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DURABILITY OF WOOD-PLASTIC COMPOSITES
EXPOSED TO FREEZE-THAW CYCLING

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Laurent Matuana
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DURABILITY OF WOOD-PLASTIC COMPOSITES EXPOSED TO FREEZE-THAW CYCLING

By

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ABSTRACT

DURABILITY OF WOOD-PLASTIC COMPOSITES EXPOSED TO FREEZE-THAW CYCLING

By

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Two studies were used to assess the durability of wood-plastic composites (WPCs) exposed to accelerated freeze-thaw cycling. A counter-rotating twin-screw extruder was used to process various formulations of WPCs, which were then exposed to accelerated freeze-thaw testing according to ASTM standard D-6662. This method includes exposure to water submersion, freezing, and thawing as one complete cycle. The effects of 2 to 15 freeze-thaw cycles were observed for the density, dimensional stability, flexural strength and stiffness, porosity, and microscopic appearance of WPCs containing both maple and pine wood flour. Of the composite formulations tested with varied wood contents, only the lower wood content WPCs showed resistance to freeze-thaw actions. The density of all WPCs were unaffected by freeze-thaw actions. The WPCs maintained relatively stable dimensions after exposure compared to other materials such as solid wood. The flexural strength and stiffness of all WPCs were significantly decreased by as few as 2 cycles. Scanning electron microscopy confirmed similarities between water-only and full freeze-thaw cycles. The main cause of the flexural property losses was attributed to the water portion of this cyclic process, which led to decreased bonding between the wood and polymer, which also increased the porosity. The freezing (without water) had a lesser effect on WPCs compared to the water portion.

Dedicated to my friends and family

Especially Dan, Karana, Bhavesh, Katie and my mom Sue

Without whom I would have never made it this far

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LIST OF ABBREVIATIONS

CCA	Chromated Copper Arsenate (wood preservative)
EMC	Equilibrium Moisture Content
EPA	(United States) Environmental Protection Agency
FT	Freeze-Thaw only cycle, without water exposure
HDPE	High-density Polyethylene
LDPE	Low-density Polyethylene
LVL	Laminated Veneer Lumber
MDF	Medium Density Fiberboard
MF	Melamine Formaldehyde
MOE	Modulus of Elasticity (stiffness)
MOR	Modulus of Rupture (strength)
OSB	Oriented Strand Board
PE	Polyethylene (high-density or low-density)
PF	Phenol Formaldehyde
phr	Parts per hundred parts of resin
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
RH	Relative Humidity
SEM	Scanning Electron Microscopy
UF	Urea Formaldehyde

UV -- Ultraviolet (rays or light)

W -- Water-only cycle, without exposure to freezing

WFT -- Water-Freeze-Thaw cycle, full cycle exposure

WPC -- Wood-Plastic Composite

Chapter 1

INTRODUCTION

Wood-plastic composites (WPCs) are relatively new products that have been developed in part due to health concerns and the phasing out of other products. WPCs are unique because they can be easily modified and customized depending on the requirements of any given application. Some already prevalent applications of WPCs include decking, docks, landscaping timbers, fencing, signposts, picnic tables, boardwalks, flooring, railroad ties, playground equipment, window and door frames, and construction molded automobile interiors, just to name a few (1-8). The combination of properties from plastics, wood and other additives can create a composite for seemingly any application and production has been growing rapidly in the United States (1-3,9-11).

Wood-plastic composites make use of would-be wood wastes as fillers or reinforcing agents in a polymer matrix. The addition of wood fibers to the neat polymer enhances the stiffness, lessens the cost compared to mineral reinforcing agents, and cause less wear on processing equipment because wood is more flexible (12-19). The plastic portion of the composite is believed to enhance the resistance to moisture, fungus, bacteria and insects which wood is susceptible to (1,2). Additives can also be mixed into WPCs, which can further enhance the properties. Lubricants and coupling agents are the most common additives that are used to ease processing and enhance mechanical properties.

Wood fibers are naturally attracted to water, whereas plastics are oil-based and are not miscible with water (20-23). Because of these differences it is difficult to obtain bonding between the wood and plastic components. Coupling agents are used to enable and enhance the bonding between the hydrophilic wood fibers and hydrophobic polymer matrix (20-23). The coupling agent acts by bonding to the wood and make it appear more plastic-like (21-23). Coupling agents are most commonly used with polyolefins, such as ethylene or propylene based polymers (20-23). Coupling agents can be created from several sources, but commonly involve organic agents, the most common of which are maleated and acrylic acid-functionalized polyolefins (21-23).

Due to WPC's desirable combination of attributes, the wood-plastic composite industry is expected to become a major beneficiary of the decision made by the Environmental Protection Agency (EPA) to stop producing chromated copper arsenate (CCA) treated lumber at the end of the year 2003 (24,25). At the end of their service life, CCA treated lumber structures will need to be replaced by another product with equal properties and superior environmental preservation. Although CCA is no longer for sale, there are other pressure treated wood products available. Like CCA, there is concern that these products may leach chemicals from the wood, posing health hazards to humans and the surrounding aquatic or terrestrial environment (26). WPCs can yield properties similar to that of wood and adhesive-bound wood composite products, but with fewer environmental drawbacks. Adhesive-bound composites, such as particleboard, medium density fiberboard (MDF), or oriented strand board (OSB) are frequently bound with formaldehyde-based resins that have concerns about carcinogenous formaldehyde being emitted from the boards once in use and even later as a waste (23,27). The health and environmental concerns raised by pressure treated wood and adhesive-bound wood composites are not present when considering the use of WPCs. Consequently, wood-plastic composites offer a healthy alternative for both humans and the environment.

However, many challenges still lie ahead in the thriving wood-plastic composite market. The emerging status of this product dictates the need for more and varied research. These relatively new products are increasingly common in both interior and exterior applications, many of which are listed above. These applications often involve ground contact or above ground use where there is a risk of material deterioration. When in ground contact there is a concern of degradation from biological agents such as fungi and subterranean termites (4,5,28). Exterior applications also involve exposure to ultraviolet (UV) rays in sunlight and moisture from precipitation. Wood fibers added into a polymer matrix have been shown to act as chromophores, since they accelerate photodegradation compared to neat polymers (29,30). Among the degradative effects to the WPCs were color changes, increased brittleness, decreased elasticity, and reduced impact resistance (29). These effects can be as insignificant as aesthetic color changes or as drastic as failure of the product that can lead to injury and subsequent replacement of the degraded material. Therefore, it can be deduced that WPCs are as susceptible to degradation as solid wood, but there is much more potential for enhancement in WPCs because of the ease of modifying formulations.

Some types of exposure have been investigated and evidence has shown that there is a potential for degradation of wood-plastic composites via fungi, termites and UV light exposure (4,5,28-30). Other types of exposure, such winter climate exposure, have yet to be investigated and could result in other forms of degradation for WPCs. Considerable information is available on the durability of WPCs exposed to warm climate conditions and improvements can be made in the future. However, there is no information in the open literature on the freeze-thaw durability of wood-plastic composites. The durability of WPCs to freeze-thaw actions is vital because they are currently in exterior use in colder regions like the northern United States and Canada. The long-term response of wood-plastic composites to environmental influences would ideally be evaluated by real time observations of the materials in natural conditions for several years. However, this process would be much more extensive, involved, expensive, and would possess more inherent variation. The control of the accelerated laboratory tests allow for control of conditions to be more representative of typical conditions and the data can be obtained in a more timely manner. Additionally, the laboratory testing allows for comparison between factors that would not be possible under inherently variable exterior conditions. These reasons demonstrate that accelerated laboratory freeze-thaw tests are more practical and will be utilized here.

The results of this study are expected to show that wood-plastic composites are a durable material that is suitable for exterior applications in cold northern climates. The composites should perform as well as or better than current wood products due to the increased fungal and moisture resistance from the plastic component. Mechanical, physical, and aesthetic properties are expected to continue to be dependant upon composite composition and decrease with increasing numbers of freeze-thaw cycles. Properties of concern for losses include the strength, stiffness, and dimensional swelling. The property losses will likely manifest themselves from a loss in adhesion between the wood and plastic that will be observable via losses in density, increased porosity, and microscopic cracks visible with scanning electron microscopy (SEM). This work will hopefully lead to future work that can reduce or cause property losses to plateau over time.

As with other previously investigated agents, there is a potential for both aesthetic and structural failure of the composites exposed to freeze-thaw conditions. Since adding wood fibers already increases the brittleness, there is the concern of further increased brittleness, which often correleates with decreased mechanical properties, after exposure to cold and freeze-thaw conditions (18,19,31-33). Accelerated cyclic freeze-thaw testing will yield valuable information on the effects of cold climate conditions. This can help in assessing the possible service life of WPCs used in outdoor applications due to decreased surface quality and mechanical properties. Freeze-thaw exposure may result in diminished mechanical properties of these materials that are already being used in outdoor applications that require the retention of these properties, such as decking.

This study will enhance the understanding of the durability of WPCs exposed to accelerated laboratory freeze-thaw cycling. This study will encompass two common polymers, polyvinyl chloride (PVC) and high density polyethylene (HDPE). Furthermore, varied wood mesh sizes, wood contents, maleated polyethylene content in HDPE, and two wood species (hardwood maple or softwood pine) will be investigated. This will aid in enhancing wood-plastic composites so that they will have a prolonged service life. The conclusions from this study will result in enhanced outdoor durability for WPC building products.

OBJECTIVES

The main goal of this study was to investigate the retention of mechanical properties of extruded wood-plastic composites exposed to accelerated freeze-thaw cycling meant to simulate outdoor exposure in northern North America. This goal was fulfilled by addressing the following objectives:

i. Determine the mechanical (flexural) properties of various compositions of HDPE and PVC composites before and after exposure to accelerated laboratory freeze-thaw cycling.
ii. Establish relationships between mechanical properties of composite samples that have been exposed to varying numbers of accelerated freeze-thaw cycles.
iii. Examine the causation for mechanical property changes before and after exposure to freeze-thaw cycling as it relates to portions of exposure.
iv. Evaluate changes in dimensional stability, density and porosity before and after exposure to freeze-thaw cycling.
v. Examine the composites before and after exposure to freeze-thaw cycles for cracking and loss of adhesion on a microscopic level using scanning electron microscopy, SEM.

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Chapter 2

BACKGROUND

SOLID WOOD PRODUCTS

Wood is one of the most abundant and readily available resources that persons all over the world have for building materials. However, there are several factors that need to be addressed when considering the use of solid wood. Among the basic concepts to understand how to appropriately utilize wood are the variations in structure between species, effects of atmospheric conditions, the susceptibility to biological organisms, and preservative chemicals.

