Thermogravimetric Analysis of Rice Husk Flour for a New Raw Material of Lignocellulosic Fiber-Thermoplastic Polymer Composites*[1]

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ABSTRACT

Rice husk flours were analyzed by chemical composition and thermogravimetric methods in nitrogen atmosphere to discuss its feasibility as a raw material for manufacturing agricultural lignocellulosic fiber-thermoplastic polymer composite. It was revealed in the chemical composition analysis that rice husk flour was composed of moisture, 5.0%; lignin, 21.6%; holocellulose, 60.8%; ash, 12.6%. In the thermogravimetric analysis (TGA), thermal decomposition behavior of rice husk flour from room temperature to 350°C was similar to that of wood flour, but rice husk flour was more thermally stable from 350 to 800°C than wood flour because of higher silica content in the rice husk flour and smaller particle size of rice husk flour. The activation energy of thermal decomposition was evaluated using Flynn & Wall expression. As the thermal decomposition proceeded in rice husk flour, the activation energy of thermal decomposition appeared almost constant up to $\alpha = 0.25$, but thereafter increased. Activation energy of thermal decomposition in wood flour, however, decreased steeply up to $\alpha = 0.3$, but thereafter remained almost constant.

From the results, rice husk flour was thought be a substitute for wood flour in manufacturing agricultural lignocellulosic fiber-thermoplastic polymer composite in the aspect of thermal decomposition.

Keywords: Rice husk flour, wood flour, TGA, thermal decomposition, activation energy, Flynn & Wall expression, thermoplastic polymer composite

1. INTRODUCTION

Industrial development and rising population require more energy, goods, and foodstuffs. Simultaneously, large amount of wastes are generated and the by-products are created in several industrial sectors. Some of these by-products have already been used as raw material for fabricated products.

Rice husk is an agricultural waste material produced as by-products during rice milling process in rice-producing countries, especially in the Asian, Pacific and United States regions. According to FAO (Food and Agriculture Organization) statistical data in 2000, the annual world rice production is approximately 600

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million tons, of which 20% is wasted as rice husk (The FAOSTA Database, 2000). This rice husk is primarily used as a bedding materials for domestic animals but its industrial application is still limited. The rest of rice husk is now landfilled, but landfilling itself is becoming a social problem of demanding large areas of landfill site. Therefore, there is a tremendous need for making useful and value-added products from rice husk (Teng & Wei, 1998).

Several technologies have been proposed to solve this problem, using rice husk as a source for different industrial processes such as fuel in the rice milling industry, pozzolanic material to enhance the lime treatment of degraded soil, filler for increasing compressive strength in cement, particleboard technology and activated carbon (Vempati *et al.*, 1995).

Thermogravimetric analysis (TGA) is one of the major thermal analysis techniques used to study the thermal behaviour of carbonaceous materials. The rate of weight loss of the sample as a function of temperature and time is measured to predict thermal behaviour of the materials.

The objective of this study is to determine the mass loss rate and the kinetic parameters of rice husk flour for manufacturing agricultural lignocellulosic fiber-thermoplastic polymer composite with TGA. In addition, through comparison with wood flour, the feasibility of rice husk flour as a substitute for wood flour was discussed in the thermal stability and economic considerations.

The previous investigations on converting rice husk to energy by thermochemical processes required a fundamental understanding of its thermal properties and reaction kinetics (Mansaray & Ghaly, 1999; Teng & Wei, 1998; Liou *et al.*, 1997).

The thermal degradation characteristics of lignocellulosic materials are strongly influenced by their chemical composition such as cellulose, hemicellulose and lignin (Mansaray & Ghaly, 1999). Although the thermal degradation of some lignocellulosic materials such as wood and their components have been studied extensively, the exact mechanism and kinetics of the reactions have not yet been unveiled completely.

For activation energy of thermal decomposition, various useful TGA data were introduced and noted Flynn & Wall (Lee *et al.*, 2000; Popescu, 1996), Kissinger (Starink, 1996; Min & Ma, 2000; Lee *et al.*, 2001), Ozawa's (Popescu, 1996; Min & Ma, 2000), and other expressions. The weight loss appeared proportional to the fraction of thermal decomposition (Lee *et al.*, 2000). From this expression of weight loss, high-quality kinetic data for the thermal decomposition of the polymer materials can be obtained.

