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Hardness, Decay and Water Resistance of Polypropylene/Montmorillonite/Almond Shell Flour Composites

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The effect of montmorillonite (MMT) loading (0, 2.5, and 5 wt%) and almond shell flour (ASF) content (30, 35, and 40 wt%) on the decay resistance, hardness, water resistance of injection molded polypropylene (PP) composites was investigated. The amount of maleic anhydride grafted polypropylene was kept constant at 2% for all formulations. White-rot (*Trametes versicolor*) fungal treatment was applied to the produced composites for 14 weeks according to BS 838:1961 with the Petri dishes method. The weight loss of the composites decreased with increasing MMT content. The highest hardness (66 Shore D) was noted in the undecayed control composites (40ASF60PP0MMT) while the lowest hardness (61.3 Shore D) was recorded in the decayed control composites (30ASF70PP0MMT). The water absorption of the undecayed and decayed composites decreased with increasing amount montmorillonite at 30-40 wt% content of the ASF loading level. The water absorption of the decayed composites was higher than that of the undecayed composites but their thickness swelling was lower. Based on the findings obtained from the present study, a 35/5/65/2 formulation of the ASF/MMT/PP/MAPP can be used in outdoor applications requiring a high dimensional stability.

Keywords: *Montmorillonite, Almond shell flour, Polypropylene, Decay resistance, Hardness, Water resistance*

1. Introduction

Much work has been done in studying and developing thermoplastic/natural fibers composites, especially wood plastic composites (WPCs) which have successfully proven their high qualities in various fields of technical application, especially in load-bearing applications. New applications and end uses of wood-plastic composites have been found in decking flooring, outdoor facilities, window frames, various construction materials, and bathroom parts. Dimensional stability and biological durability are the most important characteristic of WPCs exposed to environmental conditions that determine their end use applications. Therefore, as a limiting parameter, dimensional stability and decay resistance have to be taken into account in the design of WPCs for final applications[1-15].

Nano-scale technology offers a new approach to develop high performance composites. Having a large geometric aspect ratio (length/diameter) and surface area, nano-sized filler can enhance interfacial interaction in the composite at very small loading amount. Among different nanoparticles, nanoclay has attracted more interest as filler material and extensive research are devoted on nanoclay as a filler material which is capable of providing reinforcement. Even low levels of 1 to 5 wt% have improved the strength properties of the nanocomposites. It is believed that such performance is due to the development of strong bonds amongst the nanoparticles distributed in the polymer matrix[13]. As has been reported in the literature, the incorporation of nanoclays improves the properties of WPC, including the modulus[7-18-25], flexural and tensile strengths[7-8-18], thermal properties[12-18], and lowered wettability[7-11]. One of the most common nanoclay forms is montmorillonite with a particle thickness of 1 nm and 70 to 100 nm crosswise silica platelets. The montmorillonite clay is one of the nano particles having the widest acceptability for use in polymers[26]. The choice and extensive use of the montmorillonite clay in previous researches is mainly due to the fact that it is commonly available and inexpensive[27].

Almonds are a very important crop throughout the world's temperate regions[19]. Worldwide almond production in 2009 was about 2.31 million tons from a total of 1.7 million hectares[9]. Almond (*Prunus amygdalus* L.) shell, an agricultural residue, is the lignocellolusic material forming the thick endocarp or husk of the almond tree fruit that upon processing the fruit to obtain the edible seeds is separated and since they have no important industrial usages are normally incinerated or dumped[28]. Burning agricultural residues causes environmental problems such as air pollution, soil erosion, and decreasing soil biological activity[6]. Utilizing agricultural residues not only prevents environmental concerns but also can mean farmers second income from plantation[3-24]. For this reason, the walnut shell flour generated in massive quantities by almond

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shell mills can play an important role in the manufacture of filled thermoplastic composites, thereby reducing the demand for wood material.

