

THERMOGRAVIMETRIC ANALYSIS OF RICE HUSK FLOUR FILLED THERMOPLASTIC POLYMER COMPOSITES

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Abstract

The thermal degradation and thermal stability of rice husk flour (RHF) filled polypropylene (PP) and high-density polyethylene (HDPE) composites in a nitrogen atmosphere were studied using thermogravimetric analysis. The thermal stability of pure PP and HDPE was found to be higher than that of wood flour (WF) and RHF. As the content of RHF increased, the thermal stability of the composites decreased and the ash content increased. The activation energy of the RHF filled PP composites increased slowly in the initial stage until $\alpha=0.3$ (30% of thermal degradation region) and thereafter remained almost constant, whereas that of the RHF filled HDPE composites decreased at between 30 and 40 mass% of RHF content. The activation energy of the composites was found to depend on the dispersion and interfacial adhesion of RHF in the PP and HDPE matrix polymers.

Keywords: activation energy, Flynn and Wall expression, rice husk flour, thermal decomposition, thermal stability, thermogravimetric analysis

Introduction

In recent years, natural fibers and flours have been widely used as reinforcing fillers in thermoplastic polymer composite materials. Reinforced polymer composites made using cellulose and lignocellulose materials as fillers have several advantages, such as their low cost, renewability, biodegradability and absence of associated health hazards [1]. Agricultural residues such as rice-husks, bagasse, palm oil, and wood chips are a particularly important natural resource. These natural fillers are lighter, cheaper and provide much higher strength per unit mass than most inorganic fillers such as carbon black, calcium carbonate, talc and zinc oxide [2]. Rice husk, one of several lignocellulose materials, is an agricultural industrial residue produced as a by-products during the rice milling process in rice-producing countries, especially in

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the Asian, Pacific and United States regions. According to FAO statistical data in 2000, the annual world rice production is approximately 600 million tons, of which 20% is wasted as rice husk. Most of this rice husk is either used as a bedding material for animals and burned or used for landfilling. Therefore, the use of rice husk in the manufacture of thermoplastic polymer–lignocellulosic flour composites is attracting much attention because of the potential biomass energy [3–4].

Nowadays, thermoplastic polymers are widely used in various aspects of human society. They have several good properties that make them the polymers of choice for numerous applications (e.g., excellent chemical resistance, good mechanical properties and low cost) [5]. Because of the superior properties of these materials, they have used both mixed with natural fillers and in manufactured composite forms. The use of thermoplastic polymer composites reinforced with natural fillers has been rapidly increasing in the European automotive industry [6]. Thermal analysis (TA) is used to describe the analytical method that is used to measure the physical property and chemical property of a sample as a function of temperature or mass loss. Thermogravimetric analysis (TG) is one of the thermal analysis techniques used to measure the mass change, thermal decomposition and thermal stability of composite materials. Knowledge of the kinetic parameters associated with thermal degradation constitutes an important tool in estimating the thermal behavior of composites under dynamic conditions [7–9].

The purpose of this study is to evaluate the thermal stability and kinetic parameters of RHF, which is used for manufacturing thermoplastic polymer (PP and HDPE)-agricultural lignocellulosic filler composites using TG under an inert atmosphere. In addition, to examine the effect of RHF content on degradation temperature, mass loss rate and residual mass, it is necessary to investigate its effect on the thermal stability of these composites. Different heating rates are to be expected in different areas of the sample, and it is therefore necessary to have a good knowledge of the thermal degradation behavior, because of the low thermal conductivity of PP and HDPE [8]. There are many expressions used for the evaluation of the non-isothermal kinetic parameters of the thermal degradation of these composites, but we discussed the activation energy of the composites in terms of the Flynn and Wall expression [10–12].

