Durability of Wood Flour-Plastic Composites Exposed to Accelerated Freeze–Thaw Cycling. Part I. Rigid PVC Matrix

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This study examined the effects of accelerated freeze–thaw actions on the durability of wood fiber-plastic composites. Rigid PVC formulations filled with various concentrations of wood flour (both pine and maple) were processed in a counterrotating twin-screw extruder and exposed to cyclic freeze–thaw actions according to ASTM Standard D6662. Freeze–thaw cycling was also modified by omitting portions of the test (either the water or freezing) to verify whether or not moisture was the primary cause for property loss. The durability of exposed samples was assessed in terms of flexural properties, density, and dimensional stability. Scanning electron micrographs of unexposed and freeze–thaw-exposed samples were taken to qualitatively evaluate the interfacial adhesion between the wood flour and PVC matrix. The experimental results indicated that the density was not affected by freeze–thaw cycling. The dimensional stability was also relatively unaffected, although greater wood flour content exhibited greater dimensional change. The loss in stiffness of the composites was statistically significant after only two freeze–thaw cycles, regardless of both the wood species and content. Conversely, the strength of the composites was not significantly affected by five freeze–thaw cycles at lower wood flour contents (50 and 75 phr). The deleterious effects of the freeze–thaw actions on the strength of the composites became apparent at higher wood flour content (100 phr) after only two freeze–thaw cycles for maple flour and five freeze–thaw cycles for pine flour. The property loss was attributed primarily to the water portion of the cycling, which appears to have led to the decreased interfacial adhesion between the wood flour and the rigid PVC matrix. J. VINYL ADDIT. TECHNOL., 11: 1–8, 2005. © 2005 Society of Plastics Engineers

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INTRODUCTION

Recently, wood fiber-plastic composites (WPCs) have been gaining popularity in a variety of applications because WPCs combine the desirable durability of plastics with the cost-effectiveness of wood fibers as a filler or reinforcing agent [1–5]. The addition of wood fibers leads to an improvement in the stiffness of the composite, while lowering the abrasiveness on processing equipment [6–8] compared to mineral fillers. Because of these attributes, WPCs are being used in a variety of innovative applications, such as decking, docks, landscaping timbers, fencing, playground equipment, window and door frames, etc. [5, 9–12]. Among these, building applications are the largest and fastest-growing market for WPCs [13]. One of the most prevalent uses is as decking and railings, which have shown strong sales and some manufacturing companies have doubled production from 2001 to 2002 [10]. This production has been forecasted to double again by the year 2005 [13]. One reason for the popularity of WPCs is the need to replace chromated copper arsenate (CCA) pressure-treated solid wood in several outdoor applications [14, 15].

This increased use of WPCs by the construction industry has resulted in concern about their durability in outdoor environments. The products may be in ground contact or in aboveground exterior use where there is a risk of material deterioration. When in ground contact, WPCs are subject to degradation from biological agents such as fungi and subterranean termites [11, 12, 16]. Exposure to the ultraviolet (UV) rays in sunlight and moisture have also been shown to cause degradation in aboveground exterior environments [17, 18].

Various climactic conditions cause millions of dollars of material damage every year, and high costs may be involved in replacing these damaged products. Therefore, when a new material is developed it is important to determine how durable the material will be in a variety of environmental conditions. Consequently, in colder regions where the freeze–thaw action is prevalent, freeze–thaw durability may be of significant importance in determining the service life of WPCs, but has not yet been assessed. Similar studies on freeze–thaw exposure of composites made with HDPE and 50% maple wood flour have been shown to have significant losses in both flexural strength and stiffness [19]. The PVC matrix has not previously been assessed to see how its performance under freeze–thaw conditions compares to that of other matrices.

Moisture sorption during simulated warm climate accelerated weathering tests has been shown to adversely affect the properties of other wood-polymer composites. Stark [20] examined the effects of moisture on the flexural properties of 40% wood flour-filled polypropylene composites and reported that composites exposed to a water bath for 2,000 h at 26.7°C experienced 39% loss in modulus and 22% loss in strength. Tensile properties and notched Izod impact strength also significantly decreased for composites soaked in the water bath [20]. HDPE filled with 65% wood lost ~40% in tensile modulus after saturation with water [21]. However, when only 30% wood filler was used with HDPE matrix, a loss of ~25% in flexural modulus was observed after exposure to boiling water for 50 h [22].

