EFFECT OF MILLED GRAPHITE COMPOSITION ON THE MECHANICAL PROPERTIES AND MORPHOLOGY OF HIGH DENSITY POLYETHYLENE (HDPE)/GRAPHITE COMPOSITE

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Abstract. High density polyethylene (HDPE)/graphite composites were made by melt blending and polymer injection process with milled graphite as a filler. The effect of milling time and composition of milled graphite to physical and tensile properties of composites were investigated. The microstructure evolution of the milled graphite and fracture surface of the HDPE/graphite composites were characterized by X-ray diffractometer (XRD) and scanning electron microscope (SEM). XRD analysis showed that the graphite peak and crystallite size of graphite decreased from 17.82 nm to 15.15 nm with increasing of milling time. The reduction in fragmented size of graphite was also observed in SEM micrograph with increment of milling time. The mechanical properties study of HDPE/graphite composites represents the considerable effect of milled graphite on the increasing of Young's modulus. For sample that filled with 4 wt.% of 50 hours milled graphite, the Young's modulus was 1295 N/mm^2, a 24 % enhancement than the HDPE without graphite filler. The addition of milled graphite has improved mechanical properties of HDPE/graphite composite and suitable as a candidate for structural application.

Keywords: Mechanical milling, milled graphite, high density polyethylene, tensile properties, Graphite/polymer composite

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Introduction

The demand for the composite materials in primarily structure applications is constantly increasing day by day due to their high strength and weight ratio and ability to tailor material properties. Conventional materials are unable to meet these demands. Improvements in mechanical properties of composite materials such as stiffness, strength and fracture toughness are being increasingly made feasible by advancement in composite manufacturing technologies [1]. Generally, polymer matrix composites (PMC) are obtained by adding of some basic structure material in the form of particles, filaments, fibres, or a mesh into the matrix composite. Polymer matrix composites consist of thermoset or thermoplastic matrix reinforced with filler that used as the reinforcement phase including carbon, polymer, glass and many others. These including polymer matrix such as epoxies and phenolics, polystyrene (PS), polyethylene (PE), polymethylmethacrylate (PMMA) [2], nylon-6 and polypropylene (PP) are the widely used as polymer-based nanocomposite [3].

According to Peacock and Calhoun [4], high density polyethylene (HDPE) is widely used thermoplastic due to its appropriate crystallinity, melting point, processability and low in price. The composite that made from polyethylene has better properties and extensively been applied in various applications due to their high crystallinity, pipes and moulded items are stiff with excellent resistant to permeability by aqueous fluids. HDPE is blended with different filler of monomeric or polymeric materials to achieve the combined properties for specific application.

The utilization of polymer/graphite composites in aerospace industries, structural, and sporting equipment has been around for some considerable time [5]. It has been recognized that the characteristic of polymer composites mixed with filler are significantly affected by the composition and distribution of the fillers. The incorporation of graphite in the polyethylene polymer improved the thermal conductivities, mechanical properties and tribological response as the graphite content increased [6,7,8]. The mechanical properties of polymer composites filled with fine particle rely heavily on the size, particle–polymer matrix interface adhesion and particle loading. Mechanical milling method is a method to reduce the size of graphite particles. Upon high-energy mechanical milling of graphite, several processes occur such as continuous fracturing of graphite particles and plastic deformation that can induce crystalline defect and vacancies. The crystallite size of milled graphite can be reduced and is highly dispersed in the polymer composites [9]. The introduction of this milled graphite as a filler has become beneficial since it can improve the properties of polymer composites. With the reduction of processing steps by applying melt blending method for polymer composite production will further reducing the cost [10].

In this research, polymer composites of HDPE mixed with varies composition of milled graphite were produced using melt mixing method. Graphite powder was milled until 50 hours of milling time. The influence of the milled graphite content on the mechanical and morphology of polymer composites was evaluated.

