DURABILITY OF WOOD FLOUR-RECYCLED THERMOPLASTIC COMPOSITES UNDER ACCELERATED FREEZE-THAW CYCLING

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ABSTRACT

This study investigated the durability performance of wood-plastic composites (WPCs) exposed to accelerated water submersion, and freeze-thaw cycling conditions. WPCs were made from virgin/ or recycled high-density polyethylene (HDPE) and polypropylene (PP) with pine (*Pinus radiata*) sawdust through hot-press moulding. Surface colour, flexural properties, dimensional stability, microstructures of interface, and thermal properties of composites were examined after the accelerated freeze–thaw (FT) cycling. It was found that water absorption and thickness swelling after 24 h water soaking of FT weathered composites were increased compared to corresponding control samples for all composite formulations. Flexural strength and stiffness were decreased; however, elongation at break was increased after the FT cycling. Scanning electron microscopy (SEM) images of fractured surfaces of weathered composite samples confirmed a loss of interfacial bonding between the wood flour and the polymer matrix. Differential scanning calorimetry (DSC) analysis showed the decrease in enthalpy and crystallinity of composites as compared to the neat PP and HDPE, with slight decrease in melting temperature. Crystallinity of the FT weathered composites for both virgin polymer (PP and HDPE) matrices increased, however composites with recycled polymer matrices decreased compared to corresponding control samples. These findings are found valid for composites made of both the virgin and recycled plastics.

1. INTRODUCTION

Wood-plastic composites are emerging as an important eco-material in the construction industry. Despite significant success in the processing, a lack of understanding of the durability performance of WPCs has limited its outdoor applications. The exposure of WPCs to environmental conditions such as humidity, temperature and sunlight alters its chemical and physical properties. Past studies have shown that a change in moisture and/or elevated temperatures may have an adverse effect on the physical and mechanical properties of WPCs [1, 2]. The durability performance of WPCs made from thermoplastics with organic fillers (such as wood , natural fibres and rice hull) exposed to biological organisms [3, 4] and ultraviolet radiation [5, 6] have been thoroughly investigated. However, there is little known about the durability and stability of WPCs under freeze-thaw weathering conditions [7, 8]. Pilarski *et al.* reported that the loss in flexural strength and modulus were 5% and 37%, respectively, for extruded composites made of virgin HDPE and pine wood flour with a lubricant (in the ratio of 44:50:6) which had been exposed to 15 accelerated cycles of water submersion, freezing and thawing [7]. In a separate study by Pilarski *et al.*, extruded pine wood-flour reinforced rigid PVC composites showed a significant loss in stiffness after 5 accelerated freeze-thaw cycles [8]. If WPCs are to be used in colder regions where they experience periodic wetting, freezing and drying during their service life, its service performance with respect to the material composition, processing methods and environmental conditions are to be fully known. In particular, the freeze-thaw durability of WPCs

made from recycled plastics and sawdust through hot-pressed moulded composites is presently not known. A separate study by Adhikary *et al.* [9], demonstrated that mechanical properties of composites made from recycled HDPE and sawdust were comparable to composites based on virgin HDPE. Hence, this work aimed to evaluate the freeze-thaw durability of bio-composites based on sawdust and matrices of virgin and recycled HDPE and PP. A detailed investigation was carried out to evaluate the properties and aesthetic changes to the composites under accelerated FT cycling.

2. EXPERIMENTAL

2.1 Materials and composite preparation

Radiata pine (*Pinus radiata)* sawdust was collected from local sawmill, dried and then ground to finer flour of 35-45 mesh sizes (diameter: 0.18-0.5mm). Both virgin as well as recycled HDPE and PP polymer were used. Recycled HDPE (rHDPE) and recycled polypropylene (rPP) granules were derived from post-consumer waste plastics, and thoroughly washed with water. Virgin form of HDPE and PP were also used for comparative study. Virgin HDPE (grade GM4755F) had a melt flow index (MFI) of 0.1 g/10min at 190°C and its density is 949 kg/m^3 and virgin PP (Hyundai Séetec M1600) had a MFI of 25 g/10min at 190°C and density of 900 kg/m^3. The corresponding MFI value for the rHDPE was 0.072 g/10min and that for the rPP was 21g/10min. A coupling agent used was maleated polypropylene (MAPP) (Epolene G-3015 polymer).

