ACCELERATED WEATHERING OF RUBBER WOOD-REINFORCED RECYCLED POLYPROPYLENE COMPOSITE

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ABSTRACT

The successful development of durable wood-plastic composite (WPC) cladding poses a challenge, hence investigating the effects of water immersion-freeze-thaw treatment on the physical properties, flexural strength (FS), and morphology of wood-recycled polypropylene composites. The behavior of wood plastic composite is difficult to predict due to the complexity of the structure of the material. Wood consists of cells (fibers) arranged in an intricate pattern, and the behavior of the material is a result of the behavior of the cells and the cell arrangement. In this study, different approaches were employed to analyze various degradation in the wood plastic composite. This study shows whether the flexural strength and thermal stabilization of the WPC will reduce or boost after introduction to water immersion-freezing-thaw cycling, as well as the degree of modifications in the ground characteristics (shade and roughness) of the composites after introduction to water immersion. This research is composed of new research on the weathering of wood-polymer composites (WPCs) and the findings of this research will be derived from rapid laboratory studies.

Keywords: Chemical contents, Mechanical, Physical properties, Recycle polypropylene, Rubber-wood flour, Wood-plastic composites
INTRODUCTION

The wood/plastic composite (WPC) is an environmentally friendly composite with high performance and added value. It is made from wood flour (WF) and thermoplastic mixed with a certain proportion of coupling agent, lubricant, stabilizer, etc. under injection molding, extrusion, and another forming process (Tajvidi and Haggdan et al. 2009). WPC shares the wood texture of original solid wood products as well as excellent mechanical properties, workability, corrosion resistance, water tolerance, and fireproofing.

Under the background of scale commercialized application of wood/plastic products, it has become a research hotspot to improve the quality and cut down the production cost of the wood/plastic products. The principal research approaches include increasing the additive amount of wood flour, reducing the additive number of plastics, adding padding, and improving the production process (Toghyani et al., 2017).

Wood-plastic composite is a low-carbon and environmentally friendly material that refers to a composite material that contains wood and plastic. Among the numerous advantages of WPCs includes, lightweight, corrosion resistance, dimensional stability, and recyclable, which is widely used in outdoor construction, logistics, and decoration, etc., WPC products have commonly substituted for solid wood in today’s applications, which can effectively solve waste fiber and plastic products caused by the waste of resources and the problems of environment pollution (Ge et al., 2018).

Previous studies on rubber wood showed various climatic conditions caused millions of dollars of material damage every year, and high costs may be involved in replacing these damaged products. Hence when new material is developed it is important to determine how durable the material will be in a variety of environmental conditions (Butylina and Kärki, 2011; Butylina and Kärki, 2014). Consequently, in colder regions where the freeze-thaw action is prevalent, freeze-thaw durability may be of great importance in determining the service life of WPCs (Calorimetry, 2001; Butylina and Kärki, 2014), since it is prone to degradation by many kinds of fungi. A combination of moisture content, temperature, biological activity, etc. can and will affect the mechanical and physical properties of a wooden element and mostly of a wooden structure (Chen et al., 2016; Friedrich and Luible, 2016a).

The durability of WPCs has been studied, focusing on the characterization of moisture-induced reductions in mechanical properties, thickness swelling, rate of water transport, and fungal resistance of synthetic polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) matrix composite. The poor freeze-thaw resistance that is common with WPCs has been noted as a primary durability concern (Butylina and Kärki, 2014; Chaudemanche et al., 2018). Wood reinforcement is subject to expansion upon the absorption of moisture. The moisture absorbed by the WPCs expands upon freezing, causing the development of internal stresses that causes cracking in the surrounding polymer matrix (Chen et al., 2016; Friedrich and Luible, 2016a). Researchers reported that the limited degree of bonding between the hydrophilic “water-loving” wood and the hydrophobic “water-hating” plastics can also be disrupted by physical activities such as freezing and thawing. This would be a critical performance issue in temperate exposures (Chen et al., 2016; Friedrich and Luible, 2016a). According to previous research, testing of small samples showed some loss in properties after freeze-thaw cycling; however, there were no significant effects on the flexural
properties of freeze-thawed cycled commercial samples (Butylina and Kärki, 2011; Luible, 2016b). Others have shown losses in flexural strength and stiffness of 5% and 15%, respectively, after exposure to five freeze-thaw cycles (Chen et al., 2016; Friedrich and Luible, 2016a). A large portion of the mechanical property loss was associated with moisture absorption rather than the freeze-thaw cycle (Srubar, 2015).

