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High-Density Polyethylene Based on Exfoliated Graphite Nanoplatelets/Nano-Magnesium Oxide: An Investigation of Thermal Properties and Morphology

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Abstract

In this study, high-density polyethylene (HDPE)/exfoliated graphite nanoplatelet (xGnP) composites reinforced with a 2 wt.% concentration of nanomagnesia (n-MgO) were fabricated using an injection moulding machine. The thermal properties and morphological structures of the composites were investigated. The XRD results showed the peaks of xGnP and n-MgO, where the intensity of the xGnP peaks became stronger with adding increasing amounts of xGnP into the polymermatrix. In terms of morphology, some agglomeration of particles was observed within the matrix, and the agglomeration decreased the thermal properties of the composites. The nanocomposites showed less thermal stability than the pristine polymer. The reduction in the onset temperature compared to that of neat HDPE was attributed to less adhesion between the fillers and the matrix. In addition, the crystallinity was reduced by the addition of fillers.

Keywords

High-Density Polyethylene, Exfoliated Graphite Nanoplatelets, Magnesium Oxide Nanoparticles, TGA, XRD, SEM

1. Introduction

In the last era, the plastic industry had witnessed rapid growth in the production of synthetic polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl alcohol (PVA) and polyvinyl chloride (PVC). Accordingly, plastics have become inseparable and indispensable components of society. The use of plastics has significantly increased to meet the demands of society by enabling affordable manufacturing of numerous products for packaging, safety and protection, service, lightweight components in cars and aircraft, mobile phones, construction, medical devices, toys and other uses [1] [2]. Among the different types of polymers, high-density polyethylene (HDPE) plays a vital role in thermoplastic industries due to its superior physical and mechanical properties. However, the adoption of HDPE in structural applications is limited due to the need for better mechanical properties. To overcome this drawback, the mechanical properties of HDPE could be improved using different additives, such as glass fibre, carbon fibre, and carbon black, for reinforcement [3]. Recently, a new promising type of reinforcement, exfoliated graphite nanoplatelets (xGnPs), has been commonly used. The use of xGnPs for reinforcement has resulted in outstanding properties for HDPE matrices [3]-[9]. xGnPs are notable for having a semi-metallic character and are is commonly comprised of less than 10 layers of graphene with thicknesses that do not exceed a few nanometres, while their other two dimensions can reach up to a few hundred microns [10]. Additionally, xGnP is considered an ideal reinforcing material that enhances the thermal, mechanical and electrical properties of a polymeric matrix [11] [12]. Nanoparticle MgO materials are widely utilized metal oxides that can be easily synthesized using inexpensive raw materials such as brines, magnesium salts and magnesium-bearing minerals [13]. MgO materials are usually selected due to their superior properties, such as high strength, modulus, melting point, and hardness and exceptional thermodynamic stability. Accordingly, MgO was chosen to be used as a suitable reinforcement in this study [14].

The thermal degradation of polymers has been studied in recent decades [15]-[20]. Due to the low thermal degradation resistance of organic-based polymers, thermal stability is one of the most studied characteristics. Recent studies have stated that the addition of nanomaterials, such as carbon nanotubes, nanoclays, and graphene, to polymers would improve the thermal stability of a studied polymer. The incorporation of inorganic fillers, such as GNPs, has been shown to further enhance many of these properties, including thermal properties [21] [22]. Furthermore, studies discussing the adoption of MgO as ananofiller for HDPE-xGnP composites are very limited in the literature. Accordingly, the aim of this work is to investigate the thermal properties of HDPE-xGnP/n-MgO composites.

2. Experimental Procedures and Methods

2.1. Materials

n-MgO and xGnP with a purity of 99.9% were used in this study as filler materials. The n-MgO and xGnP were purchased from Tritrust Industrial Co., China. The xGnP has a diameter of 10 μm and a thickness of 5 nm, whereas the MgO nanoparticles have a particle size of 10 nm. The HDPE matrix particles were supplied by SABIC, Kingdom of Saudi Arabia.

2.2. Fabrication of Composites

In this study, the different weight percentages of xGnP and n-MgO reinforcement used are shown in Table 1.

