

Relationship between structural and mechanical properties of polyethylene matrix nanocomposites

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Abstract

This study examined the impact of incorporating graphene nanoplatelets (GnP) into high-density polyethylene (PE) to create nanocomposites, with and without a compatibiliser. We specifically focused on the impact of structural crystallinity on the mechanical properties of the nanocomposites. These nanocomposites exhibited a much higher Young's modulus compared with pure PE. Specifically, the Young's modulus increased exponentially with the addition of a compatibiliser and linearly without it. One explanation for this exponential rise in Young's modulus is that the crystal's compacted polymer chain structure improved its stiffness, facilitating effective load transfer. Additionally, a poor distribution of GnP in the nanocomposites with a filler content of 0.5 and 1 wt.%, both with and without a compatibiliser, led to a decreased stress and strain at break. However, at higher filler contents, well-distributed GnP play a key role in enhancing stress and strain at break.

Keywords: Nanocomposites, Graphene nanoplatelets, Crystallinity, Mechanical properties

1. Introduction

In recent years, thermoplastic matrix nanocomposites have received significant attention. In particular, high-density polyethylene (PE), a low-cost semicrystalline polymer, is widely used as a host polymer in several kinds of nanocomposites. Recently, it has been concluded that the addition of nanomaterials, including graphene, carbon nanotubes, fullerene, and clay, to PE or modified PE improves the physical properties of nanocomposites [1-4].

Because of its availability and good physical properties, graphene, a single atomic layer of sp^2 hybridised carbon atoms arranged in a honeycomb structure, has recently been the focus of many studies. Specifically, its large theoretical surface area of about 2600 m^2/g , as well as its good thermal, electrical, and mechanical properties, make it well suited for potential applications in a wide range of polymer matrix nanocomposites [5].

Several factors must be considered to fully harness the unique properties of graphene, particularly in bulk systems, with adequate dispersion being a key challenge. Various preparation strategies have been reported in the literature [6], with molten-state processing being the most suitable for industrial-scale applications [7]. The influence of graphene on the solid-state mechanical properties, such as tensile modulus and strain or stress at break, has been extensively studied in the literature [8]. Improved mechanical characteristics were observed when fillers were well dispersed and exfoliated [9]. However, at high filler contents, graphene tends to re-aggregate to form clusters within the matrix.

The end-use properties of materials are significantly influenced by the crystallinity of PE; many chemical and physical properties of polymers are strongly influenced by their crystallinity. X-ray diffraction, differential scanning calorimetry, and Fourier transform infrared spectroscopy can provide valuable information about the crystalline structure and morphology of materials.

X-ray diffraction (XRD) is used to study the crystallinity and crystalline size of polymer matrix nanocomposites, as well as the effect of nanofiller incorporation on the crystal structure of polymers. Tarani et al. [10] found that the crystallinity of PE depends on the size and content of graphene nanoplatelets. According to Qi et al. [11], the heterogeneous nucleation effect of graphene may increase the temperature at which PE crystallises, along with the thickness and crystallinity of the lamellae in nanocomposites. The impact of graphene on PE crystallinity has been covered in several studies [11-14]. However, there is little research on the relationship between crystallinity and the mechanical properties of PE nanocomposites.

In the present work, a study of the structural and mechanical properties of high density polyethylene-graphene nanocomposites was carried out. Different mass fractions of graphene and compatibiliser were used to understand the influence played by each. The relationships between crystallinity and the elastic and nonlinear mechanical properties of nanocomposites are discussed.

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2. Experimental

2.1 Materials

Commercial high-density polyethylene supplied by POLYMED (Sonatrach, Algeria) with the product code HDPE 5502, was used in this study as a matrix material. The density was $\rho = 0.955 \text{ g/cm}^3$ and the melting temperature was $T_m = 140^\circ\text{C}$. As mentioned by Liu et al. [15], the number average molar mass was 17,300 g/mol and the mass average molar mass was 135,000 g/mol.

Polar graphene N008-100-P10 was purchased from Angstrom Materials, Ohio. The company states that the thickness of these GnP ranged from 15 to 100 nm and their x - y dimensions were less than 7 μm . The approximate percentages of carbon and oxygen were 99.0% and 1%, respectively.

