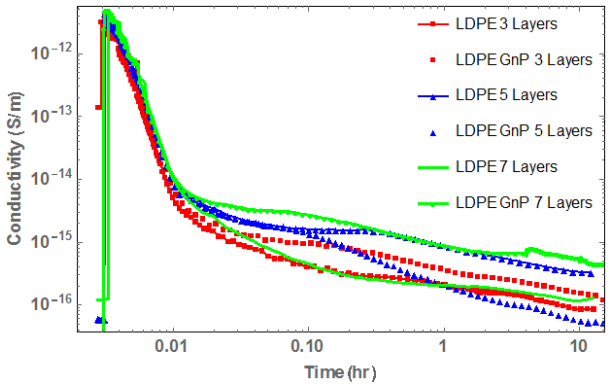

Fig. 6 – DC Conductivity GnP LDPE laminates at 10kV/mm.

4.3 Field dependence of DC Conductivity

The field dependence of DC conductivity was measured in a stepwise manner at the range 8 - 50 kV/mm at 30 °C for the extruded samples and the laminates. Figure 7 illustrates the results obtained for the extruded samples.

One may notice here an appearance of nonlinear behavior, where at a lower field range all the nanocomposites exhibit lower conductivity than that of pure LDPE. With the increasing field strength above 20 kV/mm, a nonlinear behavior starts to dominate the process with a crossover effect is visible around this field value. This behavior appears to be strongest for samples with the highest filler content (11 wt.%) of GnP.

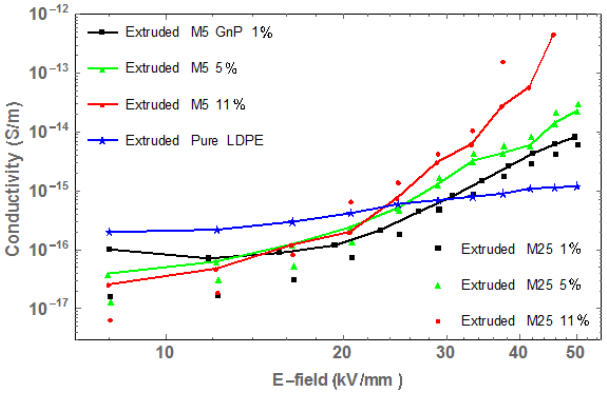

Fig. 7 – DC Conductivity step measurement of extruded samples.

One may consider here the charge transport based on internal injection from localized states at the GnP-LDPE interfaces, where charge carriers are forced to cross the energy barrier between GnP surfaces and the polymer matrix. Tunneling of charges through this barrier and further through polymer matrix may be the dominating mechanism, responsible for the observed nonlinear behavior of the conductivity. At low field, the interface barriers hinder the charge movement, while when the electric field increases the charge carriers gain sufficient energy for crossing them. Moreover, a slight influence of the flake size can also be observed. The GnP M25 nanocomposites show the lowest conductivity at low electric fields, while switching to the highest levels at high field regions.

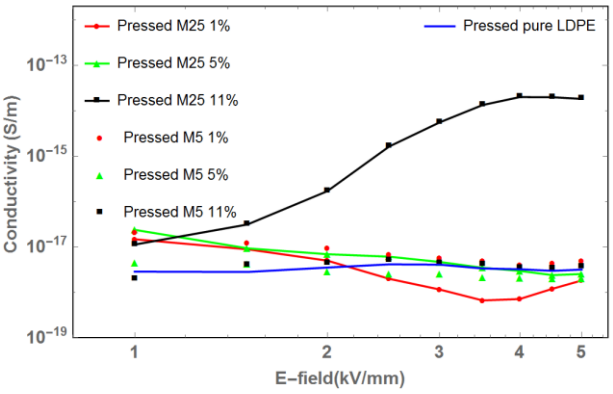

Fig. 8 – DC Conductivity step measurement of pressed samples.

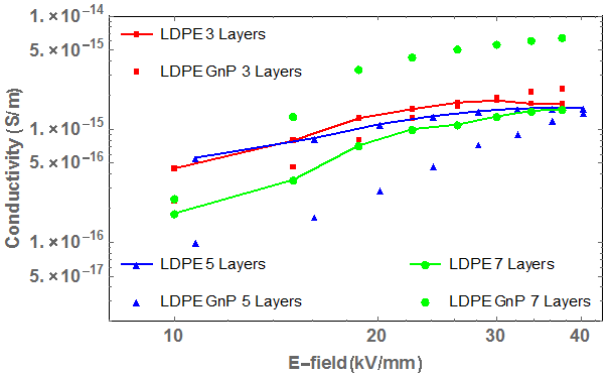

Fig. 9 – DC Conductivity step measurement of the laminates.

Figure 8 shows the conductivity versus electric field for the pressed samples. The field range is here limited to 1 – 5 kV/mm because of frequent sample breakdowns. At such low fields the nonlinear effect is practically not visible except for the pressed 11 wt.% GnP M25 samples.

Figure 9 presents the field dependent conductivities for the graphene LDPE laminates. A slight nonlinear behavior occurs for the samples with the highest graphene content.

5. Conclusions

The influence of manufacturing process on DC conductivity of GnP-LDPE nanocomposites is presented. The results show that melt extrusion process allows obtaining strong anisotropy of nanocomposites and thus yielding a nonlinear behavior of the conductivity, in which GnP interfaces play an important role in the control of charge transport. The presented effect can be interesting for possible future applications of GnP based nanocomposites within HVDC technology.

Acknowledgments

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