Water absorption behavior and mechanical properties of lignocellulosic filler–polyolefin bio-composites

Han-Seung Yang [a], Hyun-Joong Kim [a,*], Hee-Jun Park [b],
Bum-Jae Lee [c], Taek-Sung Hwang [d]

[a] *Laboratory of Adhesion and Bio-Composites, Major in Environmental Materials Science, Seoul National University, Seoul 151-921, South Korea*
[b] *Field of Engineering, Iksan National College, Iksan 570-752, South Korea*
[c] *Department of Fine Chemical Engineering & Chemistry, Chungnam National University, Daejeon 305-335, South Korea*
[d] *Department of Chemical Engineering, Chungnam National University, Daejeon 305-335, South Korea*

Available online 16 February 2005

Abstract

To determine certain physical properties, viz. the thickness swelling and water absorption, and mechanical properties, viz. the tensile strength and Izod impact strength, of lignocellulosic filler reinforced polyolefin bio-composites, polyolefin was used as the matrix polymer and rice-husk flour as the reinforcing filler. Wood flour was also used as a reinforcing filler, and commercial particleboard, medium-density fiberboard and solid woods (red pine and birch) were also included in this study, in order to obtain comparative water absorption behavior measurements. Test samples were prepared, in order to determine the physical and mechanical properties of the bio-composites as a function of filler loading and according to filler type as well as with respect to the thermoplastic polymer itself. The thickness swelling and water absorption of the bio-composites slightly increased as the filler loading increased, but to a negligible extent as compared with the wood-based composites (particleboard and fiberboard) and the solid woods (red pine and birch). The mechanical properties of the composites decreased as the filler loading increased, but the composites had an acceptable strength level. It was concluded that these bio-composites are suitable to be used for the interior of bathrooms, wood decks, food packaging, etc.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Thickness swelling; Water absorption; Lignocellulosic filler; Polyolefin; Thermoplastic polymer; Physical properties; Mechanical properties; Bio-composite

1. Introduction

The need for materials unharmful to the body and yet having appropriate properties has increased due to a lack of resources and increasing environmental pollution; thus, composites prepared from recycled materials are actively being sought after [7]. Especially, many synthetic polymeric materials are produced by combining with various reinforcing fillers to improve their mechan-ical properties and obtain the desired properties. Among these reinforcing fillers, active research is under way concerning the use of lignocellulosic materials, which are among the most environmentally friendly agro-wastes, as a substitute for synthetic materials [3]. The cost of producing composites comprising natural products such as lignocellulosic materials as the reinforcing filler and thermoplastic polymer as the matrix polymer is quite low. Furthermore, these materials can easily be obtained from waste products and have a minimal effect on the environment, due to their biodegradable properties; thus, in recent years, the emphasis has increasingly been placed on these composites, which may well play a

major role in resolving some of the pressing environmental issues with which we are confronted in the future [3–6].

Instead of the inorganic materials and synthetic fibers which were previously added to plastics as fillers, lignocellulosic materials offer many environmental benefits when used as reinforcing fillers for plastics, including their making the final product lightweight, decreasing the erosion of the manufacturing machinery, low cost, biodegradability, and absence of production of residue or toxic by-products when burnt [4]. Due to these benefits, continual development has been seen in the industry of wood–plastic composites, which saw active development after the 1980s leading to these composites being used extensively in automobile parts, window frames, various construction materials and bathroom parts. Wood–plastic composites with excellent moisture stability have the potential to create a new trend in construction materials and bathroom parts.

Compared with the reinforcing fillers previously used to fill plastics, i.e., inorganic materials and synthetic fibers, lignocellulosic material is composed of a hydro-

philic natural polymeric material possessing many –OH groups, which is able to combine with water molecules. When a composite containing lignocellulosic material is used in moist areas, the composite absorbs water. However, it is believed that no significant change occurs in the microstructure of the composite, because the reinforcing filler is encapsulated in the hydrophobic matrix polymer. In this study, the mixing ratio of reinforcing filler was studied as a function of the thermoplastic polymer type, as well as the physico-mechanical properties of the composite according to the compatibilizing agent content,

Table 1
Chemical constituents of the lignocellulosic fillers (rice-husk flour, wood flour and rice-husk powder)

	Holocellulose	Lignin	Ash	Others
RHF[a]	59.9	20.6	13.2	6.5
WF[a]	62.5	26.2	0.4	10.9
RHP[b]	60	20	17	3

Values are percentage by weight.
[a] Spec. from Saron Filler Co.
[b] Rice-husk powder from Ref. [3].

(a) Thickness swelling

(b) Thickness swelling (log-scale plot)

