

Outdoor durability of wood–polymercomposites

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7.1 Introduction

Wood–plastic composite (WPC) lumber is promoted as a low-maintenance, high-durability product (Clemons, 2002). However, after a decade of exterior use in the construction industry, questions have arisen regarding durability. These questions are based on documented evidence of failures in the field of WPC decking products due to such impacts as polymer degradation (Klyosov, 2005), wood decay (Moms and Cooper, 1998), and susceptibility to mold which negatively impact the aesthetic qualities of the product. The industry has responded to problems associated with first-generation products by improving WPC formulations. Manufacturers have also made great strides in making more reasonable claims and in educating consumers on the proper care and maintenance of WPC products to maintain the aesthetic quality of the surface finish. Research groups throughout the world are working toward a fundamental understanding of WPC durability that will help improve and/or identify new strategies for protecting WPCs. WPC durability will continue to be an important subject regarding the use of these products in building construction and other related applications in the field.

7.2 Characteristics of raw materials

This section will discuss the characteristics of wood and plastics that make them susceptible to degradation, and the degradation mechanisms of each component. A discussion of structure and composition of wood and polymers in WPCs can be found in Chapter 1.

7.2.1 Wood

Weathering

Wood is very susceptible to the effects of weathering including the primary impacts of ultraviolet (UV) light, oxidation, rain, and combinations of light,

oxidation, and rain. Wood is hygroscopic, readily absorbing moisture due to the prevalence of hydroxyl groups. All wood components are also susceptible to degradation by UV radiation. However, lignin is primarily responsible for UV absorption. Of the total amount of UV light absorbed by wood, lignin absorbs 80–95% (Fengel and Wegener, 1983). Chromophoric functional groups present in lignin can include phenolics, hydroxyl groups, double bonds, and carbonyl groups. In addition, lignin can form free radicals as intermediates. Photodegradation of wood begins with an attack on the lignin-rich middle lamella. Longer exposure leads to a degradation of secondary walls (Fengel and Wegener, 1983). UV light degrades lignin into water-soluble compounds that are washed from the wood with rain, leaving a cellulose-rich surface with a fibrous appearance.

The effects of UV degradation are largely surface phenomena. UV light cannot penetrate deeper than 75 μm into wood. However, studies investigating depth of degradation show that degradation occurs deeper than this. The result is a proposed mechanism where wood components at the surface initially absorb UV light, and then an energy transfer process from molecule to molecule dissipates excess energy to create new free radicals. In this way, free radicals migrate deeper into wood and cause discoloration reactions (Hon and Minemura, 2001). After long exposure times, lignin content through the thickness of wood changes gradually even beyond the discolored surface layer, with less lignin at the surface and more in the center portion (Hon and Minemura, 2001).

Photodegradation leads to changes in wood's appearance such as discoloration, roughening and checking of surfaces, and destruction of mechanical and physical properties. All wood species eventually will fade from a brown, red, or yellow color to a light grey during weathering. Wood weathering is visually apparent in untreated wood and in WPCs that do not contain a colorant.

Biological attack

The natural origin of wood predisposes it to degradation by a variety of biological deterioration agents. Wood chemical components provide a food source for a variety of biological organisms including insects, fungi, bacteria, and marine borers.

Brown-, white-, and soft-rot fungi (see below) all contribute to the decay of wood. The conditions essential for fungal growth in wood are food, sufficient oxygen, suitable temperature, and adequate moisture. Wood itself provides the necessary food, and oxygen is readily available in the environment. A wood moisture content of approximately 20% is required for decay. Below this level degradation due to fungal attack will not occur, and fungi that may have already begun to grow will cease growing (Naghipour, 1996). As a general rule, if wood is kept dry, i.e. moisture content below 20% then fungi typically will not attack wood. However, in unprotected outdoor or marine exposures, wood can be

exposed to high levels of moisture that provide the necessary conditions for biological attack.

Fungi that attack wood include the decay fungi and stain or mold fungi. Decay fungi have the most deleterious impact on wood in service because the organisms consume the primary wood chemical components. Decay fungi are grouped into three types including white-rot, brown-rot (both basidiomycetes), and soft-rot (ascomycetes). White-rot fungi primary attack lignin and leave behind a cellulose-rich residue, while brown-rot primarily attack carbohydrates and leave behind a lignin-rich residue. Brown-rot fungi attack mainly softwood while white-rot fungi attack primarily hardwoods. However, each fungal type can be found on both softwoods and hardwoods (Ibach, 2005). Soft-rot fungi typically produce chains of cavities with conical ends in the secondary wall of wood (Daniel, 2003). Stain or mold (mildew) fungi will use extractable materials from wood as a food source. Mildew does not impact the strength properties of wood but does have a negative impact on the aesthetic quality of a wood surface.

Mold requires similar conditions for growth as decay fungi. However the food sources for mold include stored sugars, starches, and other compounds. Similar to decay fungi, mold growth on wood also appears above the threshold of 20% moisture content. Although mold does not usually affect the strength of wood, it can increase the absorptivity, making the wood more susceptible to moisture (Ibach, 2005). Discoloration from the spores is usually confined to the surface.

Insects that attack wood include termites, wood destroying beetles, carpenter ants, and carpenter bees. Marine borers that attack wood include shipworms (teredineds) and piddocks (pholads).

7.2.2 Polymers

Polymers degrade by chemical, mechanical, photo(light)-induced, and/or thermal modes. The major polymer matrices used in WPCs include high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), and polyvinyl chloride (PVC). More recent work describes the use of nylon as a polymer matrix for WPCs (Chen and Gardner, 2008). Polymer additives used in WPC processing include lubricants, colorants, light stabilizers, anti-oxidants and coupling agents. Specific additives or combinations of additives can potentially contribute to degradation. For the most part, polymers and polymer additives are much less susceptible to biological attack than wood; but polymers, like wood, are susceptible to the weathering effects of UV light and oxidation.

PE and PP are linear molecules consisting of carbon and hydrogen. The energies of photons in the UV region (290–400 nm) are significantly higher than bond energies typically found in PE and PP (e.g. C–C and C–H bonds).

