Biodegradability and Mechanical Properties of Agro-Flour–Filled Polybutylene Succinate Biocomposites

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ABSTRACT: The objective of this study was the production of rice husk flour (RHF) and wood flour (WF) filled polybutylene succinate (PBS) biocomposites as alternatives to cellulosic material filled conventional plastic (polyolefins) composites. PBS is one of the biodegradable polymers, made from the condensation reaction of 1,4-butanediol and succinic acid that can be naturally degraded in the natural environment. We compared the mechanical properties between conventional plastics and agro-flour–filled PBS biocomposites. We evaluated the biodegradability and mechanical properties of agro-flour–filled PBS biocomposites according to the content and filler particle size of agro-flour. As the agro-flour loading was increased, the tensile and impact strength of the biocomposites decreased. As the filler particle size decreased, the tensile strength of the biocomposites increased but the impact strength decreased. The addition of agro-flour to PBS produced a more rapid decrease in the tensile strength, notched Izod impact strength, and percentage weight loss of the biocomposites during the natural soil burial test. These results support the application of biocomposites as environmentally friendly materials. J Appl Polym Sci 97: 1513–1521, 2005

Key words: biocomposites; biopolymers; agro-flour; biodegradable; mechanical properties

INTRODUCTION

In recent years, as a result of growing environmental awareness, agro-fillers have been increasingly used as reinforcing fillers in thermoplastic composite materials. Agro-fillers are composed of cellulosic and lignocellulosic materials, such as wood flour (WF), rice husk flour (RHF), wheat straw, and bagasse. Agro-fillers, available in fiber and powder form, can be used as reinforcement for thermoplastic composites.[1,2] Thermoplastic polymers derived from petroleum-based synthetic resources, such as polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polystyrene (PS), have generally been used as matrix polymers. However, these polymers do not degrade easily in the natural environment, resulting in various forms of environmental pollution. To solve this problem, the use of environmentally friendly degradable polymers is considered as an alternative to conventional plastic materials.[3,4]

Nowadays, there is great interest in the development of biodegradable polymers as a solution to environmental problems. Most of the biodegradable synthetic polymers are mainly aliphatic polyesters produced by microbiological and chemical synthesis, natural polymer-based products, and their blends. Polybutylene succinate (PBS) is one of the aliphatic thermoplastic polyesters with a range of desirable properties including biodegradability, melt processability, and both thermal and chemical resistance. PBS is produced through the condensation reaction of glycols such as 1,4-butanediol and aliphatic dicarboxylic acid such as succinic acid used as principal raw materials. Aliphatic polyesters can be naturally degraded into the natural environment by bacteria and fungi.[3,5–7] In recent years, many attempts have focused on making aliphatic polyester composites from cellulosic materials with low cost, renewability, biodegradability, and nontoxicity.[8,9] RHF and WF are two of the agro-materials that can be used as reinforcing fillers in biodegradable polymer biocomposites. Rice husk is an agricultural waste material generated in rice-producing countries, especially in the Asian, Pacific, and North American regions. Most of this rice husk is used as a bedding material for animals and the industrial applications of this material are limited. Therefore, the use of rice husk in the manufacture of agro-material–filled biodegradable polymer biocomposites is attracting much attention because of the potential biomass energy.[10]

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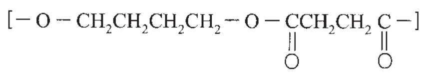


Figure 1 Chemical structure of polybutylene succinate (PBS).

In the present article, we discuss the biodegradability and mechanical properties of agro-flour–filled PBS biocomposites. We used aliphatic thermoplastic polyester (PBS) as a matrix polymer and RHF and WF as reinforcing fillers. We evaluated the biodegradability and mechanical properties of the RHF-filled PBS biocomposites as a function of the RHF content and mesh size. In addition, the biodegradability and mechanical properties of the resulting WF-filled PBS biocomposites were compared with those of the RHF-filled PBS biocomposites.

EXPERIMENTAL

Materials

Polybutylene succinate [PBS; melt flow index: 20 g/10 min (190°C/2160 g); density: 1.22 g/cm^3; number-average molecular weight (M_n): 5.5 × 10^4] was supplied by SK Chemical Co. (Seoul, South Korea). The chemical structure of PBS is presented in Figure 1. The agro-fillers used as the reinforcing filler were rice husk flour (RHF) and wood flour (WF). These fillers were obtained from Saron Filler Co. and Korea Forest Research Institute, South Korea, respectively. The particle sizes of RHF were 80 to 100 and 200 mesh; the particle size of WF was 80 to 100 mesh. The chemical constituents of agro-fillers are listed in Table I.

