

Development of Low Density Polyethylene /Graphene Nanoplatelets with Enhanced Thermal Properties

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Abstract—The polymer technologies have evolved due to the vast applications of polymer nanocomposites with improved properties such as mechanical and thermal stability to replace the conventional materials. The aim of this study is to develop low density polyethylene (LDPE) / graphene nanoplatelets (GNP) with enhanced thermal properties. Different loadings of GNP (0, 0.5, 1.0 and 1.5 wt%) were incorporated into the LDPE through melt mixing technique using a twin-screw extruder with the screw speed at 50 rpm to produce LDPE/GNP polymer nanocomposites. The degradation behavior of LDPE/GNP was characterized by thermogravimetric analysis (TGA), while the melting temperature (T_m), recrystallization temperature (T_c) and crystallinity (X_c) of polymer composite were analyzed by differential scanning calorimeter (DSC). The results exhibited that T_c decreased by the incorporation of GNP as compared to the pure LDPE. Degree of crystallinity of LDPE/GNP composites was observed to be lower than the pure LDPE. However, the thermal stability of LDPE was slightly increased with the increased loadings of GNP. The overall test showed the increase thermal properties of LDPE/GNP polymer nanocomposite.

Keywords—low density polyethylene; graphene nanoplatelets; thermal property

I. INTRODUCTION

Polyethylene (PE) production is the biggest production of polymer that produced around the world, with a total over 90 million metric tons per annum. Since PE was accidentally discovered in 1933, it has evolved into an important material to a modern life. The first commercialized product of PE was a low density polyethylene (LDPE) produced from the free radical polymerization. Shortly thereafter, new polymerization chemistries that employed chromium catalysis and Ziegler Natta [1] catalysis expanded the product space. Improved polymer performance based on new catalysts and application technologies have made it possible to have the diversity of use of LDPE. LDPE is an essential material to be used for power transmission, food packaging, consumer goods, electronics, household goods, industrial storage and transportation industries [2]. Development in technology continues to improve functionality of PE by making it the most efficient use of natural resources petroleum and natural gas. PE is produced by the polymerization of ethylene, which is the building block

called a monomer [3]. Ethylene has the chemical formula (C_2H_4) and each molecule of ethylene consists of two methylene (CH_2) groups connected by a double bond. Different type of PE can be produced by variety of methods such as radical polymerization, anionic addition polymerization, cationic addition polymerization or ion coordination polymerization [4].

The purpose of using graphene nanoplatelets (GNP) is to strengthen PE [5]. One of the advantages of GNP is easier to be dispersed in water and other organic solvents, as well as in different matrixes, due to the presence of the oxygen functionalities. Good dispersity remains as a very important property of GNP when mixing it with polymer matrixes when trying to improve electrical [6], [7] and mechanical properties [8]. Functionalization of GNP can fundamentally change GNP properties. The chemically modified polyethylene [9] could then potentially become much more adaptable for a lot of applications [10]. There are many ways in which GNP can be functionalized, depending on the desired applications [11]-[13].

The main objectives of this work were to investigate the effect of the addition of GNP to LDPE. The optimal %wt GNP addition was studied to achieve an enhanced LDPE/GNP nanocomposite performance. Different LDPE/GNP nanocomposites with various GNP wt% loadings were prepared and their thermal properties were investigated and compared with the virgin LDPE.

II. EXPERIMENTAL DETAILS

A. Material and Method

Materials used in this research are low density polyethylene (LDPE) and graphene nanoplatelets (GNP). LDPE is not reactive at room temperature, quite flexible and tough because of having melting temperature of 110 °C and glass transition temperature of -125 °C. A counter rotating twin-screw extruder was utilized due to the availability of equipment in the laboratory for blending the polymer matrix that attached with a die mould for moulding. Thermogravimetry analysis (TGA) and Differential Scanning Calorimeter (DSC) were employed to characterize the thermal properties of the polymer matrix.

B. Blend Preparation and Compounding

The compositions of LDPE and GNP were varied as listed in Table I. The total weight of a sample was 250g.