Clemons and Ibach [23] preconditioned 50% pine flour-filled HDPE composites for fungal testing and observed that more moisture was absorbed during ambient temperature water soak than during cyclic boiling tests. However, the cyclic boiling tests did more damage to the samples. Composite samples preconditioned for five cycles of ambient temperature water and then 65% relative humidity (RH) at 27°C showed a 23.5% decrease in flexural strength [23].

Rapid hourly freeze–thaw changes from –10°C to 15°C following a 2-week water soak showed a decrease in tensile strength for 50% straw-PE composites [24]. This loss in tensile strength was attributed to either previous water or fungus exposure and not to the freezing [24]. Karbhari et al. [25] observed prevalent microcracking in E-glass vinylester composites that were cycled between –10°C and 22.5°C. There was also evidence of fiber-matrix debonding, and salt water had a more prevalent effect than deionized water; however, no causation for either observation was given [25].

The processing method was also shown to have an effect on moisture absorption of WPC products. Extruded composite samples absorbed more moisture than compression or injection-molded samples [23]. Several authors have also reported an increase in water uptake as the fiber loading increased in WPCs, regardless of fiber and matrix types [8, 20, 26, 27]. The increased fiber content allows for more fibers to undergo fiber wicking, so the moisture uptake is continually increasing with time [8]. Different lignocellulosic fillers have been shown to lead to varying degrees of water absorption, likely due to the varied adhesion between the fiber and the polymer matrix [27]. Composites made with wastepaper had greater water absorption than those manufactured with wood flour or cellulose fibers [27]. For aspen wood-polypropylene composites, a maleated polypropylene compatibilizer has been shown to reduce swelling and moisture uptake [8].

Although the durability of WPCs exposed to biological organisms and ultraviolet light has been extensively investigated [8, 12, 17, 18, 20–24], little information is available in the open literature on the freeze–thaw durability of these composites. This study was aimed to assess the effects of accelerated freeze–thaw cycling on the density, dimensional stability, and flexural strength and stiffness of rigid PVC filled with various concentrations of pine or maple wood flour. Particular emphasis was placed on understanding the effects of the number of freeze–thaw cycles and moisture absorption on the properties of the composites.

TABLE 1. Formulations used for rigid PVC/wood-flour composites.

Ingredients	Concentration (phr)
PVC (K-value = 66) (Oxyvinyls)	100
Tin stabilizer (PlastiStab 2808) (OMG Americas)	2
Calcium stearate (Synpro)	1.5
Paraffin wax (Gulf Wax)	2
Processing aid (Paraloid K-120)[a]	2
Processing aid (Paraloid K-175)[a]	2
Impact modifier (K-334)[a]	10
40 mesh maple or pine wood flour (American Wood Fibers)	50, 75, 100

[a]Supplied by Rohm & Haas Co., Philadelphia, PA.

EXPERIMENTAL

Materials

The 0.425 mm (40 mesh) maple and pine wood flours were utilized as hardwood and softwood species, respectively. The wood flour was oven dried at 105°C for ~48 h before processing to remove moisture. The PVC matrix and other additives used in the manufacture of the composites are listed in Table 1.

Compounding and Extrusion of Composites

A 10-L high-intensity mixer (Papenmeier, Type TGAHK20) was used for room-temperature dry blending of the PVC matrix, dried wood flour (pine or maple), and other additives at the concentration levels listed in Table 1. Once mixed, the compounded materials were fed into a 32-mm conical counterrotating twin-screw extruder (C.W. Brabender Instruments, South Hackensack, NJ) with a length-to-diameter ratio of 13:1. This twin-screw extruder was equipped with an unpressurized vent to allow residual moisture to escape and was powered by a 7.5 hp Intelli-Torque Plasti-Corder Torque Rheometer. The rotational speed of the screws was maintained at 50 rpm throughout processing. However, the extruder's temperature profiles were varied as follows.

The first portion of this study examined the effect of wood flour content (50–100 phr) on the physical and mechanical properties of the composites exposed to five freeze–thaw cycles. For this study, the temperature profile from the hopper to the horizontal die was set at 190/175/170/180°C. The rectangular die created samples with a nominal width and depth of 2.54 cm (1″) and 0.95 cm (3/8″), respectively.