The wood flour was compounded either with the recycled or virgin thermoplastics granules in a co-rotating twin-screw extruder (screw diameter: 19 mm, L/D ratio: 30). The extruded strand was passed through a water bath and palletised. The WPCs formulations studied were given in Table 1. The compounded composite pellets were consolidated by hot press moulding in an aluminium mould. Firstly, the pellets were hot-pressed (at 180°C for HDPE series and 200°C for PP series) under a pressure of 5 mega-pascal (MPa), and was followed by cold pressing under the same pressure to produce composite panels. These panels were conditioned at a temperature of 23±2^{o}C and relative humidity (RH) of 50± 5% for at least 40 h prior to testing.

2.2 Accelerated weathering tests

The composite samples were exposed to accelerated water immersion, freeze–thaw (FT) cycles in accordance with the ASTM standard for polyolefin-based plastic lumber decking boards (ASTM D6662–01). One complete weathering cycle consisted of 3 separate stages: (i) water soaking until the equilibrium moisture content (EMC) was reached. The water submersion of the cycle was conducted at a temperature of 21±3°C. Each sample was submersed and weighed every 24 h until the weight gain was less than 1.0 % to achieve an EMC (ii) freezing for 24 h which was conducted in a GE chest freezer with the temperature controlled at -27±3°C and (iii) thawing for 24 h in a controlled environment (21±3°C and 50± 5% RH). In this study, 12 full freeze–thaw cycles was investigated to simulate variable extreme weather conditions.

2.3 Testing and characterization

Moisture absorption and thickness swelling tests were conducted in accordance with ASTM D570-98. 3-point bending was carried out with a Universal Testing Machine (MTS858 Desktop load frame with 2.5 kN load cell) at a crosshead speed of 2.8mm/min

as outlined in ASTM D790. The FT weathered composite samples were tested with weathered face in tension side.

Table 1 WPCs formulation (percent by weight)

Composite sample code	Polymer type	Polymer content (%)	Wood flour (%)	Coupling agent (%)
Wood flour-HDPE composites				
rHDPE100	Recycled	100	0	0
vHDPE100	Virgin	100	0	0
vHDPE60W40	Virgin	60	40	0
vHDPE50W50	Virgin	50	50	0
rHDE50W50	Recycled	50	50	0
rHDPE47W50CA3	Recycled	47	50	3
Wood flour-PP composites				
rPP100	Recycled	100	0	0
vPP50W50	Virgin	50	50	0
rPP50W50	Recycled	50	50	0
rPP45W50CA5	Recycled	45	50	5

The fractured surfaces of the bending test specimens were investigated using a high-resolution field emission scanning electron microscopy (FE-SEM). The surface color of the composite samples was determined according to the Commission International d'Eclairage (CIE) color system (CIE 1976) as given in the ASTM D2244 by using a Minolta Spectrophotometer (Model CM-2500d). As defined by the CIE, L^* is used to represent the lightness, and a^* and b^* are the chromaticity coordinates. Discoloration (ΔE) of the weathered samples was calculated from the following equation:

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \qquad (1)$$

DSC analysis was conducted by using a Q1000 by TA Instruments. 3-5 mg of samples was scan from 50 to 200°C at a heating rate of 2°C/min. After being held isothermally at 200°C for 5 min, samples were then cooled down at 2°C/min. Samples were then reheated to 200°C at 2°C/min (2nd run). Crystallization temperature (T_c) and enthalpy (ΔH_c) were measured from the first cooling run, while melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from second heating run. The crystallinity (X_c) was determined using the following equation:

$$X_c = \frac{\Delta H_{f100}}{\Delta H_f * w} \qquad (2)$$

where, ΔH_f is the heat of fusion of the neat thermoplastic or composites and ΔH_{f100} is the theoretical heat of fusion for a 100% crystalline polymer (ΔH_{f100}=293 J/g for HDPE and ΔH_{f100}=205 J/g for PP) [10] and w is the mass fraction of thermoplastic in the composite samples.

