Dielectric properties of graphene nanoplatelets filled LDPE

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Abstract - **This work presents studies on electrical properties of nanocomposites of low density polyethylene (LDPE) filled with graphene nanoplatelets (GnP) of different content. As compared to pure LDPE, significant reductions of the conductivity are found for the composites at relatively low electric fields (below 20 kV/mm). A crossover effect is however seen at higher fields (above 20 kV/mm), where a strong field dependent non-linear behavior dominates, yielding higher conduction currents that increase with increasing filler content. Results of investigations of dielectric response confirm the differences found in polarization currents during the measurements of dc conductivity.**

Keywords – Graphene nanocomposites, low density polyethylene, dc conductivity, dielectric response

I. INTRODUCTION

The use of graphene as a filler is gaining more and more attention in recent years due to its special electrical and mechanical properties. Meanwhile, the requirements set on HVDC cable insulation systems are increasing, for reaching higher and higher voltage levels, among which the insulation and field controlling cones of cable terminations and joints appear to be the most challenging parts. Polymer based composites filled with conducting or semi-conducting particles, for example SiC, ZnO or carbon black, are mainly utilized for this purpose and the required non-linear electrical properties are obtained thanks to the percolating structure of the filler particles. High filler loads (30 – 40 wt%) are normally required for achieving effective non-linear characteristics in these materials, which however also changes their processing and mechanical properties as well as dielectric losses [1, 2]. For reducing the filler load while maintaining the other properties on desired level various ideas are considered. In this work we investigate the possibility arising from using graphene nanoplatelets (GnP) as the filler in low density polyethylene (LDPE) based nanocomposites and report on the impact of the filler on dielectric properties, including both dc conductivity and dielectric frequency response. The dc conductivity of all specimens were measured at different electric fields, up to 66 kV/mm. In addition, measurements of dielectric response in frequency range of 1 mHz – 1 kHz were also performed. The paper concentrates on presenting and discussing how the filler content influences the measured dielectrical properties.

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II. MATERIAL SPECIMENS

The manufacturing process of the studied speciemens is illustrated in Fig 1. It follows the technique used by Drzal et al [3]. Low density polyethylene (LDPE) pellet were used as the base materials. It was criogenically grounded into powder (average diameter of the particles 0.5 mm). Exfoliated graphene nanoplatelets (GnP) with an average thickness of approximately 6-8 nanometers and a typical surface area of 120 to 150 m^2/g with particles diameter of 5 microns [4] were applied as the filler.

Mixing of LDPE powder with exfoliated GnP was performed in acetone using an overhead stirrer rotating at 500 rpm for 40 minutes. Thereafter, the mixed materials were dried in an oven at 60 °C for 20 hours. Two extrusion processes were performed using a single srew Brabender extruder 19/25D. In the first process pellets of the masterbatch were manufactured, which thereafter were used to obtain thin films with an average thickness of 0.1 mm. The extruder temperatures from the hopper to the die were respectively: 115, 130, 140 and 140 °C. A constant speed of 5 rpm was kept in the compression screw.

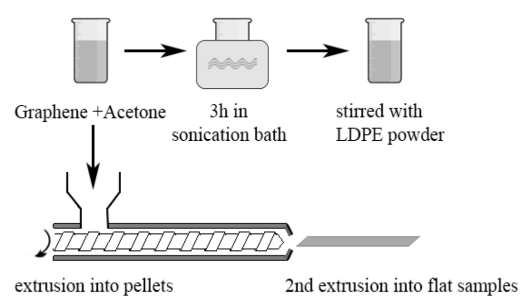

Fig. 1. Stages of specimens manufacturing process.