Polymer blend formulation was compounded by GNP to LDPE reinforce (0, 0.5, 1.0, and 1.5 wt%) using a five -stage twin screw extruder. Table 1 shows the details sample formulation of GNP to LDPE. The barrel temperature profile adopted during compounding of all blends was 135 °C at the feed section and decreased to 110 °C at the die head. The higher temperature at the feeding zone was set to ensure complete melting of mixtures in the barrel zone. The screw rotation of the extruder was fixed at 50 rpm. After blending all the materials, the sample was collected from the die block moulding of the extruder. The collected sample was allowed to cool and kept under ambient temperature. The extruded LDPE/GNP nanocomposite strands with a diameter 15-30mm and cut into pellets form using a palletizer cutter machine. The LDPE/GNP pellets were then moulded into test specimens using hot compressed moulding machine.

TABLE I. SAMPLE FORMULATION OF GNP TO LDPE

Composition	Extruder speed (rpm)	GNP wt%	LDPE wt%
LDPE	50	0	100.0
99.5LDPE/0.5GNP	50	0.5	99.5
99.0LDPE/1.0GNP	50	1.0	99.0
98.5LDPE/1.5GNP	50	1.5	98.5

C. Thermal Analysis

Thermogravimetric analysis (TGA) is a technique that measures the mass and the change in mass of the sample during heating as a function of time and/or temperature. Decomposition of the mass sample can occur due to the chemical reactions or physical changes during heating. The evaluation of thermal stability of LDPE and blends was carried out with a HITACHI/STA7000 apparatus. Sample (12±0.2 mg) was added to the alumina crucibles and an empty alumina crucible was used as a reference. The sample was heated from the ambient temperature of 25 °C until to 900 °C at the scanning rate of 10 °C /min under nitrogen gas. The sample temperature weight, derivative and the heat flow were also recorded [14].

D. Thermal Degradation

The crystallization behaviour of blend components was demonstrated on compression moulded specimens. Differential scanning calorimetric (DSC) measurements were taken under nitrogen atmosphere on samples of 5-8 mg using a Perkin Elmer/ DSC8000 apparatus. Samples were placed in standard aluminium pans with pierced lids and heated to 250 °C at a scan rate of 10 °C/min. The samples were cool down to room temperature at the same rate and then underwent second heating cycle at 10 °C/min. The glass transition, crystallization temperature and melting temperatures were determined. Polymer crystallinity was determined by DSC using the heat associated with melting (fusion) of the polymer. Equation (1) shows the calculation of the degree of crystallinity (Xc) [15]:

$$X_c = \frac{\Delta H}{(1-\phi)\Delta H^0} \quad (1)$$

where ΔH is the apparent enthalpy of fusion per gram of composite, ΔH^0 is the heat of fusion of a 100% crystalline PE was taken as 293 J/g [16], and ϕ is the weight fraction of the filler in the composites.

III. RESULT AND DISCUSSIONS

A. Thermal Properties: Differential Scanning Calorimeter(DSC)

Fig. 1 shows DSC thermograms obtained for various LDPE/GNP composites. Plot of a heat flow versus temperature showed that LDPE/GNP composites underwent all three transitions of glass transition, crystallization and melting.

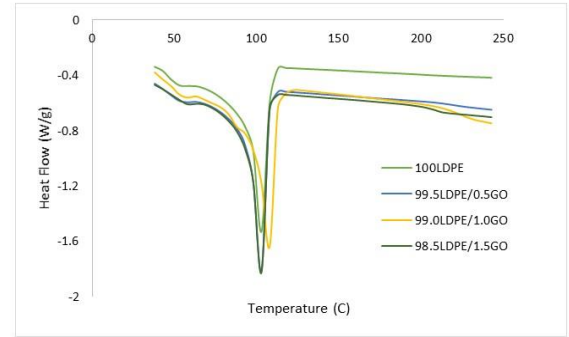


Figure 1. Heat flow (W/g) vs temperature (°C).

Table II shows the respective data of the glass transition temperature (Tg), cold crystallization (Tc) and percentage of crystallinity (Xc %) for each LDPE/GNP composites.