Materials and Methods

HDPE type Etilinas HD5740UA supplied by Polyethylene Malaysia Sdn. Bhd was used as polymer matrix. The mass density and melting temperature of this HDPE were $0.964 g/cm^3$ and 132ºC respectively. Graphite powder was used as filler with the average particle size about <50µm, its purity was 99.5% and bulk density of 20-30g/100ml from R&M Chemical Sdn. Bhd.

Graphite powder was prepared via ball-milling technique as reported by [11]. After milling, the structural parameters of milled graphite powder were characterized by X-ray Diffractometer (XRD) Rigaku Mini Flex II and Scanning Electron Microscope (SEM), JEOL JSM-6360LA. The preparation of HDPE/graphite composite consists of two steps which are compounding and forming process. During compounding process, milled graphite powder was incorporated into HDPE to produce HDPE/graphite composite and this process was done by using the Brabender mixer W 50 EHT. This process was conducted by using rotor blade with speed of 50 rpm, the temperature at 130º and the mixing time of 8 minutes. The composites were compounded according to the ratios in Table 1. The tensile bar shape was formed by using Haake MiniJet II injection molding machine and tensile test was conducted by using universal tensile machine (UTM), model M350-10 CT.

Table 1. Composition of various wt% of graphite in HDPE

Sample	HDPE (g)	Graphite (wt%)	Graphite (g)
1	35.00	0	0.000
2	34.65	1	0.354
3	34.29	2	0.714
4	33.92	3	1.082
5	33.54	4	1.458

Results and Discussion

Figure 1 shows the effects of mechanical milling on the morphology of milled graphite in different time milling. The unmilled graphite particles have a flaky appearance with sharp edges in the initial stage (Figure 1(a)). A clear alteration in the shape of graphite particles was observed with increasing milling time [6, 11]. After 50 hours of milling time (Figure 1(f)), the graphite particles are highly layered and flat with average particles size that less than 1 µm have been observed. Several processes occur during milling between grinding balls such as continuous fracturing, crushing of graphite particles due to ball impact and plastic deformation that can induce crystalline defect and vacancies. Therefore, it can be realized that 50 hours of effective mechanical milling reduce particles size significantly [12].

XRD patterns of 50 hours milled graphite and HDPE/graphite composite up to 4 wt % of milled graphite are shown in Figure 2. According to Li et al. [13], the existence of two strong crystalline peaks was observed in 2θ diffraction peaks at 21.5° and 23.8° are the characteristic of (110) and (200) planes in a HDPE region. A small peak at $2\theta = 26.4°$ in HDPE/milled graphite corresponded to characteristic of graphite as reported by Patiño-Carachure et al. [14]. Therefore, this has not only confirmed the existence of graphite in the HDPE/graphite composites but also shows the crystalline phase with the sharp peak occurred. Composites with 4 wt. % of milled graphite show a more pronounced peak than lower percentage of milled graphite. It shows that the intense peak of graphite increased with increasing the concentration of graphite. The higher intensity for uppermost graphite content can be assigned to the larger number of graphite layers. The intensity of the graphite peak increases as a function of the mixing ratio, indicating that graphite and pure HDPE are mixed in homogenous state [15].

