THERMOGRAVIMETRIC ANALYSIS OF RICE HUSK AND SAWDUST FILLED POLYOLEFIN MATRIX COMPOSITES

PHÂN TÍCH NHIỆT TRỌNG LƯỢNG COMPOSITE NỀN POLYOLEFIN ĐỘN TRẤU VÀ MÙN CƯA

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Abstract - The thermal behaviour of bio-fillers and bio-filler/polyolefin composites were studied with thermogravimetric analysis. The thermal analysis of the fillers showed rice husk has thermal resistance comparing to sawdust. In the air atmosphere, the main peak of rice husk degradation shifted to lower temperature values compared to that in nitrogen atmosphere. The residues of rice husk at 700^{o}C in the air atmosphere were lower than that in nitrogen atmosphere. Moreover, the effects of filler type and loading as well as polymer matrix type and modification on the thermal properties of the three composite systems including rice husk/polypropylene composite, rice husk/polyethylene composite and sawdust/polyethylene composite were evaluated. It was found that the thermal stability of the composites decreased with increase of filler loading from 30 wt% to 50 wt%. However, the thermal stability and degradation temperature of the composites with compatibilizers were slightly higher than those of the composites without compatibilizers.

Key words - sawdust; rice husk; polyethylene; polypropylene; composite; compatibilizer; thermogravimetric analysis

Tóm tắt - Đặc tính nhiệt của độn sinh học và composite độn sinh học/polyolefin được nghiên cứu bằng phân tích nhiệt trọng lượng. Phân tích nhiệt của độn cho thấy trấu chịu nhiệt tốt hơn mùn cưa. Trong môi trường phân tích nhiệt là không khí, đỉnh phân hủy nhiệt chính của trấu dịch chuyển về phía nhiệt độ thấp hơn so với trong khí quyển nitơ. Hàm lượng tro của trấu ở 700^{o}C trong môi trường phân tích nhiệt là không khí thấp hơn trong khí quyển nitơ.Hơn nữa, ảnh hưởng của loại và hàm lượng độn, cũng như loại nền polymer và sự biến tính nhựa nền đến tính chất nhiệt của ba hệ composite bao gồm trấu/polypropylene composite, trấu/polyethylene composite và mùn cưa/polyethylene composite được đánh giá. Kết quả cho thấy rằng độ ổn định nhiệt của composite giảm khi hàm lượng độn tăng từ 30 % đến 50 % trọng lượng. Tuy nhiên, độ ổn định nhiệt và nhiệt độ phân hủy của các composite khi có mặt chất tương hợp cao hơn một ít so với composite không có mặt chất tương hợp.

Từ khóa - mùn cưa; trấu; polyethylene; polypropylene; composite; chất tương hợp; phân tích nhiệt trọng lượng

1. Introduction

Bio-materials used as fillers in polymer matrix composites are natural compounds, mainly containing cellulose, hemicellulose and lignin. Their degradation takes place at a relatively low temperature, around 200^{o}C [1]. Therefore, bio-fillers are subjected to thermal degradation during composite processing with the majority of the thermoplastic polymers. The degradation of bio-fillers resulting from high processing temperature may lead to undesirable properties, such as odor and browning along with a reduction in mechanical properties of the bio-composite [2, 3]. Therefore, it is important to understand and predict the thermal decomposition processes of bio-fillers so that this knowledge can aid to better design a composite-obtaining process and estimate the influence of the thermal decomposition of bio-fillers on composite properties [4].

Thermal analysis is becoming an increasingly useful tool for material characterization, particularly in the development of new materials. It is essential to monitor not only the final properties of the composite but also the basic raw materials through the processing procedure to the end product. Optimization of the processing temperature and time with an understanding of matrix, reinforcing element and interface between matrix and filler, can lead to the best balance of composite properties [5]. Thermogravimetric analysis (TGA) can measure the moisture content, thermal cleavage, thermal degradation temperature and thermal stability of composite materials [6, 7].