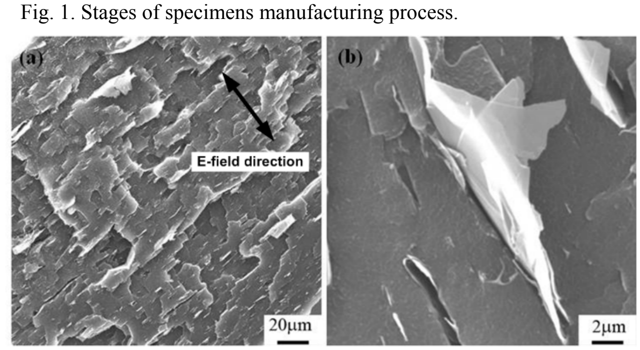

Fig. 2. SEM images of freze-fractured surface of 7.5 wt% LDPE-GnP composites (a) dispersion of filler in the polymer matrix and (b) low adhesion between GnP particle and LDPE.

In total 4 different LDPE-GnP composite specimens were parepared, containing different filler contents: 1, 3, 5 and 7.5 wt %. In addition, pure LDPE specimens were also prepared with the same extruding procedure as a reference.

To check the structure of the prepared specimen, including the distribution and possible agglomeration of the GnP filler, scanning electron microscopy (SEM) was used. Fig. 2 (a) shows a SEM image of the 7.5 wt% composite specimen, in which alignment of GnP particles along extrusion direction becomes evident. Fig. 2 (b) shows possible formation of cavities in the composite on the border between filler and polymer matrix.

III. Experimental Setups

A. DC conductivity measurement

The dcconductivity measurement setup is shown in Fig. 3. Keithley Electrometer (6517B) is used to measure the current flowing through the specimen placed in a shielded electrode system. To obtain a broad range of used electric fields, both the electrometer internal voltage supply (up to 1 kV) and a high voltage DC supply (Glassman FJ60R2, 60kV, 2 mA) were utilized. An overvoltage protection together with low pass filters were also integrated into the setup for preventing possible damages in case of specimen breakdown and for filtering out high frequency noise.

The used shielded electrode system is similar to a conventional three electrode system. The difference is that a shielding plate covers the back side of the measuring electrode for avoiding external capacitive couplings. To further reduce the external noises, the whole electrode system was placed in a grounded stainless steel box. To control the temperature of the measurement, an oven was used and the electrode system with inserted specimen were kept in the oven for at least 1 hour before each measurement.

A LabVIEW based software was utilized for recording and processing the data in real-time. In dc conductivity measurement, an extensive averaging is often required for increasing the signal to noise level. An algorithm optimizing the necessary averaging was applied by evaluating the standard deviation of every incoming data point.

B. Dielectric frequency response measurement

The dielectric response measurements were performed by IDAX 300 dielectric spectroscopy analyzer using the same shielded electrode system as the one used for dc conductivity measurements. The advantage of using it in the dielectric response measurements is elimination of parasitic capacitances. The measurements were performed at room temperature (22 °C), and the applied voltage was 200 V_{peak}.

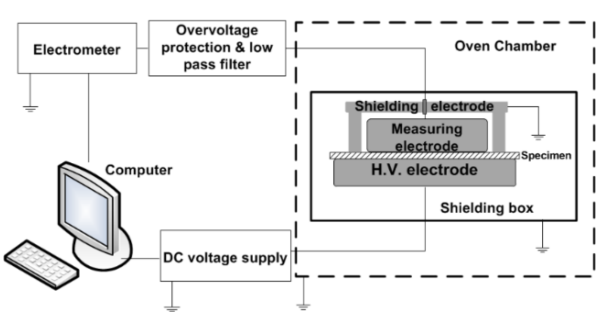

Fig. 3. Setup of dc conductivity measurements.

IV. Results and Discussions

A. DC Conduction at Low Fields

The low field behavior was studied by measuring dc current response at three temperatures: 30, 50 and 70 °C and the electric field strenght over the specimens were kept at 9 kV/mm. For taking care of slightly varying specimen thickness, the results are presented in the following as apparent dc conductivity.

Fig. 4 shows the apparent conductivity calculated by using the current values obtained during 3 hours lasting measurements. At each temperature level, similar conductivity level was obtained for all the LDPE-GnP composite specimens, independently of the filler content. Certainly, the curves shown are affected by the in parallel ongoing polarization of the samples, especially at shorter measuring times, but the difference of the conductivity as compared to the pure material becomes evident and it increases with inreasing temperature.

