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# Highly Structured Graphene Polyethylene Nanocomposites

Karolina Gaska<sup>a\*</sup>, Roland Kádár<sup>a</sup>, Xiangdong Xu<sup>b</sup>, Stanislaw Gubanski<sup>b</sup>, Christian Müller<sup>c</sup>, Santosh Pandit<sup>d</sup>, Venkata R. S. S. Mokkalapati<sup>d</sup>, Ivan Mijakovic<sup>d</sup>, Andrzej Rybak<sup>e</sup>, Artur Siwek<sup>e</sup>, Magnus Svensson<sup>f</sup>,

<sup>a</sup> Chalmers University of Technology, Dept. of Industrial and Materials Science, Division of Engineering Materials, Polymeric Materials and Composites, SE 412 96 Göteborg, Sweden

<sup>b</sup> Chalmers University of Technology, Dept. of Electrical Engineering, Division of Electric Power Engineering, High Voltage Engineering, SE 412 96 Göteborg, Sweden

<sup>c</sup> Chalmers University of Technology, Dept. of Chemistry and Chemical Engineering, Division of Applied Chemistry, Polymer Technology, SE 412 96 Göteborg, Sweden

<sup>d</sup> Chalmers University of Technology, Dept. of Biology and Biological Engineering, Division of Systems and Synthetic Biology, SE 412 Göteborg, Sweden

<sup>e</sup> ABB Corporate Research Center, PL 31038 Krakow, Poland

<sup>f</sup> Wellspect HealthCare, SE 43121 Mölndal, Sweden

\*gaskak@chalmers.se

**Abstract.** This research presents an overview of the properties of highly structured, low density polyethylene-graphene nanoplatelets (LDPE-GnP). The influence of nanofiller content, size and processing conditions on the material properties have been investigated. Therefore, rheological and thermal nanocomposite properties were investigated. So-called dry-coating method has been used in order to prepare masterbatches which were thereafter extruded by means of single screw extruder resulting in a strong anisotropy in the extruded samples. Graphene nanoplatelets were oriented in the extrusion direction for all shear rates and flow histories investigated, as confirmed by scanning electron microscopy. The rheological percolation was determined via nonlinear parameters to be around 11wt%. Thermal conductivity measurements revealed strong anisotropy with in-plane conductivity increasing with GnP content.

**Keywords:** nanocomposites, graphene nanoplatelets, extrusion

**PACS:** 81.05.ue, 81.05.Qk,

## INTRODUCTION

Graphene has found applications in most of the scientific fields today. It has been shown that graphene-based materials have a wide range potential in variety of applications such as supercapacitors, packaging, filtering membranes, flexible electronics and heat sinks [1]. In the recent years graphene has gained attention as a possible nanofiller for polymer matrix nanocomposites due to its unique thermal, electrical and mechanical properties [2, 3]. Polyolefin composites are mainly produced by means of melt extrusion, compression molding or film blowing methods. The processing methods very often have significant influence on resulting material's morphology. The large deformations which are present during the processing, determine resulting materials morphology [3, 4, 8]. Therefore, a characterization of rheological properties of polymer nanocomposites is crucial in order to understand the complex matrix-filler and filler-filler interactions. In particular, Fourier-transform rheology can be used to determine the percolation threshold, morphological changes and microstructural interactions in percolated systems, the influence of various particle characteristics and modeling the rheological material response [4, 6, 7].

The main purpose of this study is to develop an understanding of the influence of manufacturing process as well as properties of used GnP on effective thermal and rheological properties of manufactured nanocomposites.

## MATERIALS

Low density polyethylene (LDPE - Borealis AB) in the form of pellets was used as a polymer matrix. Graphene nanoplatelets (XG Sciences) GnP M5 and GnP M25 with average flakes size 5  $\mu\text{m}$  and 25 $\mu\text{m}$  respectively were used.

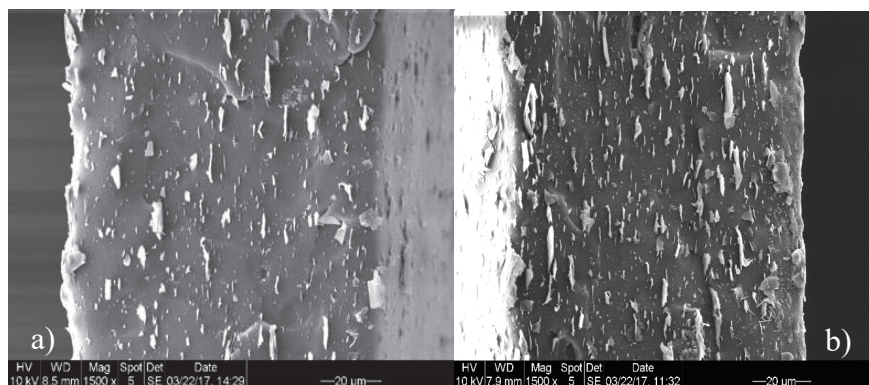
Properties of the nanoplatelets and molecular weight parameters of the LDPE, measured by means of Gel Permeation Chromatography and DSC, are presented in Gaska et al. [3, 5]