Types of Wood

Wood is defined as a cellular, ligno-cellulosic material (1), but encompasses many different species, that in actuality are not very similar. Different species, growing conditions, and defects all result in products that have vastly different structures and properties, which make every piece of wood unique. Most commonly, broad delineations are made into hardwoods and softwoods, but there are numerous differences within these categories as well (2). Hardwoods are commonly known as deciduous trees that shed their leaves, whereas softwoods are evergreen trees that have needles, which can be retained for several years.

Wood is an anisotropic material, meaning that it has 3 different properties depending on the orientation of the wood (1-3). The longitudinal, tangential and radial surfaces shown if figure 2.1 all display different components of wood and therefore have different properties (2,3). Differences are prevalent even within wood obtained from the same tree. The annual rings visible on the transverse surface of wood represent changes in wood structure from earlywood to latewood (figure 2.1) and the center portion of the tree known as heartwood is different from the surrounding sapwood (figure 2.2) (1,2). There are also several cell types, particularly in hardwoods that cannot all be distinguished with the naked eye (2). Changes in grain, knots, decay and other defects can also affect the appearance and properties of wood.

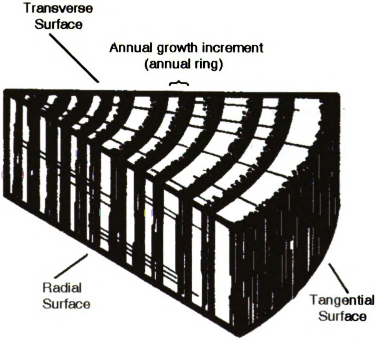


Figure 2.1 The three surfaces of wood, transverse, radial, and tangential. Also an annual growth ring is shown with the lighter earlywood and darker latewood. Image taken from Haygreen & Bowyer (2).

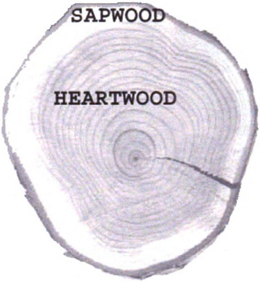


Figure 2.2 The interior wood of a tree is known as the heartwood, and the surrounding lighter colored wood is the sapwood.
Image modified from Society of Wood Science and Technology.
http://www.swst.org/teach/teach1/structure1.ppt#1

The structure of wood is most easily compared to a bunch of straws that are stacked in bundles, end to end (1). This structure allows for conductance of water and nutrients within the tree. Softwoods are mostly composed of fiber tracheids, which stack in this manner, that are strength-giving fibers with the ability to conduct water (1). Figure 2.3 shows the thin walls of softwood fibers and the numerous connections between the fibers, or pits. Hardwoods do not have as many as many pits as the softwoods due to their variety of components (1). Softwoods' mostly homogenous structure, straight-grain and long fibers make it ideal for uses such as construction beams, poles, pilings, decks, siding, exterior moldings and premium papers (2). These uses necessitate that it is graded on strength with appearance as a secondary concern (2).

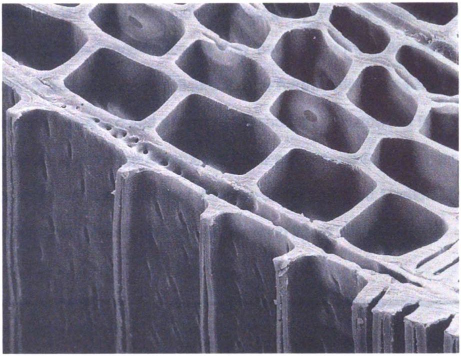
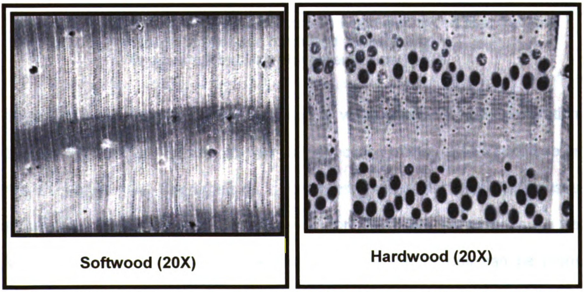


Figure 2.3 Fiber tracheids appear like boxes on the transverse side of softwoods and have small holes, or pits, connecting them. The large boxes to the left of the image are earlywood, whereas the smaller boxes on the right are from the latewood. Image taken from Haygreen and Bowyer (2).



Softwood (20X)

Hardwood (20X)

Figure 2.4 The structure of softwoods (left) is much more simple than that of hardwoods (right), which contain more types of cells. The large holes in the hardwood are the vessel elements for conduction.
Image modified from Society of Wood Science and Technology.
http://www.swst.org/teach/teach1/structure1.ppt#1

Hardwoods are a much more diverse group than softwoods, with varied structures and appearances because they have many more components (1,2). The variety of cells (as seen in figure 2.4) in hardwoods means that fibers are more randomly dispersed and are generally shorter (1). Hardwood fibers are also not used for as much conduction since there are vessels that form conduits for this purpose (1). A comparison of the size of the softwood tracheid, hardwood fiber, and hardwood vessel elements is shown in figure 2.5.

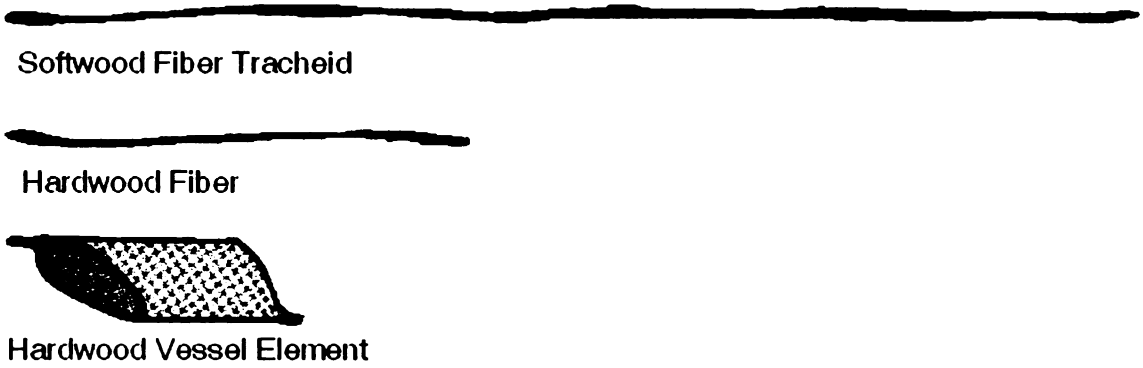


Figure 2.5 The relative difference in sizes between a softwood fiber tracheid, hardwood fiber and hardwood vessel element.
Image modified from Haygreen & Bowyer (2).

Structures within hardwoods that are used to verify species include perforation plates between these vessels, as well as the location of the vessels in diffuse or ring-like patterns (2). The variations in hardwoods make them desirable for uses where their uniqueness can be observed for decorative purposes such as furniture, cabinets, flooring and paneling. However, hardwoods can be more dense than softwoods, which makes them more desirable for uses as railroad ties and less popular species are frequently used for industrial pallets (2). For most applications, though, it is most important for hardwoods to be free from defects and have clear surfaces.

All wood is composed of three primary constituents. Cellulose, hemicellulose, and lignin are all present in wood, although to differing extents depending on species and growing conditions (2). Table 2.1 shows the relative content of these three components for hardwoods and softwoods. Cellulose is about half of the weight of any wood and is comprised of glucose units produced during photosynthesis (2). Cellulose is not a large molecule and can only reach about 10 µm in length and 8 Å in diameter (2). Hemicellulose closely resembles cellulose, but is comprised of different sugars and has a lower molecular weight, in part, due to chain branching (2). Lignin is essentially the glue that holds the wood structure together and is found throughout the wood (2). Less than one percent of the tree is comprised of extractives (2,4). These extractives give each tree a unique odor, color, and appearance (2,4). Extractives consist of non-structural elements within the wood and include elemental compounds or chemicals that help contribute to natural resistances and tolerances of the wood (4,6).

Table 2.1 The relative content of cellulose, hemicellulose, and lignin in hardwoods and softwoods. Table modified from Haygreen and Bowyer (2).

Type	Cellulose	Hemicellulose	Lignin
Hardwood	40 – 44 %	15 – 35 dry wt.%	18 – 25 %
Softwood	40 – 44 %	20 – 32 dry wt.%	25 – 35 %

Properties of Wood

Important properties for consideration with wood include compressive, tensile, and flexural strength and stiffness, impact strength, durability, shear strength and toughness (1). However, wood is anisotropic and will behave differently depending on the direction in which it is loaded for property testing (1-3). Other materials that provide alternatives to wood such as plastic, metal and cement are isotropic so the mechanical properties are typically the same in all three directions (2), which can make them more desirable than solid wood. Since wood is a naturally occurring material there are several other factors that can affect these already differing properties. Among the concerns for mechanical properties in wood are exposure to moisture, temperature, chemicals, and loading, as well as inherent defects (2,3).

Perhaps one of the greatest concerns when using wood is the exposure to moisture since properties vary with the atmospheric and wood moisture contents (1,3). Since wood is a hygroscopic material, it will obtain and release moisture from its surroundings (1). This is a well known phenomenon with wood and often results in the shrinking and swelling of its dimensions (2). Changes in the presence of moisture in wood below about 25% moisture content, also known as the fiber saturation point (FSP), influences the strength and elastic properties of wood (2). The lower the moisture content below FSP, the higher these properties will be since the water is no longer present to obstruct fiber bonding (2). Different species differ in their ability to gain and release moisture because of their differing structures, so some species may be more desirable where moisture changes will be present (3). The necessary mechanical and dimensional properties for wood products in their end use must be related to what moisture it will be exposed to in order to determine what species best fits those needs.

While indirectly related to the ability to hold moisture, temperature also affects wood properties. High temperatures decrease mechanical properties and the presence of a high moisture level makes wood more sensitive to property loss at high temperatures (2). Generally exposure over 100°C will result in some destruction of the wood structure (2). Exposure to extreme conditions like steam can result in permanent irreversible damage to the structure of wood and loss of the majority of its strength (1). In addition to the concerns for property loss from moisture changes, the effects from temperature changes can make the use of wood difficult without proper scrutiny and observation.

Exposure to alkaline and acidic environments is another weakness of wood, although it is more resistant to acidity than steel (2). Chemicals are known to deteriorate the cell walls in wood and result in a loss of strength since the cell walls provide structural support (2). The insertion of fasteners into wood can also result in more localized deterioration from the reaction of metal with its environment (2). Nails, bolts and screws can interact with moisture and wood-bound extractives to degrade the wood and lose their holding power, but coatings are used to inhibit this trend (2). The environment to which wood is exposed to should be carefully monitored to ensure that fasteners are intact and that wood has not degraded, otherwise a material with superior chemical resistance is necessary.