Chain scission and crosslinking are two opposite reactions; chain scission reduces the molecular weight of the polymer while crosslinking results in increased molecular weight due to free radicals recombining and creating new polymer chains. Crosslinking does not affect polymer crystallinity, while chain scission can increase crystallinity due to short chains being more mobile and crystallizing more easily (Matuana and Stark, 2011; Ge et al., 2018). Changes caused by UV radiation harm the characteristics of the polymer. The change in the crystallinity of the polymer contributes to the simultaneous cracking of the surface (Rahman et al., 2013; Martins et al., 2017). Hot pressing is an easy manufacturing method for making wood-plastic composites. In addition to the flexibility in altering the density of the produced panels, the technique offers the added benefit of the possibility of producing layered panels with higher mechanical properties in a one-step process that many manufacturers want (Rahman et al., 2013; Rao, 2018).

Although WPCs based on polypropylene were manufactured using rubber-wood flour and their properties evaluated, there is very limited or no information on the characteristics of WPCs recycled polypropylene-based. Therefore, this study aimed to produce experimental WPC samples using rubber-wood fiber and recycled polypropylene as the material, to investigate the mechanical properties of wood-plastic composites exposed to accelerate freeze-thaw cycling meant to simulate outdoor exposure to a different temperature.

MATERIALS AND METHODS
The recycled polypropylene (rPP) was used as a polymeric matrix with a melt flow index of 12 g/10 min, and a density of 0.83 g/cm³ supplied from Withaya Intertrade Co., Ltd, Thailand for the samples. Rubber-wood flour (RWF), used as the reinforcing material, is supplied by a local furniture manufacturer in Trang, Thailand. The size of the rubberwood flour particles was smaller than 180 mm (<80 mesh) and dried in an oven at a temperature of 110 °C for 8 h to reduce the moisture content to less than 3%. Maleic anhydride-grafted polypropylene (MAPP) with a rate of 8–10% Sigma-Aldrich, Missouri, USA was used as the coupling agent. Paraffin wax as a lubricant was purchased from Nippon Seiro Co., Ltd. Yamaguchi, Japan. The ultraviolet stabilizer purchased from TH Color Co., Ltd. Samutprakarn, Thailand was also used as a light stabilizer additive in the samples. The sample was supplied in pellets by the university of Songkhla Thailand.

Manufacture of the composite sample
The ratios of the materials used in this study were recycled PP: 50.3%, RWF: 44.5%, MAPP: 3.9%, UV: 0.2% and Lub: 1% by weight. In the first stage, WPCs pellets were manufactured before they were compounded into composite samples employing a twin-screw extruder, Model CTE-D25L40 (Srivabut and Hiziroglu, 2018). The temperature from the feeding to the dead zone was controlled in the range of 170 to 200°C, while the screw rotation speed was fixed at 50 rpm. In the next stage, the WPCs pellets were carefully dried before use in an oven at a temperature of 50°C for 24 h. The samples were compressed in a hot press having a temperature of 190°C at a pressure of 870 psi for 30 min with.
a sequence of pre-heating, compressing, and cooling. Finally, the specimens were machined complying with ASTM D638 standards before any tests were carried out.

**Water absorption and thickness swelling of the sample**

Water absorption (WA) and thickness swelling (TS) of the specimens were carried out according to ASTM D570-88. The specimens with dimensions 10 mm × 20 mm × 3 mm were cut from the panels. Five replications of each combination were dried in an oven at a temperature of 50 °C for 24 h, until constant weight. The weight and thickness of dried specimens were measured to a precision of 0.001 g and 0.01 mm, respectively. The specimens were then placed in water and kept at room temperature for 13 weeks. For each measurement, the specimens were removed from the water tank, wiped off with tissue paper, and immediately weighed. The percentage of water absorption and thickness swelling was calculated using Eqs (1).

\[
WA = \frac{W_1 - W_0}{W_0} \times 100 - 1
\]

Where WA is the water absorption, \(W_0\) is the initial mass of the sample and \(W_1\) is the mass of the samples after immersing in water Eqs (1).

\[
TS = \frac{T_1 - T_0}{T_0} \times 100 - 2
\]

Where TS is thickness swelling at a given time \(t\), \(T_0\) is the initial dry weight, and \(T_1\) is the soaked weight of the specimen, both at the given time \(t\) Eqs (2).

