LIGNOCELLULOSIC FILLER/ RECYCLED HDPE COMPOSITES: EFFECT OF FILLER TYPE ON PHYSICAL AND FLEXURAL PROPERTIES

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The aim of the research was to study the potential of lignocellulosic fillers such as flour of rice hull, wood saw dust, sanding flour from Medium Density Fiberboard (MDF), and sawdust from particleboard as reinforcement for recycled high density polyethylene. Natural filler HDPE composites were made from recycled HDPE and lignocellulosic fillers at 60% by weight filler loadings using a dry blend/hot press method. In all compounds 3 per hundred compound (phc) Maleic Anhydride Polyethylene (MAPE) was used. Nominal density and dimensions of the panels were 1g/cm³ and 35×35×1 cm. Physical properties of panels including short and long-term of water absorption and thickness swelling and mechanical properties, including flexural modulus, flexural strength, strain at yield, and energy to yield point were studied. Composites containing sanding flour from MDF showed higher short-term values of water absorption and thickness swelling. For the long term, such as maximum values of water absorption and thickness swelling and diffusion coefficient, composites including wood sawdust showed higher values, and composites contain rice hulls exhibited the lowest values. In addition, composites made from sanding flour from MDF showed high value of the swelling rate parameter. Water absorption behavior of studied composites followed Fick’s model. The flexural properties of composites were investigated with reference to the effect of filler type. Composites containing sanding flour from MDF and particleboard sawdust exhibited better flexural properties than others and composites containing wood sawdust showed the lowest values.

Keywords: Wood plastic composites; Lignocellulosic filler; Recycled HDPE; Water absorption; Flexural properties; Dry blend/hot press method

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INTRODUCTION

There is currently worldwide interest in manufacturing composite materials from waste industrial and agricultural materials due to increasing demands for environmentally friendly materials. However, technology is evolving that holds promise for using waste lignocellulosic materials and plastics to make an array of high performance composite products that are themselves potentially recyclable (Rowell et al. 1991). Wood-plastic composites are products that can be well suited for using waste materials. The utilization of waste lignocellulosic materials for manufacturing of wood-plastic composites has been
much studied (Youngquist et al. 1994; Ashori and Nourbakhsh 2009, 2010; Yang et al. 2004, 2006; Zabihzadeh 2010). Composites made from lignocellulosic materials are now becoming popular due to their advantages, especially in wood-limited countries. There are different resources in the world that can be useful for wood-plastic composites manufacturing. In Iran the agricultural residue rice hull has been produced at about 3.5 million tons per year (Najafi 2007). As another example, in a Medium Density Fiberboard (MDF) mill in Iran, when MDF panel was sanded by sanding machine, 5 kg / sheet sanding flour of MDF was generated (Najafi 2007). The various waste products, consisting of wood or particle board sawdusts were also produced in carpentry workrooms. They are easily available, biodegradable, and inexpensive.

In WPC manufacturing, virgin plastics are commonly used. In addition, essentially any recycled plastic that melts and can be processed below the degradation temperature of lignocellulosic fillers (around 200 °C) is likely to be suitable for manufacturing WPCs. Plastic wastes are one of the major components of global municipal solid waste and present a promising raw material source for WPCs thanks to their large amount of daily generation and low cost. For example, a city in a developed country with a population of 3 million inhabitants produces around 400 tonnes of plastic waste per day with an annual increase of 25% (Avila and Duaret 2003). The utilization of recycled plastics for the manufacture of WPCs has been studied by a number of authors (Chow et al. 1998, Kamdem et al. 2004; Kazemi Najafi et al. 2006; Jayaraman and Bhattacharyya 2004). Hence, the development of new value-added products (WPCs), with the aim of utilizing the lignocellulosic waste and low cost recycled plastic would be desirable.

Wood-plastic composites can be manufactured using a variety of production techniques. The dry blend/hot press method is a simple technique. An advantage of dry blend/hot press is flexibility in changing the density of the composites (Najafí 2007). Although there has been considerable research devoted to the utilization of lignocellulosic filler in thermoplastic composites, there is little experimental data pertaining to composites made with fillers that were manufactured by a dry blend/hot press method (Zabihzadeh et al. 2011).

