Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 157–160

THERMAL PROPERTIES OF LIGNOCELLULOSIC FILLER-THERMOPLASTIC POLYMER BIO-COMPOSITES

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In the TG analysis of the bio-composites, their thermal stability was found to slightly decrease and the ash content to increase as the lignocellulosic filler loading increased. This is a logical consequence of the lower thermal stability of the lignocellulosic filler compared to that of the matrix polymer. The dispersion and interfacial adhesion between the lignocellulosic filler and thermoplastic polymer were important factors affecting the thermal stability of the composite system. In order to improve their compatibility and interfacial adhesion, the incorporation of a compatibilizing agent into the lignocellulosic material-thermoplastic polymer composites is recommended. In the TMA analysis, the thermal expansion of the composites was found to decrease with increasing filler loading and incorporating compatibilizing agent. Lignocellulosic filler is a suitable material for preventing the thermal expansion of the composite materials caused by atmospheric changes.

Keywords: *bio-composite, lignocellulosic filler, thermal expansion, thermal stability, thermoplastic polymers*

Introduction

Recently, lignocellulosic materials such as wood fiber, wood flour and agricultural residues have been widely used as reinforcing fillers in natural filler-thermoplastic polymer bio-composites. These bio-composites, which are made using lignocellulosic materials as reinforcing fillers, are inexpensive, biodegradable, thus causing minimal environmental pollution, and non-toxic to the human body [1, 2]. Agricultural residues, such as rice husk, sugar cane, bagasse, etc., are very important natural materials, and their ability to act as substitutes for wood fiber/wood flour is of great utility, because of the lack of forest resources and increasing levels of environmental pollution. These natural materials are lighter, less expensive and provide much higher strength per unit mass than inorganic reinforcing fillers, such as carbon black, calcium carbonate, talc and zinc oxide [3]. Most of all, rice husk, an agricultural industrial residue which is easy to obtain, is one of several lignocellulosic materials, which is produced as a by-products during the rice milling process in rice-producing countries [4]. This rice husk is mainly utilized as natural reinforcing filler in the form of rice husk ash through the burning process, due to its high silica content but, in the present study, rice husk flour was used, in order to simplify the manufacturing process. A thermoplastic polymer, a polyolefin, was used as a matrix polymer to compound with the natural fillers for the purpose of manufacturing the bio-composite. The use of natural filler-thermoplastic polymer bio-composites has been rapidly increasing in the field of constructions (wood decks, window frames, bathroom interiors, etc.) and the automotive industry (Dashboard *etc.*) [5]. In addition, some industries, particularly the marine and chemical industries, have also used these composite systems [6]. In these composite systems, thermal properties, such as thermal stability and thermal expansion, are very important factors that affect the quality of the final products. For example, the thermal deformation of bathroom interiors can be brought about by the hot vapor generated during a shower, Dashboard is affected by the high temperature inside the vehicle during the summer. Moreover, the thermal stability of these composite systems is very important because these materials must bear up against heat during a fire.

In this study, the thermal properties of bio-composites, made using lignocellulosic materials as the reinforcing filler, are examined, in order to measure their physical and chemical properties as a function of the temperature and mass loss. Thermogravimetric analysis (TG) is one of the methods of thermal analysis which can be used to measure the mass change, thermal decomposition and thermal stability of composite materials [7]. Thermomechanical analysis (TMA) is the method of measuring the thermal expansion of the composites as a function of temperature.

The purpose of this study is to evaluate the thermal stability and thermal expansion of lignocellulosic material (wood flour, rice husk flour) filled polyolefin

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1388–6150/$20.00

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composites according to the filler loading and the presence of compatibilizing agent, using the TG and TMA analysis methods.

Experimental

Materials

The polypropylene (PP) used in this study was supplied by Hanwha L&C Corp., South Korea, in the form of homopolymer pellets with a melt flow index of 12 g/10 min (230°C, 160 g) and a density of 0.91 g cm^{-3}. The low-density polyethylene (LDPE) was supplied by LG Chem. Ltd., South Korea, in the form of homopolymer pellets with a density of 0.918 g cm^{-3} and a melt flow index of 24 g/10 min (230°C, 160 g).

