

# Thermal behavior of Flame Retardant Filled PLA-WF Bio-Composites<sup>\*1</sup>

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## ABSTRACT

This study examined the thermal stability of PLA-WF bio-composites. Wood flour (WF)-filled PLA bio-composites were reinforced with the flame retardants, Melamine pyrophosphate (MPP), resorcinol bis (diphenyl phosphate) (RDP) and zinc borate (ZB). The flame retardant was compounded with PLA and natural biodegradable filler. The thermal properties of the biodegradable polymer and bio-composites reinforced with the flame retardant were measured and analyzed by DSC, DMA and TGA. The results showed that the flame retardant-reinforced biodegradable bio-composite exhibited improved thermal properties.

*Keywords* : thermal property, bio-composites, flame retardant, poly lactic acid, wood flour

## 1. INTRODUCTION

Petroleum-based synthetic polymers have several advantages, such as excellent chemical resistance, good mechanical properties and low cost, and are used in a variety of applications. However, excessive use of petroleum-based synthetic polymers causes problems, such as environmental pollution from polymer waste in landfill (Kim *et al.*, 2005; Kim *et al.*, 2005). The problem of environmental pollution has become an important issue and various solutions have been suggested, one of which is the use of composites made from a biodegradable matrix

polymer and a natural reinforce filler. Biodegradable polymers have high mechanical properties that are similar to petroleum-based synthetic polymers (Mohanty *et al.*, 2000). The natural filler supports the biodegradable matrix polymer but has the limitation of low cost, non-toxic, low density and reduction of weight (Lee *et al.*, 2006). These biodegradable bio-composites have several advantages, such as good mechanical properties, wide productivity, low density, high specific stiffness and light weight (Huda *et al.*, 2005). However, biodegradable bio-composites generally have weak thermal stability, which is one of barriers to their wider

<sup>\*1</sup> Received on March 3, 2009; accepted on March 12, 2009

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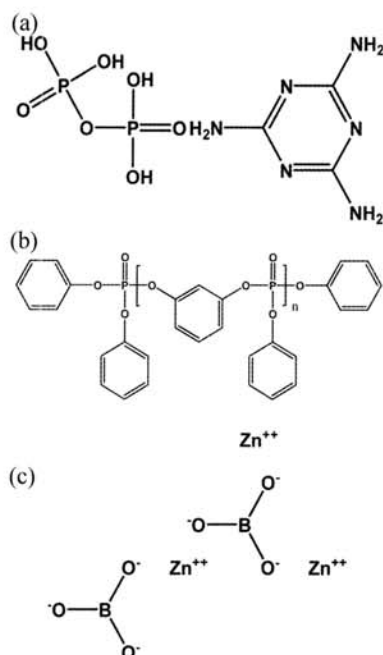


Fig. 1. Chemical structures of (a) melamine pyrophosphate (MPP), (b) resorcinol bis(diphenyl phosphate) (RDP), and (c) zinc borate (ZB).

use. Therefore, a variety of methods have been made to improve the thermal properties of bio-degradable polymers, such as the use of additives, mechanical treatment and reinforcement in the polymerization stage (Nikolic *et al.*, 2001; Loo *et al.*, 2005; Kim *et al.*, 2007).

Flame retardants hinder the combustion of polymer materials generally by volatilizing after absorbing heat through an endothermic reaction and remove the heat of polymer combustion. They react with the residues, such as char or a gas foam layer, which can effectively hinder the heat and fuel transfer process during combustion, leading to the self-extinguishment of burning materials (Agrawal *et al.*, 1991; Camino *et al.*, 1991; Zhu *et al.*, 1996). This mechanism can be effective in reinforcing the thermal stability of bio-composites.

This study investigated the thermal stability of

wood flour (WF) filled poly lactic acid (PLA) bio-composites with the addition of flame retardants, such as melamine pyrophosphate (MPP), resorcinol bis (diphenyl phosphate) (RDP) and zinc borate (ZB). The change in the thermal properties of PLA and PLA-WF bio-composites, such as  $T_m$ , storage modulus, and weight loss, were examined.

