Mechanical and Thermal Properties of Liquefied Wood Polymer Composites (LWPC)[*1]

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ABSTRACT

The influence of liquefied wood (LW) on the mechanical and thermal properties of liquefied wood-polymer composites (LWPC) was investigated in this study. The thermal behaviors of LWPC were characterized by means of thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses. LW showed significant effects on the mechanical strength properties. The increase of flexural MOE and Young's modulus was related to the increase of stiffness of LWPC. The effect of LW was also significant on the flexural and tensile MOR. The impact strength decreased with the increase of LW application level. With the increased stress concentration by the poor bonding between LW and polymer, the impact strength of LWPC decreased, compared with that of high-density polyethylene (HDPE). The thermal stability of LWPC decreased with the increase of LW content up to 40%. The melting temperature of HDPE decreased with the increase of LW loading level. Enthalpy of HDPE also decreased with the addition of LW. This study proves the thermal stability necessary for the consolidation of composition materials.

Keywords : Liquefied wood-polymer composites, high-density polyethylene, Flexural strength, tensile strength, impact strength, TGA, DSC, weight loss, melting temperature

1. INTRODUCTION

In terms of effective utilization of biomass, liquefaction of wood resources converts lignocellulosic wastes such as sawdust into substances soluble in organic solvent and liquefying agent. Lignocellulosics can be completely liquefied without leaving any residues. Practically, liquefied wood (LW) is produced after removing the liquefying agent and organic solvent (Shiraishi *et al.*, 1985; Pu *et al.*, 1993; Lin *et al.*, 1994; Doh *et al.*, 1995; Kurimoto *et al.*, 1999).

The use of LW for thermoplastic composites is highly beneficial, improving the toughness and strength of pure polymers. LW may show the similar effect of filler as wood flour or fiber for thermoplastic polymers. These materials are biodegradable as well as nontoxic. In addition, these composites can be easily processed by the injection- or compression-molding (López-Manchado *et al.*, 2000). In order to be applicable

Table 1. Rheomixing and injection moulding conditions in this study

Rheomixing			Injection moulding		
Heater position	Temp. (°C)	Speed (rpm)	Heater	Temp. (°C)	Pressure (psi)
Barrel 1	170	15-25	Front	180	
Barrel 2	180		Middle	190	
Barrel 3	190		Nozzle	200	
Die	200		Injection pressure		1,000
			Device pressure		1,500

for a massive and economic production the thermoplastic polymer must be economic, easily available and well established.

Additional information regarding the mechanical properties such as flexural, tensile, and impact strength can shed more light about the manufacture of LWPC. Most of the polymers are generally subjected to a degradation of the mechanical and physical properties with the increase of temperature. Because of thermal stress during the manufacturing of composite materials, it is necessary to identify the effects of the temperature.

Thermogravimetric analysis (TGA) is one of the thermal analysis techniques used to quantify weight change and thermal decomposition of the sample (Mansanray et al., 1998). On the other hand, Differential Scanning Calorimetric (DSC) analysis provides the melting temperature (T_m) at which a transition occurs. It also provides the enthalpy ΔH associated with the transition. Studies of the dependence of ΔH on temperature can also be used to attain the change in heat capacity that occurs during melting. Understanding these parameters helps a characterization of the thermal stability of a given material. Recently, the authors have reported on the thermal properties of polymer composites filled with wood flour, rice husk, and sisal fiber (Coutinho et al., 1998; Nair et al., 2001; Eom et al., 2004; Yang et al., 2004).

However, little work was reported on the thermal behavior of LWPC. In this study, high-density polyethylene was used as a polymer matrix and liquefied wood mill as the lignocellulosic material for LWPC. The objective of this work is to investigate the mechanical and thermal properties of the LWPC and the prospect of LW as a reinforcing filler.

2. MATERIALS and METHODS

2.1. Materials

High-density polyethylene (HDPE) was obtained from Dae-Lim Industrial Co., South Korea. HDPE has a melt index of 7.5 g/10 min with a density of 0.938 g/cm^3. Wood mill was manufactured from municipal wood wastes in Korea Forest Research Institute, Korea. The wood mill was mixed with phenol at the mixture ratio of 1:3, and then added with 2.0 wt % sulfuric acid as a catalyst based on the weight of phenol in a rotary-digester of 20 L for 90 min. Thereafter, dissolute and residues were separated by a centrifuge and filtered through a 25G2 glass filter and the LW was recovered. Unreacted phenol was eliminated by using a rotary-vacuum evaporator at 170~180°C. Finally, a LW lump was obtained and granulated.