(c) Water absorption

(d) Water absorption (log-scale plot)
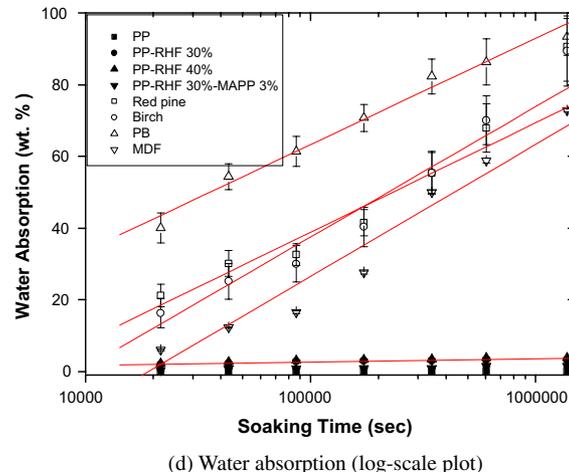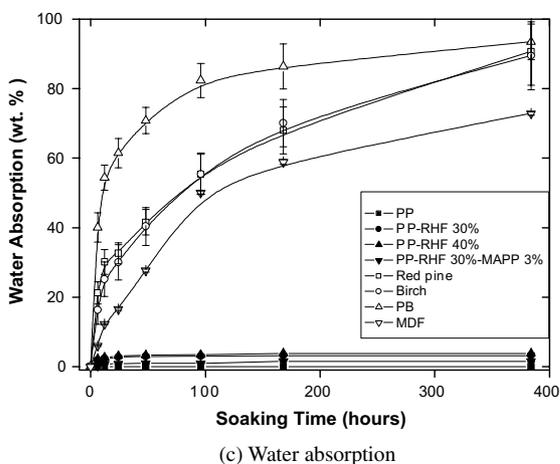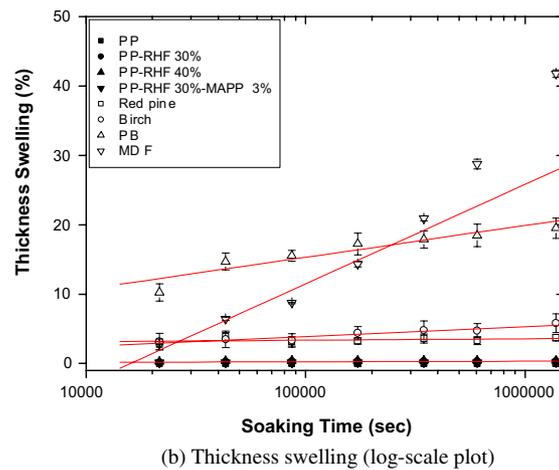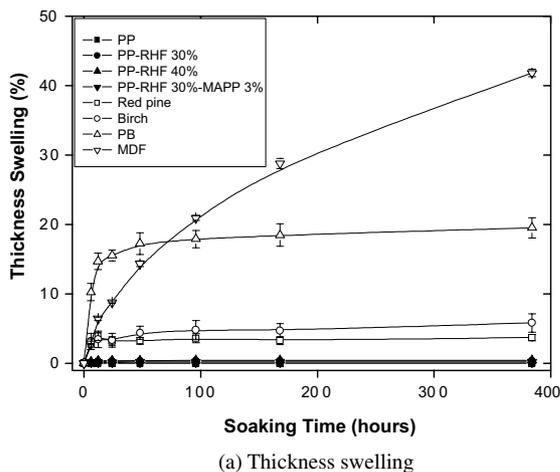
Fig. 1. Thickness swelling and water absorption of the PP–RHF bio-composites and control samples.

using a thermoplastic polymer as the matrix polymer and a lignocellulosic material (rice-husk flour and wood flour) as the reinforcing filler, with the goal of using the results of this study as basic data for future studies on the development of bio-composites containing lignocellulosic material as the reinforcing filler.

2. Experimental procedure

2.1. Matrix polymer

The thermoplastic polymer polypropylene was supplied by Hanwha L&C Corp., South Korea, in the form of homopolymer pellets with a density of 0.91 g/cm^3 and a melt flow index of 12 g/10 min (230 °C/2160 g). 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/2160 g). The high-density polyethylene (HDPE) was supplied by LG Chem. Ltd., South Korea, 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 (230 °C/2160 g).

2.2. Reinforcing filler

The lignocellulosic materials employed as the reinforcing filler in the composites used to obtain the comparative data were rice-husk flour (RHF) and wood flour (WF), for which the particle sizes were 80 to 100 mesh. The RHF and WF were supplied by Saron Filler Co., South Korea. The chemical constituents of the fillers are shown in Table 1.

2.3. Compatibilizing agents

The compatibilizing agent, MAPP (maleated polypropylene), was obtained from Eastman Chemical Products, Inc., in the form of Epolene G-3003^{TM}, which has an acid number of 8 and a molecular weight of 103,500. MAPE (maleated polyethylene) was obtained from Uniroyal Chemical, Inc., in the form of Polybond-3009^{TM}.
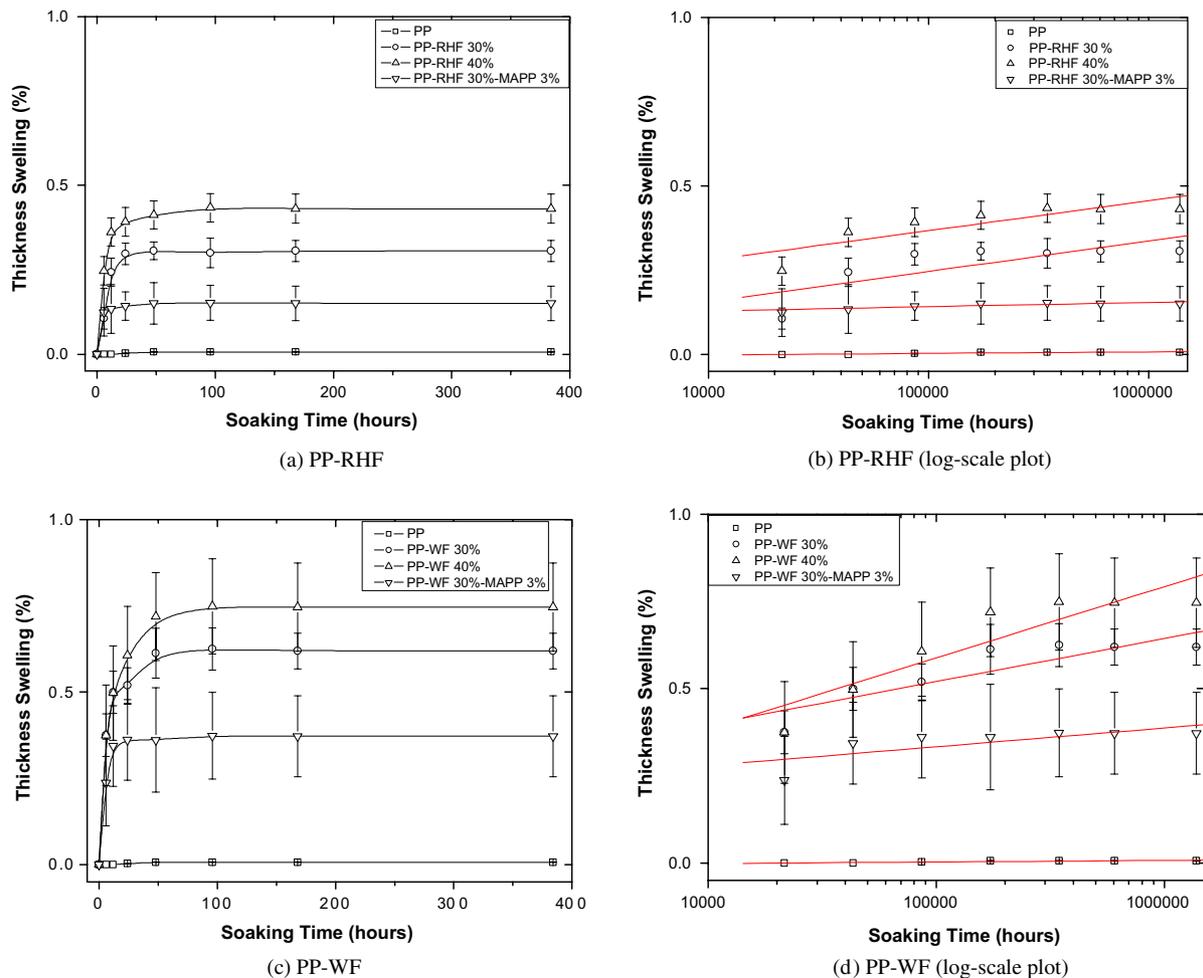
Fig. 2. Thickness swelling of the lignocellulosic filler–PP bio-composites at different filler loadings.