The reinforcing filler was rice husk flour (RHF) and wood flour (WF) obtained from Saron Filler Co., South Korea. The particle size of these lignocellulosic fillers ranged from 80 to 100 mesh.

The compatibilizing agent (MAPP: maleated polypropylene) was obtained from Eastman Chemical Products Inc.; Epolene G-3003™ has an acid number of 8, and a molecular mass of 103 500.

Compounding

The RHF and WF were oven dried to 4% or less moisture content at 100°C for 24 h, and then stored over a desiccant in a sealed polyethylene bag. PP and LDPE were mixed with the RHF and WF in an extruder, and the blending temperature was maintained at 200°C for PP and 140°C for LDPE. The major type of laboratory size extruder that was used was a twin-screw type, which is widely used to blend thermoplastic polymer composites reinforced with natural fillers. 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. After pelletizing the polymer, the pellets were conditioned before testing at 23±2°C, 50±5% RH for at least 40 h according to the ASTM D 618-99 [8]. These pellets were prepared with four different filler loadings (10, 20, 30 and 40 mass%) and a compatibilizing agent (MAPP) content of 3 mass% (30 mass% of filler loading) for the tests performed using TG and TMA.

Thermogravimetric analysis

The TG measurements were carried out using 10~13 mg of the lignocellulosic filler-LDPE bio-composites at a heating rate of 40°C min^{-1} in a N_2 atmosphere using a thermogravimetric analyzer (Rheometric Scientific TG1000). 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.

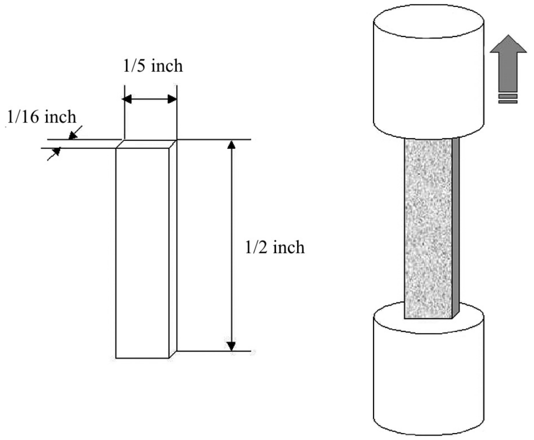

Fig. 1 Dimensions of TMA sample and testing method

Thermal expansion

The thermal expansion coefficients of the lignocellulosic filler-polypropylene bio-composites were measured by manufacturing samples in the form of bars with dimensions of 1/5– by 1/2– by 1/16 inch, as shown in Fig. 1, and then tested by TMA (using a thermomechanical analyzer), with tension mode being used for the measurements of the thermal expansion. The samples were heated from room temperature to 100, cooled to –50, then heated to 100°C for the secondary scanned test, and finally cooled to room temperature. The tests were accomplished during second heating on a sample oriented along the length of the bar, namely the y-axis.

Results and discussion

Thermogravimetric analysis

Figure 2 shows the TG curves of the lignocellulosic fillers (RHF and WF). The graph exhibits two mass loss steps, an initial mass loss below 100°C, which is due to the gradual evaporation of moisture, and a second mass loss from approximately 150 to 500°C, which is due to the decomposition of the three major constituents of the lignocellulosic fillers, namely cellulose, hemicellulose and lignin. Lignocellulosic materials are chemically active and decompose thermochemically in the range of 150 to 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 [7]. The ash in the RHF is mainly composed of silica (96%). The amount and distribution of silica in the RHF have a significant effect on the properties of the composite products, such as the interfacial adhesion between the RHF and the

