Thermal Behavior of Hwangto and Wood Flour Reinforced High Density Polyethylene (HDPE) Composites[*1]

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ABSTRACT

The thermal properties of wood flour, Hwangto, and maleated polyethylene (MAPE) reinforced HDPE composites were investigated in this study. The thermal behavior of reinforced wood polymer composites was characterized by means of thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses. Hwangto and MAPE were used as an inorganic filler and a coupling agent, respectively. According to TGA analysis, the increase of wood flour level increased the thermal degradation of composites in the early stage, but decreased in the late stage. On the other hand, Hwangto reinforced composites showed the higher thermal stability than virgin HDPE, from the determination of differential peak temperature (DT_p). Decomposition temperature of wood flour and/or Hwangto reinforced composites increased with increase of heating rate. From DSC analysis, melting temperature of reinforced composites little bit increased with the addition of wood flour or Hwangto. As the loading of wood flour or Hwangto to HDPE increased, overall enthalpy decreased. It showed that wood flour and Hwangto absorbed more heat energy for melting the reinforced composites. Hwangto reinforced composites required more heat energy than wood flour reinforced composites and virgin HDPE. Coupling agent gave no significant effect on the thermal properties of composites. Thermal analyses indicate that composites with Hwangto are more thermally stable than those without Hwangto.

Keywords : Hwangto, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), maleated polyethylene, melting temperature (T_m), enthalpy

1. INTRODUCTION

Composites with desired properties can be made by incorporating particulate fillers into a polymer matrix to suit various applications. There has been an elevating utilization of composites in various fields ranging from a residential building to automobile industries. Especially, bio-based polymer composites have been in demand on the housing and construction market in recent years, since they are environmentally compatible and energy conserve (Hatakeyama *et al.*, 2004). Even though the wood polymer composites (WPC) is still a sec-

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tion of the forest products industry, relatively low density and safe handling as well as utilization of natural fibers make it attractive to manufacturers and consumers of WPC (Bhattacharyya *et al.*, 2003). Agrofibers used in WPC are most often incorporated in particular form up to the loading level of 50% by weight (Clemons, 2002).

An important trait of polymer is the capacity to modify their natural physical properties by the addition of fillers, making their characteristic processing ease. In polymeric materials, inorganic particles are used as fillers to improve the strength, stiffness, toughness, dimensional stability, wear and lubrication, and resistance to UV radiation (Thomas *et al.*, 2003). It was also found that thermal decomposition temperature increased with increasing inorganic filler content, indicating that composites with fillers are more durable (Hatakeyama *et al.*, 2004; Linfu *et al.*, 2005).

Hwangto is a reddish brown soil which loam is weathered by water and wind for a long time naturally and is a sediment which has particle size of 0.002~0.005 mm diameter (Bates and Jackson, 1987, Cho *et al.*, 2003). Traditionally Hwangto as an environmentally friendly inorganic material has been used for floor heating system and siding. The Hwangto has been widely applied for wide applications with some advantageous properties such as the radiation of far-infrared, adsorption-condensation-precipitation of a toxic substance (Kim, 1998; Ikhsan *et al.*, 1999). It was also reported that Hwangto shows the high sound and impact absorption, thereby showing the proper flexibility and releasing the burden of the human body and activating the metabolism (Chorover and Sposito, 1995; Jung *et al.*, 1997).

Hwangto has been practically used as a finishing material for residential structures. Recently, many researchers have worked for the development of new material for better indoor environment and for the partial substitution of cement and concrete, using loess. As a matter of interest in green cement, the characteristics of concrete mixed with Hwangto and cellulose fiber were analyzed (Yang *et al.*, 2006). In addition, there are attempts to develop the cement and concrete composites with Hwangto and to wide applications to construction material (Choi *et al.*, 2000; Ryu and Seo, 2000).