Compounding and sample preparation

RHF and WF were dried to 1–3% moisture content using an air-dryer oven at 105°C for 24 h and then stored in sealed polyethylene bags in an environmental controller before compounding. The compounding of PBS with RHF and WF, which is performed in a twin-screw extruder, is similar to polymer blending. The laboratory-size extruder was a twin-screw extruder, which blends aliphatic thermoplastic polyester with agro-filler, using three general processes: melt blending, extrusion, and pelletizing. Compounding was performed at 140°C for 3 min with a screw speed of 300 rpm. The extruded strand was pelletized and dried at 80°C for 24 h. The dried pellets were stored in sealed polyethylene bags to avoid moisture infiltration. These composites with four different filler loadings (10, 20, 30, and 40 wt %) were prepared for measuring mechanical properties and biodegradability. Extruded pellets were injection molded into tensile (ASTM D638) and Izod impact (ASTM D256) test bars using an injection-molding machine (Bau Technology, Seoul, South Korea) at 140°C with an injection pressure of 1200 psi and a device pressure of 1500 psi. After injection molding, test bars were conditioned before testing at 50 ± 5% relative humidity (RH) for at least 40 h according to ASTM D 618-99.

Mechanical property tests

The tensile test for biocomposites was conducted according to ASTM D 638-99 with a Universal Testing Machine (Zwick Co., Bamberg, Germany) at a crosshead speed of 100 mm/min and a temperature of 24 ± 2°C. Notched Izod impact strength was measured on an impact tester (Dae Yeong Co., Kyongbuk, South Korea) by ASTM method D 256-97 at room temperature. Five measurements were conducted and each value obtained was determined by the average of five samples.

Biodegradability

The biodegradability of the biocomposites was measured during natural soil burial for 4 months. After each soil burial test of 10, 20, 30, 40, 60, 80, 100, and 120 days, the buried specimens were dug out each day, washed in distilled water, and dried in an air-drying oven at 60 ± 2°C for 24 h before undergoing weight loss and mechanical property tests. The percentage weight loss was estimated using an electronic balance. Mechanical property tests after natural soil burial test were performed on tensile and notched Izod impact strength, measured according to mechanical property test methods. Five measurements were conducted for

TABLE I
Chemical Constituents of Agro-Flours

	Other components	Holocellulose	Lignin	Ash
Rice husk flour[a]	5.0	60.8	21.6	12.6
Wood flour[a]	10.9	62.5	26.2	0.4
Rice husk flour[b]	6.3	59.9	20.6	13.2

[a] Rice husk and wood flours from Kim and Eom.[23]
[b] Specification from Saron Filler Co. (South Korea).

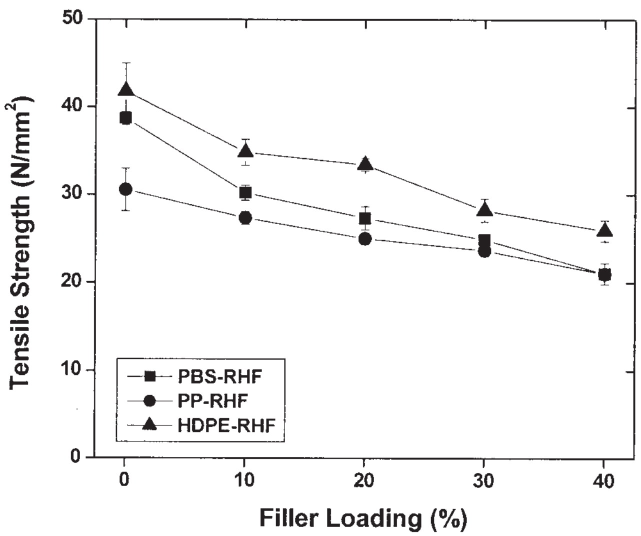


Figure 2 Comparison of tensile strength of RHF (rice husk flour) filled PP, HDPE, and PBS biocomposites. PP-RHF and HDPE-RHF: Results of reference [22].

tensile and impact strength sample after the natural soil burial test.

Morphological test

Scanning electron microscopy (SEM) was used to measure the fracture and degraded surfaces of the tensile and notched Izod impact specimens. Electron micrographs were obtained using a scanning electron microscope [JEOL-5410 LV (Tokyo, Japan); NICEM at Seoul National University] on specimens collected before and after biodegradation testing in natural soil. Before the measurement, the specimens were coated with gold (purity, 99.99%) to eliminate electron charging.

RESULTS AND DISCUSSION

Mechanical properties

Tensile strength

Figure 2 shows the tensile strength of RHF (80–100 mesh) filled PP, HDPE, and PBS composites at different filler loadings and a crosshead speed of 100 mm/min. The tensile strength of RHF-filled PBS biocomposites was higher than that of RHF-filled PP composites and lower than that of RHF-filled HDPE composites. These results support the application of agro-flour–filled PBS biocomposites as an alternative to conventional plastic materials. The tensile strength of agro-flour (RHF and WF) filled PBS biocomposites at different filler loadings is shown in Figure 3. As RHF loading increased, the substantial decrease in tensile strength could be attributed to weak interfacial adhesion between RHF and the matrix polymer, which promotes microcrack formation at the interfacial area.[8] On the contrary, the tensile strength slightly decreased with increasing WF content, up to a filler loading of 10 wt%, after which it remained almost constant. The tensile strength of WF-filled PBS biocomposites was higher than that of RHF-filled PBS biocomposites. This result may have been affected by the chemical constituents of agro-flour, which is composed mainly of holocellulose and lignin. Hemicellulose may act as a link between the cellulose and amorphous lignin. Lignin not only holds the agro-flour together, but also acts as a stiffening agent for the cellulose molecules within the agro-flour cell wall. Thus, the strength of the agro-flour can be affected by the content of holocellulose and lignin. Because of the higher holocellulose and lignin content of WF, the tensile strength of WF-filled PBS biocomposites was slightly higher than that of RHF-filled PBS biocomposites.[11,12]

