Durability of Wood Flour-Plastic Composites Exposed to Accelerated Freeze–Thaw Cycling. II. High Density Polyethylene Matrix

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ABSTRACT: This study examined the durability of extruded HDPE/wood-flour composites exposed to 15 accelerated cycles of water submersion, freezing, and thawing, according to ASTM standard D6662. The durability of both maple and pine composites was assessed by testing the flexural properties and density. Mercury intrusion porosimetry and scanning electron microscopy were also used to evaluate the interfacial adhesion between the matrix and wood flour before and after exposure to accelerated freeze–thaw cycling. Freeze–thaw actions had no apparent effect on the density of the composites after exposure, regardless of the wood species. However, these actions led to moisture uptake, which decreased the interfacial adhesion and increased the pore size and quantity in the composites, which resulted in a significant loss in flexural properties. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 100: 35–39, 2006

Key words: freeze–thaw cycling; degradation; moisture; wood plastic composites; porosity; flexural properties

INTRODUCTION

Wood-plastic composites (WPCs) have become prevalent in many building applications partially due to the need to replace pressure-treated solid lumber.[1–3] Several applications of WPCs require outdoor exposure or ground contact, where the material is susceptible to various weakening agents, such as fungi and insects.[4–6] The weather itself may also cause the product to deteriorate, which is evident in work done on moisture and ultraviolet radiation.[7,8] However, the effect of exposure to cold winter conditions is not well-documented. Although WPCs are typically seen as combining the best properties of wood and plastic, their combination makes a brittle product, which may become more brittle by cold exposure and further decrease the mechanical properties.[9–11] Since these products are used in building applications the retention of strength is essential.

Our preliminary study showed that rigid PVC/wood-flour composites exposed to freeze–thaw cycling loose some of their mechanical properties.[12] The in-depth study conducted with PVC filled with maple and pine wood flour showed significant losses in both flexural strength and stiffness after exposure to various numbers of freeze–thaw cycles.[13] Additionally, this study showed the development of cracking and de-bonding inside of the composite, which was attributed to the absorption of water during weathering.[13] Although PVC was previously examined, the majority of the WPCs in North America, over 70%, are manufactured with polyethylene thermoplastics.[14] This study was aimed to further investigate the effects of accelerated freeze–thaw cycling on the density and flexural properties of HDPE composites filled with 50% maple or pine wood flour after exposure to extreme conditions. Since the previous studies examined the effect of varying numbers of freeze–thaw cycles, this work focused on the extreme case of 15 freeze–thaw cycle exposures.

EXPERIMENTAL

Materials

Because of the popularity of polyethylene resins in the wood-plastic composite market,[14] HDPE, designated as FORTIFLEX™ B53–35H-FLK from B.P. Solvay Polymers (Houston, TX), was used as the polymeric matrix. The polymer was in flake form with a melt flow index of 0.49 g/10 min and density of 0.9 g/cm^3. The 0.425 mm (40 mesh) maple and pine wood flours were obtained from American Wood Fibers (Schofield, WI) to compare hardwood and softwood species. The wood flour was oven-dried at 105°C for ~48 h before processing to remove moisture. The TPW104 lubricant

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from Struktol® Company (Stow, OH) was used to reduce friction between components and equipment, which eased processing. This lubricant is a blend of aliphatic carboxylic acid salts and mono and diamides.

Compounding and extrusion of composites

A 10 L high intensity mixer (Papenmeier, Type TGAHK20) was used for room temperature dry blending of the HDPE matrix, dried wood flour, and lubricant. The formulation of the composites was maintained at 50% wood flour (maple or pine), 44% HDPE, and 6% lubricant by total weight of the composites. The compounded materials were fed into a 32 mm conical counter-rotating twin-screw extruder (C.W. Brabender Instruments Inc.) 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 heating profile, from the hopper to the horizontal die was 190, 175, 170, and 165°C with a rotational speed of the screws maintained at 40 rpm throughout processing. The rectangular die created samples with a nominal width and thickness of 2.54 cm (1″) and 0.95 cm (3/8″), respectively.