The weighed powders were mixed using a mechanical disperser to obtain a homogeneous distribution of the filler materials in the HDPE matrix. Subsequently, the mixed powders were put into a Battenfeld HM 1000/750 injection moulding machine to produce the samples. Injection moulding was carried out using an L/D ratio of 22, screw diameter of 45 mm, a clamping force of 10 tons, barrel and nozzle temperatures of 230˚C, pressure of 3000 psi, and mould temperature of 20˚C. The different HDPE-xGnP/n-MgO composites shown in Table 1 were examined to investigate the effect on the thermal properties of HDPE-xGnP composites of the addition of n-MgO.

2.3. X-Ray Diffraction Analysis (XRD)

XRD (Schimadzu 7000, Japan) was used to confirm the existing phases of the composites. Wide-angle X-ray diffraction (WAXD) patterns, which provide the characteristics of the nanoparticles, were obtained with an X-ray diffractometer equipped with CuKα radiation. The survey scan was run between 10˚ and 90˚ with a scanning speed of 2˚ per minute.

2.4. Scanning Electron Microscopy (SEM)

The samples were prepared by fracturing (cryo-fracturing) the samples into 1 cm long pieces at the neck portion of tensile samples and attaching each to a 12.5 mm diameter Al stub with sticky 12 mm diameter C tabs. The samples were Au-Pd sputter-coated for 1 - 2 minutes at a deposition current of 25 mA and a partial pressure of ~0.1 TorrAr. The samples were then transferred to be examined by SEM.

2.5. Fourier Transform Infrared (FTIR)

A spectrogram of the composite surface was collected using an FTIR 783 Perkin Elmer spectrometer. Each spectrum was obtained for 24 scans between 4000 and 400 cm^{-1} at intervals of 1 cm^{-1} with a resolution of 4 cm^{-1}. An FTIR spectroscopic study was performed to assess the structural degradation of the immersed samples or changes in the chemical structure.

2.6. Thermogravimetric Analysis (TGA)

TGA was performed using a TGA Q500 instrument. The samples were placed in

Table 1. Composition of composites (all in weight %).

Sample	HDPE (wt.%)	xGnPs (wt.%)	n-MgO (wt.%)
Neat HDPE	100	0	0
HDPE-1G-2MgO	97	1	2
HDPE-2.5G-2MgO	95.5	2.5	2
HDPE-5G-2MgO	93	5	2

a platinum crucible and heated in a nitrogen-filled environment with a heating rate of 20˚C/min from room temperature to 600˚C. The initial weights of the samples were approximately 22 mg. The data extracted from the test were used to plot both the weight loss as a function of temperature and the thermogravimetric analysis/derivative thermal gravimetry (TGA/DTG) relations.

3. Results and Discussions

3.1. X-Ray Diffraction Analysis

Wide angle X-ray diffraction (WAXD) is a widely applied technique in the study of intercalation or exfoliation and has an advantage for composite characterization. X-ray diffraction (XRD) is used to explain the intercalation or exfoliation structures by utilizing methods for the inter-gallery spacing calculations, which are responsible for identification of the composite structures [2]. Using this technique, it is useful to identify and present the amount of inter-planner spacing (d-spacing) of the inter-gallery for different particle loading composites as well as for the neat polymer.

Figure 1 shows the XRD patterns of the neat HDPE and HDPE/xGnP/n-MgO composites with different amounts of fillers. From the XRD patterns obtained, xGnP and n-MgO were found in samples b to d, as shown in Figure 1. It is clear that the xGnP peaks were detected ata two theta of 26.6˚ in all composite samples, which matches the previous study [23]. In contrast, n-MgO was observed at a two theta of 42.9˚, which suggests the face-centred cubic crystalline phase (JCPDS No 45-0496) [24]. In addition, the intensity of the xGnP peak became stronger with increasing amounts of xGnP added into the HDPE matrix, whereas the intensity of the n-MgO peak was relatively consistent, as shown in Figure 1. Table 2 represents the change of the basal spacing (d_{001} spacing) of the composites, which was calculated by Bragg's Law using the values extracted from the XRD patterns according to literature [25]. The d-spacing can be described as