3. RESULTS AND DISCUSSION

3.1 Color analysis

The discoloration (ΔE) values for composites were calculated after 7 and 12 FT cycles (Fig. 1). It was observed that the surface color change (ΔE) of the composite varies with the composite formulation, and increased with increasing FT cycles. Most of the color change occurred in the first 7 FT cycles after that change is small. The MAPP additions were not observed to prevent surface discoloration, however does reduce the color change of the composites. The lightness values (ΔL*) increased for all composites except for vHDPE based composites, indicating that the surfaces of most of the composites became lighter with the FT weathering. The vHDPE based composites observed negative values indicating that darkening of the composite takes place. This variation in ΔL* values might have been due to differences in the initial color of the composites samples. The vHDPE-based composites were wood color, while the other composites were all dark black in color. Also, MAPP addition in the formulation significantly reduced the ΔL* values of the composites. For example, addition of 3 wt. % MAPP in the 50 wt. % wood flour composite with rHDPE, the surface lightening was reduced from 3.9 to 0.4 after 7 FT cycles and 5.2 to 0.9 after 12 FT cycles. It was observed that the PP-based composites fade at a more rapid rate than HDPE-based composites. An increased lightness of the composites is mainly due to bleaching of the wood component while darkening may be attributed to an increase in surface oxidation [11]. Changes in the chromaticity coordinates (a* and b*) were insignificant for the FT cycles tested.

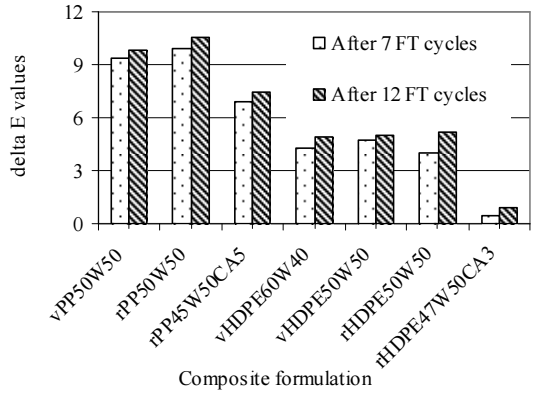

Figure 1: Discoloration (ΔE) values of WPCs after 7 and 12 FT weathering cycles

3.2 Water absorption and thickness swelling

In general, FT weathering cycles increased the tendency for water absorption in the submersion tests although the increase is also a function of the wood flour content and polymer used (Fig. 2). Water absorption of the composites after weathering increased with increasing wood-flour content. This is attributed to a greater number of voids present in composites that have been exposed to weathering. During FT cycling there is increased incremental intrusion (pore volume in the wood particle) and decreased bonding between the wood flour and matrix that increases the amount and rate of moisture uptake [7]. Although incorporation of MAPP reduces water absorption, its influence is reduced after FT cycling. It was observed that MAPP coupled (3 wt. %) composite appear to accelerate the degradation during FT cycling when compared with

non-coupled composites (*e.g.* rHDPE50W50). A similar result was observed for MAPP-coupled wood-PP composite. The thickness swelling after 24 h water submersion also increased for the weathered composites for all composite formulations (Fig. 3). The MAPP coupled composites did not exhibit greater resistance to thickness swelling than non-coupled composites. This is probably due to the degradation of the interface with repeated FT cycling which exposes the wood cellulose for water uptake.

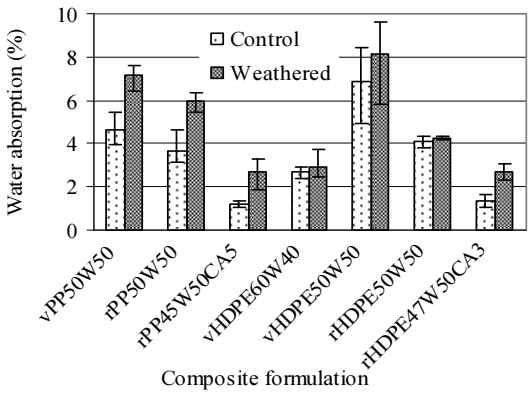

Figure 2: Water absorption by control and weathered WPCs after 24 h water soaking test