At 30 °C, the peaks appearing within the first 10 s of the measurements are due to stabilization of the electrometer. As the current in this time is mainly due to the ongoing polarization, the differences in its level (apparent conductivity level) correlate well with level of filler content, indicating a possible difference in

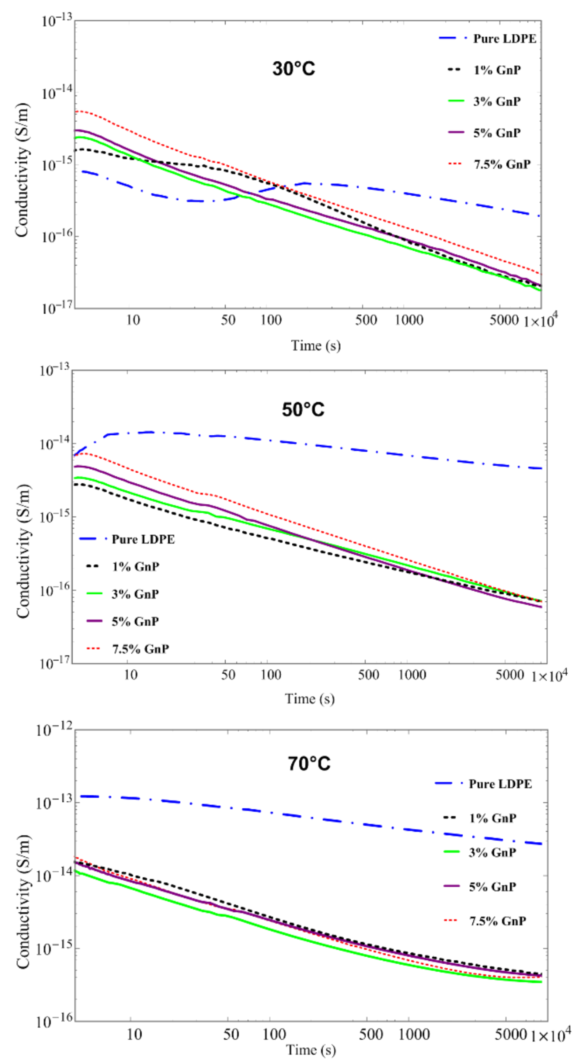

Fig. 4. Time variations of apparent dc conductivity for pure LDPE and LDPE-GnP compositesat 30, 50 and 70 ^{0}C and 9 kV/mm.

material's permittivity. However, the second peak appearing at around 200 s in the pure specimen is possibly caused by the movement of injected charge that reaches the measuring electrode (space charge limited regime). The same behaviour is only weakly marked in the 1 wt% LDPE-GnP specimen and not present in all the others, indicating that the space charge movement through the samples may be of different nature, i.e. accumulated at the interface between filler and base material [5].

When increasing the temperature to 50 °C, the transit time of space charge is shorter, i.e. about 10 s. At the same time the difference of the current level between pure and filled materials becomes larger, but the current levels measured on the LDPE-GnP specimens at 50 °C remain similar as the results obtained at 30 °C. At 70 °C, the charge movement peak lies with the electrometer stabilization time, while the level of polarization current in the pure material is again higher. By assuming the time of space charge drift to occur at 1 s at 70 °C, charge mobility μ in the pure LDPE specimen can thus be estimated according to the time of flight principle as:

$$\mu = \frac{l^2}{V \cdot t_{tr}} \quad (1)$$

where l is sample thickness, V is applied voltage and t_{tr} is estimated time to the current peak.

Fig. 5 shows the estimated charge mobilities of the pure LDPE specimens as a function of reciprocal temperature. As an exponential relation is observed, the activation energy of the charge mobility can be calculated by applying Arrhenius equation:

$$\mu(T) = Ae^{(-\frac{E_a}{k_B T})} \quad (2)$$

where, A is the pre-exponential factor, in this case the reference charge mobility $\mu_{0;}$ k_B is Boltzmann's constant $8.617 \cdot 10^{-5}$ eV/K, and T is the absolute temperature. The calculated activation energy of the charge mobility E_a becomes 1.1 eV.