However, the excitation of single bonds requires an amount of energy that is also significantly higher than the bond energy (Gugumus, 1995). Therefore, photodegradation of polyolefins is caused mainly by the presence of chromophores, functional groups that readily absorb UV light, introduced during polymer manufacturing, processing, or storage. They include catalyst residues, hydroperoxide groups, carbonyl groups, and double bonds (Gugumus, 1995). Photodegradation of the chromophores yields free radicals, which then give rise to compounds containing hydroxyl groups, carbonyl groups, and vinyl groups (Wypych, 1995). As semicrystalline polymers, the packing of the crystalline phase is much tighter than that of the amorphous phase. Oxygen diffusion into crystalline segments is restricted (Wypych, 1995). Comparing PE and PP, the degree of branching determines the oxidation rate; more branching results in more labile hydrogen atoms attached to the tertiary carbon atoms.

PVC contains C–Cl, C–C, and C–H bonds. None of these absorb UV radiation. PVC is degraded by residual solvents, unsaturations, irregularities in polymer structure, and thermal history. Photodegradation proceeds via a free radical pathway and leads to dehydrochlorination, chain scission, and cross-linking. Incorporation of a plasticizer increases the rate of oxygen diffusion (Wypych, 1995).

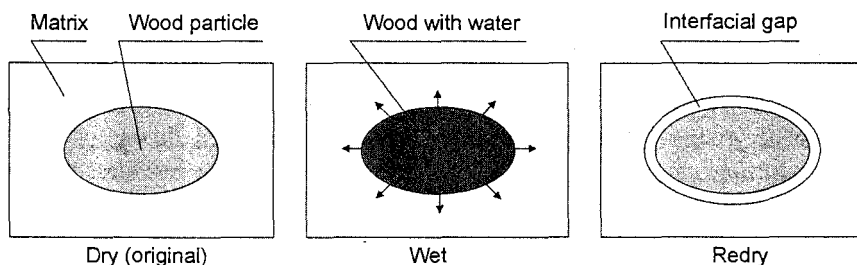
Indications of photodegradation include oxidation of the polymer, changes in crystallinity, and structural changes such as crosslinking and chain scission. Photodegradation is a surface phenomenon and can lead to the formation of surface cracks, embrittlement, and loss of strength and modulus of elasticity (MOE).

7.3 Changes in composite properties with exposure

Environmental, biological, chemical, mechanical, photo(light)-induced, and/or thermal modes of degradation all contribute to the degradation of WPCs. Outdoor durability, by its very nature, exposes WPCs to degradation modes that can act synergistically.

7.3.1 Moisture effects

In WPCs, the hydroxyl groups on wood or other lignocellulosic materials are primarily responsible for the absorption of water, which causes the wood to swell. When WPCs are exposed to moisture, the swelling wood fiber can cause local yielding of the plastic due to swelling stress, fracture of wood particles due to restrained swelling, and interfacial breakdown (Joseph *et al.*, 1995). Figure 7.1 illustrates this mechanism. Initially, there is adhesion between the wood particle and matrix in a dry WPC. As the wood particle absorbs moisture, it swells. This creates stress in the matrix, leading to the formation of microcracks. It also creates stress in the wood particle, causing damage. After drying the



7.1 Schematic of moisture damage mechanism in WPCs.

composite, there is no longer adhesion at the matrix and wood particle interface. Cracks formed in the plastic and the interfacial gap contribute to penetration of water into the composite at a later exposure.

Damage that occurs during moisture exposure degrades mechanical properties. Microcracks in the matrix and damage to wood particles cause a loss in MOE and strength. Interfacial damage is primarily responsible for a loss in composite strength. The effects can be dramatic. For example, after soaking 40% wood flour filled PP composites in a water bath for 2000 hours, the water absorption of the composites was 9%. This corresponded with a 39% decrease in flexural MOE and a 22% decrease in flexural strength (Stark, 2001).

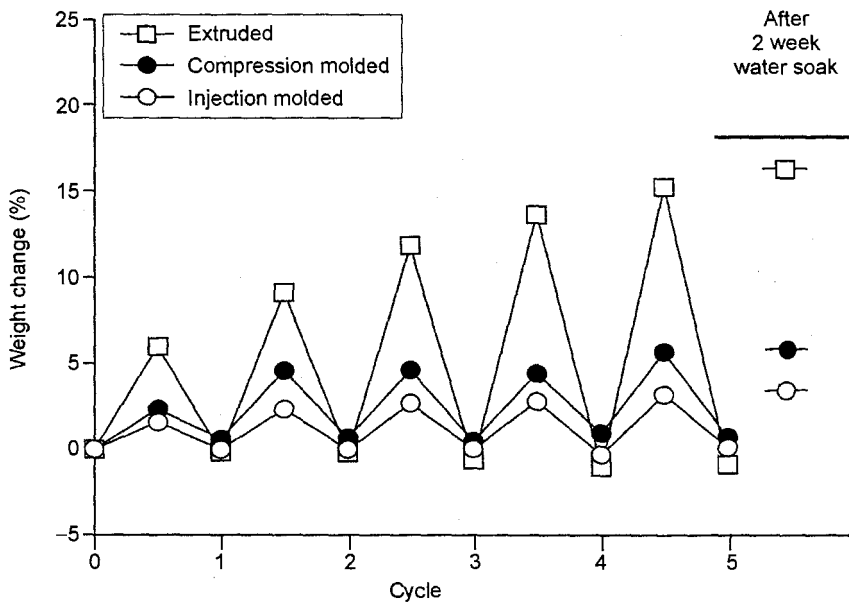
The amount of moisture absorbed by WPCs can be influenced by wood flour content, wood particle size, processing method, and additives. Steckel *et al.* (2007) examined the effects of wood flour content, particle size, coupling agent, and milling of the original surface on the moisture absorption of WPCs. After soaking the composites in distilled water, it was reported that increasing wood flour content, removing the original composite surface, and increasing the particle size increased the equilibrium moisture content of the composite while adding a coupling agent decreased it (Table 7.1; Steckel *et al.*, 2007). Lin *et al.* (2002) also found that increasing wood flour content and, to a smaller extent, increasing particle size increases the moisture absorption of WPCs. Lignocellulosic type also changes water absorption properties. Tajvidi *et al.* (2006) demonstrated that PP containing kenaf fiber and newsprint absorbed more moisture than WPCs, while composites containing rice hulls absorbed less. Because the diffusion of water into WPCs is slow, it can take some time to reach equilibrium moisture content. As the thickness of WPCs increases, the distribution of absorbed water in the material becomes non-uniform with higher moisture content in the outer surface layer than in the core (Wang and Morrell, 2004).

