INVESTIGATION ON RICE HUSK/POLYOLEFIN COMPOSITES

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ABSTRACT

This article presents some characteristics of the rice husk filler and the composites based on rice husk filler and polyolefin (Polyethylene and polypropylene). Filler morphology investigation showed angular shapes, some particular surface characters and some other properties of rice husk filler. The influences of rice husk content and compatibilizers on mechanical properties of the composites were investigated. An increase in rice husk content led to increased modulus and decreased tensile, bending and impact strengths of the composites in the case without modification. However, the presence of the compatibilizers based on maleic anhydride grafted polyolefin caused an increase in tensile, bending and impact strengths of the composites. Furthermore, some additives such as processing stabilizer, UV stabilizer and fungal resistance agents were also added in order to improve some properties of rice husk/polyolefin composites during processing and using. The experimental results indicated that the addition of the additives improved significantly some properties of the composites.

Keywords: Rice husk; Polyethylene, Polypropylene; Composite; Compatibilizer; Additive

1. INTRODUCTION

In recent years, bio-flour filled thermoplastics have received considerable attention because they have several advantages, such as renewable resource, light weight, low cost, reasonable strength and stiffness, recyclability, biodegradability… Various types of bio-fillers have been exploited including wood, hemp, sisal, flax, rice husk, jute and others.

Rice husk is the major agricultural residue produced with huge amount in Vietnam as a byproduct during the rice milling. The rice husk yield in Vietnam was over 8 million tons in 2012[1] and its amount will increase in the next future. However, they have been used ineffectively. Only some are used for daily cooking in the rural areas, the others have been dumped in rivers or burnt in open piles that cause the environmental problems.

The most common thermoplastics used as matrices for the bio-fillers are polyethylene, polypropylene and poly(vinyl chloride). In this study, polyethylene (PE) and polypropylene (PP) were chosen as the polymer matrices for the composites. The bio-filler used was rice husk.

However, the non-polar characteristic of the polyolefin matrix results in an incompatibility with the polar rice husk filler leading to poor adhesion of the filler/matrix interface. Therefore, there have been many studies on improving the interfacial interaction between the polyolefin matrix and bio-filler. According to the previous studies the best solution to the problem was using a proper coupling agent such as maleic anhydride grafted polyolefin [2, 3]. In this study, therefore, maleic anhydride grafted polyethylene and maleic anhydride grafted polypropylene were used as compatibilizers for polyethylene and polypropylene matrix composites, respectively.

To improve some properties of rice husk/polyolefin composite during processing and using, on the other hand, some additives including processing stabilizer, UV stabilizer and fungal resistance agent were also used in this study.

The objective of this study is to assess some characteristics of rice husk filler as well as the influences of filler, compatibilizer and additive content on the properties of the rice husk/polyolefin composites and to compare some properties of these composites to other materials, such as wood, plastics.

2. EXPERIMENTAL

2.1. Materials

Polypropylene Advanced PP–1100N and high density polyethylene EL-Lene HDPE H5818J were supplied by Advanced petrochemical Co. and SCG Plastics Co., respectively. Maleic anhydride grafted polyethylene (MAPE) named Polybond 3029 and maleic anhydride grafted polypropylene (MAPP) named Polybond 3200 were provided by Chemtura Co. Some additives, including processing stabilizer (Songnox 1010) and UV stabilizers (Songlight 7700, Songsorb 3260) were provided by Songwon Co., fungal resistance agent (zinc borate) was supplied by Riedel-de Haën, Germany.

Rice husk (RH) was collected from a Rice mill factory in Danang, Vietnam. Rice husk was ground, screened and classified into four mesh sizes (20÷35, 35÷45, 45÷80 and >80). RH particle fillers were then dried in oven at 80^{o}C for 24h before preparing composite samples.

2.2. Methods

2.2.1 Preparation of the composites

Composites were produced in a two-stage process. In the first stage, rice husk and polyolefin were compounded with and without compatibilizer, additives using the twin-screw extruder Rheomex CEW100 QC, Haake, Germany. The compounding temperature (mixing zone) was 160^{o}C (For PE matrix) and 190^{o}C (for PP matrix) at a screw speed of 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 being injection molded. The composite specimens were prepared using the injection molding machine MiniJet II, Haake, Germany. The molding temperature was 180^{o}C (for PE matrix) and 190^{o}C (for PP matrix) at an injection pressure of 800 bars [4].