Elvaloy@15024S, a copolymer of ethylene and methyl acrylate from DuPont, China, was the compatibiliser used in this investigation.

2.2 Preparation of nanocomposites

All composites were made using the melt intercalation technique in a Brabender plastograph mixer at an imposed temperature of 160°C . The blade rotational speed was 50 rpm for a total time of 10 min. Every sample was exposed to the same shear and temperature conditions.

The different samples were ground and processed by compression moulding at 160°C between 2-mm thick plates using a hydraulic press. The pressure was increased incrementally from 0 to 10 MPa to prevent the formation of air bubbles. The composition of all samples is listed in Table 1.

Table 1 Compositions of all materials (mass fraction).

	PE	GnP	C
PE	100	0	0
GnP PE	99.5	0.5	0
	99	1	0
	98	2	0
GnP C PE	97.5	0.5	2
	95	1	4
	90	2	8

2.3 Characterisation

Wide-angle X-ray diffractograms of graphene, the matrix, and nanocomposites were obtained using an X'Pert PRO MRD diffractometer equipped with Panalytical's XRD Data Collector systems and the Panalytical HighScore Plus software (Cu K α radiation 1.5418 \AA , 40 kV, and 30 mA) in the 2θ range of 2° – 70° at scan rate of $0.017^\circ/\text{s}$. Bragg's law (Equation 1) was used to calculate the interlayer spacing (d):

$$2d \sin \theta = \lambda \quad (1)$$

Tensile tests were performed on a universal testing machine MTS, using normalised specimens (ISO-527-2) of the studied composites. A constant crosshead speed of 5 mm/min, corresponding to a strain rate of 10^{-3} s^{-1} , was selected. The deformation was measured by a video extensometer to avoid errors due to the sliding of the specimen relative to the grips. For all samples, at least two tensile tests were systematically performed. The Young's modulus, E , stress at break σ_r , and strain at break ε_r were determined from the resulting stress-strain curves.

3. Results and discussions

3.1 Structural properties

XRD offers important insights into the material's structural properties. Its objective is twofold: evaluate the dispersion state of GnP in polymer matrices and assess how GnP affect the crystalline microstructure of the polymer matrices within composites. The XRD patterns of all the composite samples, virgin graphene, and PE are shown in Figure 1.

The XRD pattern of PE, as indicated by the red line in Figure 1, shows two distinct peaks at $2\theta \sim 21.0^\circ$ and $2\theta \sim 24.02^\circ$, which correspond to the Bragg reflections of the orthorhombic phase of PE (110) and (200), respectively. Two additional peaks, positioned at $2\theta \sim 30.2^\circ$ and $2\theta \sim 36.4^\circ$, represent the (210) and (020) Bragg reflections, respectively. These results are in good agreement with previous results reported on high density polyethylene [16-18].

The diffraction pattern for GnP (illustrated by the black line in Figure 1) shows a pronounced peak at $2\theta \sim 26.4^\circ$ (with a corresponding d -spacing of 0.335 nm). This peak is attributed to the stacking of individual graphite layers, which corresponds to the literature results reported on GnP [19, 20]. Other peaks appeared at about $2\theta \sim 44.4^\circ$ and $2\theta \sim 54.7^\circ$, corresponding to inter-planar distances of 0.123 and 0.085 nm, respectively.

The patterns of the nanocomposites showed the superposition of diffractograms for GnP and PE at different intensities. Furthermore, the diffraction peaks of GnP that were expected to appear at $2\theta \sim 44.7^\circ$ and $2\theta \sim 54.7^\circ$ were not observed in diffractograms of the nanocomposites, which is partially attributed to the little amount of graphene distributed throughout the PE matrix.

The crystallite size of the GnP PE nanocomposites (L) was estimated from the (110), (200), and (002) reflections using the Scherrer equation (Equation 2) [21]:

$$L = \frac{K \times \lambda}{\beta \times \cos \theta}$$

(2)

where β is the line width (full width at half maximum) in radians, λ is the X-ray wavelength, K is the coefficient taken to be 0.89, and θ is the diffraction peak. The results are summarised in Table 2, showing the crystallite sizes perpendicular to the (110) and (200) planes for PE, GnP PE, and GnP C PE nanocomposites, as well as the (002) plane for GnP.