The content of the compatibilizing agent was 3% by weight of the test sample.

2.4. Sample preparation

RHF and WF were oven dried at 100 °C for 24 h to adjust their moisture contents to 4% or less, and then stored over a desiccant in sealed containers. The polypropylene and high-density polyethylene were blended with RHF and WF. A laboratory-size, twin-screw extruder was employed to compound the RHF and WF with the PP and HDPE used as matrix polymers. The extruded strand was pelletized and stored in sealed packs containing a desiccant. Four levels of filler loading (10, 20, 30 and 40 wt.%) were used in the sample preparation. The low-density polyethylene was blended with RHF and WF. A laboratory-size, twin-screw extruder

was employed to compound the RHF and WF with the LDPE used as a matrix polymer. The extruded strand was pelletized and stored in sealed packs containing a desiccant. Five levels of filler loading (10, 20, 30, 40 and 60 wt.%) were included in the sample preparation. The tensile strength and Izod Impact test specimens were prepared using an injection molding machine at 200 °C (PP and HDPE) and 140 °C (LDPE) at an injection pressure of 1200 psi using a device pressure of 1500 psi. After molding, the test specimens were conditioned before testing at 23 ± 2 °C, 50 ± 5% RH for at least 40 h according to ASTM D 618-99 [2].

2.5. Dimensional stability and water absorption behavior

The thickness swelling and water absorption tests were conducted according to ASTM D 1037–99 [2].