Moisture exposure that is cumulative can cause some irreversible damage to WPCs. Clemons and Ibach (2004) subjected 50% wood flour filled HDPE composites to five moisture exposure cycles. Each cycle consisted of 2 hours of boiling and 22 hours of drying. After each boiling cycle, the final moisture content of the composite was higher than for the previous cycle (Fig. 7.2).

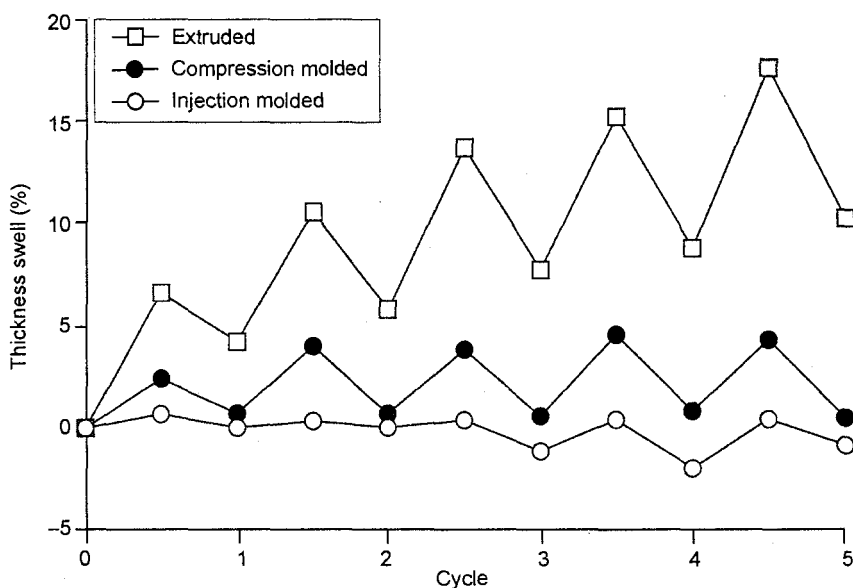
Table 7.1 Average moisture content of PP-based composites soaked in distilled water for 238 days (adapted from Steckel *et al.*, 2007)

Wood flour content (%)	Wood flour particle size	Coupling agent (%)	Surface treatment	Moisture content (%)
25	Coarse	0	None	5.08 (0.03)
25	Coarse	0	Milled	6.33 (0.21)
25	Coarse	3	None	4.42 (0.1 6)
25	Coarse	3	Milled	5.75 (0.05)
25	Fine	0	None	4.76 (0.1 7)
25	Fine	0	Milled	5.73 (0.04)
25	Fine	3	None	4.43 (0.06)
25	Fine	3	Milled	5.1 9 (0.20)
50	Coarse	0	None	13.33 (0.34)
50	Coarse	0	Milled	14.1 2 (0.43)
50	Coarse	3	None	10.92 (0.27)
50	Coarse	3	Milled	12.56 (0.1 6)
50	Fine	0	None	11.51 (0.16)
50	Fine	0	Milled	12.41 (0.07)
50	Fine	3	None	10.77 (0.1 7)
50	Fine	3	Milled	11.51 (0.1 0)

Values in parentheses are one standard deviation.



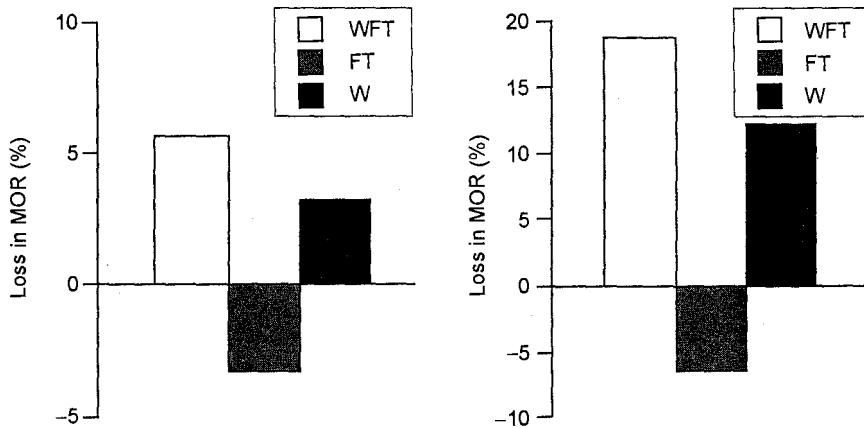
7.2 Moisture sorption of 50% wood flour filled HDPE during five moisture cycles consisting of 2 hours of boiling followed by 22 hours of drying (Clemons and Ibach, 2004).



7.3 Thickness swell of 50% wood flour filled HDPE during five moisture cycles consisting of 2 hours of boiling followed by 22 hours of drying (Clemons and Ibach, 2004).

Thickness swell also occurred (Fig. 7.3). Drying composites that absorbed more water, i.e. extruded composites, did not result in the composite returning to its original thickness.

Moisture exposure also becomes important in cold climates during freeze-thaw cycles. Freeze-thawcycling WPCs results in a loss of mechanical properties (Panthapulakkal *et al.*, 2006; Pilarski and Matuana, 2005, 2006). Standard freeze-thawcyclical testing consists of three parts: (1) water soak until weight gain in a 24 hour period is not more than 1%; (2) freezing for 24 hours at -29°C ; and (3) thawing at room temperature for 24 hours (ASTM D6662). WPCs comprising 46% pine wood flour filled PVC were exposed to five freeze-thaw cycles. After exposure, the modulus of rupture (MOR) decreased 13% and the MOE decreased 30%. To better understand the effect moisture has on freeze-thawcycling, Pilarski and Matuana (2005) performed two variations of the water soak/freeze-thaw test in addition to the standard test. In the first variation, the water soak portion of the test was removed. Therefore, the composites were exposed to only freeze-thawcycles. For the second variation, the freezing and thawing portions were removed. Composites were exposed only to the water soak. Figure 7.4 shows the loss in MOR and MOE after the standard water soak/freeze-thawcycle and the two variations. The authors concluded that the water soak portion of the cycling process had the greatest impact on flexural properties. This was attributed to moisture influencing interfacial adhesion between PVC and wood flour.



