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Physical Properties of Agro-Flour Filled Aliphatic Thermoplastic Polyester Bio-Composites*[1]

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ABSTRACT

The purpose of this study was to investigate the water absorption and thickness swelling of bio-composites at room temperature. These properties of bio-composites mainly depend on the ability of the agro-flour to absorb water through hydrogen bonding between water and the hydroxyl groups of the holocellulose and lignin in the cell wall. As the content of agro-flour increased, the water absorption and thickness swelling of the bio-composites increased. The effects of agro-flour content and rice husk flour (RHF) particle size on the water absorption and thickness swelling of the bio-composites were evaluated. In general, wood-based materials showed significantly higher water absorption and thickness swelling than the bio-composites. This might be attributed to the ability of the polybutylene succinate (PBS) hydrophobic polymer to prohibit the water absorption and thickness swelling of the bio-composites. Therefore, the use of agro-flour filled PBS bio-composites, which exhibit improved dimensional stability in comparison with wood-based materials, is recommended.

Keywords : bio-composites, agro-flour, water absorption, thickness swelling, hydrogen bonding

1. INTRODUCTION

In recent years, due to the surge environmental awareness, cellulosic fillers have been increasingly used as reinforcing fillers in thermoplastic composite materials (Yang *et al*, 2004). The majority of available thermoplastic polymers are widely used in modern society because they possess certain properties that make them suitable for various applications (e.g. excellent chemical resistance, good physical properties and low cost). However, most synthetic polymers are extremely resistant to microbial attack, and the non-biodegradability of most commercially available plastics has resulted in many environmental problems associated with their disposal. Recycling would provide a solution to this environmental problem (Masahiko, 2002). However, only a very small proportion of non-biodegradable plastics is recyclable and consequently most synthetic plastics end up in landfills. As the consumption of synthetic polymers increases,

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the disposal of the associated waste matter is proving to be an increasingly taxing problem, due to the difficulty of finding available landfill areas. Therefore, the substitution of these synthetic polymers by biodegradable polymers has become a topic of great interest in recent years, with the object of reducing the dependence on landfills. PBS (polybutylene succinate) is a commercially available biodegradable polymer with many interesting properties, such as biodegradability, melt processing, and chemical resistance (Kim *et al.*, 2003 ; Wu *et al.*, 2003).

Nowadays, most researches in this field are focused on aliphatic polyester composites made from agro-materials, such as cellulosic and lignocellulosic materials with low cost, renewability, biodegradability, and non-toxicity. Tserki and Lee (2003) studied the use of biodegradable polymer bio-composites made from cellulosic materials as reinforcing fillers. Rice husk flour (RHF) and wood flour (WF) are two such agro-materials which can be used as reinforcing fillers in biodegradable polymer bio-composites. Rice husk is an agricultural waste material generated in rice-producing countries, especially in the Asian, Pacific, and United States regions. Most of this rice husk is used as bedding material for animals but the industrial applications of this material are limited (Lee *et al.*, 2003; Rajan *et al.*, 2002). The use of rice husk in the manufacture of agro-material filled biodegradable polymer bio-composites is attracting much attention because of its potential supply as a biomass material (Lee *et al.*, 2003).

One of the main disadvantages of using cellulosic materials as fillers is their high water absorption, which originates from their inherent numerous hydroxyl groups. Moisture penetration into bio-composites occurs via the direct diffusion of water molecules into the filler and matrix polymer interface (Ichazo *et al.*, 2001; Pavlidou *et al.*, 2003). Moreover, Son *et al.* (2003) indicated that the thickness swelling of paper sludge-thermoplastic polymer composites increased with the increase of paper sludge content.

The objective of this study was to discuss the feasibility of manufacturing agro-flour filled PBS bio-composites as alternatives to cellulosic material filled conventional plastic (polyolefin) composites in terms of dimensional stability. Therefore, we evaluated the physical properties (water absorption and thickness swelling) of the RHF filled PBS bio-composites as a function of the RHF content and the mesh size. These physical properties of RHF filled PBS bio-composites were also compared with those of WF filled PBS bio-composites at the same particle size (80～100 mesh).