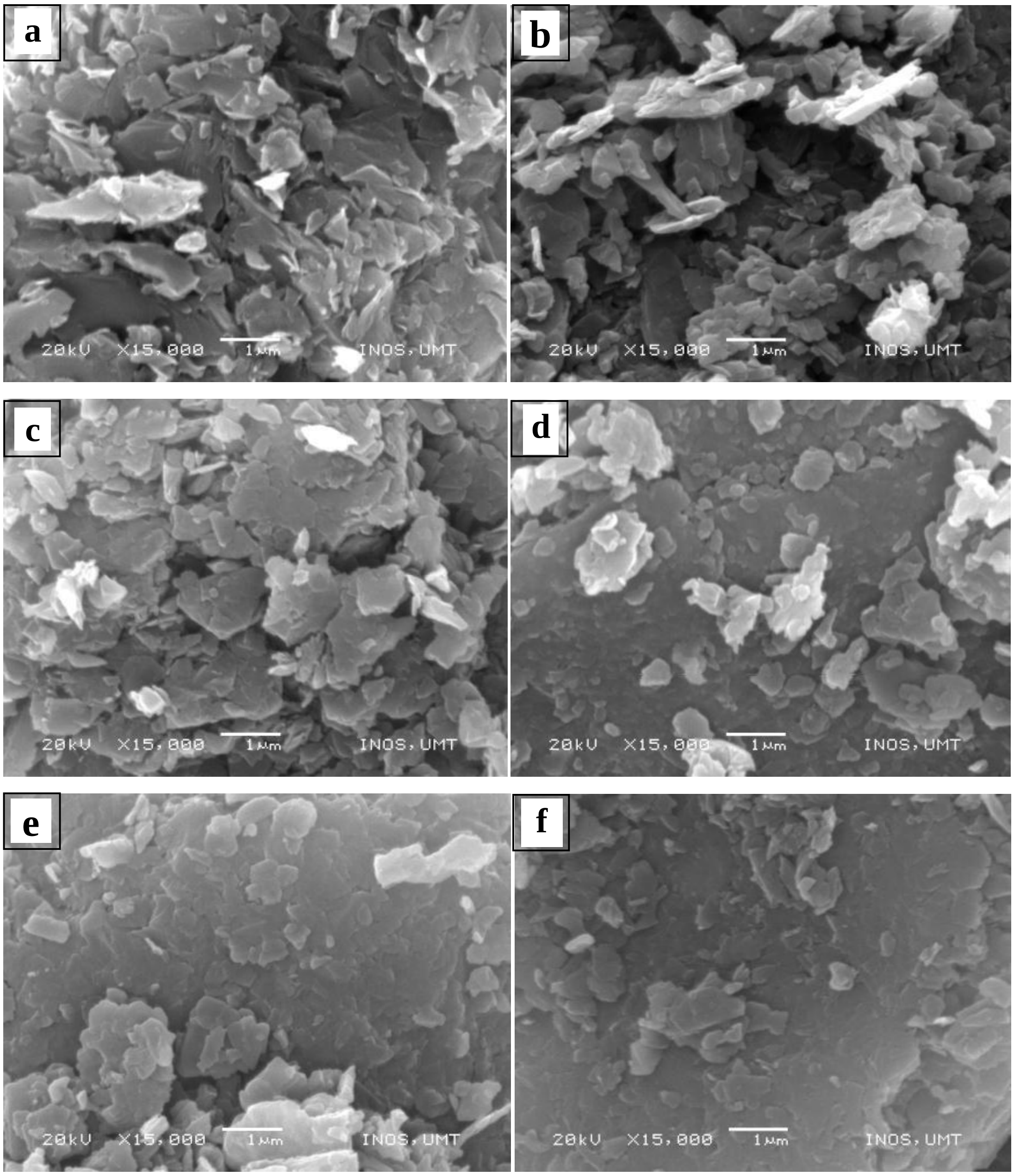

Figure 1. SEM micrographs of (a) unmilled graphite, (b) 10 hours, (c) 20 hours, (d) 30 hours, (e) 40 hours and (f) 50 hours of milled graphite.