This report describes two objectives; (1) to investigate the influence of fungal decay on the weight loss of almond shell flour filled polymer composites (2) to determine the effect of montmorillonite and almond shell flour on the hardness, water absorption, and thickness swelling of the composites prior to and after incubation with white-rot fungus.

2. Material and Methods

2.1. Materials

The polymer matrix used in this study was polypropylene (PP) with a melt flow index of 7-10 g/10 min, and a density of 0.87 g/cm^3 (supplied by Arak petrochemical Co., Iran). The montmorillonite modified with a dimethyl-dehydrogenated tallow, quaternary ammonium with a cationic exchange capacity of 125 meq/100 g clay, density of 1.66 g/cm^3, and a d-spacing of d_{001}=31.5 nm was obtained from Southern clay Products Co, Texas, USA, with trade name Cloisite 15 A. Maleic anhydride grafted polypropylene (PP-g-MA) was provided by Solvay Co, Belgium, with trade name of Priex 20070 (melt flow index of 64 g/10 min, density of 0.91 g/cm^3, and a grafted maleic anhydride 1 wt%) was used as coupling agent.

Almond (*Prunus dulcis* (Mill.)) shell was used as lignocellulosic filler in the thermoplastic composites. Almond shells were hammer milled to obtain almond shell flour (ASF). The ASF passing through a 40-mesh (0.42 mm) screen and retained on a 60 mesh (0.25 mm) screen were used in the experiments.

2.2. Methods

2.2.1. Production of injection molded composite specimens

Before preparation of composite specimens, almond shell flour (ASF) was dried in an oven at 65 ± 2 °C until it reached a constant weight. Then polypropylene, almond shell flour, coupling agent and montmorillonite were weighed and bagged according to formulations given in Table 1. The mixing was carried out with a counter-rotating intermeshing twin-screw extruder (Model T20, 1990, Dr. Collin GmbH, Germany) which its barrel temperature ranging from 155 to 190 ˚C at six zone, from feeding zone to the die zone, at a screw speed of 70 rpm. The pasty compound produced was cooled to room temperature and then grinded to produce suitable granules for further processing. Grinding was carried out in a laboratory mill (Wieser, WGLS 200/200 Model) and the granulated materials were dried at 105 °C for 4 hours. Test specimens were prepared by injection molding machine (Model EM80, Aslanian Co., Iran) set at 160-180 °C temperature was used to prepare test specimens. At each molding operation a complete set of specimens for different tests are produced. Finally, specimens were conditioned at a temperature of 23 °C and relative humidity of 50% for at least 40 h, according to ASTM D 618-99 prior to testing. The densities of the composites varied from 1.00 to 1.07 g/cm^3.

2.2.2. Decay test

Malt extract agar was used at a concentration of 48 g/L as the culture medium. Purified white-rot (*Trametes versicolor*) fungus was used in this study as the biological degradation agent. The purified white-rot fungus was transferred to Petri dishes containing malt extract agar under sterile hood using sterile pincers. The dishes were kept at 25 ºC for one week until the culture medium was fully covered by the fungus. The cultured fungus was transferred into Petri dishes containing the culture medium that were incubated for one week at 25 ºC. Then, the test specimens were transferred into the Petri dishes. The Petri dishes containing the fungus and the wood plastic composite specimens were stored in an incubator for 14 weeks at 25 ºC and 75% relative humidity.

2.3. Measurements

2.3.1. Weight loss

Dry weights of the specimens were measured at 103 ± 2 ˚C for 24 h. The weight losses were calculated according to equation (1),

$$\text{Weight loss } (\%) = \frac{(Mb - Ma)}{Mb} \times 100 \tag{1}$$

where *Mb* and *Ma* denote the oven-dry weights prior to and after incubation with fungus, respectively.

2.3.2. Hardness

Inspiring by the Shore-D method, the hardness property of specimens was tested according to ASTM D 2240 specifications using a Santam device. Four specimens with dimension of 50 mm x 13 mm x 5 mm were tested for each composite formulation.

Table 1. WPC formulations for the composition of the studied formulations.