Applying a continual load or stress to wood over extended periods of time can result in a loss of properties or fatigue (2). Time is a foe of most materials because it allows for so many changes to take place. The invasion of microorganisms, drastic temperature changes, changes in moisture content, exposure to chemicals, and exposure to other degrading agents are all likely given enough time (2,3). All or most of these effects will take place during the service life of wood and necessary actions, such as chemical treatment, need to be taken to ensure against these effects.

Natural defects in wood can be a result of animals, insects, decay, or growth history and also can cause mechanical property loss in wood products (2,3). Factors in the history of a tree's growth, like broken branches can cause knots or other defects (2,3). Knots are the most common defect that decreases wood strength (2). Knots and human error in processing of wood can also result in abnormal grain patterns, which further reduce properties (2,3). Living creatures can harm trees in many ways like by inflicting wounds and damaging wood by burrowing or causing pockets of pitch to form to repel insects (3). Decay can also occur within a tree, primarily from the presence of fungi (2,3). Decay is prohibited in structural lumber and may be much worse than anticipated due to its ability to decrease impact strength and toughness (2). Most of these natural defects are preventable, but require appropriate recognition and treatment to ensure that wood is a practical material for building uses.

Deterioration of Wood

Since wood is part of a natural and organic environment, it is susceptible to degradation from many types of organisms, some of which were previously mentioned. The sapwood portion of trees is most commonly used and is susceptible to deterioration from fungi, insects, bacteria, and marine borers when exposed outdoors (2,4-6). Some wood species possess an inherent resistance to these factors from extractives that the tree produces, but these are typically held in the less desirable heartwood (4,6). Additionally, these naturally resistant trees are not readily available in most locations and are generally in short supply (5). Since the susceptible sapwood portion of the tree is used most often, it is imperative that proper chemical preservation be done to prevent against unnecessary wood degradation. Selecting a readily treatable species and selecting proper preservatives can help ensure against untimely failure due to exposure in biologically adverse environments (2,5). There are also concerns of non-biological agents that affect wood, particularly heat and fire (2). Other concerns for wood degradation were previously discussed and include chemical exposure, metal corrosion, as well as surface weathering and UV exposure over time (2).

The most common cause of wood deterioration is fungi because they can lead to molds, stains and structural decay (6). Fortunately, fungi require more than just the food supply from the wood to survive. Fungal growth requires warm, moist, and oxygen rich environments to survive (2,6). Given proper storage, seasoning and handling procedures there is no reason that wood should be attacked by fungi (6). However, this is not always the case and wood products are often left susceptible to fungi. Decay fungi collapse the wood structure and soft-rot fungi penetrate into the surface of the wood to cause losses in strength (2). Decay fungi are divided into further categories that attack either the cellulose and hemicellulose portions of the cell or the lignin that holds the cells together (2). Regardless of which type, decay initially reduces the ability to withstand impact, also known as toughness, and then proceeds to reduce flexural strength properties until there is eventually no strength left in the wood (6).

Wood is also exposed to a wide variety of insects when in outdoor use. Insects can attack standing trees, cut logs, or lumber products and include carpenter ants, termites, beetles, and some species of bees (2,3,6). These insects cause a variety of holes, burrowing galleries, stains and pitch or gum pockets (6). Small creatures in seawater can have similar effects on wood products used in marine applications. Wood used for posts or pilings in marine exposure are susceptible to attack from shipworms and pholads that are similar to mollusks, as well as crustaceans (2,6). These creatures, particularly shipworms, attack untreated wood so rapidly that it will not even last a year in salty or brackish waters (2,6). Since no wood in North America is naturally resistant to these marine borers, chemical treatment is necessary to prevent their degradation (2,6). Due to wood's inherent susceptibility chemical preservation is essential.

Preservation of Wood

Wood preservatives are widely used to prevent against the effects of the above-mentioned deteriorating organisms. The American Wood Preservers Association or AWPA, and the EPA regulate the use of wood preservatives since they are considered pesticides and can be hazardous if improperly utilized (5). The chemicals used for treatment are divided into two categories - oilborne and waterborne preservatives. Oilborne preservatives use an oil to transport the preservative chemicals into the wood and have no interaction with the wood structure itself (3). However, waterborne preservatives do interact with the cell walls in the wood because they are transferred by water (2,3).

Among the most common preservatives used to prevent against fungal and insect attack are pentachlorophenol, creosote and chromated copper arsenate or CCA (2,7). Pentachlorophenol is not usually categorized as either oilborne or waterborne because it can be used with a variety of volatile carriers (2,5). Creosote is the most common oilborne preservative and has a high toxicity, low volatility, easily penetrates and has a long-term record of usage (5). Like creosote, oilborne preservatives are effective at resisting weathering and decay they also emit odors, cannot be painted, have a dark brown-black color, are not clean to handle or touch, and have poor fire performance (5).

There are a variety of common waterborne preservatives, such as CCA, which involve mixtures of copper, chromium and arsenic that are used when cleanliness, low odor emissions and paint-ability are of concern (5). However, waterborne preservatives are water-based and have concerns for leaching,

strength reduction, and need to be dried before being put in end-use (2). These products need to be dried before use in any application because changes in moisture content affect the dimensional stability of wood, as was previously described (2). Other pest specific waterborne preservatives are also becoming popular, such as the use of boron treatments for resistance against subterranean termites (5,8). Inevitably, the type of exposure that the wood product will be used in determines the necessary chemical and degree of retention (2,5).

For example, chemical treatment to resist attack by marine borers is an involved process compared to the treatment of wood used in terrestrial exterior applications. Normally a dual treatment of a waterborne preservative like ACA or CCA, and then treatment with creosote until no more chemical will be absorbed is necessary to ensure proper marine protection (2,5,6). The efficacy of this treatment is still not absolute since climactic conditions and marine borer presence vary greatly around the United States (2,6). These differences mean that treated pilings will have differences in preservative leaching rates and subsequent differences in service lifetime (2,6).

Leaching is a concern when using most chemicals for wood preservatives, due to the inability of wood to retain the chemicals over time. Leaching is encouraged by the presence of rain and moisture in outdoor exposure and many studies have focused on the ability of various chemicals to be retained (9,10). In 1984 the EPA released an assessment of the use of preserved wood products and came to the conclusion that preservative chemicals are effective, although they can adversely affect human health by direct or indirect contact, and that stricter regulations are needed for handling and treating processes to protect people and the environment (2). Preservatives may be effective, but there is no long term solution to maintaining our environmental conditions and using chemically-treated solid wood products.

Additionally, waterborne preservatives, unlike oilborne preservatives, interact with the cell walls of the wood and thereby can affect the mechanical properties (3,5). High temperature and pressures used for treatment, as well as the presence of high levels of chromium can cause reactions between chemicals and the wood's cell walls, which can lead to decreased mechanical properties (2). Mechanical properties are all affected differently, but generally flexural strength, tensile strength perpendicular to the grain, impact strength and energy absorption related properties are the most affected, with losses ranging from 0% to 50% under less desirable conditions (3). The main factors that can contribute to a loss in these mechanical properties are the treatment method, retention, preservative chemistry, drying conditions before and after treatment, size of material, quality or grade of material, species, and the use of incising (3). The use of incising, or puncturing the wood surface to improve treatability and retention, are of utmost concern for these property losses (3).

As well as the chemical's toxicity, the method of application and the degree to which the chemical penetrates and is retained in the wood is essential to the properties and efficacy of the treatment (2,5). There are a variety of ways that chemicals can be applied to ensure proper penetration, which will not be covered here. Obtaining thorough protection of the wood is dependant upon many of the same factors that affect strength retention including the species, penetrability of heartwood, proportion of heartwood/sapwood, and moisture content (5). Wood species vary in their ability to resist penetration by chemicals and the inner heartwood portion of most species is less receptive than the sapwood (2). Consequently, proper species selection can be helpful in maintaining strength properties while adding resistance to biological agents.

Summary

The use of solid wood products depends on a variety of factors, most of which cannot be predicted due to the organic nature of wood. Wood can come from several types of trees from numerous locations and there will be few commonalities between them, although they are all susceptible to several factors in outdoor environments as cut lumber or wood products. Factors like moisture, temperature changes, fungi, and insects are inevitable in outdoor exposure, yet there is no absolute way to protect wood. Chemical preservation methods are commonly used but involve the use of harmful chemicals that can cause property loss and often leach out of the wood after treatment. The use of chemical treatment is not an exact science because the treatability varies between species and even between logs of the same species. If processed properly solid wood can be effectively used in countless applications, however the service life can be cut short from biological organisms. Wood is affordable and readily available compared to alternatives like steel or concrete, but the inherent variability and susceptibility may lead to the need to pursue other alternatives.

WOOD-BASED COMPOSITES

Due to the inability to obtain solid wood in desired dimensions and the production of wood wastes from machining and processing, the development of wood-based composites began. Trees that were originally used in the United States had much greater dimensions than it is possible to obtain now due to rotation lengths and demand (2). Consequently, composite products based on wood, with some of its appearance and mechanical properties were created. Wood-based composites use wood in a variety of shapes and sizes to enhance wood utilization and create products in sizes that were previously not possible. The creation of wood-based composites has resulted in numerous thermoset resins being developed, as well as several dimensions of wood being used.

Wood Adhesives

Numerous adhesives have been developed in an attempt to better bind wood pieces together. These resins vary in the way they function, their origins, solidification method, and prevalence in the marketplace. The majority of resins are organic polymers, which are simple molecules that have been bound together by functional groups (11). Although natural resins have been used, the vast majority of these polymers are now synthetic, mostly due to the enhanced moisture resistance of synthetics (11-13). Synthetic adhesives can also be designed to be stronger, more rigid, and more durable than the wood that they are bonding, whereas natural resins can have inherent variability (11).

New binders and binding systems are always being developed, but none have had a significant effect in penetrating the market (12). The majority of adhesives, 59% in 2001, were synthetic amino resins like urea formaldehyde (UF), melamine formaldehyde (MF), etc. (12). A close second with 32% of the 2001 total was phenol formaldehyde (PF), whereas only 5% of adhesives used were isocyanates with the rest of the resins having only a negligible influence (12). These three resins; UF, PF, and isocyanates, will be discussed in more detail later. Isocyanates, UF, PF, and MF are all examples of thermoset resins, which undergo irreversible chemical changes and cross-link after reaction (11,13). Thermoset resins are known for high strength properties, moisture resistance, chemical resistance, and rigidity under load (11). There is also a smaller group of thermoplastic resins that are used in these composites, but they soften under heat and are less common (11).