2. MATERIALS and METHODS

2.1. Materials

Polybutylene succinate (PBS) was supplied by SK Chemical Co., South Korea. It has a melt flow index of 20 g/10 min (190°C/2, 160 g), a density of 1.22 g/cm^3), and a number average molecular weight (M_n) of 5.5×10^4. The agro-flours used as reinforcing filler were rice husk flour (RHF) and wood flour (WF). These fillers were obtained from SARON FILLER Co., and the Korea Forest Research Institute, South Korea, respectively. The RHF were 80 to 100 and 200 mesh in particle size. The particle size of the WF was 80 to 100 mesh.

2.2. Compounding

The RHF and WF were dried to a 1～3% moisture content using a drying oven at 105°C for 24 hrs and then stored in sealed polyethylene bags in an environmental controller prior to compounding. The compounding of PBS with RHF and WF was performed in a twin screw extruder, like polymer blending. The laboratory size extruder was a twin screw extruder which blends the polybutylene succinate (PBS) with the agro-fillers, using three general processes: melt blending, extrusion, and palletizing. 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 hrs. The dried pellets were stored in sealed polyethylene bags to avoid moisture uptake. The bio-composites were prepared with four different filler loadings (10, 20, 30 and 40 wt.%).

2.2. Test Specimens

The extruded pellets were injection molded into test bars for measuring their physical properties (ASTM D 1037-99) by an injection molding machine (Bau Technology, South Korea) at 140°C, an injection pressure of 1,200 psi, and a device pressure of 1,500 psi. Water absorption and thickness swelling were measured in the rectangular samples of 15 mm×10 mm×3 mm. After injection molding, the test bars were conditioned before testing at 50±5% RH for at least 40 h according to ASTM D 618-99.

2.3. Physical Properties Test

The thickness swelling and water absorption tests were conducted according to ASTM D 1037-99. Rectangular specimens having a size of 100 mm×25 mm×5 mm were used in the thickness swelling and water absorption tests. Samples of each type were immersed in water at 25°C for up to 250 hrs. At each testing time, the samples were removed from the water and patted dry. The mass change of samples was recorded using an electronic balance at each testing time. Commercial particleboard, MDF and solid woods (red pine and birch) were also tested as control samples. The specific gravities of particleboard, MDF, red pine and birch were

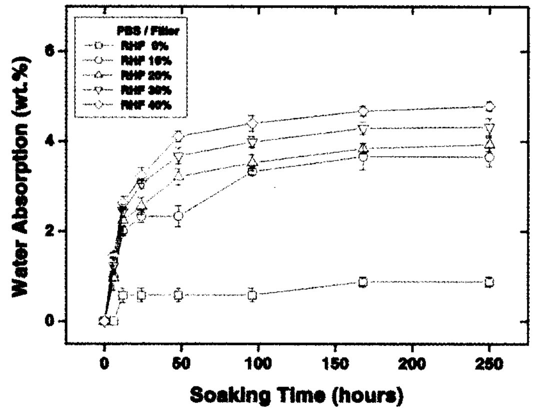

Fig. 1. Water absorption of RHF (200 mesh) filled PBS bio-composites.

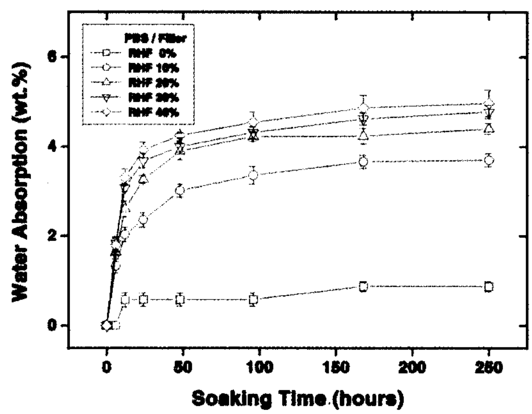

Fig. 2. Water absorption of RHF (80~100 mesh) filled PBS bio-composites.

0.60, 0.92, 0.47 and 0.49, respectively.