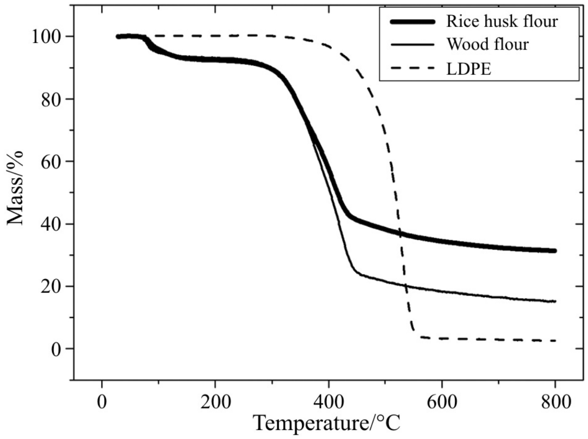

Fig. 2 TG curves of RHF, WF and LDPE at a heating rate of 40°C min^{-1} in a N_2 atmosphere

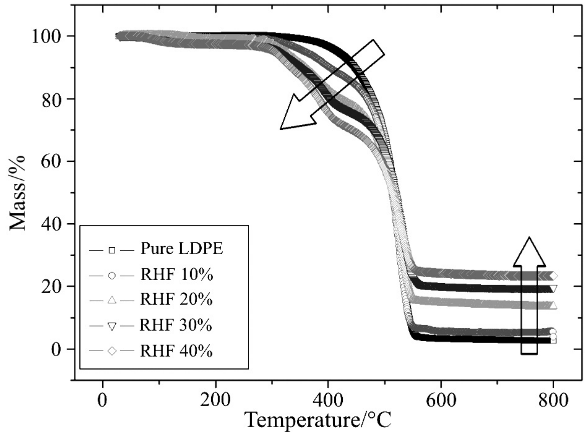

Fig. 3 TG curves of RHF filled LDPE composites, at a heating rate of 40°C min^{-1} in a N_2 atmosphere

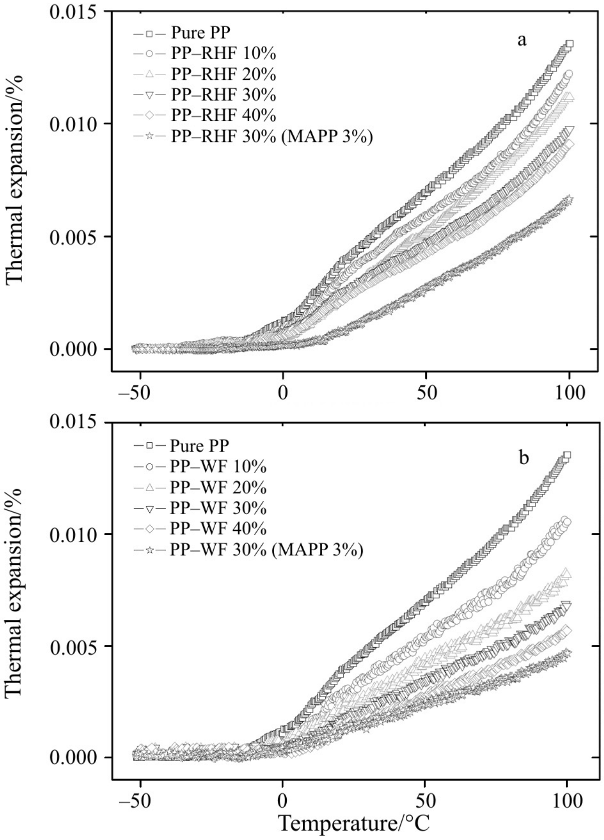

Fig. 4 Thermal expansion of the RHF-PP and WF-PP composites: a – RHF-PP composites, b – WF-PP composites

polyolefin matrix polymer, in the case of RHF-polyolefin bio-composites. Because of its higher cellulose content, WF exhibits slightly higher thermal stability than RHF [7]. The mass loss of pure LDPE takes place very slowly at temperatures below 400, but above 400°C this process occurs very rapidly. This result demonstrates that the thermal stability of RHF and WF are lower than that of LDPE. The thermal degradation of LDPE 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 [7].

The mass loss of the composites made using RHF as the reinforcing filler and LDPE as the matrix polymer at different filler loadings and one heating rate (40°C min^{-1}) are shown in Fig. 3. As the filler loading increased, the thermal stability of the composites slightly decreased, whereas the final ash content increased. These results show that the thermal stability of the composites decreased as the lignocellulosic filler content increased, which is a logical consequence of the lower thermal stability of the lignocellulosic filler compared to that of the polyolefin, whereas the thermal degradation of the composite was retarded above 500°C, because of the increased ash content.