Freeze–thaw cycling

Freeze–thaw cycling was done in accordance with a modified ASTM D6662–01,[15] the standard for polyolefin-based plastic lumber decking boards. One complete freeze–thaw cycle consisted of three parts: (i) a water soak until equilibrium moisture content (EMC), (ii) exposure to freezing for 24 h, and (iii) thawing for 24 h. The number of freeze–thaw cycles was maintained at 15 cycles to examine extreme conditions, since intermediate cycles have already been examined.[13]

The water submersion part of the cycle was conducted in room temperature water (~21°C). Samples were weighed every 24 h until the weight gain was less than 1%, which implied that the sample had reached its EMC. A general electric 0.38 m^3 (13.4 ft^3) chest freezer controlled to –27°C ± 2°C was used for the freezing portion of the cycle. Lastly, the samples were thawed in a walk-in conditioning room at 23°C ± 2°C and 50% ± 4% relative humidity.

Property testing

The three-point flexural tests were carried out in the walk-in conditioning room using an Instron 4206 testing machine (with Series IX software), according to ASTM standard D6109–97,[16] the standard test methods for flexural properties of unreinforced and reinforced plastic lumber. Fifteen replicates were tested and data was collected on modulus of rupture (MOR or flexural strength) and modulus of elasticity (MOE or flexural stiffness).

The density profile across the thickness of the sample was determined using an automated and nondestructive X-ray Density Profiler (Model QDP-01X equipped with Version NT 1.14 software), following the approach described by the manufacturer (Quintek Measurement Systems, Inc., Oak Ridge, Tennessee, 1999). Five replicates were tested for each formulation.

Statistical analysis

Design-Expert v.6 software from the Stat-Ease Corp. (Minneapolis, MN) was used to perform statistical analyses to determine the effect of freeze–thaw cycling on properties of the composites. A two-sample t test and Duncan's multiple range tests were employed to determine the statistical differences among the variables investigated at a 95% significance level. Comparisons were done between exposed and unexposed samples as well as between wood species for density and flexural properties.

Porosimetry

Porosity testing was conducted by the Micromeritics Instrument Corp. to quantify the porosity in the samples before and after freeze–thaw exposures. Samples had a nominal size of 2.54 cm (1″) thick by 0.95cm (3/8″) wide from the die on the extruder. The sample was cut from near the middle of the sample after flexural testing. The broken end was cut off and then a 2.54 cm (1″) length was cut. One sample each of the unexposed (control) and 15 freeze–thaw exposures were tested for composites with both maple and pine wood flour. An AutoPore IV 9250 was used for testing, which has a maximum pressure capability of 414 MPa (60,000 psi). Mercury was used for all pore intrusion, since it cannot move through the samples by capillary action.

Penetrometers were used to hold the individual samples when they were exposed to mercury intrusion and had a nominal volume of 6 mL. Initially, the penetrometers were placed in low pressure chambers to force mercury into the larger macropores, and then they were individually moved into high pressure chambers for mesopore testing and the majority of the data collection.

Microscopy

Scanning electron microscope (SEM) images of unexposed and exposed samples were taken to verify whether or not freeze–thaw actions affected the interfacial adhesion in the composites. Images were taken of the broken surface after flexural testing of the composites with maple flour, since the most significant flexural loss was observed with these samples. The

TABLE I
Changes in Physical and Mechanical Properties in HDPE Composites Before and After Exposure to Freeze-Thaw Cycling

Flexural and physical properties	Composites with maple flour[a]		Composites with pine flour[a]	
	0 (control)	15 cycles	0 (control)	15 cycles
MOR (MPa)	$20.73^{A} \pm 2.26$	$16.31^{B} \pm 1.40$	$24.68^{C} \pm 1.04$	$23.47^{D} \pm 0.51$
MOE (GPa)	$1.63^{A} \pm 0.33$	$0.83^{B} \pm 0.11$	$2.21^{C} \pm 1.04$	$1.38^{D} \pm 0.07$
Density (g/cm^3)	$0.89^{A} \pm 0.03$	$0.90^{A} \pm 0.02$	$0.99^{B} \pm 0.003$	$1.01^{B} \pm 0.02$

[a] Means with the same letter are not significantly different based on Duncan's grouping.