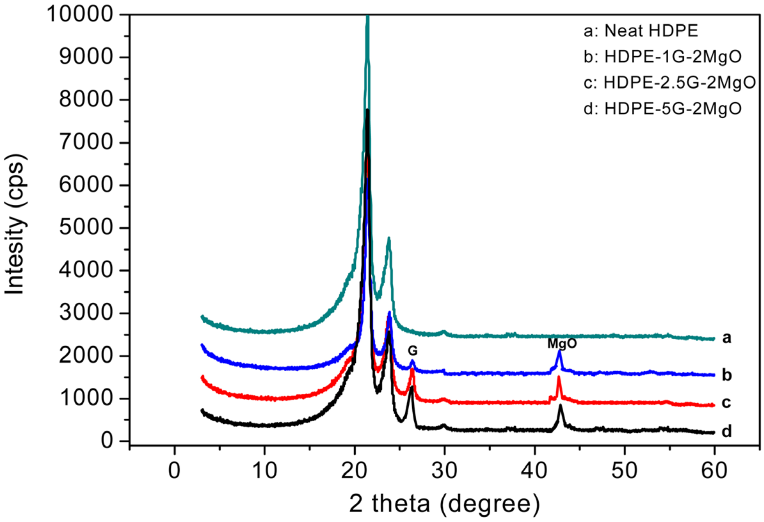


Figure 1. XRD patterns of neat HDPE and its composites.

Table 2. XRD d-spacings of various HDPE and its nanocomposite samples.

Samples	2 Theta	d-spacing [Å]
100 wt. % HDPE	21.48	4.13
HDPE/1xGnP/2n-MgO	21.50	4.12
HDPE/2.5xGnP/2n-MgO	21.53	4.12
HDPE/5xGnP/2n-MgO	21.52	4.12

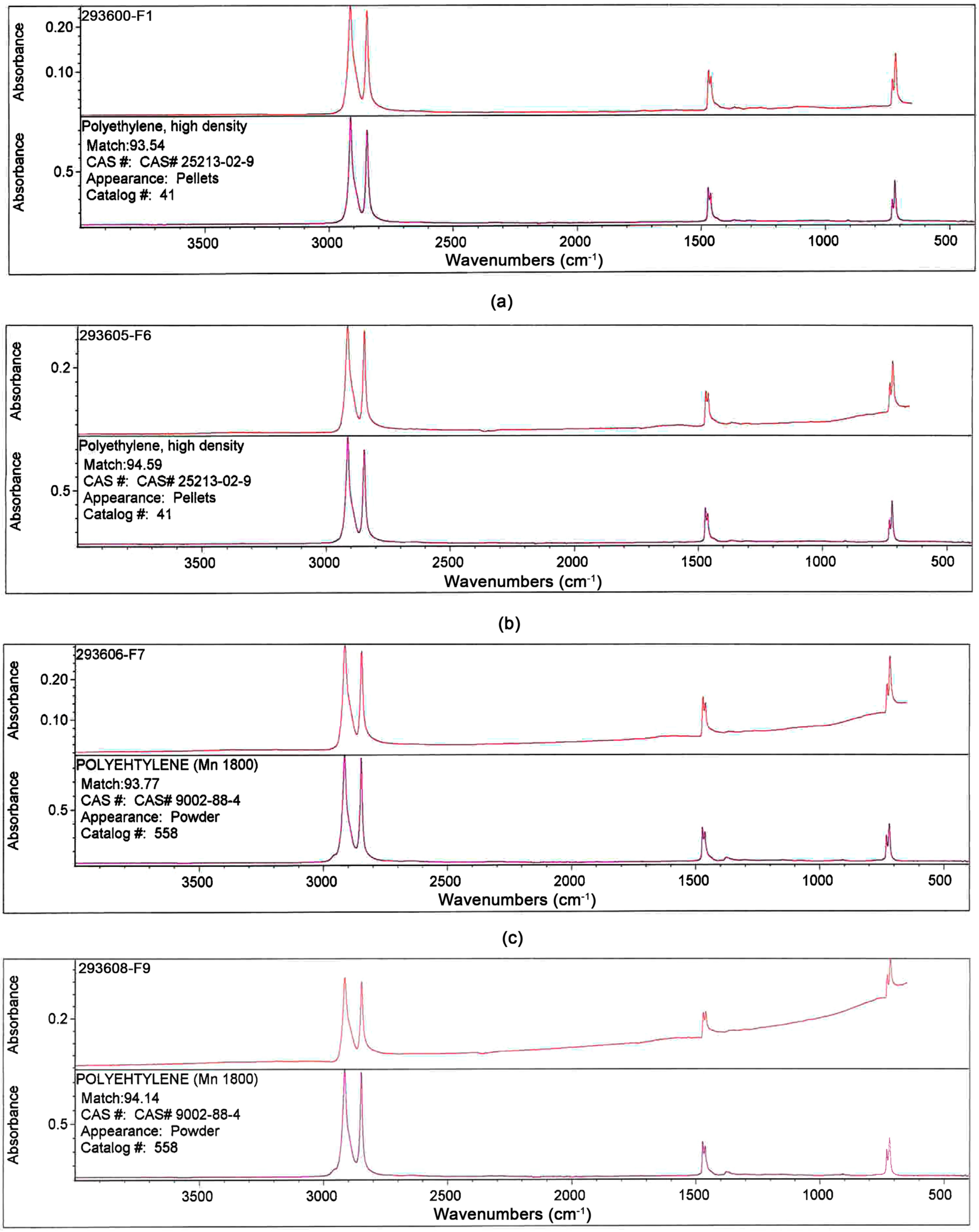
the distance between planes of atoms that gives rise to diffraction peaks. Each peak in a diffractogram results from a corresponding d-spacing. The planes of atoms can be referred to as a 3D coordinate system and can be described as a direction within the crystal. Therefore, the d-spacing, in addition to having a dimension, which is usually given in Ångstroms, can be labelled with a plane direction, hkl. With the development of nanotechnology, an increasing number of materials with d-spacings in the nanometre range have been made.