Graphene nanoplatelets were dispersed into acetone and stirred by high shear rotor stator mixer for 20 minutes at 10 000 rpm, then sonicated for 3h, 90W. Thereafter graphene-acetone suspension was mixed with LDPE in the powder form for 1h at 500 rpm using overhead stirrer until total solvent evaporation. Obtained this way masterbatches were dried in an oven at 60 °C for 24 h. The Brabender 19/25D single-screw extruder (screw diameter  $D=19$  mm and a screw length of 25 D) equipped with conveyor belt was used. GnP-LDPE masterbatches were extruded twice by means of barrier screw with compression ratio 5:1[3]. The first extrusion process has been carried out to compound the masterbatches, the second extrusion process was carried out in order to obtain samples in the shape of tapes with an average thickness of  $0.1\text{ mm} \div 0.3\text{ mm}$  and width around 70mm. The extrusion temperatures were as follows: 115, 130, 130 and 140 °C from the feeding section to the extruder die. The constant screw speed of 5 rpm was kept during the extrusion process. The produced composites contain 1%, 5% and, 11 wt% of GnPs.

## RESULTS AND DISCUSSION

### Morphology

The morphology of the LDPE-GnP nanocomposites has been studied by means of a FEI/Philips Field Emission Scanning Electron Microscope using freeze fractured samples. The representative SEM images of LDPE/GnP/M5 and LDPE/GnP/M25 with 5% of filler content are shown on Figure 1. It can be seen from the SEM images that graphene nanoplatelets are well distributed throughout the LDPE matrix. The nanoplatelets are aligned along the extrusion flow direction. This effect was also observed in our earlier study [3, 5]. The difference in size between fillers is visible, however some agglomerates are present in both samples.