TABLE II. THERMAL STABILITIES OF LDPE/GNP COMPOSITES

Composition	Tg (°C)	Tc (°C)	Xc (%)
LDPE	97.22	105.18	33.69
99.5LDPE/0.5GNP	95.41	104.35	31.88
99.0LDPE/1.0GNP	86.23	109.25	32.34
98.5LDPE/1.5GNP	95.98	104.32	31.06

Cold crystallization peak of pure LDPE occurred at 105.18 °C and shifted to higher temperatures with increasing of GNP (1.0) in the LDPE/GNP composites indicating a clear nucleating effect of GNP filler over polymer matrix. However, Tc peak of LDPE/GNP was shifted to lower temperatures (GNP 0.5 and 1.5) in the LDPE/GNP composites due to the rejection from the crystalline phase [17]. Lee *et al.* also reported that the crystallization

temperature decreased by the incorporation of nanofiller as compared to pure LDPE [18]. Besides, the deviated data at 1.0% GNP loading showed exactly different to other samples of LDPE/GNP composite might be caused by some impurities included during conducting DSC analysis.

Glass transition value of pure LDPE was 97.22 °C and reduced further for all LDPE/GNP composites with the lowest T_g value at 86.23 °C of 99.0LDPE/1.0GNP. Reference [19] stated that the reduction of T_g for LDPE composites could be related to the polymer chain in that composites that had more free volume than in pure LDPE.

Fig. 2 shows the crystallinity of LDPE/GNP composite. The degree of crystallinity can be calculated from the enthalpy of melting transition. LDPE/GNP composites exhibited a higher degree of crystallinity that of pure LDPE. Such behaviour of the higher degree of crystallinity could be due to the presence of GNP acted as a nucleating agent.

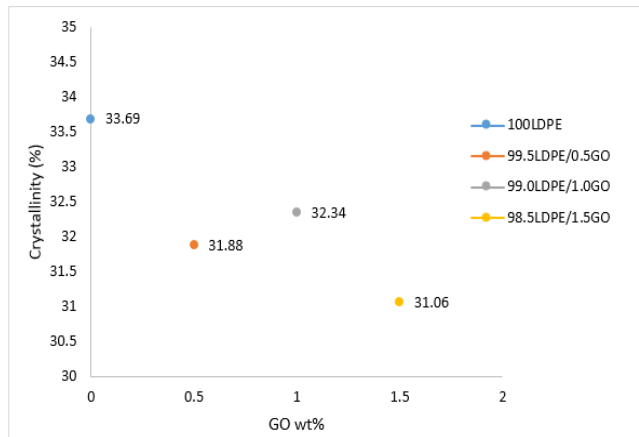


Figure 2. Crystallinity of LDPE/GNP composites.

B. Thermal Properties: Thermogravimetric Analysis (TGA)

Fig. 3 shows the TGA curves of pure LDPE and LDPE/GNP composites. TGA was performed to determine the thermal stability of LDPE and GNP blends.

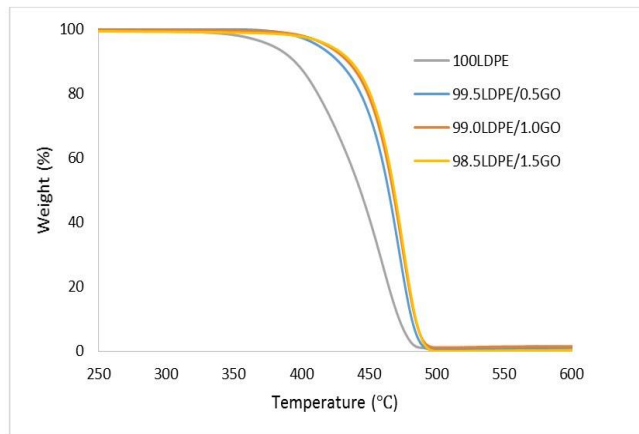


Figure 3. TGA curves of pure LDPE and LDPE/GNP composites.

The pure LDPE appeared to start decomposing rapidly at about 395 °C and the decomposition process finished at about 490 °C. However, the additions of GNP have shifted the composition curves of TGA to the higher temperature. Therefore, results of TGA showed an improvement in the thermal stability of the LDPE/GNP composites.