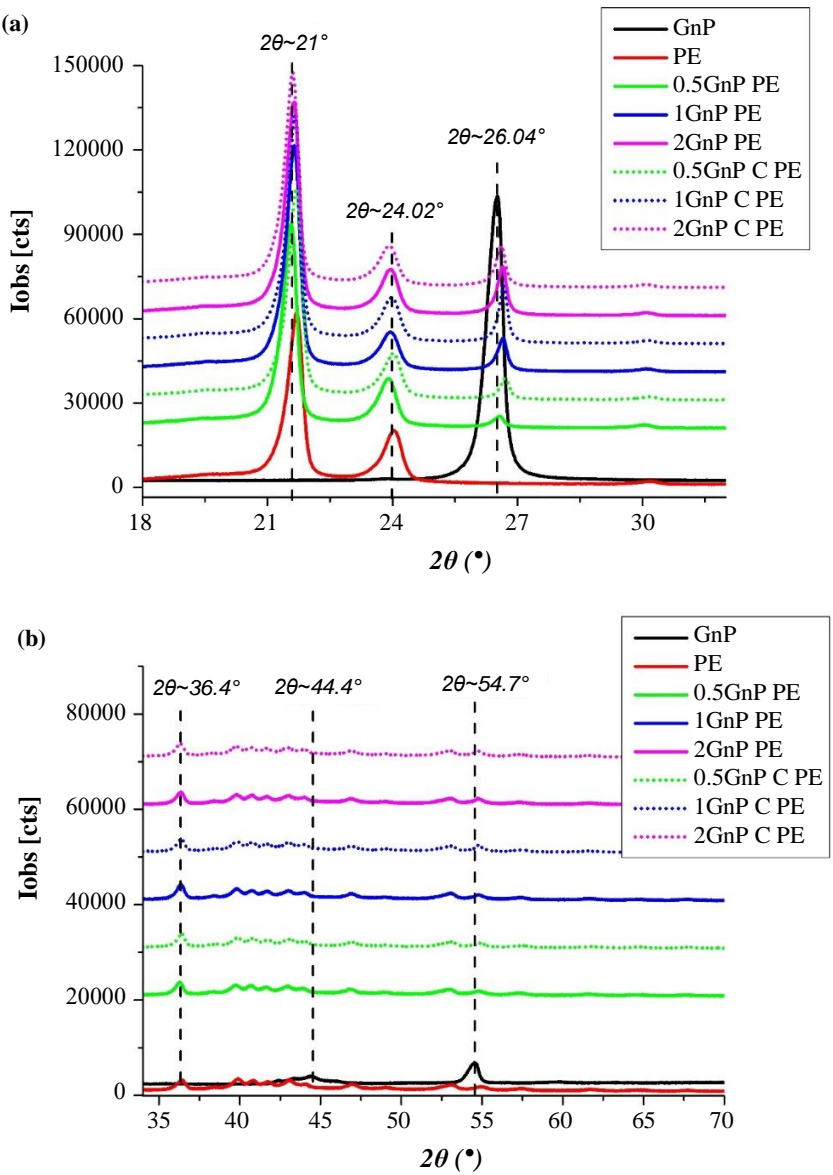


Figure 1 XRD patterns of GnP PE nanocomposites.

Table 2 XRD parameters calculated by the Scherrer–Debye equation.

	$L_{110} (\text{\AA}^\circ)$	$L_{200} (\text{\AA}^\circ)$	$L_{002} (\text{\AA}^\circ)$
PE	195	165	--
0.5GnP PE	208	166	261
1GnP PE	209	158	295
2GnP PE	211	168	315
0.5GnP C PE	--	--	--
1GnP C PE	210	162	318
2GnP C PE	215	162	319
	216	162	339

The crystallite size (L) perpendicular to the (110) and (200) planes of pristine PE are on the order of 165 and 195 Å, respectively. These values are consistent with the typical characteristics of PE, a popular polymer distinguished by its distinct crystalline structure and semi-crystalline nature.