Polypropylene (PP) and high density polyethylene (PE) are among the most important commercial plastics currently used as the matrix polymer in bio-filler composites due to their mechanical/thermal properties and low density at competitive price [8, 9]. Rice husk (RH) and sawdust (SD) are agriculture and forestall wastes, which are produced in high amounts in Vietnam and worldwide, and are totally biodegradable in the natural environment. Therefore rice husk and sawdust are promising bio-fillers for composites to replace conventional materials such as wood, plastic, inorganic filled composite in the fields of construction materials, furniture and many plastic products [10].

The purpose of this study is to evaluate the thermal behavior of bio-material (rice husk and sawdust) filled polyolefin (PP, PE) composites according to the filler loading and the presence of compatibilizers, using the TG analysis method.

2. Experimental

2.1. Materials

Polypropylene Advanced PP–1100N and high density polyethylene EL-Lene H5818J were supplied by Advanced Petrochemical Co. and SCG Plastics Co., Ltd-Thailand, respectively. Two compatibilizers, maleic anhydride grafted polypropylene (MAPP) Polybond 3200 and maleic anhydride grafted polyethylene (MAPE) Polybond 3029, were provided by Chemtura, USA.

Rice husk was obtained from a rice mill factory in Danang, Vietnam and then was ground. Sawdust from Acacia auriculiformis tree was collected from a wood processing factory in Danang, Vietnam. Rice husk and sawdust were sieved (particle size <500µm) [11, 12, 13] and then were dried in oven at 80^{o}C for 24h before preparing the composites.

2.2. Methods

2.2.1. Preparation of the composites

Composites were produced in a two-stage process, as optimized in a previous study [11, 12, 13]. In the first stage, bio-fillers and polyolefin were compounded without and with compatibilizer (2wt% for PP matrix composite and 4wt% for PE matrix composite) using the twin-screw extruder Rheomex CEW100 QC, Haake, Germany. The mixing zone temperature of the extruder was 160^{o}C for PE and 190^{o}C for PP matrix composites. The rotation speed of the screws was 50 rpm. In the second stage, the extrudate in the form of strands was cooled to room temperature and then granulated.

The compound granules were dried at 80^{o}C for 24 h before injection molding. The specimens were prepared using an injection molding machine MiniJet II, Haake, Germany at cylinder temperatures of 180^{o}C for HDPE and 190^{o}C for PP matrix composites under an injection pressure of 800 bar.

2.2.2. Thermogravimetric analysis (TGA)

The samples used for the thermogravimetric analysis were cut from the extruded pellets. Approximately 10 mg of each sample was used. The thermogravimetric analysis (TGA Q500 V6.7 Build 203) was carried out under nitrogen (N_2) and air atmospheres in a temperature range of 23°C to 700^{o}C. The heating rate of the analysis was 10°C/min.

3. Results and discussion

3.1. Thermogravimetric analysis of fillers

The results of the thermal analysis of rice husk and sawdust are shown in Figure 1. The TA and DTG curves of the fillers in nitrogen as well as air atmosphere showed the weight loss between 40°C and 100°C, which corresponds to the vaporization of water. A second mass loss from approximately 150°C to 500°C is due to the decomposition of the three major constituents of bio-fillers, namely cellulose, hemicellulose and lignin. Bio materials are chemically active and decompose thermochemically in the range of 150°C to 500°C; hemicellulose mainly between 150°C and 350°C, cellulose between 275°C and 350°C and lignin, with higher thermal stability, between 250°C and 500°C [14, 15, 16].

The thermal behavior of RH and SD fillers differed above 350^{o}C in nitrogen and 320^{o}C in air atmosphere. RH had higher thermal resistance than SD, which may be due to higher silica content of RH. At 700°C, the ash content of RH is much higher than that of SD. The ash in the RH is mainly composed of silica (96 wt%). The amount and distribution of silica in the RH have a significant effect on the properties of the composite products, such as the interfacial adhesion between the RH and polyolefin matrices (PE, PP) [17].