The main objective of this research was to study the potential of agricultural residues and industrial waste as reinforcement for recycled HDPE composites.

**EXPERIMENTAL**

**Materials**

Recycled high density polyethylene (HDPE) was used as plastic matrix in lignocellulosic filler/HDPE composites. The recycled HDPE was obtained from milk bottles with a melt flow index of 18 g/10 min (170 °C).

Four different waste materials were used as filler for the composites: Sanding flour of MDF was generated in a factory producing medium density fiberboard, Amol, Iran. Wood sawdust was produced from band saw. Flour of rice hull was produced from a rice grinding mill as agriculture residual. Particleboard saw dust was obtained as waste from a circular sawing operation. Also, in all of studied composites 3 per hundred
compound (phc) of Maleic Anhydride Poly-ethylene (MAPE) with the commercial name Borcoat™ ME0433 and density 0.934 g/cm³ was used as coupling agent.

Panel making

The fillers were oven-dried for 24 hours at 103 ± 2°C. Filler size distribution of the material was determined by screening through predetermined mesh size screens. The results are presented in Table 1. In this study the materials to be used as fillers were produced without any essential change. Figure 1 shows light microscopic photos of the fillers (4X). The oven-dried flour with a moisture content of less than 3% and recycled HDPE powder and constant value of MAPE were weighed for each formulation according to Table 2. Wood-plastic panels were manufactured using a dry blend/hot press method. Dried powder of high density polyethylene and MAPE and dried flour of lignocellulosic materials were separately mixed in a high-speed mixer at 1500 rpm for 5 min. Nominal density and dimensions of the panels were 1g/cm³ and 350×350×11mm, respectively. A forming frame (measuring 350×350×11mm) was placed on a stainless steel caul plate. The surfaces of the caul plate were sprayed with mineral oil releasing agent to reduce the adhesion between the wood-plastic composites and the caul plate. Mixed materials poured into the frame and spread to fill the frame evenly. Two 0.3 cm spacers were taped to each side of the forming frame. These prevented the hot press from closing completely and reduced the probability of the formation of internal air void in the panel during the release of gases that might otherwise have penetrated the mat and caused undesirable defects. After the completion of forming, the top caul plate was placed on the mat, and the entire assembly was placed into an oil-heated press. The temperature of the hot press was maintained at 190 ºC, and the pressure was constant at 35 (bar). The press cycle consisted of two phases. The first phase involved closing of the press for 20 minutes. In the second phase, the press was opened and the spacers were removed from the assembly, and subsequently the press was closed completely for 5 additional minutes. Then, the cauls plate assembly containing the molten wood-plastic was removed from the hot press and placed in a cold press to allow the composites to harden under pressure. About 5 cm wide edges of each board were trimmed off to remove the low density and poor bonding area of boards. Three WPC boards were manufactured for each formulation. The boards were conditioned at constant room temperature (25 ºC) and relative humidity (65%) for two weeks prior to testing.

Fig. 1. Microscopic photos of the fillers (4X)
Table 1. Filler Size Distribution of the Ingredients Used to Make Composites (% total weight/mesh)

<table>
<thead>
<tr>
<th>Type of filler</th>
<th>&lt;18</th>
<th>18-30</th>
<th>30-60</th>
<th>60-100</th>
<th>&gt;100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sanding flour of MDF</td>
<td>18</td>
<td>24</td>
<td>26</td>
<td>29</td>
<td>3</td>
</tr>
<tr>
<td>Wood Sawdust</td>
<td>12</td>
<td>40</td>
<td>38</td>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>Flour of Rice hull</td>
<td>—</td>
<td>34</td>
<td>39</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>Particleboard sawdust</td>
<td>2</td>
<td>18</td>
<td>40</td>
<td>26</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 2. Composition of Evaluated Formulations (% total weight)