To further investigate the temperature dependence of the measured conductivity, the volume conductivity values at 3 hours of measurement are shown as a function of reciprocal temperature in Fig. 6. The slope of the plot represents the thermal activation energy of the conductivity, which can also be calculated by using Arrhenius dependence. The calculated on this basis activation energy of the pure LDPE is about 1.1 eV, i.e. practically the same as the activation energy of charge mobility. For all the LDPE-GnP composites it is about 0.7 eV. The obtained activation energy of dc conductivity for the pure LDPE is similar as indicated in the literatures [6, 7]. Thus, one may suggest that, at low electric field, LDPE filled with GnP results lower DC conductivity compare to the pure LDPE, but the amount of fillers content (between 1-7.5 wt%) does little influence on it.

B. DC Conduction at High Fields

In order to identify the presence of field activated conductivity, the measurements were performed in a way, where the applied voltage was gradually increased in steps of about 4 kV/mm between 8 and 66 kV/mm and the duration of each step was 30 minutes. All the measurements were performed at room temperature (22 °C). The current behaviour during one such a step with applied electric field of 43 kV/mm is exemplified in Fig. 7. It clearly shows a change in the effect of the filler, as compared

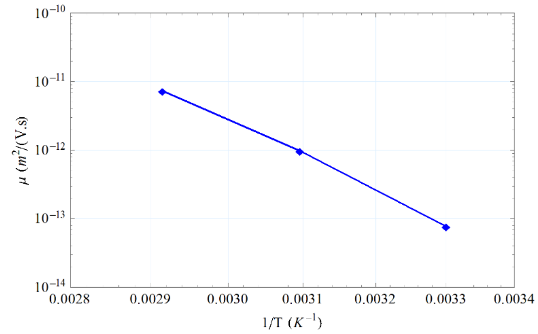

Fig. 5. Temperature dependence of charge mobility in pure LDPE.

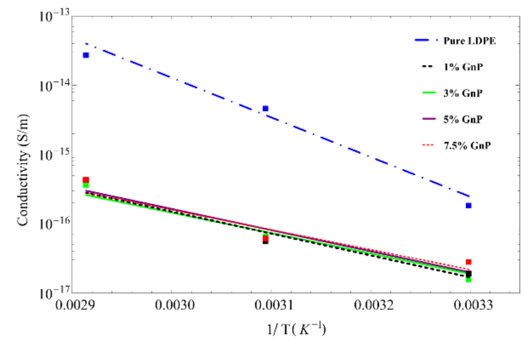

Fig. 6. Temperature dependence of apparent dc conductivity (current at 3 hours) for pure LDPE and LDPE-GnP composites.

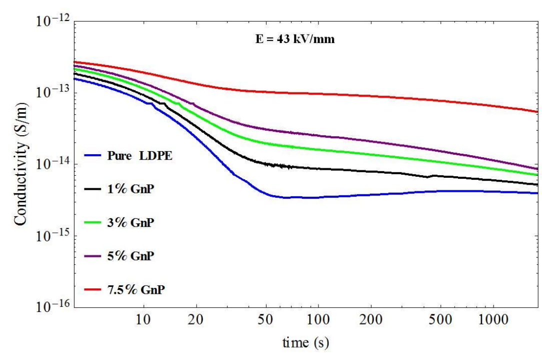

Fig. 7. Time variations of apparent dc conductivity for pure LDPE and LDPE-GnP composites at 43 kV/mm and 22 °C.