3.2. Fourier Transform Infrared (FTIR) Analysis

Figure 2 shows the FTIR spectra of neat HDPE and its composites. The peak of HDPE was somewhat altered with the addition of graphite and a constant amount of magnesium oxide nanoparticles. The absorbance level was slightly decreased by the incorporation of high amounts of graphite. The reduction was not significant as the molecular structure was relatively constant. In summary, differences in the peaks of the composites were not clearly observed, which indicates the stability of the polymer molecular structure. Of note in this paper, the FTIR spectra are presented as the absorbance percentage as a function of wavelength, not as the transmittance percentage as a function of wavelength. Therefore, if we carefully look at the FTIR spectra, the spectra show a decrease in the absorbance percentage with increasing filler content. Furthermore, this decrease in intensity can be attributed to a decrease in the number of free polyethylene chains, meaning a number of the polymer chains were coordinated to the carbon particles, and hence, the flexibility and molecular motion of the polymer chain are restricted.

3.3. Thermal Properties

The TGA/DTG analysis of monolithic HDPE and HDPE/xGnP/n-MgO composites during heating from 20˚C to 600˚C/min are shown in Figure 3. From Figure 3, it is clear that the addition of graphite and magnesium oxide nanoparticles into the HDPE matrix resulted in a slight increase in the thermal stability. Additionally, the onset temperature of the neat polymer was 465˚C, whereas for HDPE/1xGnP/2n-MgO and HDPE/2.5xGnP/2n-MgO, the onset temperatures were 464˚C and 464˚C, respectively. By incorporating 5 wt.% graphite and 2 wt.% magnesium oxide into the HDPE matrix, the onset temperature was improved to 466˚C. The char yield of the composites was significantly increased in a manner proportional to the graphite content. Crystallinity tended to be reduced