7.4 Loss in flexural properties after exposure of 46% pine wood flour filled PVC composites to water soak/freeze–thaw cycling (WFT), freeze–thaw cycling (FT), and water soak cycling (W) (adapted from Pilarski and Matuana, 2005).

7.3.2 Thermal changes

Thermal response of polymers can impact mechanical properties, especially creep, and physical properties, i.e. coefficient of thermal expansion which can impact in-service properties of WPCs. Depending on the particular climatic exposure, WPCs used in decking applications can experience temperatures ranging from -30°C to 50°C . The primary thermal changes impacting WPC properties include thermal expansion, mechanical creep, and thermal-oxidative degradation. Increased temperatures can also act synergistically with other chemical degradation mechanisms to increase reaction rates.

extruded solid deck boards made from either HDPE or PP containing at least 50% wood flour and 50% polymer/additives (O'Neill and Gardner, 2004). As an example, for PP-based deck boards, the coefficient of thermal expansion is greatest in the thickness direction ($30.03 \times (1/^{\circ}\text{F}) \times 10^{-6}$) followed by the width ($23.61 \times (1/^{\circ}\text{F}) \times 10^{-6}$) and is the least in the length ($11.53 \times (1/^{\circ}\text{F}) \times 10^{-6}$) or machine direction of the boards. Both the polymer chains and wood flour align with the flow of extrusion and this behavior is believed to contribute to the anisotropic thermal behavior of extruded deck boards. Thermal expansion behavior of WPC deck boards becomes important during installation because improper gapping can lead to warping.

Mechanical creep

Thermoplastic materials such as WPCs will experience changes in mechanical (stiffness) properties as a function of increased temperature. Materials under a mechanical load that might perform adequately at normal service temperatures may experience creep under loads for extended periods of time and at higher temperatures (Brandt and Fridley, 2003).

Thermal-oxidative degradation

Recently, a thermal-oxidative degradation issue in WPC deck boards was reported (Klyosov, 2005). WPC deck boards not containing sufficient levels of antioxidant exposed to extreme temperatures in the Arizona desert were experiencing crumbling and subsequent board failure. The failures were attributed to free radical oxidative degradation mechanisms that were exacerbated by high temperatures.

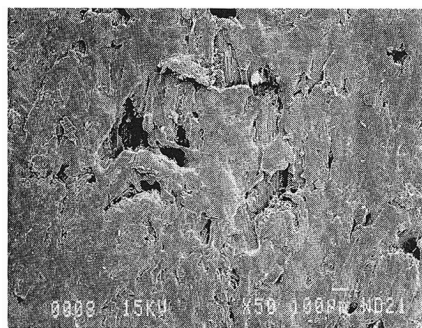
7.3.3 Weathering

Primary weathering variables include solar radiation, temperature, and water. Secondary variables include seasonal and annual variation, geographical differences, atmospheric gases, and pollution changes. The large number of variables accounts for the high variability in weathering studies, and does not readily allow for comparison among natural weathering studies. Results obtained are specific for the location and timeframe of the test.

Accelerated weathering is a technique used to compare performance by subjecting samples to cycles that are repeatable and reproducible. Primary weathering variables can all be measured during accelerated weathering. During accelerated weathering, test standards are typically followed that prescribe a schedule of radiation (ultraviolet, xenon-arc, etc.) and water spray (number and time of cycles).

WPCs exposed to weathering may experience color change, which affects their aesthetic appeal, as well as mechanical property loss, which limits their performance. Changes in mechanical properties after weathering can be due to changes such as composite surface oxidation, matrix crystallinity changes, and interfacial degradation. Although photodegradation of both polymers and wood has been extensively examined, the understanding of WPC weathering continues to evolve as several research groups work on characterizing and understanding changes that occur when WPCs weather.

Weathering results in the destruction of the WPC surface (Fig. 7.5). Wood particles exposed at the surface absorb water and swell. In addition, the plastic matrix cracks upon UV exposure. In combination, the result is a flaky, cracked surface. As WPCs weather, the surface chemistry changes. Oxidation at the surface is one measure of degradation; its increase can be followed throughout weathering. Fourier transform infra-red (FTIR) spectroscopy is one tool that can



(a)



(b)



(c)



(d)

7.5 Micrographs of extruded 50% wood flour filled HDPE composites before weathering (a) and after 1000 hours (b), 2000 hours (c), and 3000 hours (d) of weathering (adapted from Stark et al., 2004).

be used to determine changes in surface chemistry during weathering. Peaks that appear on spectra are assigned to functional groups present at the composite surface. This method has been used to study surface oxidation and matrix crystallinity changes in weathered WPCs (Stark and Matuana, 2004a, 2004b; Muasher and Sain, 2006).

Weathering variables act independently and synergistically to degrade WPCs. In the following example, Stark (2006) exposed extruded WPCs (50% wood flour filled HDPE) to two accelerated weathering cycles for approximately 3000 hours. The first weathering cycle included water spray cycles (12 minutes of water spray every 2 hours); in the second weathering cycle there was no water spray. The change in composite properties is shown in Table 7.2 (Stark, 2006).

The color of the composite clearly lightened after weathering, i.e. increase in lightness (L^*). However, the increase in L^* was much less when the samples were exposed only to UV light, demonstrating that water spray had a large effect on color fade. Flexural MOE and strength decreased when the composites were exposed to UV radiation with water spray (Table 7.2). Exposing the WPCs to UV radiation resulted in only a small decrease in MOE and no significant change in

Table 7.2 Percentage change in extruded 50% wood flour filled HDPE composites after 3000 hours of accelerated weathering (adapted from Stark, 2006)

Property	Weathering cycle	
	UV + water spray	UV only
Lightness (L^*)	+46	+13
MOE	–52	–12
Strength	–34	+1 ^{NS}

NS: Change not significant at $\alpha = 0.05$.

strength. Exposure to UV radiation with water spray resulted in more destruction in mechanical properties than exposure to UV radiation only (Stark, 2006).