This study was performed to develop the multifunctional wood polymer composites as the construction materials with Hwangto, since very little data were available on the relation between loess and filler reinforced polymer composites. The objective of this study was to investigate the influence of wood four, Hwangto, and MAPE on the thermal behavior of reinforced HDPE composites.

2. MATERIALS and METHODS

2.1. Sample Preparation

High density polyethylene (HDPE) from LG Petrochemical Co. (Korea), has a melt flow index of 5.5 g/10 min and a density of 0.961 g/cm^3. Particle size of wood flour (WF) as a filler supplied from Il-Song Wood Flour Co., Korea, was in the range of 80~100 mesh per 25.4 mm. Wood flour was manufactured from mixed hardwood and softwood panels. Maleated polyethylene (MAPE) as a coupling agent was obtained from Honam Petrochemical Co, Korea. The melt flow index and density of MAPE were 1.0 g/10 min and 0.920 g/cm^3, respectively. Hwangto of 1,400 mesh per 25.4 mm was obtained from Hwangto Nara Co, Korea. Major chemical components of the Hwangto were presented in Table 1.

Table 1. Chemical components of Hwangto (Unit: %)

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ig.loss
42.5	36.6	0.23	4.05	0.57	0.69	0.41	0.18	14.8

2.2. Compounding and Manufacture of Pellets

Wood flour was dried to moisture content of 2~3% using an oven-drier at a temperature of 80°C for 24 hours. Wood flour, Hwangto, and MAPE were blended with HDPE in a Hakke Rheomix (Germany) for 20 min at 40 rpm and 170°C. HDPE (60, 70, 80, 90, and 100 weight % based on total weight), WF (0, 20, 30, and 40%), Hwangto (0, 10, and 20%), and MAPE (0 and 3%) were loaded at the various combinations. The mixture of raw materials was cooled in the air and then granulated in the cutting mill (Fritsch Co., Germany).

Brabender® stand-alone extruder (Germany) has a single screw to extrude the pellets. This extruder had a screw diameter of 19 mm with a L/D ratio of 25 and a circular nozzle of 6 mm in diameter. The extrusion temperature was 180°C. The extrudate in the form of strands was cooled in the air and pelletized with Brabender® pelletizer (Germany). The resulting pellets for tensile test specimens were dried at 80°C for 24 hrs before being injection-molded using an injection-molding machine (Korea Manufacturing Technology Center, Korea). Molding temperature of all pellets was approximately 195°C.

2.3. TGA Analysis

TGA measurements using a Thermogravimetric Analyzer (TA Instrument SDT Q600, USA) were carried out at four heating rates of 5, 10, 15, and 20°C/min under a nitrogen flow rate of 5 ㎖/min. Thermal degradation of each sample was carried out in the range of 30~600°C. The weight loss (%) as a function of temperature was analyzed to determine thermal degradation rate (% weight loss/min), differential peak temperature (DT_p) acquired from the differentiation of the weight loss by time, and residual weight at 600°C.

2.4. DSC Analysis

Differential Scanning Calorimetry (TA Q10, TA instrument, USA) was used to investigate the thermal behaviors of composites at four different heating rates of 5, 10, 15, and 20°/min. Melting temperature (T_m) and enthalpy (J/g) were determined at the heating rate of 10°C/min. Each test specimen using a sealed aluminum capsule was weighed to about 7 mg and was scanned at a single heating rate and scanning temperature of 30 to 200°C. These different heating rates (5, 10, 15, and 20°/min) were applied to determine the activation energy (E_a) of each composite by using the Kissinger equation of $y = -\ln(\beta/T_p^2)$ versus $x = 1/T_p$ and fitting a straight line. The E_a was determined from the slope of a straight line: where, β: heating rate (°C/min), T_p: peak temperature at the exothermic peak (K), E_a: activation energy of thermal decomposition (KJ/mol), and R: gas constant (8.314 J/mol) (Park *et al.*, 1999: Park and Wang, 2005).