Thermal expansion

The thermal expansion of the lignocellulosic filler-polypropylene composites was measured on the second heating and is shown in Fig. 4, and the thermal expansion coefficients of the composites are shown in Table 1. The thermal expansion coefficients of the composites decreased with increasing filler loading. Lignocellulosic filler is a suitable material for preventing the thermal expansion caused by cold and warm atmospheric changes. The sample with a filler loading of 30 and a MAPP content of 3 mass% expanded the least. This means that the strong bonding between the hydrophilic lignocellulosic filler and the hydrophobic matrix polymer induced by MAPP restricted the thermal expansion [9–10].

The typical TMA curve for the thermal expansion of the lignocellulosic filler-PP composite is shown in Fig. 5, and the thermal expansion coefficient of the composite is represented by the slope of the curve. The thermal expansion of the composites varied only slightly up to 0°C, which is the glass tran-

Table 1 Coefficient of thermal expansion of the lignocellulosic filler-PP composites

Filler loading	Coefficient of thermal expansion (10^{-6}/°C)	
	0 to 25°C	25 to 100°C
Pure PP	14.8	13.0
RHF 10 mass%	12.9	11.7
RHF 20 mass%	10.2	12.0
RHF 30 mass%	9.9	9.7
RHF 40 mass%	9.0	9.1
RHF 30 mass% MAPP 3 mass%	3.9	7.9
WF 10 mass%	12.3	10.3
WF 20 mass%	8.4	8.1
WF 30 mass%	7.1	6.8
WF 40 mass%	6.1	6.0
WF 30 mass% MAPP 3 mass%	4.8	4.6
Solid wood (Longitudinal direction)	3.2~5.6	
Solid wood (Radial direction)	22~35	
Solid wood (Tangential direction)	31~45	
LDPE	16~18	
HDPE	11~13	
EVA (ethylene vinyl acetate)	16~20	

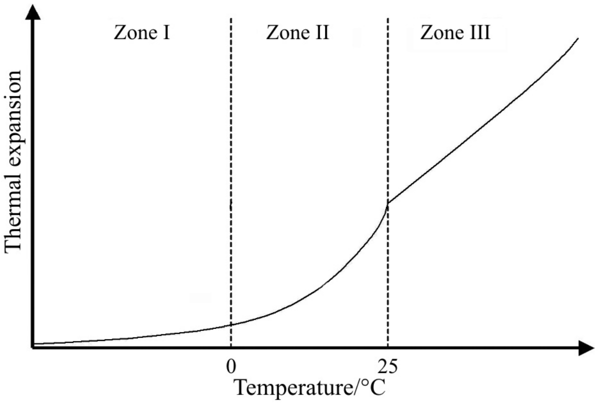

Fig. 5 Typical thermal expansion curve of the lignocellulosic filler-PP composites

sition temperature of PP (zone I). Subsequently, the slope was steep up to room temperature (zone II) and then gentle up to 100°C (zone III). Generally, the thermal expansion of the lignocellulosic filler-PP composites increased with increasing temperature.

Conclusions

The thermal stability of RHF and WF was lower than that of pure LDPE. As the filler loading increased, the thermal stability of the composites slightly decreased, whereas the ash content increased, which is a logical consequence of the lower thermal stability of the lignocellulosic filler. The thermal expansion of the composites decreased with increasing filler loading and increasing compatibilizing agent content. Lignocellulosic filler is a suitable material for preventing the thermal expansion of the composite materials caused by cold and warm atmospheric changes. In order to improve their compatibility and interfacial adhesion, the incorporation of a compatibilizing agent into the lignocellulosic material-thermoplastic polymer bio-composites is recommended.

Acknowledgements

This work was supported by a Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (M01-2004-000-20097-0) and H.-S. Kim is grateful for the graduate fellowship provided by the Ministry of Education through the Brain Korea 21 project.

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Received: January 05, 2005
In revised form: March 10, 2005

DOI: 10.1007/s10973-005-6525-y