Figure 3 shows the tensile strength of RHF-filled PBS biocomposites according to filler particle size. A slight increase in tensile strength with smaller RHF particle size is evident (200 mesh), indicating that the smaller RHF offers a larger specific surface area in the biocomposites than that of the larger RHF, at the same weight fraction. As the surface area increases, good particle dispersion in the matrix polymer enhances interfacial adhesion between the filler and matrix polymer.[13,14]

The tensile stress–strain curves of RHF (200 mesh), RHF (80–100 mesh), and WF (80–100 mesh) filled PBS biocomposites are shown in Figure 4(a), (b), and (c), respectively. In general, the stress–strain behavior of these biocomposites is nonlinear, mainly because of the polymer matrix deformation. As the filler loading increased, the tensile stress and strain of all biocom-

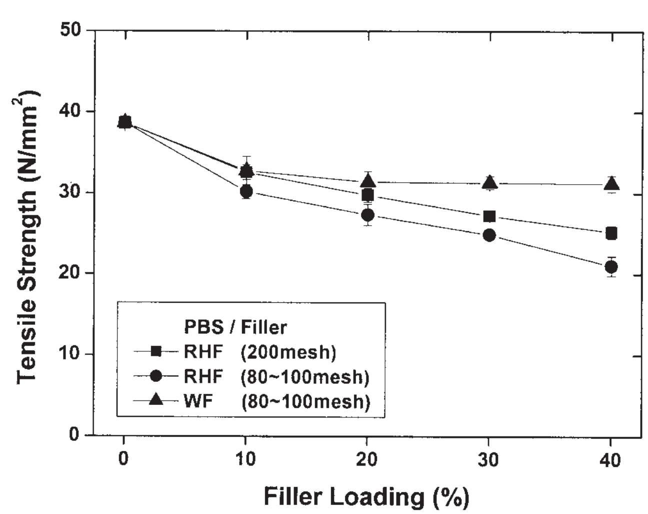


Figure 3 Comparison of tensile strength of RHF and WF (wood flour) filled biocomposites.

