Tailoring polymer nanocomposite microstructure by controlling orientation, dispersion and exfoliation of GnP in LDPE via extrusion flow

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ABSTRACT

The orientation of low density polyethylene - graphite nanoplatelets polymer nanocomposites during extrusion flow was considered in this study, with the purpose of controlling the nanocomposite orientation and dispersion for desired extrudate properties. The emphasis was on orientation of the nanofillers as a function of the composition of the nanocomposite, die apparent shear rate and draw ratio. Scanning electron microscopy analysis of the extrudates revealed a strong orientation of the nanoplatelets in the flow direction provided the concentration of fillers is low enough to avoid agglomeration. The achieved orientation was independent of the applied shear rates and filler type, however, a slight de-orientation could be achieved by imposing of draw ratios greater than 1. The orientation of the fillers in the flow direction could be observed as early as the transition zone during screw channel flow, with the platelets oriented along the secondary flows therein formed.

INTRODUCTION

Graphene stands out as potential nanofiller in polymeric melts due to its outstanding mechanical, dielectric, barrier, thermal, etc. properties.[1] However, significant challenges remain to be overcome in the development of graphene-based consumer products. In the case of polymer-based nanocomposites, three main challenges can be envisioned: (i) graphene preparation, (ii) its incorporation into polymers and (iii) tailoring the microstructure during processing to achieve the desired properties. The main issues regarding the preparation of graphene refers to the absence of affordable large quantities of defect-free single layer graphene.[2] Thus, most efforts are directed toward investigated few-layers thick graphene nanoplatelets also called graphite nanoplatelets (GnP). The incorporation of graphene into polymers is a critical step for the properties of the nanocomposites and several options are available, such as in-situ polymerization, solution blending, melt blending etc.[3] Melt blending is a fast and simple route for preparing master batches for polymer melts albeit its exfoliation is typically extremely low. Overall, the degree of exfoliation and the quality of dispersion is a function of the preparation of the graphene and its incorporation into polymers. Thereafter, the processing stage is of utmost importance for obtaining graphene-enhanced properties in polymer nanocomposites. By method of processing, the microstructure can be tailored to attain the desired material properties by deagglomerating the particles, improving dispersion and, ensuring the desired orientation of the nanofillers in the melt. For example, to attain good electrical properties the platelets must be percolated and randomly oriented, whereas the platelets must be oriented perpendicular to the direction of gas diffusion to attain good barrier properties. Thus, with respect to processing it is of utmost importance to understand the flow field - filler interaction in polymer melt nanocomposites. In this context, in this publication we explore the orientation dynamics during the extrusion flow of polyethylene - graphite nanoplatelets nanocomposites.

EXPERIMENTAL

Two variants (M5 and M25) of Grade-M XGNP graphite nanoplatelets (GnP) were used and their main characteristics are presented in Table 1, as provided by the supplier. A packaging grade polyethylene with a long chain branched molecular architecture, i.e. low density polyethylene was used as matrix. Master batches of high filler concentrations (e.g. 16.7 wt%) were produced via melt mixing in a twins screw extruder with the melt zone temperature set to 190°C. The effect of concentration was studied by diluting the master batch to concentrations of 7.5 wt% and 1.5 wt% of both M25 and M5. The dilution was performed in a single screw extrusion with a compression screw (compression ratio of 2:1) and Maillefer screw with a Saxton mixing element and a 3 mm die. The dilution was achieved by several runs for each batch. A compression screw (compression ratio of 2:1) was used for the final extrusion flow study, equipped with dies of dimensions 10 mm x 0.45 mm and 20 mm x 0.45 mm.

For both dilution and shaping, a Brabender single screw extruder 19/25D (barrel diameter of 25 mm and barrel length of 25 × 19) was used. The extruder was equipped with Terwin 2000 series (model 2076) melt pressure sensors with maximum pressure of 700 bar for inline rheometry. Shear viscosity and normal stress difference measurements via the 'hole effect'[4,5] were performed, however they are not discussed in this publication. The extrusion setup is complemented by two Brabender conveyor belts with belt speeds of 6 m/s and 18 m/s, respectively and rollers to impose a draw ratio, and an inline visualization system for monitoring the onset of instabilities.[4] Overall, the influence of the apparent (die) shear rate,

