Thermo-Gravimetric Stability of High Density Polyethylene Composite Filled with Olive Shell Flour

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Abstract Thermal behaviors of high density polyethylene (HDPE) composites filled with olive shell flour (OSF) have been measured applying the thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Addition of the OSF into the HDPE matrix reduced the melting temperature, melting enthalpy and crystallinity of the HDPE composite. The effect of the used coupling agent was not significant to the melting temperature and slightly (10%) decreases the melting enthalpy of the polymer composite. However the use of coupling agent reduced crystallinity of 25- % and 50- % filled polymer composite by 14- % and 36- %, respectively. Addition of the OSF into the HDPE matrix reduced the starting of degradation temperature due to its low thermal stability when compared to neat HDPE. OSF filled HDPE had three main decomposition peaks, two for OSF around 260°C and 330°C and one for HDPE around 478°C. Addition of coupling agent to the polymer composite did not affect the starting degradation temperature since the coupling agent (a random ethylene copolymer incorporating a monomer) has the same thermal behavior as neat HDPE. Moreover, the residue contents above 500°C increase systematically with the increase of OSF content.

Keywords TGA, DTGA, DSC, HDPE, Olive shell flour, Coupling agent

1. Introduction

Wood-plastic composite (WPC) products such as weather-resistant decking were first widely marketed in the early 1990s. The product concept has evolved rapidly into railing, fencing, trim, automotive parts, and other applications [1-3]. Adding wood to plastic to make WPC reduces the formula cost, raises the modulus of elasticity, and lowers the coefficient of thermal expansion [4-6]. Wood is not the only natural fiber used in plastics composites [7-9], but it is the most common. Wood used for WPCs is ground, screened, and dried prior to extrusion [10]. The main natural fibers used to reinforce thermoplastics mainly include wood, cotton, flax, hemp, jute, sisal, and oil palm fibers [11-12]. Less common Fibers, such as curaua, henequen, fique, buriti, olive husk, and kapok are recently being studied as potential reinforcement owing to their reasonable mechanical properties [13-15]. The relatively low thermal stability of these fibers could be a limitation to their composites [16-18]. Olive oil waste, one of several less common lignocellulose materials, is an agricultural industrial residue produced as a by-product during the olive milling process in olive oil-producing countries, especially in the Mediterranean region.

Limited works, covering the thermogravimetric stability of polymer composites reinforced with less common lignocellulosic fibers [19-21], have so far been dedicated to these composites in spite of their potential use [22-24]. The thermal stability of such composites needs to be investigated for practical use [25]. The general properties and, in particular, the TG/DTG analysis of novel composites based on these fibers have to be assessed [26-28]. Olive fruit composed of mainly three parts endocarp, mesocarp, and exocarp or stone, pulp and skin.

The present work is dedicated to analyze the thermo-gravimetric stability of the less common lignocellulosic material prepared from HDPE composites filled with OSF (pulp and skin). The effect of OSF filler content in the presence and in the absence of coupling agent on degradation temperature, mass loss, and residual mass of the polymer composite will be under investigation.

2. Experimental Section

2.1. Materials

The composites were prepared using homopolymer HDPE (ExxonMobil HDPE HMA 018) as polymer matrix with density of 0.954 g/cm^3, T_m = 131.7°C and T_g = -117°C. This HDPE is an easy flow grade with a melt flow index of 30 g/10 min (according to ASTM D1238 standard) to

facilitate the dispersion and processability of the composite material. Fusabond M603 resin (density: 0.94 g/cm^3, melt flow rate (190°C/2.16kg) is 25g/10min and Tm 108°C), a random ethylene copolymer incorporating a monomer, which is classified as being a maleic anhydride equivalent, was kindly provided by Dupont Company and used as coupling agent to improve the interface adhesion and to promote the compatibility of powder/matrix composite. Olive waste was kindly provided by local olive oil processing plant in Jerash region/Jordan and used after certain conditioning as an organic filler material.

2.2. Methods

2.2.1. Olive Pulp and Skin Flour Preparation

Olive waste was obtained from the residues of the olive oil production. After the separation of the olive oil, the residue is composed of skin, pulp, and stone. The solid residue was used without any chemical or solvent treatment. Then the residue was dried and separated into shell (pulp and skin) and stone by means of screening ventilation. The resulting shell residues were grounded into fine flour that represents about 10-15% of the whole olive fruit. Olive shells which contain only pulp and skin were grinded using Pulverisette 9 vibrating cub mill (Fristch, Germany). The obtained particles size was measured with a set of sieves from 140 to 325 meshes. OSF was oven dried at 103°C± 2°C for 24 h to adjust moisture content. The bulk density was also found to be 0.71 g/cm^3.