3. RESULTS and DISCUSSION

3.1 Water Absorption

Figs. 1, 2, and 3 show the effect of filler loading on the water absorption curves of the agro-flour filled PBS bio-composites over a period of 250 hrs. As the filler loading increased, the water absorption of the bio-composites slightly increased. The water absorption of the pure PBS, however, was very low due to its

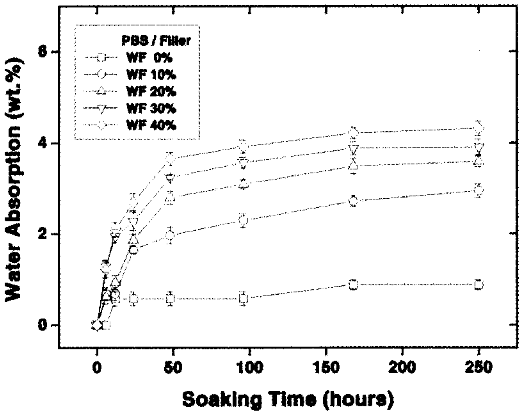

Fig. 3. Water absorption of WF (80∼100 mesh) filled PBS bio-composites.

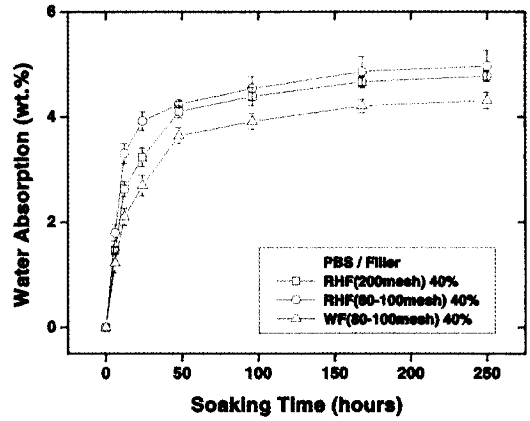

Fig. 4. Comparison of water absorption of agro-flour filled PBS bio-composites at 40 wt.% filler loading.

hydrophobic nature. On the other hand, the water absorption of bio-composites significantly increased in the initial stage up to 50 hrs and thereafter remained almost constant. The water absorption of bio-composites is mainly due to hydrogen bonding of the water molecules to the hydroxyl (OH) groups present in the cellulosic cell wall materials and to the diffusion of water molecules into the filler/matrix interface. Cellulosic materials are complex substances constituted of cellulose, hemicellulose, lignin, and extractives. Cellulose is the main component of cell walls and has three free hydroxyl groups per anhydroglucosic unit. It can be seen that the free hydroxyl groups in the cellulose form hydrogen bonds during the process of soaking in water. Therefore, we found that the water absorption of bio-composites increased with the increase of agro-flour content because of more numerous OH groups at higher agro-flour contents (Ichazo *et al.*, 2001; Pavlidou *et al.*, 2003; Hon *et al.*, 1991).

Fig. 4 shows the water absorption of agro-flour filled PBS bio-composites at 40 wt.% filler loading at different filler particle sizes. It can be seen that the water absorption is slightly higher for the larger RHF particle size (80∼100 mesh). Consequently, we can conclude that the bio-composite from RHF with a larger particle size contains larger cavities than that from RHF with a smaller particle size for the same weight fraction. As the particle size decreases, the filler possesses a higher surface area, resulting in the increased interaction between agro-flour surfaces in the PBS matrix. This result is reflected in the slightly increased tensile strength of the bio-composites with a smaller RHF particle size (Stark *et al.*, 1997; Rozman *et al.*, 2003), and the higher interaction between the agro-flour and the matrix polymer results in lower water absorption at the filler/matrix interface. Also, it is possible to observe that the water absorption of the RHF filled PBS bio-composites is a little higher than that of the WF filled PBS bio-composites. This is due to the higher specific gravity of WF compared with RHF. The specific gravity of cellulosic materials decreases with the increase of moisture content (Rowell *et al.*, 1984).