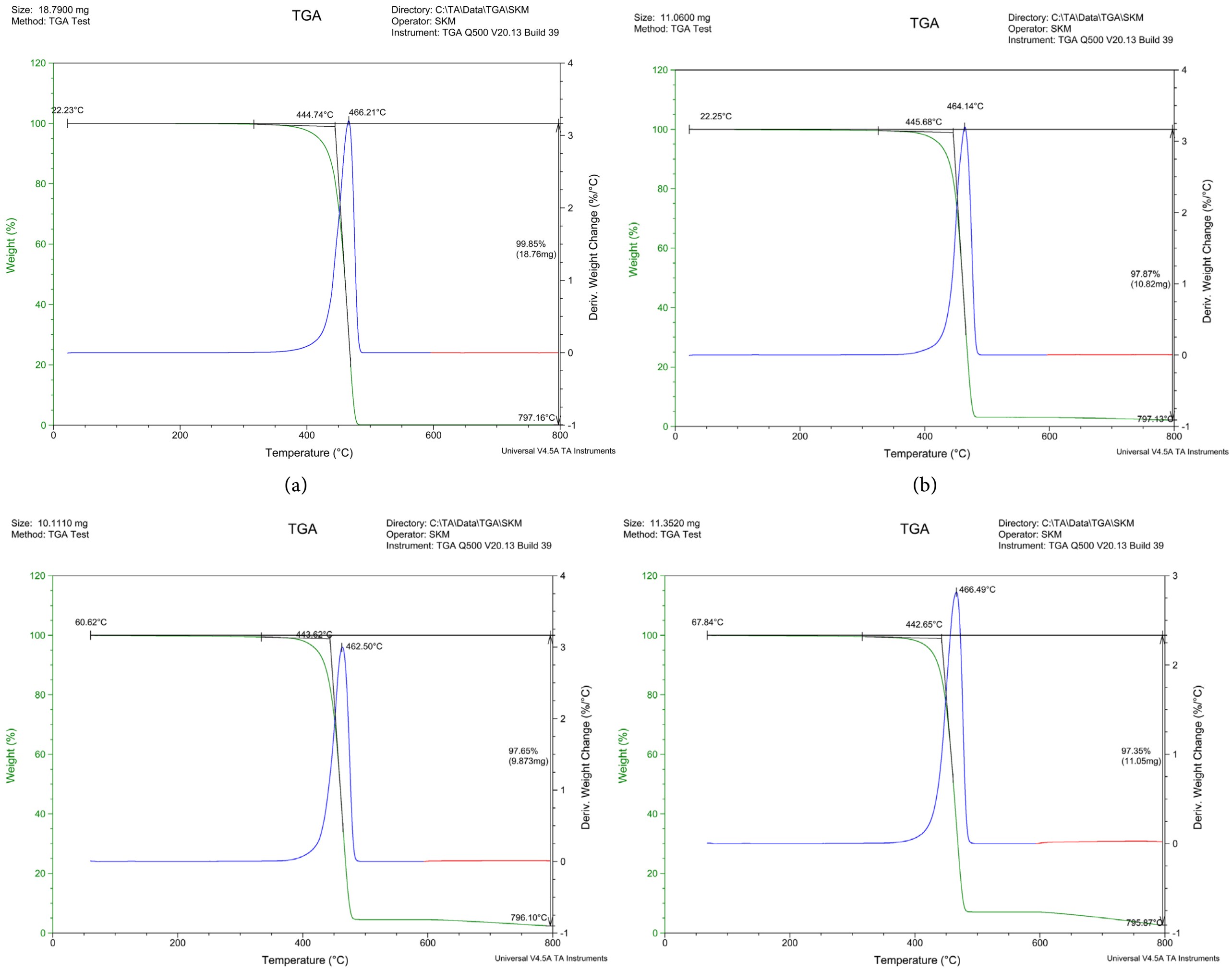
(a)

(b)

(c)

(d)

Figure 2. FTIR images of HDPE and its composites: (a) 100 wt.% HDPE, (b) HDPE/1xGnP/2n-MgO, (c) HDPE/2.5xGnP/2n-MgO, and (d) HDPE/10xGnP/2n-MgO (too bad resolution-not clear).



(a) (b)

(c) (d)

Figure 3. TGA results of (a) 100 wt.% HDPE, (b) HDPE/1xGnP/2n-MgO, (c) HDPE/2.5xGnP/2n-MgO, and (d) HDPE/5xGnP/2n-MgO.

by increasing the composite loading, as shown in **Table 3**, which agreed with the literature that composites with plate-like particles have a reduced degree of crystallinity [26]. There is a robust relationship between **Figure 3** and **Table 3**. The melting temperature (Tm), crystallization temperature (Tc) and degree of crystallinity are observed and calculated from the TGA curves.