2.2.2. Compounding and Composite Processing

Table 1. Formulation of Composite Samples

Composite Type	Olive shell flour	HDPE	Coupling agent
0F0C	0	100	0
0F5C	0	95	5
5F0C	5	95	0
5F5C	5	90	5
25F0C	25	75	0
25F5C	25	70	5
50F0C	50	50	0
50F5C	50	45	5

Before processing; HDPE and flour are dried at 103°C ± 2°C for 24 h. Compounding is achieved by a parallel co-rotating twin screw extruder (TSE 20, L/D: 40:1, diameter 22 mm, 8 × 78 mm^2 flat die) with 7 heating zones (temperature profile: 160°C /180°C/180°C / 175°C /175°C / 170°C / 180°C). Screw speed rate is 60 rpm and feed rate is 3 kg/h. After extrusion, compression molding is then carried out on digital thermal (XH-406B) press machine. Plate temperature is set at 160°C and the mold temperature is maintained at 150°C. The compression cycle time is fixed at 90 s. OSF and coupling agent contents vary in the 0–50 wt. % and 0-5 wt. % range in HDPE matrix respectively. The

formulations of composites were summarized in Table 1. Sheet samples from each obtained polymer composite recipe were prepared by using aluminum mold in a compression-molding machine (XH-406B).

2.3. Thermogravimetry and Differential Scanning Calorimetry

TGA of the samples was done according to (ASTM E 1131) in a NETZSCH TG 209 F1 Iris® ASC thermal analyzer. Approximately 4–6 mg samples were scanned from room temperature to 600°C under nitrogen atmosphere with 50 mL/min flow rate and at a heating rate of 10°C/min. Values for the onset degradation temperature and peak temperature were determined from the derivative TGA curves.

DSC analysis was performed according to (ASTM E 473-85) in a NETZCH DSC 204 Phoenix® ASC. The test specimens weighing about 4-6 mg in an aluminum crucible were heated up to 200°C with the heating rate of 10°C/min and kept at this temperature for 3 min to remove thermal history. Then the specimens were cooled down to -130°C with the cooling rate of 10°C/min and kept at this temperature for 3 min. Subsequently, the nonisothermally crystallized specimens were reheated up to 225°C with the heating rate of 10°C/min. All heating-cooling runs were carried out under nitrogen (N$_2$) atmosphere at a flow rate of 50 ml/min to prevent oxidation of the specimens. Degree of crystallinity (Xc) was determined from the melting enthalpy values using the equation 1:

$$Xc = \frac{\Delta Hm}{\Delta Ho \times w} \times 100\% \qquad (1)$$

Where, ΔHm is melting enthalpy of the specimens (J/g), ΔHo is the enthalpy value of melting of a 100% crystalline form of HDPE (287.3 J/g) [29], and w is the weight fraction of polymer into the composite material.

3. Results and Discussions

3.1. TGA & DTGA

TGA analysis was performed on OSF, unfilled HDPE, OSF filled HDPE composites, and OSF filled HDPE composites modified with (Fusabond 603) coupling agent. Figure 1 and 2 represent the TGA thermographs of the HDPE and OSF/HDPE composites in the absence and in the presence of coupling agent, respectively. The effect of the OSF content was clear in initiation the degradation at lower temperature when compared to that of pure HDPE polymer Figure 1 and the degradation temperatures were reduced as the OSF content increase. The low degradation temperatures of OSF are due to hemicellulose, cellulose, and lignin components which have low decomposition temperatures. As a result; filler content with low degradation temperatures reduces thermal stability of the polymer composite which is in good agreement with those results obtained by Nayak SK. et al. and Mäder E. et al. [30, 31].

On the other hand, addition of 5% coupling agent to the polymer composite with different filler loading levels (i.e. 0, 5, 25 and 50%) did not change the degradation behavior of the composite samples Figure 2. Moreover; the increase in the polymer composite residues after 500°C was evident as filler content increased for both uncoupled and coupled polymer composites.

Figure 3-6 show the TGA and DTG thermographs of the representative samples respectively. The thermal stability of the OSF, HDPE, and OSF/HDPE composite without and with coupling agent was investigated by using TGA and DTG.