All adhesives function by two methods, i.) molecular size remains the same and ii.) molecular size changes through reaction (1). Phenolic resins are the most common of the second type, where the molecules increase in size until they are cured, which offers the greatest interaction with the wood and processing (1). These reactions can take place in a variety of processing environments. The most prevalent types of processing with wood adhesives involve radio-frequency curing, steam injection, and continuous or batch platen pressing (12,14). Once they are adhered by one of these methods, the resins then solidify to form a composite product. Solidification can occur via heat loss, solvent loss, chemical reaction, or a combination thereof (1). The one problem with resin solidification experienced under all these conditions is shrinkage due to crystallization or resin solvent loss (1). This is a common problem because most wood adhesives use water as a carrier because it is cheap, non-toxic, and easily absorbed by wood (11). As the water is evaporated, dimensional changes within the composite can lead to undesirable stresses within the product (1).

Resins are also categorized by their uses. Structural, semi-structural and non-structural applications are all determined by the resins ability to transfer load within the composite and maintain the integrity (11). Adhesives require different properties, so a unique resin is often created to fit into one of these categories depending on the application (11,15). The concern is that non-structural adhesives with the least resistance to service exposure, lowest rigidity and weakest bonds also have the most tolerance of wood variation, assembly, and curing conditions (11). Modifications are done on resins to try to change this.

Adhesives are modified to improve their workability, mechanical properties, shelf life, durability, and cost-effectiveness ratio (11,13). This can involve the addition of extenders, reinforcing fibers, fillers, catalysts, hardeners or other resins (11). Although natural resins have been mostly replaced with synthetic resins, they are often still used as components in these types of resin blends. Natural adhesives that are used for resin modifications include lignin, tannin, caseins, soy, animal blood, and pyrolysis oils (12). Components like lignin and pyrolysis oils can be used as substitutes for up to 50% of PF resins in some cases (12). Animal blood is considered "indispensable" as an additive for industrial and construction plywood made with foamed PF resins (12).

Synthetic chemicals used in wood adhesives are toxic to people if in a high enough concentration and exposed for a long enough time (11). Generally, the cured state of adhesives is considered safe, but this is not always the case. Resins like PF efficiently consume formaldehyde during reaction and have little concern of gas emission (11). However, UF is not as efficient as reacting and can release low concentrations of formaldehyde gas that react with proteins in the body and are suspected to be a carcinogen (11,15).

Urea formaldehyde, UF is typical of the most common group of resins used in North America (12,13). A reaction between urea and formaldehyde can bond up to four formaldehyde molecules to the urea before it is neutralized to produce a final resin content of about 65% resin solids (13). UF is the cheapest of the common resins, but looses its bond strength in the presence of water, is brittle once cured, has an acidic nature that makes bonding difficult with oily or high extractive containing woods, and as previously mentioned can emit formaldehyde gas (1,11,13,15). Because of its affordability and poor water resistance, UF is typically used for interior applications like hardwood plywood, medium density fiberboard (MDF) in furniture or paneling, and particleboard used in furniture or underlayment (1,13,14). As with other resins, UF can be modified. Modification is typically done to enhance its moisture resistance (13).

There are 2 types of phenol formaldehyde, PF, that are commonly used, a resole and a novolac (1,13). These resins are made of the same components, however the resole has less phenol than formaldehyde. The proportions of phenol and formaldehyde are reversed for the novolac (1,13). The resole only needs heat to solidify and has a very limited storage life, conversely since the novolac lacks formaldehyde it has a very long shelf life, but needs formaldehyde added to get hardening (1,13). Due to its superior moisture resistance and strength retention compared to UF, PF is typically used for exterior applications like plywood and oriented strand board (OSB) (13,14). PF is a desirable resin because it is easy to process, low cost, has low formaldehyde emissions, and is resistant to water, weather, and high temperature (15).

One of the most common isocyanates is polymeric methylene diphenyl diisocyanate, PMDI (11,13). PMDI is widely used because of its ability to develop strong and durable bonds even when the wood has a high moisture content, while possessing a lower volatility and toxicity compared to other isocyanates (11-13). The use of PMDI is also encouraged because it is free of formaldehyde and does not need a solvent or additives (13). Diisocyanates like this are potentially hazardous and highly reactive, but are considered safe once they are bonded (11).

There are several drawbacks and hazards with wood adhesives, as there are with wood preservatives. The toxicity and susceptibility concerns (e.g. UF with moisture) are being addressed and new resin formulations are constantly being developed. The variety of resins for wood composites means that there are an equal number of products that can be produced. The following sections on veneer and particle/flake products are a broad overview and do not cover all of the uses of adhesive-bound composites. The main wood composites that will be covered, in order of manufacturing quantity in 1998, are plywood, OSB, particleboard, MDF, hardwood plywood, and laminated veneer lumber (LVL) (12).

Veneer Products

Veneer is produced by rolling a log on a lathe with a special cutter and shaving off thin layers of wood about 1/16th of an inch thick called plies (2,16). The veneer can then be used to make either plywood or LVL among other products, although only plywood and LVL will be covered here. Veneer allows composite materials to have the same appearance as solid wood, but with larger dimensions and fewer imperfections in wood quality and appearance.

To make plywood, these plies are stacked perpendicular to each other so that the grains of the wood is alternating on every other level (2,13,14). These alternating layers allows for good strength properties, improved dimensional stability, and help increase the isotropy (2,13,14). Softwood plywood has experienced competition from OSB and has needed to reduce production costs and improve products to stay competitive (16). A major problem for plywood is with the raw materials used, as with solid wood, the appearance and quality of the available wood is decreasing (13,17). Also, because of the raw material shaped as plies, plywood is confined to the dimensions of roughly 4 by 8 feet (17). The properties of the plywood are rated on grades A through D and depend upon the wood species, material quality, orientation of the plies, type and amount of adhesive, curing conditions, and pressing conditions (2,13,14).

Softwood veneer panels, which are preferred for structural applications compared to hardwood panels, are almost exclusively bound with synthetic PF resins (12). Hardwood plywood is generally manufactured for decorative, non-structural uses and because of its applications is typically bound with UF (12,14). Not all plywood, hardwood or softwood, is comprised entirely of veneer plies. Often times a filler of particleboard is used for the core of the panel and the exterior is faced with veneer plies (2,16). This is often done for a major competitor of hardwood plywood, where MDF is faced with veneer to give it a desirable solid wood appearance (13).

Laminated veneer lumber (LVL) is also made with wood veneer plies, although it is not always a panel like plywood (2,18). In LVL plies are all oriented in the same direction in an effort to simulate solid wood with enhanced properties (2,13,16-18). Since LVL is a manufactured product, the length can range up to 80 feet, which solid wood cannot easily obtain (17,18). As with plywood, LVL uses PF resin, but the veneer plies are generally thicker and range from 1/10th to 1/6th of an inch (2,12,18). LVL does cost more than solid wood, but it has already been dried to uniform moisture content, imperfections from growth like knots are no longer localized, and it can be made in a continuous process to larger dimensions than solid wood (2,17,18). Because of this, production has been growing in North America despite the fact that LVL is mostly used for specialized applications (12). Since many of these applications are load-bearing, the adhesive used must be reliable and evenly cured (18). LVL is still competitive in the marketplace because of the reduced availability and increasing price of solid wood that LVL simulates (18).

Plywood and LVL are not the only products made with veneer, although they are certainly the most common. Other veneer-based products include wood I-joists, parallel strand lumber, laminated strand lumber, and Com-Ply® Panels. Information about these products is available in other publications (2,16-18).

Particle and Flake Products

Wood waste is commonly used for products such as particleboard, but wood can be made into several different shapes and sizes. Ideally these wood pieces will be of uniform size and relatively homogeneous. Factors like wood species and particle type can greatly affect the final product (2). To achieve homogeneity, wood pieces may be processed at the manufacturing plant using various milling equipment to control the particle size and geometry (2,14). Products like particleboard and MDF utilize sawdust, planer shaving and other mill residues that have been screened for compatibility (13,14,16). Flakes are used to make OSB and are created from roundwood that has been processed through a flaking or chipping machine to produce thin wafers of wood about 3 inches long and 0.03 inches thick (2,13,14). The emergence of OSB has been fueled primarily due to the lack of veneer sized logs because OSB can use essentially any grade or size of tree (13,14). Although not specifically a wood waste, the wood used for OSB is generally under-utilized and this is a value-added usage of wood (13).

A close second to the combined production of plywood and LVL is OSB (12). OSB has been a main competitor of veneer panel products and is not far behind veneer panels in production (12,13). The flakes are mechanically oriented to increase properties and typically bound with PF resin, although there is some use of PMDI generally in the inner layers (2,12-14). There are 3 to 5 layers in an OSB panel, which like plywood are placed perpendicular to other layers with the faces being parallel to each other (2,13). The percent resin content used in OSB can vary within and between panels, but typically ranges from 2 to 6% depending on the application, with more resin used for higher durability products (12). The major drawback of OSB is that it lacks dimensional stability and can experience irreversible thickness swelling (2,13). Despite this, OSB has become well used in construction for roofing, walls, and floor sheathing (14). Although commonly used for products made from particles, the use of a continuous press system is only recently becoming popular for OSB production (12,14).

The use of wood residues is more common in particleboard or MDF where smaller wood particles are desired (2,14). Of all the wood particles used in these manufacturing processes, only about 1/10th comes from virgin roundwood that is not a waste (2). UF resins are most commonly used for particleboard and MDF, which combined made up almost as much of the composite market as OSB in 1998 (12). The use of PF is also sometimes used in particleboard for exterior uses (2). Over 90% of particleboard and MDF products have overlays or finish coatings applied to them for uses in furniture (12,14).

Particleboard is a general category that can contain products with different appearances depending upon the particle's size and geometry, the density it is pressed to, and the amount of resin used (2,16). Since particleboard is commonly used for interior furniture, the surface properties are of concern. Consequently, particleboard is made of 3 to 5 layers where the face is different than the core (2,13,14). The core of particleboard is comprised of coarser fibers, while the surface has smaller particles to increase smoothness and strength (2,14). The particles are pre-coated with the adhesive and are then laid out into a mat that is processed in a continuous or platen pressing system (2,14). Although less common, there are also extrusion pressing systems that are used (13,16).

To make MDF, individual fibers or fiber bundles are used with a synthetic resin, in a dry process similar to that used for hardboard (2,13,16). Compared to particleboard, MDF is more difficult to process because pressurized refiners are needed to produce the pulp that is used (2). Sugar cane stalks, called bagasse, have also been successfully used to make MDF (16). Although the pulping to obtain fibers is an added step, otherwise the processes for making MDF and particleboard are quite similar. In the United States over 70% of the MDF is used for furniture and cabinetry (2). Unlike particleboard, MDF is more easily machined, has smoother more paintable surfaces, and does not need edge banding to mask its appearance (2,13). Variations in raw wood materials are also better tolerated in MDF production than particleboard although it cannot be too drastic because of interactions with the UF resin (16).