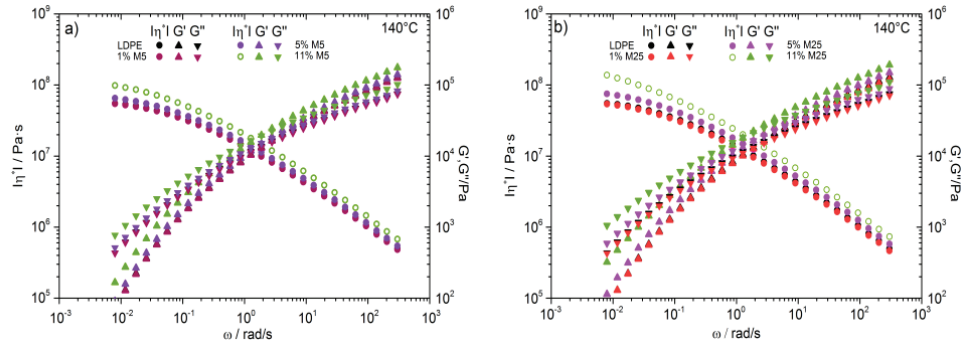


**FIGURE 1.** SEM pictures for composites filled with 5wt% GnP M5 (a) and GnP M25 (b).

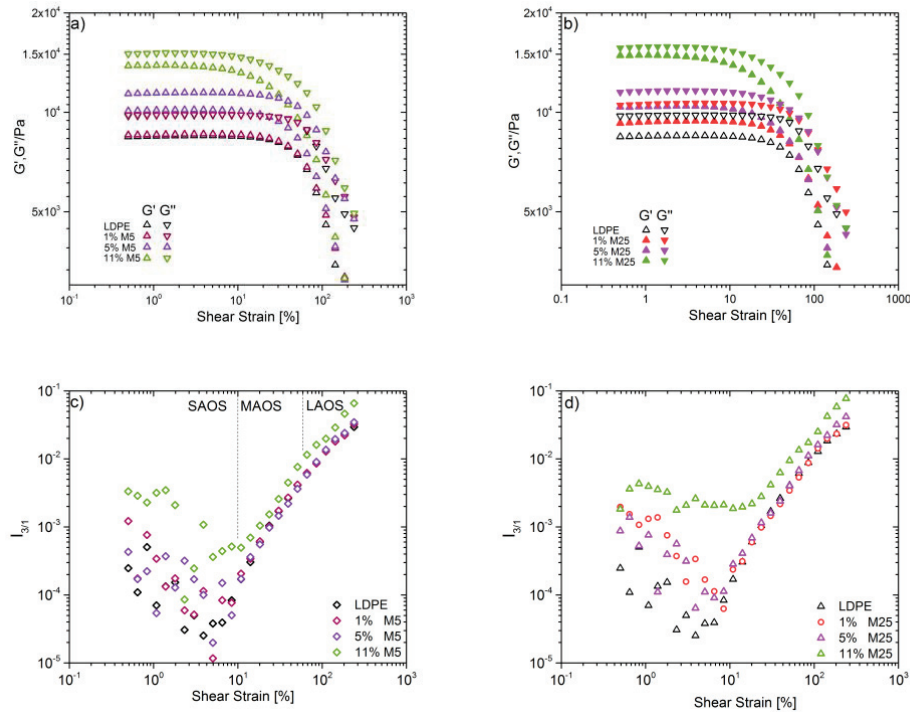
### Rheological Properties

The rheological characterization of the nanocomposites was conducted by means of an Anton Paar MCR702 TwinDrive rheometer with 25 mm diameter plate-plate geometry and 1 mm gap. Linear and nonlinear viscoelastic oscillatory shear tests were performed in order to determine the influence of graphene with different particles' size on composites rheology. The results are presented in Figures 2-3.

Storage modulus  $G'$ , loss modulus  $G''$  and complex viscosity as functions of angular frequency are presented on Figure 2. An increase (terminal region) in  $G'$  and  $G''$  with increasing filler content is visible for both types of graphene. In the low frequency range, which could correspond to creation of a rheological percolation network, the increase is most pronounced for 11wt.% of filler content. However, the existence of a plateau in the storage modulus cannot be inferred from the data. Also, moderate increases in the complex viscosity are recorded, slightly higher for LDPE/GnP/M25 samples.



**FIGURE 2.** Storage modulus  $G'$  and loss modulus  $G''$  as functions of angular frequency (a) LDPE/GnP/M5, complex viscosity as a function of angular frequency for samples LDPE/GnP/M25.



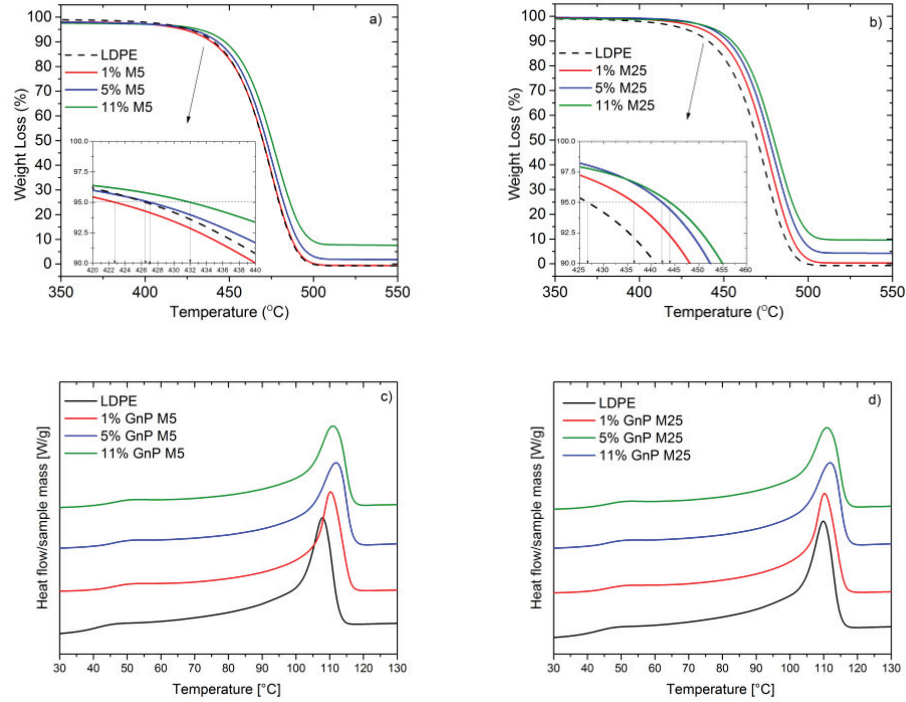
**FIGURE 3.** Storage modulus  $G'$  and loss modulus  $G''$  as a function of shear strain (a) LDPE/GnP/M5, (b) LDPE/GnP/M25 and relative third harmonic content  $I_{3/1}$  as function of shear strain (c) LDPE/GnP/M5 and (d) LDPE/GnP/M25.