Thermo gravimetrical analysis is a good technique to evaluate thermal stability of materials.
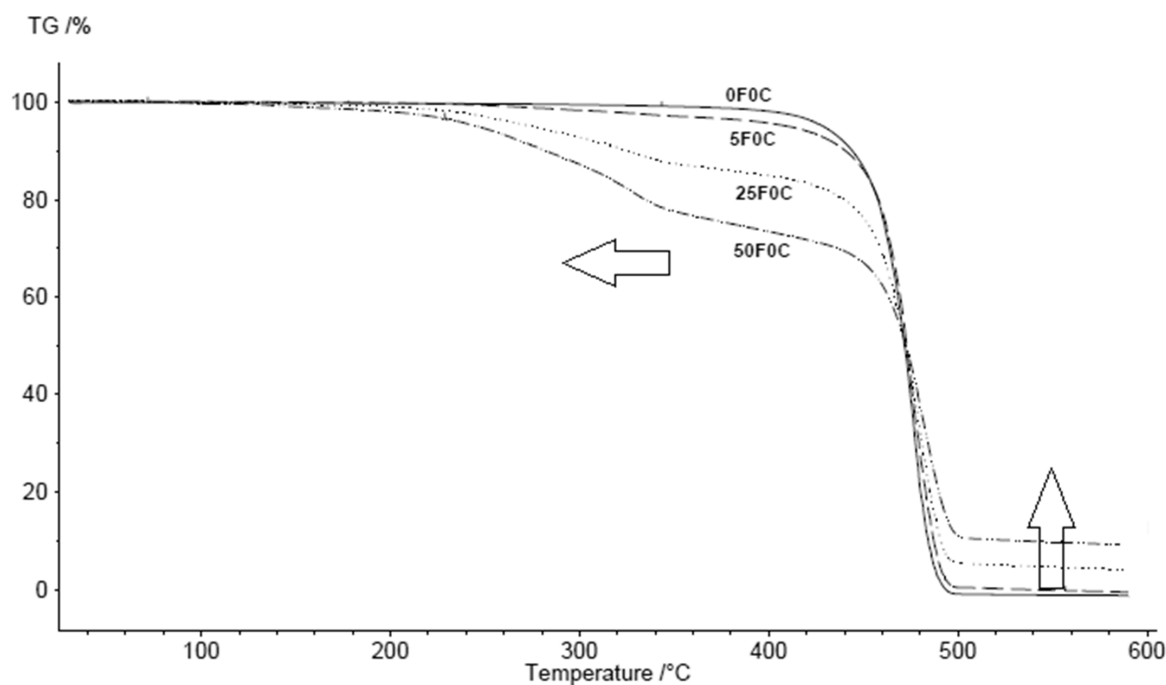
Figure 1. TGA themograph of OSF/HDPE composite without coupling agent
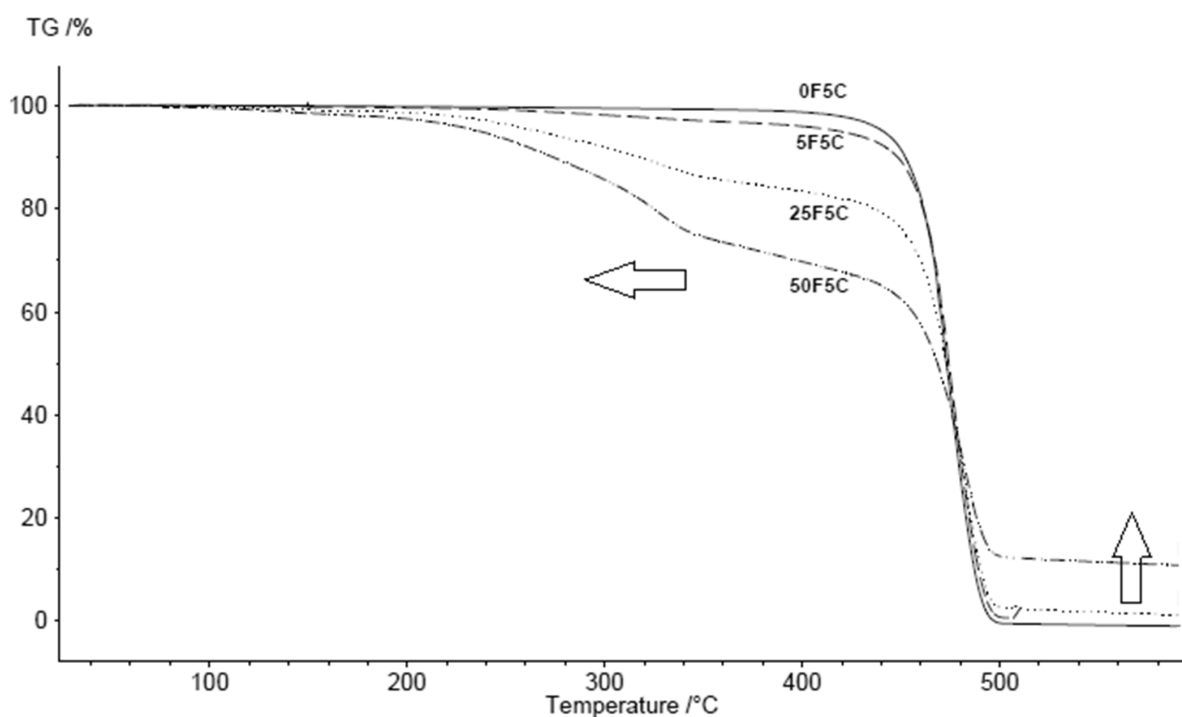