## 2. EXPERIMENTAL

### 2.1. Materials

Poly lactic acid (PLA) was supplied by Nature Works Co., USA. PLA has an MFI of 15 g/10 min (190°C/2, 160 g) and a density of 1.22 g/cm<sup>3</sup>. Wood flours (WF), as the reinforcing natural-filler, were obtained from Saron Filler Co., South Korea. The AS additives to reinforce flame retardation, melamine pyrophosphate (MPP), resorcinol bis (diphenyl phosphate) (RDP) and zinc borate (ZB) were supplied by Chempia Co., South Korea. Fig. 1 shows the chemical structure of the flame retardants.

### 2.2. Compounding and Making Specimens

PLA was blended with WF, MPP, RDP and ZB in a laboratory-sized, co-rotating, twin screw extruder (Bau Technology, South Korea) using three general processes: melt blending, extrusion and pelletizing. The weight ratio of PLA to WF was 70 to 30. Two types of flame retardant, MPP and RDP were applied at 5 wt%, 10 wt% and 10 wt% with 3 phr ZB based on the total weight of resin such as PLA and PLA-WF bio-composites. The extruder barrel was divided into eight zones with the temperature in each zone being individually adjustable. The materials were blended with a screw speed of 250 rpm at 185°C. After extruding, the blended ma-

## Thermal behavior of Flame Retardant Filled PLA-WF Bio-Composites

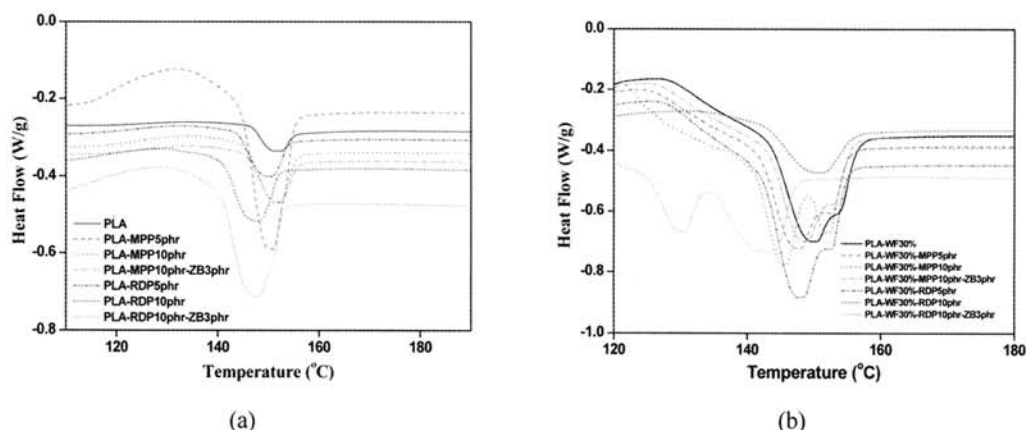


Fig. 2. DSC curves of (a) PLA and (b) PLA-WF bio-composites.

terials were cooled with water, and pelletized. The pellets were dried at 60°C for 24 hrs. The dried pellets were made into specimens for dynamic mechanical analysis (DMA) with an injection molding machine at a heating temperature of 185°C, an injection pressure of 1,200 psi and a device pressure of 1,500 psi.

### 2.3. Differential Scanning Calorimetry (DSC)

DSC was carried out using a TA Instrument DSC Q1000 in NICEM, at Seoul National University, South Korea. Each sample was scanned from -80 to 200°C at a heating rate of 10 °C/min and then cooled at the same rate under a nitrogen atmosphere. The thermal properties, melting temperature ( $T_m$ ) and glass temperature ( $T_g$ ), were determined from the second scan.  $T_m$  was considered the maximum of the endothermic melting peak from the second heating scan, and a deflection of the baseline was observed at the  $T_g$  from the second cooling scan.

### 2.4. Dynamic Mechanical Analyzer (DMA)

DMA was carried out using a TA Instrument

DMA Q800. The storage modulus, loss modulus and loss factor ( $\tan \delta$ ) of the composites was measured in type of dual cantilever. The measurements were carried out from -20.0°C to 140.0°C at a heating rate of 2.0°C/min and at a frequency of 1 Hz.