In this study, as a new concept, various sizes of rice husk flour were selected as the thermally stable filler in manufacturing thermoplastic polymer composites. Fillers can be roughly classified into two types, based on function: one for improvement of service properties (reinforcing filler) and the other for reduction of the material cost (diluent or non reinforcing filler). Agricultural lignocellulosic materials, recently, are being considered as the reinforcing filler for thermoplastic polymers with relatively lower melting point like polypropylene, high and low density polyethylene in manufacturing composites. Especially, the possibility of rice husk flour as a filler for the substitute of wood flour in thermoplastic polymer composites was discussed.

2. MATERIALS and METHODS

2.1 Materials

2.1.1 Rice husk flour

Four types of rice husk flours, which obtained from Saron Filler LTD in Ansung, Korea, were as follows: F type (under 325 mesh), AA type (under 200 mesh), A type (100~200 mesh), and B type (50~100 mesh). These were conditioned to the moisture content of 6% and ash content of 13%. Only B type of rice husk flour was selected for the comparison with wood flour.

2.1.2 Wood flour

Wood flours of mixed softwood species made in Germany were offered by S-Wood LTD in Chonan, Korea. Wood flour of 50~100 mesh size was used to compare with rice husk flour of B type.

2.2 Methods

2.2.1 Chemical composition analysis

After acquisition, rice husk flours were immediately dried in an air forced drying oven at 105°C for 24 hours to the desired moisture content and for avoiding their deterioration by higher moisture content. After drying, the rice husk flours were stored in polyethylene bag. For separating ash, lignin and holocellulose, the samples were treated through the ASTM standard D1102-84 'Standard Method of Static Tests of Ash in Wood' (ASTM 1995) and TAPPI T13 wd 74 'Fibrous Materials and Pulp Testing, Lignin in wood' (TAPPI 1994-1995).

2.2.2 Thermogravimetric analysis

Rice husk flours and wood flour were analyzed thermogravimetrically in nitrogen atmosphere at four heating rates: 5, 10, 20 and 40°C/min. The samples weighing approximately 10 mg were heated at the preselected heating rates from room temperature to 800°C with Thermogravimetric Analyzer (Rheometric Scientific TGA 1000, NICEM, Seoul National University). A high-purity nitrogen gas consisting of 99.5% N_2 and 0.5% O_2 was used as an inert purge gas to displace air in the pyrolysis zone for avoiding unwanted oxidation of the sample. A constant flow was fed at a rate of 20ml/min to the system from a point below the sample.

2.2.3 Activation energy of thermal decomposition

To evaluate activation energy, Flynn & Wall expression (Lee *et al.*, 2000) was used as follows:

$$E_a = \frac{-R}{0.457}\,\frac{d(\log\beta)}{d(T^{-1})}$$

E_a = activation energy of thermal decomposition
R = gas constant
β = heating rate
T = absolute temperature

For activation energy (E_a), a linear relationship between $\log\beta$ and 1/T at a selected fraction of thermal decomposition was displayed and E_a was then evaluated from the slope. The selected fraction ranged from 0.10 to 0.50 and the resulting values of the activation energy for each fraction were compared.

3. RESULTS and DISCUSSION

3.1 Chemical composition analysis

The chemical composition of the rice husk

Table 1. Chemical composition of rice husk and wood flours. (Unit: %)

Code	Moisture	Lignin	Holocellulose	Ash
Rice husk flour	5.0	21.6	60.8	12.6
Wood flour	10.3	26.2	62.5	0.4

flour and wood flour used in this study are listed in Table 1. As shown in Table 1, the content of lignin and holocellulose of rice husk flour was a little lower than that of wood flour. Ash content of rice husk flour, however, was much higher than of wood flour because of silica (SiO_2) with 96% of ash (Liou *et al.*, 1997). The content of ash after pyrolysis was found to be 12.6%, like the result of Liou *et al* (1997).