2.2.2. Average width, length and aspect ratio analysis of rice husk filler

To evaluate the average width and length, RH fillers after grinding were classified by screening into four mesh size ranges 20÷35, 35÷45, 45÷80 and >80 (approximately 500÷850 µm, 350÷500 µm, 180÷350µm and <180 µm, respectively). An imaging analysis system was used for measuring the width and length of rice husk particles. The system consists of a Keyence VHX-100 digital microscope, Germany. For the measurement, about 500 mg filler were randomly selected after classifying by the sieve opening, each filler sample was placed on a glass dish under the microscope. The optical light was adjusted to achieve the best focusing alignment and image resolution. The filler images taken with a digital camera were used to measure the length and width of individual filler. A minimum of 100 filler particles were measured for each sample for determining the average length and width values.

The aspect ratio was described as the ratio of length and width for each filler particle. A minimum of 100 filler particles were measured for each sample.

2.2.3. SEM analysis

Studies on the morphology of fillers and the tensile fracture surfaces of the composites were carried out using a FE-SEM (Ultra 55, Carl Zeiss SMT AG, Germany).

2.2.4. Mechanical testing

Tensile and bending tests were carried out with a Universal Testing Machine AG-X plus, Shimadzu, Japan according to ISO 527-3 and ISO 178, respectively. Izod impact test was conducted with HIT 50P, Zwick/Roell, Germany according to ISO 180 at room temperature. Each value obtained represented the average of five samples at least.

2.2.5. Accelerated UV weathering

Composite samples were placed in a xenon arc-type light exposure apparatus and operated according to ASTM D2565. Samples were mounted on a drum that rotated around the chamber at 1 rpm, in four rows. The samples were rotated periodically to ensure that all samples were exposed to the same irradiance. The exposure cycle consisted of 108 minutes of light exposure and 12 minutes of simultaneous water spray and light exposure. Samples were removed after 250, 500, 1000 and 2000 hours of exposure for analysis.

2.2.6. Optical Properties

A CM-3600d Fa Konica Minolta spectrophotometer was used to measure color of the composite specimens using the CIE LAB color system. L*, a* and b* were measured for five replicate samples. The total change in color (ΔE) after weathering was calculated in according to DIN 6174 using the following equation:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \qquad \text{(Eq. 1)}$$

Where: ΔL, Δa và Δb represent the differences between the initial and final values of L*, a*, and b*, respectively (Fig 1).

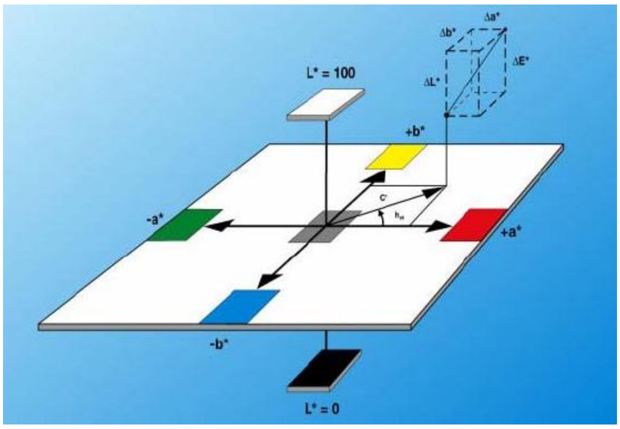


Fig 1: CIE - L*a*b*

2.2.7. Accelerated decay test

Susceptibility to biodegradation was assessed according to ASTM D 2017. The specimens with dimension of 80 x 10 x 4 mm were dried at 50°C to a constant weight and conditioned at a standard environment of 27 ± 2°C. After cooling, the test specimens were exposed to the white rot fungus *Phanerochaete chrysosporium* and the brown rot fungus *Trichoderma spp*. After 12 weeks, the specimens were brushed free of mycelium. The specimens were then reconditioned to a constant weight at the standard environment before the percentage of weight loss due to fungal decay was determined.