### 2.5. Thermo Gravimetric Analysis (TGA)

TGA (Q-5000 IR, TA Instrument, USA) was used at NICEM, Seoul National University, South Korea. The sample was measured in nitrogen gas at a heating rate of 20°C/min, from 35°C to 700°C. The sample weight was 8~14 mg.

## 3. RESULTS and DISCUSSIONS

### 3.1. Differential Scanning Calorimetry (DSC)

The thermal properties, such as melting temperature ( $T_m$ ) and glass temperature ( $T_g$ ) of the PLA and PLA-WF bio-composites were measured from DSC analysis. Fig. 2 show the heating thermograph of PLA and PLA-WF bio-composites according to the amount of flame retardant added. Table 1 summarizes the thermal

Table 1. DSC data of the PLA and PLA-WF bio-composites (second heating scan)

	$T_g$ (°C)	$T_{m1} \sim T_{m2}$ (°C)
PLA	59.1	152.1
PLA-MPP5phr	58.0	150.2
PLA-MPP10phr	58.8	151.4
PLA-MPP10phr-ZB3	58.9	151.8
PLA-RDP5phr	53.3	150.2
PLA-RDP10phr	47.8	147.9
PLA-RDP10phr-ZB3phr	47.7	147.8
PLA-WF30%	58.0	149.9 ~ 153.6
PLA-WF30%-MPP5phr	56.7	147.6 ~ 152.0
PLA-WF30%-MPP10phr	56.5	145.3 ~ 151.3
PLA-WF30%-MPP10phr-ZB3phr	57.0	148.5 ~ 152.2
PLA-WF30%-RDP5phr	56.3	147.7 ~ 152.4
PLA-WF30%-RDP10phr	52.9	150.7
PLA-WF30%-RDP10phr-ZB3phr	40.5	130.3 ~ 143.8

properties of the flame retardant filled PLA and PLA-WF bio-composites obtained from DSC. The  $T_m$  of the MPP filled PLA specimens was lower than that of the neat PLA. However, as soon as the MPP content was increased from 5 phr to 10 phr, the  $T_m$  of MPP filled PLA specimens increased. The  $T_m$  of the 10 phr MPP and 3 phr ZB-filled PLA specimens was slightly higher than that of the 10 phr MPP filled PLA specimen. It was expected that MPP and ZB would reinforce the thermal stability of the PLA with their heat resistance (Kandola *et al.*, 2001; Cai *et al.*, 2008). The  $T_m$  of the RDP filled PLA specimen also was lower than that of neat PLA. The  $T_m$  of the RDP filled PLA decreased with increasing RDP content, and the addition of ZB exacerbated the decrease in  $T_m$ .

In Fig. 2(b), the  $T_m$  of PLA-WF bio-composites were slightly lower than that of the PLA

specimens but the change was not significant. The  $T_m$  of the PLA-WF bio-composites showed two peaks except for that of the PLA-WF with 10 phr RDP bio-composites. This may be due to the rapid decrease in molecular mass and the breaking of the chains into shorter dimensions, resulting in a rearrangement into a more organized structure during mineralization (Iovino *et al.*, 2008). Several  $T_m$  of the sample were not clearly separated, which may be due to the relatively rapid ramping of the heating temperature. The MPP filled PLA-WF bio-composites showed a similar tendency to that of the MPP filled PLA specimens. The  $T_m$  of the RDP-filled PLA-WF bio-composites also decreased. In particular, the RDP 10 phr and ZB 3 phr PLA-WF bio-composites showed a large decrease. This shows the anti-synergic effect among WF, RDP and ZB.

In Table 2, the  $T_g$  of the PLA and PLA-WF bio-composite showed a similar tendency to  $T_m$  of the PLA and PLA-WF bio-composites. The  $T_g$  of the PLA specimens was slightly higher than that of the PLA-WF bio-composites, and the  $T_g$  of the MPP filled samples was higher than that of the RDP filled specimens. The  $T_g$  of the MPP filled PLA and PLA-WF bio-composites were lower than that of the neat PLA and PLA-WF bio-composites. However, the addition of ZB increased the  $T_g$  of the MPP filled PLA and PLA-WF bio-composites. This was attributed due to the heat resistance of ZB and MPP, and the synergic effect of MPP and ZB (Kandola *et al.*, 2001; Cai *et al.*, 2008). The anti-synergic effect between RDP and ZB could also be confirmed as a decrease in the  $T_g$  of RDP and ZB filled PLA.