<table>
<thead>
<tr>
<th>number</th>
<th>Recycled HDPE (%)</th>
<th>Flour (%)</th>
<th>MAPE(phc)</th>
<th>Type of flour</th>
<th>code</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>60</td>
<td>3</td>
<td>MDF¹</td>
<td>RPE²/MDF</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>60</td>
<td>3</td>
<td>WF³</td>
<td>RPE/WF</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>60</td>
<td>3</td>
<td>RH⁴</td>
<td>RPE/RH</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>60</td>
<td>3</td>
<td>PB⁵</td>
<td>RPE/PB</td>
</tr>
</tbody>
</table>

¹ – MDF as sanding flour from Medium Density Fiberboard; 2 – RPE as recycled High density poly-ethylene; 3 – WF means wood saw dust; 4 – RH as Flour of Rice hulls; 5 - PB means sawdust from particleboard.

Physical tests

Short-term (after 2 and 24 hours immersed in water) water absorption and thickness swelling tests were carried out according to the ASTM D1037 specification, and long-term (after 2, 4, 6.5, 9.5, 12, 24, 35, 48, 72, 96, 120, 168, 192, 336, 504, 672, 840, 1008, 1176, 1344, 1512, 1680, 1848, and 2016 hours immersed in water) water absorption and thickness swelling tests were carried out according to the ASTM D7031 specification. Five specimens of each panel were selected and dried in an oven for 24 h at 103±2°C. The weight and thickness of dried specimens were measured to a precision of 0.001 millimeter or gram. The specimens were then placed in distilled water and kept at room temperature. For each measurement, specimens were removed from the water and the surface water was wiped off using blotting paper. The weight and thickness of the specimens were measured at different times during the time immersion. The measurements were terminated after the equilibrium weight and thickness of the specimens were reached. The values of the water absorption and thickness swelling in percentage were calculated using Equations 1 and 2,

\[ W_A(t) = \left( \frac{W(t)}{W_0} - 1 \right) \times 100 \]  \hspace{2cm} (1)

\[ TS(t) = \left( \frac{H(t)}{H_0} - 1 \right) \times 100 \] \hspace{2cm} (2)

where \( W_A(t) \) is the water absorption at time \( t \), \( W_0 \) is the initial weight of specimens, and \( W(t) \) is the weight of specimens at time \( t \) (Eq. 1). \( TS(t) \) is the thickness swelling at time \( t \), \( H_0 \) is the initial thickness of specimens, and \( H(t) \) is the thickness of specimens at time \( t \) (Eq. 2).
Mechanical test (Flexural properties)

Three-point static bending tests were carried out according to the ASTM D7031 specification. Five replicates of each panel were tested. The samples had nominal dimensions of 220×50×11 mm, and a computer-controlled INSTRON machine (MODEL 5567) was used. The speed of the crosshead was set at 8.1mm/min. Data were collected and used to calculate the modulus of elasticity (MOE) and modulus of rupture (MOR).

RESULTS AND DISCUSSION

Short-Term Water Absorption

The short-term water absorption and thickness swelling of composites immersed in water at 2 and 24 hours are given in Figs. 2 and 3, respectively. As it is clearly seen, generally water absorption and thickness swelling increased with immersion time. After 24 hours immersion the values of water absorption and thickness swelling were greater than at 2 hours. Figures 2 and 3 show that there were no obvious differences between the water absorption and the thickness swelling histograms. The hydrophilic nature of lignocellulosic fillers tends to promote water absorption and thickness swelling in studied WPCs because most plastics have a hydrophobic nature and show negligible water absorption and thickness swelling (Espert et al. 2004). Because the fraction of natural filler in the studied composites was kept constant, the different results observed for various lignocellulosic composites can be attributed to the type of filler. Also, Figs. 2 and 3 show the effect of the lignocellulosic fillers on short-term water absorption and thickness swelling composites made of different fillers with recycled HDPE. At 2 or 24 hours immersion time, composites containing sanding flour from MDF as filler exhibited high values of water absorption and thickness swelling.