The picture in Fig 1 shows the differential of thermal degradation of rice husk filler in the nitrogen and air atmospheres. In nitrogen atmosphere, a high temperature main peak and a low temperature shoulder peak of filler were observed at about 340^{o}C and 298^{o}C, respectively. The shoulder peak was overlapped in the main peak because the degradation region of hemicellulose was close to that of cellulose, and the content of hemicellulose in both fillers was less than that of cellulose. The first thermal degradation step or regime of weight loss, in the active zone could be attributed to the decomposition of hemicellulose and the initial stages of cellulose decomposition, whereas the second thermal degradation step in the active zone is attributed to the final stages of cellulose decomposition and the initial stages of lignin decomposition. It can be deduced from the above results that the hemicellulose and cellulose components of the rice husk are the main contributors to the evolution of the volatile compounds (active zone), while lignin is mainly responsible for the char portion of the product (passive zone) [18].

However, in the air atmosphere the main peak of rice husk degradation shifted to lower temperature values, which were 320^{o}C, compared to that in nitrogen atmosphere. Besides of the first main peak of thermal degradation, there was the second main peak (438^{o}C) probably associated to thermal oxidation degradation of char. Therefore, the residues of RH filler at 700^{o}C in the air atmosphere (19.86%) were lower than that in nitrogen atmosphere (35.72%).

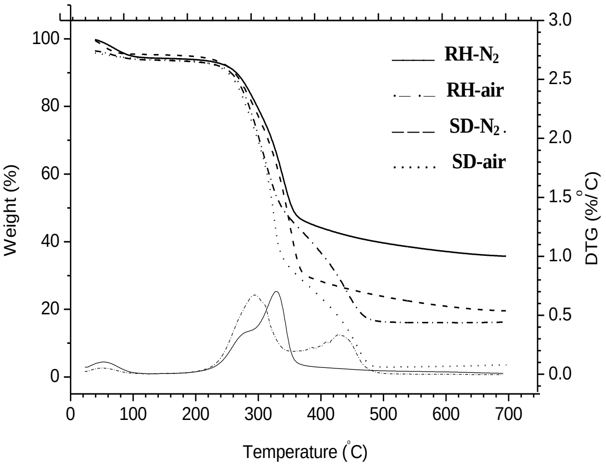

Figure 1. *TGA curves of sawdust, rice husk and DTG curves of rice husk in nitrogen and air atmospheres*

3.2. Thermogravimetric analysis of filler/polyolefin composites

Figure 2÷8 shows the TGA and DTG curves of the polyolefin, filler and the composites with filler content ranging from 30 wt% to 50 wt% in nitrogen and air atmospheres. Rice husk and sawdust decomposed at lower temperature than polyolefins (PE and PP) which started to decompose at above 400^{o}C. TGA results in Figure 2 show that PP decomposed quite easier than PE. In nitrogen atmosphere, thermal degradation of PP and PE occurs very rapidly at 468^{o}C and 488^{o}C, respectively. Furthermore, thermal resistance of PP decreased significantly in the air atmosphere. Decomposition of both polyolefins (PP and PE) started at 250^{o}C. While PP degraded strongly, PE decomposed gradually. The maximum decomposition rates of PP and PE in the air were 371ºC and 399ºC, respectively. Both PP and PE decomposed almost completely. Residues of both polyolefins at 700ºC were <2% in nitrogen and <1% in air atmosphere. However, at 700°C, rice husk and sawdust decomposed only about 65% and 80% in nitrogen, 80% and 92% in air atmosphere, respectively.