### 3.2. Dynamic Mechanical Analyzer (DMA)

The storage modulus of the PLA bio-composites was obtained from DMA. Fig. 3 shows the

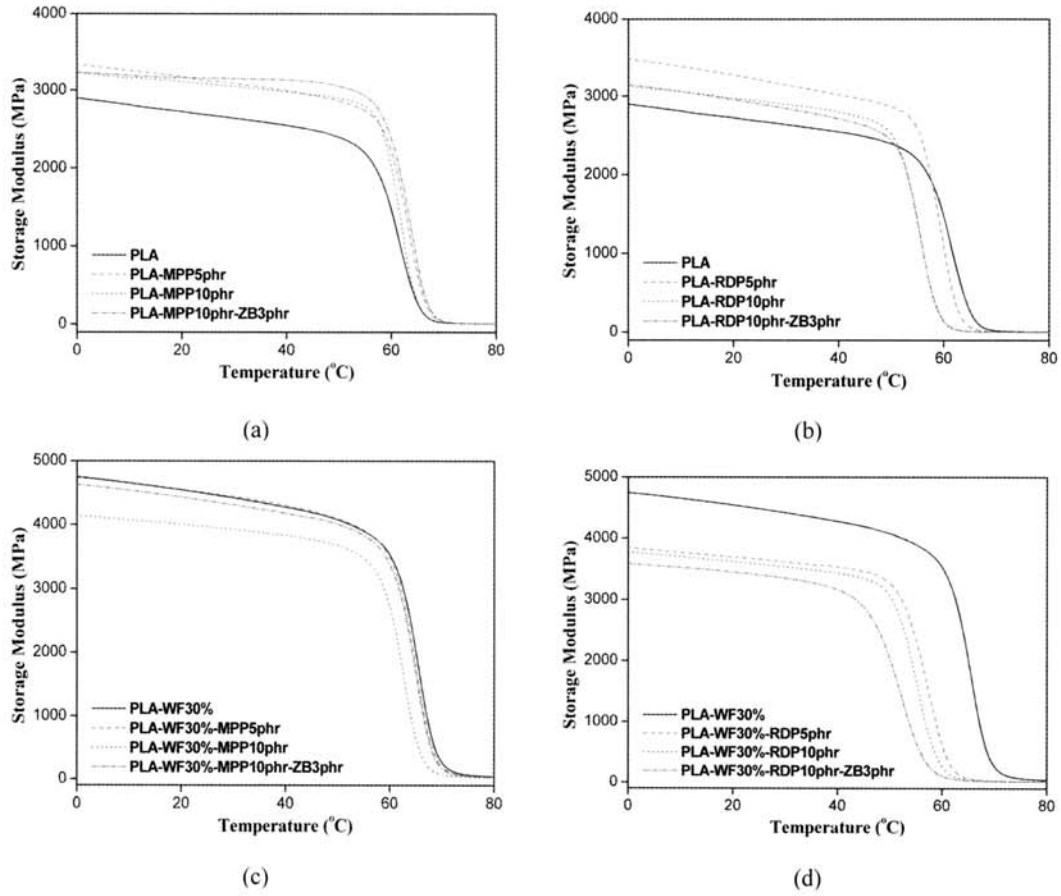


Fig. 3. Storage modulus of (a) MPP filled and (b) RDP filled PLA and (c) MPP filled (d) RDP filled PLA-WF bio-composites.