3. RESULTS and DISCUSSION

3.1. TGA Analysis

Test data on weight loss, residual weight, and differential peak temperature (DT_p) acquired from the differentiation of the weight loss by the time are summarized in Table 2. Virgin

Table 2. Results of thermal analysis of wood flour and Hwangto reinforced HDPE composites at the heating speed of 10 °C/min

HDPE (%)	WF (%)	HT (%)	MAPE (%)	TGA analysis				DSC analysis	
				Temp. @5% wt loss (°C)	Temp. @50% wt loss (°C)	Residue @600°C (%)	DT_p[1] (°C)	T_m[2] (°C)	Enthalpy (J/g)
-	100	-	-	166.6	329.2	-0.1	335.1	N/A	N/A
-	-	100	-	379.5	N/A	90.2	N/A	N/A	N/A
100	-	-	-	359.5	441.7	0.1	458.2	134.8	243.3
-	-	-	100	417.2	461.9	0.2	464.5	119.2	93.2
90	10	-	-	335.2	450.9	-0.1	457.9	136.4	228.1
90	-	10	-	342.9	451.2	8.2	478.9	136.9	242.4
80	20	-	-	304.5	436.4	-0.1	458.1	138.4	197.7
80	-	20	-	377.3	465.5	17.7	477.5	138.6	221.5
80	10	10	-	323.8	461.5	7.6	462.1	136.6	194.1
80	10	10	3	310.4	464.8	8.9	472.8	133.1	194.6
70	30	-	-	290.2	444.4	1.6	472.3	137.1	182.1
70	20	10	-	308.2	464.5	9.2	479.6	138.0	189.3
70	20	10	3	310.5	469.2	9.2	483.3	135.8	184.5
60	40	-	-	283.9	447.4	0.3	474.6	134.7	148.4
60	30	10	-	289.8	460.5	8.7	477.2	134.5	151.6
60	30	10	3	295.8	462.8	12.5	475.4	135.9	160.3
60	20	20	-	306.4	475.3	18.8	482.6	134.5	151.6
60	20	20	3	312.7	470.4	14.7	482.3	136.2	153.7

[1] Differential peak temperature. [2] melting temperature. WF: wood flour, HT: Hwangto, MAPE: maleated polyethylene.

HDPE was used as a control for comparison with the wood flour/Hwangto/HDPE reinforced composites. Wood flour and Hwangto showed the weight loss of 5% at 166°C and weight loss of 50% at 329°C, respectively. Inorganic Hwangto showed the residual weight of 90.2% at 600°C, indicating the higher thermal stability.

Fig. 1 represents the thermogram of TGA for HDPE at the different level of wood flour (0 to 40%) and a heating rate of 10°C/min up to 600°C. As the increase of wood flour level increased the thermal degradation of composites in the early stage, but decreased in the late stage. It can be seen that the thermal stability of wood flour is lower than that of PP. Tar and ash content after thermal degradation over 500°C, however, increased with increase of wood flour level.

TGA results of wood flour, Hwangto, and MAPE reinforced HDPE composites were shown in Fig. 2. Hwangto (10% and 20%) reinforced HDPE composites showed the lower weight loss than virgin HDPE, showing the higher thermal

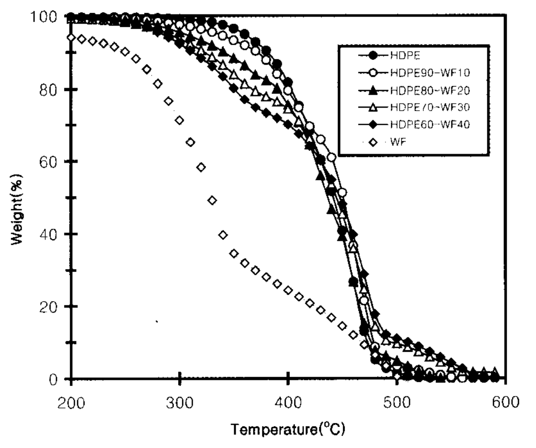


Fig. 1. TGA results of wood flour reinforced HDPE composites. HDPE: high density polyethylene. WF: wood flour.