Treatment code	Almond shell flour (ASF) content (wt%)	Polypropylene (PP) content (wt%)	MAPP [1] (wt%)	Montmorillonite content (wt%)
WPC-control	30	70	2	0
WPC-control	35	65	2	0
WPC-control	40	60	2	0
WPC-2.5NC	30	70	2	2.5
WPC-2.5NC	35	65	2	2.5
WPC-2.5NC	40	60	2	2.5
WPC-5NC	30	70	2	5
WPC-5NC	35	65	2	5
WPC-5NC	40	60	2	5

[1] MAPP = maleic anhydride grafted polypropylene.

2.3.3. Water absorption and thickness swelling

The water absorption (WA) and thickness swelling (TS) measurements for 24 h immersion in distilled water at room temperature, and 2 h immersion in boiling water were carried out according to ASTM D 7031. Four specimens of PP/ASF composite were dried in an oven for 24 h at 103 ± 2 ºC. The specimens were then placed in distilled water and boiling water one. At the end of immersion period, the specimens were removed from the distilled water and boiling water; and the surface water was wiped off using blotting paper and wet mass values were determined. The specimens were weighed to the nearest 0.01 g and measured to the nearest 0.001 mm immediately. The specimen thickness was determined by taking a measurement at a specific location, the diagonal crosspoint, on the specimen.

2.3.4. Morphological analysis

Small specimens of 1 mm × 1 mm × 1 mm were cut from the composite strips, dried gently in an oven and then coated with gold alloy. The surfaces of the specimens were observed by scanning electron microscopy (SEM, model Philips XL 30) at a voltage of 17 kV.

2.3.5. Statistical analysis

Statistical analysis was conducted using the SPSS program in conjunction with analysis of variance (ANOVA). Duncan's multiple range test (DMRT) was used to test statistical significance at $\alpha = 0.05$ level. For each treatment level, four replicate specimens were tested.

3. Results and Discussion

3.1. Effect of montmorillonite on weight loss of PP/ASF composites

The influence of montmorillonite loading on the weight loss of wood flour/polypropylene composites exposed to white-rot fungus is shown in Figure 1. The weight loss decreased with the increase of montmorillonite content. The lowest weight loss was found in the specimens containing 2.5 wt% montmorillonite and 35% ASF. The weight loss of the specimens with montmorillonite was significantly lower than that of previous studies[14,16]. For example, Hosseinihashemi *et al.*[14] investigated the weight loss of bagasse fiber/plastic composites. They reported that the both lowest (3.2%) and the highest (7.2%) weight loss were observed in the white-rotted composite specimens for 8 and 16 weeks fungal exposure times, respectively. The adequate conditions for fungal growth and attack including wood as food, sufficient oxygen, suitable temperature and moisture are a necessary[22]. A problem associated with using natural fibers in composites is their high moisture absorption and dimensional instability (swelling). Swelling of fibers can lead to micro-cracking of the composite and decrease of mechanical properties[23]. However, moisture content and much of the micro-cracking as a function for fungal attack can be attributed to decay of WPCs. Therefore, the first step in preventing decay is to prevent or limit moisture sorption[21]. The presence of the montmorillonite makes the WPC less accessible for the fungus through reduction of oxygen content, moisture uptake and nutrient shortage[17].

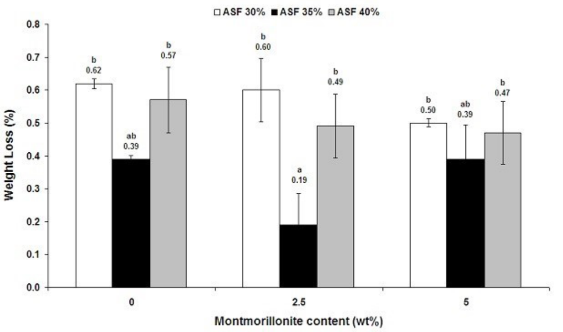


Figure 1. The average and standard errors for the weight loss measurements of the composites. Results with different letters are significantly different. The same letters in each column indicate that there is no statistical difference ($p< 0.05$) among the composite groups.