Summary

The development of wood-based composites bound with thermoset resins has successfully counteracted some of the difficulties with solid wood. Composite products can create large panels and products from small pieces of wood (2). Also, high percentages, over 70%, of the raw materials are in the final product so there is much less waste (2). In fact wastes from solid wood processing are often used in particleboard and MDF manufacturing (2,13,14). Composites may be more expensive than solid wood, but the strength, uniformity, and dimensional possibilities make it a valuable substitute (2). Solid wood has several previously mentioned drawbacks, particularly the decreasing quality of trees. Composite materials are superior because they can offer the same properties, but the quality is controlled by resins and manufacturing, which are easily alterable instead of inherently variable growing conditions (2). The main problems that remain for the development of thermoset bound composites like plywood, OSB, MDF, and particleboard are the toxicity and cost of raw materials. There are continually developing adhesives of several types, but the inertia of the market to incorporate them and continue with the same old adhesives is inconceivable. Although certainly more customizable and functional than solid wood, there are still health concerns that need to be addressed for these resins.

WOOD-PLASTIC COMPOSITES

Wood-plastic composites (WPCs) are an up-and-coming field of products that alleviate the susceptibility of solid wood and the toxicity of wood adhesives and preservatives. There are a variety of mineral and natural fillers/fibers that have been incorporated into composites around the world (13), but the focus here will be on wood. Essentially anything can be combined into wood-plastic composites, so the scope needs to be limited to that pertinent to this work. The variety of polymers, additives, and fillers used in wood-plastic composites means that they can be open to several types of degradation. Given time to assess these hazards and customize formulations, wood-plastic composites have the potential to become durable materials with fewer concerns than current products. As with wood-based composites, there are countless combinations of materials that are categorized as wood-plastic composites. This discussion certainly does not encompass the diversity of products or current research.

Development of Wood-Plastic Composites

WPCs combine the desirable durability of plastics with the cost effectiveness and strength of natural ligno-cellulosic fibers as fillers or reinforcing agents (13,19-21). Similar to the particle composites previously discussed, wood-plastic composites can use virgin, waste, or recycled components (12,14,22). As of 1998, recycling was still growing slowly, but materials like polyethylene terephtalate (PET), high-density polyethylene (HDPE), polypropylene (PP), and low-density polyethylene (LDPE) were available as recycled materials (12). The natural fibers can be from anything ranging from virgin wood, recycled pallets, recycled newspaper, or other virgin ligno-cellulosic fibers described later (12,14). This variety of resources can be used because there is no current standard or restriction on manufacturing WPCs (13).

Although wood-based composite products are typically more isotropic in nature than solid wood, plastic products are isotropic with no variation in any direction (2). Unlike the other wood-based composites, WPCs use thermoplastic resins, which soften when heated and solidify when cooled (14). As long as the melting point of the thermoplastic is less than the degrading point of the natural fibers (about 200°C), the two can successfully be combined (1,12,14,20). Common thermoplastics include HDPE, LDPE, PP, polystyrene (PS), and polyvinyl chloride (PVC) (13,14). During manufacturing these plastics serve to transport the wood or cellulosic filler, but in the final product the fiber filler bears the load to enhance the strength (2).

The combination of the wood and plastic in a composite allows for a new construction material that was not previously available, with tailor-made properties (23). Benefits of wood-plastic composites compared to neat plastics are improved machinability, enhanced thermal stability, and increased stiffness (13,14). Compared to solid wood, wood-plastic composites have several benefits such as moisture resistance, less water uptake, reduced thickness swelling, and insect and fungal resistance (13). These attributes are ascribed to the plastic matrix thoroughly encapsulating and protecting the wood or natural fibers from moisture that they readily absorb (13). However, the temperature sensitivity of the plastic portion is often more of a concern than any possible moisture that the wood may uptake (14). Additionally, these composites possess excellent fastener (nail, screw, etc.) retention and the ability to be sanded, stained, painted and finished for aesthetic purposes, although it is not necessary for proper protection (13).

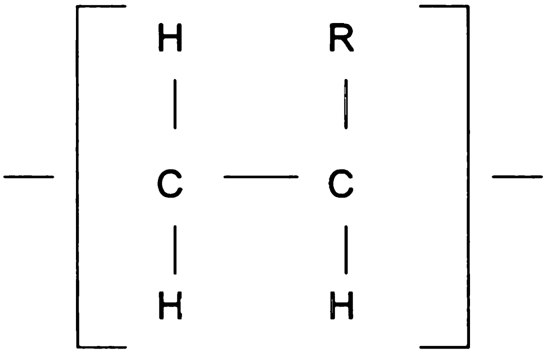
Since wood-plastic composites are a relatively new product, they are not without some problems that need to be solved. Problems that need to be resolved for WPCs include low impact resistance and increased brittleness compared to unfilled thermoplastics and high density (14,24,25). Currently, impact resistance and brittleness concerns are being addressed by using additives, which will be discussed later. The high density and weight of WPCs is being approached by creating microcellular voids and microstructure, using a process called foaming (26). This has also inadvertently acted to increase ductility and impact resistance, but may reduce strength and stiffness (26).

Raw Materials Used in Wood-Plastic Composites

As the name implies, wood-plastic composites are composed primarily of wood and plastic. There are, however, several other additives that are used to enhance processability and properties of the final product. The most common plastics, or polymers, as well as common fillers and additives will be covered here. Fillers that are used in polymer-based composites besides wood will also be briefly mentioned to show the diversity and possibilities in this field.

Polymers

Polymers are isotropic, meaning that they have the same properties no matter what the direction of the applied force (2,27). This should hold true for wood-plastic composites too because they are processed into homogenous materials (14). As of 2001, the majority of wood-plastic composites produced in North America, over 80%, were made from polyolefins (23). Polyolefins are a specific type of thermoplastic, the most prevalent of which are polyethylene and polypropylene (27). PVC has also been used in this work and will be discussed as well. A generic structure for PE, PP, and PVC is shown in figure 2.6.



$$-\left[\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{C}}}\right]-$$

substitute for R	polymer formed
H	PE
CH_3	PP
Cl	PVC

Figure 2.6 The structure of polymers commonly used in WPCs.

High density polyethylene, or HDPE, is produced from polymerizing ethylene into a linear chain by using a special Ziegler-Natta catalyst (27). This catalyst can be regulated to control the density and thereby the amount of crystallinity that is possible (27). The more crystalline the polymer is the higher density it can be and the mechanical properties (i.e. stiffness, strength, etc.) will be higher (27). The ability of HDPE to achieve 65-90% crystallinity means that it is a good moisture barrier, can resist chemicals, and it is also opaque and easily machinable (27). These properties are primarily affected by the molecular weight and distribution thereof. As the molecular weight increases the mechanical properties also increase (27). The only fault with HDPE is that it is susceptible to stress cracking, so the crystallinity needs to be obstructed or reduced by processing conditions or adding comonomers (27).

Polypropylene, PP, is in the same polyolefin family as HDPE, but varies in structure because it has a methyl group (CH_3) attached to the main carbon chain as seen in figure 2.6. The location of the methyl groups in PP can make an atactic, isotactic or syndiotactic product (27). Atactic PP has the methyl group randomly located, isotactic PP has the methyl on alternating carbons, and methyl groups in pairs next to pairs of hydrogens forms the less common syndiotactic PP (27). Catalysts are also used for PP to ensure that the product is isotactic, which allows for increased crystallinity compared to atactic or syndiotactic PP (27). The increased crystallinity in isotactic PP means that the mechanical properties are improved compared to when there is less crystallinity (27). Compared to HDPE, PP is lower density, has a higher melt temperature and higher stiffness in its neat state (27).

PVC is similar to PP, but has a chlorine atom instead of the methyl group as seen in figure 2.6. However, unlike PP it is not possible to achieve full crystallinity because of the large size of the chlorine group (27). The small degree of syndiotacticity that is possible in PVC allows for just the slightest amount of crystallinity (27). Thus PVC is mostly amorphous (not crystalline) and relies upon the strength of the polar chlorine bonds for its mechanical properties (27,28). The main concern with PVC is its thermal stability because it can decompose at temperatures as low as 100°C (27,28). To process PVC requires stabilizers because of this. Plasticizers are also used to manufacture PVC because it acts as a lubricant between molecules to increase flexibility (27,28). Other additives are also commonly added to PVC, which combined all serve to determine the properties of the final product (27,28).

Additives

Since the plastic portion of WPCs is oil-based and the wood portion has an affinity for water, the two do not naturally bond to each other (12,27,29). Because of this difference in polarity and structure, the wood and plastic components can be difficult to adhere to each other (12,27-31). This can result in poor properties of WPCs compared to neat polymers, but the properties can be improved by several additives (27-29). Additives can serve many functions, such as to improve processability, impact strength, cost effectiveness, flame resistance, UV resistance, resistance to oxidation, and mechanical or optical properties and decrease shrinkage (27-34). Several of the additives that are used for neat polymers and also in WPCs include coupling agents, lubricants, impact modifiers, UV stabilizers, and flame retardants (14,28-34).

Coupling agents are the most common additive used to enhance the bonding between the hydrophilic natural fibers and hydrophobic plastic molecules

(12,14,27,30,31). Typically, coupling agents are used with polyolefins and are a variation of the polymer's structure (30,31). For example, HDPE and PP are often modified with a maleic anhydride, which make a molecule that is polar on one end, but non-polar on the other end (30,31,33). This allows for the polar end to bond to the wood and the remaining non-polar end bonds to the polymer and creates a bond between the otherwise incompatible wood and plastic portions (12,30,31,33). The enhanced bonding formed by coupling agents increases the stiffness, strength, and impact strength (34). This improvement is a result of the wood fibers breaking and the plastic deforming instead of a loss of bonding between the fiber and matrix that would be observed without the presence of a coupling agent (34).

Some additives simply function as their names imply. This group includes lubricants, flame retardants, and UV stabilizers. In order to have a desirable appearance, lubricants are needed to decrease sticking and increase the flow or processability (27). There are two main types of lubricants, external and internal, which both aid the processability of the polymer melt and enhance surface appearance, but do so by different mechanisms (14,27). UV stabilizers and also antioxidants ensure that damaging ultraviolet rays do not deteriorate the structure of polymer (27). All polymers are affected differently by UV radiation, but color changes, decreased flexibility, and severed polymer chains are common (27).

Impact modifiers also have an effect similar to what the name implies, however it encompasses a very broad group. The effect of impact modifiers depends on if they act as crosslinked or uncrosslinked modifiers, their compatability with PVC, and the content (28-29). Generally crosslinked modifiers yield better results at lower contents and can show more impact strength improvement (25). Impact modifiers also enhance the bonding by creating a network of elastomers, so they can increase the strength and stiffness (25,27-29). Despite their name, some work has shown that impact modifiers do not actually increase ductility or reduce the density, but they increase the structure, resistance, and strength of WPCs (25,29).