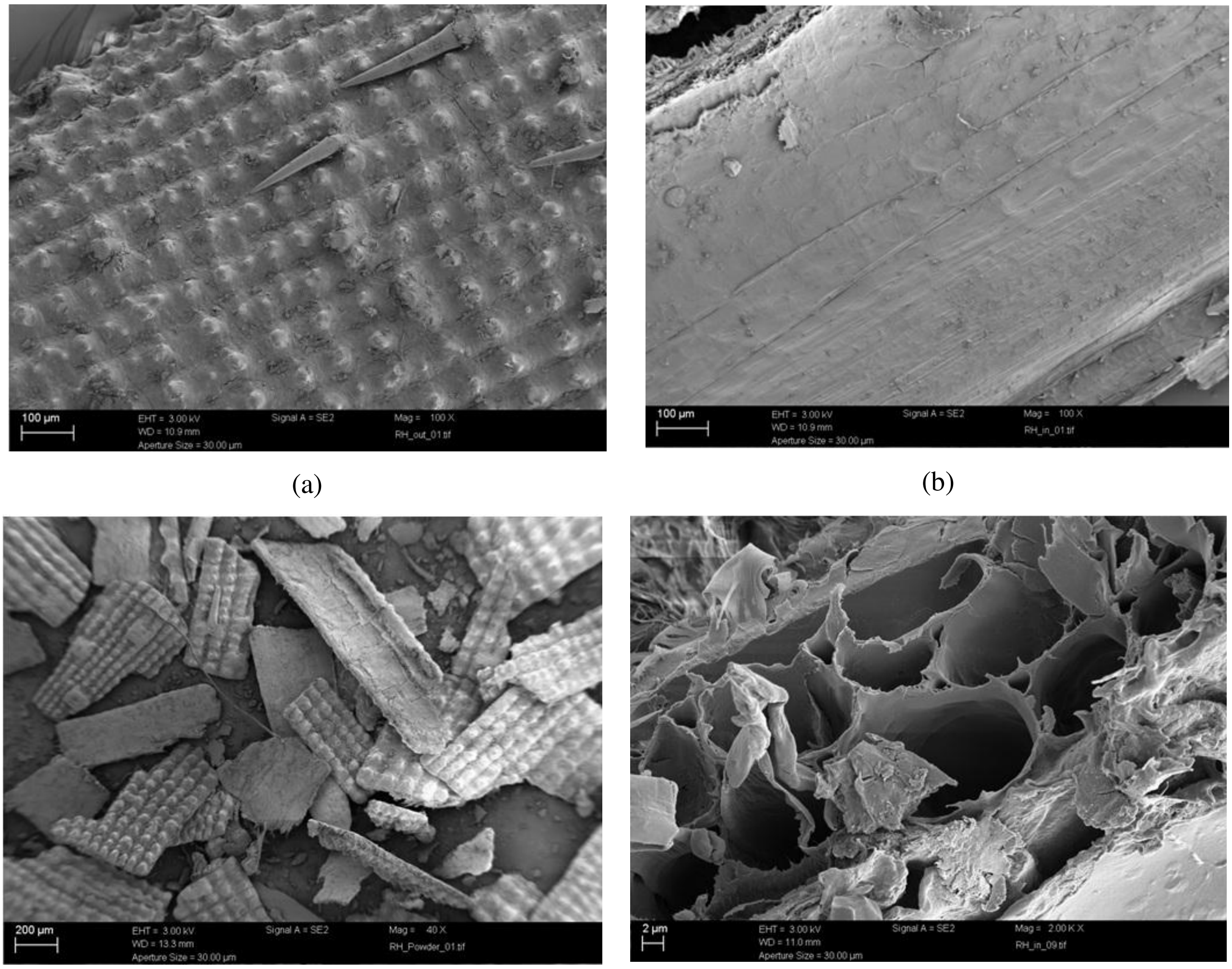
2.2.8. Water absorption test

The water absorption tests were conducted according to ASTM D 1037–99. Water absorption was determined by immersing the specimens in distilled water at room temperature. The weight change was periodically measured. The difference between the mass after a given time of immersion and the initial mass compared to the initial mass led to the determination of the water absorption. A minimum of three specimens were tested for each sample.

3. RESULTS AND DISCUSSION

3.1. Some properties of rice husk

Figure 2a, b show the morphology by means of SEM images of both sides of rice husk. It can be seen that the external surface of RH is very rough with many aligned knob (Fig.2a). Hair-like structures were also observed in the gaps between the ridges in some regions, while the internal surface of RH is smoother with no knob on the surface (Fig.2b). The filler surface layer is relatively minor portion of filler but it plays an important role in wettability and surface tension. It has long been postulated that the inner RH surface contains lipid and proteinaceous compound and the lipid molecule is usually bonded to the protein molecule by ester or thioester bond [5]. The amount of lipid on the filler surface has influence on hydrophobicity and surface tension. The more amount of lipid on the filler surface means the more hydrophobic and more surface tension as well as smoother the RH inner surface forming a thin film.



(a) (b)

(c) (d)

Fig 2: Morphology of (a) outer, (b) inner, (c) particles and (d) cell structure of rice husk

For the composite material, filler size and shape are one of the most important factors. Figure 2c shows SEM images of RH particles after grinding. Most of rice husk particles after grinding have rectangular shape and different sizes. Like other natural fibers, rice husk has cellular structure and an empty lumen with a diameter about 10÷20 µm exists in each single fiber (Fig. 2d).