dynamic storage modulus of the flame retardant filled PLA and PLA bio-composites as a function of temperature. The storage modulus of the flame retardant added PLA specimens was higher than that of the neat PLA (Fig. 3(a)). This was attributed to the improvement of thermal stability of the specimens by the flame retardants. In Fig. 3(a), the storage modulus of the 10 phr MPP-filled PLA over the same temperature was slightly lower than that of the 5 phr MPP-filled PLA. It is believed that the increase in MPP content has little effect on the ratio storage modulus of PLA. The storage modulus of the 10 phr MPP and 3 phr ZB-filled PLA specimen

was lower than that the only 10 phr MPP-filled PLA until 30°C, but was highest in after 50°C. This may be due to reinforcement of the thermal stability from ZB. The storage modulus the RDP filled PLA was lower than that of the MPP filled PLA except for PLA containing 5 phr RDP until 30°C. The storage modulus of the 10 phr RDP-filled PLA and 10 phr RDP and 3 phr ZB-filled PLA specimens was lower than that of the 5 phr RDP-filled PLA specimens, and the storage modulus of the 10 phr RDP and 3 phr ZB-filled PLA specimen was higher than that of the 10 phr RDP-filled PLA specimen until 10°C. However, the ratio of the storage

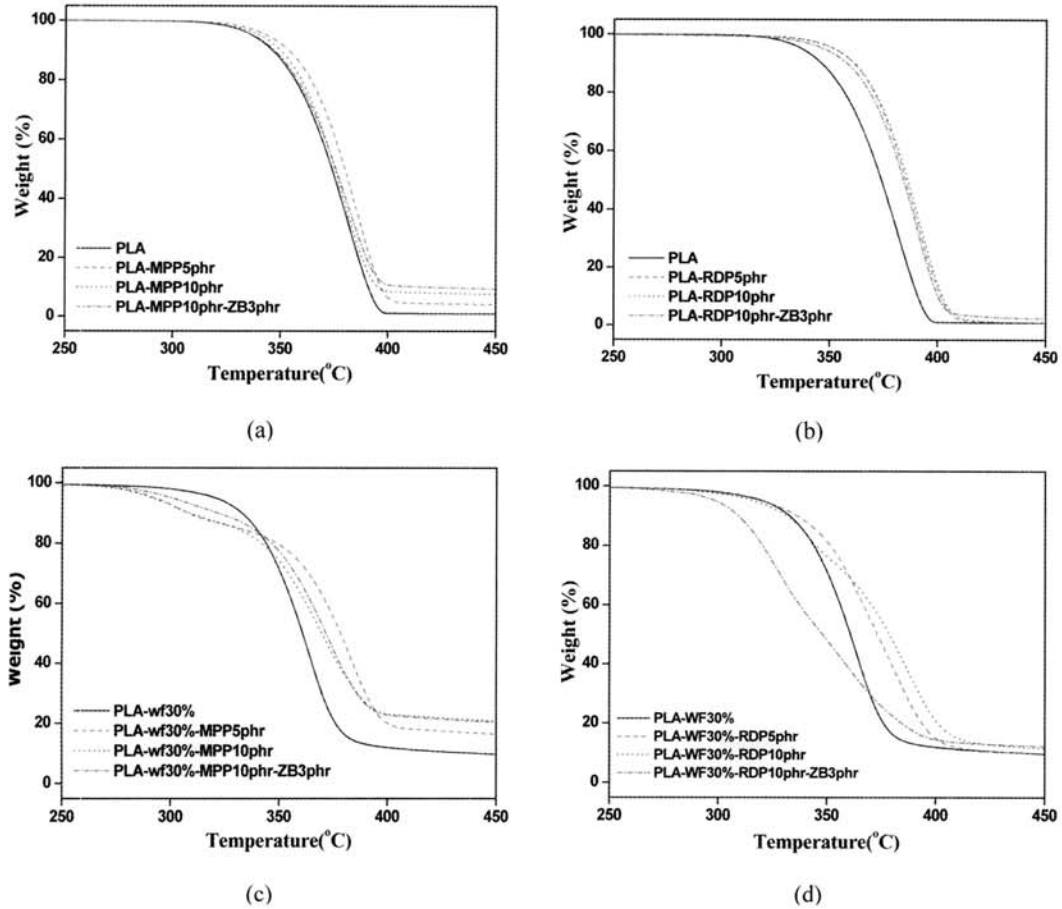


Fig. 4. TGA curves of (a) MPP filled and (b) RDP filled PLA and (c) MPP filled (d) RDP filled PLA-WF bio-composites.

modulus of PLA with 10 phr RDP and 3 phr ZB-filled PLA specimens was lower than that of the 10 phr RDP-filled PLA specimens after 10°C. Therefore, the content of RDP and ZB in the RDP filled PLA had little effect on the storage modulus.