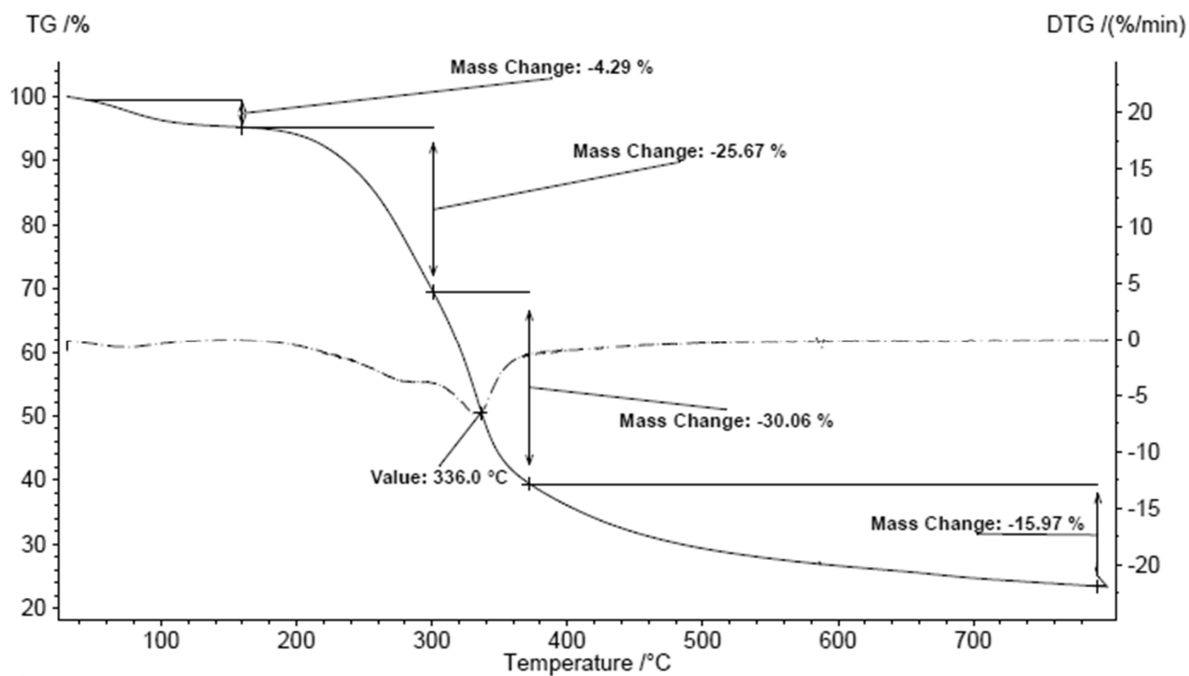**Figure 2.** TGA themograph of OSF/HDPE composite with 5% coupling agent
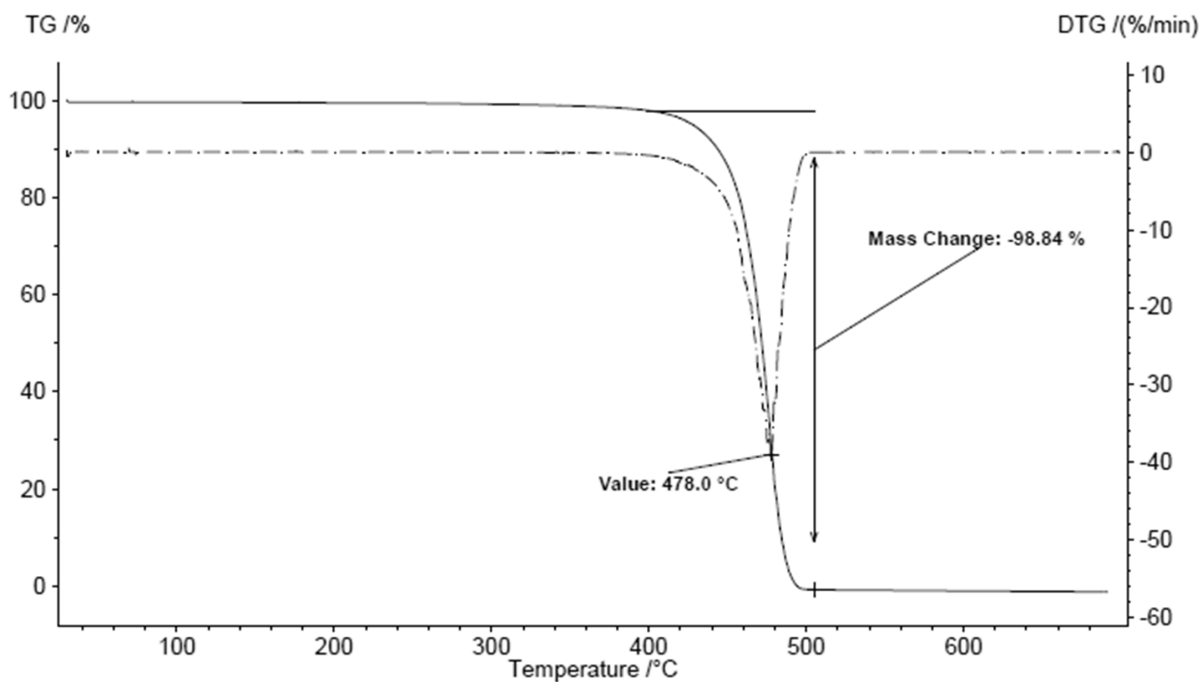
Figure 3.   TG and DTG thermographs of OSF
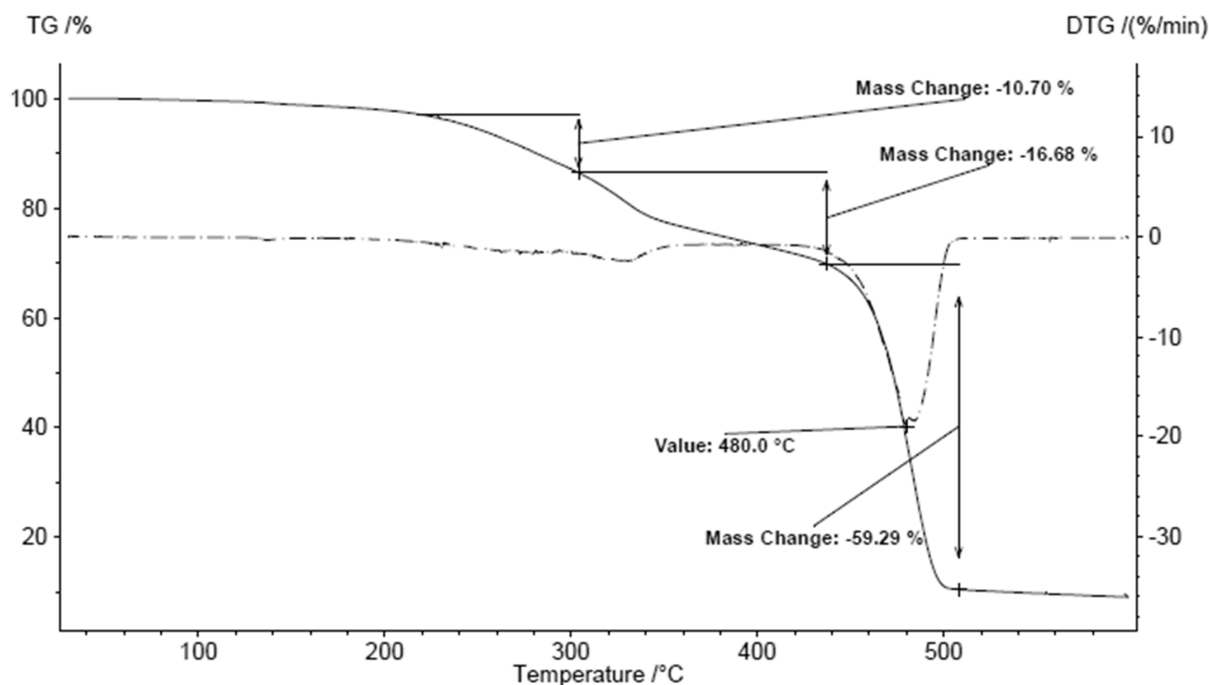
Figure 4.   TG and DTG thermographs of pure HDPE