For the second part of this study, the wood content was maintained at 100 phr and the number of freeze–thaw cycles was varied at either 0 (control), 2, 5, 8, or 12. Although excellent quality samples were previously produced with 50 and 75 phr wood flour in the first part of this study, the increased melt viscosity with 100 phr wood flour made processing at the lower temperature profile difficult and the appearance of the final sample suffered accordingly (poor surface quality, rough and tearing edges). Consequently, a different temperature profile was selected for the second part of this study, with varied numbers of freeze–thaw cycles. The processing temperature profile from the hopper to the die was set at 190/185/180/180°C. The same die discussed above was used.

Freeze–Thaw Cycling

Freeze–thaw cycling was done in accordance with a modified ASTM D6662-01 [28], the Standard for Polyolefin-Based Plastic Lumber Decking Boards. One complete freeze–thaw cycle consisted of three parts: 1) a water soak until equilibrium moisture content (EMC); 2) exposure to freezing for 24 h; and 3) thawing for 24 h. The water submersion part of the cycle was conducted in ambient room temperature water (~21°C) in a workshop environment. Each sample was submerged for 24 h intervals until the weight gain was less than 1%, which implies that the sample has reached its EMC. The freezing was conducted in a GE 0.38 cubic meter (13.4 cu. ft.) chest freezer controlled to –27°C ± 2°C. Lastly, the samples were thawed in a walk-in conditioning room at 23°C ± 2°C and 50% ± 4% RH.

Modified Freeze–Thaw Cycling

Our preliminary study showed that rigid PVC/wood-flour composites exposed to freeze–thaw cycling lose some of their mechanical properties [29]. This loss in mechanical properties is thought to be largely due to the effect of moisture, since moisture changes can lead to a degradation of interfacial properties in composites [25]. To verify whether or not moisture is the primary cause of the observed property loss, freeze–thaw cycling was modified by omitting portions of the test (either the water or freezing part) as follows:

i) The freeze–thaw-only (FT) cycle had the freezing and thawing portions of the exposure. The water portion was omitted to find out if freezing had a significant effect on the mechanical property loss.
ii) The water-only (W) cycle had the water submersion and conditioning at 23°C ± 2°C and 50% ± 4% RH portions. The omission of the freezing portion would show if exposure to water caused a significant amount of the mechanical property loss.

This part of the study used composites with 100 phr wood flour manufactured in the second part of the study (high-temperature profile) and the cycle length for both the FT and W cycles was kept constant at five cycles.

Property Testing

The three-point flexural tests were carried out in the walk-in conditioning room at 23°C ± 2°C and 50% ± 4% RH on an Instron 4206 (Canton, MA, with Series IX software) testing machine. The crosshead rate was 4.5 mm/min in conformance with ASTM Standard D6109-97 [30], the Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastic Lumber. Unless otherwise mentioned, at least eight replicates were tested to obtain an average value for each formulation. Data were collected on modulus of rupture (MOR or flexural strength) and modulus of elasticity (MOE or flexural stiffness). Per the standard [30], all unexposed and freeze–thaw exposed samples were stored in the walk-in conditioning room described above for at least 48 h prior to property testing.

Dimensional stability was measured in conformance with ASTM Standard D6341 as mentioned in D6662-01 [28] using digital calipers for measurements of thickness and width before and after exposures for possible thickness swelling and width changes. Five replicates were tested to obtain an average value for each formulation.

The density profile across the width of the sample was determined using an automated and nondestructive X-ray Density Profiler (Model QDP-01X equipped with v. NT 1.14 software) following the approach described by the manufacturer (Quintek Measurement Systems, Oak Ridge, TN). Five replicates were tested for each condition shown.

Statistical Analysis

To determine the effect of freeze–thaw cycling on flexural properties of the composites with various wood flour contents, a two-sample *t*-test was carried out with an α significance value of 0.05, comparing the exposed and unexposed data. Comparisons were only performed within species type and between the unexposed control and samples exposed for five freeze–thaw cycles of each wood content addition level (50, 75, and 100 phr). All statistical analyses were performed using Design Expert software (v. 6) from Stat-Ease (Minneapolis, MN).

The statistical analysis for the effect of the number of freeze–thaw cycles on the properties of the composites was also performed, using the same software. A two-sample *t*-test with $\alpha = 0.05$ was used to compare each cycle exposure to the unexposed control. Comparisons were only performed within species type and between unexposed and exposed samples. Ten replicates were tested to obtain an average value for each exposure cycle.