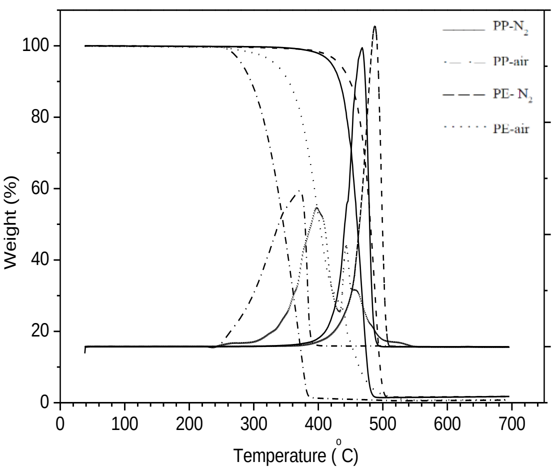

Figure 2. *TGA and DTG of PP and PE in nitrogen and air atmospheres*

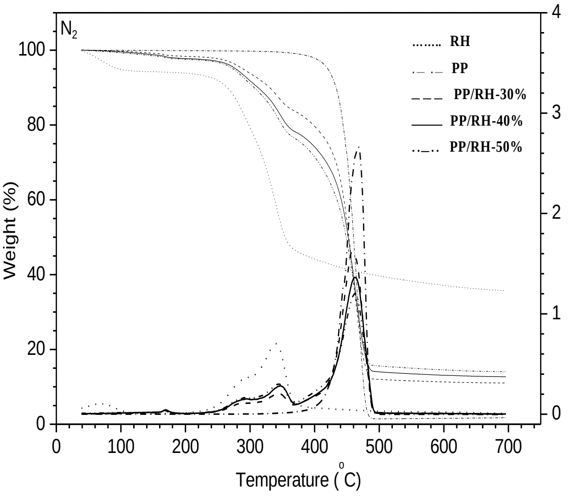

Figure 3. *TGA and DTG of RH, PP and the PP/RH composites in nitrogen atmosphere*

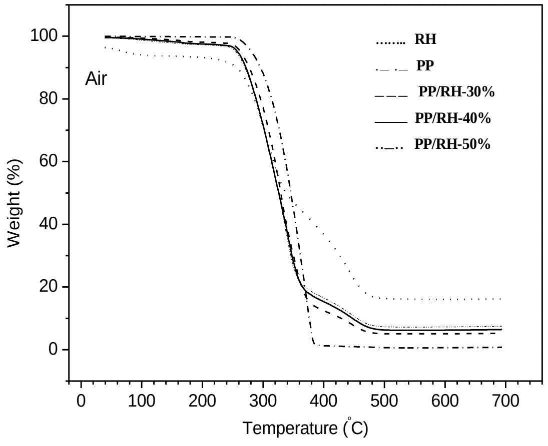

Figure 4. *TGA of RH, PP and the PP/RH composites in air atmosphere*

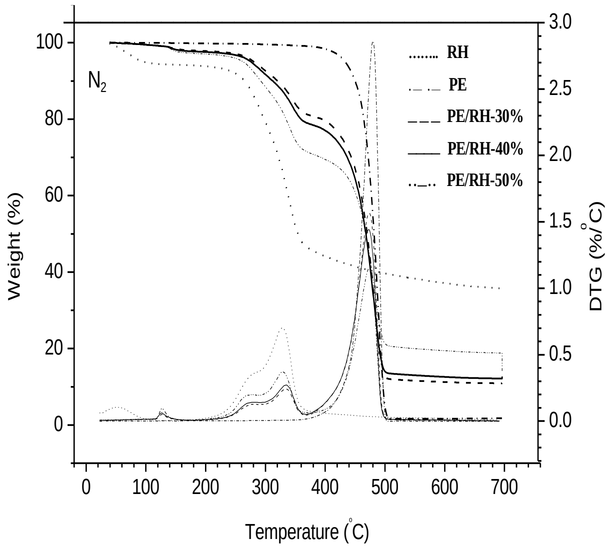

Figure 5. *TGA and DTG of RH, PE and the PE/RH composites in nitrogen atmosphere*