Experimental

Materials

The reinforcing filler was RHF obtained from Saron Filler Co., South Korea. The particle sizes of this filler were from 80 to 100 mesh. The chemical constituents of the fillers (rice husk flour; RHF, wood flour; WF) are listed in Table 1. Polypropylene (PP) and high-density polyethylene (HDPE) were purchased from Hanwha L&C Corp., South Korea. PP was purchased in the form of homopolymer pellets with a melt flow index of 12 g/10 min (230°C/2.160 g) and a density of 0.91 g cm⁻³. HDPE was purchased in the form of homopolymer pellets with a density of 0.957 g cm⁻³ and a melt flow index of 15 g/10 min.

Table 1 The chemical constituents of the WF and RHF

	Others	Holocellulose	Lignin	Ash
*Rice husk flour	5.0	60.8	21.6	12.6
*Wood flour	10.9	62.5	26.2	0.4
**Rice husk flour	6.3	59.9	20.6	13.2

*rice husk and wood flours from [3]

**Specification from Saron Filler Co.

Compounding

The rice husk flour (RHF) was dried to 1–2% moisture content using in an air dryer oven at 100°C for 24 h and then stored in a polyethylene bag in an environmental controller. The process of mixing the PP and HDPE with the RHF in a two-roll rheomixer is similar to that used for polymer blending. The blending temperature was maintained at 200°C and a rotor speed of 20 rpm was used for 15 min. The major type of laboratory size extruder was a single screw type, which is used to blend thermoplastic polymer composites reinforced with natural fillers, using three general processes: melt blending, extrusion and pelletizing. The extruded strands were pelletized and stored in sealed packs to prevent moisture infiltration. Pellets are the typical end product from direct extrusion production lines. These composites were prepared with four different filler loadings (10, 20, 30 and 40 mass%) for investigation using TG.

Thermogravimetric analysis (TG)

The TG measurements were carried out using 10–13 mg of the composites at five different heating rates of 2, 5, 10, 20 and 40°C min⁻¹ in a N₂ atmosphere using a thermogravimetric analyzer (Rheometric Scientific TG1000, Nicem at Seoul National University). The TG was conducted with the compounds placed in a high Quality nitrogen (99.5% nitrogen, 0.5% oxygen content) atmosphere with a flow rate of 20 mL min⁻¹ in order to avoid unwanted oxidation.

Activation energy of thermal decomposition

To calculate the activation energy of the thermoplastic polymer composites (PP and HDPE) reinforced with RHF, the following Flynn and Wall expression was used [12].

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

where E_a =activation energy of thermal decomposition, R =gas constant (kJ mol⁻¹), β =heating rate, T =absolute temperature (K).

To obtain the activation energy (E_a), this expression, which is based on the relationship between $\lg\beta$ and $1/T$ for a selected fraction of the thermal decomposition was displayed in the form of a graph and E_a was then evaluated from the slope. The selected

fraction ranged from 0.05 to 0.50 and the determining values for the activation energy of each fraction were compared. This method represents a simple and rapid method for finding the activation energy from a plot of mass loss vs. temperature using data obtained at several heating rates.

Results and discussion

Thermogravimetric analysis

Figure 1a shows that the TG curves of both RHF and WF exhibit two mass loss steps. The initial mass loss below 100°C is due to the gradual evaporation of absorbed moisture. The second mass loss from approximately 150 to 500°C is due to the decomposition of the three major constituents of the natural fillers. Natural fillers are composed of cellulose, hemicellulose and lignin. Our results were in good agreement with the theoretical stoichiometric values, based on the fact that lignocellulose materials are chemically active 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. At 800°C, the ash content of RHF is much higher than that of WF. Ash in the RHF is mainly composed of silica (96%). The amount and distribution of silica in the rice husk is likely to be an important factor in determining the properties of the composite products, for example, in interfacial adhesion between RHF and thermoplastic matrix polymer in the manufacture of thermoplastic polymer-RHF composites. Table 1 shows that the content of holocellulose and lignin in RHF is a slightly lower than that in WF. Because of the higher cellulose content of WF, the thermal stability of WF is a slightly higher than that of RHF [3–5, 13].