TABLE 2. Density of rigid PVC/wood-flour composites before and after exposure to five full freeze–thaw cycles.

	Density (g/cm^3)					
	50 phr		75 phr		100 phr	
Samples	Control	5 Cycles	Control	5 Cycles	Control	5 Cycles
Composites with maple flour	1.15	1.14	1.21	1.23	1.08	1.10
Composites with pine flour	1.13	1.15	1.21	1.21	1.12	1.15

Ten replicates were also used for the modified freeze–thaw cycles, water-only (W) and freeze–thaw-only (FT), which were compared to the five full freeze–thaw cycles with all of the components (water–freeze–thaw). Samples exposed to both five W and five FT cycles were also compared to the unexposed controls using the same two-sample *t*-test ($\alpha = 0.05$).

Microscopy

Scanning electron microscope (SEM) images of unexposed and exposed samples (both full and modified freeze–thaw cycles) were taken to verify whether or not moisture changes affected the interfacial adhesion in the composites. Images were taken of the broken surface after flexural testing. Since the most detrimental effect of freeze–thaw cycling on flexural properties was seen in rigid PVC filled with 100 phr maple flour, representative images were taken only from these composites. These samples were oven-dried at 105°C for 24 h to remove moisture, and were then gold-coated, for conductance, immediately before insertion into the SEM. Gold coating was done using a deposition of 20 mA for two runs of 4 min each. A JEOL JSM-6400 SEM was used with accompanying analySIS software for image acquisition. The acquired images had a resolution of 2048 $\times$ 1536 pixels with a pixel dwell time of 50 μs. The accelerating voltage was set to 15 kV, with a condenser lens of 11 and a working distance of 39 mm.

RESULTS AND DISCUSSION

Effect of Wood-Flour Content

Freeze–thaw actions did not appear to have a substantial effect on the density of rigid PVC/wood-flour composites. The test results show that the densities were similar for both the unexposed and full freeze–thaw cycle-exposed samples, irrespective of wood flour content and species (Table 2).

Table 3 summarizes the changes in dimensional stability of rigid PVC/wood-flour composites after exposure to five complete freeze–thaw cycles. The overall dimensional stability was relatively unaffected by the freeze–thaw cycling, regardless of wood species. Even after five freeze–thaw cycles, the width and thickness changed less than 1.3% and 2.2%, respectively, for the most severely affected composition of rigid PVC filled with 100 phr maple flour (Table 3). It was also observed that both the thickness and width changes due to freeze–thaw cycling increased with wood flour content. Increasing the wood flour content in the PVC matrix allows more water absorption and potentially diminished encapsulation of the wood flour by the matrix, thus leading to greater dimensional changes.

The percent loss in MOR and MOE of rigid PVC/wood-flour composites filled with both maple and pine species exposed to five full freeze–thaw cycles were compared to the unexposed control and the results for the various wood flour addition levels are summarized in Table 4. Rigid PVC/wood-flour composites with lower wood flour contents (50 and 75 phr) of either wood species retained their strength after exposure to five freeze–thaw cycles. The loss in the MOR of the composites exposed to five freeze–thaw cycles was statistically significant only for 100 phr of wood flour content for both wood species (Table 4). This trend was expected because the more wood present in the sample, the greater the uptake of moisture and therefore a more prevalent decrease in mechanical properties [8, 20, 26, 27]. Unlike the flexural strength, five freeze–thaw cycles caused a significant loss in the MOE for all composites, regardless of wood species and content (Table 4). The stiffness of rigid PVC/wood-flour composites with 100 phr maple and pine decreased by 34% and 30%, respectively, after exposure to five full freeze–thaw cycles. Although a statistical comparison between the maple and pine was not performed, the results listed in Table 4 indicate that the composites with maple wood flour were more detrimentally affected by five freeze–thaw cycles than the pine wood flour composites.

As previously mentioned, the degraded mechanical properties of rigid PVC-wood flour composites after accelerated freeze–thaw cycling is thought to be largely due to a degradation of interfacial adhesion in the composites as a result of exposure to moisture. During freeze–thaw exposure, the samples cycled through environments of soaking in a water bath until equilibrium moisture content, freezing at –27°C

TABLE 3. Changes in dimensional stability of rigid PVC/wood-flour composites after five cycles of full freeze–thaw (WFT) exposure.