(a) LDPE-RHF

(b) LDPE-WF
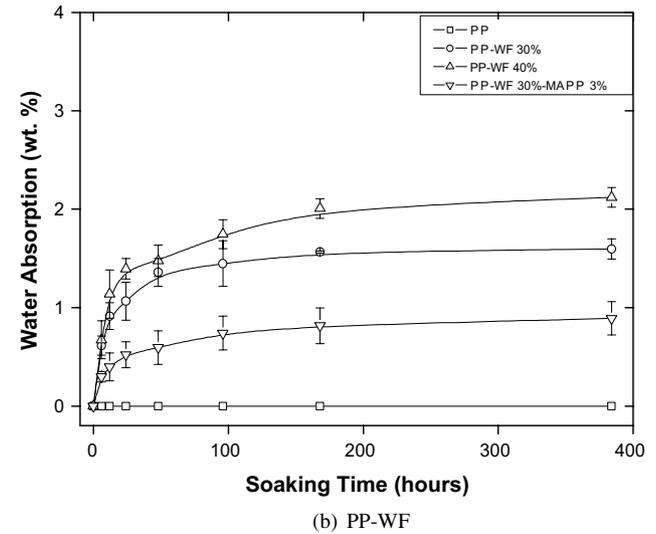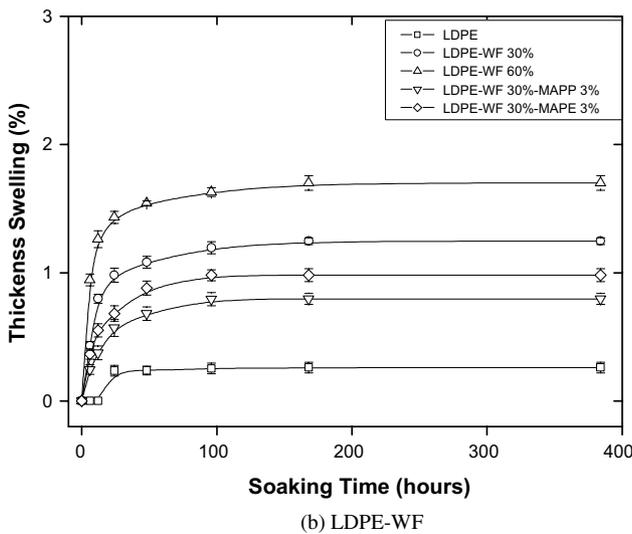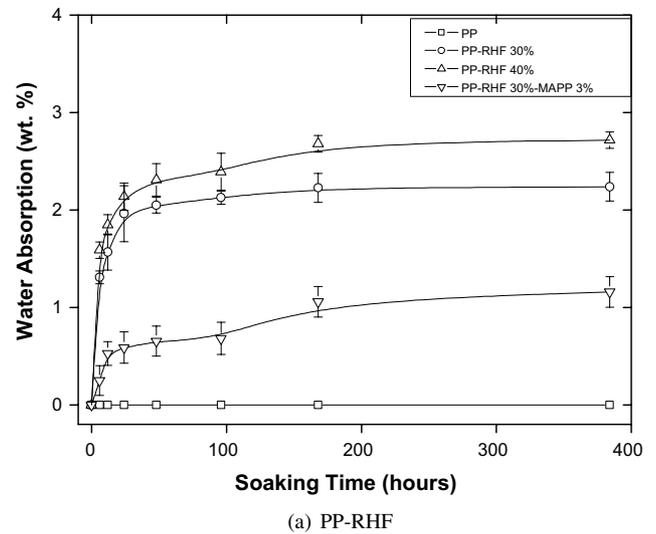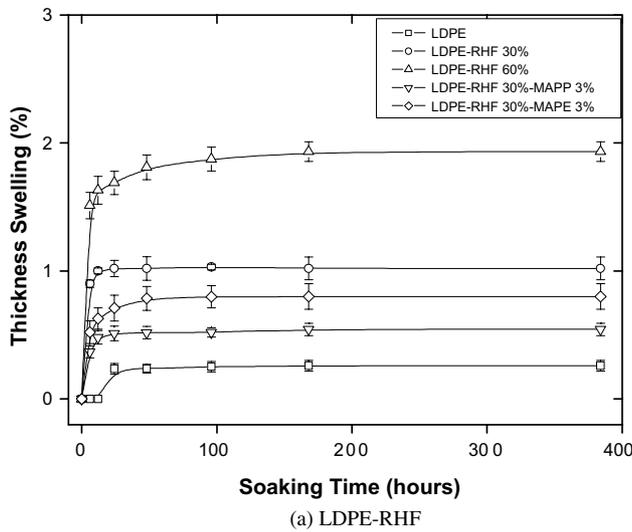
Fig. 3. Thickness swelling of the lignocellulosic filler–LDPE biocomposites at different filler loadings.

(a) PP-RHF

(b) PP-WF

Fig. 4. Water absorption of the lignocellulosic filler–PP bio-composites at different filler loadings.

Samples of each type of bio-composite were soaked in water. Commercial particleboard (PB), medium-density fiberboard (MDF) and solid woods (red pine and birch) were also tested to obtain comparative data. The specific gravities of the PB, MDF, red pine and birch were 0.60, 0.92, 0.47 and 0.49, respectively. At each testing time, samples were removed from the water, patted dry and then weighed. Each value obtained represented the average of five samples.

2.6. Mechanical testing

The tensile tests were conducted according to ASTM D 638-99 [2] with a Universal Testing Machine. The tests were performed at a crosshead speed of 100 mm/min and at room temperature. The notched Izod impact strength tests were conducted according to ASTM D 256-97 [1] at room temperature. Each value obtained represented the average of five samples.