2.2. Manufacture of LWPC Pellets

The extruder had a single screw type which blended HDPE with LW mill. LW mill of 100 mesh was mixed with HDPE at the mixture ratios of 1:9, 2:8, and 3:7 in a Hakke Rheomix for 20 min and at 200°C (Table 1). The mixture of LW and HDPE was cooled in the air and then granulated in the cutting mill.

Extrusion of the granulate was performed on a Brabender[R] stand-alone extruder. This extruder had a screw diameter of 19 mm with an L/D ratio of 25 and a circular nozzle of 6 mm in diameter. The extrudate was cooled in the air and pelletized. The resulting pellets were extruded in the form of tensile, flexural, and impact test specimens on a Nissei NC-8300PZ injection-moulding machine (Table 1).

2.3. Mechanical Strength Testing

Flexural properties for LWPC were measured according to ASTM D-790 (ASTM, 2000a). Dimension of a specimen for flexural tests was 80.0 mm × 4.0 mm × 10 mm (length × thickness × width). Tests were conducted using a Universal Testing Machine at a speed of 200 mm/min on the samples with a span of 64 mm (5 replications).

Tensile tests for LWPC were conducted in accordance with ASTM D-638 (ASTM 2000b). Test specimens were molded in a mould whose cavity has these dimensions as follows; W= 13.0 ± 0.03 mm, L=57.0 ± 0.08 mm, G=50.0 ± 0.02 mm, T=3.0 ± 0.08 mm, where W=width of narrow section, L=length of narrow section, G =gage length, and T=thickness of narrow section. The tests were conducted using a Universal Testing Machine at a speed of 200 mm/ min on the samples with an initial length of 214.0 mm (5 replications).

Notched Izod impact tests were conducted according to ASTM D-256 (ASTM 2000c). The tests were performed with an XJ-40A pendulum apparatus using a specimen with notch depth of 2 mm (5 replications).

2.4. Thermogravimetric Analysis and Differential Scanning Calorimetry

TGA measurements using a Thermogravimetric Analyzer (TA Instrument SDT Q600) were carried out 5~10 mg of LWPC and HDPE at a heating rate of 10°C/min. LW, LWPC, and HDPE were subjected to TGA at a constant flow rate (10 mℓ/min) of nitrogen gas. Thermal decomposition of each sample was conducted in a scheduled temperature range of 30~600°C. The continuous records of weight loss and temperature were determined and analyzed to determine the following TGA indices: thermal degradation rate (% weight loss/min), initial degradation temperature and residual weight at 600°C.

DSC measurements were made on a DSC Q10 (TA instrument) thermal system. Each test specimen (10 ± 0.5 mg) was positioned at a heating rate of 10°C/min and a scanning temperature of 30 to 200°C.

2.5. Data Analysis

Tukey's Studentized-Range test ($\alpha = 0.05$) was used to compare the difference among treatment means (Wozniak et al., 1994).

3. RESULTS and DISCUSSION

3.1. Mechanical Properties

3.1.1. Flexural strength

The flexural strengths of LWPC were measured by a Universal Testing Machine (Table 2). Fig. 1 shows the relationship between the flexural properties and the HDPE with and without LW. The maximum flexural MOE

Table 2. Mechanical properties of LWPC

Polymer	LW (%)	Flexural MOE (kgf/cm^2)	Flexural MOR (kgf/cm^2)	Young's Modulus (kgf/cm^2)	Tensile MOR (kgf/cm^2)	Notched Impact strength (kgfcm/cm^2)
HDPE	0	6,652 a	356.4 a	3,387 a	258.2 a	N.B.
	10	9,747 b	348.1 a	7,380 b	219.9 b	1.72 a
	20	14,008 c	327.8 b	8,994 c	217.1 b	1.46 b
	30	14,702 d	228.7 c	9,386 d	198.7 c	1.27 c

Each mean for flexural, tensile, and notched impact strength properties represents five replicates of the LWPC. N.B. indicates not broken. Means within each column followed by the same letter are not significantly different (ANOVA, Tukey's Studentized-Range test, $\alpha = 0.05$).
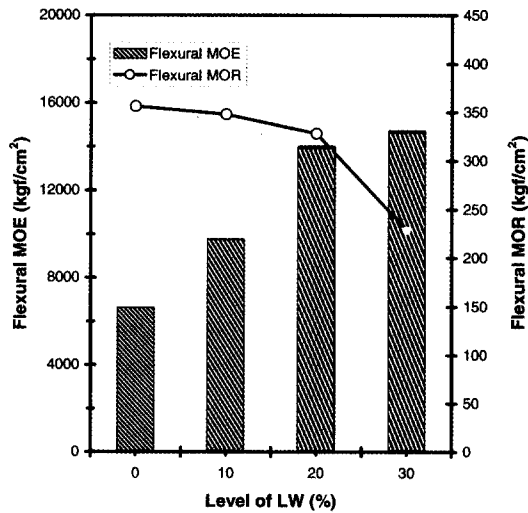

Fig. 1. Flexural MOE and MOR of HDPE and LWPC with various loading levels of LW.

