

## Thermal Degradation Behavior of Polypropylene Base Wood Plastic Composites Hybridized with Metal (Aluminum, Magnesium) Hydroxides

Jae Gyoung Gwon,<sup>1</sup> Sun Young Lee,<sup>2</sup> Jung Hyeun Kim<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, University of Seoul 130-743, Seoul, Korea

<sup>2</sup>Functional Materials Laboratory, Division of Environmental Material Engineering, Korea Forest Research Institute, 130-712 Seoul, Korea

Correspondence to: J. H. Kim (E-mail: jhkimad@uos.ac.kr)

**ABSTRACT:** The effect of hybridization of wood fibers and metal hydroxides on the thermal stability of polypropylene (PP) based plastic composites is studied through thermo gravimetric analysis (TGA). The wood fiber increases thermal stability of the metal hydroxide hybridized WPC including aluminum hydroxide (AH) and magnesium hydroxide (MH). Hybridization with the AH increases decomposition temperature of the maximum loss rate ( $T_{max}$ ) of the PP due to reinforcement of residue, but the onset-temperature of the PP decomposition is nearly shifted. However, hybridization with the MH increases both the onset-temperature and the  $T_{max}$  of the PP thermal degradation. Both AH and MH fillers increase the  $T_{max}$  of the PP matrix decomposition with increment of their contents. Besides, the MH case shows higher thermal stability of the PP resin in WPC decomposition than the AH case at the same loading level. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40120.

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### INTRODUCTION

Wood plastic composites (WPC) manufactured by combining wood fibers and polymers have gradually gained popularity in commercial markets for automobile (interior panels, trunk liners, spare tire covers, and package trays) and construction (deck boards, stairs, post sleeves, and hand rails) fields.<sup>1,2</sup> So far, most studies<sup>3–7</sup> about the WPC have focused on chemical treatments of the wood fibers or addition of coupling agents to improve physical and mechanical properties of final products through overcoming incompatibility between hydrophilic wood fibers and hydrophobic polymer. Our previous studies also showed that tensile and flexural strengths of WPC incorporated with the hydrophilic fillers were significantly improved (up to about 50%) through chemical modification of the fillers.<sup>3,4</sup> However, studies enhancing thermal stability of WPC during high temperature degradation are relatively sparse in comparison with the above mentioned ones.

Investigations of the fire performance of polymers as well as the general WPC researches are important to fortify their heat resistance in various applications. Intumescent, inorganic, and halogenated additive-type flame retardants have been mainly adopted for improving flame retardancy of the polymers.<sup>8,9</sup> The halogenated type retardants effectively delay flame spreading, but their usages have been inhibited by environmental regula-

tions due to emission of lots of smoke and corrosive gases arisen from their pyrolysis.<sup>8</sup> So, the inorganic and intumescent flame retardants have been widely used in various polymers as halogen-free alternatives.<sup>10–12</sup> The traditional intumescent flame retardants consist of acid, char, and gas sources could be improper to apply for the WPC systems. Generally, it is well known that wood fiber is a char former<sup>13–15</sup> and the char formation mechanism can be activated in existing the acid source in the intumescent flame retardant. The fast pyrolysis of wood fibers at high thermal environment for manufacturing WPC materials can induce high viscosity, which is hard to extrude molten mixture. During the processing condition, thus various volatile gases are produced simultaneously by forming char, and they can also reduce mechanical properties of end products. Therefore, addition of the inorganic flame retardant such as metal hydroxides in the WPC systems could be a good solution for enhancing fire performance of the WPC.

Our attempt for enhancement of flame retardancy of WPC is focused on hybridization of wood fibers and metal hydroxides such as aluminum hydroxide (AH) and magnesium hydroxide (MH). The metal hydroxides can release water vapor above their decomposition temperature due to their endothermic reaction. In addition, their solid residues after the reaction can reduce the heat release rate from the burning polymer.<sup>16</sup>

**Table I.** Characteristics (Size and Distribution) of Fillers

Materials	$d_{10}$ ( $\mu\text{m}$ )	$d_{50}$ ( $\mu\text{m}$ )	$d_{90}$ ( $\mu\text{m}$ )	$d_M$ ( $\mu\text{m}$ )	Span factor
ABOCEL® C100	11.18	55.38	175.65	76.54	2.97
AH	15.48	53.28	85.73	52.99	1.31
MH	2.20	6.28	14.73	7.56	1.99

$d_{10}$ ,  $d_{50}$ , and  $d_{90}$  are particle diameters at 10, 50, and 90% cumulative size,  $d_M$ : mean particle diameter.