Figure 5. TG and DTG thermographs of 50% OSF filled HDPE compsoitewithout coupling agent (50F0C)
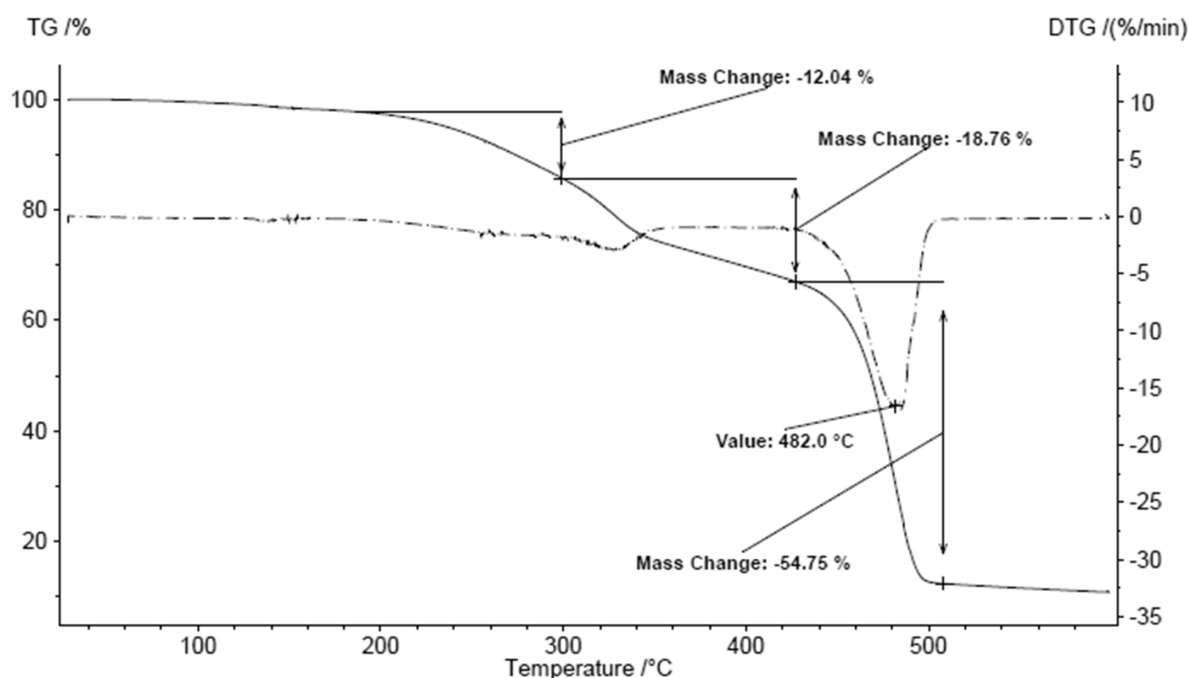