Rice husk flour, thus, appeared similar in the chemical composition, except for ash content.

3.2 Thermogravimetric analysis

Figure 1 shows two points as follow; rice husk flour and wood flour are similar between room temperature and 350°C but are different at higher temperature of 350°C or higher in thermal behaviour. This was thought to be caused by higher silica content in rice husk flour. The thermogravimetric behaviors of rice husk and wood flours at the heating rate of 40°C/min from room temperature to 350°C were similar but were different from 350 to 800°C, which seemed to be caused by the higher silica content in the rice husk. At 800°C, ash content of rice husk flour was 40% but that of wood flour was below 20%. These results agreed with the reports of Marcovich, Roboredo & Aranguren (2001) and Mansaray & Ghaly (1998). Furthermore, Shafizadeh & DeGroot (1976), Antal (1983), and Mansaray & Ghaly (1998) described that three major constituents of cellulose, hemicellulose, and lignin in the lignocellulosic materials were chemically active

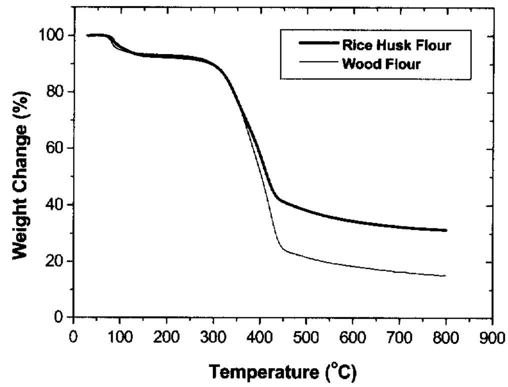

Fig. 1. Comparison of thermograms between rice husk flour and wood flour.

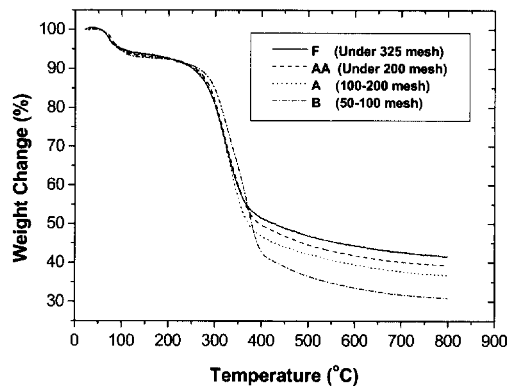

Fig. 2. Thermograms of rice husk flour by particle size.

and decompose thermochemically between 150 and 500°C; hemicellulose mainly between 150 and 350°C, cellulose between 275 and 350°C, and lignin between 250 and 500°C.

The thermogravimetric behaviors of rice husk by the flour types (F; under 325 mesh, AA; under 200 mesh, A; 100~200 mesh, B; 50~100 mesh) in nitrogen atmosphere are shown in Figure 2. Rice husk flour of large particle size was more degradable at higher temperature of 350°C or higher than at lower temperature up to 350°C. This was thought to be attributed to the burning of organic materials such as cellulose and lignin by friction of saw when rice husk milling process, resulting in higher silica content but lower organic materials content in the rice husk flour of smaller particle size.

3.3 Activation energy of thermal decomposition

TGA curves for the rice husk flour at four heating rates are shown in Figure 3. As the heating rate increased, decomposition temperature (T_d) increased. The T_d was obtained from the point where the weight loss increased. This has already known to be influenced by the heating rate of pyrolysis by other researchers (Mansaray & Ghaly, 1998; Liou *et al.*, 1997; Teng & Wei., 1998). The initial degradation temperature of rice husk flour decreased as the heating rate increased, as expected in the literature.

The temperature at $\alpha = 0.1$ (10% thermal degradation region) by the four heating rate was measured where the line crossed the TGA curve. To obtain activation energy of thermal decomposition, these data obtained were converted to a $\log\beta$ and 1/T (Lee *et al.*, 2000), as listed in Table 2.