3. Results and discussion

3.1. Thickness swelling and water absorption

Figs. 1–6 show the values of the thickness swelling and water absorption for the composites, which vary depending upon the filler loading, the incorporation or not of a compatibilizing agent and the type of matrix polymer. As shown in Figs. 2–6, the thickness swelling and water absorption of the bio-composites increased with increasing filler loading, but were nevertheless very low as compared with the control samples (wood particleboard, MDF and solid woods), as shown in Fig. 1, because the matrix polymers are hydrophobic, whereas the control samples are hydrophilic [6]. The shapes of the graphs in Figs. 1–6 are nearly logarithmic. The thickness swelling and water absorption of the wood particleboard, MDF and solid woods are significantly higher than those of the bio-composites, as shown in the log-scale graphs of Fig. 1. The gradients of the
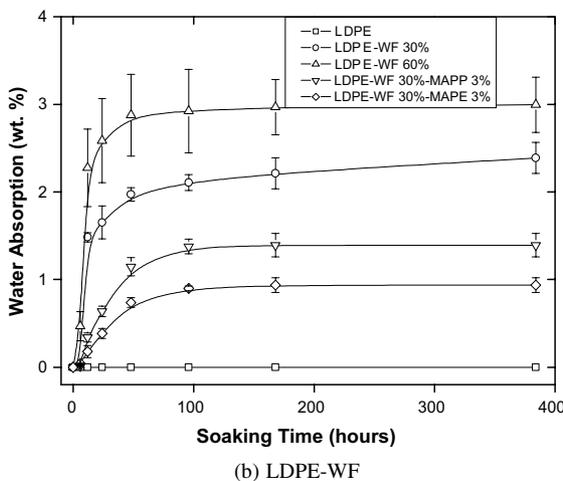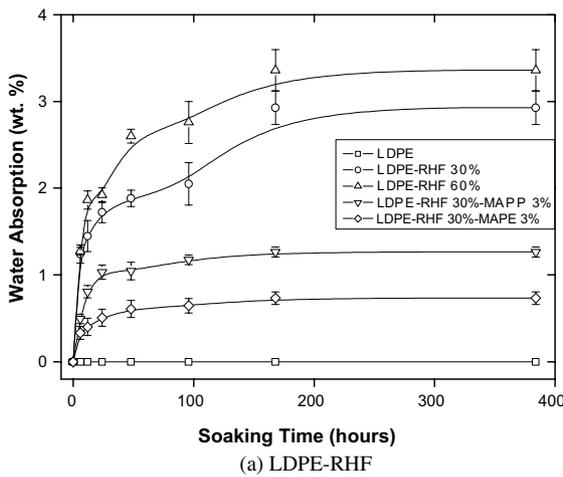
Fig. 5. Water absorption of the lignocellulosic filler–LDPE bio-composites at different filler loadings.
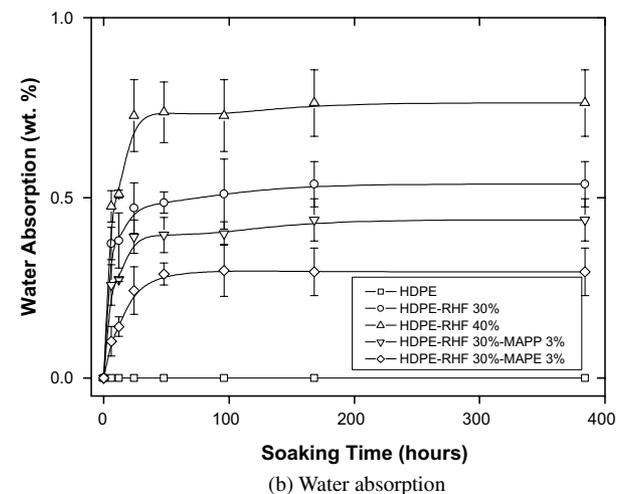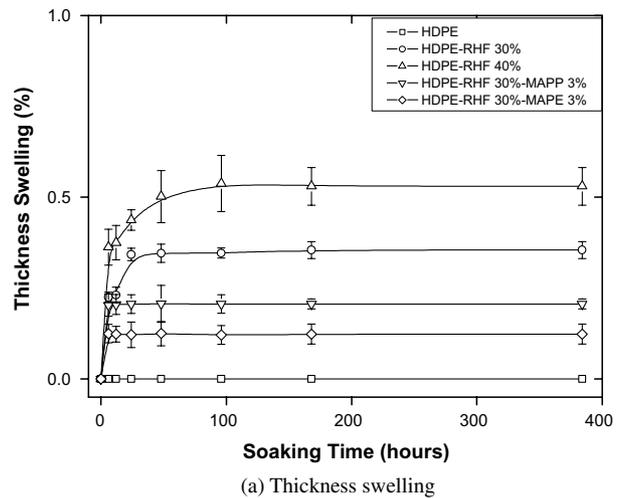
Fig. 6. Thickness swelling and water absorption of the HDPE–RHF bio-composites at different filler loadings.

thickness swelling graphs for the wood particleboard, MDF, red pine, birch and bio-composite (PP–RHF 30 wt.%) are 4.59, 14.37, 0.21, 1.42 and 0.09, respectively, while those of the water absorption graphs are 29.64, 39.28, 30.53, 36.36 and 0.89, respectively. The linear fit regressions of the log-scale graphs of Fig. 1 are as follows:

Thickness swelling
   PB: $y = -7.66 + 4.59x$, $R^2 = 0.92874$
   MDF: $y = -60.36 + 14.37x$, $R^2 = 0.93486$
   Red pine: $y = 2.29 + 0.21x$, $R^2 = 0.89019$
   Birch: $y = -3.23 + 1.42x$, $R^2 = 0.94128$
   Bio-composite (PP–RHF 30 wt.%): $y = -0.21 + 0.09x$, $R^2 = 0.75318$

Water absorption
   PB: $y = -85.03 + 29.64x$, $R^2 = 0.99058$
   MDF: $y = -170.52 + 39.28x$, $R^2 = 0.97926$
   Red pine: $y = -113.95 + 30.53x$, $R^2 = 0.95427$
   Birch: $y = -144.40 + 36.36x$, $R^2 = 0.97703$
   Bio-composite (PP–RHF 30 wt.%): $y = -1.89 + 0.89x$, $R^2 = 0.96672$

The PP and HDPE composites containing 30% lignocellulosic filler by weight showed less thickness swelling and water absorption than those containing 40% of the filler. As shown in the log-scale graphs of Fig. 2, the gradients of the thickness swelling graphs for PP–RHF 30 wt.%, PP–RHF 40 wt.% and PP–RHF 30 wt.%–MAPP 3 wt.% are 0.09, 0.10 and 0.01, respectively, while the gradients of the thickness swelling graphs for PP–WF 30 wt.%, PP–WF 40 wt.% and PP–WF 30 wt.%–MAPP 3 wt.% are 0.12, 0.20 and 0.05, respectively. The PP–RHF 30 wt.% bio-composite exhibited less thickness swelling than the PP–RHF 40 wt.% bio-composite. The PP–RHF 30 wt.%–MAPP 3 wt.% bio-composite exhibited significantly less thickness swelling than the other PP–RHF bio-composites, because the MAPP chemically bonded with the –OH groups in the lignocellulosic filler and this limits the water absorption, as shown in Fig. 7. The PP–WF bio-composites showed the same results as the PP–RHF composites. The linear fit regressions of the log-scale graphs of Fig. 2 are as follows:

Thickness swelling of PP–RHF bio-composites
   PP–RHF 30 wt.%: $y = -0.21 + 0.09x$, $R^2 = 0.75318$
   PP–RHF 40 wt.%: $y = -0.08 + 0.10x$, $R^2 = 0.84441$
   PP–RHF 30 wt.%–MAPP 3 wt.%: $y = 0.08 + 0.01x$, $R^2 = 0.84257$
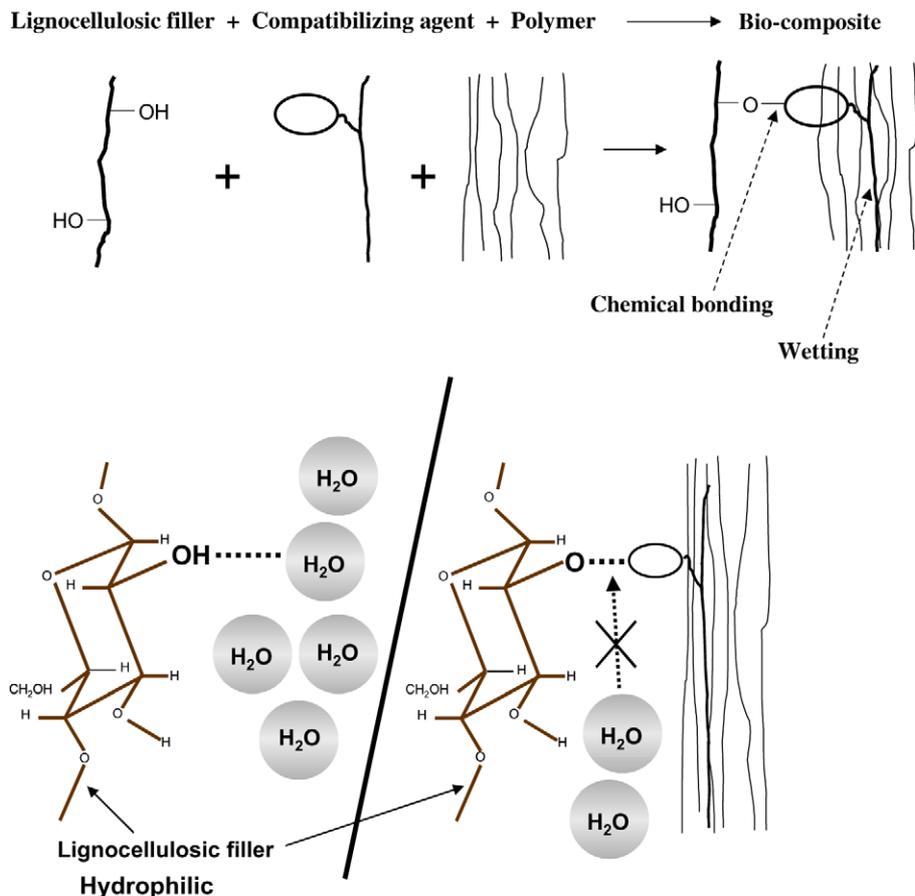
Fig. 7. The function of the compatibilizing agent in the lignocellulosic filler–polyolefin composite system.

Thickness swelling of PP–WF bio-composites

PP–WF 30 wt.%: $y = -0.10 + 0.12x$, $R^2 = 0.89196$

PP–WF 40 wt.%: $y = -0.43 + 0.20x$, $R^2 = 0.90452$

PP–WF 30 wt.%–MAPP 3 wt.%: $y = 0.06 + 0.05x$, $R^2 = 0.73508$

The LDPE composites containing 30% lignocellulosic filler by weight also exhibited less thickness swelling and water absorption than those containing 60% of the filler, because of the increased number of micro voids caused by the larger amount of poor bonded area between the hydrophilic filler and the hydrophobic matrix polymer. Water is easily absorbed by these voids. The thickness swelling and water absorption of the lignocellulosic filler–LDPE composites were higher than those of the lignocellulosic filler–PP composites. This was attributed to the weak interfacial adhesion between the PE chains and the lignocellulosic filler [6]. A significant difference was observed between the bio-composites and the control samples, in that the control samples showed much higher values of thickness swelling and water absorption than the bio-composites, and continued to absorb water at the end of the test, as shown in Fig. 1. From these results, it can be confirmed these bio-composites are suitable for use in damp places, such as the interior of bathrooms, wood decks, food packaging, etc. The bio-composite samples containing MAPP and MAPE showed lower thickness swelling and water absorption, as shown in Figs. 2–6. In Figs. 8 and 9, it can be seen that the thickness swelling and water absorption of the composites at the end of test (final TS and WA) are directly proportional to the filler loadings, and that the compatibilizing agents have a positive effect on the thickness swelling and water absorption. The strong interfacial bonding between the filler and matrix polymer caused by the compatibilizing agents limits the thickness swelling and water absorption of the composites.
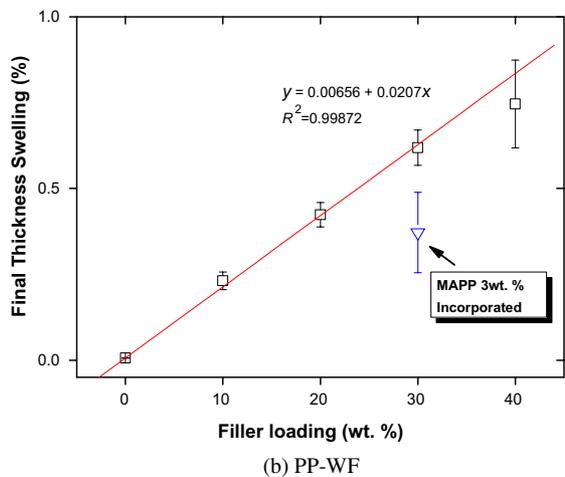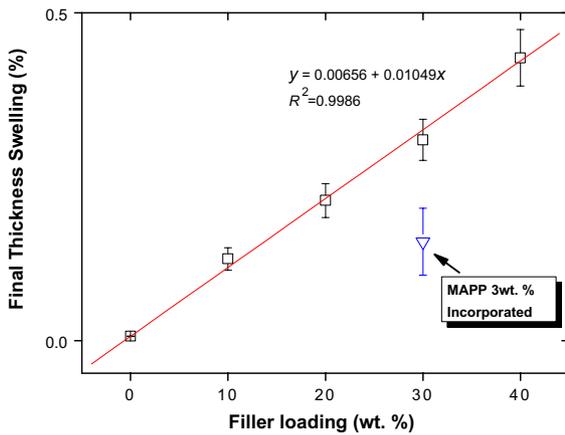
(a) PP-RHF

$y = 0.00656 + 0.01049x$
$R^2 = 0.9986$

MAPP 3wt. % Incorporated

(b) PP-WF

$y = 0.00656 + 0.0207x$
$R^2 = 0.99872$

MAPP 3wt. % Incorporated

Fig. 8. Thickness swelling of the lignocellulosic filler–PP bio-composites at the end of the test as a function of the filler loading.