Figure 6. TG and DTG thermographs of 50% OSF filled HDPE compsoite with 5% coupling agent (50F5C)

The residue weight of samples at different temperatures was obtained accordingly. The thermal degradation of OSF can be divided into main three stages Figure 3. Up to 100°C, about 4.3% weight loss is noted corresponding to the moisture departure, which is a common feature for lignocellulose fibers [32]. Thermal degradation of OSF started at 200°C and continued up to 400°C with two successive peaks; one at 280°C and the other at 336°C with weight loss of about 26% and 30% respectively. The decomposition peak at 280°C is associated with the thermal degradation of hemicelluloses which are the most thermally sensitive components in the lignocellulosic filler [17, 33]. The third decomposition stage around 336°C, assigned to the thermal decomposition of cellulose and lignin [34]. The weight loss which appeared as a shoulder between 400°C and 500°C was noted with 12% weight loss related to the third stage and probably associated to the joint lignin degradation.
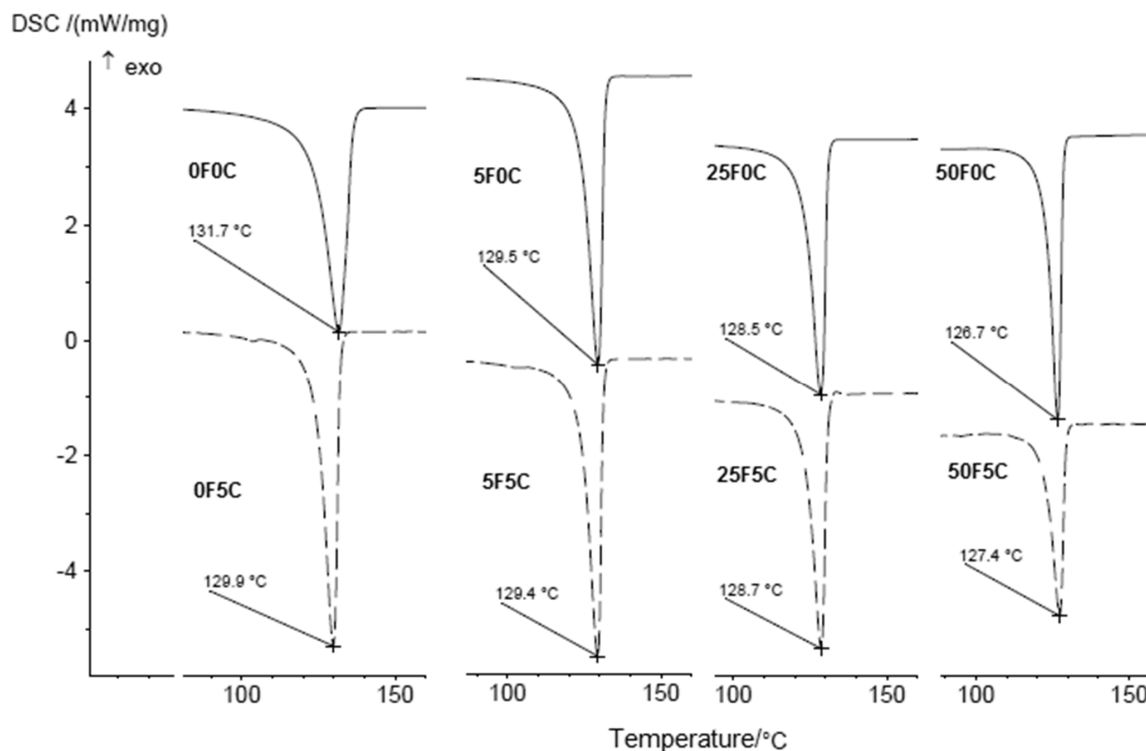
Figure 7. DSC thermographs of OSF/HDPE composites with and without coupling agent

Table 2. Thermal Parameters of OSF/ HDPE Composites Extracted from TGA and DTG Thermographs

Composite Type	Peak Temperature (ºC)			Weight Loss (%)			Residue after 500ºC (%)
	1st peak	2nd peak	3rd peak	1st peak	2nd peak	3rd peak	
0F0C			478			98.8	1.2
0F5C			474			98.5	1.5
5F0C		330	474		5.8	93.6	1.0
5F5C		330	476		4.6	93.4	2.0
25F0C	260	340	480	6.3	10.8	75.5	7.4
25F5C	260	340	480	6.4	12.0	77.9	3.7
50F0C	260	330	480	10.7	16.7	59.3	13.3
50F5C	260	330	482	12.0	18.8	54.8	14.4
Olive Flour	260*	336	580	30.0*	30.0	16.0	24.0**

* Include 4.3 % peak below 100°C, ** Residue % after 800°C.