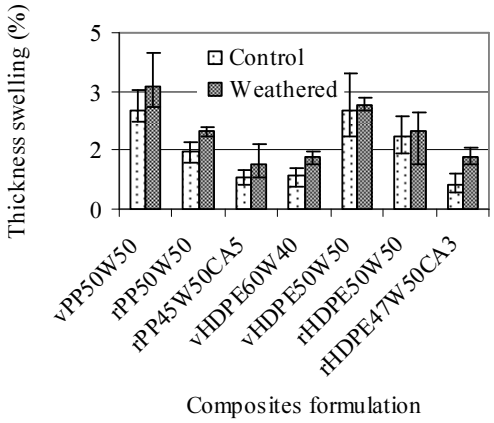

Figure 3: Thickness swelling of control and weathered WPCs after 24 h water soaking test

3.3 Flexural properties

Generally, a significant decrease in the flexural strength (MOR) of both wood-HDPE and wood-PP composites was observed after 12 FT cycles (Fig. 4). The decrease in MOR was higher in the wood-PP composites (4-18 MPa) compared with the wood-HDPE composites (1-5 MPa). In addition, the MOR degradation were greater for the composites based on the virgin polymer compared with recycled polymer for a wood flour content of 50 wt. %. The addition of MAPP (3 or 5 wt. %) in the composite formulation did not protect from the flexural properties degradation. The Young's modulus (E) was found to decrease after FT cycling for all composite formulations (Fig. 5). The E decreased by up to 66.5% and 60% for wood-HDPE and wood-PP composites, respectively. However, MAPP coupled composites exhibited the greatest decrease in E when compared to the non-coupled composites. The yield strength of the FT weathered composites was also reduced; however, elongation at break was increased slightly for most of the samples. The property degradation of WPCs is mainly attributed to the degradation of wood component as previous studies by Pages *et al.* [12] have confirmed that the tensile properties of HDPE samples remained almost constant after 90 days of weathering in Canadian winter (freeze-thaw condition). As the incorporation of the wood fibre in composites enhances moisture uptake, and in the presence of moisture, the hydrogen bonds between wood and polymer are disturbed and hydrogen bonds instead reform with the water molecules, decreasing the flexural properties [2]. Secondly, degradation of interfacial adhesion, and increased pore size and pore number in the composites also can contribute to the degradation of flexural properties [8].