The mass loss steps of pure PP and HDPE occur very slowly under 500°C, but above 500°C this process occur very rapidly. The mass loss of PP and HDPE started at 472 and 517°C, and were completed at 578 and 597°C, respectively. Our results

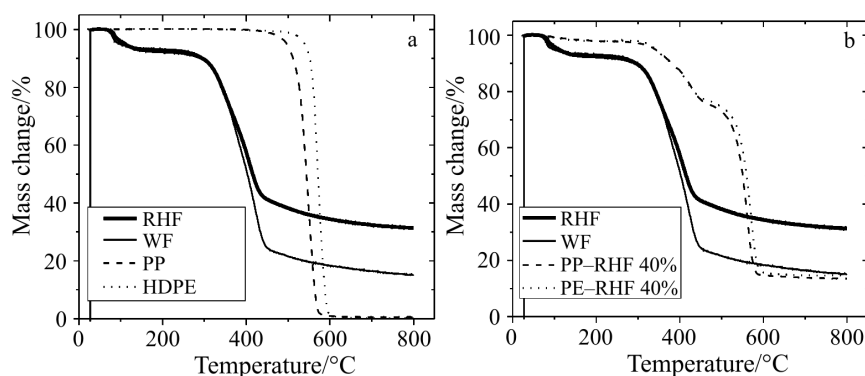


Fig. 1 a – TA curves of WF, RHF, PP and HDPE, at the heating rate of $40^{\circ}\text{C min}^{-1}$ in an N_2 atmosphere. b – TA curves of WF, RHF and RHF filled PP and HDPE composites (40 mass% filler loading) at a heating rate of $40^{\circ}\text{C min}^{-1}$ in an N_2 atmosphere. Results of wood and rice-husk flour [3]

show that the thermal stability of RHF and WF are lower than that of PP and HDPE. The thermal degradation of PP and HDPE can take place through random chain scission and a radical chain mechanism. However, the major source of thermal degradation in RHF and WF is the degradation of holocellulose and lignin. Figure 1b shows that the effect of mixing PP or HDPE matrix resin with RHF (filler loading: 40 mass%) was to improve the thermal stability of the composites in comparison with that of WF and RHF [14–17].

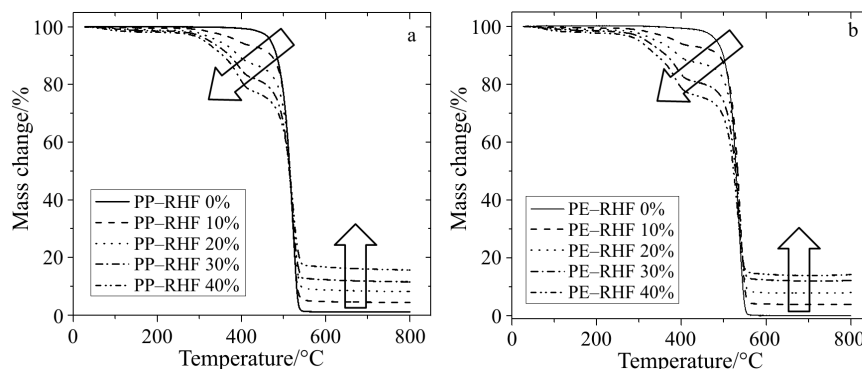


Fig. 2 TA curves of a – RHF filled PP, b – RHF filled HDPE composites, at a heating rate of $10^{\circ}\text{C min}^{-1}$ in an N_2 atmosphere

The mass loss of the composites made of PP or HDPE to which RHF was added at different filler loadings and one heating rate ($10^{\circ}\text{C min}^{-1}$) are shown in Figs 2a and b. As the filler loading increased, the thermal stability of the composites decreased and the ash content increased. The results show that the thermal stability of the composites decreased as the RHF content increased. This is a logical consequence of the lower thermal stability of the RHF.