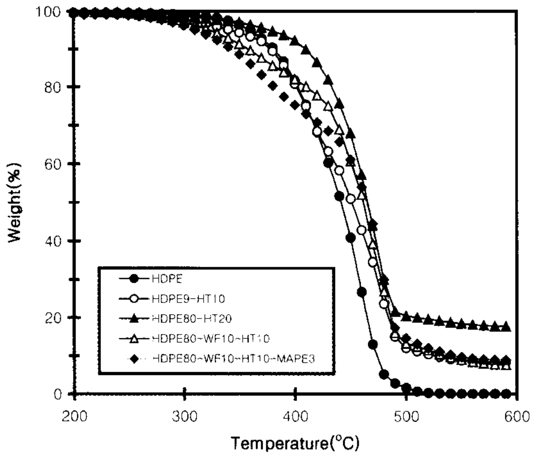


Fig. 2. TGA results of wood flour, Hwangto, and MAPE reinforced HDPE composites. HDPE: high density polyethylene, WF: wood flour, HT: Hwangto, MAPE: maleated polyethylene.

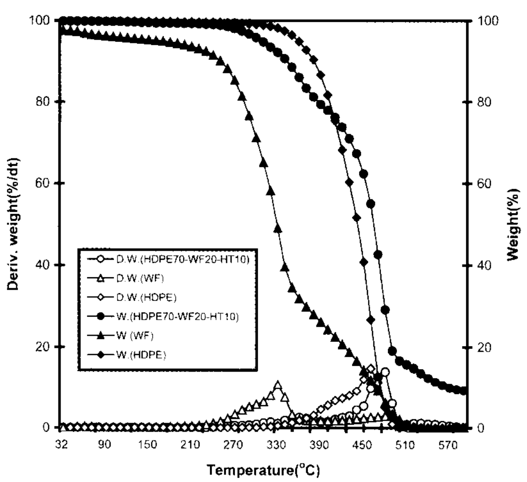
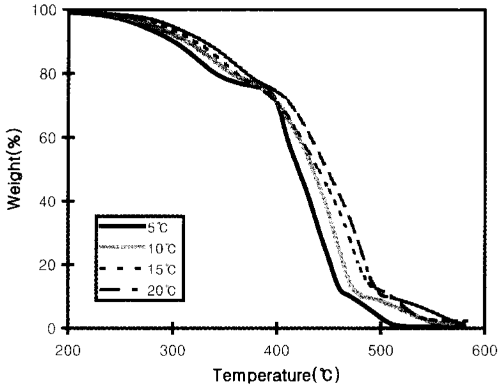


Fig. 3. TGA results (weight (%) and derivative weight (%/dt)) of wood flour and Hwangto reinforced HDPE composites. HDPE: high density polyethylene, WF: wood flour, HT: Hwangto.

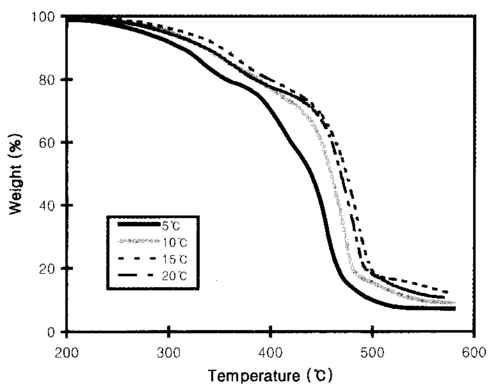
stability at a given temperature after 400°C. After 500°C, residual weight increased with increasing the content of wood flour and Hwangto. At a weight loss level of 50%, decomposition temperature of composites with Hwangto was higher 10~24°C (Table 2). It represents that the addition of Hwangto improved the thermal stability of HDPE.