Table 1 shows the average length and width as well as aspect ratio of rice husk particles.

Particle size of RH filler ranging from 20 mesh to 35 mesh with the average length of 640 µm and the average width of 320 µm can be oversize and make the abrasion of processing machines due to high silica content. Therefore, RH fillers with the particle size above 35 mesh (under 500 µm) were chosen for preparing the composite samples.

Table 1: Size intervals and particle size distribution, aspect ratio of RH particles

Mesh	µm	Length (µm)	Width (µm)	Aspect ratio
20÷35	500÷850	640	320	2.02
35÷45	350÷500	402	208	2.82
45÷80	180÷350	360	148	2.75
>80	<180	251	116	2.39

Furthermore, the average aspect ratio of rice husk filler (under 3) is quite small comparing to other natural fibers. The smaller aspect ratio value of RH compared with other fibers indicated the "square-like" feature of RH particles [6].

3.2. The rice husk/polyolefin composites

3.2.1. Effect of filler content

The mechanical properties of the filler/polymer composites depend strongly on the particle size, degree of dispersion, interfacial adhesion and particle loading [7, 8]. Effect of filler content on mechanical properties of the rice husk/polyethylene composite (RH/PE) and the rice husk/polypropylene composite (RH/PP) are shown in figures 3÷4.

In the case without any modification, the interfacial adhesion between the polar rice husk filler and the apolar polyolefin matrix is poor. When rice husk content increases, weak interfacial adhesion area increases resulting in a decrease of the tensile and bending strengths (Fig.3).

The impact strength of a composite is influenced by many factors, including the toughness properties of the reinforcement, the nature of the interfacial region and frictional work involved in pulling the fiber out of the matrix. The nature of the interface region is of extreme importance regarding the task of determining the toughness of the composite [9, 10]. The notched Izod impact strength of rice husk/polyolefin composites is presented in Fig. 4. The impact test determines the amount of energy absorbed by a material during fracture. This absorbed energy is a measure of a given material's toughness and acts as a tool to study the brittle-to-ductile transition [11]. It was found that an increase in the filler content resulted in a decrease in the impact strength of the composites in the case of without any modification.

However, the addition of fillers to the polyolefin matrices increases the modulus significantly. Raising the filler content improves the stiffness of the composites. It can be seen in Fig.4 that the bending modulus of rice husk/polyolefin composites increases when rice husk content increased. Modulus reflects the capability of both filler and polymer matrix to transfer the elastic deformation in the case of small strains without interface fracture.

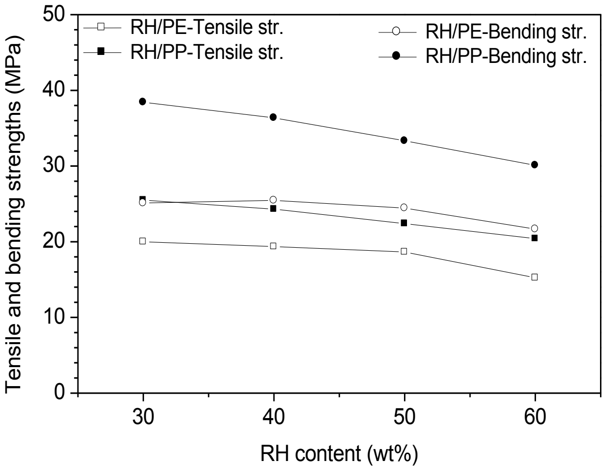


Fig 3: Effect of rice husk content on tensile and bending strengths of the composites

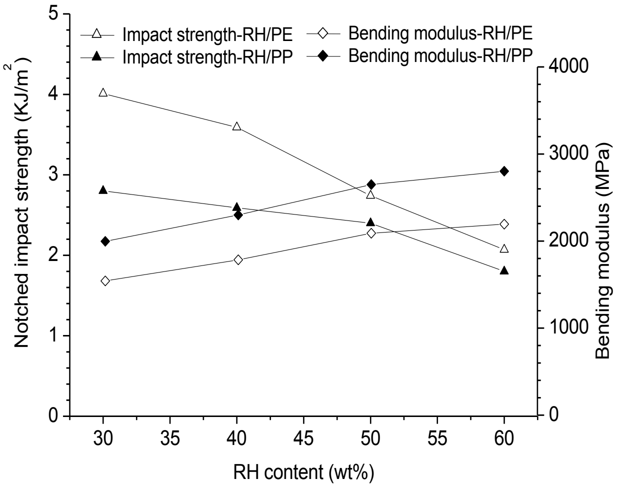


Fig 4: Effect of rice husk content on impact strength and bending modulus of the composites

3.2.2. Effect of compatibilizer content

To improve the bonding strength between the rice husk and polyolefin, matrix modification was done by using compatibilizers. Figure 5 shows the effect of compatibilizer content on mechanical properties of the composites containing 50 wt.% rice husk filler.