Percent change in properties from the control	Composites with maple flour			Composites with pine flour		
	50 phr	75 phr	100 phr	50 phr	75 phr	100 phr
Thickness swell (%)	0.73	1.28	2.17	0.55	0.97	1.72
Width change (%)	0.19	0.32	1.32	0.17	0.44	0.85

TABLE 4. Flexural properties of rigid PVC/wood-flour composites before and after five cycles of full freeze–thaw (WFT) exposure.

	Composites with maple flour			Composites with pine flour		
Properties	50 phr	75 phr	100 phr	50 phr	75 phr	100 phr
MOR of unexposed samples (MPa)	36.61	46.40	31.55	40.30	43.57	37.60
MOE of unexposed samples (GPa)	2.04	3.38	2.54	2.35	3.33	3.34
Loss in MOR (%)[a] after WFT exposure	4.22[NS]	5.91[NS]	15.19[S]	2.22[NS]	8.49[NS]	12.53[S]
Loss in MOE (%)[a] after WFT exposure	16.8[S]	22.13[S]	33.93[S]	9.96[S]	18.11[S]	29.79[S]

[a]NS means that the change is not statistically significant, whereas S implies that the difference is statistically significant at values of "Prob>|t|" less than 0.05.

for 24 h and thawing at 23°C and 50% RH for another 24 h. The majority of this cycling is changing moisture contents, which have been shown to adversely affect the properties of other wood–plastic composites [20, 23–25, 29]. Moreover, visual observations show a distinctive change in appearance and lightening in color of exposed samples. Most of the samples had developed tearing and rough edges following exposure to five freeze–thaw cycles compared to the control. These rough edges are likely a result of moisture changes and fiber-matrix debonding [25].

Effect of Number of Freeze–Thaw Cycles

As mentioned, processing conditions had a prevalent effect on the surface quality and appearance of the composite samples made with 100 phr wood flour. Composite samples used in the second portion of this study were processed using a higher temperature profile (190/185/180/180°C) due the increased melt viscosity of the blend with 100 phr wood flour. Consequently, the processing was much easier and the samples had more thorough edge adhesion than those previously manufactured with the lower temperature profile (190/175/170/180°C). These samples were exposed to various numbers of freeze–thaw cycles (0, 2, 5, 8, or 12) and the measured flexural properties are listed in Table 5. Both flexural strength and stiffness significantly decreased with increasing numbers of freeze–thaw cycles.

For 100 phr maple flour-filled rigid PVC samples, the loss in flexural properties (both MOR and MOE) of the exposed samples was significant when statistically compared to the control even after two freeze–thaw cycles. Composites with 100 phr pine flour also showed a significant decrease in strength and stiffness after freeze–thaw exposures, although slightly less pronounced than maple composites. After exposure to two full freeze–thaw cycles the loss in flexural strength was only 3.5%, which is not statistically significant when compared to the unexposed control. However, a significant loss in strength occurred after five full freeze–thaw cycles and all cycles thereafter. Unlike for strength, the loss in flexural stiffness of pine flour-filled rigid PVC was significant after only two full freeze–thaw cycles and leveled off after about eight freeze–thaw cycles. Consequently, it is assumed that composites with pine flour are not likely to lose much more than 20% of their stiffness. This significant loss in the flexural properties of rigid PVC/wood-flour composites may be a cause for concern with these materials being used in decking and other construction/semistructural applications.

Modified Freeze–Thaw Cycles

To determine the cause of the above-mentioned loss in mechanical properties in rigid PVC wood-flour composites, the full freeze–thaw cycle was broken down into its components. Either the water or freezing portion of the full freeze–thaw cycle was omitted and the number of cycles was held constant at five.

Figure 1a shows the effect of the freeze–thaw cycle portions on the flexural properties of PVC filled with 100 phr maple flour. The freezing portion (FT only cycle) had

TABLE 5. Effect of the number of freeze–thaw cycles on the flexural properties of rigid PVC/wood-flour composites.