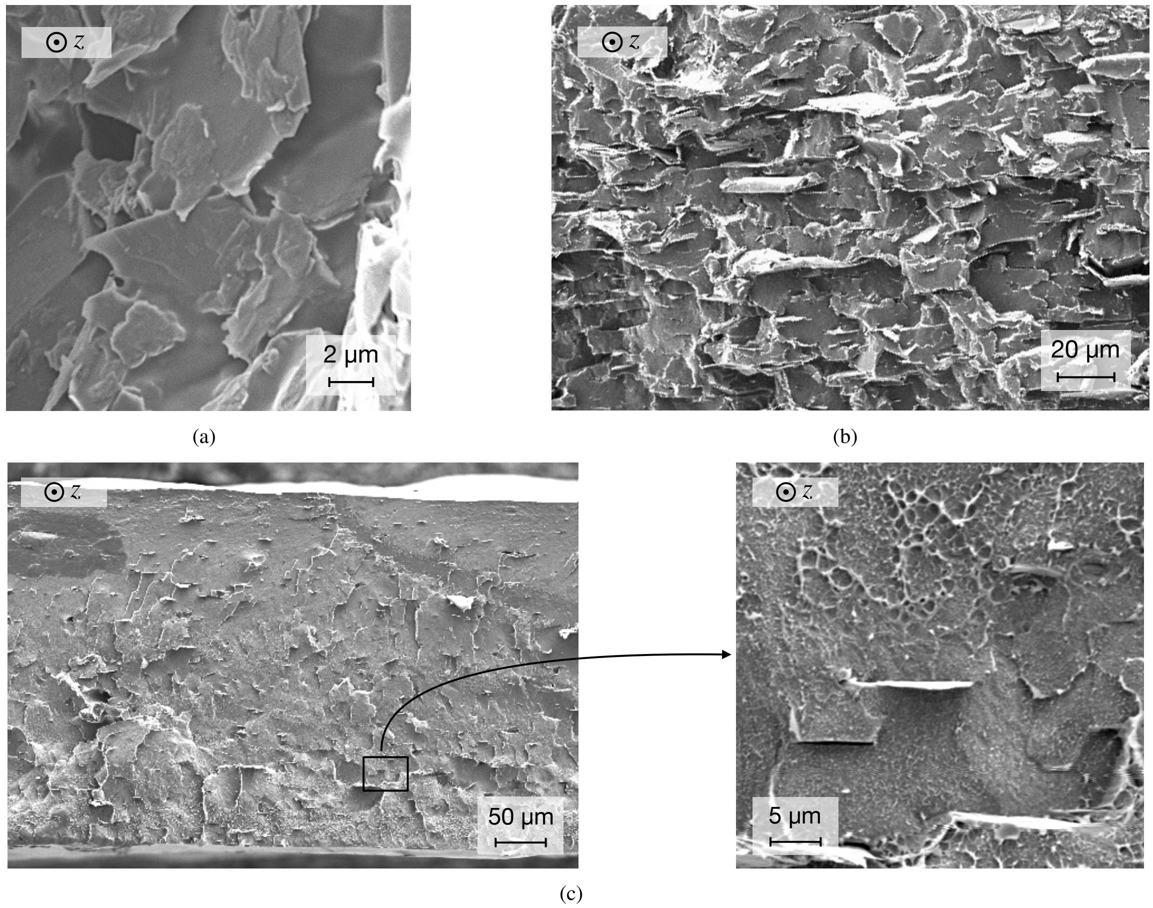
Table 1. The main characteristics of the graphite nanoplatelets (GnP) used in the present study, as provided by the supplier.

Grade	Average particle diameter μm	Surface area (BET) m^2g^{-1}	Average thickness nm	Density kg/cm^3
M5	5	120 - 160	6 - 8	2.2
M25	25	120 - 160	6 - 8	2.2

defined[6] as $\dot{\gamma}_a = 6Q/WH^2$, where Q is the volumetric flow rate entering the die and W and H are the width and height of the slit die, and of the draw ratio defined as v_2/v_1, where v_2 is the linear velocity between the rollers and v_1 is the average velocity inside the extrusion die. Scanning electron microscopy (SEM) analysis was performed on the extruded films in order to assess the orientation of the GnP.