Fig. 3(b) shows the storage modulus of the PLA-WF bio-composites that was higher than that of the PLA specimens and it may be due to the increase of stiffness of PLA-WF bio-composites from natural filler loading which allow effective stress transfer from the PLA matrix to the flours (Huda *et al.*, 2005). And the

aspect of the DMA curve of the PLA bio-composites was generally similar to that of the PLA polymer in that an increase in the content of flame retardant decreased the storage modulus and ZB had a synergic effect with MPP and an anti-synergic effect with RDP.

### 3.3. Thermo Gravimetric Analysis (TGA)

The weights loss of the PLA bio-composites caused by thermal degradation was examined by TGA. Fig. 4 shows a thermograph of PLA with

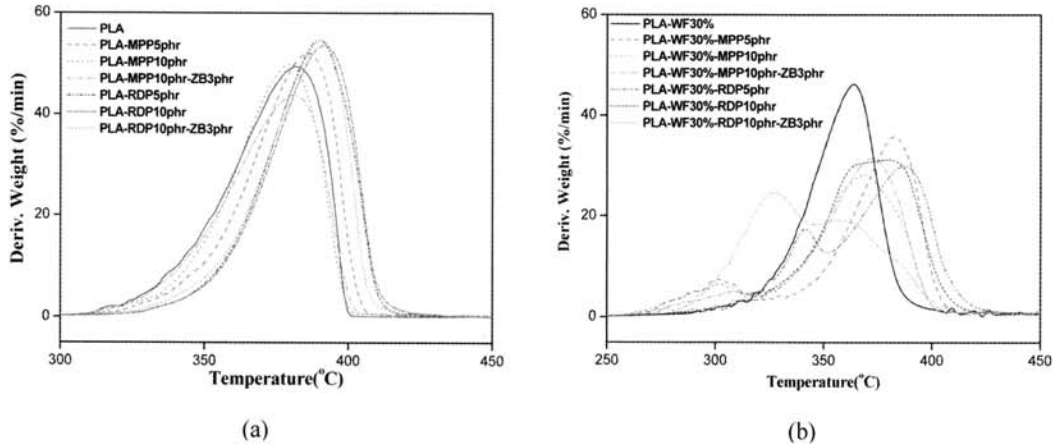


Fig. 5. Derivative thermo gravimetric curve ( $DTG_{max}$ ) of (a) PLA and (b) PLA-WF bio-composites.

the flame retardant. In Fig. 4(a), the weight loss of the samples began from approximately 300°C, and only one peak was observed in the derivative thermo gravimetric curve ( $DTG_{max}$ ) temperature at approximately 380°C (Fig. 5(a)). This tendency was attributed to the properties of PLA and the flame retardants, as shown in Fig. 6. The decreasing rate of the flame retardant-added PLA specimens was lower than that of the non flame retardant filled PLA sample. This is due to the thermal volatilization of MPP through an endothermic reaction (Kandola *et al.*, 2001). The weight loss of the 10 phr MPP-filled PLA and 10 phr MPP and 3 phr ZB filled PLA specimens were more than that of the only 5 phr MPP-filled PLA. This may be due to the increase in the MPP content, and is supported by the fact that thermal decreasing rates of the 10 phr MPP-filled PLA and 10 phr MPP and 3 phr ZB-filled PLA specimens were smaller than that of the 5 phr MPP-filled PLA. In the end of thermal degradation, there was more residue in the additive-filled PLA than that of the neat PLA because of char and inorganic residue from the thermal reaction of MPP. The 10 phr MPP and 3 phr ZB-filled PLA showed a lower degradation rate and more

residue than that the 10 phr MPP PLA. Therefore, ZB reinforced the flame retardation effect of MPP.