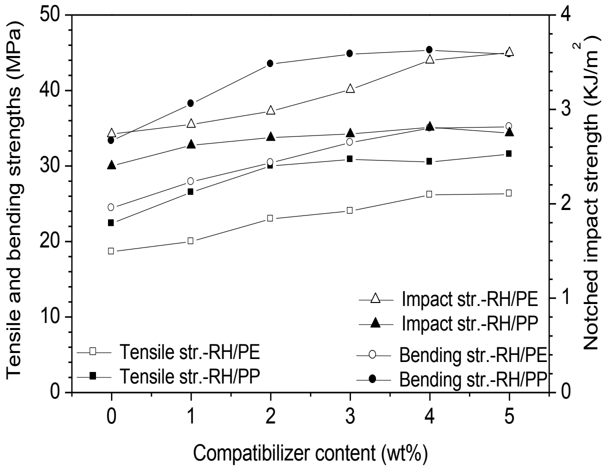


Fig 5: Influence of compatibilizer content on the strengths of the composites

Tensile, bending and impact strengths increased while adding compatibilizers and levels off at above 4wt% MAPE for PE matrix composite and 2wt% MAPP for PP matrix composite. The increase in strengths of the composites is due to the improved interfacial adhesion between the RH filler and polyolefin matrix. The maleic anhydride groups of MAPE, MAPP interact with the polar RH filler surface (via chemical coupling or hydrogen bonding), while the polyolefin chains of MAPE, MAPP diffuse into the polyolefin matrix. Therefore, the interfacial strength is improved, which was also shown in some literatures [4, 5].

3.2.3. Morphological study

Figure 6 shows the tensile fracture surfaces of the composites at 50 wt.% filler without and with compatibilizers (4 wt% for PE matrix composite and 2 wt% for PP matrix composite).

The composites without compatibilizers (Figure 6-left) displayed a rough morphology with the presence of many voids between the filler particles and the polymer matrix, clearly indicating the poor interaction between them. From Figures 6 (right), it is possible to verify that the presence of compatibilizers reduced the voids sizes as well as amount and turned the surface more homogeneous confirming its effect on promoting adhesion in the interfacial region.