Although the WPC materials have been widely commercialized, they are so sensitive to flame environment that their usages in many applications have been limited.<sup>17</sup> In addition, only a few studies about thermal decomposition of the metal hydroxides in the WPC systems have been reported. The WPC materials are more fire-sensitive than the wood itself because common polymers have higher heating values than wood fiber.<sup>13</sup> Therefore, this study is aimed at exploring the effect of hybridization of wood fibers and metal hydroxides on thermal stability of polypropylene (PP) base WPC through thermo gravimetric analysis (TGA). The effect of loading contents of the wood fibers and the metal hydroxides on thermal stability of WPC is also studied.

## EXPERIMENTAL

### Materials

PP (HJ 700, Samsung total) was used as a base material. Its melt flow index was 22 g/10 min at 230°C, and its density was 0.91 g/cm<sup>3</sup> at room temperature. Wood fiber (ABOCEL® C100, JRS, Germany) was used, and its grain size and bulk density are 31–100  $\mu\text{m}$  and 172 g/L, respectively. AH and MH provided by Samchun Pure Chemical were used for improving thermal stability of WPC materials. Their chemical formulae are Al(OH)<sub>3</sub> and Mg(OH)<sub>2</sub>, respectively. The filler characteristics (mean size and distribution) were measured by a laser diffraction method with a particle size analyzer (CILAS 1064, France), as summarized in Table I.

### Composite Preparation

The composite formulations including contents of PP, wood fiber, and metal hydroxides are summarized in Table II. An intermeshing corotating twin-screw extruder (19 mm diameter, 40 L/D ratio, Bautek, Korea) and a pelletizer (Bautek, Korea) were used in manufacturing the WPC blends. Wood fibers and metal hydroxides were dried at 80°C in the convection oven for 24 h to remove moisture prior to use. The compounding temperature was 170–185°C with screw speed at 150 rpm for 1 kg/h production.

### Thermal Analysis

Thermal decomposition curves of all samples were obtained from TGA (TA instrument) with a heating rate of 10°C min<sup>-1</sup> under nitrogen atmosphere. The temperature range was scanned from 50 to 650°C.

## RESULTS AND DISCUSSION

### Thermal Degradation Behavior of the Base Materials

Thermal degradation behavior of composite materials is complex because all constituent materials have their own thermal

degradation mechanisms. Thus, examination of thermal behavior of the base components is very important to understand the thermal stability of final composite materials. In this respect, thermogravimetric analysis can provide useful information for ultimate applications of the wood fiber reinforced plastic composites. Figure 1 shows thermal degradation curves of the base materials used in fabrication of WPC, under dehumidified N<sub>2</sub> atmosphere. As can be seen in Figure 1(a), PP is completely degraded before the temperature reaching around 460°C, whereas AH and MH reveal substantial amounts of residue after the primary decomposition process due to the remaining metal oxide materials. Furthermore, wood fiber shows gradual weight loss as the temperature increases after the first reduction step. As well known, lignocellulosic materials such as wood and plant fibers mainly consist of three components (cellulose, hemicelluloses, and lignin).<sup>18</sup> The cellulose and hemicelluloses decompose primarily into carbonaceous residues at high temperature conditions, and those residues secondarily produce carbon monoxide, carbon dioxide, methane, methanol, water, and acetic acid during the accelerated degradation step.<sup>14</sup> In the range of the degradation, the lignin can also decompose into methoxy phenols.<sup>17</sup> The carbonaceous residues formed by degradation of wood fibers can decompose into carbon free radicals over about 400°C.<sup>15</sup> Therefore, weight loss in degradation curve for the wood fiber continues from the temperature (about 385°C) where the carbonaceous residues are produced to the temperature (>650°C) where the residues are completely removed.