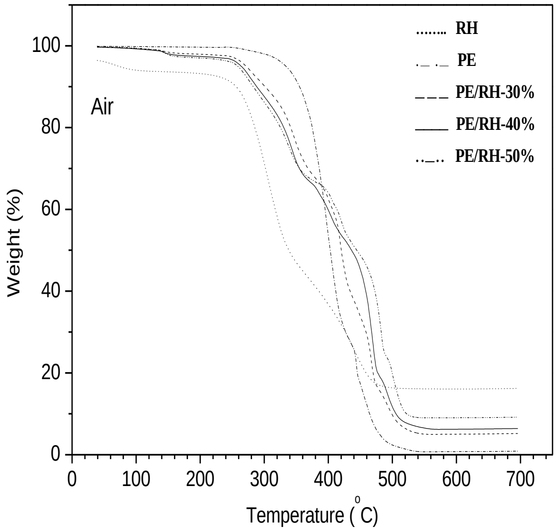

Figure 6. *TGA of RH, PE and the PE/RH composites in air atmosphere*

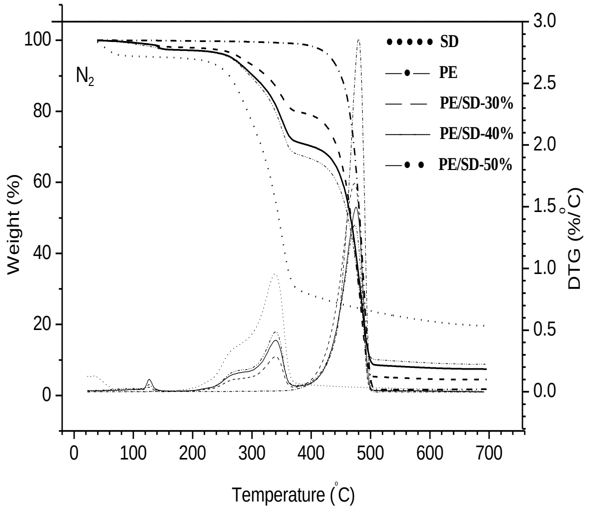

Figure 7. *TGA and DTG of SD, PE and the PE/SD composites in nitrogen atmosphere*

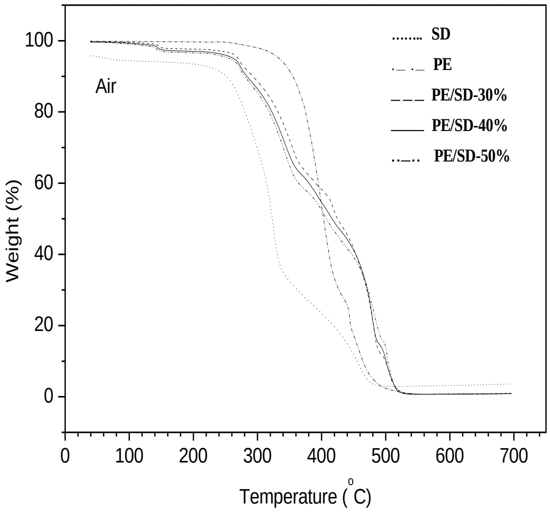

Figure 8. *TGA of SD, PE and the PE/SD composites in air atmosphere*

In the case of filler/plastic mixtures, DTG profiles show two regions of thermal decomposition that consist of the profile of filler and plastic as seen in Figure 3, 5, 7. As the filler loading increased, the thermal stability of the composites slightly decreased, whereas the final ash content increased (table 1, figure 1, 3 ÷ 8). These results show that the thermal stability of the composites decreased as the bio-filler content increased, which is a consistence of the lower thermal stability of the bio-filler compared to that of the polyolefin. The residues of rice husk composites (10.91÷18.82 wt% in nitrogen and 5.51÷9.42 wt% in air atmosphere) were much higher than those of sawdust composites (4.48÷8.75 wt% in nitrogen and 0.97÷1.29 wt% in air atmosphere) due to high ash content of rice husk compared to sawdust.