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 2 runs of 4 min each. A JEOL JSM-6400 SEM was used with accompanying analySIS software for image acquisition. The accelerating voltage was set to 15 kV, with a condenser lens of 11 and a working distance of 39 mm.

RESULTS AND DISCUSSION

Only the extreme case of 15 full freeze–thaw cycles was examined in this study. Results from a previous study with rigid PVC/wood-flour composites indicated a general trend of increasing property loss with increasing numbers of freeze–thaw cycles.[13] However, there was a plateau effect after a threshold of about 5 cyclic exposures were completed. Consequently, these HDPE/wood-flour composites were exposed to 10 more cycles than those with PVC for a total of 15 cycles to simulate the most extreme effects possible so that the maximum property loss was certain to be observed.

Changes in density and flexural properties in HDPE/wood-flour composites before and after exposure to freeze–thaw cycling are summarized in Table I. The observed loss in flexural properties was considerably larger for the composites with maple flour than those with pine flour. Composites made with maple wood flour lost about 21% of their strength and almost 50% of their stiffness, whereas composites with pine flour only lost about 5% in strength and near 38% of their stiffness. These losses are all significant compared with their unexposed counterparts (control samples). The greater flexural property loss in maple flour filled HDPE composites compared with those with pine was likely a result of their lower density and greater porosity (discussed in the following section). This favored water uptake and decreased interfacial bonding after freeze–thaw exposure in maple composites.

The density within either species composite was unaffected by freeze–thaw cycling exposure (Table I). However, the composites with pine flour were of high density and therefore less porous than those with maple flour. This made pine samples less sensitive to the damage caused by freeze–thaw exposure. High density WPCs absorb less moisture,[17] which is the primary cause of mechanical property loss. As expected, composites with pine wood flour reached the EMC faster and subsequently gained less moisture per cycle (3.1 wt % versus 4.6 wt % for maple) than those with maple flour. Consequently, the higher density pine composites were more likely to retain most of their flexural properties, particularly their bending strength. Greater moisture uptake observed in maple composites may be indicative of decreased bonding between the matrix and filler, which resulted in the greater flexural property loss.

Porosimetry

Porosimetry was conducted for quantitative evaluation of the porosity in the samples before and after 15 freeze–thaw exposures. Figure 1 illustrates graphs of pore size (diameter) class versus incremental intrusion (pore volume) for composites with both wood species. A distinct difference between the exposed and unexposed samples is clearly seen in the range between about 1 μm and 6 μm. As the incremental intrusion increased, there were more pores of that particular diameter. In other terms, exposure to freeze–thaw cycles increased the incremental intrusion, implying that more pores were created in this range, regardless of wood species. This general increase in porosity was likely due to a decrease in bonding between the matrix and fibers after exposure. Moreover, this loss in bonding resulted in a small amount of debris being present in the water after the submersion portion of the cycle, which could be the material that was previously in the newly created porous spaces. The increase in the size and number of pores correlates with the loss in mechanical properties.

The denser composites with pine flour had fewer and smaller sized pores compared with the maple composites. The higher density and lower overall porosity allowed pine composites to resist moisture uptake and better retain interfacial bonding. This was expected, since the decrease in flexural properties was not as drastic for the pine samples as for the maple.