Fig. 2. Water absorption of composites after 2 and 24 hours immersed in water
As it is shown in Fig. 1, sanding flour from MDF generally consists of fibrous matter, and it can absorb moisture more readily rather than other fillers. According to Figs. 2 and 3 composites made from rice hull showed the lowest water absorption and thickness swelling values. Rice hull is a non-wooden filler and has somewhat different chemical composition as compared to wooden fillers. This result may be due to presence of minerals as significant chemical constituents of rice hulls (Klyosof 2007).

![Fig. 3. Thickness swelling of composites after 2 and 24 hours immersed in water](image)

**Long-Term Water Absorption**

Figures 4 and 5 show long-term water absorption and thickness swelling of composites after 2016 hours immersed in water. Generally water absorption and thickness swelling increased with immersion time, reaching a certain value beyond which no more weight and thickness increased.

![Fig. 4. Long-term water absorption of composites after 2016 hours immersed in water](image)
Unlike the results for short-term water absorption and thickness swelling, composites including wood sawdust showed higher values for long-term water absorption and thickness swelling. In fact, the higher values for wood sawdust/recycled HDPE composites can be related to larger particle size (Table 1) and more hygroscopic chemical constituents (Klyosof 2007). Figures 4 and 5 show that the composites including rice hulls had longer equilibrium time (time to reach to equilibrium water absorption and thickness swelling). The composites including rice hulls swelled and gained weight very slowly.

![Graph showing long-term thickness swelling of composites after 2016 hours immersed in water.](image)

**Fig. 5.** Long-term thickness swelling of composites after 2016 hours immersed in water

The analysis of the water diffusion mechanism in composites was performed based on Fick's Theory. Diffusion can be distinguished theoretically by the shape of sorption curve represented by Eq. 3,

$$\frac{M_t}{M_s} = kt^n$$

where $M_t$ is the moisture content at time $t$, $M_s$ is the moisture content at the equilibrium, and $k$ and $n$ are constants. If the value of coefficient $n$ gets smaller than 0.5, then water absorption behavior follows the Fickian diffusion process (Espert et al. 2004). To understand the mechanism of the water absorption in composite materials, the experimental data were fitted to the Eq. 4 which is derived from Eq. 3 (Espert et al. 2004).

$$\log\left(\frac{M_t}{M_s}\right) = \log k + n \log t$$
The diffusion coefficient is the most important parameter in the Fickian model. The water diffusion coefficient was calculated using the Eq 5.

\[
\frac{M_t}{M_e} = 4 \left( \frac{D}{L \pi} \right)^{0.5} t^{0.5}
\]  

(5)

In this equation \(M_t\) is the moisture content at time \(t\), \(M_e\) is the moisture content at equilibrium, \(L\) is thickness of samples, and \(D\) is the water diffusion coefficient (Espert et al. 2004).

Table 3 shows diffusion parameters for the studied composites. The values of \(n\) indicate that the water absorption in lignocellulosic filler / HDPE composites followed a Fickian process. It can be seen that the diffusion coefficient of composites including wood sawdust was the highest. This result can be attributed to big size of wood sawdust particles (Table 1). The lowest value diffusion coefficient in composites containing rice hulls as filler can be due to chemical constituents that have been discussed.

### Table 3. Diffusion Coefficient for Studied Composites

<table>
<thead>
<tr>
<th>Composites Code</th>
<th>(n)</th>
<th>(\log_k)</th>
<th>(k(h^2))</th>
<th>Diffusion Coefficient (m²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPE/MDF</td>
<td>0.168</td>
<td>-0.544</td>
<td>0.286</td>
<td>6.74E-12</td>
</tr>
<tr>
<td>RPE/WF</td>
<td>0.408</td>
<td>-1.296</td>
<td>0.050</td>
<td>7.57E-12</td>
</tr>
<tr>
<td>RPE/RH</td>
<td>0.479</td>
<td>-1.523</td>
<td>0.030</td>
<td>5.14E-12</td>
</tr>
<tr>
<td>RPE/PB</td>
<td>0.478</td>
<td>-1.485</td>
<td>0.033</td>
<td>6.97E-12</td>
</tr>
</tbody>
</table>