These findings are in close agreement with those in the study by Wegrzyn *et al.* [27].

3.4. Microstructure

To investigate the surface morphology of the composites, SEM micrographs were taken for the monolithic HDPE and HDPE-xGnP/n-MgO composites, as shown in **Figure 4**. **Figure 4(a)** reveals some white strand regions as a characteristic of polymer materials. The composites with 1 and 2.5 wt.% xGnP exhibited good dispersion/distribution of fillers in the matrix, which shows no evidence

Table 3. Thermal properties of HDPE and its corresponding composites.

Samples	Tm (˚C)	Tc (˚C)	Crystallinity (%)
100 wt.% HDPE	131	117	62.83
HDPE/1xGnP/2n-MgO	131.53	117.31	62.22
HDPE/2.5xGnP/2n-MgO	130	118	61.6
HDPE/5xGnP/2n-MgO	118.74	130	61.5

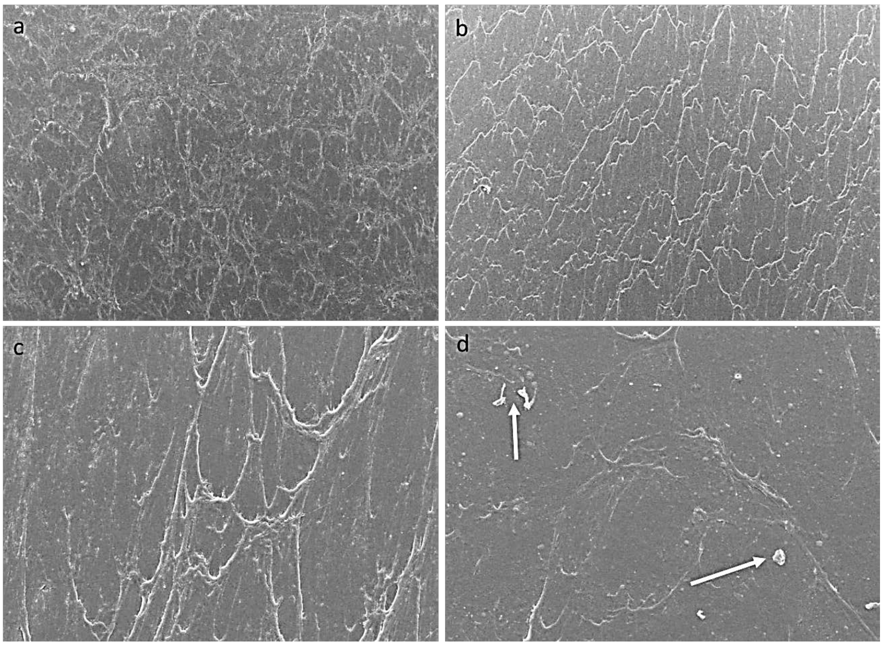


Figure 4. SEM images of HDPE and its composites: (a) 100 wt.% HDPE (2 mm), (b) HDPE/1xGnP/2n-MgO (2 mm), (c) HDPE/2.5xGnP/2n-MgO (400 μm), and (d) HDPE/5xGnP/2n-MgO (400 μm).

of aggregation. This is due to the high affinity between the particles and polymer during fabrication at the optimal injection conditions. Furthermore, less intercalation was obtained in the polymers with the addition of 5 wt.% xGnP, which could be associated with eitherparticle agglomeration or the possibility of losing the platelet morphology of xGnP, leading to the development of a rolled-up structure or folds during preparation and dispersion differences [3]. It is worth mentioning here that achieving a homogeneous dispersion is the most challenging obstacle in obtaining an efficient reinforced polymer, especially in the case of non-polar polymers such as polyethylene (PE) [2] [28].

4. Conclusion

HDPE/xGnP/n-MgO composites were fabricated using an injection moulding machine. The present results show that the combination of xGnP and n-MgO filler provides varying degrees of reduction in the thermal properties of composites. Generally, all of the composite samples revealed lower thermal properties compared with the monolithic HDPE. This reduction can be attributed to the agglomeration of particles within the matrix as a consequence of inadequate matrix-reinforcement adhesion. Other preparation method such as *in situ* polymerization, can be utilised for investigating the intercalation level.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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