Using the same method, the temperatures at different α were obtained. And the relationships between $\log\beta$ and 1/T, based on Figure 5, are also listed in Table 2. Because decomposition at the early stage was affected by the moisture, the fixed conversions, α, were selected from 0.1 to 0.5.

The activation energy for each α was calculated from the slope of each straight line, as listed in Table 4.

The TGA curves for the wood flour by the heating rate are shown in Figure 4. The activation energy of thermal decomposition and relationship between $\log\beta$ and 1/T for wood flour are shown in Figure 6 and Table 5, respectively.

The activation energies of the thermal decomposition curves for the rice husk flour and wood flour at degradation conversion (α) are shown in Figure 7. As the thermal decomposition proceeded in the rice husk flour, the activation energy remained almost constant up to α = 0.3, and thereafter began to increase. However, activation energy of thermal decomposition for wood flour decreased steeply up to α = 0.3, and thereafter remained almost constant.

During thermal decomposition of rice husk flour, the thermal degradation rate increased as the heating rate increased. Mansaray & Ghaly (1998) reported that the higher the cellulose

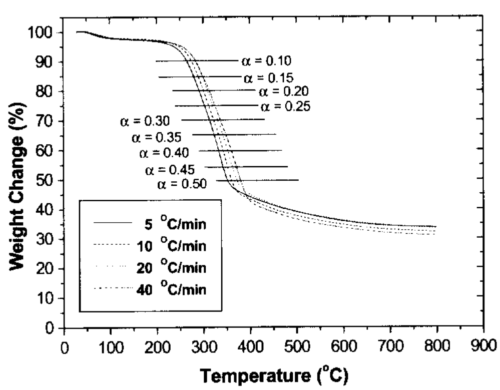

Fig. 3. Thermograms of rice husk flour by heating rate.

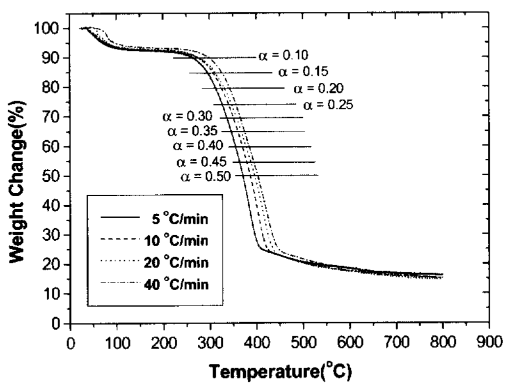

Fig. 4. Thermograms of wood flour by heating rate.

Table 2. Relationship between log β and 1/T in rice husk flour.

log β	1/T × 10^3 (K^{-1})								
	α = 0.10	α = 0.15	α = 0.20	α = 0.25	α = 0.30	α = 0.35	α = 0.40	α = 0.45	α = 0.50
0.699	1.857	1.810	1.772	1.737	1.704	1.676	1.652	1.628	1.603
1.000	1.824	1.779	1.743	1.711	1.679	1.650	1.625	1.603	1.581
1.301	1.795	1.751	1.717	1.685	1.654	1.625	1.601	1.577	1.551
1.602	1.795	1.750	1.709	1.672	1.641	1.610	1.582	1.558	1.533

Table 3. Relationship between log β and 1/T in wood flour.

log β	1/T × 10^3 (K^{-1})								
	α = 0.10	α = 0.15	α = 0.20	α = 0.25	α = 0.30	α = 0.35	α = 0.40	α = 0.45	α = 0.50
0.699	1.863	1.760	1.709	1.672	1.642	1.615	1.592	1.571	1.553
1.000	1.825	1.726	1.674	1.637	1.605	1.580	1.555	1.534	1.515
1.301	1.828	1.711	1.659	1.621	1.589	1.562	1.538	1.515	1.495
1.602	1.753	1.672	1.626	1.594	1.568	1.545	1.522	1.501	1.481

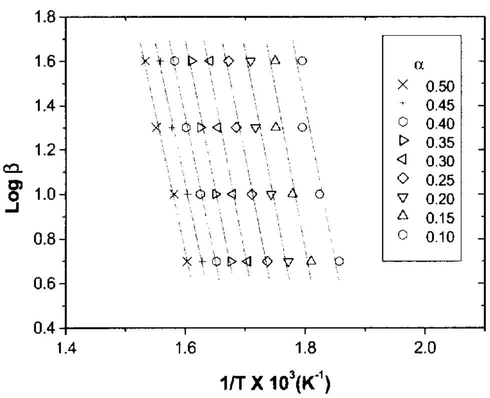

Fig. 5. Isoconversional curves of rice husk flour by Flynn & Wall expression.