3.2. Effect of montmorillonite on hardness of undecayed and decayed PP/ASF composites

Hardness is an important test for different applications of wood flour/polypropylene composites. The influence of montmorillonite loading on the hardness of PP/clay/almond shell flour composites exposed to the white-rot fungus is shown in Figure 2. The results showed that the hardness of the specimens increased with the increase of the montmorillonite content. The highest hardness was determined for the specimens containing 5 wt% montmorillonite and 30 wt% ASF. This is due to the fact that montmorillonite protects the WPCs against fungal attack through reduction of oxygen content, moisture uptake and nutrient shortage which are necessities for fungus function[17]. The fungus only attacks to the lignocellulosic material, in particular lignin[20]. Since due to exposure to fungus, the surface layers in contrast with the core layers undergo more damage, the hardness of the WPCs increased with increase of montmorillonite content.

3.3. Effect of montmorillonite on water absorption of undecayed and decayed PP/ASF composites

The influence of montmorillonite on the WA of the undecayed and decayed PP/ASF composites is presented in Figures 3 and 4. In general, the incorporation of montmorillonite into the composition at all levels of ASF

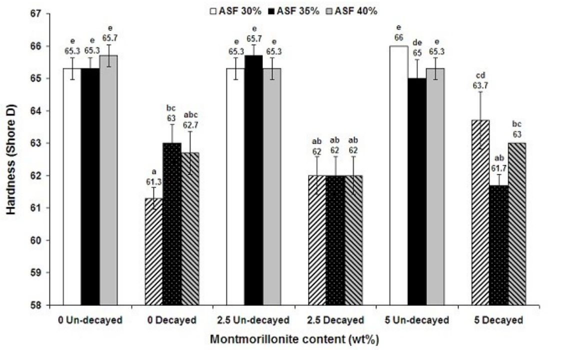


Figure 2. The average and standard errors for the hardness measurements of the composites. Results with different letters are significantly different (MMT: montmorillonite).

decreased the WA of the composites for immersion in normal water and boiling water. In particular this was observed for the specimens soaked in boiling water. For example, the WA values of the composites produced with 0, 2.5, or 5 wt% montmorillonite and undecayed wood (35 wt%) were found to be 1.45%, 1.16%, and 1.16% while it was found 1.45% for the control specimens. The WA values of the composites produced with 5 wt% were found to be lower than that of the composites produced with 2.5 wt%. The WA difference between the ASF/PP system and the ASF/PP/clay systems was increased with time, and the influence of the clay content from 2.5 to 5 wt% on WA was small. The WA of ASF/PP composites containing 2 wt% clay increased with time, but this property for the composites containing 2.5 wt% and 5 wt% montmorillonite increased very slowly. At this stage, moisture most likely penetrated deeper into the composites where the exfoliated clay could create longer moisture diffusion paths and slow moisture penetration. Generally increased clay content and keeping the amount of coupling agent in polyolefins can occur a difficulty in the montmorillonite exfoliation process.

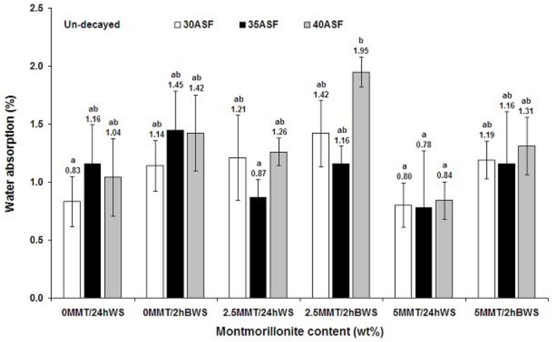


Figure 3. The average and standard errors for the water absorption (2 h boil water soaked and 24 h water soaked) measurements of the un-decayed composites).