According to Table 2, adding graphene to a PE matrix, both with and without a compatibiliser, can impact the interplanar distances between distinct crystallographic planes, which in turn may affect the crystalline structure of nanocomposites. When graphene is added

to PE, L_{110} tends to slightly increase, increasing from 208 Å for 0.5 wt.% GnP (i.e., 0.5GnP PE) to 211 Å for 2 wt.% GnP. However, L_{200} varies more significantly, decreasing from 166 Å for 0.5 wt.% GnP to 158 Å for 1 wt.% GnP and then increasing to 168 Å for 2 wt.% GnP.

GnP C PE nanocomposites also exhibit variations in L_{110} and L_{200} , with crystallite size increasing as a function of filler content, ranging from 210 Å to 216 Å for the (110) plane and decreasing to 162 Å for the (200) plane.

The increase in crystallite size perpendicular to the (110) plane suggests that the presence of GnP in the case of GnP PE and GnP C PE has a dilating effect. This means that the polymer chains in nanocomposites are less tightly packed in this direction. In the case of GnP C PE, this increase is more pronounced. These findings imply that the inclusion of GnP encourages the development of bigger crystalline domains in this direction. This could be because GnP act as nucleating agents, promoting the development and expansion of crystallites [22].

In contrast, the increase in crystallite size perpendicular to the (200) plane decreased in the GnP C PE nanocomposites compared to pure PE. This reduction indicates that the crystallite size in this direction is smaller. This might be explained by interactions or obstacles caused by the evenly dispersed GnP when a compatibiliser is present [23], resulting in a more compact arrangement of polymer chains in this direction. Consequently, the growth of crystallites slows along this direction during the crystallisation process, possibly as a result of the close proximity of GnP. Insufficient filler dispersion in GnP PE nanocomposites significantly complicates this process.

Additionally, the L_{002} of GnP increases with increasing filler content for GnP PE and GnP C PE nanocomposites, indicating that GnP have a more agglomerated structure in 2GnP PE and 2GnP C PE nanocomposites [24]. The change in crystallite shape will have a significant impact on the mechanical behaviour of these materials.

3.2 Mechanical properties

The Young's modulus, which characterises the material's rigidity, corresponds to the slope of the linear segment in the low-strain region of the stress-strain curve. The maximum point before the breaking of the sample is defined as the stress and strain at break. Figure 2 presents the normalized Young's modulus of nanocomposites as a function of GnP content. The data are shown as normalised values to reduce experimental errors.

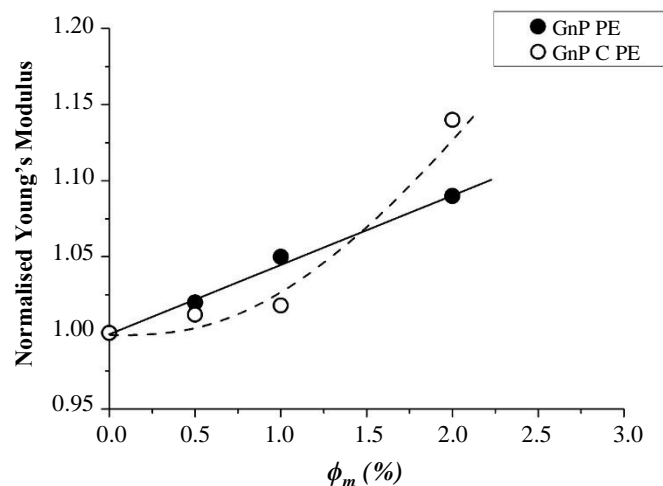


Figure 2 Normalised Young's modulus as a function of filler content.

The Young modulus of GnP PE nanocomposites increases with increasing GnP content. For example, the addition of 0.5 wt.% GnP increased the tensile modulus of PE from 1183 to 1218 MPa. This enhancement can reach 10% for 2GnP PE nanocomposites relative to pure PE.