	Composites with maple flour[a]					Composites with pine flour[a]				
	Number of freeze–thaw cycles					Number of freeze–thaw cycles				
Properties	0	2	5	8	12	0	2	5	8	12
MOR (MPa)	33.81	31.49[S]	29.76[S]	29.73[S]	28.66[S]	38.93	37.57[NS]	36.71[S]	35.98[S]	35.39[S]
MOE (GPa)	2.71	2.22[S]	2.05[S]	1.95[S]	1.90[S]	3.37	2.94[S]	2.74[S]	2.68[S]	2.71[S]

[a]NS means that the change compared to the control is not statistically significant, whereas S implies that the difference is statistically significant at values of "Prob>|t|" less than 0.05.

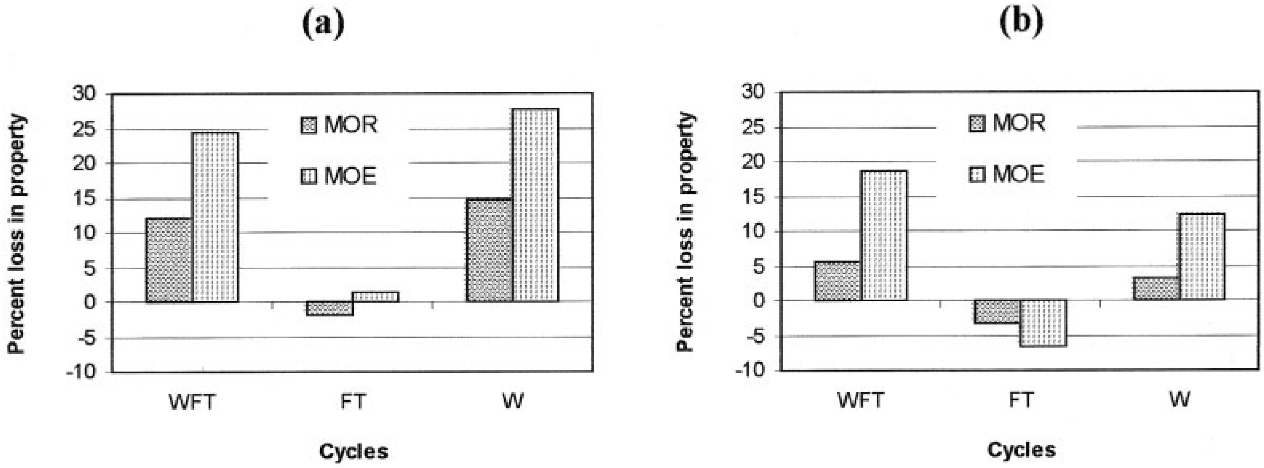

FIG. 1. The effect of each freeze–thaw cycle portions on the loss of flexural properties of rigid PVC filled with 100 phr wood flour: (a) maple and (b) pine. WFT cycle represents the full freeze–thaw cycle (water soak–freeze–thaw), W cycle includes only the water soaking and conditioning at 23°C ± 2°C and 50% ± 4% RH portions (without freezing), and FT cycle includes freezing and thawing only (without water soak). The cycle length for WFT, W, and FT cycles was kept constant at five cycles.

very little effect on the flexural properties of the composites and was not statistically different from the control. Five FT only cycles actually showed a slight increase in MOR compared to the unexposed control. This insignificant increase in MOR leads us to believe that the freezing portion of the full freeze–thaw cycle does not significantly affect the flexural properties of the composites with maple flour. However, the water portion of the cycle (exposed to five W cycles) had a significant impact on the flexural properties of the composites compared to the unexposed control. Flexural properties of the composites exposed to five full freeze–thaw cycles (water, freezing and thawing, or WFT) were not statistically different from those exposed to water-only cycles (with no freezing). Consequently, the loss in both MOE and MOR of the composites filled with 100 phr maple flour could be attributed to the water portion of the full freeze–thaw cycle process.

Rigid PVC filled with 100 phr of pine flour showed a slightly different trend than that observed with maple flour (Fig. 1b). Compared to the unexposed control, both the flexural strength and stiffness of the composites filled with pine flour increased after exposure to five freeze–thaw-only (FT) cycles. However, this increase in flexural properties was not statistically significant compared to the control, meaning that flexural property loss cannot be attributed to the freezing portion of the cycle. The loss in MOE of the composites exposed to five water-only (W) cycles was statistically the same as that of five full freeze–thaw (WFT) cycles. For the loss in MOR, however, five water-only cycles produced significantly different results compared to five full freeze–thaw (WFT) cycles. Nevertheless, the significance level for the MOR values was 0.0483, which is very close to the necessary 0.050 to be statistically the same. Since the freezing part of the cycle is known to have no effect, the flexural property loss is attributed to the water submersion part of the full freeze–thaw cycle for 100 phr pine-filled rigid PVC as well.