As was previously mentioned, PVC requires several additives to ease processing and enhance its properties that are not used or as common with other polymers. PVC additives include plasticizers, heat stabilizers, and colorants among many others (27-29). Plasticizers function to reduce the rigidity of PVC, which increases the flexibility and processability, while reducing the required processing temperatures (27-29). The increased processability is a result of decreased viscosity from the low molecular weight plasticizer (28,29,32). The vast majority of plasticizers, over 80% are used with PVC because without plasticizers PVC is essentially useless due to its brittle nature and processing difficulties (27). Heat stabilizers are needed to prevent PVC from degrading because it is heat sensitive (27-29). While colorants serve no purpose in the mechanical properties of the composite, they are often used for aesthetic purposes so that painting and other finishing techniques are not necessary (27,32).

Although not truly an additive, occasionally other polymers can be added to a neat polymer to form a blend. For example, PP often has 1.5 to 7% of ethylene monomers, the building blocks for PE (27). This incorporation of similar monomers allows PP to retain the majority of its structure but effectively reduces the crystallinity (27). The reduced crystallinity results in less brittleness, higher clarity, and lower density because the crystallites are not as organized and packed together (27).

Fillers and Fibers

As with additives, fillers can serve to reduce the cost, improve some of the properties of neat polymers, or both (27,32). Fillers fall into 2 groups, inorganic minerals and organic natural fiber fillers (27). Regardless of the type, the fiber fillers carry the structural load in composites, assuming they are properly bound to the polymer matrix (2,32). They are also available in a variety of shapes and sizes with names like whiskers, fibers, particles, and flakes (32). Continuous fibers provide more improvement in mechanical properties, but have a higher cost associated with them than chopped fibers (27,32). The shorter chopped fibers or particles are easier to process than long fibers, which tend to break or agglomerate and not disperse as readily (13,14,29,32). The higher aspect ratio (length to diameter) of long fibers generally provides better reinforcement (13,20,27). However, a compatibilizer, intensive mixing, or special feeding equipment is often needed to help with the dispersion of long fibers (13,20). Another alternative when using long fibers is to have them woven into a mat and then form the final product (32).

Mineral fillers have been the most widely used in the past, although natural fillers are becoming more prevalent because they are lower cost (13). Common mineral fillers include calcium carbonate, glass fibers, clay, talc, silica, carbon fibers, and mica (13,27). There are some problems with mineral fillers compared to natural fillers, although they can provide better reinforcement. Minerals tend to be denser, end products will be heavy, and manufacturing equipment wears down from processing (13).

Wood and natural fillers also have benefits over mineral fillers, such as their low cost, low density, light weight, low abrasiveness, increased flexibility, and that they are made from renewable resources makes them readily available and recyclable (13,14). Natural fibers also have a high specific strength and stiffness, so for a small piece of fiber the strength is still quite high (13). Common natural fibers that are being used for current research are wood, kenaf, jute, flax, hemp, soybean hulls, etc. (13,14,22,35). One problem with natural fibers like these is that the moisture can easily ruin the surface or part quality as excess moisture evaporates during processing (14,29). This necessitates the use of ovens to dry the fillers before processing or using machinery equipped with venting for processing (14,29). The lack of attraction between the wood and fiber, which was previously discussed may also be improved by modifying the fibers with a chemical treatment (29,33). Wood fibers that were previously used as CCA treated lumber have been shown to be effectively incorporated into WPCs with improved flexural strength and stiffness compared to WPCs made with virgin wood flour (36).

Wood flour, particles, or fibers are easily accessible and common fillers for thermoplastic composites (14). As with particleboard the wood can be a result of planer shavings, chips, or sawdust (14). They can also be obtained in a variety of species and sizes (14). Generally softwood species are preferred to hardwoods to make for easier processing and better mechanical properties (29). The addition of wood fillers leads to an improvement in the stiffness of the composite while lowering the abrasiveness on processing equipment compared to mineral fillers (22,37,38). However, the strength may be reduced and the brittleness increased as the wood fiber content increases (24,25,29). There are an infinite number of additives and concentrations that make the properties of WPCs easily customizable to any application, but the sacrifice of trade-offs such as these need to be evaluated.

Degradation of Wood-Plastic Composites

As mentioned in Chapter 1, wood-plastic composites are used in a variety of indoor and outdoor applications. The use of WPCs, particularly in outdoor applications, raises concerns about their durability and property retention. As with solid wood, there are concerns for marine, fungal, insect, and UV damage. Since WPCs are a relatively new field these problems are just being discovered. There are a variety of additives that have been developed to help with some of these problems and more can be developed in the future to prevent against potential problems as they are discovered.

The plastic component of WPCs surrounds the wood, which helps to reduce the moisture problems and subsequent attacks seen in solid wood (13). The reduced moisture presence and resistance of plastic means that there is less likelihood for fungal and insect attack (13). There has been some early work done on fungus and WPCs that have shown the potential for fungal attack (39,40). More recent work on commercially available products has shown that WPCs have a slow moisture uptake, although after continuous submersion they can still achieve a moisture content high enough for fungal colonization (41). Also, when there is incomplete encapsulation of the fibers by the polymer, there is a probability for fungal attack and thereby discoloration is likely (42). The lack of proper encapsulation allows for greater moisture uptake and microscopic cracks which act as entry points for the fungus (42). If the wood is properly encapsulated, WPCs show a greater weight loss [from fungal consumption of wood components] at higher wood contents because there is more food available for the fungi (43).

In order to help prevent against fungal colonization, there has been some use of new additives. Biocides have been added to several different combinations of WPCs and tested against both brown- and white- rot fungi (43-45). Zinc borate is the most commonly used biocide and has shown protection against a brown-rot fungus at levels as low as 1% for 50% wood content in the composites (44). Additionally, there has been evidence to show that there is little concern of biocide leaching at effective loading levels of zinc borate (45). The concern for fungal attack in WPCs was one issue that was discovered early.

Consequently, there has been more time to conduct research and an answer to this problem seems to be near at hand.

There are still concerns for other types of degradation with WPCs. These concerns are primarily related to the wood component that was discussed earlier, although there are some drawbacks of plastics that need to be addressed as well. Along with fungal attack, there is also concern of attack from subterranean termites (46). Marine applications also raise concerns for attack by creatures including marine borers. Plastics like PVC have been used to jacket solid wood pilings and have been shown to effectively reduce attacks by marine borers (6). Likely a solid plastic coating would have a similar effect for WPCs. However, this plastic casing is still susceptible to mechanical damage (6), so it is not the final solution to marine borer resistance because more modification needs to be done on the formulation to ensure mechanical properties are retained.

When in use for exterior applications, as WPCs often are, sunlight and its UV rays are of concern as well as the moisture from precipitation. Most polymers, but particularly polystyrene (PS) are susceptible to degradation from UV light (47). The UV light is absorbed by the polymer and can result in yellowing and increased brittleness (47). This is preventable in polymers with the use of additives, most of which turn the absorbed radiation into heat, so no chemical change is observed (47). Previous research with WPCs has shown that the incorporation of wood into the polymer matrix increases the rate of photodegradation compared to neat polymers (48-50). The effects on WPCs can range from aesthetic to mechanical failures of the product, but it is unknown as to whether or not the incorporation of plastic additives like benzophenone derivatives can help reduce the damage from UV light WPCs like it does in neat polymers (47-50). WPCs made with CCA-treated wood have shown increased photo-protection compared to WPCs with virgin wood flour (37), so perhaps chemical treatment is a possible solution. It has been established that WPCs absorb more UV light than particleboard because of the addition of the plastic (36), so further research is warranted.

Other factors that could affect WPCs that have not been extensively investigated exist as well. Both wood and plastics are susceptible to degradation in the presence of chemicals (2,47). Exposure to chemicals can cause the wood structure to collapse and polymers to show local plasticization and cracking under lower than ordinary loads (2,47). Most polymers used for WPCs (PP, PS, PE, and PVC) are also susceptible to thermal degradation. Additives are common and have been previously discussed to prevent against this, particularly for PVC (27-29,47). Thermal degradation often results in breakage or degradation of the polymer structure (47). In the extreme case of PVC, hydrochloric acid can be released as the polymer chain is broken apart (28,29,47). Further research needs to be done on these and other additive related issues to determine solutions for degradation from these forces.

Processing of Wood-Plastic Composites

Thermoplastic polymers, and therefore WPCs, can be processed in a variety of ways depending upon their final applications. Parts made from the previously described polymers (HDPE, PP, and PVC) which are also used for WPCs are commonly processed by injection molding, extrusion, and compression molding (27,28,32,47). These three techniques are used to manufacture the majority of plastic objects (32). Extrusion is a continuous process, whereas both compression and injection molding are batch processes (47). Extrusion is preferred for long parts; injection molding is good for complex shapes and very high volumes, whereas compression molding works well for large molded shapes (32). There are also other options such as pultrusion, transfer molding, thermoforming or calendering, which will not be discussed here (14,27,32,47). The choice of method relates strongly to the item being made and the viscous properties of the polymer composite melt (47). The desired properties of the final product may also be considered because each method produces differing amounts of fiber orientation, which can result in anisotropic products (32). The same methods of processing that are used for polymers also apply to WPCs, although an initial compounding step is needed to ensure proper dispersion of fibers and additives (14). This compounding step may involve dry-blending, molten-dispersion mixing in a continuous or batch process, or pelletizing (14).

Extrusion

Extrusion is perhaps the most widely used method for plastic processing and creates products formed into profiles, pipes, sheets, or rods (32,47,51). An extruder has three main parts, the hopper, barrel, and die (47). The hopper feeds pelletized, granulated, or ground materials into the heated barrel, although some extruders are equipped to feed already molten mixtures to the barrel (32,47,51). The barrel is equipped with either one or two screws depending upon the processing. A twin-screw extruder is needed when temperature sensitive and viscous melts are being processed (47). Since these are both attributes of WPCs, a twin-screw extruder is preferred and has been used for this work.

The screws are custom made for each extruder and contain feeding, compression and metering sections (32,47). The depth and distance between the channels in the screw are essential to how the material will flow through the extruder (51). The initial feeding section is often cooled to ensure that the polymer does not melt too early and clog the feeding (51). The feeding section moves materials to the compression section, also known as the transition section, which begins melting the polymer (47,51). Normally a series of heaters and coolers are needed to ensure that the temperatures are properly maintained through this region of the barrel (32,51). The metering section begins to taper in diameter and combined with shear forces inside the extruder force the melt out of the extruder and into a shaping die (32,47). The finished shape is then water-cooled as it comes out to retain its dimensions and is then cut to length (32,47,51). Although solid formed components were the focus here, films, sheets,

and coatings can also be created using extruders with different dies (51). An example of an extruder's cross section with these sections is shown in figure 2.7. The drive provides power to the extruder, thermocouples ensure that the temperature is properly regulated, and the adapter provides a connection for the die (27).