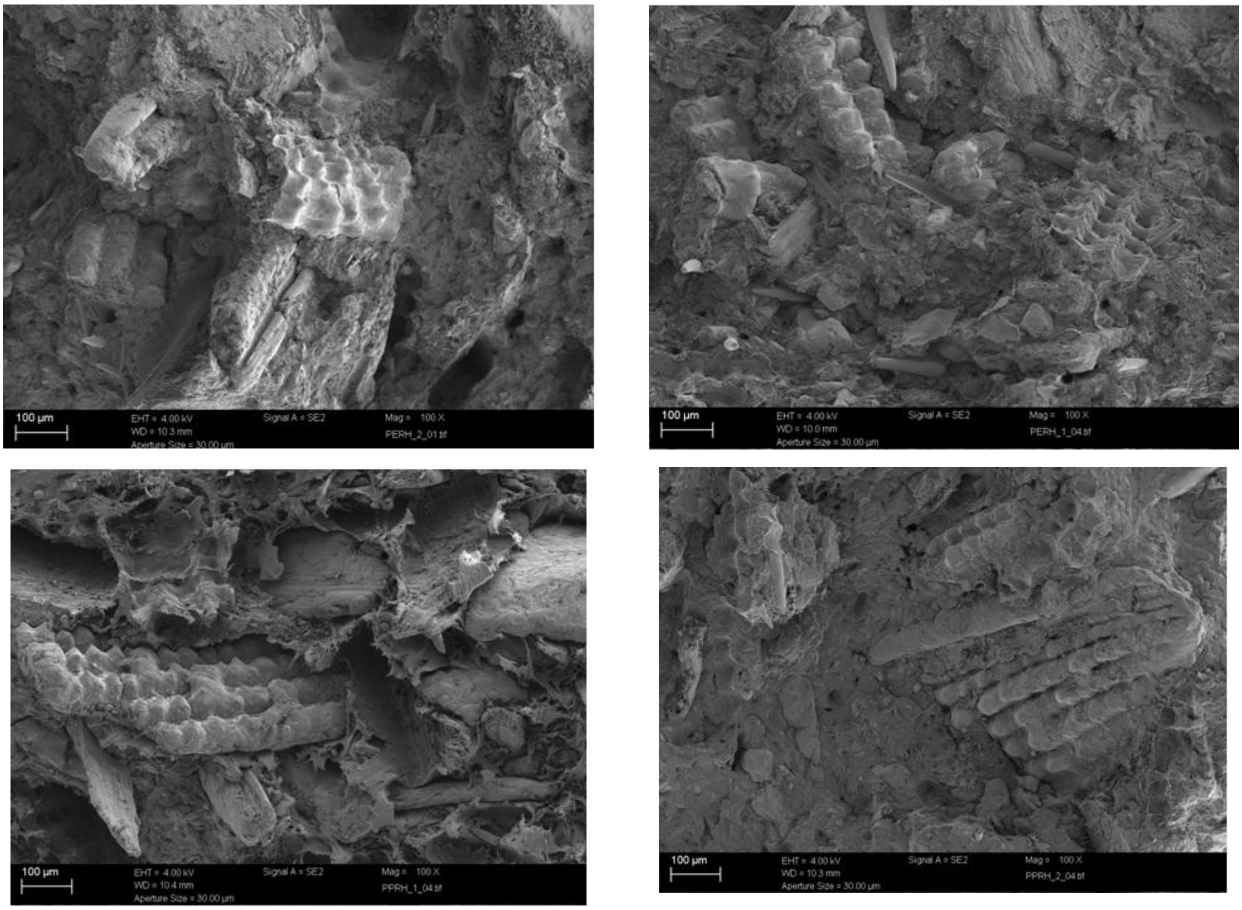


Fig 6: SEM micrographs of tensile fracture surfaces of the RH/PE composites (top), the RH/PP composites (bottom) without (left) and with compatibilizers (right)

3.2.4. Optical and mechanical property changes during accelerated weathering

To improve some properties of the composites during processing and using, some additives were also added with the content as seen in Table 2.

Table 2: Formulas for producing the RH/polyolefin composites

Components	Composite samples			
	RH/PE (%)	RH/PE +Add (%)	RH/PP (%)	RH/PP +Add (%)
Rice husk	50	50	50	50
Polyethylene	46	42.5	-	-
Polypropylene	-	-	48	43.9
MAPE	4	4	-	-
MAPP	-	-	2	2
Songnox 1010	-	0.5	-	0.7
Songlight 7700	-	0.5	-	0.7
Songsob 3260	-	0.5	-	0.7
Zinc borate	-	2	-	2

Color changes:

Fig. 7 shows the changes in total color (Delta E-ΔE) of neat polyolefin (PE, PP) and RH/polyolefin composites with and without additives at different exposed time. The Delta E values of all samples generally increased with increasing exposed time. The neat PE, PP samples exhibited less color changes than the PE, PP matrix composite samples. Among the composite samples, the PP matrix composite without additive exhibited the most severe color changes. The value of Delta E changed significantly in the first 1000h and then leveling off. In contrast, the PE matrix composite has more color stability and the value of Delta E increased gradually with the exposed time. The addition of the additives improved significantly the color stability of the composites.

Changes of mechanical properties:

Similarly, bending and impact strengths of the polypropylene matrix composites decreased much more than the polyethylene matrix composites after accelerated UV weathering for 2000h. The strengths of both composite systems improved while adding the additives (Fig.8).

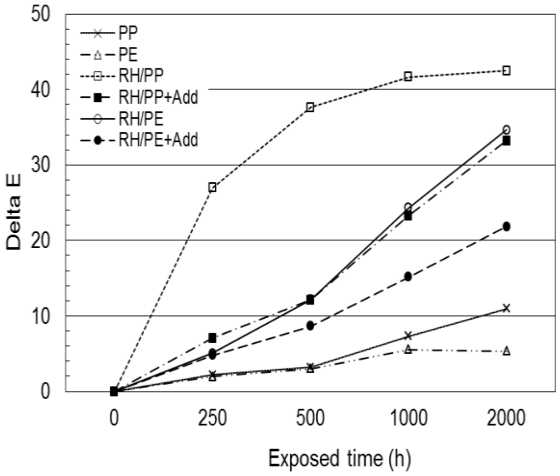


Fig 7: Changes in total color parameters of the neat polyolefin and the RH/polyolefin composites