Fig. 2. Young's modulus and tensile strength of HDPE and LWPC with various loading levels of LW.

(14,702 kgf/cm^2) and MOR (356.4 kgf/cm^2) were obtained by the LWPC with 30% LW and 0% LW, respectively. The flexural MOE of LWPC improved by adding LW up to 30%. The increase of flexural MOE of LWPC by the addition of LW was in the range of 46.5~ 121.0%. It indicates that the increase of flexural MOE values is related to the increase of stiffness of LWPC, due to the addition of LW. On the other hand, the flexural MOR decreased by adding LW up to 30%. The decrease of flexural MOR by the addition of LW was in the
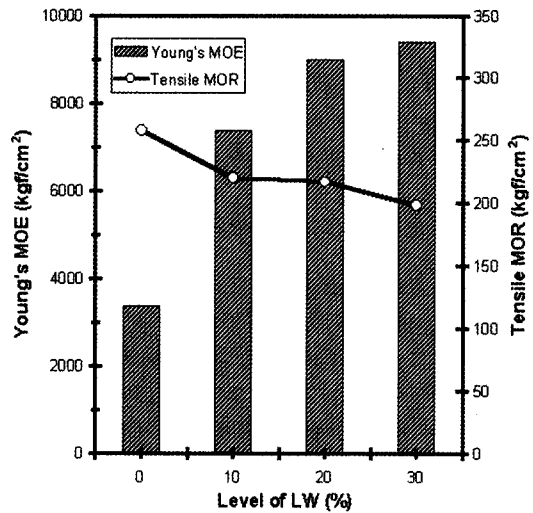
range of 2.3~35.8%, indicating the decrease of bonding strength between pure HDPE and LW.

3.1.2. Tensile strength

Tensile strengths for LWPC were reported in Table 2 and Fig. 2. The maximum Young's modulus (9,386 kgf/cm^2) and tensile MOR (258.2 kgf/cm^2) were observed by LWPC with 30% LW and a control group, respectively. It was observed that Young's modulus showed the increase of 117.9~177.1%, due to the addition

Table 3. Results of TGA analysis of LWPC

Polymer	LW (%)	T_p^a (°C)	Degradation (%)	Residue at 600°C (%)
HDPE	0	466.09	28.25	-0.703
	10	469.90	36.98	1.006
	20	471.75	32.98	-0.774
	30	473.68	41.31	3.939

[a] indicates the peak temperature of TGA analysis.

of LW up to 30%. It is also explained by the increase of stiffness of LWPC, due to LW. The tensile strength by the addition of LW increased significantly, showing the similar effect of reinforcing filler such as wood flour or fiber (Lee et al., 2004). The decrease of tensile strength showed that the LW gives no good reinforcement with the polymer matrix.

3.1.3. Impact strength

Notched impact strengths for LWPC were reported in Table 2. HDPE without LW were so high that it was not broken under the maximum load. As the LW content increased, impact strengths of LWPC were decreased. It is assumed that high flexibility of HDPE attributes to the high impact strength of polymer matrix. It may attribute to the increased stress concentration by the decreased uniformity of polymer and liquefied mixture. It is also considered that the reduced flexibility of polymer matrix is another reason for the decreased impact strengths.

3.2. Thermal Properties

3.2.1. TGA induction time

Weight loss of a virgin polymer and LWPC as a function of time or temperature is commonly determined by the technique of TGA and is an irreversible process due to thermal degradation. TGA curves of LW, HDPE, and
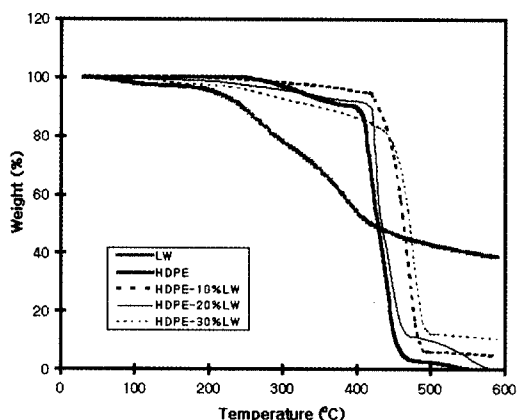

Fig. 3. TGA results of LW, HDPE, and LWPC with various loading levels of LW.