Figure 3 (a) and (b) show the dynamic moduli dependence on the applied strain amplitude at constant angular frequency across the linear and nonlinear regimes for samples filled with GnP M5 and M25 respectively. The corresponding relative third higher harmonic ( $I_{3/1}$ ) of the shear stress material response signal are shown in Figure 3 (c) and (d). We refer to nonlinear material parameters due to their higher sensitivity for the detection of percolation [4, 6, 7] Results in Figure 3 (c) and (d) show a change in scaling law in the LAOS (large amplitude oscillatory shear) regimes with increasing filler concentration. Moreover, plateau at the SAOS–MAOS (small and medium amplitude oscillatory shear respectively) transition region may signal rheological percolation above 5wt.%. Especially for samples LDPE/GnP/M25 the plateau is clearly visible which may be attributed to the influence of the filler size.

## Thermal Properties

The thermogravimetric analysis (TGA) has been carried out by means of Mettler Toledo TGA/DSC 3+. The filler content and the degradation temperature of all specimens were studied. These measurements were carried out on

2 ÷ 5 mg samples in nitrogen atmosphere with heating rate 20 °C/min in the temperature range from 30 °C - 900 °C. The results are presented on figure 4 (a) for LDPE/GnP/M5 and LDPE/GnP/M25 (b). One can notice that degradation temperature  $T_{5\%}$  increases with increasing filler content, namely the addition of 11% causes its increase by 5.5<sup>0</sup>C in the case of using GnPs M5 and 17.5<sup>0</sup>C for GnPs M25. These results are consistent with author's other studies [5] and suggest that GnP flakes prevent the diffusion of flammable gasses into the composite body and increase the thermal stability of the composite. Moreover, graphene flakes may reduce the mobility of polymer chains within the matrix, therefore the degradation temperature increases.



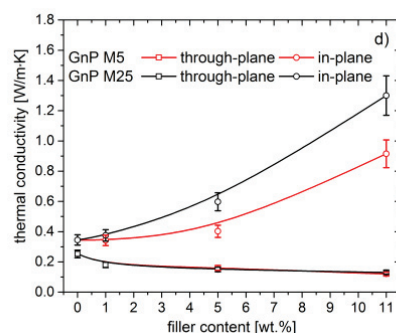
**FIGURE 4.** TGA curves measured for specimens filled with M5 GnP (a) and M25 GnP (b) DSC second heating thermograms for specimens filled with M5 GnP (c) and M25 (d).

The impact of GnPs nanofiller on composite crystallinity was also investigated by means of Mettler Toledo TG-DSC2 instrument. The samples were measured in the temperature range as follows: -50 °C to 150 °C with a scan rate of 10 °C/min in a heating-cooling-heating cycle under nitrogen atmosphere. The size of DSC second heating thermograms present melting peaks which size slightly decrease with increasing filler content. This behavior is attributed to the decrease in degree of crystallization of LDPE [3] (Figure 4 c and d). One may conclude that the higher concentration of graphene may hinder the growth of the crystallites as the graphene flakes may prevent the diffusion of polymer chains to grow crystallites.

Thermal conductivity was measured by means of Hot Disc Thermal Constants Analyser 2500 S according to ISO Standard 22007-2. The instrument used allows to determine thermal conductivity of anisotropic samples. Figure 5 shows thermal conductivity of the LDPE/GnP/M5 and LDPE/GnP/M25 nanocomposites and the reference pure LDPE.

Thermal conductivity increases in-plane direction whereas in through-plane direction slight decrease is visible. This behavior corresponds to the morphology of extruded films presented in this paper (Figure 1). The thermal conductivity along extrusion direction for all the measured samples increased together with filler content and for the sample with 11 wt% M25 the increase is the most pronounced.





**FIGURE 5.** thermal conductivity of the composites

One can conclude that the conductive paths are more likely created along polymers processing direction and are created in a more efficient way using flakes with bigger diameter [9]. Whereas, interfacial scattering processes of phonons between GnP and LDPE can be much stronger in through-plane direction due to much bigger interface area as for parallel direction therefore strong scattering of phonons may yield to the decrease of effective thermal conductivity in this direction [5, 9].

## CONCLUSIONS

In this study the influence of GnPs with different particles size M5 and M25 on low density polyethylene produced by means of melt extrusion process has been investigated. The studied composites' morphologies show good filler dispersion as well as strong anisotropy in its orientation which is a result high shear stresses acting on a material during extrusion process. It can be observed that thermal degradation temperature slightly increased with the increasing filler content whereas crystallinity decreases. A strong anisotropy in the thermal conductivity is also achieved, showing a strong increase of thermal conductivity along extrusion direction.

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