Activation energy of thermal decomposition using Flynn and Wall model based on thermogravimetric data

To determine the detailed kinetic parameters of the composites, such as the activation energy, TG was performed to analyze their thermal degradation behavior at different heating rates in a nitrogen atmosphere. All the experiments were carried out under the same conditions using a non-isothermal method. Figures 3a and b show the thermal degradation curves for the RHF filled PP and HDPE composites (filler loading: 10 mass%) at five different heating rates. As the heating rate increased, the decomposition temperature (T_d) increased, and the T_d was found from the point where the mass loss started to increase. The same results are shown in Figs 4a and b (filler loading: 40 mass%). The results of the experiment designed to measure the effect of filler loading on the thermal stability of the composites are shown in Figs 3a, b and 4a, b. It is clear that the initial degradation temperature and thermal stability of the composites decreased as the filler loading increased. This means that the degree

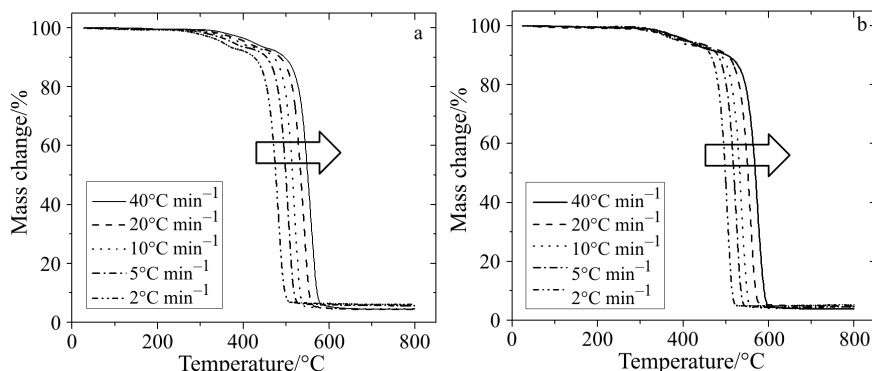


Fig. 3 TA curves of a – RHF filled PP, b – RHF filled HDPE composites (10 mass% filler loading) by heating rate

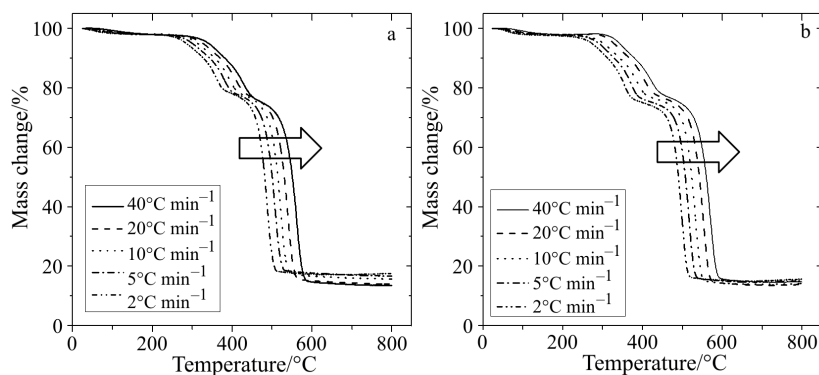


Fig. 4 TA curves of a – RHF filled PP, b – RHF filled HDPE composites (40 mass% filler loading) by heating rate

of compatibility and interfacial bonding is dependent on the mixing ratio of RHF. It can be seen that the incompatibility between the hydrophilic RHF and the hydrophobic thermoplastic matrix resin results in there being poor interfacial adhesion. For this reason, as the filler loading increased, the thermal stability of the composites decreased more and more [3, 18, 19].