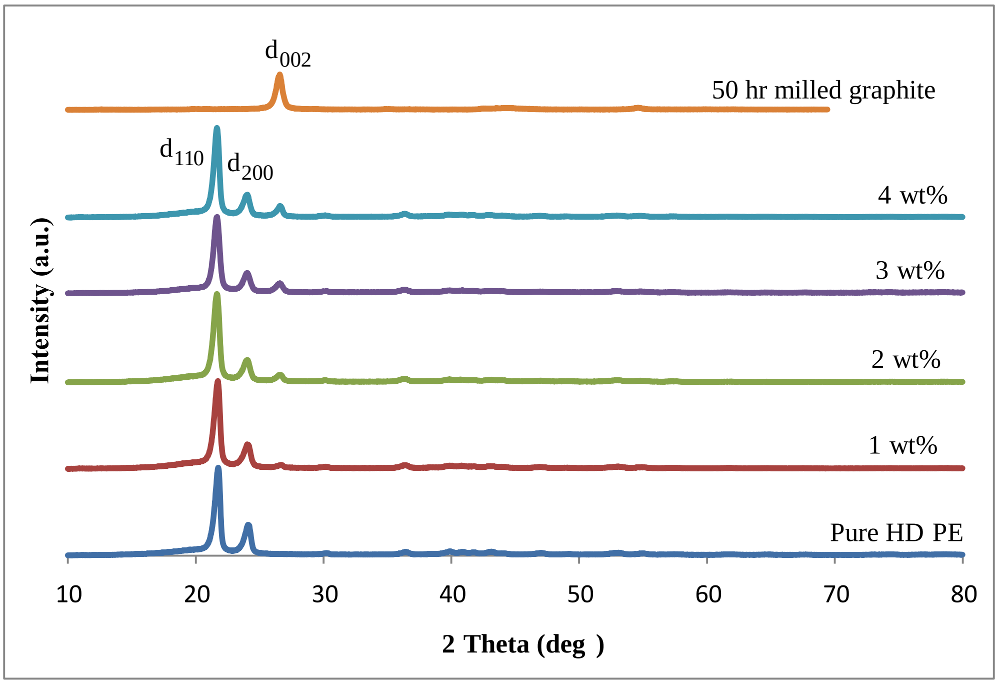

Figure 2. XRD patterns of HDPE/graphite composite for 50 hours milled graphite.

Morphology of fracture surface of HDPE/milled graphite composites. SEM micrographs of the tensile fracture surface of pure HDPE and HDPE/unmilled graphite composites are shown in Figure 3. For pure HDPE, it indicates no unknown particle inside the material. The morphological changes with introduction of graphite filler and different content of it in composites. Agglomeration of graphite particles occur in HDPE/unmilled graphite composites, and this could be ascribed to the Van der Waal bonds between graphite particles [16]. Due to the graphite particles agglomeration, it is usually resultant in decline of the polymer composite's mechanical properties. However, for HDPE/milled graphite composites, reduce indication of rough graphite particles was observed with good uniform dispersion than HDPE/unmilled graphite (Figure 4(a-d)). Polymer composite should have a uniform distribution of filler because of the stress field that can focused around any agglomerates, such that initial cracks will spread easily and swiftly, causing premature failure [17]. Also, uniform dispersion can improve the mechanical properties of the composites where it can be proved from the tensile testing.