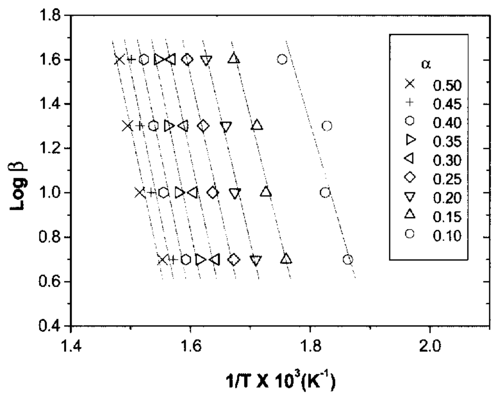

Fig. 6. Isoconversional curves of wood flour by Flynn & Wall expression.

content of the wood flour, the higher the thermal degradation rate. This means that rice husk flour contains more silica than wood flour as a raw material, resulting in lower thermal degradation in manufacturing of high temperature process of thermoplastic polymer composites.

3.4 Isothermal test of TGA

For utilizing rice husk flour as the raw material of agricultural lignocellulosic fiber-thermoplastic polymer composites, isothermal test was prerequisite at the probable temperatures in the composite manufacture. When agricultural lignocellulosic fiber-thermoplastic polymer composites are manufactured, the inner temperature of rheomixer or extruder, even though it may depend on polymer type, are in the range of 150 to 250°C (Son, 2000) for at least 15 minutes.

Table 4. Activation energy of thermal decomposition in rice husk flour by Flynn & Wall expression.

α	Linear expression	Activation energy (kJ/mol)
0.10	Y = -0.0714 X + 1.8999	1.299
0.15	Y = -0.0691 X + 1.8520	1.257
0.20	Y = -0.0714 X + 1.8174	1.299
0.25	Y = -0.0734 X + 1.7857	1.335
0.30	Y = -0.0711 X + 1.7513	1.294
0.35	Y = -0.0741 X + 1.7255	1.348
0.40	Y = -0.0777 X + 1.7044	1.414
0.45	Y = -0.0784 X + 1.6817	1.426
0.50	Y = -0.0797 X + 1.6587	1.450

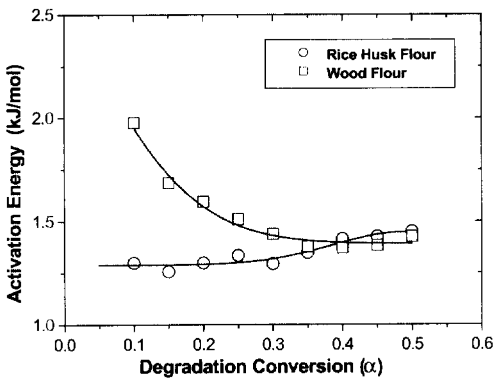

Fig. 7. Comparison of activation energy of thermal decomposition between rice husk flour and wood flour.

Rice husk flour of B type and wood flour were tested at 130, 180, 200, 230, 240 and 250 °C for 40 minutes to compare thermal stability in consideration of actual manufacturing processes. The results obtained are shown in Figures 8 and 9. The harshest temperature condition was regarded to be 250°C (Son, 2000). It, however, was revealed that thermal degradation of only 2.5% occurred in this harshest condition for 15 minutes. Rice husk flour, as the substitute for wood flour, proved to have the potential because they showed similar tendency in thermal decomposition at the

Table 5. Activation energy of thermal decomposition in wood flour by Flynn & Wall expression.