**Mechanical properties of the samples**

The flexural properties of composites were measured on a Universal Testing Machine (UTM) ag-1/100KN (Shimadzu Corporation, Japan). The specimens were dried in an oven at a temperature of 50 °C for 24 hours, before the tests. The flexural test, a three-point bending test was carried out based on ASTM D790-92 at a cross-head speed of 2 mm/min, using a span of 80 mm. Specimens for bending test had nominal dimensions of 15 mm ×100 mm × 4 mm. All tests were performed at room temperature with five replications of each combination of 12 samples.

**Microscopic evaluation of the samples**

Scanning electron microscopy (SEM) was performed with a Jeol JSM-5800 LV operating at 10kV. Before the analysis, the fracture surface was covered with a layer of gold using a sputter coater. Elemental analysis of mineral-containing composite was performed with SEM coupled to an energy-dispersive X-ray spectrometer (EDS). The scanning data will be analyzed at the magnification of 100× and 200×. Approximately 8-10 SEM images were taken and analyzed for each composite formulation.

**FTIR Analysis**

A Spectrum 100 FTIR spectrometer (Perkin-Elmer, UK) equipped with an attenuated total reflection (ATR) accessory (Perkin Elmer) was used for the surface analysis of the composite. The spectra were collected by co-adding 14 scans at a resolution of 4 cm\(^{-1}\) in the range from 4000 to 400 cm\(^{-1}\). All spectra were normalized by 2917 cm\(^{-1}\) (CeH band), the specific peak intensity of PP. This peak was selected as the reference peak because it changed the least during
weathering. For the estimation of the degree of aging of the samples the area of the carbonyl groups region, 1800-1600 cm\(^{-1}\) was calculated. Five replicates for each type of composite were measured.

**Differential scanning calorimetry (DSC)**

DSC tests were carried out according to standard ASTM D3418-15 (Calorimetry, 2001) to assess material behavior at different temperatures using a Differential Scanning Calorimetry, DSC-7 (Perkin Elmer, USA). The test consists of heating and cooling the test material at a controlled rate in an insulated environment under a specified purge gas at a controlled flow rate and continuously monitored with a suitable sensing device the difference in heat input due to energy changes in the material between the reference material and test material. In this case, the air was used as the purge gas as it is present in the nominal production environment and the heating cycle was set to 25–200\(^{\circ}\)C due to fiber degradation at higher temperatures. The heating and cooling rate was set to 10\(^{\circ}\)C/min, which is the default value in the standard. The percentage crystallinity of maxing (Cm) was evaluated according to Eq (3).

\[
C_m(\%) = \frac{\Delta h_f}{\Delta h_{of}} \times 10^{-3}
\]

Where Dhf is the enthalpy of fusion and Dhof is the enthalpy of fusion of perfectly 100% crystalline polypropylene (Dhof = 165 J/g).

**Micro-hardness properties**

Micro-hardness tests helped to measure the hardness of the WPC. Hardness is determined when force is applied by an indenter to the surface area of the material. In this study a load of 0.05g will be applied for the 30s using a micro Vicker hardness testing machine, HM-200 Series made in Japan.

**RESULT AND DISCUSSION**

The experimental outcomes were evaluated for five samples of each experiment with a 5%-fold significance level (a = 0.05).

**Water absorption, thickness swelling, and mass changes**

The wettability of the composites is displayed in Fig 1 & 2. This shows the immersion period of 6 days, it was enough for the stabilization of the water absorption and thickness swelling parameters. Moreover, the amount of absorbed water and swelling started to increase faster after the second day of immersion. The highest wettability for the WPC was found in the fifth cycle compared to the first cycle of water absorption (Mazzanti and Mollica, 2017). Since both specimens were exposed on both sides, the moisture absorption of the specimen is two-dimensional. In addition, the composites showed low mechanical properties, which was explained by the loss of WF/matrix bonding.

Moisture absorption has a great impact on the properties of weathered composites (Turku and Timo, 2018). The study revealed that freeze-thaw cycling on wood and recycled plastic-based composites showed that more moisture was absorbed when subjected to freeze-thaw compared to the original weight of the specimen. Properties loss after the complete cycling was similar to the property’s loss after solely water immersion (Adhikary and Staiger, 2013). However, properties loss after freeze-thaw cycling without water immersion periods was negligible. Absorbed
moisture degrades interfacial interaction in the composite, reducing stress transfer and, hence, lowering the mechanical properties (Butylina and Kärki, 2014). Also, the presence of water made wood particles swell which causes stress in the matrix and micro-cracking formation.