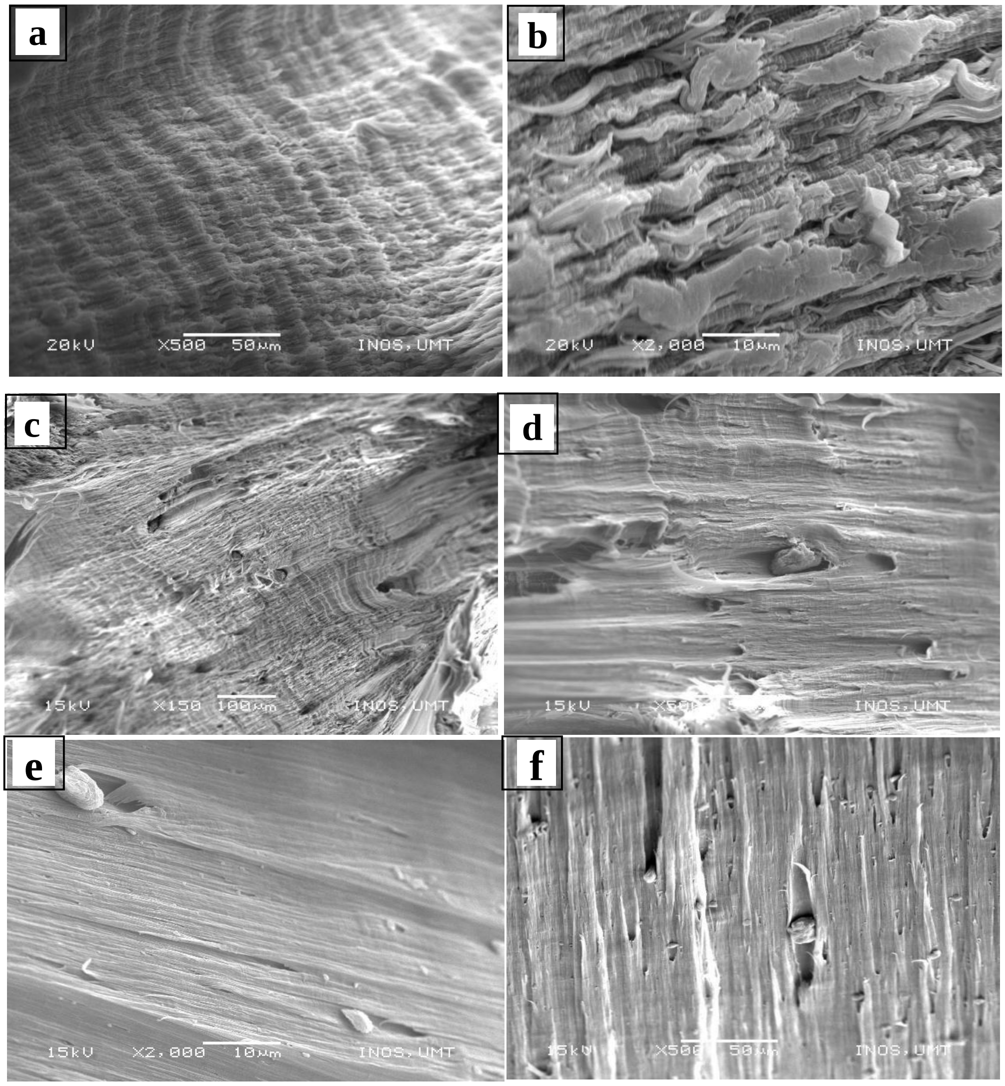

Figure 3. SEM micrographs of pure HDPE with magnification of (a) x500, (b) x2000, fractural surfaces for HDPE/unmilled graphite composites with concentration (c) 1 wt. %, (d) 2 wt. %, (e) 3 wt. %, (f) 4 wt. % of unmilled graphite.