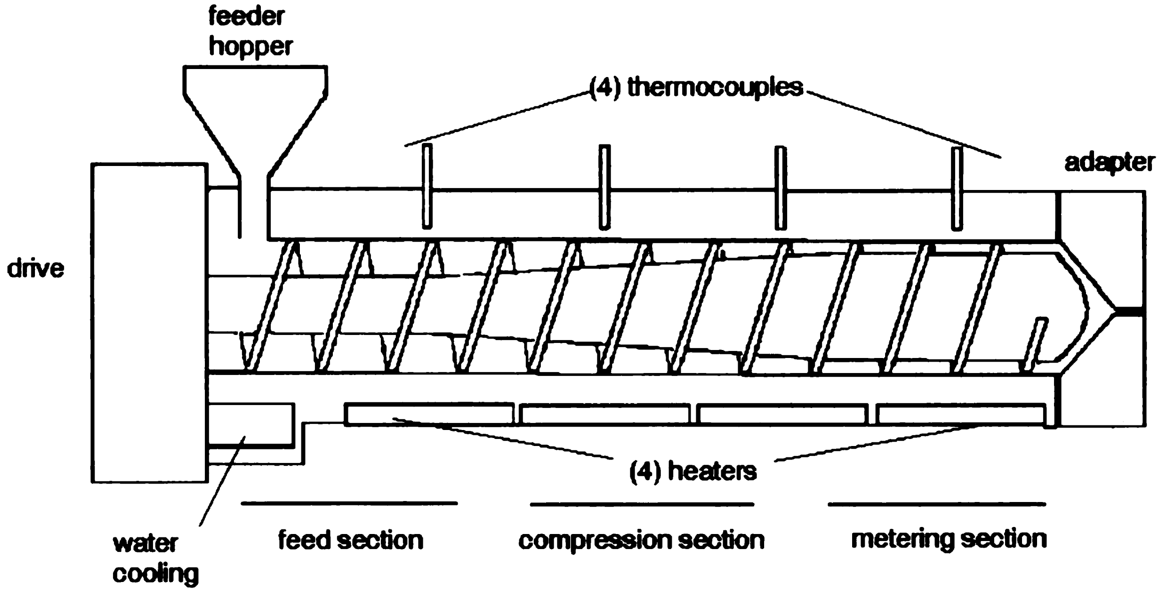


Figure 2.7 A cross section of an extruder showing all of the components including the screw down the middle of the barrel.
Image slightly modified from Hernandez, Selke, and Culter (27).

Extrusion may be difficult to set-up, but often requires little monitoring once in progress, although there are a few concerns for the use of extruders. When using an extruder it is important to ensure that the feed stock has components that are all about the same size, otherwise there will be uneven melting, dispersion and flow (51). The flow of materials through the extruder also needs to be monitored to ensure that there are enough raw materials present to be fed into the later zones and that materials are not stuck in the threads of the screw (51). The screws also need to be checked for damage that can occur from abrasive (mineral) fibers (32). For production of polymer compositions like WPCs, which can emit gases during production, a vent about ¾ of the way down the barrel is needed to allow gases to escape so that the final product will not be damaged or contain voids (51). The final shape of the product mainly depends upon proper venting and the die. However, shrinkage during cooling occurs from the presence of crystallinity and needs to be considered when designing a die and determining cooling treatments (51). This makes amorphous polymers, like PVC, desirable for the production of shaped extrudates (51).

Injection Molding

Injection molding involves the use of a screw similar to that in the extruder to melt the pellets, granules, or ground materials (32,47). As with the extruder, friction and shear are created inside the barrel and create a uniform mixture of the molten polymer with the fibers suspended inside (32). A forward movement of the screw then forces the melt through a gate into a mold under high pressure to form the desired part or parts depending upon the mold used (47). This movement helps to create microstructure within the piece as the fibers are oriented and move in the polymer melt (32). As with extrusion there is also a concern of shrinkage with crystalline polymers. To prevent shrinkage in injection molding, a packing state with high pressure is used to counteract any contracting that may otherwise take place (32). The part is then cooled and ejected (32). Components manufactured by injection molding may be limited to non-load bearing applications because of poor mechanical properties that result if fiber content, length, alignment, and degradation are not properly considered (32).

One of the main problems with injection molding is that only a few polymers are commonly used. This is because of the interactions between the hot polymer melt and the cold mold walls that can lead to "freezing" and impede proper flow (32). Injection molding does have standard built-in vents to allow for the displacement of air from in the cavity and the polymer melt (32), but this is useless if the melt cannot completely fill the mold. The cost of molds can also be quite high and they need to be able to withstand high temperature and pressure while retaining the ability to produce nearly identical molded parts (32,47). Another small problem is that the molds waste material to flow through runners and gates to get to the portion of the mold that forms the desired part (47). This can be alleviated by using hot runners, so the loss of material is significantly decreased. Injection molding does provide short cycle times and the potential for high volume production, as long as these costs and problems can be properly considered (32).

Compression Molding

Compression molding is becoming less common, but is the oldest, cheapest and easiest form of polymer processing (32,47). Although injection molding is preferred for processing thermoplastics, compression molding is often used for processing thermosets or when other forms of processing are too costly (47). Both molded and flat panel parts can be made via compression molding (32,51). The materials used in compression molding may involve a woven mat with long fibers, or a nonwoven mat that has been dry-blended and loosely laid together (14,32). Generally the nonwoven mat is preferred because it allows for a wider use of fibers, fillers, and additives to be incorporated (14). This mat, also called a charge, is placed between the two sides of the mold cavity (32). The mold cavity then closes, but there are two options for what happens next in WPC production depending upon when the heat is applied. The first option involves consolidation, then heating to melt the thermoplastic, and lastly cooling the press to solidify and remove the composite (14). The other choice is to heat the material first in an oven or press, and then transfer the hot material to a cool press where it is consolidated and cooled (14). Generally it is preferred to heat and cool a consolidated mat in one step like the first option (32). Regardless of the method, the concept of heating the WPC so that the thermoplastic flows around the fibers is the same. Enough heat needs to be provided so that this flow happens before the cooling stage is initiated (32). Unlike injection molding, the orientation of fibers from compression molding is negligible and does not affect the final properties of the panel or molded part (32).

Compression molding has been partially phased out due to injection molding because injection molding can produce similar parts with more automation (32). Compression molding does still have the advantage that there are fewer stress points than in injection molding because of the lesser amount of deformation (32). Also, compression molding allows longer fibers to stay intact since they do not have to flow through the gate and higher fiber contents can be used because flow is not as much of a concern (32). Compression molding also yields parts with very low dimensional tolerance requirements and has more repeatability over time even under fast production times (32).

Testing of Wood-Plastic Composites

The phrase 'mechanical properties' is often used when referring to the strength, stiffness, impact strength, etc. of materials. They are also called strength properties or by the name of the individual property of concern. These properties are essentially the same for all materials that are used for the same applications regardless of whether they are wood, plastic, a composite thereof, or a different material like steel, concrete, etc. A thorough discussion of common and less common properties was found for wood, but it can be extended to WPCs since they are used for the same applications and need the same properties.

In the course of this text the phrase mechanical properties was often used to refer to the flexural strength and stiffness. The flexural strength and stiffness are used to reflect the maximum load that a material can retain under a bending procedure (3). The bending involves both compressive forces on the top of the sample and tension forces on the bottom of the sample (2). Figure 2.8 shows a sketch of how flexural testing is conducted with a force, F, applied to the middle of a sample set across a span denoted by the supports. One test can yield both the flexural strength (MOR) and stiffness (MOE), both of which are calculated in the untis of psi or MPa. Since WPCs are most commonly used for decks, their ability to resist loading in this manner is of utmost concern. Consequently, flexural testing was the primary test done throughout this work to determine mechanical property retention.

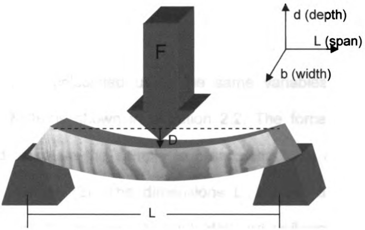


Figure 2.8 A schematic drawing of flexural testing with variables labeled for calculating flexural strength (MOR) and stiffness (MOE).
Image was modified from the Society of Wood Science and Technology.
http://www.swst.org/teach/teach2/properties2.ppt#1

The result of a flexural test is a graph similar to that shown in figure 2.9. The x-axis is the strain or deflection and the y-axis is stress or load. Either way the same graph results. If the graph is stress vs. strain, then the flexural stiffness (MOE) can be calculated as the slope of the line, the stress divided by the strain up to the proportional limit (2). The proportional limit, shown in figure 2.9 is where the linear portion of the stress-strain curve ends and it becomes curvilinear (2).

The MOE can also be calculated by using equation 2.1. The variables are illustrated in figure 2.8, where F represents the force applied, D is the deflection caused by the load at midspan, L is the span, and I is the moment of inertia (2).

$$MOE = \frac{FL^3}{48ID} \qquad I = \frac{bd^3}{12} \qquad \text{(Equation 2.1)}$$

The MOR is calculated using the same variables as the MOE. The calculation for MOR is shown in equation 2.2. The force, F, this time is the maximum load to cause the sample to break, and L, b, and d are the same dimensions as before (2). The dimensions L, b, and d are used in these equations because the samples being tested are uniform rectangles with the same cross sectional sizes (2). If the samples had a different shape, then different equations would be needed to calculate the MOE and MOR (2). Flexural testing also assumes that the sample is supported only by the span supports and that the sample does not slip from these supports during testing (2).

$$MOR = \frac{1.5FL}{bd^2} \qquad \text{(Equation 2.2)}$$

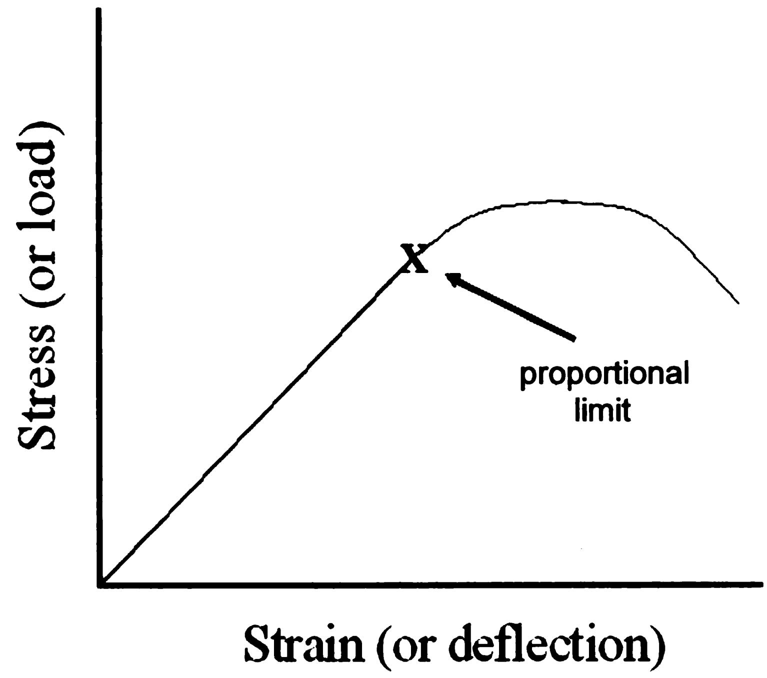


Figure 2.9 The stress-strain curve or load-deflection curve that results from flexural testing of strength and stiffness.
Image was modified from the Society of Wood Science and Technology.
http://www.swst.org/teach/teach2/properties2.ppt#1

The tensile properties are also used by themselves to determine the ability of a material to stretch in a vertical direction in each of the anisotropic directions (3). Compressive forces are often checked by themselves too. Compressive forces are applied in all anisotropic directions to determine the ability of each direction to resist compression (3). Isotropic materials like plastics, and presumably WPCs, are only tested in one direction for these tests.