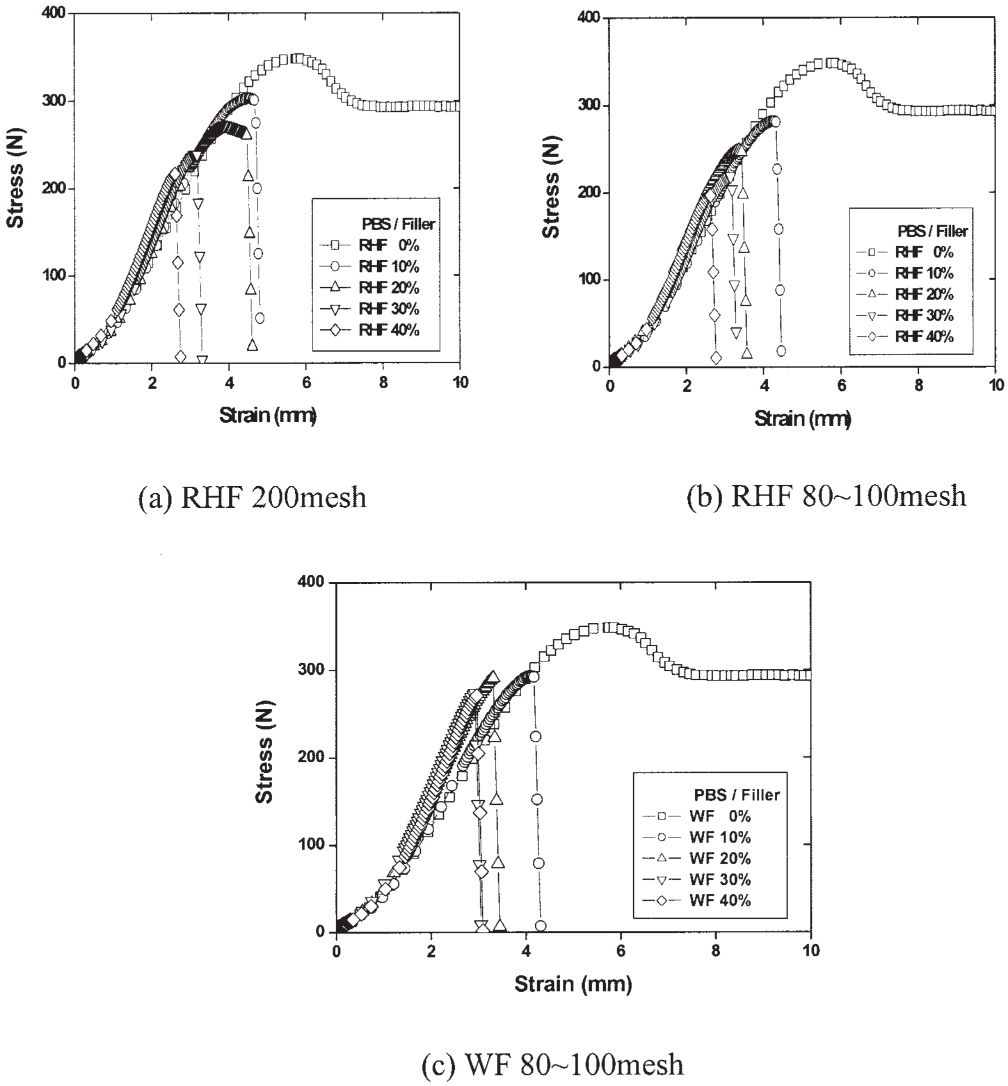


Figure 4 Stress—strain curves of agro-flour–filled PBS biocomposites.

posites dramatically decreased when compared with those of neat PBS. This is attributed to poor compatibility between the polar hydrophilic agro-flour and the nonpolar hydrophobic PBS matrix. The content of agro-flour in the biocomposites reduced their ductility and increased their brittleness under tensile deformation.[15]

Izod impact strength

Figure 5 presents the notched Izod impact strength of RHF (80–100 mesh) filled PBS, PP, and HDPE composites. The Izod impact strength of RHF-filled PBS biocomposites was lower than that of RHF-filled PP and RHF-filled HDPE composites because of the very brittle characterization of PBS. The impact strength of biocomposites is affected by the matrix polymer rather than by the addition of the filler in composites system. Therefore, we can compare the tensile and impact

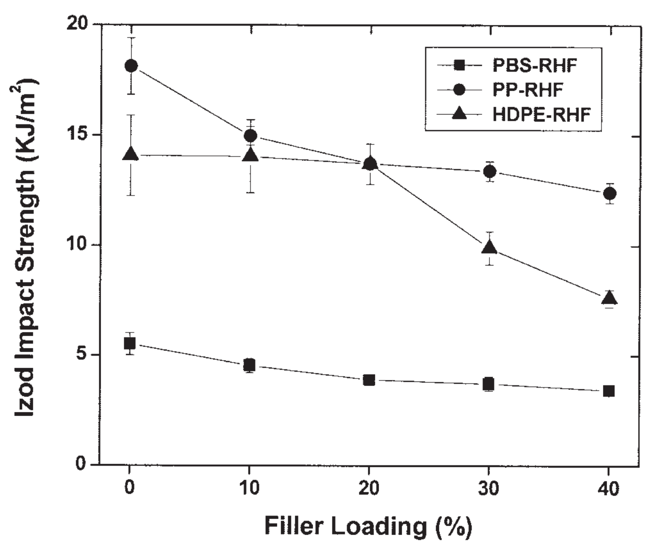


Figure 5 Notched Izod impact strength of RHF (80–100 mesh) filled PBS, PP, and HDPE biocomposites. PP-RHF and HDPE-RHF: Results of reference [22].

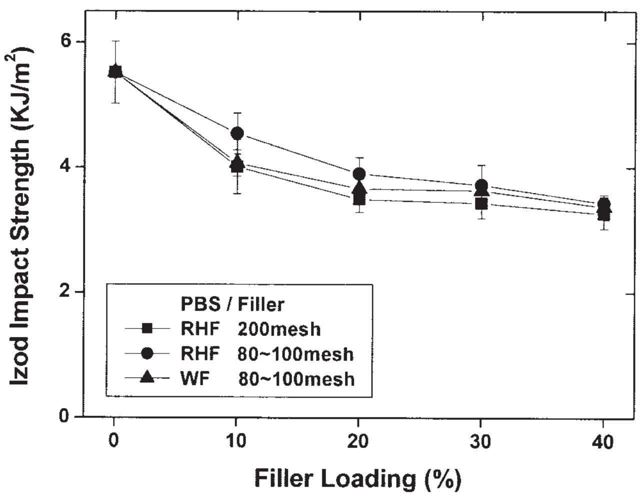


Figure 6 Comparison of notched Izod impact strength of agro-flour–filled biocomposites at different filler loadings.