The water absorption curves of agro-flour filled PBS bio-composites and control samples are shown in Fig. 5. The control samples show much higher water absorption than the bio-composites, and they were not saturated with water even at the end of test. Generally, the

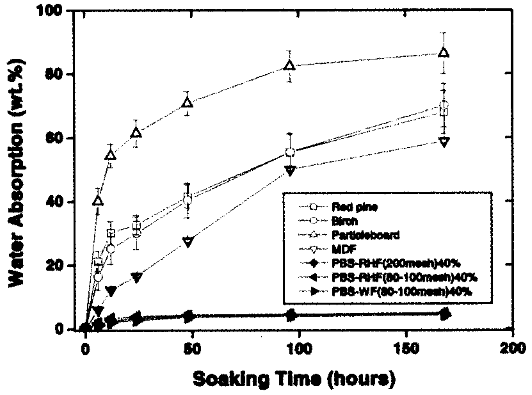

Fig. 5. Comparison of water absorption of agro-flour filled PBS bio-composites and wood-based materials.

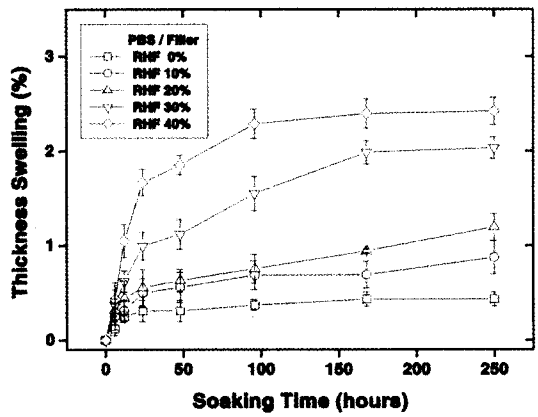

Fig. 7. Thickness swelling of RHF (80～100 mesh) filled PBS bio-composites.

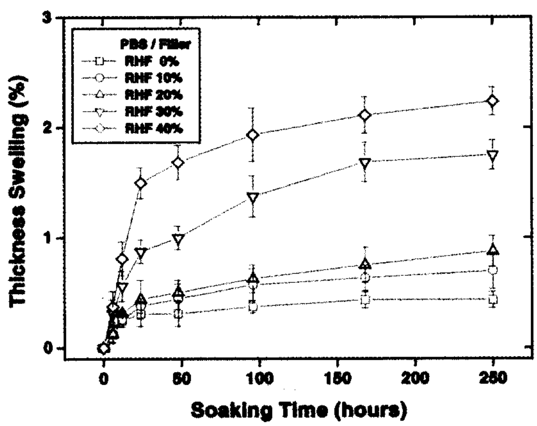

Fig. 6. Thickness swelling of RHF (200 mesh) filled PBS bio-composites.

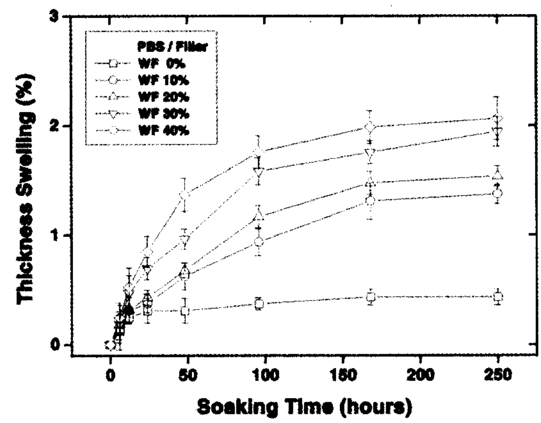

Fig. 8. Thickness swelling of WF (80～100 mesh) filled PBS bio-composites.

main disadvantage of wood-based materials is their poor dimensional stability because of their high water absorption. From this result, we can expect that bio-composites would be suitable for use as interior panels and food packing materials, etc.