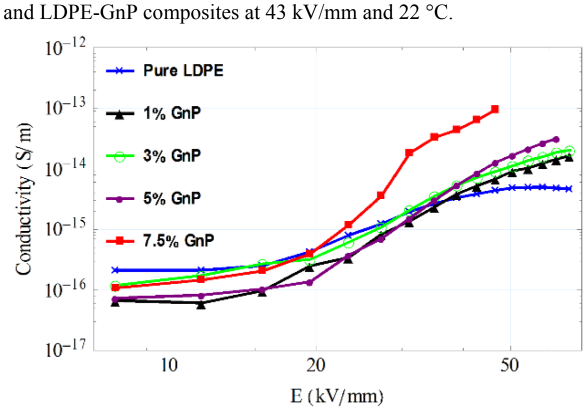

Fig. 8. Field dependence of apparent dc conductivity at 22 °C for pure LDPE and its GnP composites (at 30 min).

to the low field conditions, where the level of the current increases with increasing filler content.

Fig. 8 plots the calculated conductivities (at 30 minutes) as a function of applied electric fields for all the investigated specimens. One may observe in the figure that a nonlinear behaviour starts to dominate at the field strength of about 20 kV/mm. In addition a clear crossover effect appears, where the lower at low fields conductivity of the filled composites becomes higher as compared to the conductivity of pure LDPE and the order of the increase is related to the GnP filler content. The specimen containing 7.5 wt% GnP shows the strongest non-linear field depended behavior. There also seems to exists a tendency for the conduction to saturate at fields about 40 kV/mm and above.

C. Dielectric Response

The results of dielectric response measurement are shown in Fig. 9. The dielectric constant ε' and losses tan δ increase with the increase of the filler content. These results matches well the current difference observed at the beginning of dc conductivity measurements, where the dominance of polarization current component is strong. The difference in dielectric constant may be related to the aspect ratio of the fillers [8]. Fillers with a high aspect ratio can yield an increase of the dielectric constant of polymer composites and the used GnP have aspect ratio of 625.

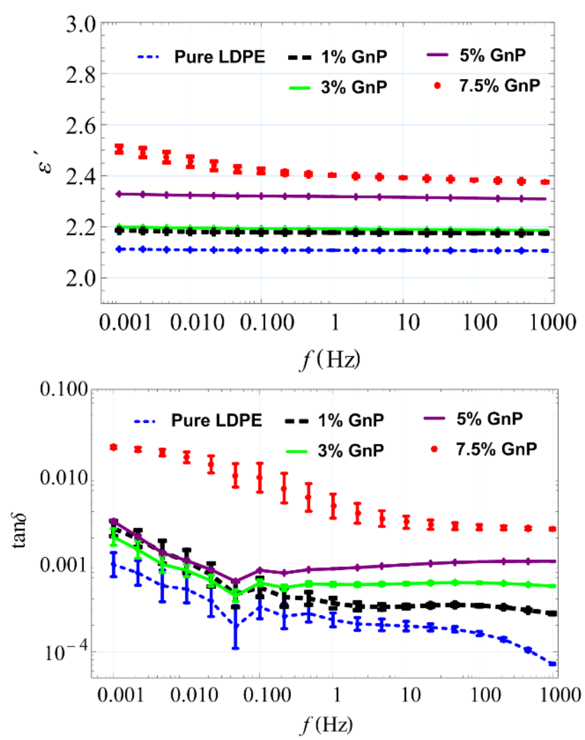

Fig. 9. Relative permittivity (ε') and dissipation factor (tan δ) at 22 °C for pure LDPE and its GnP composites (error bars represent deviation for 3 specimens).

V. SUMMARY

GnP filled LDPE composites show interesting non-linear field dependent behaviour. Significantly lower conductivity, as compared to pure LDPE, is observed in them at low electric fields (<10 kV/mm) while higher conductivity is measured at higher electric field (> 20 kV/mm). At the low field, the possible explanation is that interfaces between LDPE and filler particles limit space charge movement and thus the current. In parallel, increase in dielectric constant and loss are also observed with the increase of GnP filler content. The presented findings indicate that using the lowest filler content provides strong reduction of dc conductivity at low electric fields. However, to obtain a strong non-linear field dependent behavior, a higher filler content is required.

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