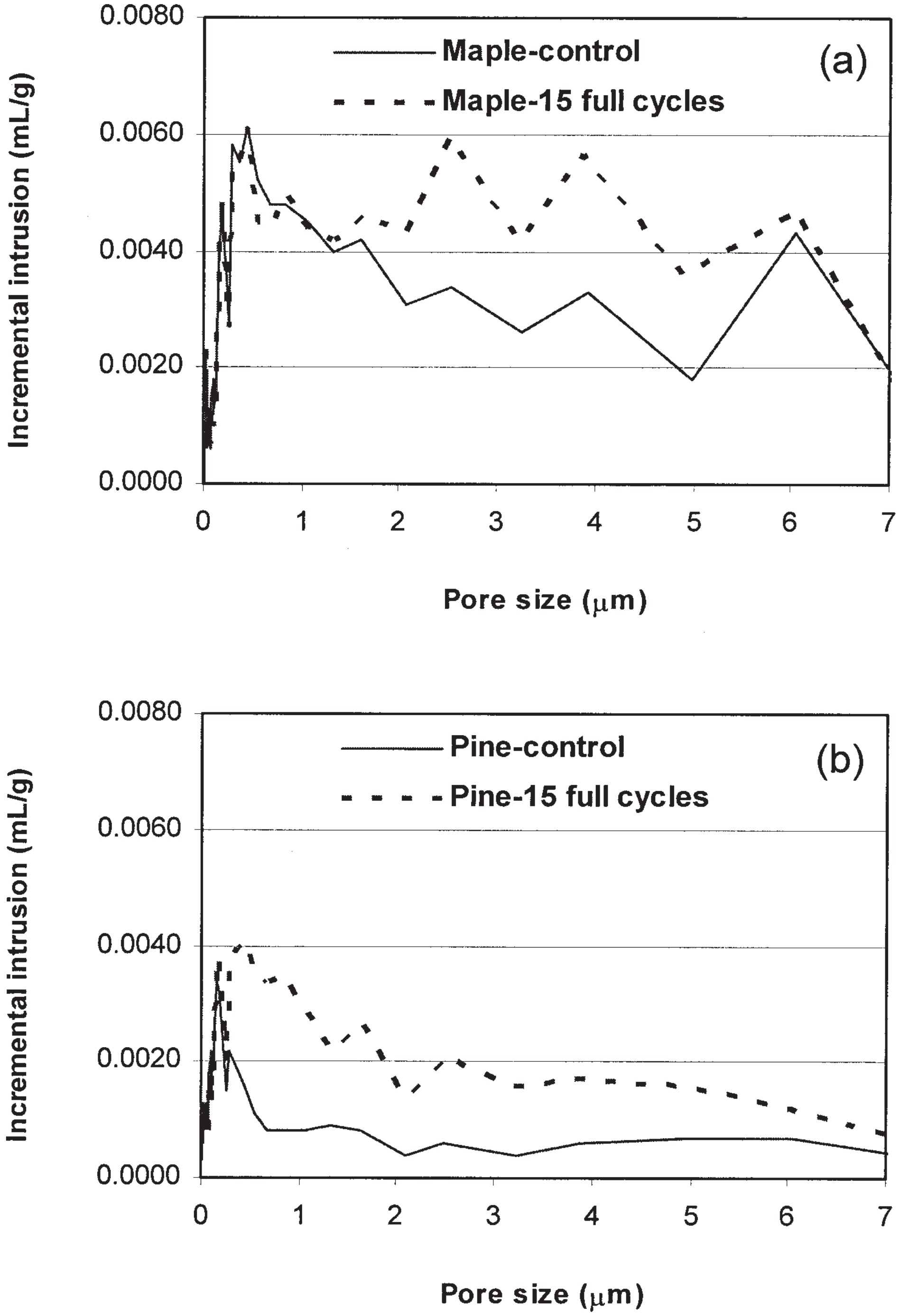

Figure 1 The effect of freeze–thaw cycling on the porosity: (a) maple–HDPE composites and (b) pine–HDPE composites.

Scanning electron micrographs

SEM was used to evaluate the interfacial adhesion between the matrix and fibers to determine the main cause for property loss for the exposed composites. In previous work, SEM images of rigid PVC/wood-flour composites showed that freeze–thaw cycling reduces the bonding between the matrix and fibers, thus reducing the flexural properties.[13]

The HDPE matrix behaved similarly to PVC and SEM images shown in Figure 2 support the finding of our porosity investigation (Fig. 1). The unexposed sample showed a considerable amount of fiber and matrix breakage with very little intact material on the surface [Fig. 2(a)] as a result of good adhesion between the maple wood fibers and HDPE matrix. Conversely, exposure to 15 freeze–thaw cycles decreased bonding between the matrix and fibers as clearly shown in Figure 2(b) where intact fibers as well as a cavity where an intact fiber was pulled out from the matrix are seen. This loss in bonding supports the porosity