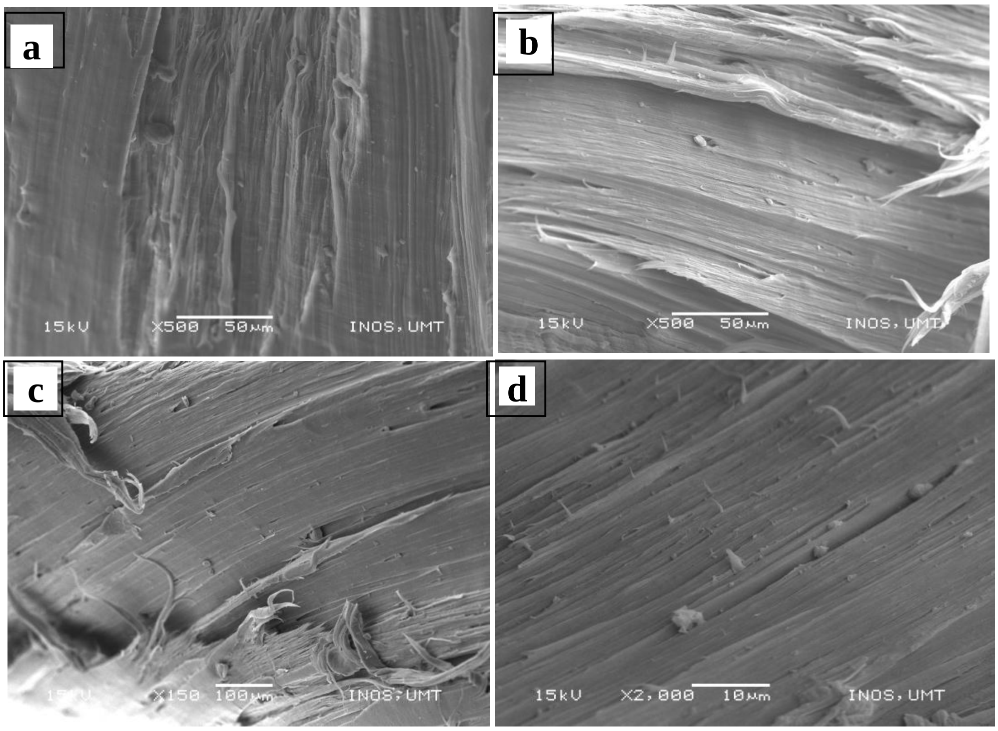

Figure 4. SEM micrographs of fractural surfaces for HDPE/milled graphite (50 hour of milling) composites with concentration of (a) 1 wt. %, (b) 2 wt. %, (c) 3 wt. %, (d) 4 wt. %.

Mechanical properties. Figure 5 shows modulus of elasticity of the composites for unmilled and milled graphite. It can be seen that modulus of elasticity increases with an increased in graphite content. The highest value of modulus of elasticity, 1295 N/mm^2 is attributed to the HDPE/graphite composites with 4 wt. %. The increase in the modulus of elasticity related to the stiffness of the matrix due to the addition of graphite as filler. Modulus of elasticity is improved significantly by adding varied size of particles to a polymer matrix since hard particles have much stiffness values than the matrix [7,18]. This implies that the dispersion of graphite in HDPE provides an effective reinforcement effect. The improvement of modulus of elasticity is due to the good distribution of graphite particles and good interfacial adhesion between the particles and HDPE matrix. In that case, the movement of polymer chains is limited during applying forces [19].

Figure 6 shows the modulus of elasticity of HDPE/milled graphite composite with various milling time in 4 wt. %. The modulus of elasticity of the HDPE/milled graphite composites increased with increasing the milling time and more pronounced for sample with 50 hours of milled graphite. This fact associated with the smaller crystallite size of graphite and particles size reduction after milling [8] that established during mechanical milling process [20]. The low modulus of elasticity would be due to the agglomeration of graphite, weak interfacial bonding at the graphite and HDPE matrix interfaces. Therefore, the improvement in modulus is important because it can be attributed to the high aspect ratio of graphite as well as to the uniform distribution and good adhesion between graphite and HDPE matrix [19]. Besides, it is also known that the size of particle plays an important role on the reinforcement mechanism. Mechanical stress during milling reduced the particles size so that it can managed to distribute itself in a homogeneous and uniform manner, intercalating itself within the macromolecular structure during melt mixing [12]. This has also provided good load transfer from the matrix to the graphite particles.