It can be seen that HDPE was thermally stable up to a temperature of 400°C Figure 4, and then dramatically started to degrade following one step with maximum weight loss rates appearing at 478°C in the DTG curve. The degradation, involving a mass loss of about 99%, is attributed to the thermal cracking of the hydrocarbon chains and the production of oxygenated hydrocarbons, CO, CO_2, and H_2O [35] which ends approximately around 510°C. The incorporation of OSF reduces the degradation temperature of the material and accelerates the initial degradation of HDPE matrix in the composite. This phenomenon was also observed in wood flour-HDPE composite.

Introduction of OSF into HDPE decreased the decomposition temperature of OSF/HDPE to 260°C. It could

be due to the presence of hemicelluloses and lignin with degradation temperature of 260°C and 330°C respectively, which could produce free radicals and accelerate decay of the composite [19, 36-37]. Composite materials started degrading around 260°C and 330°C for both uncoupled and coupled polymer composites Figure 5-6. Addition of wood into the thermoplastic matrix induced HDPE to degrade thermally at low temperatures. It is reported that thermal degradation of wood produces free radicals which accelerate the reaction of thermal degradation of polyethylene at high temperatures [21, 38-39].

Figure 5 shows the TGA and DTGA thermographs of the OSF/HDPE composites in the absence of coupling agent. The three main decomposition peaks was shown on DTGA

thermograph. The first two peaks were around 260°C and 330°C while the third peak was around 480°C. It is believed those first two peaks at 260°C and 330°C in composite were mainly come from the degradation of OSF where, the main decomposition temperatures for OSF positioned at 260°C and 336°C Figure 3. The third decomposition temperature peak for HDPE based composites was close to the decomposition temperature 478°C of HDPE Figure 4. Similar results were also observed for polymer composite in the presence of coupling agent Figure 6 which indicates the insignificant effect of the used coupling agent in changing the thermal behavior of the polymer composite.

Results for other polymer composite formulations with the main degradation characteristics were summarized in Table 2. It can be seen that for low level 5% OSF loaded polymer composite only two main degradation peaks appeared due to peaks overlapping, whereas three main degradation peaks appeared for polymer composite with medium and high OSF loading levels 25% and 50%. Furthermore, it can be observed that addition of OSF to the polymer prohibits complete degradation of the matrix at 500°C and an increase in ash content was noticed with the increase in filler content.

3.2. DSC

Lignocellulosic materials are complex materials that consist mainly of cellulose, hemicellulose, and lignin. Cellulose represents the crystalline structure of wood while the hemicelluloses and lignin are amorphous structures [23, 40]. The thermal properties of OSF/HDPE composite with different filler loading levels were also studied by DSC and the corresponding thermographs are given in Figure 7. A strong endothermic peak average value around 130°C is visible, which is most likely associated with the melting of the crystalline domains of the polymer composite. The melting peak temperature T_m of OSF/HDPE composites decreased with the addition of OSF Figure 8. However, T_m values of the composite did not significantly change with the incorporation of coupling agent.
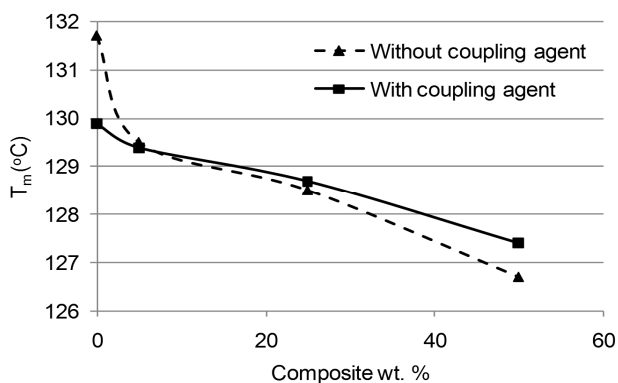

Figure 8. Composite melting temperatures vs. OSF content with and without coupling agent

For example, the T_m of OSF/HDPE polymer composites 5F0C decreased from 131.7°C to 129.5°C as 5 wt. % OSF was added into the polymer matrix. On the other hand, an addition of 5% coupling agent to the polymer composite 5F5C showed insignificant change on the melting temperature of the polymer composite with $T_m = 129.4$°C. This would probably due to the effect of the coupling agent on the filler-polymer matrix which enhances the intermolecular forces and stop the reduction in melting when compared to uncompatiblized polymer composite behavior.

The melting enthalpy (ΔH_m) of OSF/HDPE decreased with the addition of OSF Figure 9. For example polymer composite 50F0C showed a decrease in melting enthalpy (108j/g) on the order of 43% when compared to the corresponding value of the neat HDPE polymer (189j/g).
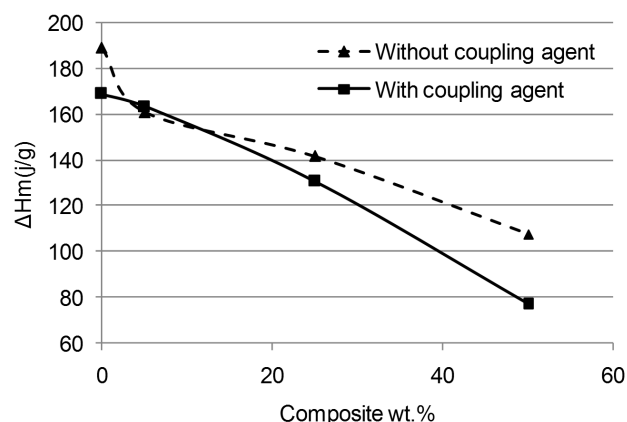
Figure 9. composite melting enthalpies vs. OSF content with and without coupling agent

Addition of coupling agent did not significantly change the melting enthalpy at low level filler loading but showed a potential decrease when polymer composite filled with 50% OSF. The reduction in melting enthalpy values can be explained by the amount of free volume between HDPE chains capable of allowing OSF to be intermixed. As the volume of the OSF increases, less polymer intermolecular free volume is capable of dissipating the filler via the physical interaction between OSF filler and HDPE polymer [7, 41].