The color of WPCs primarily reflects the color of the wood during weathering, although some whitening is due to stress cracking of the matrix. Water and UV radiation jointly contribute to increasing composite L^* . Exposure to UV radiation degrades lignin leaving loose fibers at the composite surface. Water spray cycles wash away loose fibers, exposing more material for degradation. The result is a cyclical erosion of the surface (Williams *et al.*, 2001). Additionally, washing the surface can remove some water-soluble extractives that impart color (Stark, 2006). W radiation and water also act synergistically to degrade WPCs in the following ways. Exposing WPCs to UV radiation degrades hydrophobic lignin, leaving hydrophilic cellulose at the surface and increasing surface wettability, causing the surface to become more sensitive to moisture (Kalnins and Feist, 1993). Swelling of the wood fiber also facilitates light penetration into wood and provides sites for further degradation (Hon, 2001).

Fiber swelling due to moisture absorption is primarily responsible for the loss in mechanical properties after weathering. Cracks form in the HDPE matrix due to swelling of the wood fiber and contribute to the loss of composite MOE and strength. The loss in strength is due to moisture penetration into the WPC, which degrades the wood–HDPE interface, decreasing the stress transfer efficiency from matrix to the fiber. Synergism between UV radiation and water also contribute to mechanical property losses by eroding the surface and increasing surface wettability as described above, causing exposure to UV radiation with water exposure to be much more damaging than exposure to UV radiation only (Stark, 2006).

7.3.4 Biological attack

Decay

Wood decays when its moisture content exceeds approximately 20%. In WPCs, it can be assumed that the plastic matrix does not absorb moisture. Therefore, a

50% wood filled WPC must reach a moisture content of about 10% for decay to occur (i.e. the wood component reaches a moisture content of 20%). However, the moisture content is typically measured for the bulk of the material. The slow diffusion of water through WPCs results in higher moisture contents at the surface than in the core (Wang and Morrell, 2004). In the field, the moisture content of the bulk WPC material may be significantly lower than the expected point at which decay begins.

The wood component in WPCs is responsible for its susceptibility to fungal attack. In the winter of 1996/1997, brown-rot and white-rot fungi were observed on a commercial WPC after 4 years of service in Florida (Morris and Cooper, 1998). This observation led to the study of WPC decay. Because moisture is the critical factor, it is not surprising that the variables that influence moisture sorption, including fiber content and encapsulation, also influence decay. Mankowski and Morrell (2000) studied three commercial WPC products made from a combination of wood and HDPE. A sample from each product was soaked in water for 30 minutes, sterilized, and exposed to brown-rot or white rot fungi for 12 weeks. They showed that composites with more wood experienced a higher moisture content and also more decay. Verhey *et al.* (2001) manufactured WPCs with 30, 40, 50, 60, and 70% wood. After exposure to a white-rot or brown-rot fungus for 12 weeks, the composites with higher wood contents generally had more weight loss, and higher weight losses were observed after exposure to brown-rot fungi versus white-rot fungi (Table 7.3). Investigations into the effect of particle size on decay resistance of WPCs demonstrated that weight loss due to fungal decay decreased as wood particle size decreased (Verhey and Laks, 2002). This was attributed to better encapsulation of smaller wood particles by the plastic matrix.

Table 7.3 Percentage weight losses from wood flour/PP composites after 12 weeks exposure to fungi (adapted from Verhey *et al.*, 2001)

Test fungus	Wood content (%)	Surface preparation	
		Unsanded	Sanded
White-rot	30	1	1
	40	1	1
	50	1	1
	60	2	5
	70	3	15
Brown-rot	30	8	8
	40	12	11
	50	14	16
	60	40	33
	70	54	58

WPCs decay only at the surface layer. Stakes cut from a commercial WPC consisting of approximately 56% wood and 44% PE were installed in the ground in Hilo, Hawaii and analyzed after 10 years of exposure. Evaluation of the in-ground portion of the stakes using SEM revealed surface pitting due to loss of wood particles. Only 5 mm in from the surface, there was no evidence of microbial attack (Schauwecker *et al.*, 2006). This was attributed to limited moisture movement into the WPC.

Much of the loss in mechanical properties due to fungal attack can be attributed to moisture absorption. Following the procedure of Clemons and Ibach (2004), Schirp and Wolcott (2005) evaluated HDPE-based WPCs containing either 49% or 70% wood filler after exposure to modified agar-block tests for 3 months. Tests were conducted with a white-rot fungus, brown-rot fungus, or no inoculation to determine the contributions of wood decay and moisture exposure to changes in mechanical properties of WPCs. Loss of stiffness occurred for each of the formulations after exposure, while loss in strength occurred only for WPCs containing 70% wood fiber. The reported losses in mechanical properties were due primarily to moisture absorption.

Mold

Because mold has received attention as a potential health hazard, it has become more important to understand mold growth on WPCs. Much of the ongoing work has been proprietary. Dawson-Andoh *et al.* (200516) exposed wood flour filled HDPE composites to mold fungi. They were able to relate moisture exposure to mold growth and found more evidence of mold growth when composites were directly in contact with moisture versus exposed to an environment with a high relative humidity. Additionally, pre-conditioning WPCs through either exposure to UV weathering or freeze-thaw cycling was shown to have minimal effect on mold growth (Dawson-Andoh *et al.*, 200516).

Laks *et al.* (2005) investigated the effect of several variables on mold growth on extruded wood flour filled HDPE composites. After 8 weeks of exposure, mold was hardly noticeable on composites containing 30% or 50% wood flour, very noticeable on WPCs containing 60% wood flour, and completely covered WPCs containing 70% wood flour. Lubricants are often used to aid in extrusion. Laks *et al.* (2005) evaluated two, ethylene bis-stearamide wax and zinc stearate. They suggested that the amine in each of these lubricants may provide sufficient nitrogen for more rapid colonization of mold fungi.