LWPC are shown in Fig. 3. The TGA curves of those materials show a single stage of weight loss. The initial weight loss of LW started approximately up to 200°C, due to the heat of evaporation of moisture in the sample and the initial decomposition of holocellulose. The severe weight loss from 210 to 410°C is due to the major components of wood, namely holocellulose and lignin. It can be deduced that holocellulose components of LW are the major contributors to decomposition between 200 and 400°C, whereas lignin is mainly responsible for the char formation of the LW over 400°C. From these results, the chemical modification of major components of LW occurred during manufacturing LW with phenol and sulfuric acid, resulting in the lower decomposition temperature.
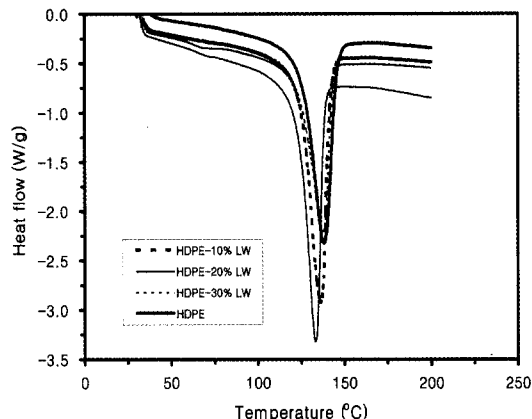
Fig. 4. DSC results of HDPE with various loading levels of LW.

The weight loss of HDPE started 425°C and the thermal stability of HDPE with LW was higher than that of pure HDPE. The thermograms of TGA for HDPE at the different level of LW (0~30%) and at a heating rate of 10°C/min were shown in Fig. 4. As the LW level increased, thermal stability of composites decreased. This result indicates that the compatibility and interfacial bonding decreased by mixing both LW and HDPE. It shows that the thermal stability of LWPC is lower. Char and ash content after thermal degradation over 500°C, however, increased with increase of LW level.

3.2.2. DSC-Melting temperature

Fig. 4 shows a heating thermogram of LW,

LDPE, and HDPE with LW used in this study; a single peak was obtained. This is actually a characteristic of semi-crystalline polymer and is visible as an endothermic peak. The temperature corresponding to the peak represents the melting point^{TM} of the composite materials concerned (Table 4). The addition of LW to pure polymer showed no significant effect on the melting point of polymer. When heating a binary blending (pure HDPE:LW) of a specific blending ratio (90/10% w/w) for HDPE, the melting point decreased virtually 0.2~1.3°C. The melting point of HDPE decreased 4.8°C by adding LW of 20%, but it increased 0.4°C, compared with pure HDPE. Nevertheless, it is worth pointing out that there is some incompatibility between virgin polymer and LW.

An enthalpy of caloric processes by measuring the heat flow between sample and reference with isothermal heating was determined (Table 4). The area under the peak is the enthalpy of the transition (Fig. 4). The enthalpy of pure HDPE at transition temperature was the highest (165.5 J/g). When LW of 10~30% was added to pure HDPE, overall enthalpy decreased, indicating the decreased thermal stability.

4. CONCLUSIONS

LW showed significant effects on the flexural, tensile, and impact strength properties of LWPC. The increase of flexural and Young's

Table 4. Results of DSC analysis of LWPC

Polymer	LW (%)	$T_m{}^a$ (°C)	Enthalpy (J/g)
HDPE	0	138.03	165.5 @125.4°C
	10	136.27	163.2 @124.6°C
	20	133.23	160.3 @123.7°C
	30	139.38	149.6 @127.3°C

[a] indicates the melting temperature of DSC analysis.

modulus MOE by the addition of LW is related to the increase of stiffness of LWPC, due to the reinforcing effect acquired by LW. The impact strength from HDPE with high flexibility was comparatively high. Due to the increased stress concentration by the poor bonding between LW and HDPE, the impact strength of LWPC decreased. The thermal stability of LWPC decreased with the increase of LW loading. In fact, melting points of HDPE decreased with the increase of LW loading. Overall enthalpy decreased as LW of 10~30% was added to pure HDPE, indicating the decreased thermal stability.

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