strengths of biocomposites with those of conventional plastic materials. This result supports the application of agro-flour–filled PBS biocomposites as packing materials, disposable products and other films. Recently, PBS has not been widely used in significant quantities for biodegradable polymer applications because of its high cost. Recently, however, this cost barrier has been overcome by blending the PBS with agro-flour. The notched Izod impact strength of the biocomposites, shown at different filler loadings in Figure 6, decreased as the agro-flour content increased. Generally, notched impact strength is a measure of crack propagation. The poor interfacial adhesion between agro-flour and the matrix polymer causes microcracks when impact occurs, thus allowing the cracks to easily propagate. Figure 6 also shows the effect of particle size on notched Izod impact strength. As the particle size increased, the notched Izod impact strength slightly increased. This result was expected because the crack propagates at the weaker RHF–PBS interface as well as through the biopolymer. Because of cracks traveling around the RHF particles, the fracture surface area increases with increasing particle size. Therefore, more energy is required to fracture the impact specimen with larger particles.[13,14]

Morphological study

SEM examinations were conducted to evaluate the energy absorption mechanism such as fiber matrix debonding and flour removal. The tensile fracture surfaces of the RHF 200 and 80–100 mesh filled PBS biocomposites at 40 wt % filler loading are shown in Figure 7. Cavities can be seen between RHF and the matrix polymer. The presence of these cavities clearly indicates the poor interfacial adhesion between the agro-flour and the matrix polymer. As the filler loading increased, the agro-flour particles become the main component and some traces can be seen where the agro-flour has been removed. This result contributes to the poor stress transfer from matrix polymer to agro-flour leading to poor tensile properties. The effect of filler particle size on the tensile fracture surface of the biocomposites is also shown in Figure 7. The pulled out traces and the particles were bigger in the larger particle size RHF (80–100 mesh) filled PBS biocomposites than in the smaller particle size RHF (200 mesh) filled PBS biocomposites. This result confirms that the tensile strength of RHF (200 mesh) filled PBS biocomposites is slightly higher than that of RHF (80–100 mesh) filled PBS biocomposites and that smaller particle size offers better dispersion between agro-flour and the matrix polymer.[1]

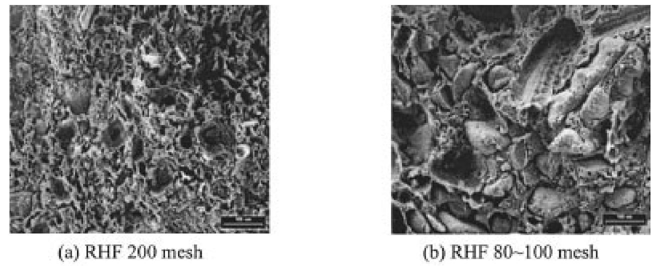


Figure 7 SEM micrographs of morphology of the tensile fracture surfaces of (a) RHF (200 mesh) and (b) RHF (80–100 mesh) filled PBS biocomposites.

Figure 8 shows the notched Izod impact fracture surfaces of RHF (80–100 mesh) filled PBS at 200 × magnification. The SEM micrograph of morphology clearly shows the fractured surface at the notched tip where, under the effect of stress concentration, the crack easily propagates at the weaker point of PBS when impact occurs. As the filler loading increased, increasing pulled out traces of agro-flours can be seen in the micrographs of the biocomposites. This result suggests that the notched Izod impact strength of the reinforced biocomposites decreased with increasing agro-flour volume fraction and thereby increased the brittleness of the biocomposites.[1,16]

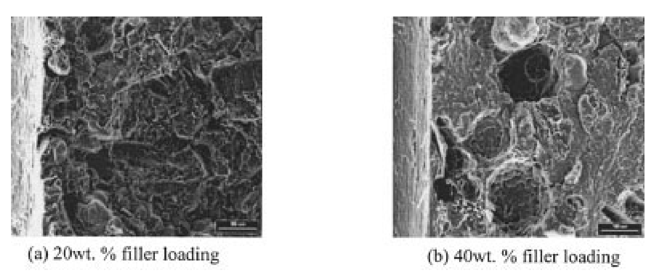


Figure 8 SEM micrographs of morphology of the Izod impact fracture surfaces of RHF (80–100 mesh) filled PBS biocomposites.

Biodegradability

Tensile strength

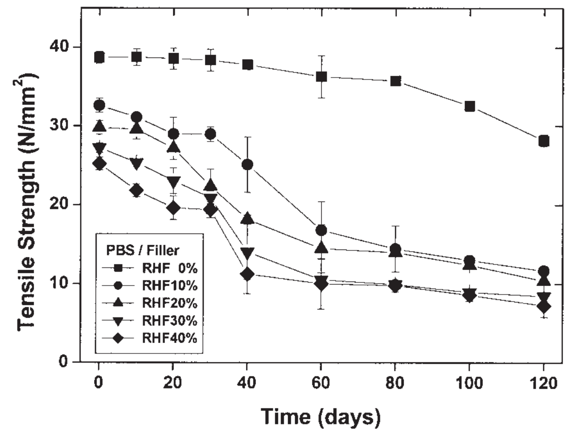
The tensile strength of the biocomposites as a function of natural soil burial time is shown in Figure 9(a)–(c). There was no change in the tensile strength of the pure PBS until 30 days, after which there was a slight change because of the increasing hydrolysis of the ester groups of the pure PBS. We can expect that the biodegradability of PBS is initiated with random chain scission by microorganisms in natural soil and is followed by reduction in molecular weight. The addition of WF and RHF to the PBS resulted in a more rapid decrease in the tensile strength of the biocomposites during the natural soil burial test.[6,17] We can expect that RHF and WF added to the PBS would be selectively hydrolyzed and that this would create localized micropores in the biocomposites. Furthermore, this result is probably explained by the absorption of water during soil burial with consequent weakening of the agro-flour–filled PBS biocomposites. The tensile strength of the biocomposites after 40 days of soil burial test is also presented in Figure 9(a)–(c). It is evident that, after 40 days, the tensile strength of the biocomposites was significantly decreased because hydrolysis of the ester groups of the biocomposites increased and hydrolysis of agro-flour of the biocomposites also increased by microorganisms in natural soil.[6,18]