(a) PP-RHF

$y = 0.0005 + 0.06904x$
$R^2 = 0.9994$

MAPP 3wt.% Incorporated

(b) PP-WF

$y = 0.0005 + 0.05304x$
$R^2 = 0.99917$

MAPP 3wt. % Incorporated
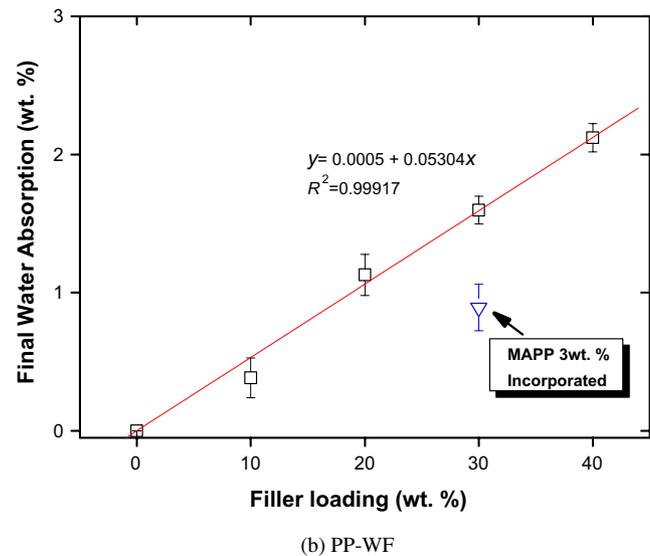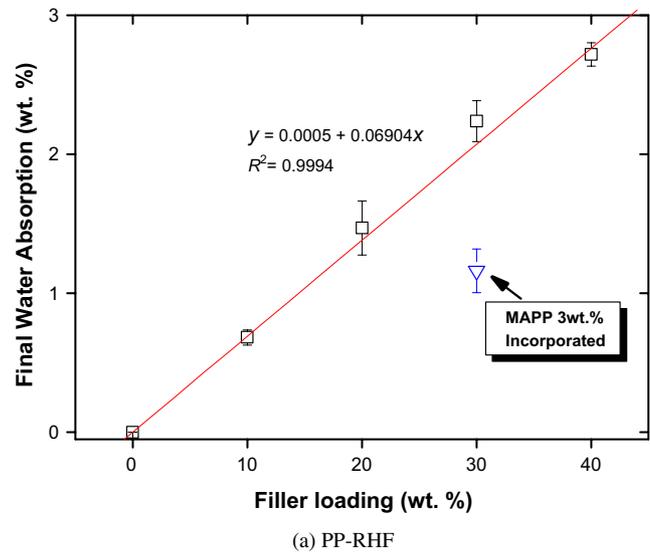
Fig. 9. Water absorption of the lignocellulosic filler–PP bio-composites at the end of the test as a function of the filler loading.