The temperatures at $\alpha=0.05$ (5% of thermal degradation region) for the five heating rates were measured where the line crossed the TG curve. The temperatures at various values of α for different heating rates were measured by the same method for all of the samples. From this study, we obtained the conversion values (α) at 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50%, respectively, for the RHF filled PP and HDPE composites, which are shown in Figs 5a, b and 6a, b. As can be seen in Figs 5a and b, the temperature at the lowest values of α , from 0.00 to 0.10, representing the early stage of thermal decomposition, was affected by the moisture content and the major constituents of the RHF. At the lower RHF content, the thermal decomposition of the composites occurs very rapidly due to there being a majority of matrix resin, and

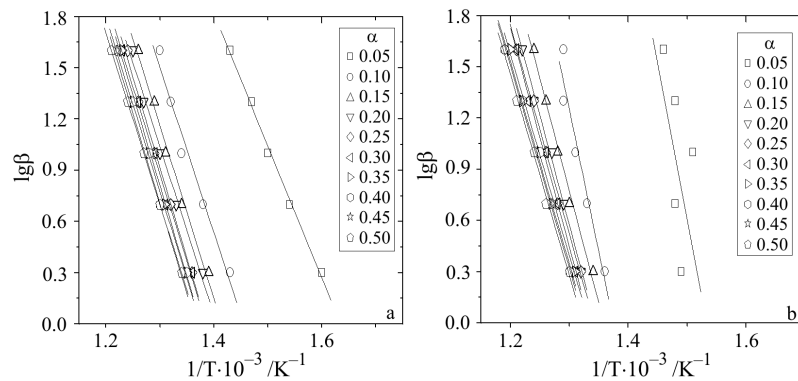


Fig. 5 Isoconversion curves of a – PP-RHF, b – HDPE-RHF composites (10 mass% filler loading) by Flynn and Wall expression

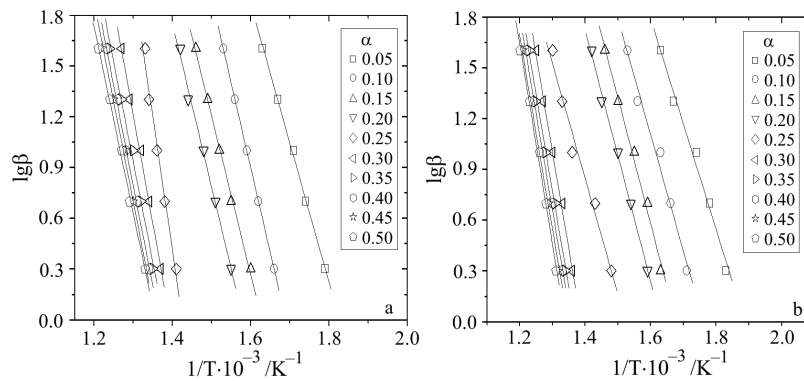


Fig. 6 Isoconversion curves of a – PP-RHF, b – HDPE-RHF composites (40 mass% filler loading) by Flynn and Wall expression

therefore the values for the fixed conversion factor, α , were selected from a range of 0.15 to 0.50. On the other hand, as the RHF content increased, the linear fittings are more broadly distributed, over a wider range of temperatures and values of α , from 0.05 to 0.25. It can be seen that the thermal stabilities and degradation temperatures of the composites were determined by the RHF content.

The activation energy of the thermal decomposition curves for the RHF filled PP and HDPE composites at degradation conversion (α) are shown in Figs 7 and 8. As the thermal decomposition proceeded in the RHF filled PP composites, the activation energy increased slowly in the initial stage until $\alpha=0.3$ and thereafter remained almost constant, but Figs 8 and 9 show that as the filler loading increased, the activation energy of the RHF filled HDPE composites decreased. In particular, the degradation temperature and the activation energy of the RHF filled HDPE composites significantly decreased at values of α from 0.00 to 0.25 and thereafter increased steeply up to $\alpha=0.5$ [3, 12].