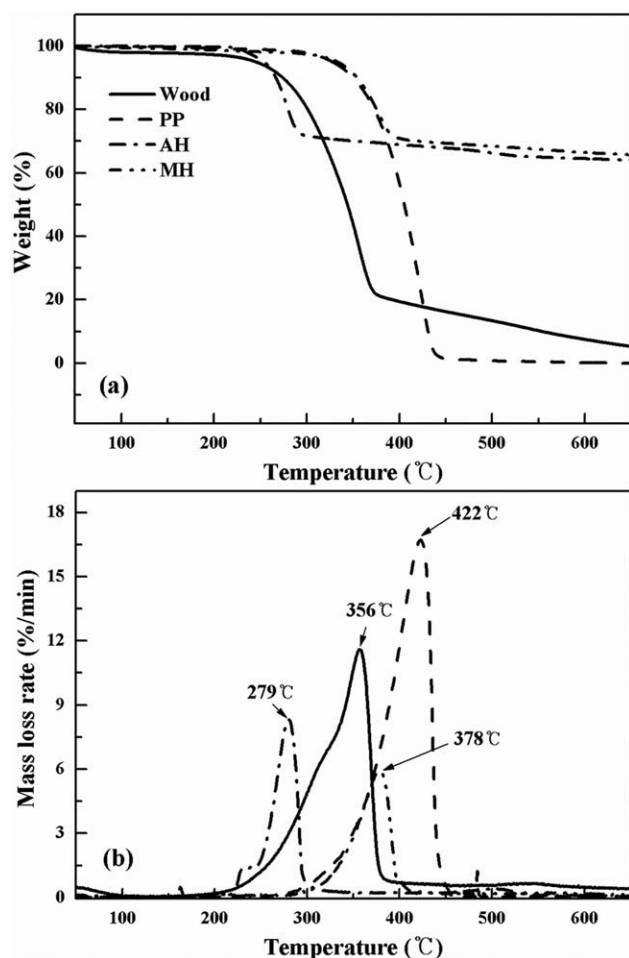
In addition, in Figure 1(b), the mass loss rate is plotted as a function of temperature, and it clearly demonstrates different decomposition temperatures of all constituent materials (wood fiber: 200°C–385°C, PP: 276–465°C, MH: 277–394°C, and AH:

**Table II.** Compositions of the Composites

Wood (wt %)	PP (wt %)	Additives <sup>a</sup> (wt %)
10	90	0
30	70	0
50	50	0
50	47	3
50	41	9
50	35	15
50	29	21

<sup>a</sup> Additives = Al(OH)<sub>3</sub>, Mg(OH)<sub>2</sub>.

Weight percents are based on the composite total weight.