In Fig. 4(b), the decreasing rate of the flame retardant added PLA specimens was lower than that of the non flame retardant filled PLA samples. The thermal degradation of the flame retardant filled PLA ended later than that of the neat PLA and MPP-filled PLA at the same content. In Fig. 5(a), the RDP filled PLA specimens also showed a single peak in the derivative thermo gravimetric curve ( $DTG_{max}$ ) at approximately 390°C, which was higher than that of PLA and MPP-filled PLA. This was attributed to the flame retardant mechanism of RDP that volatilized and form a gas phase (Murashko *et al.*, 1999). This was confirmed from the weight loss of each material shown in Fig. 6 The TGA curve of PLA with 10 phr RDP was similar to that of PLA with 5 phr RDP but there was a slight increase in flame retardation. It is expected that the contents of RDP influenced the flame retardation slightly. However, compared to the 10 phr RDP filled-PLA specimen, the degradation ratio and residue of PLA with 10 phr RDP and 3 phr ZB was higher. It is possible that the anti-syner-



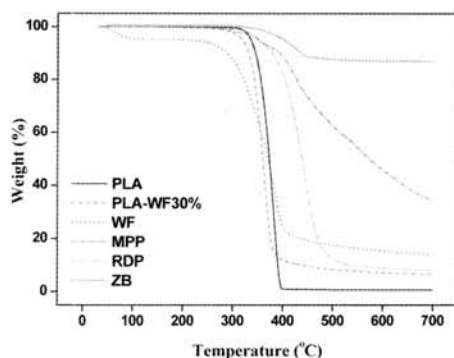


Fig. 6. TGA curves of the materials.

gistic effect between RDP and ZB influenced the flame retardation of PLA.

Fig. 4(c) shows the PLA-WF bio-composites. The weight loss of the PLA-WF bio-composites began earlier than that of PLA. In addition, the two peaks were observed in the derivative thermo gravimetric curve ( $DTG_{max}$ ) of the flame retardant filled PLA-WF bio-composites (Fig. 5(b)). This may be due to the degradation of the hemicellulose, cellulose and lignin constituents in the bio-composites and reaction of flame retardant for degradation (Kim *et al.*, 2005). This tendency is supported by the TGA curve of WF, as shown in Fig. 6. The MPP- and MPP with ZB filled PLA-WF bio-composites showed more weight loss than the neat PLA-WF bio-composites until 340~350°C. However, after 350°C, the weight loss of flame retardant filled PLA was less than that of the non-flame retardant filled PLA-WF. This TGA curve of the flame retardant filled PLA-WF bio-composites may be due to the flame retardation mechanism of MPP and ZB. The early weight loss indicates the volatilization of the flame retardant, which decreased the thermal degradation through an endothermic reaction (Kandola *et al.*, 2001). On the other hand, the flame retardation of 10 phr RDP and 3 phr ZB filled PLA-WF bio-composite, like that of the 10 phr RDP and 3phr ZB-filled PLA specimen,

was less than the other flame retardant filled PLA-WF bio-composites. This might also be due to the anti-synergistic effect between RDP and ZB.

In the TGA curve, RDP had a larger flame retardation effect on the neat PLA than MPP. However, the TGA curve of the PLA-WF bio-composites showed that the RDP filled PLA WF30% bio-composite exhibited similar weight loss to that of the MPP filled PLA WF bio-composites with the exception for volatilization of the flame retardant in the early stages (Fig. 4(d)).

## 4. CONCLUSION

The  $T_m$  of the flame retardant filled PLA and PLA-WF bio-composites was lower than that of the neat PLA bio-composites, but the decrease of that was slight change. The storage modulus of PLA was higher than that of PLA-WF bio-composites. MPP, RDP and ZB reinforced the thermal stability of the PLA and PLA-WF bio-composites. Therefore, the thermal stability of the PLA and PLA-WF bio-composite was affected by a flame retardation mechanism from an endothermic reaction. RDP stabilized the PLA polymer and MPP reinforced the stability of the PLA-WF bio-composites. However, the addition of both RDP and ZB decreased the thermal stability of the PLA and PLA-WF bio-composites. This might be due to an anti-synergistic reaction between RDP and ZB. In contrast, the supplemental addition of ZB to the MPP filled PLA polymer and PLA-WF bio-composites decreased the thermal degradation of the PLA polymer and PLA-WF bio-composites.