Insects and marine borers

Insect attack of wood can include attack by termites, beetles, and ants. There is little information in the area of insect attack on WPCs, but one on-going study reported termite activity after 3 years in-ground exposure in Mississippi (Ibach

and Clemons, 2004). After the first and second year of in-ground exposure, there was no reported termite attack on 50% wood flour/HDPE composites. After the third year, nibbles of up to 3% cross-section were reported.

Marine borer attack includes attack of wood by shipworms and crustaceans. Although marine borers present a problem to untreated wood, they are not considered a threat to WPCs based on limited field studies. Pendleton and Hoffard (2000) exposed HDPE composites containing 50% or 70% wood flour to a natural marine environment in Pearl Harbor, Hawaii. After 1, 2, and 3 years the WPC specimens showed no visible marine borer attack (Pendleton and Hoffard, 2000).

7.4 Methods for protection

7.4.1 Moisture effects

Changes in processing conditions

Injection molding, compression molding, and extrusion are processing methods commonly used for manufacturing WPCs. Primary processing variables include temperature and pressure. Both processing methods and variables within a processing method greatly influence composite morphology and durability. Figures 7.2 and 7.3 clearly show that the weight change and dimensional change of extruded WPCs is higher than for compression molded and injection molded WPCs during cyclical water exposure. This is largely due to a polymer-rich surface layer and lower void content of compression molded and injection molded WPCs compared with extruded composites (Clemons and Ibach, 2004). As reported in Table 7.1, removing the polymer-rich surface layer from injection molded WPCs results in increased moisture contents (Steckel *et al.*, 2007).

Fiber modification

The hygroscopicity of wood can be reduced by replacing some of the hydroxyl groups with alternative chemical groups. Acetylation has been an active area of research in improving the moisture performance of wood and wood composites. Acetic anhydride reacts with hydroxyl groups in the wood cell wall to yield and acetylated fiber. For example, acetylating pine wood fiber reduced its equilibrium moisture content at 90% relative humidity and 27°C from 22% to 8% (Rowell, 1997). This method has been investigated to a more limited extent to provide moisture resistance to WPCs. For example, a 50% wood fiber filled PP composite absorbed 5% moisture after soaking for 34 days while a 50% acetylated wood fiber filled PP composite absorbed only 2.5% (Abdul Khalil *et al.*, 2002).

Additives

Coupling agents are commonly used to improve bonding between the hydrophobic matrix and hydrophilic wood fiber. This has been the most active area of research in employing an additive to provide moisture resistance to WPCs. Coupling agents can reduce the amount of moisture WPCs absorb by reducing gaps at the wood–matrix interface and by reducing the number of hydroxyl groups available for hydrogen bonding with water. However, the decreases in water absorption can be minor. Steckel *et al.* (2007) examined the moisture sorption properties of several WPCs using a full factorial design and determined that wood flour content had the largest influence on equilibrium moisture content, followed by removal of the original polymer-rich composite surface. The inclusion of a coupling agent and reducing particle size had a much smaller effect on equilibrium moisture content (Table 7.1). Panthapulakkal *et al.* (2006) examined water absorption of 65% rice husk filled HDPE composites. After immersion in water for 1608 hours the control composites absorbed 14% water. Composites containing a coupling agent absorbed either 12% or 9% depending on the coupling agent used. However, the use of a lubricant as a processing aid negated any positive effect of the coupling agent. Lin *et al.* (2002) reported an 18% decrease in moisture absorption when 2% coupling agent was added to 15% wood flour filled PP composite. Coupling agents may be more effective at mitigating changes in strength and modulus after exposure to cyclical freeze–thaw testing. The increase in weight change of rice husk filled HDPE composites was 9.6% after 12 freeze–thaw cycles. Adding a coupling agent resulted in increases of 3.3–3.5% (Panthapulakkal *et al.*, 2006).

7.4.2 Thermal changes

Methods for protection of thermal changes in WPCs are primarily formulation based and need to consider protection of both the wood and the polymer components. Thermoplastic polymers can experience thermal oxidative effects during processing especially for PVC–wood composites. Both antioxidants and thermal stabilization aids can be added to WPC formulations to decrease thermal degradation during processing. In addition to protecting the polymer during processing, antioxidants can also help protect the polymer matrix during environmental exposure.

Using a plastic matrix that is not as susceptible to thermal changes may be an important way to provide thermal stability in the future. Chen and Gardner (2008) manufactured WPCs using a nylon matrix. The storage modulus of nylon–wood composite was found to be more temperature stable than pure nylon 66 and wood flour reduced the physical aging effects on nylon in the wood composites. Comparing the nylon–wood composite thermal mechanical

properties with other, similar glass-filled nylon composites shows that nylon–wood composites are a promising low-cost material for industrial applications.

Thermal expansion in WPCs can be reduced by creating a cellular or foamed microstructure (Finley, 2000). Since wood is more thermally stable with temperature than plastic, WPCs with higher wood contents should exhibit lower coefficients of thermal expansion. Mechanical creep in WPCs can be reduced by crosslinking the polymer and this has been demonstrated for HDPE-based WPCs (Bengtsson *et al.*, 2006). Thermal-oxidative degradation can be reduced by the addition of antioxidants (Klyosov, 2005).