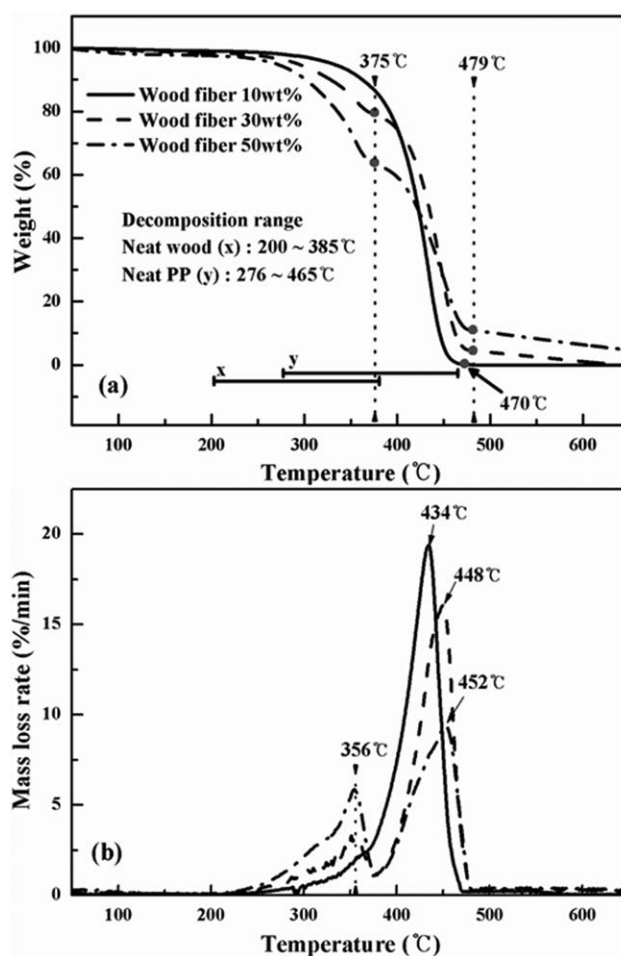


**Figure 1.** Thermal degradation curves of the base materials used in fabrication of WPC.

209–295°C). In addition, their maximum mass loss rates ( $T_{max}$ ) are observed at 356, 422, 378, and 279°C, respectively.

#### Thermal Degradation Behavior of WPC

As already shown in Figure 1, the wood fiber and PP resin have their own distinctive temperature ranges for the degradation processes. Thermal stability of WPC materials combining those two base components is much dependant on the amount of wood fiber. Figure 2 shows thermogravimetric analysis results of WPC containing various amount of wood fiber as a function of temperature. Figure 2(a) demonstrates one step weight loss for the wood fiber 10 wt % composite and two step weight losses for the wood fiber 30 and 50 wt % composites. The increased carbonaceous residues with increasing content of wood fibers can play a important role as a heat resistant material.<sup>2</sup> The resulting degradation temperatures (465°C for the only PP case) increase to 470, 480, and 480°C for the wood fiber 10, 30, and 50 wt %, respectively. Therefore, thermal protective carbonaceous layer produced from the degradation of wood fibers can enhance the thermal stability of the PP base WPC materials. However, the increment of the degradation temperature of WPC at 10 wt % is relatively small compared with the cases with 30 and 50 wt % wood fiber cases. In addition, the starting temperature of degradation on the PP matrix resin was also



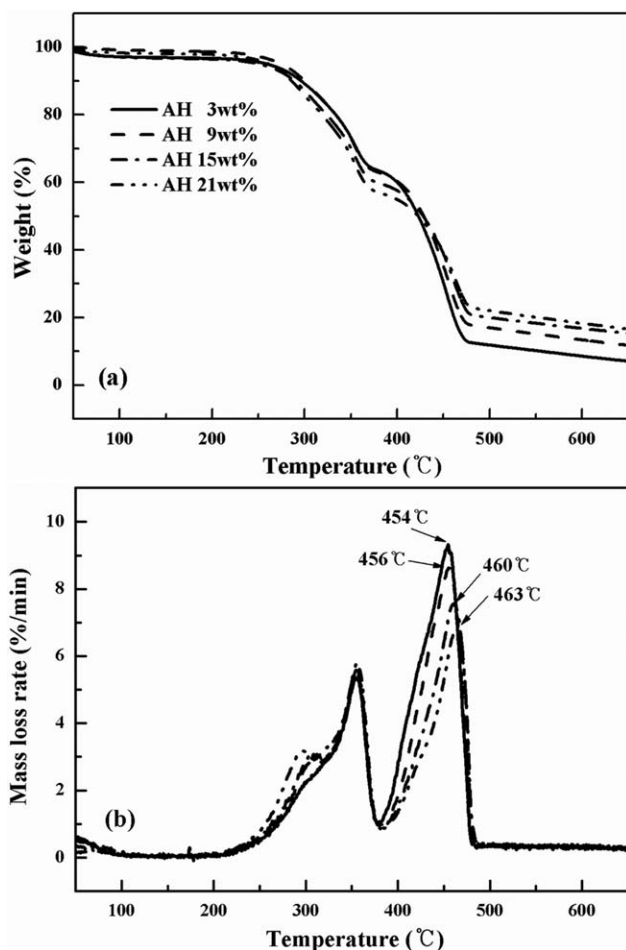
**Figure 2.** Thermogravimetric analysis results of WPC containing various amount of wood fiber as a function of temperature.

increased about 100°C for the 30 and 50 wt % wood fiber cases. Therefore, the higher amount of wood fiber content in WPC leads the better thermal stability by delaying degradation of the base resin.