Notched Izod impact strength

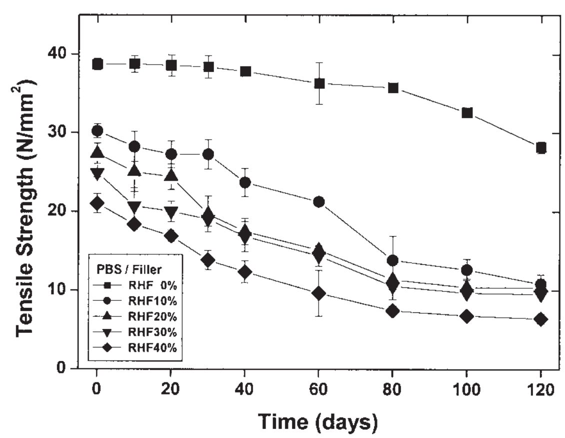
The notched Izod impact strength of the agro-flour–filled PBS biocomposites in natural soil environment for 120 days is shown in Figure 10(a)–(c). After 10 days, the Izod impact strength of PBS significantly decreased, and thereafter remained constant. It is evident that the hydrolysis of the PBS ester groups is attributed to the breaking up of the polymer into smaller units. As the degradation proceeded, the microorganisms became very active and the biocomposites became very brittle. With increasing filler loading, the Izod impact strength of the biocomposites slightly decreased. This decrease in Izod impact strength can be accounted for by the low Izod impact strength of pure PBS.[3,17]

Weight loss

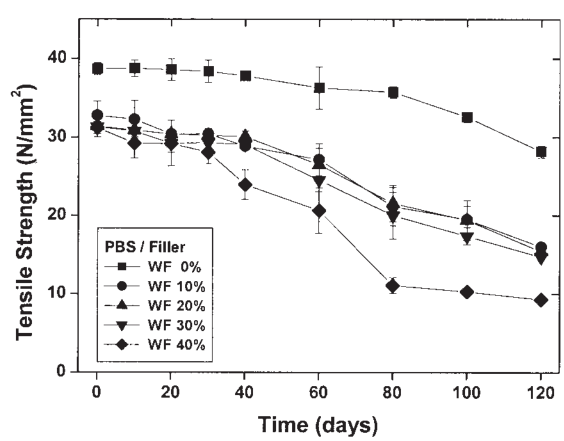
The percentage weight loss for agro-flour–filled PBS biocomposites is shown in Figure 11(a)–(c). It can be seen that the percentage weight loss of the biocomposites increased with increasing agro-flour incorporation. The percentage weight loss of PBS takes place by a hydrolysis mechanism. Hydrolysis occurs at the ester linkages, which allows the PBS molecular weight to be decreased by fungi and bacteria in the natural soil