Micro-cracks lead to further ingress of water into the composite after exposure to water. The effects of water are often irreversible, while the characteristics of the products are not retrieved after boiling. Besides, the sample was put in a freezing oven at a temperature of 50°C for 24hrs, this method was performed for three days to obtain a decrease in the moisture content of the sample (Rahman et al., 2013; Rao, 2018). However, Figure 3 Shows percentage changes, as the moisture content decreased from positive to negative from day one to day three. It was also observed that the specimen has undergone some shrinkage as a result of drying which shows that there was a reduction in the swelling until an equilibrium was reached.

Figure1: Change in water absorption of WPC at room temperature compared with PP (ordinary Polypropylene)
Figure 2: Percentage change in thickness swelling of WPC and PP during the freeze-thaw process

Figure 3: The percentage changes in the mass of WPC and PP after drying
**Flexural properties**

A significant decrease in flexural strength was observed after the complete freeze-thaw cycle. The decrease in strength was higher in the composite subjected to freeze-thaw compared to the reference specimen. Furthermore, the young modulus was found to decrease after the freeze-thaw cycle. The mechanical properties degradation of the wood plastic composite is attributed to the wood component degradation as stated in previous research. (Butylina, Martikka and Kärki, 2011). The flexural properties that were lost to the strength are believed to be due to the presence of moisture, interface degradation, and increased pore size and number due to repeated freeze-thaw cycles also can contribute to the degradation of flexural properties (Butylina and Kärki, 2011; Adhikary and Staiger, 2013).

It was observed in Fig 3. As stated earlier that the flexural properties declined for strength and modulus, respectively. However, the flexural modulus (FM) of some samples and the flexural strength (FS) of some of the samples gained strength slightly.

![Figure 4](image-url)

**Figure 4:** The typical flexural properties of the wood polymer composite after five freeze-thaw cycles.

**Morphology (SEM)**

Photograph of the composite surface with the SEM technique shows significant changes in the composite surfaces. Before the weathering Fig 4. The surfaces of the samples were smooth; the wood flour particles were covered with the matrix (Turku and Timo, 2018; Wang et al., 2017). After the weathering, cracks, and holes could be found on all surfaces of the studied composites.

It was observed that there was a loss of bonding between fiber and matrix (a, b, c, d), in the first, third, and fifth cycles respectively, characterized by the apparition of voids that are noticed compared to the untreated WPC (Turku et al., 2017; Yang et al., 2012). The fibers appear degraded with a complete lack of resin layer and the microfibrils can be observed. The ruptured ends of the composite were not plane with some parts pulled out.
Figure 5: The flexural surface fractured of WPC subjected to various water absorption freeze-thaw (WFT) cycles, (a) untreated, (b) after 1 cycle, (c) 3 cycles, and (d) 5 cycles

FTIR Test

FTIR spectra of the wood plastic composite produced with solvent and extracted wood flour before and after weathering are presented in Figure 6. The peaks at 399.134 cm\(^{-1}\), attributed to the linkage between the wood and the polymer, decreased drastically upon weathering. It indicates the degradation of wood, in particular, the degradation of cellulose (Chen et al., 2016). The band's strength, however, at 399.193–7000.34 cm\(^{-1}\), which was assigned to the carbonyl groups (carboxylic acids at 399.193 cm\(^{-1}\) and esters at 7000.34 cm\(^{-1}\)), increased intensely (Rao, 2018; Matuana and Stark, 2011). This indicates that oxidation and photodegradation of cellulose occurred as a cause of weathering (Turku and Kärki, 2016).

A significant decrease in the intensity of peaks at 399.193 cm\(^{-1}\) (C–O in cellulose and primary alcohols of lignin) occurred on the surface of WPCs after exposure to freeze-thaw (Matuana and Stark, 2011; Turku and Kärki, 2016). The formation of the peak in Figure 7. implied an increase and decrease of absorption respectively, except for the ordinary PP (reference sample), all-composite shows positive at peak 299.193 cm\(^{-1}\) – 7000.34 cm\(^{-1}\), it is associated with OH stretching in hydroxyl groups originating from cellulose which is corresponded with the previous research by (Peng and Cao, 2015).
Thermal properties

The temperature and humidity graph of the WPCs before and after the freeze-thaw periods shows that the use of chemical fillers has a beneficial effect on heat characteristics but may reduce the strength and ductility of the filled plastics. It can be seen that WPCs with distinct chemical components displayed mildly greater levels of melting temperature, enthalpy, and crystallization relative to separate samples (Srivabut and Hiziroglu, 2018; Mrad et al., 2018). In contrast, the cooling temperature of the control samples presented slightly lower values as compared with freeze-thaw samples.