7.4.3 Weathering

Changes in processing conditions

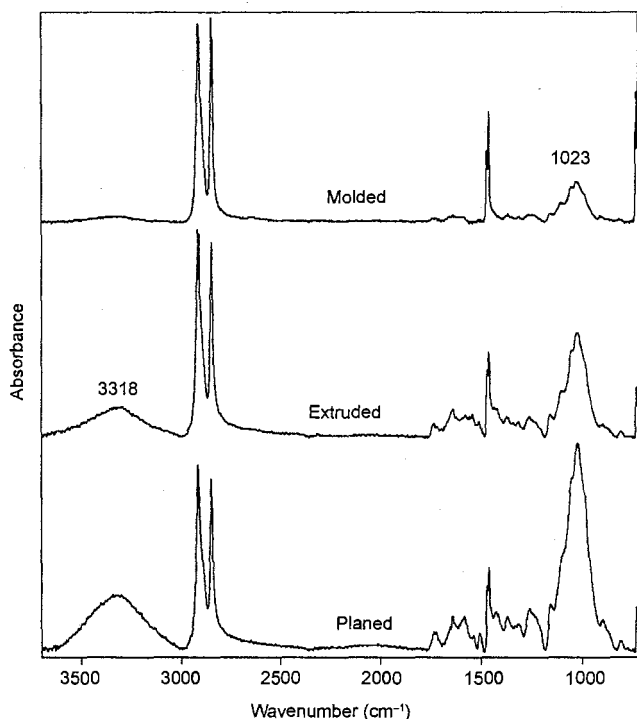
Higher processing pressures and temperature during injection molding compared with extrusion result in more plastic at the surface. The presence of a hydrophobic surface delays some changes that occur during weathering by preventing some degradation due to water exposure.

As processing conditions change, the changes in WPC surface components and morphology that influence moisture performance also influence weathering performance. In the following example, Stark *et al.* (2004) characterized this difference by analyzing FTIR spectra. Figure 7.6 illustrates the changes in composite surface components when 50% wood flour filled HDPE composites were injection molded, extruded, or extruded with the surface removed (planed). The FTIR spectra of the planed surface had larger peaks associated with wood (a broad peak at 3318 cm^{-1} and a strong peak at 1023 cm^{-1}) compared with the injection molded surface. This suggested more wood at the surface of the planed samples and a plastic-rich layer at the surface of the injection molded samples (Stark *et al.*, 2004).

The changes in the surface were related to weathering performance. Weathering resulted in composite lightening; WPCs lightened to a similar L^* after 3000 hours of weathering. Weathering resulted in a decrease in both flexural strength and MOE (Table 7.4). The relative flexural properties show that the retention of flexural properties was higher for injection molded composites, followed by extruded and planed composites (Stark *et al.*, 2004).

Additives

The first plan of attack to improve the weatherability of WPCs is often to add photostabilizers. Photostabilizers are compounds developed to protect polymers and combat W degradation. They are generally classified according to the degradation mechanism they hinder. Ultraviolet absorbers (UVAs) and free radical scavengers are important photostabilizers for polyolefins. Commercial UVAs are readily available as benzophenones and benzotriazoles (Gugumus,



7.6 FTIR spectra of injection molded, extruded, and planed WF/HDPE composites. The broad peak at 3318 cm^{-1} and the sharp peak at 1023 cm^{-1} are due to the wood component (adapted from Stark *et al.*, 2004).

1995). A relatively new class of materials, hindered amine light stabilizers (HALS), has also been extensively examined for polyolefin protection as free radical scavengers (Gijssman *et al.*, 1993; Gugumus, 1993, 1995). Pigments physically block light, thereby protecting the composite from photodegradation.

Table 7.4 Relative flexural properties of 50% wood flour filled HDPE composites manufactured by injection molding, extrusion, or extrusion with the surface removed (planed) after accelerated weathering (adapted from Stark *et al.*, 2004)

Exposure time (hours)	Strength (MPa)			MOE (GPa)		
	Injection molded	Extruded	Planed	Injection molded	Extruded	Planed
0	1	1	1	1	1	1
1000	0.88	0.77	0.66	0.81	0.81	0.60
2000	0.82	0.65	0.63	0.67	0.67	0.47
3000	0.68	0.66	0.63	0.57	0.57	0.48

Many photostabilizers that were developed for use in unfilled polyolefins are being adapted for use in WPCs and this is an active area of research. Pigments, UV absorbers, and hindered amine light stabilizers have been used with some success in mitigating changes that occur during WPC weathering.

Pigments were shown to mitigate the increase in lightness and significantly increase the flexural property retention of WPCs after accelerated weathering (Falk *et al.*, 2000). Lundin (2001) investigated the effect of hindered amine light stabilizer (HALS) content on the performance of WPCs. The author reported that the addition of HALS to the composites did not affect color change caused by accelerated weathering and slightly improved the mechanical property retention (Lundin, 2001). Stark and Matuana (2003) examined the effect of a low molecular weight HALS, a high molecular weight HALS, a benzotriazole ultraviolet absorber (UVA), and a pigment on the changes in lightness and mechanical properties of WPCs after weathering. Only the UVA and pigment significantly reduced composite lightening and loss in mechanical properties. Regardless of molecular weight, HALS was found to be ineffective in protecting the composite against surface discoloration and flexural property loss. Muasher and Sain (2006) also evaluated the performance of HALS and UVAs in stabilizing the color WPCs. They found that high molecular weight diester HALS exhibited synergism with a benzotriazole UVA.

FTIR identified functional groups present on the surface of unexposed and weathered WPCs. Following carbonyl growth indicated that both the pigment and UVA delayed the eventual increase in surface oxidation and decrease in HDPE crystallinity that would occur at later exposure times (Stark and Matuana, 2004a). Following this approach, Muasher and Sain (2006) also used FTIR to evaluate carbonyl growth in photostabilized WPCs. They identified a correlation between carbonyl growth and photostabilizer effectiveness at reducing color fade.

Table 7.5 illustrates the percentage change in property that occurs after injection molded, photostabilized WPCs weather (Stark and Matuana, 2006). The results clearly showed that composites with an ultraviolet absorber (UVA) or pigment (P) lightened less than unstabilized composites. The pigment (P) was more efficient at preventing composite lightening than WA. Lightness (L^*) decreased with increase in pigment concentration. By contrast, increasing UVA content had little, if any, effect on L^* . Composites with the least amount of lightening had a combination of UVA and P. It was concluded that WA reduced lightening by absorbing some UV radiation, resulting in less UV radiation available to bleach the wood component, while P physically blocks UV radiation, which also results in less available W radiation to the wood component. In addition, P masked some lightening (Stark and Matuana, 2006).