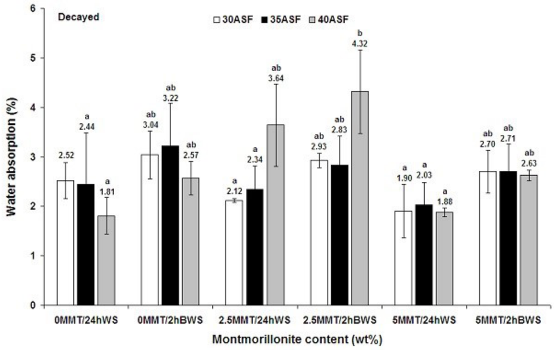
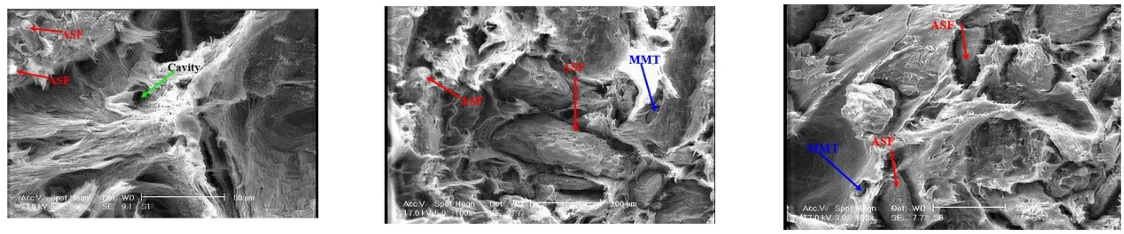


Figure 4. The average and standard error for water absorption measurements (2 h boil water soaked and 24 h water soaked) measurements of the decayed composites).

The water absorption of thermoplastics filled with lignocellulosic depends on the gaps and flaws at the interfaces, micro-cracks in the matrix formed during the compounding process, fine pores, and the number of free hydroxyl groups of the lignocellulosic[4]. The presence of voids and defects located in the filler/matrix interface was due to poor dispersion of the filler in the polymer matrix. The improvement in the WA of the undecayed and decayed composites filled with montmorillonite was attributed to the fact that the montmorillonite decreased the voids and defects filler/matrix interface. This was observed in the SEM images of the composite specimens (Fig 5).

The incorporation of the montmorillonite up to 5 wt% into the composition decreased the WA of the decayed composites at 30 wt% and 35 wt% levels of the ASF (Fig. 4). As the amount of the ASF increased to 40 wt%, there was no positive effect of the montmorillonite on the WA of the composites. Significant differences ($p<0.05$) in the WA values are presented in Figure 4. The WA of the undecayed composites was lower than that of the decayed composites. White-rot fungi deplete all components of the wood cell wall during decay, but some species cause selective removal of the lignin in wood. In the white-rot, the lignin in the wood cell wall being decayed is completely depleted, but some white-rot fungi can degrade the lignin in the wood preferentially to cellulose[10]. It can be said that the removal of lignin as a hydrophobic component and the preservation of much of the holocellulose as a hydrophilic component tend to favor increased water absorption of white-rotted PP/ASF specimens. Thus, the water absorption of white-rotted PP/ASF specimens was higher than control PP/ASF specimens after 24 h immersion in distilled water. Because an increase of water absorption causes an increase of thickness swelling, therefore the TS of white-rotted PP/ASF specimens was higher than control PP/ASF specimens after 24 h immersion in distilled water.

Various possible reasons for the greater water absorption and moisture penetration into the PP/ASF specimens exposed to white-rot fungus in an incubator could be proposed, where the main mechanism is the diffusion of water molecules



A) 0%MMT65%PP35%ASF2%MAPP (Control) B) 2.5%MMT65%PP35%ASF2%MAPP C) 5%MMT65%PP35%ASF2%MAPP

Figure 5. The SEM images of the cross section of the composite specimens (MMT: montmorillonite; PP: polypropylene; ASF: almond shell flour; MAPP: coupling agent).

inside the micro voids and gaps between polymer matrix and ASF[29]. In addition, it might alternatively be proposed that rotting created channels for the water to enter into the PP/ASF structure.