Table 1. *Residues (wt%) of fillers, plastics and the composites at 700ºC in nitrogen and air atmospheres*

Atmosphere	Nitrogen	Air
PP	1.75	0.75
PE	1.76	0.99
RH	35.72	19.76
SD	19.57	7.77
PP/RH-30%	11.03	5.54
PP/RH-40%	12.70	6.86
PP/RH-50%	14.06	8.06
PE/RH-30%	10.91	5.51
PE/RH-40%	12.15	6.74
PE/RH-50%	18.82	9.42
PE/SD-30%	4.48	0.97
PE/SD-40%	7.42	1.01
PE/SD-50%	8.75	1.29

3.3. Influence of compatibilizers on thermal behavior of the composites

For investigation of the influence of compatibilizers on thermal behavior of the composites, the compounds were produced with the formulas in Table 2 [11, 12, 13].

Table 2. *Formulas for producing the composites*

Material	Composition (wt%)					
	PP/RH	PP/RH (MA)	PE/RH	PE/RH (MA)	PE/SD	PE/SD (MA)
RH	50	50	50	50	-	-
SD	-	-	-	-	50	50
PP	50	48	-	-	-	-
PE	-	-	50	46	50	46
MAPP	0	2	-	-	-	-
MAPE	-	-	0	4	0	4

The TGA curves of the composites without and with compatibilizers (MA) (2 wt% - optimal content for PP matrix composites and 4 wt% - optimal content for PE matrix composites) are shown in Fig 9.

The thermal stability and degradation temperature of the composites with compatibilizers (PP/RH (MA), PE/RH (MA) and PE/SD (MA)) were slightly higher than those of the composites without compatibilizers (PP/RH, PE/RH and PE/SD). The improved thermal stability of the composites with compatibilizers was due to enhanced interfacial adhesion and additional intermolecular bonding (ester and hydrogen bonds) between hydroxyl groups of rice husk, sawdust and the anhydride functional group of compatibilizers [19]

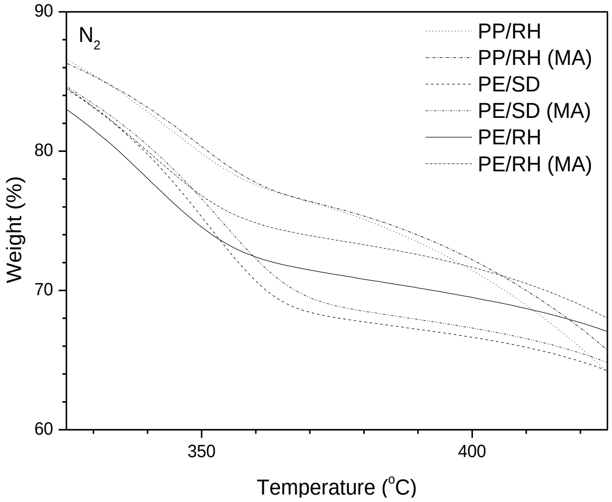

Figure 9. *TGA of three composite systems without and with compatibilizers*

4. Conclusions

Thermal degradation of bio-fillers and bio-filler/polyolefin composites is higher in the air comparing to nitrogen atmosphere due to thermal oxidative degradation. Therefore, oxygen should be absent during melting processing of the composites.

Rice husk and rice husk filled composites have higher thermal resistance comparing sawdust and sawdust filled composites due to high amount of silica.

Using compatibilizers can improve thermal stability of the composites due to enhanced interfacial adhesion at the interface between filler and matrix.

Acknowledgements: *Author is thankful to the technicians at Leibniz institute of polymer research Dresden, Germany and the students at Danang University of Science and Technology (Tran Thi Nghia, Nguyen Thanh Huan, Ngo Ngoc Hien Chuong, Pham Thai Mai Linh, Pham Thi Men, Le Van Truong) for carrying out part of the experiments.*

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(The Board of Editors received the paper on 27/04/2014, its review was completed on 19/05/2014)