The weight loss (%) and derivative weight (%/dt) as a function of time was shown in Table 2 and Fig. 3. Differential peak temperature (DT_p) was also determined by the differentiation of the weight loss by the time, representing that the higher thermal degradation occurs at higher peak temperature. Differential peak temperatures (DT_p) of wood flour and virgin HDPE were 335°C and 458°C respectively, but differential peak temperature (DT_p) of wood flour reinforced composites showed the increase of 16.4°C over virgin HDPE as wood flour of 40% was loaded. Differential peak temperature (DT_p) with Hwangto reinforced composites was 20°C higher than virgin HDPE. The addition of 3% MAPE increased the differential peak temperature in the range of 2~10°C. The highest differential peak temperature (DT_p) was obtained from HDPE 70%-WF 20%-Hwangto 10%-MAPE 3% reinforced composites, presumably due to the interaction effects of wood flour and Hwangto.

Thermal degradation curves for virgin HDPE with wood flour/Hwangto at various heating rates of 5, 10, 15, 20°C/min are shown in Fig. 4(a) and (b). Each measurement was performed with non-isothermal method. Decomposition temperature increased with increase of heating rate (Wielage *et al.*, 1999). It indicates that higher heating rate endowed the thermal stability, resulting from the decelerated decomposition rate. In other word, the thermal deformation is notably influenced by a factor of time at the different heating rates.



(a) HDPE70-WF30



(b) HDPE70-WF20-HT10-MAPE3

Fig. 4. TGA results of wood flour, Hwangto, and MAPE reinforced HDPE composites at various heating rates. HDPE: high density polyethylene, WF: wood flour, HT: Hwangto, MAPE: maleated polyethylene.

3.2. DSC Analysis - Melting Temperature, Enthalpy, and Activation Energy

Test data on melting temperature (T_m), enthalpy (J/g), and activation energy (E_a) determined at the various heating rates of 5, 10, 15, 20°C/min are summarized in Table 2. Fig. 5 shows a heating thermogram of HDPE with wood flour and Hwangto used in this study. The thermograms of HDPE with wood flour and Hwangto had the characteristic of single

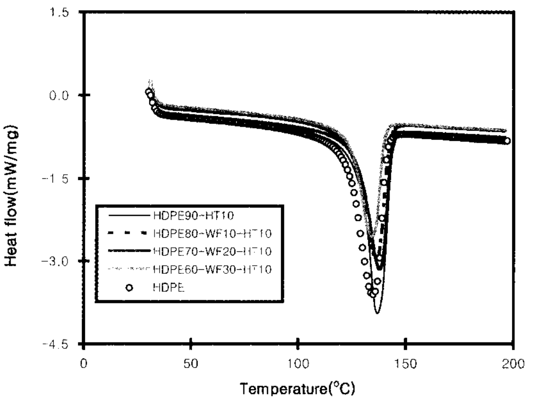


Fig. 5. DSC results of wood flour and Hwangto reinforced HDPE composites. HDPE: high density polyethylene, WF: wood flour, HT: Hwangto.

peak. The temperature corresponding to the peak represents the melting temperature (T_m) of the composite materials concerned (Table 2). Virgin HDPE showed the melting temperature of 135°C. Even though there are small variations, the melting temperature of composites increased with the addition of wood flour or Hwangto, providing the increase of thermal stability. However, the addition of wood flour and Hwangto showed no significant effect on the melting temperature of HDPE. When heating a mixture of virgin HDPE with wood flour, and Hwangto, the melting temperature decreased virtually up to 4°C (Table 2). However, it is worth indicating that there is some interaction between virgin polymer and wood flour. MAPE also showed no significant effects on the melting temperature of composites.7

An enthalpy by measuring the heat flow between a sample and a reference from isothermal heating was determined (Table 2). The enthalpy of the thermal transition is generally defined by the area under the peak. The enthalpy of virgin HDPE at transition temperature was especially highest (243.3 J/g). As the loading of wood flour to HDPE increased, overall enthalpy fairly decreased. It indicates that since enthalpy of wood flour and Hwangto is much lower than that of HDPE, wood flour and Hwangto absorb more energy for melting the composites. The enthalpy of wood flour reinforced composite was 148.4 J/g when wood flour of 40% to HDPE was added.