RESULTS AND DISCUSSION

By controlling the flow and drawing deformation rates and the material composition different microstructures can be obtained. In the case of filler concentration over 7.5wt% e.g. the master batches a strongly agglomerated microstructure was observed, e.g. see Fig. 1(a). The high filler concentration signifies also that the fillers are distributed until close to the surface of the films thus affecting their appearance. Any orientation effects observable can be related to the orientation of agglomerates along their principal axes to the flow direction. This was characteristic of the microstructure independent of the shear rates, $\dot{\gamma}_a \in [35, 350]$ s^{-1}, draw ratios applied, the maximum draw ratio being $v_2/v_1 = 5$ for $\dot{\gamma}_a = 35$ s^{-1} and the GnP grade. It should be noted that the ability of the extrudates to withstand the applied draw ratios was reduced for the filled samples compared to the unfilled samples, e.g. for LDPE the maximal draw ratio applied at $\dot{\gamma}_a = 35$ s^{-1} was $v_2/v_1 = 13$, limited only by the speed of the conveyor belt, whereas in the case of the LDPE-GnP nanocomposite sample fracture was recorded above $v_2/v_1 = 5$. For diluted GnP concentrations, i.e. 7.5wt% and 1.5wt% and in the absence of an applied draw ratio well dispersed and perfectly oriented GnP in the flow direction for all shear rates investigated, e.g. Fig. 1(b), (c) independent the GnP grade. It should be noted that even at the lowest shear rates investigated ($\dot{\gamma}_a = 35$ s^{-1}) the orientation and de-agglomeration of the fillers was observed, which can be related to the onset of nonlinear deformations in the melt (below the shear rats applied during extrusion) and the long residence time distribution associated to



(a) (b) (c)

Figure 1. Nanocomposite morphology at various compositions and in various flow conditions: (a) highly agglomerated structures with a composition of 12.5wt% GnP - M5, $\dot{\gamma}_a = 264$ s^{-1}, $v_2/v_1 = 2$, (b) highly oriented GnP - M25 in the flow direction with a composition of 7.5wt%, $\dot{\gamma}_a = 97.3$ s^{-1} and (c) highly oriented GnP - M5 in the flow direction $\dot{\gamma}_a = 1351$ s^{-1}. The z-axis in the images corresponds to the flow direction.

extrusion processing. By subjecting the composite melt to drawing in the belt zone the filler orientation was further altered. As the draw ratio increases, i.e. $v_2/v_1 > 1$, the platelets exhibited a tendency to change their orientation from the direction of the flow to match thinning profile of the films i.e. an orientation with an angle relative to the flow direction was induced. The onset of orientation was traced in-situ as far as the towards the middle of the metering zone, Fig. 2(a), zone that is responsible for the melting of the feed and due to the screw channel height, corresponds to the minimal shear rates existing in barrel. Thus, in a screw channel cross-section, the GnP are oriented in the direction of the secondary flows, Fig. 2(b).

From flow stability point of view, the onset of instabilities in the LDPE, surface distortions characterized by one characteristic frequency, was at apparent shear rates of around $\dot{\gamma}_a = 80$ s^{-1}. The presence of the GnP has a stabilizing effect on the flow, with the onset of instabilities is delayed toward apparent shear rates of over 300 s^{-1}.

SUMMARY AND CONCLUSIONS

The processing stage is of utmost importance for obtaining graphene-enhanced properties in polymer nanocomposites. By method of processing, the microstructure can be tailored to attain the desired material properties by deagglomerating the particles, improving disper-