3.4. Effect of montmorillonite on thickness swelling of undecayed and decayed of PP/ASF composites

The influence of clay on the TS property of the undecayed and decayed PP/ASF composites is shown in Figures 6 and 7. The TS values showed a similar trend to the WA values. In the all cases, the TS of undecayed and decayed PP/ASF specimens increased with increasing of montmorillonite and ASF content. The rotted specimens without montmorillonite had a lower TS as compared to the undecayed specimens (Fig. 7). The possible reason for the lower TS of white-rotted PP/ASF specimens could be the broken down nature of the almond shell fibers, such that they no longer were effective in swelling the structure. Due to their amount of hydrophilic groups hemicelluloses have excellent swelling properties. The TS of composites was due to the hydrogen bonding of the water molecules to the free hydroxyl groups present in the cellulosic cell wall materials and the diffusion of water molecules into the filler-matrix interface[2]. The lower TS of the decayed composites could be also explained by the fact that the rot-fungi degraded the hemicelluloses in the wood cell.

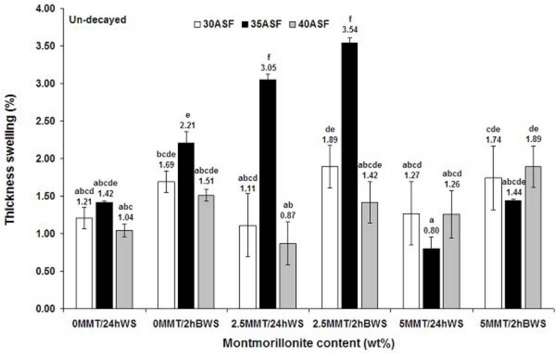


Figure 6. The average and standard errors for the thickness swelling measurements (2 h boil water soaked and 24 h water soaked) measurements of the un-decayed composites).

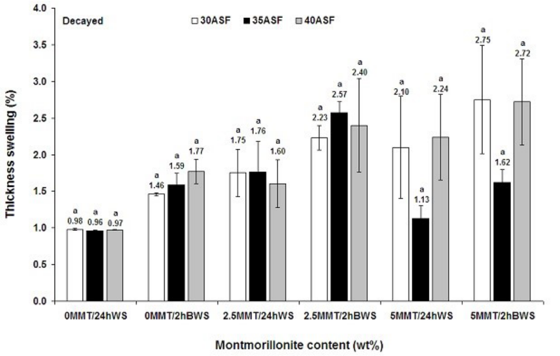


Figure 7. The average and standard error for thickness swelling measurements (2 h boil water soaked and 24 h water soaked) measurements of the decayed composites).

4. Conclusions

This study investigated the combined effect of montmorillonite and almond shell flour composites on decay resistance, hardness, and water resistance of polypropylene composites. The results showed that the incorporation of montmorillonite and almond shell flour did not significantly improve the Shore D hardness of the composites. The hardness of the decayed composites was lower than that of the undecayed composites. The weight loss of the composites decreased with increasing montmorillonite content. This revealed the thermal stability of the composites improved with the incorporation of montmorillonite. The water absorption of the undecayed and decayed composites decreased with increasing amount montmorillonite at 30-40 wt% content of the ASF loading level. This was confirmed by the SEM images, which the montmorillonite decreased the voids and defects filler/matrix interface. The 24 h water absorption and thickness swelling of the composites decreased with the addition of 5 wt% montmorillonite. The 24 h thickness swelling of the undecayed composites filled with 35 wt% almond shell flour and 5 wt% montmorillonite was lower than that of control specimens. The water absorption of the decayed composites was higher than that of the undecayed composites but their thickness swelling was lower. Based on the findings obtained from the present study, a 35/5/65/2 formulation of the almond shell flour/montmorillonite/polypropylene/MAPP can be used in outdoor applications requiring a high dimensional stability.

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