For 100 phr (about 46 wt%) pine flour-filled rigid PVC samples, a decrease of ~3.5% in flexural strength was observed in this study with exposure to five water-only cycles. This loss in MOR was considerably less than that reported by Clemons and Ibach [23] for 50% pine flour-filled HDPE matrix. A decrease of ~24.5% in flexural strength was observed after five cycles of ambient temperature water soaking followed by 65% RH at 27°C conditioning [23]. This indicates that PVC is likely a superior matrix for resistance to water-only cycling compared to HDPE matrix.

Scanning Electron Micrographs

Representative SEM images of the broken surface after flexural testing (Fig. 2) were taken to qualitatively determine the effects of the freeze–thaw cycling (full and modified cycles) on the interfacial adhesion between the wood flour and PVC matrix. As mentioned previously, the 100 phr maple-filled rigid PVC was used for imaging since the most prevalent impact on properties was seen in these samples.

For the unexposed control samples, the SEM image (Fig. 2a) shows that there was more breakage of the polymer matrix and even fibers are tearing in half. Although there were some gaps or crevices, these were probably due to manufacturing or the stresses from flexural testing, however, matrix and fibers were still well adhered to each other.

A considerable number of holes and cavities that have been formed from fibers pulling out of the matrix are clearly seen for the composite sample exposed to five full freeze–thaw cycles with water, freezing, and thawing (Fig. 2b). There are also intact fibers that are indicative of holes in the other half of the broken sample where the fibers used to be