Figure 2(b) shows the mass loss rates of WPC including 10, 30, and 50 wt % wood fibers. WPC samples reveal the two mass loss peaks from the wood fiber degradation and the PP decomposition. However, the peak for the wood fiber degradation from the wood fiber 10wt% composite is hardly seen, and it may be from the WPC degradation governed by the dominant PP decomposition. Instead, the wood fiber 30 and 50 wt % composites show increased mass loss rate in the wood fiber decomposition temperature ranges but reduced mass loss rates in PP decomposition temperature ranges. This possibly indicates that the retardation of PP decomposition is very effective from the carbonaceous residues formed from the degradation of the increased wood fiber contents. Therefore, the wood fiber used in WPC materials can give positive reinforcements in various applications for the fire possible environment.

#### Thermal Degradation Behavior of AH Hybridized WPC

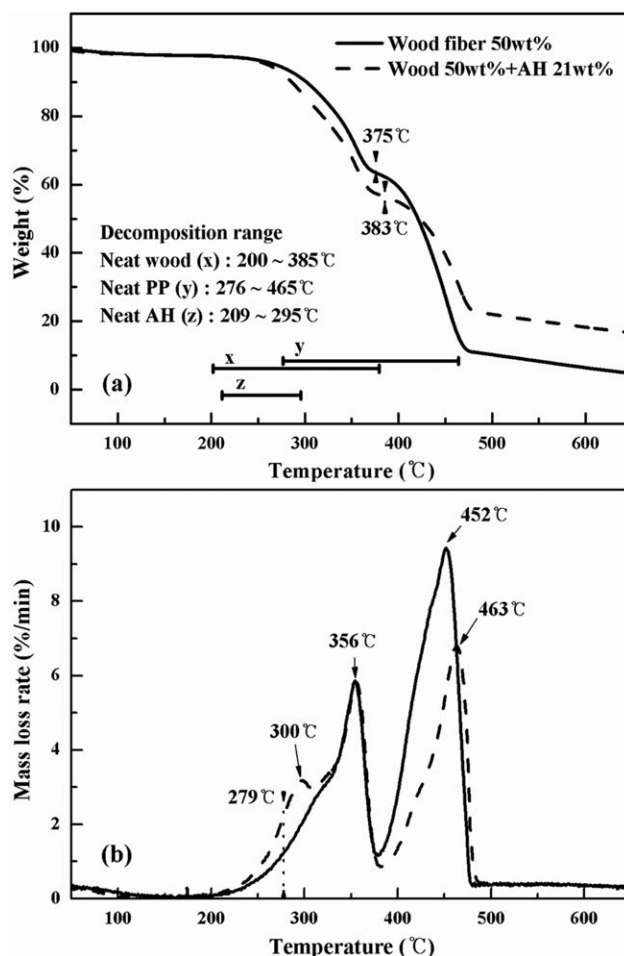
Inorganic filler hybridized polymer composites generally further retard thermal degradation of materials. Figure 3 demonstrates



**Figure 3.** Thermogravimetric analysis results of WPC containing various amount of AH at 50 wt % wood fiber content.

thermogravimetric analysis results of WPC containing various amount of AH at 50 wt % wood fiber content. As shown in Figure 3(a), the higher amount of residues is remained with the higher AH content after the second decomposition step at about 475°C due to the nature of the metal oxide filler. Interestingly, for the mass loss rate during the decomposition, slight shifting of the decomposition peak toward high temperature was observed in Figure 3(b), and the maximum mass loss rate increased to 463°C at 50 wt % wood fiber content. It is mainly believed that the higher amount of aluminum oxides produced from the AHs during thermal degradation can combine with more chars from the wood fiber degradation and thus retard the degradation rate.