For 0.5GnP C PE and 1GnP C PE, the modulus was lowered by the addition of a semicrystalline compatibiliser, a copolymer of ethylene and methyl acrylate. In this case, the Young's modulus of 2GnP C PE relative to GnP PE nanocomposites and pure PE increased by 14% and 5%, respectively.

The enhancement in stiffness of the nanocomposites is due to several reasons:

- The extremely high aspect ratio and remarkable rigidity of graphene nanoplatelets, estimated at approximately 1000 GPa according to Young et al. [25], significantly contribute to their mechanical properties.
- The presence of a wrinkled nanoscale topography leads to enhanced mechanical interlocking and adhesion at the interface between the nanoplatelets and the matrix.
- A potential variation in the crystal structure of the polymer.

On the other hand, in the case of nanocomposites that contain a compatibilising agent, the modulus is influenced by the enhanced dispersion of graphene within the matrix; the stiffness of graphene and the low viscosity of the compatibiliser result in a lower modulus of GnP C PE nanocomposites.

The relative stress at break ($\sigma_{r,c}/\sigma_{r,m}$) and the relative strain at break ($\epsilon_{r,c}/\epsilon_{r,m}$) were also examined. The properties of the composite and matrix are indicated by the indices 'c' and 'm', respectively. For pure PE, the measured stress and strain at break was 161 MPa and 1.96 mm/mm, respectively. Figure 3 displays these mechanical characteristics.

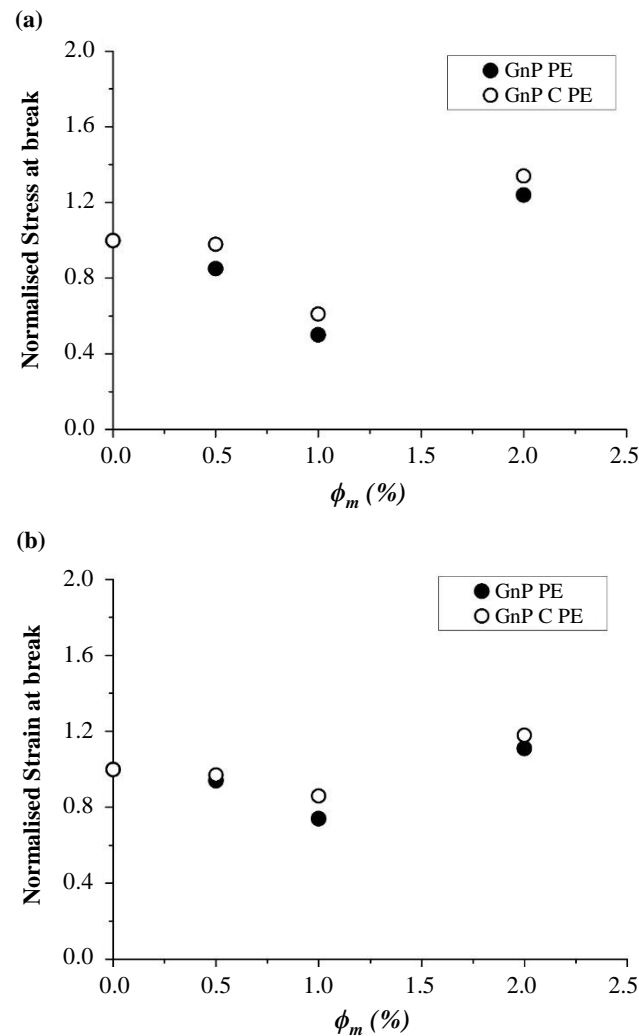


Figure 3 Normalised (a) stress and (b) strain at break as a function of filler content.

Similar trends are seen in the stress at break curve as a function of the percentage of graphene in nanocomposites with and without a compatibiliser (Figure 3a). The stress at break decreases by approximately 50% and 60% when $\phi_m = 1$ wt.% with and without a compatibiliser, respectively. Furthermore, the stress at break surpasses that of pure PE when the graphene mass fraction rises to 2 wt.%, increasing by 24% for 2GnP PE and 34% for 2GnP C PE. Similar results were observed in the work of Tarani et al. [24], who attributed the decrease of the stress at break to the low interfacial adhesion between the polymer and filler.