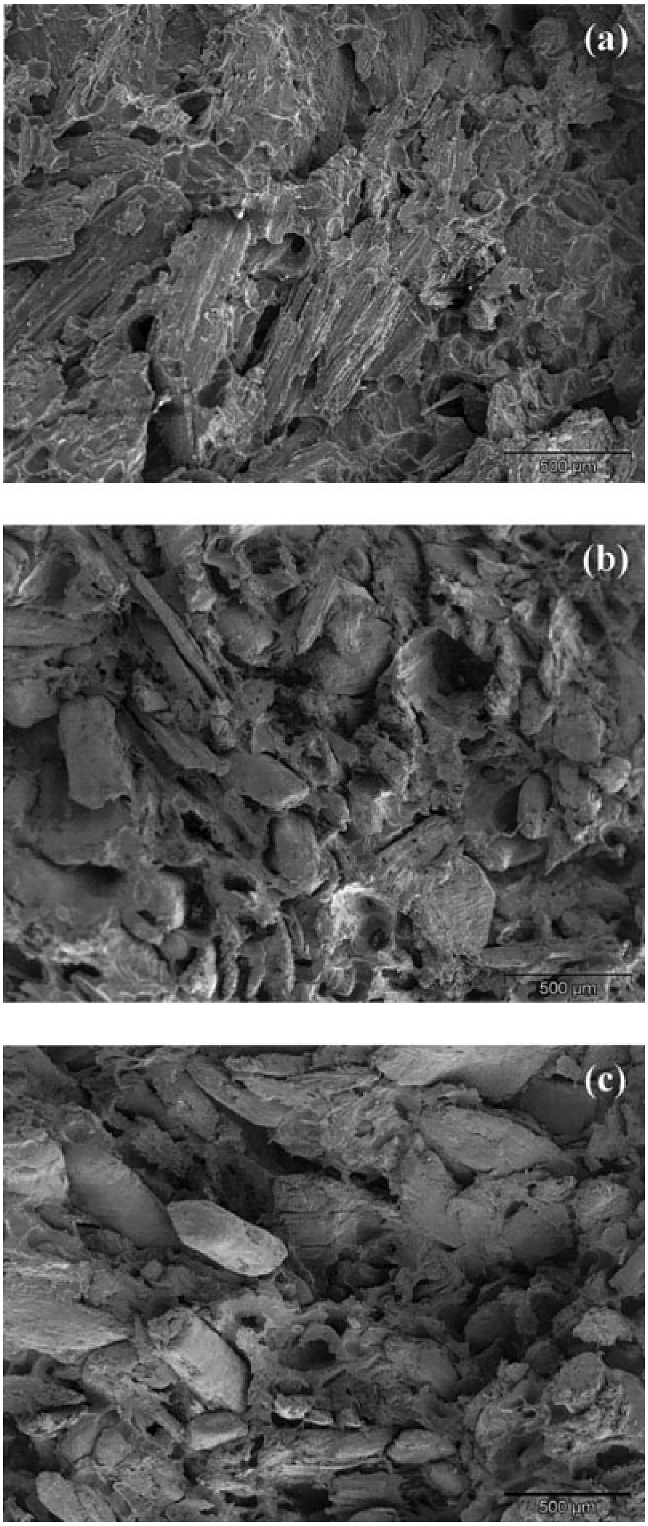

FIG. 2. SEM micrographs of rigid PVC filled with 100 phr maple wood flour: (a) unexposed control, (b) sample exposed to five full freeze–thaw cycles (water, freezing and thawing), and (c) sample exposed to five water-only cycles (W cycles without freezing).

bound. These holes and intact fibers are evidence of a loss in bonding between the fibers and the matrix for the composites exposed to five full freeze–thaw cycles. This result is consistent with findings from vinylester/E-glass composites, where microcracking and fiber-matrix debonding were observed after exposure to water [25].

The SEM image of the composite sample exposed to five water-only (W) cycles (Fig. 2c) bears a striking resemblance to that of five full freeze–thaw (WFT) cycles (Fig. 2b). As seen with five full freeze–thaw cycles (Fig. 2b), there are a lot of holes where fibers used to be and some fibers that have left holes on the other half of the broken sample, suggesting that the water-only and full freeze–thaw cycles are essentially the same. This striking resemblance further confirms that the majority of the flexural property loss is due to the water portion of the freeze–thaw cycling process.

CONCLUSIONS

This study examined the effects of accelerated freeze–thaw cycling on the durability of rigid PVC/wood-flour composites. Particular emphasis was placed on investigating the effects of wood flour content, number of freeze–thaw cycles, freeze–thaw cycle portions, and water absorption on the properties of the composites. The following conclusions can be drawn from the experimental results.

Cyclic freeze–thaw actions did not affect the density of rigid PVC/wood-flour composites at any wood flour content for either the maple or pine filler. Both the thickness swell and width changes due to freeze–thaw cycling increased with wood flour content. However, the greatest increase was still very small compared to other materials, such as solid wood.

The stiffness of the composites was significantly affected by five full freeze–thaw cycles, regardless of both the wood species and content. Conversely, the strength of the composites was not significantly affected by the freeze–thaw actions at lower wood flour content (50 and 75 phr). However, the deleterious effects of freeze–thaw cycling on the strength of the composites became apparent at the highest wood flour content (100 phr) due to the increased wood content, and therefore increased moisture uptake, which possibly caused decreased encapsulation of the wood flour by the matrix. The 100 phr maple samples did not appear as well processed as the other samples, as was evidenced by the lower than expected density. This manifested itself in lower performance after exposure in the freeze–thaw test.

The loss in flexural strength of the remade composites filled with 100 phr wood flour was statistically significant after two freeze–thaw cycles, regardless of wood species. However, maple flour-filled rigid PVC composites showed a significant loss in flexural strength after two full freeze–thaw cycles, whereas it took five full freeze–thaw cycles for the composites with 100 phr pine flour to show a significant decrease in flexural strength.

The water-only portion of the cycling process had the greatest impact upon the flexural properties and is likely attributable for the majority of the property loss due to the moisture effects on the adhesion between the matrix and wood flour. The freeze–thaw-only portion of the cycling did not significantly affect the flexural properties of the composites.

Moreover, SEM images exhibited similarities between water-only (W) cycles and full freeze–thaw (WFT) cycles. Both of these exposures showed a loss of bonding between the wood flour and PVC matrix, which resulted in cavities and intact fibers protruding from the matrix. However, the unexposed control composite exhibited matrix and fiber breakage.

Overall, rigid PVC/wood-flour composites have been shown to have been significantly impacted by cyclic water–freeze–thaw actions. With uses in outdoor exposure, such as decking, the durability of WPCs is a concern. Other types of WPCs used in outdoor exposures should be studied.

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