To clearly understand the role of AH on the thermal degradation behavior of WPC, two cases (50 wt % wood fiber only and with 21 wt % AH in 50 wt % wood fiber) are plotted in Figure 4. As shown in Figure 4(a), the PP degradation temperature shifts from 375°C for the wood fiber 50 wt % case to 383°C for the 21 wt % AH in 50 wt % wood fiber. AH absorbs heat and produces aluminum oxides ( $\text{Al}_2\text{O}_3$ ) and water vapor ( $\text{H}_2\text{O}$ ) during the thermal degradation. The oxides generated from the metal hydroxide can further combine with the char from the degradation of wood fiber, and it may reduce the mass loss rate

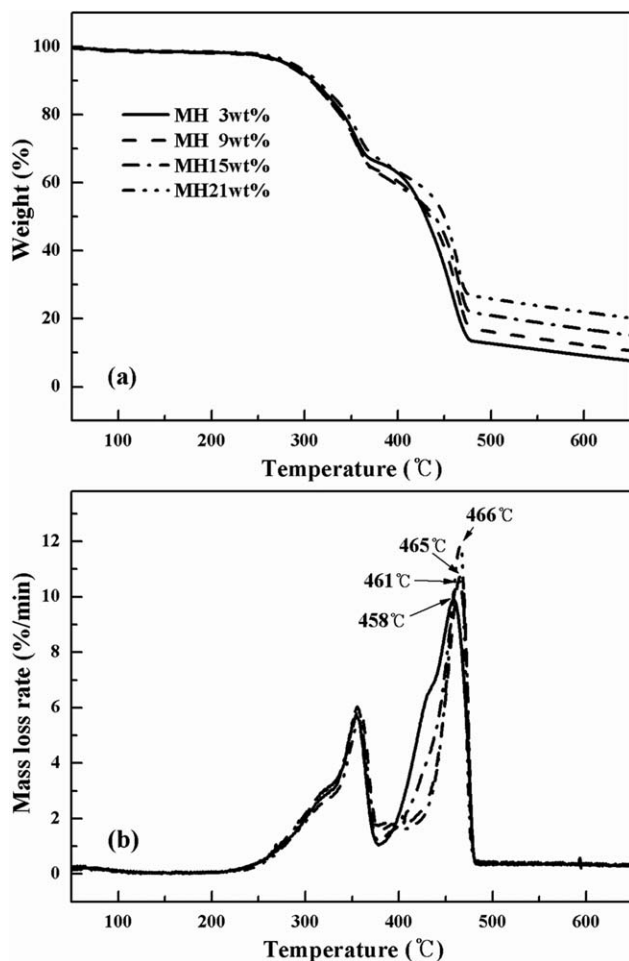


**Figure 4.** Thermal degradation behavior of WPC containing 50 wt % wood fiber only and 50 wt % wood fiber including 21 wt % AH.

and increase the decomposition temperature slightly. The temperature peak for the maximum loss rate representing PP resin decomposition changed from 452 to 463°C as shown in Figure 4(b), and it demonstrated the improved thermal stability of the PP matrix part by addition of AH filler. In addition, the mass loss peak for the AH was also shifted to 300 from 279°C for the AH only decomposition case, and it is also believed as a retarded degradation effect from the char layer formation on AH materials from the wood fiber decomposition. As a result, AH addition to the WPC can further retard decomposition of matrix polymer by improving thermal stability.