The values of \(k\) were calculated from \(10^{\log_k}\) (in Eq. 4)

Further study was conducted to model thickness swelling of studied composites that have already been reported by the authors (Najafi and Kazemi Najafi 2009). Swelling rate parameters in the model were obtained by fitting the model predictions with the experimental data. Shi and Gardner (2006) tried to quantify the thickness swelling rate of WPCs for more convenient comparisons. They developed a swelling model describing the hygroscopic swelling process of wood based composites. In this model, a swelling rate parameter \((K_{SR})\), as determined using the test data, can be used to quantify the swelling rate. The swelling model is expressed by the following equation,

\[
H(t) = H_s \left[ 1 + \left( \frac{H_s}{H_0} - 1 \right) e^{-K_{SR} t} \right]
\]  

(6)

where \(H(t)\) is the thickness swelling at time \(t\). \(H_0\) and \(H_s\) are the initial and equilibrium board thickness, respectively. \(K_{SR}\) is a constant referred to as the initial (or intrinsic) relative swelling rate. The values of \(K_{SR}\) in equation 6 depend on how fast the composites swell, and also on their equilibrium thickness swelling. Non-linear curve fitting was used to find the swelling rate parameter \((K_{SR})\) that provides the best fit between the equation and the experimental data. This algorithm seeks the parameter values that minimize the
sum of the squared differences between the observed and predicted values of the dependent variable as seen in Eq. 7,

$$SS = \sum_{i=1}^{n} \left( y_i - \bar{y}_i \right)^2$$ (7)

where $SS$ is the sum of squared difference and $y_i$ and $\bar{y}_i$ are the observed and predicted values of the dependent variable, respectively. The swelling rate parameter ($K_{SR}$) of the composites is given in Table 4. In addition, maximum values of thickness swelling are shown. Composites containing wood sawdust showed the highest thickness swelling. The minimum $K_{SR}$ was calculated for composites made of rice hull. But the maximum value of $K_{SR}$ was found in composites including sanding flour from MDF. It is important to note that in the swelling model $K_{SR}$ was obtained considering the whole thickness process until it was equilibrated. It is dependent not only on the initial rate of swelling but also on the equilibrium thickness swelling of the composites (Shi and Gardner 2006). There was less time required to reach the equilibrium thickness for sanding flour of MDF / recycled composites (Fig. 5). This can explain the very high $K_{SR}$ value determined in this type of composites. Figure 6 indicates fitting predicted thickness swelling with experimental data of recycled HDPE/particleboard sawdust composites for calculating the swelling rate parameter.

Table 4. Swelling Rate Parameters for Studied Composites

<table>
<thead>
<tr>
<th>Composites Code</th>
<th>Final Thickness Swelled (%)</th>
<th>$k_{SR} \times 10^{-3} \text{ (h}^{-1})$</th>
<th>ss</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPE/MDF</td>
<td>7.25</td>
<td>7.88</td>
<td>19.48</td>
</tr>
<tr>
<td>RPE/WF</td>
<td>13.18</td>
<td>3.34</td>
<td>31.31</td>
</tr>
<tr>
<td>RPE/RH</td>
<td>6.18</td>
<td>2.90</td>
<td>6.36</td>
</tr>
<tr>
<td>RPE/PB</td>
<td>7.65</td>
<td>3.47</td>
<td>8.75</td>
</tr>
</tbody>
</table>

The relationship between long-term water absorption and thickness swelling in composites is shown in Table 5. Thickness swelling is a response to absorbed water in composites. It is shown in Table 5 that R-squared values of all composites were above 0.97.