(a) RHF 200 mesh

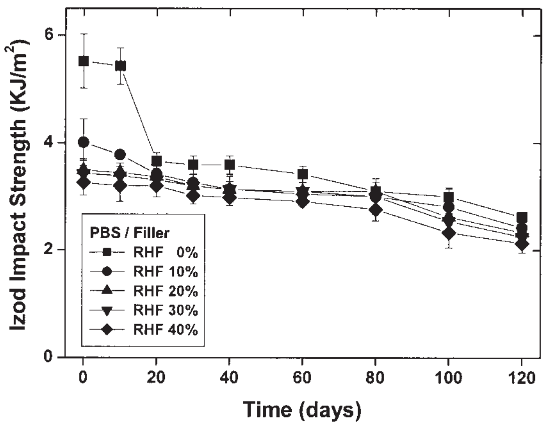


(b) RHF 80~100 mesh

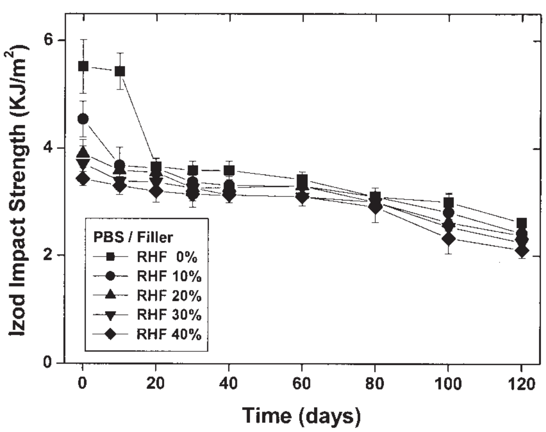


(c) WF 80~100 mesh

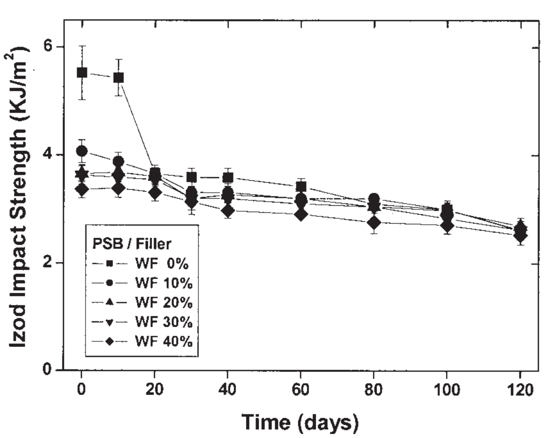
Figure 9 Effect of the duration of soil burial on the tensile strength of agro-flour–filled PBS biocomposites for 120 days.



(a) RHF 200 mesh

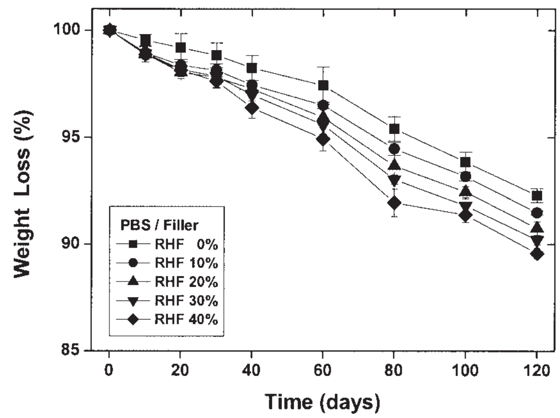


(b) RHF 80~100 mesh

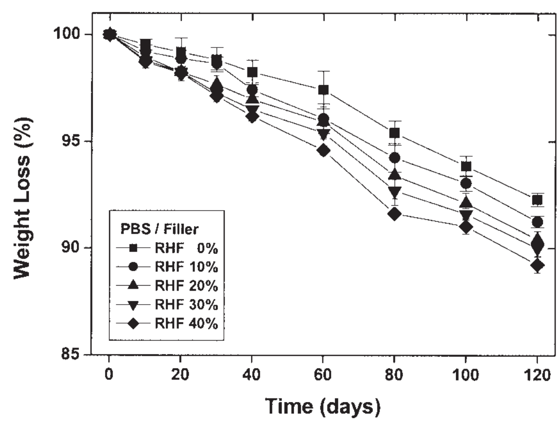


(c) WF 80~100 mesh

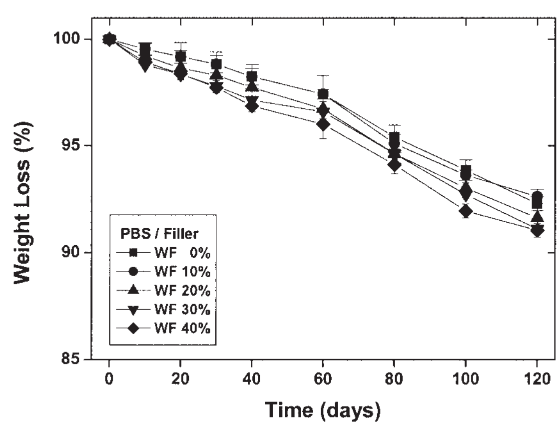
Figure 10 Effect of the duration of soil burial on the notched Izod impact strength of agro-flour–filled PBS biocomposites for 120 days.



(a) RHF 200 mesh



(b) RHF 80~100 mesh



(c) WF 80~100 mesh

Figure 11 Percentage weight loss of agro-flour–filled PBS biocomposites in natural soil.

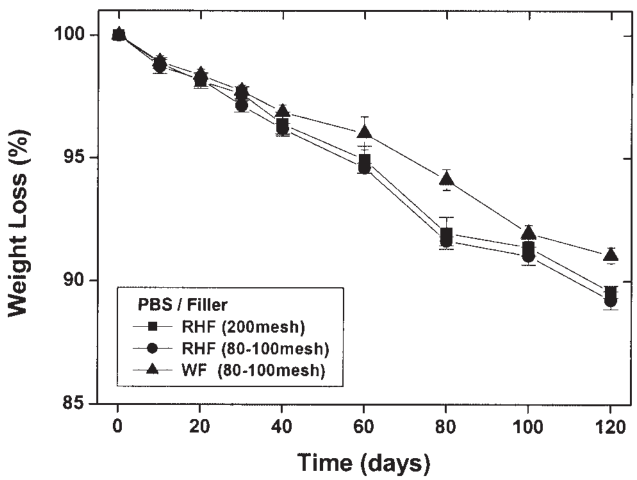


Figure 12 Comparison of the percentage weight loss of agro-flour–filled PBS biocomposites in natural soil at 40 wt % filler loading.