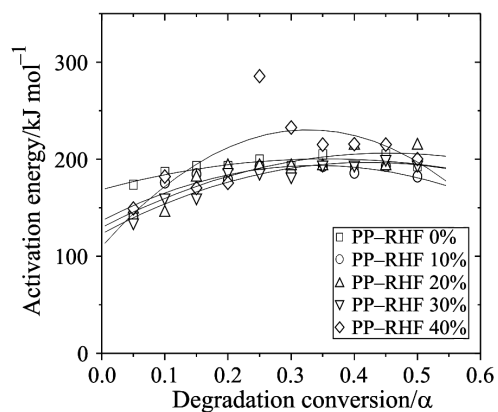


Fig. 7 Activation energy of thermal decomposition for PP-RHF composites

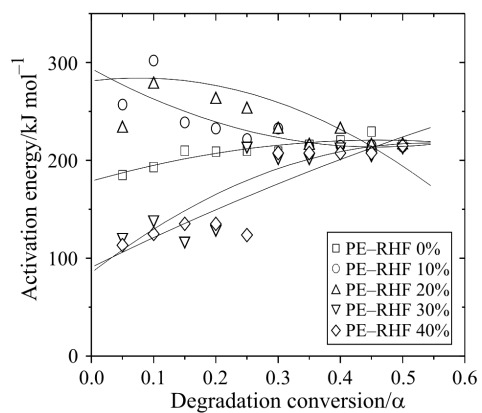


Fig. 8 Activation energy of thermal decomposition for HDPE-RHF composites

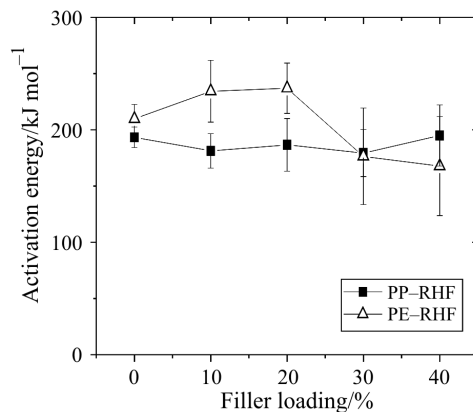


Fig. 9 Comparison of activation energy of thermal decomposition between RHF filled PP and HDPE composites

This means that the activation energy of the composites depends on the dispersion of the RHF in the PP and HDPE matrix. Therefore, at levels of between 30 and 40 mass% RHF contents, the dispersion and interfacial adhesion between the HDPE and RHF was found to be lower than that between PP and RHF. The activation energy is related to the energy barrier preventing polymer chain movement from one location to another. The strength of the interaction between the filler and the polymer mainly depends on the property of the interface. Consequently, the observed higher activation energy of the composites means not only that the dispersion of the polymer and filler was increased, but also that the interfacial adhesion was improved. The thickness swelling of the PE-paper sludge composites was higher than that of the PP-paper sludge composites. This might be attributed to the weak interfacial bonding between the PE chain and the paper sludge [16, 20, 21]. Therefore in order to improve the interaction between matrix and filler, the addition of a compatibilizing agent is recommended.

Conclusions

The thermal stability of RHF and WF was lower than that of pure PP and HDPE. Also, as the filler loading increased, the thermal stability of the composites decreased and the ash content increased. This is a logical consequence of the lower thermal stability of the RHF. As the thermal decomposition proceeded in the RHF filled PP composites, the activation energy increased slowly in the initial stages until $\alpha=0.3$ and thereafter remained almost constant, whereas in the case of the RHF filled HDPE composites with an RHF content of between 30 and 40 mass%, the degradation temperature and the activation energy significantly decreased at values of α from 0.00 to 0.25 and thereafter increased steeply up to $\alpha=0.5$. The dispersion and interfacial adhesion between HDPE and RHF was founded to be lower than that between PP and RHF. In order to improve the compatibility and interfacial adhesion, the addition of a compatibilizing agent for RHF filled PP and HDPE composites is recommended.

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