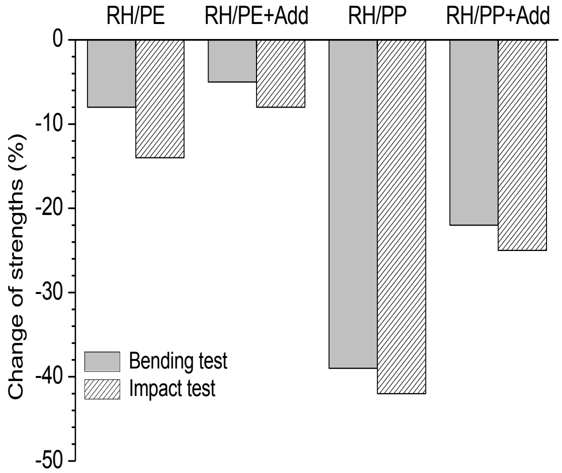


Fig 8: Changes in bending and impact strengths of the polyolefin matrix composites with and without additives

Surface characteristics

SEM micrographs in Figure 9 reveal the smooth surfaces of RH/polyolefin composites before weathering. After accelerated UV weathering for 2000 h, matrix cracks and defects appeared significantly on the surface of the polypropylene matrix composite. While the polyethylene matrix composite suffered less crack formation after 2000 h of exposure. In other words, the weatherability of the polyethylene matrix composite is better than that of the polypropylene matrix composite.

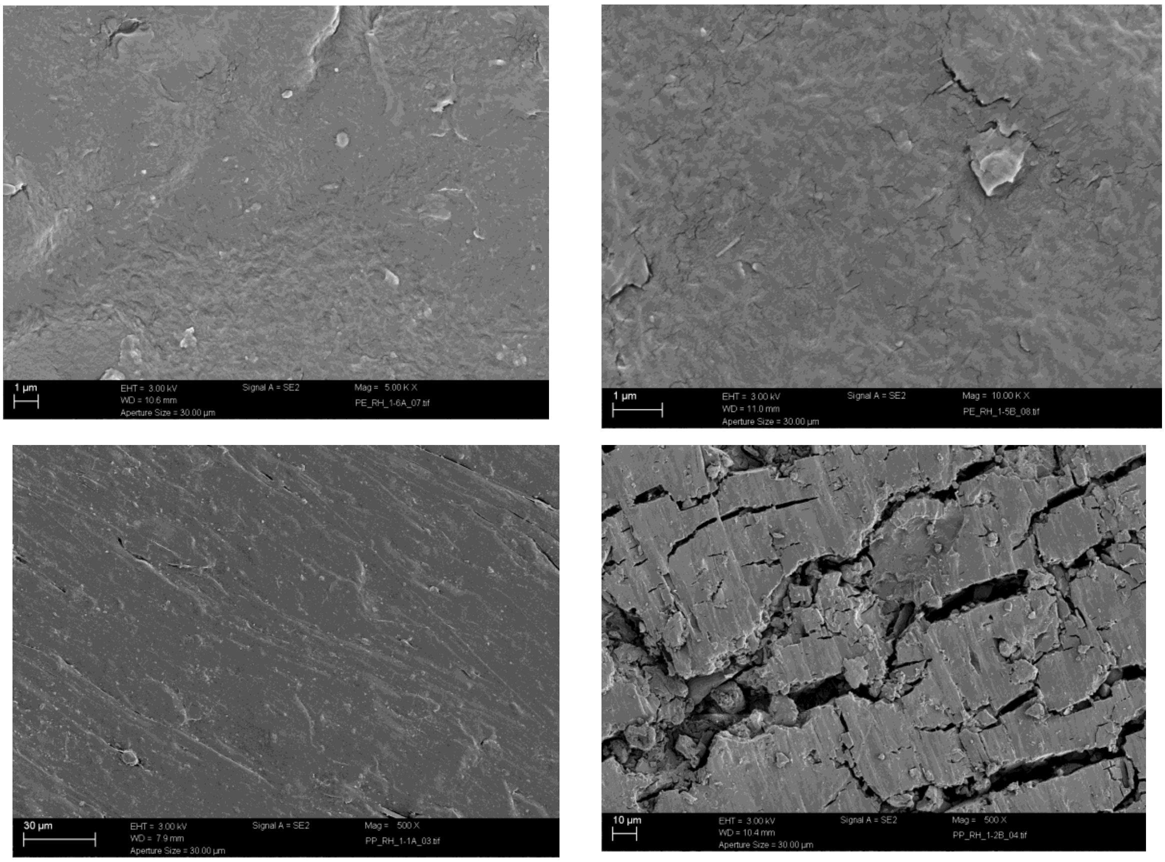


Fig. 9: SEM micrographs of the RH/PE composites (top), the RH/PP (bottom), before (left) and after accelerated weathering for 2000 h (right)

3.2.3. Fungal resistance

Weight loss is an important parameter for assessing decay of wood. For this reason, weight loss of RH/polyolefin composites containing the additives was determined and compared to Nyatoh wood, a common wood for furniture products in Vietnam. The average weight losses of the specimens after 12 weeks exposing to the white rot fungus *Phanerochaete chrysosporium and* the brown rot fungus *Trichoderma spp*. are presented in Fig. 10.