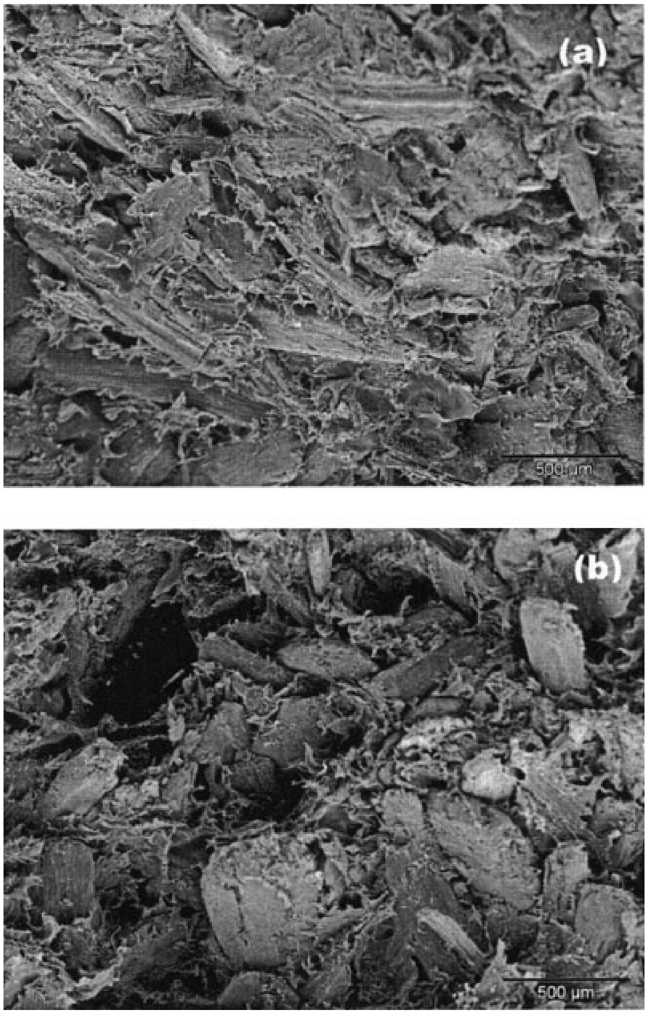

Figure 2 SEM micrographs of HDPE filled with maple wood flour: (a) unexposed control and (b) sample exposed to 15 freeze–thaw cycles (WFT, i.e., water, freezing, and thawing).

results and is consistent with previous work on the freeze–thaw cycling of rigid PVC/wood-flour composites[13] and E-glass with vinyl ester.[18]

CONCLUSIONS

The results of this study indicated that accelerated freeze–thaw cycling has a significant impact upon the durability of HDPE composites filled with 50% of either maple or pine wood flour. The HDPE/maple-flour composites showed the greatest losses of 49% in MOE and 21% in MOR after 15 accelerated freeze–thaw cycles. This property loss may cause problems if this material is used in construction applications. The pine-HDPE composites, on the other hand, performed much better for MOR with a loss of only 5%, but had a loss of 37% for the MOE.

The cycling actions had no apparent effect upon the density of either the maple or pine flour filled HDPE composites. However, a lower density was observed for maple samples compared with the pine, which resulted in increased water uptake and property loss for the composites with maple flour.

Regardless of wood species, more and larger pores were created in the composites exposed to freeze–thaw actions, particularly in the range between about 1 and 6 μm. However, the composites with maple flour had a higher porosity than those with pine flour for both the control and exposed composites, likely because of their lower density. This increased porosity was partially the cause for the lower flexural properties of the composites with maple flour.

SEM images confirmed that composite samples exposed to 15 freeze–thaw cycles had decreased bonding between the matrix and fibers as expected from porosity tests. This led to fibers extending out of the matrix and leaving cavities in the other side of the break surface after exposure. The unexposed samples (control) clearly showed the matrix and fibers breaking, so the cycling must have diminished the interfacial bonding.

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