The crystallinity (X_c) of pure HDPE 66 % decreased with the addition of the OSF to the polymer matrix Figure 10. For instance the crystallinity of the polymer composite decreased to 53%, 37%, and 19% upon addition of 5%, 25%, and 50% filler content respectively. The presence of coupling agent in OSF/HDPE composites 5F5C, 25F5C, and 50F5C resulted in an average decrease by 15% in crystallinity compared to the corresponding values of the 5F0C, 25F0C, and 50F0C polymer composites. This implies that the filler OSF and the coupling agent are prohibiting the nucleation process and hence preventing the crystal growth. This may be ascribed to the weakened nucleating ability of coupling agent and the improved interfacial adhesion between OSF and HDPE in the composites where the movement of HDPE segments are inhibited, thus leading to the reduction of the crystallinity in the polymer composites.
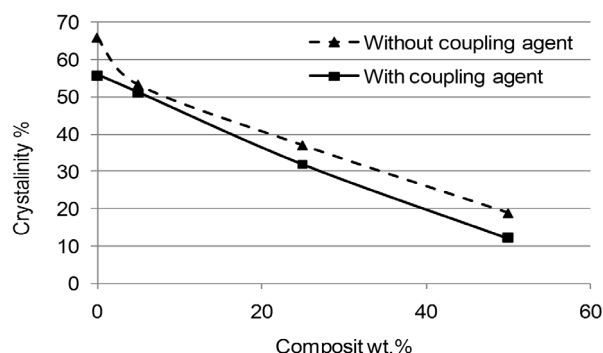
Figure 10. Composite crystallinity % vs. OSF content with and without coupling agent

The addition of OSF to HDPE matrix changes the crystallinity of HDPE. OSF has been found to physically hinder crystal growth at the higher filler loading levels and, begins to hinder the molecular motion of HDPE resulting in lower polymer crystallinity, which agrees with pervious study by El nemr et al. [13]. Furthermore, the addition of a coupling agent to OSF/HDPE seems to have played a marginal role in HDPE crystallization. The reduction of crystallinity and T_m could be due to the loss of structural integrity and debonding of the filler from the matrix, resulting from the development of shear stress at the interface due to absorbed moisture [42]. As the temperature increased, dehydration and decomposition of volatile components was observed at about 260°C, followed by rapid weight loss at about 330°C and 480°C, and finally slow decomposition corresponding to the formation of char [13, 42].

Table 3. Thermal Parameters of OSF/ HDPE Composites Extracted from DSC Thermographs

Composite Type	ΔH_m (j/g)	T_m (°C)	T_{onset} (°C)	T_{end} (°C)	T_g (°C)
0F0C	189.0	131.7	124.2	136.5	-116.7
5F0C	161.0	129.5	124.3	131.8	-116.7
25F0C	141.6	128.5	123.3	130.8	-116.2
50F0C	107.8	126.7	122.7	128.6	-118.8
0F5C	169.0	129.9	124.6	132.0	-115.6
5F5C	163.3	129.4	124.3	131.2	-119.2
25F5C	130.8	128.7	123.5	130.7	-115.4
50F5C	77.2	127.4	122.9	129.3	-116.1

Table 3 summarized the glass transition temperature of the polymer composites which extracted from DSC thermographs. A well-defined T_g values around -116°C were observed with a position being insensitive neither to the filler content nor to the coupling agent.

4. Conclusions

Knowing the effects of composite formulations on thermal stability is valuable information leading to manufacturing more thermally stable composites. OSF content was found the most influential factor as for thermal stability. The thermal stability of OSF was lower than that of pure HDPE. Moreover, as the filler loading increased, the thermal stability of the composites decreased and the ash content increased. This is a logical consequence of the lower thermal stability of the OSF. The DSC analysis showed that the melt temperatures and enthalpies of OSF/HDPE composites decreased with increasing filler content. Moreover, addition of coupling agent to composite with low and medium filler loading level 5F5C & 25F5C has insignificant effect on melting temperature and enthalpies. However a decrease in melting enthalpy was noticed for coupled composite with high filler loading level 50F5C, suggesting better dispersion of OSF particles into the matrix at low and medium filler loading level. The addition of OSF to HDPE matrix changes the crystallinity of HDPE. OSF has been found to physically hinder crystal growth with filler loading and, begins to hinder the molecular motion of HDPE resulting in lower polymer crystallinity.

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