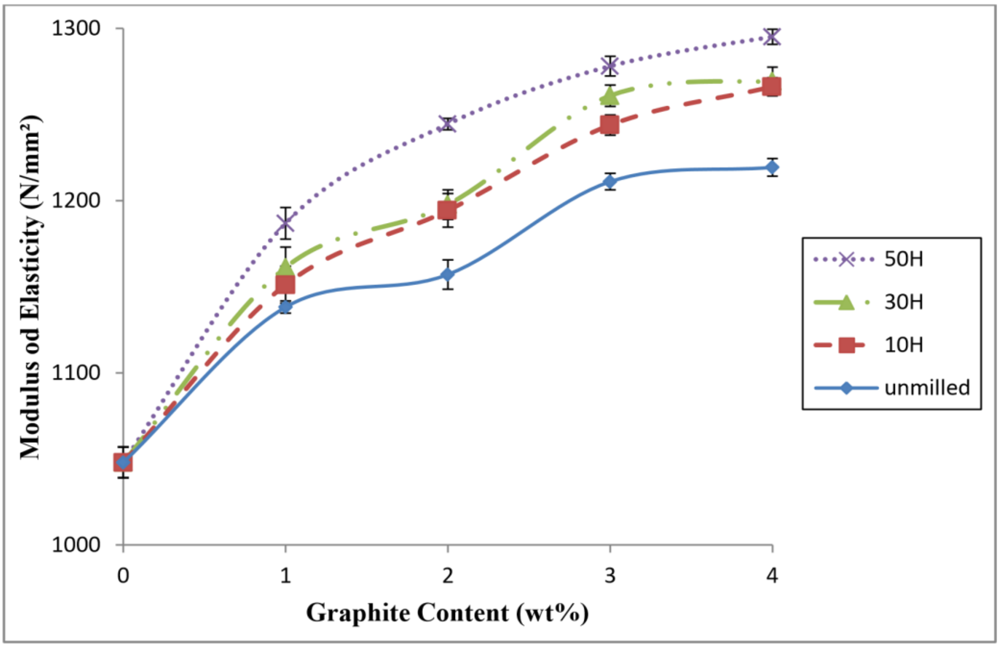

Figure 5. Modulus of elasticity of HDPE/graphite composite

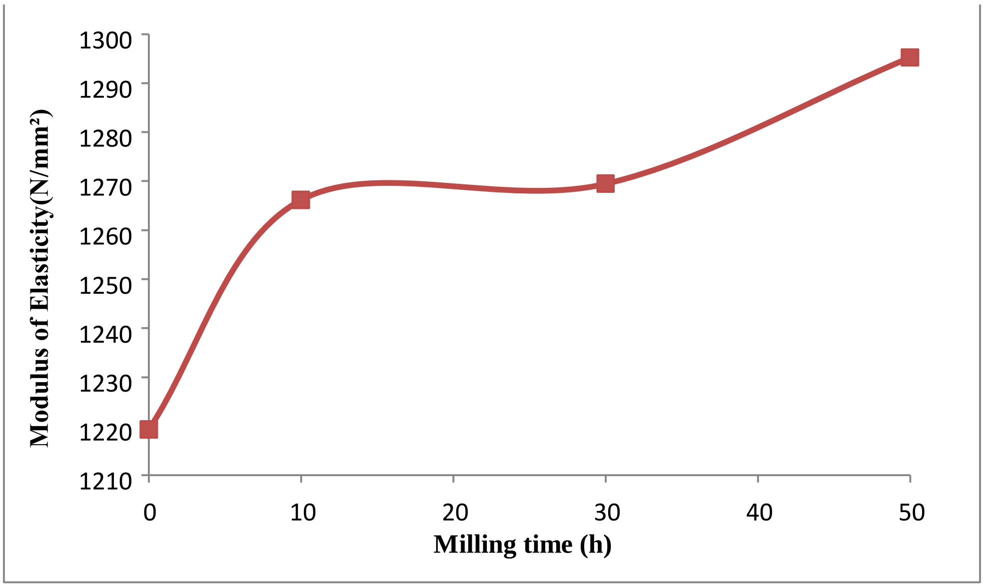

Figure 6. Young's modulus of HDPE/graphite composite with various milling time in 4 wt. %

Conclusion

In this study, the effect of graphite content in the morphology, structure changes, mechanical properties of HDPE/graphite composites was observed. Additional of graphite content resulted in a definite morphology and mechanical properties of HDPE/graphite composites. From the SEM micrographs, it can be observed that the particle size of graphite is decreasing with increasing of milling time and good distribution of graphite filler in composites. An interlinking structure with evenly distribute of graphite has been established resulting the better adhesion between graphite and HDPE matrix. Modulus of elasticity of HDPE/graphite composites was improved by the addition of graphite particles. For HDPE filled with 4 wt. % of graphite with 50 hours milling time, the highest modulus of elasticity of 1295 N/mm^2 has been observed. This is due to increase interfacial interaction between milled graphite and HDPE matrix that give better tensile properties.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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