burial test.[3,17] The weight loss of agro-flour principally involves hydrolytic depolymerization of cellulose materials to lower molecular weight compounds, finally yielding monomeric glucose units by microorganisms. In addition, major deterioration of cellulose and wood-based lignocellulosic materials is caused by microorganisms.[19,20] Figure 12 shows the weight loss of the agro-flour–filled PBS biocomposites at 40 wt % filler loading, as well as the effect of filler particle size. The weight loss of the larger particle size (80–100 mesh) filled PBS biocomposites was slightly greater than that of the smaller particle size (200 mesh) filled PBS biocomposites because the smaller particle size possesses a higher surface area, thereby increasing the contact with the PBS matrix. Thus, this accounts for the correspondingly higher weight loss of PBS biocomposites filled with larger-size particles.[21]

Biodegradability surface

Figure 13(a) shows the degradation surface of pure PBS after 100 days. The natural soil burial test is well known to be a slow process. However, it is noteworthy that the burial soil test reflects real-life conditions better than any other test. At 100 days in the natural soil, there was significant fragmentation of the surface and large holes in the PBS surface, indicating that the degradation surface of PBS was attacked by microorganisms. The degradation surface of the agro-flour–filled PBS biocomposites is shown at 40 wt % filler loading in Figure 13(b) and (c). As the content of agro-flour increased, large holes and a number of surface irregularities of agro-flour–filled PBS biocomposites increased. This result shows that agro-flour added to the PBS is selectively hydrolyzed and that this creates localized micropores in the biocomposites, giving rise to an increase in the surface area and a concomitant increase in the rate of degradation.[9,18,19] The effect of filler particle size on the degradation surface of the biocomposites is also seen. Larger pores and degradation areas are seen in the larger particle size (80–100 mesh) filled biocomposites than in the smaller particle size (200 mesh) filled biocomposites. This result shows that the addition of larger particles to PBS increased the surface area of the PBS matrix polymer.

CONCLUSIONS

As the agro-flour loading was increased, the tensile strength of the biocomposites decreased as a result of the weak interfacial bonding between filler and matrix polymer. The tensile strength of WF-filled PBS biocomposites was higher than that of RHF-filled PBS biocomposites as a result of the higher holocellulose and lignin content of WF. The Izod impact strength of RHF-filled PBS biocomposites was lower than that of RHF-filled PP and HDPE composites because of the very brittle characterization of PBS. As filler loading increased, the Izod impact strength of agro-flour–filled PBS biocomposites decreased because of the poor interfacial adhesion when impact occurred, which allowed the cracks to easily propagate. As the particle size decreased, the tensile strength of the biocomposites slightly increased because of good particle dispersion in the matrix polymer, although the impact strength decreased. As filler content increased, the SEM morphology of the tensile and impact fracture

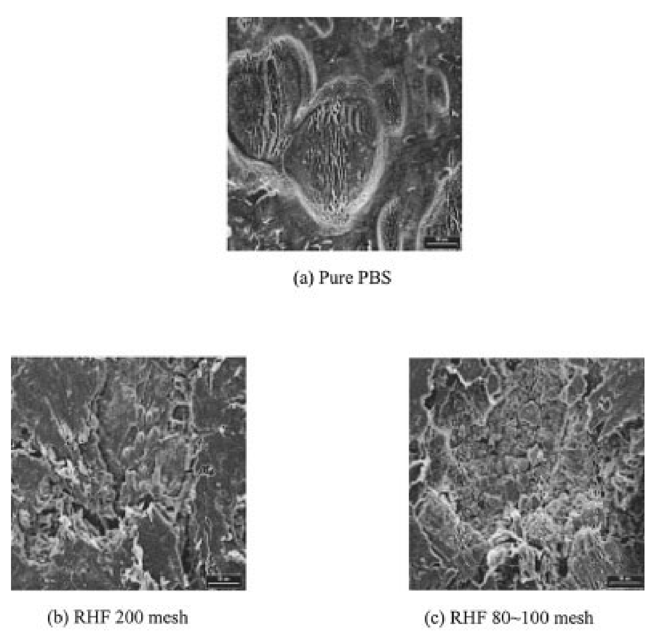


Figure 13 SEM micrographs of PBS (350×): (a) pure PBS, (b) RHF 200 mesh, and (c) RHF 80–100 mesh filled PBS biocomposites at 40 wt % filler loading after 100 days.

surface of the agro-flour–filled PBS biocomposites presented more filler particles and an increased number of holes where filler particles had pulled out. With increasing agro-flour content in the PBS biocomposites, there was a more rapid decrease in the tensile strength, notched Izod impact strength, and percentage weight loss of the biocomposites by bacteria and fungi during the natural soil burial test. These results show that agro-flour–filled PBS biocomposites are environmentally friendly and degradable materials that can be considered as alternatives to conventional plastic materials for packing, injection-molded, and disposable products.

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