Table 5. Relationship between Long-term Water Absorption (WA) and Thickness swelling (ThS) in Studied Composites

<table>
<thead>
<tr>
<th>Composites Code</th>
<th>Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPE/MDF</td>
<td>$ThS = 0.23 \text{ WA} + 0.38$</td>
<td>0.976</td>
</tr>
<tr>
<td>RPE/WF</td>
<td>$ThS = 0.35 \text{ WA} + 0.23$</td>
<td>0.986</td>
</tr>
<tr>
<td>RPE/RH</td>
<td>$ThS = 0.22 \text{ WA} + 0.29$</td>
<td>0.996</td>
</tr>
<tr>
<td>RPE/PB</td>
<td>$ThS = 0.25 \text{ WA} + 0.43$</td>
<td>0.998</td>
</tr>
</tbody>
</table>
Flexural Properties

The Modulus of Elasticity (MOE) and Modulus of Rupture (MOR) of lignocellulosic filler/recycled HDPE composites containing different fillers are presented in Fig. 7. From the curves in the figure it is evident that values in MOE and MOR increased upon filling the recycled HDPE matrix with filler types, indicating a reinforcing effect. The highest MOE values were obtained in composites containing sanding flour from MDF and also particleboard sawdust, and the lowest value in composites including wood sawdust. Similar behavior can be observed in Fig. 7, when the significant increase in MOR is plotted versus composites type. The differences in modulus and strength improvement with respect to filler type were very prominent at the lowest value. As was noted in Table 1, the size of wood sawdust filler can explain the lowest MOE and MOR values. These results also correspond to previously reported data. Zaini and others reported an increase in flexural modulus with increasing particle size for composites made with 230- to 60-mesh oil palm wood flour, and Myers and others reported decreasing flexural MOE with increasing particle size for PP filled with 40- to 20-mesh wood flour (Zaini 1995; Myers 1991). The highest MOE and MOR values in composites made from fillers such as sanding flour of MDF or particleboard sawdust can be attributed to the scantling glue that was remained with filler; such glue can become active again at sufficiently high temperature due to the hot/press method. Figure 8 shows strain at yield in lignocellulosic filler recycled HDPE composites and Fig. 9 shows energy to yield point in the studied composites. Because the fraction of lignocellulosic filler and recycled HDPE in composites were kept constant, the differences observed between various lignocellulosic composites can be attributed to the type of filler. From the plots it...
can be seen that there were significant differences in strain yield and energy to yield point between composites including sanding flour of MDF and composites containing wood sawdust. This result can be attributed to the fibrous form of sanding flour from MDF. In contrast to sanding flour from MDF, wood sawdust had the largest size among the studied fillers. In fact the lower values for wood sawdust / recycled HDPE composites can be related to the larger particle size (Table 1).

Fig. 7. MOR and MOE in studied composites

Fig. 8. Strain at yield in studied composites
CONCLUSIONS

1. Short-term water absorption and thickness swelling of all the composites were clearly dependent upon the lignocellulosic filler type. In the short term, water absorption and thickness swelling were highest in composites containing sanding flour from MDF, and the lowest values were found in composites including rice hull flour.

2. In the long term, water absorption of all the composites followed the kinetics of a Fickian diffusion process, and the thickness swelling model provided a very good prediction.

3. The water diffusion coefficient and swelling rate parameter of the composites were clearly dependent upon the lignocellulosic filler type too. Water diffusion coefficient of composites including wood sawdust was highest, and in composites containing rice hull flour showed the lowest value. The minimum $K_{SR}$ was calculated for composites made of rice hull. But the maximum value of $K_{SR}$ was found in composites containing sanding flour from MDF.

4. Maximum Values of MOE, MOR, strain at yield, and energy to yield point were obtained with composites including sanding flour from MDF and particleboard sawdust. Composites containing wood sawdust showed minimum values of MOE, MOR, strain at yield point, and energy to yield point in flexural tests.

5. Agricultural residue and industrial wastes such as flour of rice hull, wood sawdust, sanding flour of MDF, and sawdust of particleboard could in the future be good reinforcements for recycled HDPE. Using of these materials can be a resource for manufacturing of wood plastic composites. Flour of rice hull seems to have the potential for creating a suitable plastic-based composite material for consumption in wet environments. Moreover, dry blend/hot press provides the possibility of producing large panels of composites.

Fig. 9. Energy to yield point in studied composites
REFERENCES CITED


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