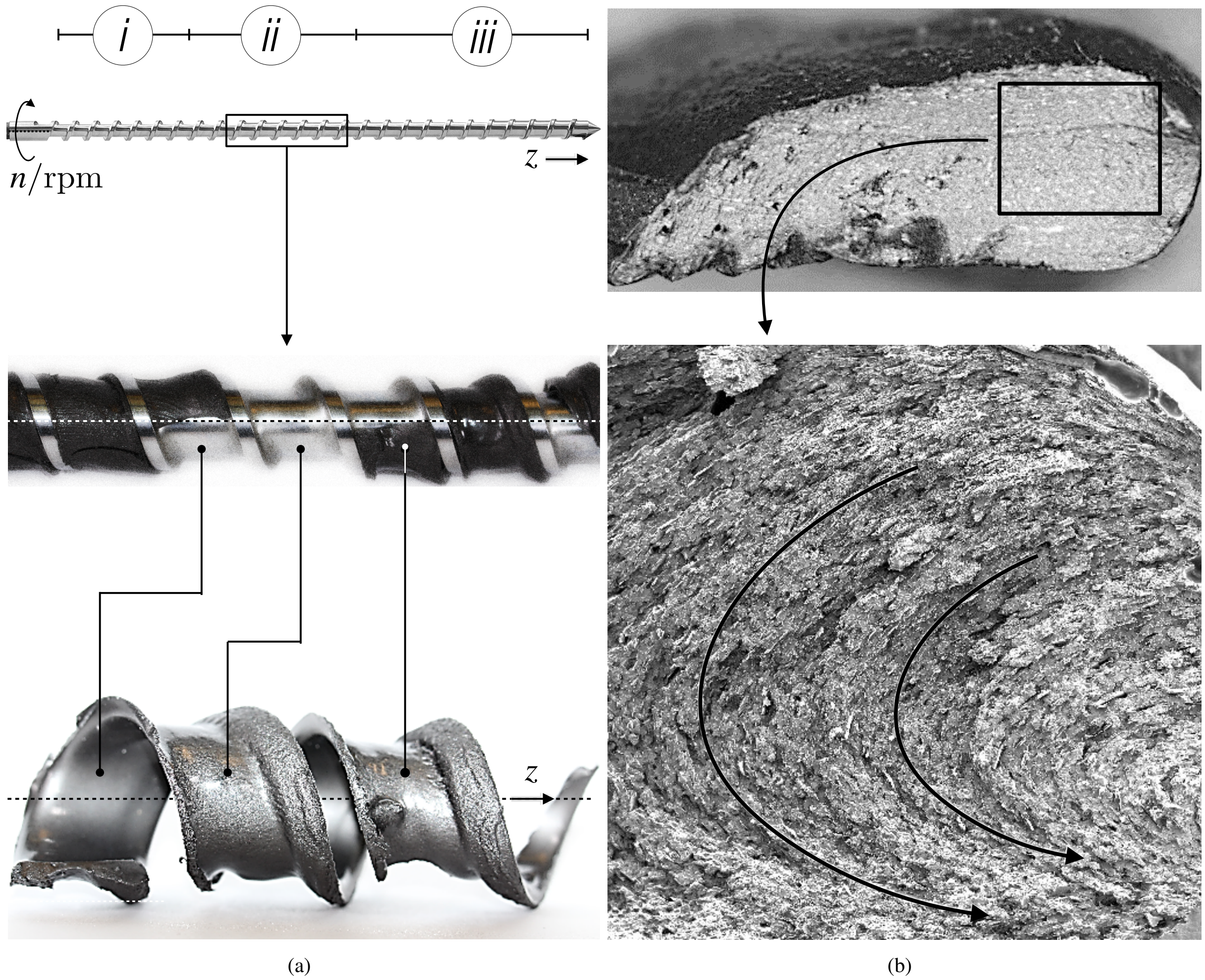


Figure 2. In-situ qualitative observations of the orientation dynamics towards the end of the metering zone, (ii), of a compression screw, compression ratio 2:1, (a), during the extrusion flow of PE-GnP nanocomposites showing the orientation of GnP along the streamlines of the secondary flows, (b). The following notations were used for the screw zones: (i) solid conveying zone, (ii) transition zone and (iii) metering zone.

sion and, ensuring the desired orientation of the nanofillers in the melt. Thus, the orientation of low density polyethylene (LDPE) - graphite nanoplatelets (GnP) polymer nanocomposites during extrusion flow was considered in this study with emphasis on orientation. A strong orientation of the nanoplatelets was achieved orientation for filler concentrations lower than 12.5 wt%, independent of the applied die shear rates and filler type. However, a de-orientation could be achieved with the application of a draw ratio. The orientation of the fillers in the flow direction could be observed as early as the transition zone during screw channel flow, with the platelets oriented along the secondary flows therein formed. Overall, extrusion flow is shown to be capable of successfully de-agglomerating the nanofillers and achieving orientation in LDPE - GnP systems, while exfoliation must be sought in the preparation stage of the nanocomposites.

ACKNOWLEDGEMENTS

The initial trials have been funded through the Vinnova Grant SIO Grafen Grant - Graphene as barrier and packaging material. The authors are grateful to Kristina Karlsson for SEM support.

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