Adding 0.5% UVA did not greatly influence the loss in MOE but did improve the loss in strength (Table 7.5). Increasing the UVA concentration to 1% resulted in further retention of MOE and strength. Adding P at 1% resulted in

Table 7.5 Percentage change in properties of photostabilized 50% wood flour filled HDPE composites after 3000 hours of accelerated weathering (adapted from Stark and Matuana, 2006)

Formulations	Change in property (%)		
	L^*	Strength	MOE
—	+115	−27	−33
0.5% UVA	+98	−20	−32
1% UVA	+107	−15	−21
1% P	+73	−13	−18
2% P	+61	−5	−18
0.5% UVA, 1% P	+59	−9	−15
1% UVA, 2% P	+50	−2 ^{NS}	−16

UVA: Hydroxyphenylbenzotriazole, Tinuvin 328, Ciba Specialty Chemicals

P: Zinc ferrite in carrier wax, Cedar TI-8536, Holland Colors Americas.

NS: Change not significant at $\alpha = 0.05$.

smaller MOE and strength losses than did adding 1% UVA. Increasing the concentration of P did not change the loss in MOE but decreased the loss in strength. FTIR work suggested that UVA and P delay changes in HDPE crystallinity (Stark and Matuana, 2004a). WA was likely consumed during weathering. Therefore, the higher concentration was required to protect against mechanical property loss for the full weathering period. The P consisted of zinc ferrite in a carrier wax. The wax may protect the WPC by creating a hydrophobic surface and resulting in less degradation of the interface (Stark and Matuana, 2006).

7.4.4 Biological attack

Decay of WPCs is a function of moisture content. Therefore, the first step in preventing decay is to prevent or limit moisture sorption. Limiting the access of nutrients, i.e. encapsulating the wood in the plastic matrix, would also provide fungal durability. Limiting oxygen availability by submersing in water decreases the opportunities for mold growth and fungal attack.

Verhey *et al.* (2001) demonstrated that sanding the surface of a compression molded WPC, i.e. removing some of the plastic film at the surface, increased the amount of decay at high wood contents (Table 7.3). Clemons and Ibach (2004) examined WPCs manufactured using extrusion, compression molding, or injection molding. Manufacturing method influenced moisture sorption (Fig. 7.2), with extruded composites absorbing more moisture than compression molded and injection molded composites. After cyclical moisture exposure followed by 12 week exposure to brown-rot fungi, the weight losses of extruded, injection molded, and injection molded samples were 22.8%, 2.4%, and 0.4%, respec-

tively (Clemons and Ibach, 2004). The difference was attributed to surface characteristics of the WPCs; a plastic layer formed at the surface of the compression molded and injection molded composites. Acetylation and silane treatment of wood fibers decreases moisture sorption, and this has been shown to be beneficial in preventing decay (Hill and Abdul Khalil, 2000).

The preservative zinc borate is often used to prevent decay and can be very effective (Ibach *et al.*, 2003; Verhey *et al.*, 2001). For example, mass loss of 50% wood flour filled PP composites was 12.9% after 12 weeks exposure to brown-rot fungi. Adding zinc borate at 1% reduced the mass loss to less than 1%; adding zinc borate at 3 or 5% resulted in virtually no mass loss (Verhey *et al.*, 2001).

There is minimal literature regarding protecting WPCs against mold growth, and much of the work that has been done to date is proprietary. Because mold and mold spores are always present in the air, it is often recommended to clean WPCs with a dilute bleach solution to remove mold that is already growing. Strategies to prevent mold growth often coincide with reducing moisture content and moisture susceptibility.

Biocides also can control mold growth. Dylingowski (2003) evaluated an isothiazole and zinc borate moldicide in a model WPC material. It was reported that isothiazole was more effective at controlling mold growth than zinc borate. Laks *et al.* (2005) evaluated chlorothalonil and zinc borate as fungicides in 70% wood flour filled HDPE composites. After 8 weeks exposure to mold fungi, mold growth was slightly noticeable on WPCs containing 1% or 1.5% chlorothalonil versus mold completely covering the control WPCs. Zinc borate was ineffective at preventing mold growth at 1% loading but, at 3% or 5% loading, mold was hardly noticeable after 8 weeks.

7.5 Future trends

The work summarized here suggests that controlling moisture is the key to not only decreasing losses in performance due to moisture absorption but also increasing weathering performance and resistance to biological attack. Therefore, it is not surprising that in the future WPCs with improved durability will be less susceptible to moisture. New methods to modify the fiber or the composite will be developed. Modifying the composite can include surface coatings, such as co-extrusion or the development of paints and coatings. Methods for embossing a grain pattern onto the surface without disrupting the protective plastic-rich layer will also provide improved moisture resistance.

Until recently most additives used in WPCs were developed for unfilled plastics. As the market has grown, the opportunities for additives suppliers to manufacture additives specifically for WPCs has grown. Additives that address some of the unique needs of WPCs are being developed and incorporated into commercial products, improving the durability of WPCs. It can be expected that

this trend will continue in the future. Improvements in lubricants, photostabilizers, and biocides will occur, along with a better fundamental understanding of how they work and interact with each other. New methods for coloring WPCs as well as new, more stable colorants will result in a more natural-looking WPC that exhibits less color fade.

Emerging fields of science such as nanotechnology will also benefit WPCs. Nanotechnology as a characterization method will allow for more fundamental understanding of how changes occur during exposure, and help to identify schemes for preventing those changes. Nanoparticles in WPCs may be able to provide increased resistance to moisture, photodegradation, and biological attack. Nanoparticles may also be used to improve thermal expansion and creep.

7.6 Sources of information and advice

To learn more about the durability of wood, readers can turn to the book chapters titled ‘Biological Properties’ (Ibach, 2005) or ‘Weathering and Photochemistry of Wood’ (Hon, 2001). Good reviews of polymer degradation can be found in the texts by Schnabel (1982) and Wypych (1995). A book chapter by Schirp *et al.* (2008) provides good discussion on the biological degradation of WPCs including a discussion of current test methods.

To keep informed on science and technology developments in wood–plastic composites including durability, readers are urged to attend the various conferences focused on this topic. Over the past several years, many international conferences per year have been focused on wood plastic composites. The International Conference on Wood & Biofiber Plastic Composites, the oldest and among the most important of these conferences, started in 1991 and provides forum on the science and technology for the processing and development of these materials.

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