α	Linear expression	Activation energy (kJ/mol)
0.10	Y = -0.1086 X + 1.9422	1.977
0.15	Y = -0.0927 X + 1.8239	1.686
0.20	Y = -0.0877 X + 1.7679	1.596
0.25	Y = -0.0831 X + 1.7266	1.511
0.30	Y = -0.0791 X + 1.6920	1.439
0.35	Y = -0.0758 X + 1.6627	1.378
0.40	Y = -0.0754 X + 1.6385	1.372
0.45	Y = -0.0761 X + 1.6178	1.384
0.50	Y = -0.0784 X + 1.6012	1.427

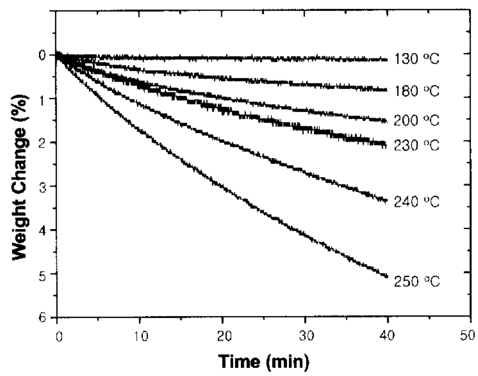

Fig. 8. Isothermal thermograms of rice husk flour by temperature.

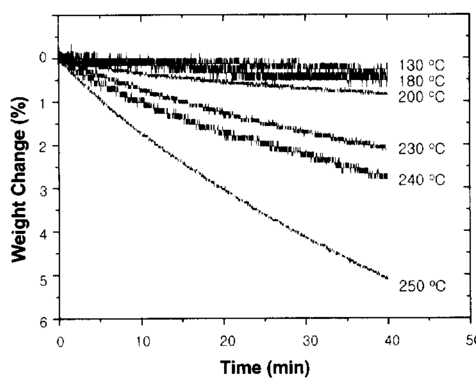

Fig. 9. Isothermal thermograms of wood flour by temperature.

probable temperature.

In this study, the thermal behavior of rice husk and wood flours were evaluated for discussing the feasibility of rice husk flour as a new raw material for agricultural lignocellulosic fiber-thermoplastic polymer composites. In future, fundamental works on physical and mechanical properties of the composites, including interfacial adhesion between agricultural lignocellulosic fibers and thermoplastic polymer chains must be followed.

4. CONCLUSION

Rice husk flour was found in chemical composition analysis to be composed of moisture, 5.0%; lignin, 21.6%; holocellulose, 60.8%; ash, 12.6%.

In thermogravimetric test, thermal decomposition of rice husk flour from room temperature to 350°C was similar to that of wood flour but rice husk flour showed approximately 60% of thermal loss in comparison with 20% of thermal loss in wood flour at the temperature of 350°C or higher. And rice husk flour with larger particle size was more considerably decomposed from 350 to 800°C because of its lower content of organic material.

As the thermal decomposition proceeded in the rice husk flour, the activation energy of thermal decomposition remained almost constant up to $\alpha = 0.25$, and thereafter began to increase. Activation energy of thermal decomposition for wood flour, however, decreased steeply up to $\alpha = 0.3$, and thereafter remained almost constant. The data obtained from activation energy of thermal decomposition appeared useful for preliminary assessment of rice husk flour as a feedstock for thermal degradation conversion system. The data also provided some pyrolysis kinetic information of rice husk and showed the fact that rice husk could be a substitute for wood flour because thermal stability of rice husk flour appeared higher than that of wood flour.

From the isothermal test of TGA, rice husk flour was known to be stable in the temperature condition of manufacturing agricultural lignocellulosic fiber-thermoplastic polymer composite like wood flour.

Thus, rice husk flour was thought to be a substitute for wood flour in manufacturing agricultural lignocellulosic fiber-thermoplastic polymer composite in the aspect of thermal decomposition.

Even though the rice husk flour appeared to have the possibility as the raw material of composites, further studies on the physical and mechanical properties of the composites and interfacial adhesion between rice husk flour and thermoplastic polymer chains must be followed in future.

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