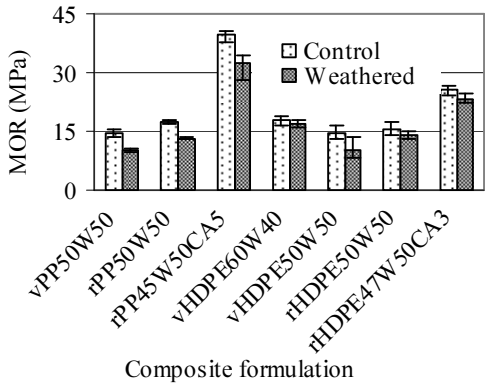

Figure 4: Flexural strength (MOR) of control and FT weathered WPCs

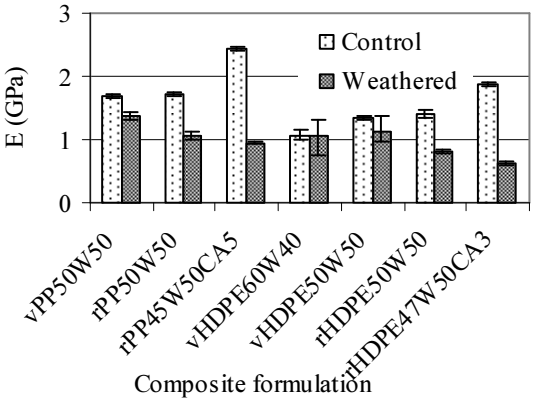

Figure 5: Flexural modulus (E) of control and FT weathered WPCs

3.4 Micro-structural characterisation

SEM images of the fractured surfaces of the flexural testing samples made of control and corresponding FT weathered composites were analysed. In general, the control sample showed a considerable amount of fibers and matrix breakage with very limited intact material on the surface. The FT weathered samples showed decreased bonding between the matrix and the fibres as reflected by the numbers of fibres being pulled out from the matrix. For example, the control sample of MAPP coupled composite made of recycled PP and wood flour (45:50 wt. %) with 5 wt. % MAPP show the very little voids and gaps at the interface, and failed with fiber breakages (Fig. 6a). On the other hand FT weathered sample (Fig. 6b) observed the interface degradation as reflected by the voids and pores, and more torn matrix with fibers pulled out from matrix rather than fiber breakages (Fig. 6b). This phenomenon is valid for all composite formulations irrespective of polymer type and form, wood fibres and coupling agent contents.

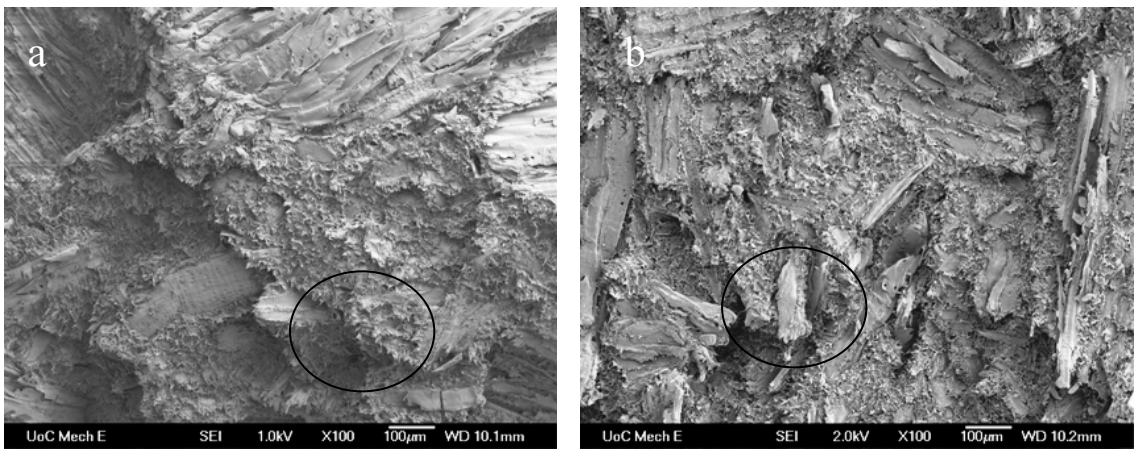

Figure 6: SEM images of rPP45W50CA5 (a) control and (b) FT exposed samples.

3.5 Thermal properties

The thermal properties of control and FT weathered composites were analysed through DSC scanning (Table 2). Fig. 7 shows the representative fusion thermograms from second heating scan for PP matrix composites. Double endothermic melting peaks were

observed for neat PP, PP based composites for both control, and FT weathered samples. The melting peak occurred ~165.7 °C corresponding to the melting of α-crystalline phase of PP polymer. While lower melting peak ~125°C is attributed to the melting of ethylene crystal units in PP copolymer segregating as a second phase in the filled composites [13]. The enthalpy of wood-filled composites was decreased as compared to the neat PP sample. An increase in enthalpy and X_c was observed for both vPP and rPP matrix composite after FT cycles. While MAPP coupled composite showed decreases in enthalpy (10.1 J/g), and X_c (10.9 %) after FT cycles. T_c (peak) and T_c (peak) of composites did not change after FT cycles.

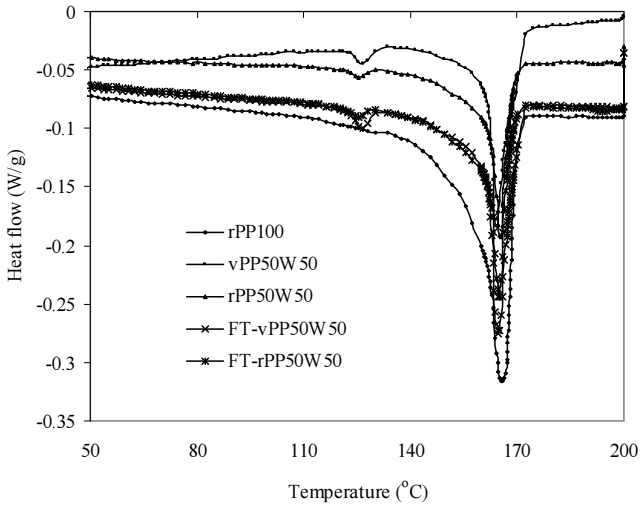

Figure 7: DSC second heating thermograms for control and weathered PP-wood flour composites.