Figure 6: FTIR spectra for WPC before and after the freeze-thaw.

Figure 7: DSC heating and cooling thermogram of WPC subjected to various water absorption freeze-thaw (WFT) cycles.
Table 1: The melting temperature (Tm) and crystallinity (Cm) of PP in the samples before and after weathering.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
<th>4Hf (j/g)</th>
<th>Cm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref- PP</td>
<td>167.07</td>
<td>132.08</td>
<td>55.45</td>
<td>33.61</td>
</tr>
<tr>
<td>Ref -WPC</td>
<td>161.33</td>
<td>119.75</td>
<td>30.99</td>
<td>18.78</td>
</tr>
<tr>
<td>WPC- cycles 1</td>
<td>161.78</td>
<td>119.82</td>
<td>37.67</td>
<td>22.83</td>
</tr>
<tr>
<td>WPC- cycles 3</td>
<td>162.52</td>
<td>120.04</td>
<td>27.87</td>
<td>16.89</td>
</tr>
<tr>
<td>WPC- cycles 5</td>
<td>160.37</td>
<td>120.52</td>
<td>26.67</td>
<td>16.16</td>
</tr>
<tr>
<td>PP- cycles 5</td>
<td>166.92</td>
<td>132.69</td>
<td>74.08</td>
<td>44.89</td>
</tr>
</tbody>
</table>

Micro-hardness properties

Microhardness averages were recorded at different cycling and standard deviation are summarized in Table 2. Aging in water for 24 hours did not change the samples. However, continuous aging in distilled water showed a reduction in the microhardness for each of the composite. The result of the microhardness showed that the sample stored in distilled water suffered a significant reduction in surface hardness compared to the reference composite. The duration of immersion is aimed at investigating surface changes in hardness that will influence mechanical wear. This study agrees with the result of other studies (Trimino and Cronin, 2018; Turku et al., 2017). A decrease in HV microhardness was found in the wood/recycled polypropylene immersed in distilled water for three weeks.

Table 2: The hardness properties of the WPC subjected to various water fatigue absorption cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (HV) (std)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref -WPC</td>
<td>22.2(0.8)</td>
</tr>
<tr>
<td>WPC- cycles 1</td>
<td>12.7 (0.1)</td>
</tr>
<tr>
<td>WPC- cycles 2</td>
<td>11.4 (0.4)</td>
</tr>
<tr>
<td>WPC- cycles 3</td>
<td>10.9 (0.1)</td>
</tr>
</tbody>
</table>
CONCLUSION

The durability performance of WPCs subjected to freeze-thaw cycles was investigated. The moisture absorption and thickness swelling of the freeze-thaw samples increased in weight after 24 hours of immersion compared to the control samples. This is due to an increase in pore number and void presence in freeze-thaw samples. The flexural strength and modulus of elasticity reduced from 15.82 Mpa to 15.46 MPa and 15.46 to 12.91 respectively after 5 freeze-thaw cycles due to the freeze-thaw. This is thought due to the plasticizing of the matrix that degraded the mechanical properties of the WPC. The thermal properties of the WPC subjected to freeze-thaw are not significantly altered indicating that freeze temperature does not cause thermal degradation on the WPC. The microscopic revealed the surface of the molded composite before and after weathering. Before the exposure to weathering, it was observed that the surface of the composite was relatively smooth, and the PP flowed over the wood particles. After weathering for 240 hours the surface of each composite was degraded. The crack appeared in the WPCs matrix, also exposure to water causes wood particles to swell. The freeze-thaw weathered sample showed decreased bonding between the matrix and the fiber as revealed by the number of fibers pulled out from the matrix. The control sample showed a little void and pores, compared to the samples subjected to freeze-thaw. The flexural analysis revealed that the moisture uptake resulted in to decrease in the flexural strength. These likewise changed the structural properties of the fiber matrix and the interface between them. Once the moisture penetrates the fiber, this causes swelling in the composite. It was also detected during the water absorption fatigue that the bonding between the matrixes decreased. The flexural strength reduces from 796.37 Mpa to 459.04 MPa after the water absorption fatigue test. The micro-hardness test of the WPCs also showed a significant reduction due to the aging period of the composite. It was observed that the longer the composite aged the lower the hardness becomes. Since the recycled WPC is equally competitive with the unrecycled WPC, the use of second-generation materials can reduce the cost of production as well as save natural resources from depletion.
REFERENCES