#### Thermal Degradation Behavior of MH Hybridized WPC

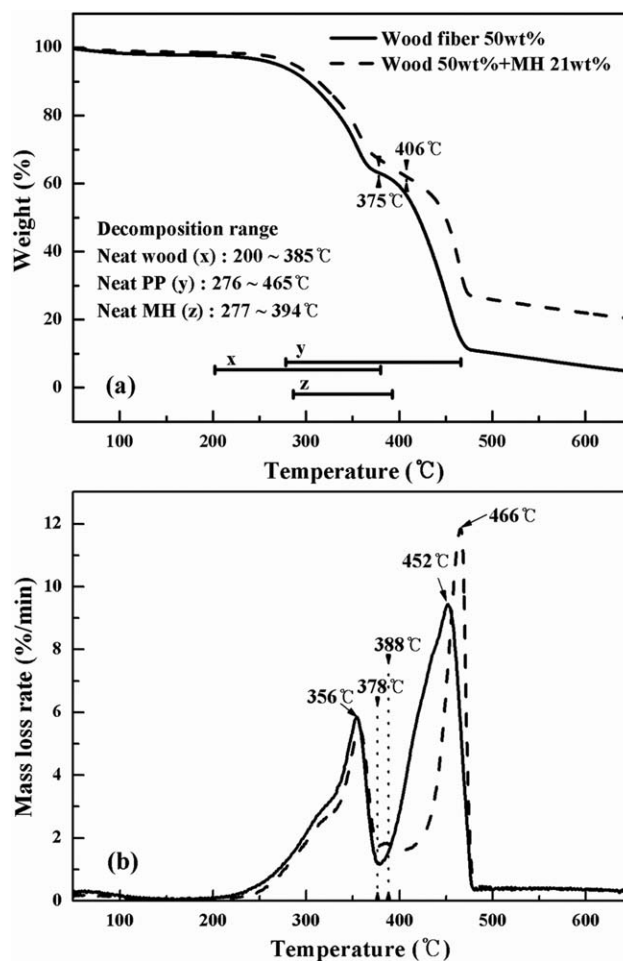
As shown in Figure 3 for the AH hybridized WPC degradation, Figure 5 shows thermal degradation curves of WPC containing various amount of MH at 50 wt % wood fiber content. In these MH filled cases, the fundamental degradation behavior is very similar to the AH filled cases, but the starting temperature for the second step degradation is slightly shifted to the higher temperature. It is believed mainly due to the higher decomposition temperature of MH filler than that of the AH filler, as explained in Figure 1. Figure 5(a) also shows a similar weight loss trend with the AH filled cases (Figure 3) after the PP resin decomposition temperature, and the residue amounts remain higher



**Figure 5.** Thermal degradation curves of WPC containing various amount of MH at 50 wt % wood fiber content.

with the higher content of filler due to the formation of magnesium oxide (MgO). Figure 5(b) shows the mass loss rate of the MH filled WPC, and the peak location of the maximum mass loss rate is very similar with the AH filled cases. However, a slight shift of the PP resin decomposition peak was observed in MH filled case to 466°C at 21 wt % MH content, comparing with 463°C peak [Figure 3(b)] for the AH filled case at the same composition. It could be attributed to the synergistic effect of higher decomposition temperature of the MH filler than the AH filler on retarded degradation of PP resin.

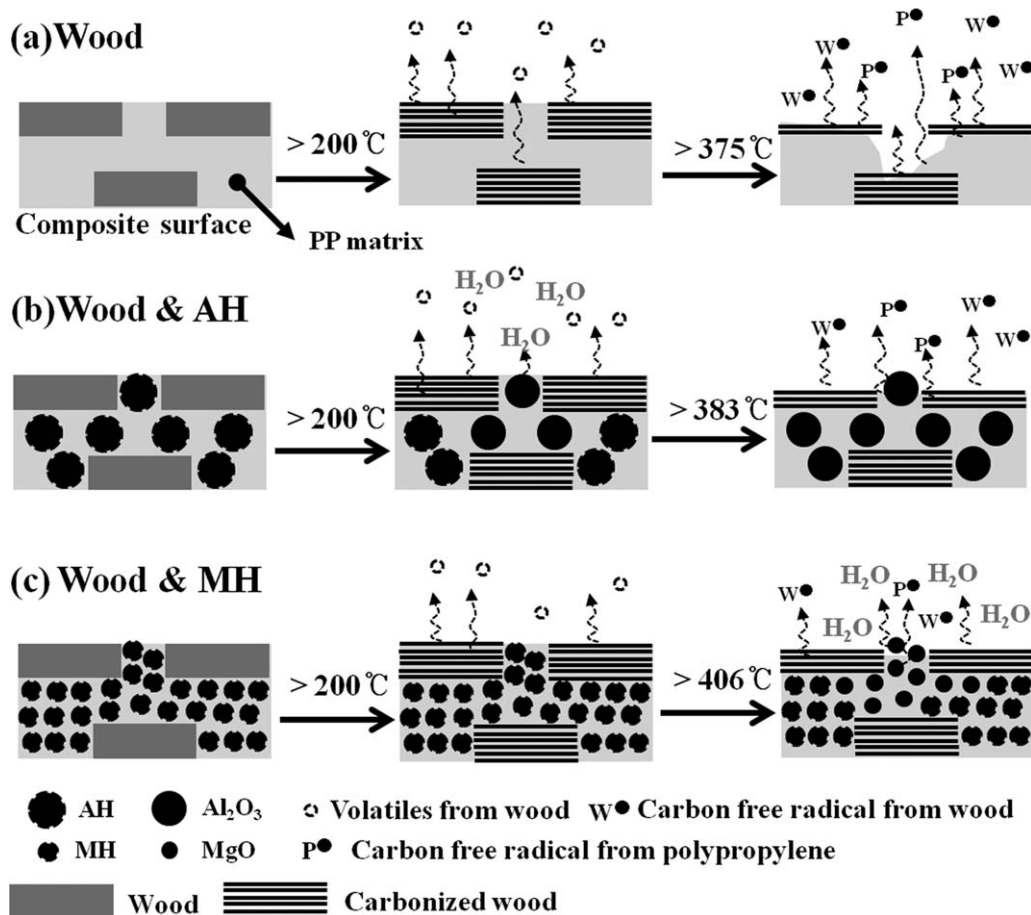
To examine more details of the MH filler effect on the WPC degradation behavior, Figure 6 shows thermal degradation curves for the wood fiber 50 wt % filled case and the MH 21 wt % filled in 50 wt % wood fiber WPC. Figure 6(a) clearly shows the change of the starting temperature of the PP resin degradation from 375°C for the only wood fiber 50 wt % filled case to 406°C for MH 21 wt % filled in 50 wt % wood fiber WPC. In addition, Figure 6(b) also shows the mass loss peak for the two cases, and the peak for the MH decomposition increased from 378°C for the only MH filler to 388°C for the MH hybridized WPC. This is believed that the decomposition products from the wood fiber can not only improve thermal