## ACKNOWLEDGEMENTS

This project was initiated through research grants (500-20070113) supported by the Korea Forest Service.



## REFERENCES

1. Agrawal, J. P., D. C. Gupta, Y. Khare, and R. S. Satpute. 1991. Zinc Borate Complex as Flame-Retardant Filler. *Journal of Applied Polymer Science* 43(2): 373~377.
2. Cai, Y. B., Q. F. Wei, F. L. Huang, and W. D. Gao. 2008. Preparation and properties studies of halogen-free flame retardant form-stable phase change materials based on paraffin/high density polyethylene composites. *Applied Energy* 85(8): 765~775.
3. Camino, G., L. Costa, and M. P. L. Dicortemiglia. 1991. Overview of Fire retardant Mechanisms. *Polymer Degradation and Stability* 33(2): 131~154.
4. Huda, M. S., A. K. Mohanty, L. T. Drzal, E. Schut, and M. Misra. 2005. "Green" composites from recycled cellulose and poly(lactic acid): Physico-mechanical and morphological properties evaluation. *Journal of Materials Science* 40(16): 4221~4229.
5. Iovino, R., R. Zujjo, M. A. Rao, L. Cassar, and L. Gianfreda. 2008. Biodegradation of poly (lactic acid)/starch/coir biocomposites under controlled composting conditions. *Polymer Degradation and Stability* 93(1): 147~157.
6. Kandola, B. K., A. R. Horrocks, and S. Horrocks. 2001. Complex char formation in flame-retarded fibre-intumescent combinations. Part V. Exploring different fibre/intumescent combinations. *Fire and Materials* 25(4): 153~160.
7. Kim, H. S., B. H. Lee, S. W. Choi, S. Kim, and H.-J. Kim. 2007. The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled polypropylene composites. *Composites Part a-Applied Science and Manufacturing* 38(6): 1473~1482.
8. Kim, H. S., H. S. Yang, and H.-J. Kim. 2005. Biodegradability and mechanical properties of Agro-Flour-filled polybutylene succinate biocomposites. *Journal of Applied Polymer Science*. 97(4): 1513~1521.
9. Kim, H.-S., H. S. Yang, H.-J. Kim, B. J. Lee, and T. S. Hwang. 2005. Thermal properties of agro-flour-filled biodegradable polymer bio-composites. *Journal of Thermal Analysis and Calorimetry* 81(2): 299~306.
10. Lee, B.-H., H.-S. Kim, S.-W. Choi, and H.-J. Kim. 2006. Improvement of interfacial adhesion for surface treated rice husk flour-filled polypropylene bio-composites. *Journal of the Korean Wood Science and Technology* 34(3): 38~45.
11. Loo, S. C. J., C. P. Ooi, and Y. C. F. Boey. 2005. Influence of electron-beam radiation on the hydrolytic degradation behaviour of poly (lactide-co-glycolide) (PLGA). *Biomaterials* 26(18): 3809~3817.
12. Mohanty, A. K., M. Misra, and G. Hinrichsen. 2000. Biofibres, biodegradable polymers and bio-composites: An overview. *Macromolecular Materials and Engineering* 276(3): 1~24.
13. Murashko, E. A., G. F. Levchik, S. V. Levchik, D. A. Bright, and S. Dashevsky. 1999. Fire-retardant action of resorcinol bis(diphenyl phosphate) in PC-ABS blend. II. Reactions in the condensed phase. *Journal of Applied Polymer Science* 71(11): 1863~1872.
14. Nikolic, M. S. and J. Djonlagic. 2001. Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene adipate)s. *Polymer Degradation and Stability* 74(2): 263~270.
15. Zhu, W. M., E. D. Weil, and S. Mukhopadhyay. 1996. Intumescent flame-retardant system of phosphates and 5,5',5'',5'''-hexamethyltris(1,3,2-dioxaphosphorinanemethan)amine 2,2',2''-trioxide for polyolefins. *Journal of Applied Polymer Science* 62(13): 2267~2280.