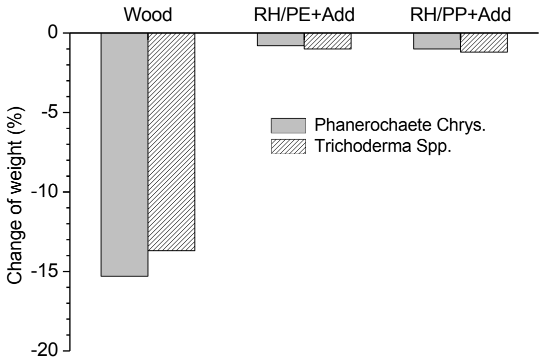


Fig. 10: Weight loss of wood and RH/polyolefin composites containing additives

After 12 weeks, the weight loss of the composites was under 1.2%, which was much less than that of wood (approximately 25%). That suggests the non-decay resistance properties of the composites.

3.2.4. Water absorption

Fig. 11 shows the values of the water absorption for the polyolefin and the composites up to 91 days immersed in distilled water. The water absorption of the polyolefin (<0.5%) is very low because the polyolefin are hydrophobic, whereas the RH/polyolefin composites (about 8%) have higher water absorption due to hydrophilic behavior of the rice husk filler. However, water absorption of the composites is much lower than that of the Nyatoh wood, approximately 140% (Fig 12).

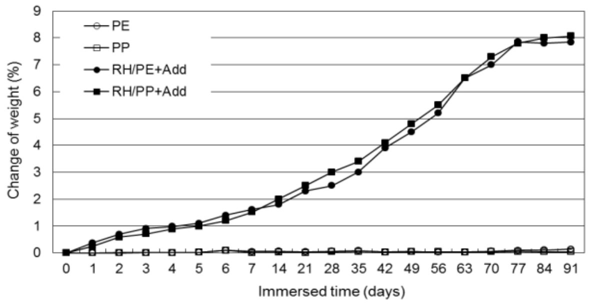


Fig. 11: Water absorption of the neat polyolefin and the RH/polyolefin composites

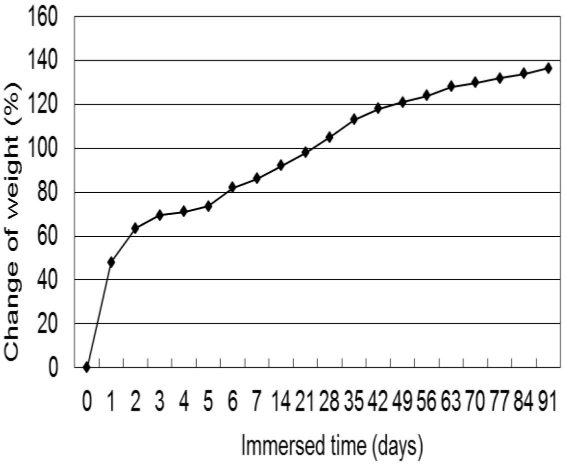


Fig. 12: Water absorption of wood

4. CONCLUSIONS

1. SEM micrographs show angular shapes, and some particular surface characters of rice husk filler.

2. As the RH filler content increased, the composites without compatibilizers showed decreased tensile, bending and impact strengths, but increased bending moduli.

3. The tensile, bending and impact strengths of RH/polyolefin composites improved with increasing compatibilizer content, due to the improvement of interface bonding between the filler and matrix.

4. SEM study confirmed the improvement of the interfacial adhesion between RH filler and polyolefin matrix.

5. The RH/polyolefin composites containing the additives had good fungal resistance and water resistance.

6. The neat polyethylene and the polyethylene matrix composite exhibited better stability under accelerated weathering, whereas the neat polypropylene and polypropylene matrix composites were destroyed seriously. Therefore, composites based on polypropylene matrix should not be used for the exterior applications.

7. The RH/polyolefin composites can be a potential material for house-wares and various construction applications (decking, railing, windows and doors, fencing…) replacing the conventional materials such as wood, plastics, metal, inorganic fiber reinforced composites…

With many advantages of RH filler, the next step of our research project is investigation on the rice husk filled composites based on cement matrix.

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