**Figure 6.** Thermal degradation behavior of WPC containing 50 wt % wood fiber only and 50 wt % wood fiber including 21 wt % MH.

stability of the PP base resin but also retard decomposition of the MH filler, and it is possibly due to the char layer derived from the wood in the composite systems.

To summarize, both metal hydroxides did not directly influence on the wood fiber decomposition, but they changed the decomposition behavior of PP resin. Especially, the MH filler improved the thermal stability of WPC materials more than the AH case. Therefore, MH hybridized WPC can be more suitable for various applications requiring thermal degradation resistance than that of AH case. In general, high content of mineral filler in composites can reduce the mechanical strength of the composites, but the reduction of the mechanical strength can be properly improved by chemical modification of the filler surfaces or addition of coupling agents. Figure 7 shows schematic illustrations demonstrating basic decomposition mechanisms of wood fiber, AH, and MH in PP matrix composites. In Figure 7(a), wood fiber decomposition in WPC produces carbonized fibers and some volatiles in the first degradation stage at temperature higher than 200°C, and it further releases decomposed radicals from wood fibers and PP matrix in the second stage at temperature higher than 375°C. However, metal hydroxides hybridized WPC results in higher temperature for the second stage decomposition than the case without metal hydroxide



**Figure 7.** Schematic illustrations demonstrating basic decomposition mechanisms of wood fiber, AH, and MH in PP matrix composites.

filler. For example, the second stage decomposition starts at 383 and 406°C for AH and MH filled composites, and these temperatures are higher than that from the wood fiber only WPC, as explained above sections. In the figure, the rough spheres represent the original metal hydroxides, but the smooth spheres do the materials after dehydrolysis process. In addition, the size of the hydroxide spheres shows the relative size of AH and MH as shown in Table I.

## CONCLUSIONS

Wood fiber, AH, and MH enhanced the thermal stability of the PP matrix in the composite systems. All cases increased the thermal stability of the PP resin by increasing their contents. The wood fiber played a role as an effective char former, and the char layer formed by the wood fiber decomposition induced increment of thermal stability of the metal hydroxide hybridized WPC. The AH component increased temperature of the maximum loss rate ( $T_{max}$ ) of the PP resin due to the residue formation, but an onset-temperature of the PP decomposition was nearly shifted. However, the MH component increased both the onset temperature and the  $T_{max}$  of the PP thermal degradation. Therefore, in metal hydroxide hybridized WPC, the MH filler could be more effective in improving thermal stability from high temperature degradation than the AH filler.

## ACKNOWLEDGMENTS

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