The strain at break shows a similar tendency, as seen in Figure 3b. For 1GnP PE and 1GnP C PE nanocomposites, there is a drop in the strain at break of around 25% and 18%, respectively. Additionally, an increase of approximately 25% for 2GnP PE and 30% for 2GnP C PE nanocomposites is observed relative to pure PE, in line with the behaviour observed for the stress at break.

The inclusion of a compatibiliser in the nanocomposites results in higher values for both stress and strain at break compared to those without a compatibiliser. This finding emphasises the influence of a compatibiliser, which improves the functionality of GnP in composite materials.

According to results from existing literature, an increase in stress and strain at break requires a good distribution of graphene particles in the polymer matrix, strong interfacial cohesion, and a high aspect ratio of the particles. We conclude that the GnP are better distributed in the PE matrix in the compatibilised nanocomposites compared with the uncompatibilised nanocomposites, contributing to favourable modifications in crystallinity and strengthening the mechanical performance of the material.

3.3 Correlation between nanocomposite structures and mechanical behaviour

The mechanical characteristics of nanocomposites are largely determined by their crystalline structure, especially in the context of polymer nanocomposites. The mechanical characteristics of PE matrix nanocomposites are significantly influenced by the interplanar distance along the (110) and (200) crystallographic planes. In this context, the following conclusions can be drawn:

- Due to a disorganised variation of crystallographic size perpendicular to the (110) and (200) planes in the GnP PE nanocomposites, we cannot precisely explain the linear increase in stiffness.
- The exponential rise in stiffness (as seen in Figure 2) in the GnP C PE nanocomposites appears to be primarily caused by a decrease in interplanar distance (as shown in Table 2) inside the (200) crystallographic plane. This reduction is caused in part by the crystal's compressed polymer chain structure, which promotes effective load transmission and increases stiffness.
- However, it is essential to note that in the case of the 0.5GnP PE and 1GnP PE nanocomposites, the poor GnP distribution and reaggregation within the polymer matrix, as evidenced in Table 2 by the increased crystallographic size L_{002} , leads to a decrease in both stress and strain at break. This is due to the agglomerates, which may act as concentration stress zones, as suggested by

Rahmaoui et al. [26]. This decrease can also be attributed to the low viscosity of the compatibiliser in compatibilised nanocomposites.

- With a 2 wt.% filler with and without a compatibiliser, the strain and stress at break are higher than that of the pure matrix, as evidenced by the large deformation after specimen necking. This is partially attributed to the appearance of an optimal point, providing an ideal distribution of graphene particles and resulting in a uniform distribution of both the crystalline and amorphous phases. The homogeneous distribution of phases, when a compatibiliser is introduced, causes a change in the PE's crystal structure, leading to a thinning of the crystallite's shape in this specific case. Furthermore, the GnP align in the direction of traction, further explaining the increase in stress at break.

These observations underscore the complex interplay between GnP dispersion, reaggregation, and overall crystalline structure in controlling the mechanical properties of the nanocomposites.

4. Conclusion

In this study, the relationship between crystallinity and mechanical properties of high-density polyethylene/graphene nanocomposites with and without a compatibiliser was studied. Compared with the pure PE matrix, the resultant nanocomposites showed noticeably higher Young's modulus values. It is important to note that the increase in Young's modulus for GnP PE nanocomposites was found to be linear, whereas the presence of a compatibiliser led to an exponential increase.

In all nanocomposites, the inclusion of GnP has a dilating effect on the crystallite size L_{110} . In GnP C PE, this increase is more pronounced. Conversely, the crystallite size L_{200} decreased in GnP C PE nanocomposites compared to pure PE. This is probably due to the obstacles introduced by well-dispersed GnP, promoting effective load transmission and increasing stiffness. Furthermore, we found that a considerable reduction in the stress and strain at break was caused by the poorly distributed GnP within the polymer matrix, especially in the case of GnP PE nanocomposites and GnP C PE with filler contents of 0.5 and 1 wt.%, both with and without a compatibiliser. However, higher filler contents resulted in a good distribution of GnP, aligning in the direction of traction and leading to even higher levels of stress and strain at break.

5. References

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