A single endothermic melting peak occurs for the control as well as FT weathered neat HDPE and HDPE based composites (not shown here). When exposed to FT cycling, there is increase in enthalpy (22.7 J/g) with vHDPE matrix, however decrease in enthalpy (~ 16.2 J/g) was observed with rHDPE matrix composites having 50 wt. % wood flour. Similarly the MAPP (3 wt. %) added composite showed decrease in enthalpy to about 9.4 J/g as compared to control sample. The T_m and T_c of non-coupled as well as coupled FT weathered composite did not change significantly. The X_c was increased remarkably (15.5 %) for 50 wt. % wood flour filled composite with vHDPE after FT cycling, however rHDPE matrix composite behave differently, where decrease in X_c was observed. The presence of MAPP (3 wt. %) in this formulation also showed decrease in X_c (6.8 %) as compared to control sample. Interestingly, the X_c of the FT weathered composites based on the virgin polymer (PP and HDPE) was increased as compared to corresponding control samples. Consequently, composites based on the recycled polymer showed decrease in X_c after FT-weathering. This is probably due to the percentage of moisture absorption and desorption by the composites during FT cycling. The exposure of highly crystalline structure of wood fiber (i.e. cellulose) and removal of amorphous component (hemicellulose and lignin) results the increase of crystallinity of the virgin polymer based composites.

Table 2 Thermal properties of control and FT weathered WPCs

Composite sample code	Control sample				FT weathered sample			
	ΔHm (J/g)	Xc, %	Tm peak (°C)	Tc peak (°C)	ΔHm (J/g)	Xc, %	Tm peak (°C)	Tc peak (°C)
rPP100	75.6	36.9	165.7	133.4				
vPP50W50	42.5	41.5	164.1	125.1	49.4	48.2	164.9	126.1
rPP50W50	33.6	32.8	165.5	130.6	39.7	38.7	165.1	130.1
rPP45W50CA5	46.6	50.5	165.0	130.2	36.5	39.6	165.1	130.0
rHDPE100	179.5	61.3	130.9	121.3				
vHDPE50W50	83.6	57.1	131.9	121.3	106.3	72.6	131.9	121.7
rHDPE50W50	89.4	61.0	130.9	121.3	73.2	49.9	130.9	121.0
rHDPE47W50CA3	96.3	69.9	130.8	121.1	86.9	63.1	130.8	121.2

4. CONCLUSIONS

The durability performance of WPCs exposed to FT cycles was investigated. The water absorption and thickness swelling of the FT weathered samples were increased after 24 h water soaking as compared to corresponding control samples. This is attributed due to an increase of pore number and pore size in the FT weathered composites. The surface of the FT weathered composites underwent colour changes with significant changes in lightness values. Flexural strength and stiffness of the weathered composites were decreased; however, elongation at break was increased. Stiffness of the composites made from recycled plastics showed a greater decrease when compared with the strength values in terms of the percentage reduction. The percentage loss in strength values is larger as compared to E values for virgin plastics matrix composites. The MAPP coupled composites showed small strength reduction as compared to stiffness for both the PP and the HDPE matrix composites. SEM images confirmed the loss of interfacial bonding between the wood flour and the polymer matrix of FT weathered composites. DSC analysis showed the decrease in enthalpy and crystallinity of composites as compared to the neat PP and HDPE, with slight decrease in melting temperature. Crystallinity of the FT weathered composites for both virgin polymer (PP and HDPE) matrices increased, however composites with recycled polymer matrices decreased compared to corresponding control samples. These findings are valid for composites made of both the virgin and recycled plastics and the property degradation for all of the composites are comparable.

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