3.2. Thickness Swelling

The thickness swelling curves of agro-flour filled PBS composites over a period of 250 hrs at different filler loadings are shown in Figs. 6, 7, and 8, respectively. It is well known that the OH groups in the agro-flour form hydrogen bonds with water. The thickness swelling of bio-composites occurs when the cell walls in the agro-flour are swelled by water (Rozman *et al.*, 2000). The results in Fig. 6 clearly show that pure PBS exhibits almost no uptake of water due to its hydrophobic nature. Also, we can see that the thickness swelling of the bio-composites increases as the content of agro-flour increases because the agro-flour is mainly composed of hydrophilic substances. These hydrophilic substances contain hydroxyl groups in the cell walls. In general, the thickness swelling of agro-

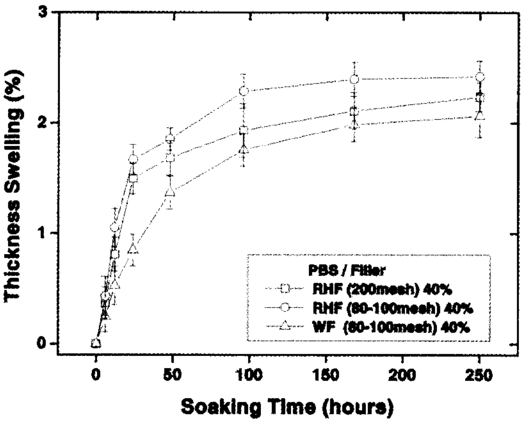

Fig. 9. Comparison of thickness swelling of agro-flour filled PBS bio-composites at 40 wt.% filler loading.

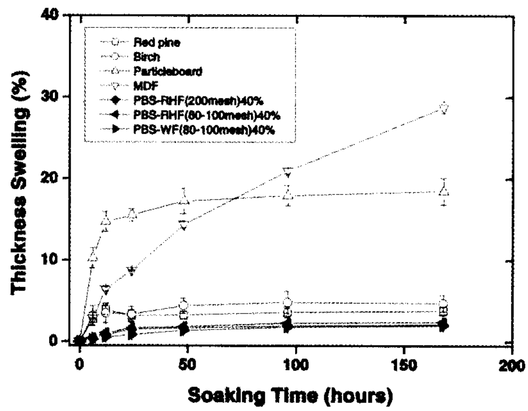

Fig. 10. Comparison of thickness swelling of agro-flour filled PBS bio-composites and wood-based materials.

flour filled PBS bio-composites increased as the water absorption increased (Son *et al.*, 2001).

Fig. 9 shows the thickness swelling of agro-flour filled PBS bio-composites at 40 wt.% filler loading at different filler particle sizes. The thickness swelling of bio-composites from the larger RHF particle size is slightly higher than that of bio-composites from the smaller RHF particle size. This fact indicates that the larger particle size results in the increased water absorption and greater swelling of the cell wall compared with the smaller particle size. The higher thickness swelling of RHF filled PBS bio-composites than that of WF filled PBS bio-composites is also shown in Fig. 9. This might be attributed to the higher specific gravity and smaller cavities in the WF cell wall. Thus, it appears the thickness swelling of bio-composites to be affected by the mechanism of water absorption by the agro-flour. The thickness swelling curves of agro-flour filled PBS bio-composites and wood-based materials are shown in Fig. 10. The wood-based materials show significantly higher thickness swelling than the bio-composites. It can be seen that the hydrophobic PBS matrix of bio-composites restricts the swelling of agro-flour. Consequently, we can conclude that the PBS matrix is able to reduce the water absorption and thickness swelling of bio-composites, and thus resulting in their lower dimensional stability in comparison with wood-based materials.

4. CONCLUSIONS

The water absorption and thickness swelling of the bio-composites are higher than those of pure PBS. The water absorption and thickness swelling of the bio-composites is mainly due to the hydrogen bonding of water molecules to the hydroxyl groups of the cellulose, hemicellulose and lignin in the cell walls of agro-flour. As the content of agro-flour increased, the water absorption and thickness swelling of the bio-composites increased. This phenomenon results from the increased number of OH group in the agro-flour with the increased filler loading. In the effect of particle size, the water absorption and thickness swelling of bio-composites with a larger RHF particle size were slightly higher than those of bio-composites with a smaller RHF particle size. Also, the water absorption and thickness swelling of RHF filled PBS bio-composites were slightly higher than those of WF filled

PBS bio-composites. This is due to the higher specific gravity in the WF in comparison with the RHF. The wood-based materials showed much higher water absorption and thickness swelling than the bio-composites. Therefore, these bio-composites were thought to be used as interior panels and packing materials, etc.

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