3.2. Mechanical properties

As the filler loading increased, thereby increasing the interfacial area, the worsening interfacial bonding between the hydrophilic filler and hydrophobic matrix polymer decreased the tensile strength, which nevertheless remained within acceptable levels [3]. The PP–RHF composites show slightly lower tensile strength than the PP–WF composites, as shown in Fig. 10, due to relatively lower holocellulose content of RHF, as shown in Table 1. The tensile strengths of the composites consisting of lignocellulosic filler (WF and RHF) and low and high-density polyethylene (LDPE and HDPE) matrixes at different filler loadings are shown in Fig. 11. The tests were conducted at room temperature. The LDPE–RHF composites also showed slightly lower tensile strength than the LDPE–WF composites, exhibiting the same tendency as that shown in Fig. 10. RHF is easily agglomerated, which is the characteristic of this filler, and the presence of these agglomerates results in the generation of flaws, which become larger in size wetting of filler by the matrix polymer macromolecules also become poor, resulting in the creation of voids between the filler and the matrix polymer. This causes the tensile strength of the RHF composites to be reduced, as compared with the WF composites [3]. The HDPE–RHF composites showed higher tensile strength than the PP–WF and PP–RHF composites, due to the tensile strength of HDPE being higher than that of PP. Generally, the tensile strength of the composites decreased with increasing filler loading, due to the poor interfacial bonding between the filler and the matrix polymer. This poor bonding causes increased micro voids in the composites, which results in increased water absorption, however the quantity of water absorbed is negligible compared with the water absorption of wood-based composites and solid woods.
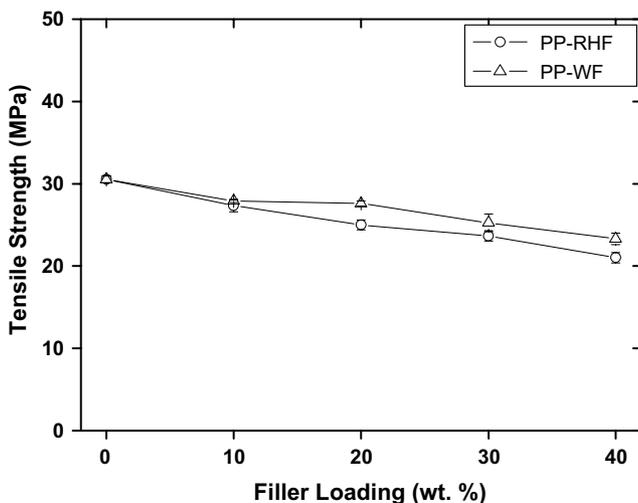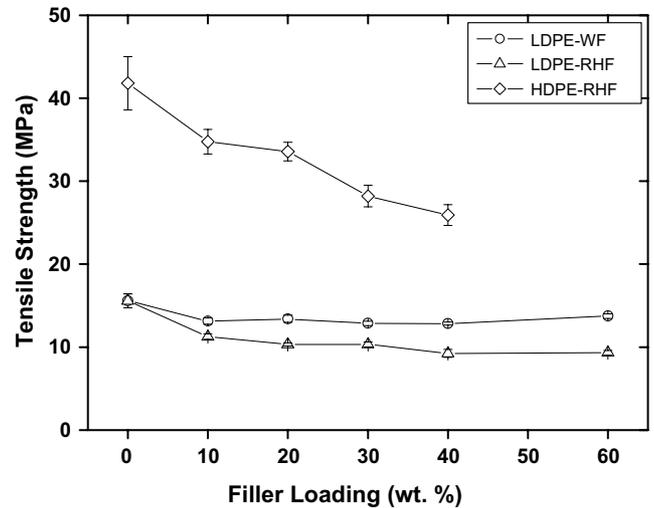
Fig. 11. Tensile strengths of the lignocellulosic filler–polyethylene bio-composites at a crosshead speed of 100 mm/min at room temperature.
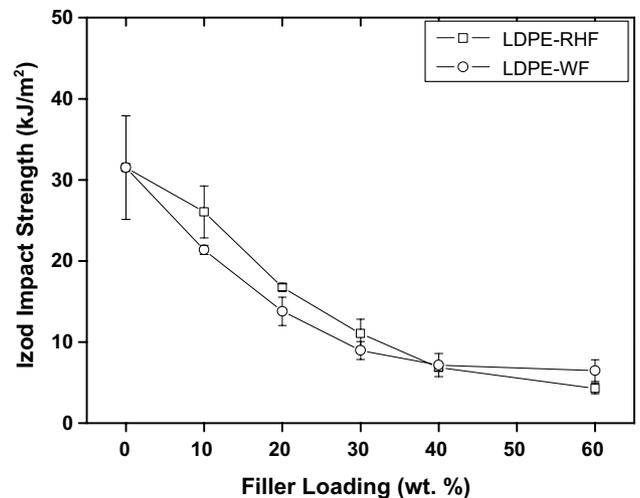
Fig. 12. Notched Izod impact strengths of the LDPE–WF and LDPE–RHF bio-composites at different filler loadings.

The Izod impact strengths of the LDPE–RHF and LDPE–WF composites at different filler loadings are shown in Fig. 12. The notched impact strengths decreased with increasing filler loading, due to the increase in size of the poor bonded area between the hydrophilic filler and the hydrophobic matrix polymer. LDPE is a very flexural matrix polymer, which causes the composites made with this material to have the highest impact strength among the unfilled samples, however as the filler loading increases, the brittleness of these composites increases.

4. Conclusion

The thickness swelling and water absorption of the bio-composites increased slightly as the filler loading

Fig. 10. Tensile strengths of the lignocellulosic filler–PP bio-composites at a crosshead speed of 100 mm/min at room temperature.

increased, but their values remained negligible as compared with those of the wood-based composites and solid woods. The compatibilizing agents had a positive effect on the thickness swelling and water absorption of these bio-composites, making them suitable for use in damp places, such as the interior of bathrooms, wood decks, food packaging, etc.

The tensile strengths of the bio-composites decreased slightly as the filler loading increased, however the composites retained an acceptable level of strength. As the filler loading increased, the poor interfacial bonding between the filler and the matrix polymer caused the tensile strength and Izod impact strength of the composites to be reduced, and this poor interfacial bonding resulted in an increase in the number of micro voids, causing increased water absorption. With the addition of the compatibilizing agent, the interfacial bonding between the filler and the matrix polymer was greatly improved, resulting in improved dimensional stabilities and water absorption behaviors.

Acknowledgements

References

[1] American Society for Testing and Materials. Annual book of ASTM standards. 100 Barr Harbor Dr., West Conshohocken, PA 19428, 1997.

[2] American Society for Testing and Materials. Annual book of ASTM standards. 100 Barr Harbor Dr., West Conshohocken, PA 19428, 1999.

[3] Hattotuwa G, Premalal B, Ismail H, Baharin A. Comparison of the mechanical properties of rice husk powder filled polypropylene composites with talc filled polypropylene composites. Polym Testing 2002;21(7):833–9.

[4] Ismail H, Nizam JM, Abdul Khalil HPS. The effect of a compatibilizer on the mechanical properties and mass swell of white rice husk ash filled natural rubber/linear low density polyethylene blends. Polym Testing 2001;20(2):125–33.

[5] Ismail H, Edyham MR, Wirjosentono B. Bamboo fibre filled natural rubber composites: the effects of filler loading and bonding agent. Polym Testing 2002;21(2):139–44.

[6] Son J, Kim H-J, Lee P-W. Role of paper sludge particle size and extrusion temperature on performance of paper sludge–thermoplastic polymer composites. J Appl Polym Sci 2001;82(11):2709–18.

[7] Yang H-S, Kim H-J, Son J, Park HJ, Lee BJ, Hwang TS. Rice-husk filled polypropylene composites; mechanical and morphological study. Compos Struct 2004;63(3):305–12.