The linear relationship between heating rate and peak temperature of composites plotted according to the Kissinger equation at various heating rates is shown in Table 3. The relationship between heating rate and peak temperature according to Kissinger equation was well fitted by the linear regression, showing the high correlation of determination (R^2). The activation energy of virgin HDPE was 259.9 KJ/mol. The activation energy of HDPE decreased with the addition of 10, 20, and 30%, but the activation energy of HDPE was much higher (447.1 KJ/mol) than HDPE at wood flour of 40%. The activation energy of HDPE with Hwangto of 10% and 20% were 196.4 and 215.0 KJ/mol, respectively. Generally, Hwangto reinforced HDPE composites provided higher activation energy (25~30 KJ/mol) than that of wood flour reinforced HDPE composites. The activation energy is defined as a kinetic parameter that represents heat energy necessary for phase conversion from solid state to liquid state. Therefore, Hwangto reinforced composites shows higher heat energy than wood flour reinforced energy, indicating higher thermal stability. On the other hand, MAPE showed no significant effect on the activation energy.

4. CONCLUSIONS

Thermal stability is a requirement and a real solution in many application fields. The property can be achieved in relatively simple and

Table 3. Linear relationship between heating rate and peak temperature of reinforced HDPE composites plotted according to the Kissinger equation

HDPE (%)	WF (%)	HT (%)	MAPE (%)	Equation by linear regression	R^2	Activation Energy (KJ/mol)
-	100	-	-	N/A	N/A	N/A
-	-	100	-	N/A	N/A	N/A
-	-	-	100	N/A	N/A	N/A
100	-	-	-	Y=31.3X-66.5	0.847	259.9
90	10	-	-	Y=20.1X-39.1	0.890	167.2
90	-	10	-	Y=23.6X-47.6	0.803	196.4
80	20	-	-	Y=25.7X-45.4	0.993	189.0
80	-	20	-	Y=25.8X-53.0	0.966	215.0
80	10	10	-	Y=22.3X-44.7	0.977	185.8
80	10	10	3	Y=18.2X-34.7	0.592	195.3
70	30	-	-	Y=28.2X-59.2	0.908	235.0
70	20	10	-	Y=26.0X-53.6	0.961	216.0
70	20	10	3	Y=43.4X-96.6	0.956	361.5
60	40	-	-	Y=53.7X-122.2	0.945	447.1
60	30	10	-	Y=23.5X-47.7	0.749	195.9
60	30	10	3	Y=38.0X-83.1	0.995	315.8
60	20	20	-	Y=34.5X-75.0	0.837	287.0
60	20	20	3	Y=43.2X-96.0	0.969	359.7

R^2 indicates the coefficient of determination. WF: wood flour, HT: Hwangto, MAPE: maleated polyethylene inexpensive ways in this study. These results were conformed by the TGA and DSC analyses. From TGA analysis, the increase of wood flour level increased the thermal degradation of composites in the early stage, but decreased in the late stage. On the other hand, Hwangto reinforced composites has the thermal stability, compared with virgin HDPE. Decomposition temperature of wood flour and/or Hwangto reinforced increased with increase of heating rate. From DSC analysis, melting temperature of reinforced composites little bit increased with the addition of wood flour or Hwangto. As the loading of wood flour or Hwangto to HDPE increased, overall enthalpy decreased. It shows that wood flour and Hwangto absorb more heat energy for melting the composites. Hwangto reinforced composites require more heat energy than wood flour reinforced composites and virgin HDPE. Conclusively, Hwangto reinforced HDPE composites provide much improved thermal properties over virgin HDPE. Coupling agent showed no significant effect on the thermal properties of composites.

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