Fig. 4 shows the DTG curves of pure LDPE and LDPE/GNP composites. DTG curves provided the variation in weight with time (dW/dT) and assisted in identifying the degradation steps of LDPE/GNP composites. Based on Fig. 4, both pure LDPE and LDPE/GNP composite have different degradation trends. The pure LDPE gave the lowest value of derivative weight at 1.51%/min while the additions of GNP gave 2.483%/min (0.5GNP), 2.588%/min (1.0GNP) and 2.684%/min (1.5GNP) derivative weight.

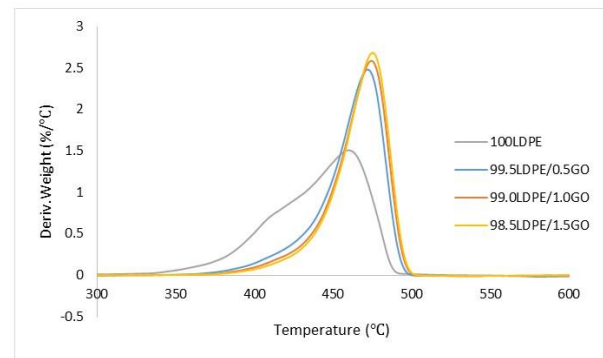


Figure 4. DTG curves of pure LDPE and LDPE/GNP composites.

Table III shows the TGA thermal stabilities of LDE/GNP blends. The onset temperature was assigned to the initial temperature of the weight loss. However, the final temperature was the observed temperature in which the end of the degradation process. The decomposition of LDPE was started at 394.74 °C and completed at 488.79 °C while LDPE/GNP for 0.5% composition blends started to decompose at 427.02 °C and completed at 491.55 °C. Therefore, the thermal stability of LDPE was slightly increased with the addition of GNP loadings. In general, T_{onset}, T_{peak} and T_{end} of blends were increased with the addition of 0.5, 1.0 and 1.5% of GNP loadings. The increased in trend behavior can be attributed by the decreasing in molecular weight as a consequence of a melt mixing process. Hence, the lower in molecular weight resulted in higher in volatility of the blends.

In the case of char residues at 900 °C, pure LDPE left minimal char residue at 0.1653%. The char yield of the composites increased in comparison to that of pure LDPE, 1.5% GNP loading gave the highest char yield at 1.915%. More char yield was possibly because of the GNP in LDPE matrix promoted the carbonization on the polymer surface. Furthermore, unburned filler and high heat resistance exerted by the filler itself additionally contributed to the higher char residue.

TABLE III. TGA THERMAL STABILITIES OF LDPE/GNP COMPOSITES

Sample	Temperature (°C)				Char Yield (%)
	T _{onset}	T _{50%}	T _{end}	T _{peak}	
LDPE	394.74	443.43	488.79	459.5	0.1653
99.5LDPE/0.5GNP	427.02	464.31	491.55	471.64	0.3510
99.0LDPE/1.0GNP	434.01	467.59	499.63	474.18	1.752
98.5LDPE/1.5GNP	436.28	468.6	492.96	474.85	1.915

Fig. 3 shows the TGA curves of LDPE/GNP composite. At higher concentration of 1.5GNP, the highest temperatures of T_{onset}, T_{peak} and T_{end} were 436.28, 474.85 and 492.96 °C, respectively.

IV. CONCLUSION

The thermal properties of LDPE/GNP composites exhibited that the incorporation of GNP has lowered the glass transition temperature values compared to that of pure LDPE. The lowered glass transition temperature could be related to the polymer chains in composites that have more free volume than in pure LDPE. Moreover, the temperature of cold crystallization and the percentage of crystallinity showed decreased values when increasing GNP loadings due to the ability of graphene particles acted as the effective nucleation sites of LDPE crystallization. Based on the TGA result, the thermal stability of LDPE was slightly increased with the addition of GNP loadings. The increased thermal stability was attributed by the decreasing in molecular weight that enhanced the volatility as a consequence of a melt mixing process. The char residue of LDPE/GNP composites increased in comparison to the pure LDPE was possibly due to the presence of GNPs in LDPE matrix that supported the carbonization on the polymer surface. In addition, unburned filler and high heat resistance exerted by the filler itself additionally contributed to the higher char residues.

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