Other common properties to check are the shear strength, impact strength and hardness (3). Shear strength is the ability to resist slippage within the sample (3). The impact strength is tested by dropping a weight onto a sample to determine how much energy can be absorbed by the material (3). Hardness is the resistance of a material to have an indentation form in it (3). During the test a ball is forced into the sample to measure the penetration (3). Contrary to some people's beliefs, hardness is not related to the title hardwood or softwood (3).

Other less common properties that can also be of concern for more specific applications include torsion, toughness, creep, fatigue, and fracture toughness, among many others (3). Torsion is the resistance to twisting and can be measured as a strength or stress (3). The energy required to cause failure from a sudden centrally-located force is the toughness (3). Creep relates to the ability of a material to hold a load over time and the amount that the sample deforms (3). Fatigue is similar to this, although cyclic loads are applied instead of a constant weight (3). Fracture toughness is a resistance of the material to form flaws which can perpetuate into total failures (3).

ASTM International has established testing methods for all of these properties and more for most common building materials. These standard testing methods relate to mechanical, physical, and aesthetic properties that may degrade over the service life of a product. Because of the variability of products such as wood to change their properties under different climactic conditions (e.g. moisture contents) these standards provide a common means to test and compare materials.

The research presented here followed ASTM standards as closely as possible, since WPCs are relatively new and have very few established standards. The flexural properties were tested using ASTM D6109, which is the standard test method for flexural properties of unreinforced and reinforced plastic lumber. Three-point bending tests were conducted and the strength and stiffness of the WPCs were determined in the manner previously mentioned. Dimensional stability, a physical property has been given little attention, but was tested according to ASTM D6341, as discussed in ASTM D6662. Another physical property, density, was also tested, although no standard test method was found. Freeze-thaw cycling was conducted in accordance with ASTM D6662, the standard specification for polyolefin-based plastic lumber decking boards. Decks have become a popular use of WPCs and this was the most closely related standard, although the sample dimensions needed to be modified.

Summary

Wood-plastic composites offer numerous advantages over solid wood, neat polymers, and wood-based composites bound with thermoset resins. Among the primary benefits is the option of several polymers, fillers, and additives to customize the final product so that it meets the requirements of end-use applications. The wood and polymer components, as well as their composites are still susceptible to various forces. Some of these forces, like fungi, have been researched and new additives are being developed for incorporation into WPCs. This work seeks to investigate another previously uninvestigated effect of freeze-thaw cycling, which may also affect (extruded) WPCs. This evaluation of effects will also be statistically modeled in an effort to determine an optimum formulation for degradation resistance.

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Chapter 3

DURABILITY OF WOOD FLOUR-PLASTIC COMPOSITES EXPOSED TO ACCELERATED FREEZE-THAW CYCLING

PART I. RIGID PVC MATRIX

This chapter is slightly modified from *Journal of Vinyl & Additive Technology* that was published in January 2005. 11 (1) : 1-8. It is co-authored by J.M. Pilarski[1] and L.M. Matuana[1].

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ABSTRACT

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 counter-rotating 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 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 indicate 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 2 freeze-thaw cycles, regardless of both the wood species and content. Conversely, the strength of the composites was not significantly affected by 5 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 become apparent at higher wood flour content (100 phr) after only 2 freeze-thaw cycles for maple flour and 5 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 rigid PVC matrix.

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 it's performance under freeze-thaw conditions compares to 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 flexural properties of 40% wood flour filled polypropylene composites and reported that composites exposed to a water bath for 2000 hours 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 approximately 40% in tensile modulus after saturation with water (21). However, when only 30% wood filler was used with

HDPE matrix, a loss of approximately 25% in flexural modulus was observed after exposure to boiling water for 50 hours (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 5 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.

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 approximately 48 hours before processing to remove moisture. The PVC matrix and other additives used in the manufacture of the composites are listed in table 3.1.

Table 3.1 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)[1]	2
Processing aid (Paraloid K-175)[1]	2
Impact modifier (K-334)[1]	10
40 mesh maple or pine wood flour (American Wood Fibers)	50, 75, 100

[1] Supplied by Rohm & Haas Co.

Compounding and Extrusion of Composites

A 10 liter 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 3.1. Once mixed, 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 any 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 5 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: (i) a water soak until equilibrium moisture content (EMC), (ii) exposure to freezing for 24 hours, and (iii) thawing for 24 hours. The water submersion part of the cycle was conducted in ambient room temperature water (approximately 21°C) in a workshop environment. Each sample was submerged for 24 hour 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 5 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 (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 8 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 hours 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 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 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 5 freeze-thaw cycles of each wood content addition level (50, 75 and 100 phr). All statistical analyses were performed using Design Expert software (Version 6) from Stat-Ease, Inc. Minnesota.

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.

Ten replicates were also used for the modified freeze-thaw cycles, water only (W) and freeze-thaw only (FT), which were compared to the 5 full freeze-thaw cycles with all of the components (water-freeze-thaw). Samples exposed to both 5 W and 5 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 hours, 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 minutes each. A JEOL JSM-6400 SEM was used with accompanying analySIS software for image acquisition. The acquired images had a resolution of 2048 x 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 3.2).

Table 3.2 Density of rigid PVC/wood-flour composites before and after exposure to 5 full freeze-thaw cycles.

Samples	Density (g/cm^3)					
	50 phr		75 phr		100 phr	
	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

Table 3.3 summarizes the changes in dimensional stability of rigid PVC/wood-flour composites after exposure to 5 complete freeze-thaw cycles. The overall dimensional stability was relatively unaffected by the freeze-thaw cycling, regardless of wood species. Even after 5 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 3.3). 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.

Table 3.3 Changes in dimensional stability of rigid PVC/wood-flour composites after 5 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

The percent loss in MOR and MOE of rigid PVC/wood-flour composites filled with both maple and pine species exposed to 5 full freeze-thaw cycles were compared to the unexposed control and the results for the various wood flour addition levels are summarized in table 3.4. Rigid PVC/wood-flour composites with lower wood flour contents (50 and 75 phr) of either wood species retained their strength after exposure to 5 freeze-thaw cycles. The loss in the MOR of the composites exposed to 5 freeze-thaw cycles was statistically significant only for 100 phr of wood flour content for both wood species (table 3.4). This trend was expected because the more wood present in the sample, the greater the uptake of moisture and, therefore, a more dramatic decrease in mechanical properties (8,20,26,27). Unlike the flexural strength, 5 freeze-thaw cycles caused a significant loss in the MOE for all composites, regardless of wood species and content (table 3.4). The stiffness of rigid PVC/wood-flour composites with 100 phr maple and pine decreased by 34% and 30%, respectively, after exposure to 5 full freeze-thaw cycles. Although a statistical comparison between the maple and pine was not performed, the results listed in table 3.4 indicate that the composites with maple wood flour were more detrimentally affected by 5 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 for 24 hours and thawing at 23°C and 50% RH for another 24 hours. 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 5 freeze-thaw cycles compared to the control. These rough edges are likely a result of moisture changes and fiber-matrix debonding (25).

Table 3.4 Flexural properties of rigid PVC/wood-flour composites before and after 5 cycles of full freeze-thaw (WFT) exposure.

Properties	Composites with maple flour			Composites with pine flour		
	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 (%)[1] after WFT exposure	4.22^{NS}	5.91^{NS}	15.19^S	2.22^{NS}	8.49^{NS}	12.53^S
Loss in MOE (%)[1] after WFT exposure	16.8^S	22.13^S	33.93^S	9.96^S	18.11^S	29.79^S

[1] 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.

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 tables 3.5 and 3.6 for maple and pine, respectively. 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 2 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 2 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 5 full freeze-thaw cycles and all cycles thereafter. Unlike for the strength, the loss in flexural stiffness of pine flour filled rigid PVC was significant after only 2 full freeze-thaw cycles and leveled-off after about 8 freeze-thaw cycles. Consequently, it is assumed that composite with pine flour are not likely to loose much more than 20% of their stiffness. This significant loss in flexural properties of rigid PVC/wood-flour composites may be a cause for concern with these materials being used in decking and other construction/semi-structural applications.

Table 3.5 Effect of the number of freeze-thaw cycles on the flexural properties of maple filled rigid PVC/wood-flour composites.

(a) Properties	Composites with maple flour[1]				
	Number of Freeze-Thaw Cycles				
	0	2	5	8	12
MOR (MPa)	33.81	31.49^{S}	29.76^{S}	29.73^{S}	28.66^{S}
MOE (GPa)	2.71	2.22^{S}	2.05^{S}	1.95^{S}	1.90^{S}

[1] 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.

Table 3.6 Effect of the number of freeze-thaw cycles on the flexural properties of pine filled rigid PVC/wood-flour composites.

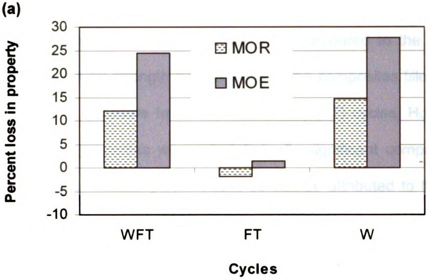
(b) Properties	Composites with pine flour[1]				
	Number of Freeze-Thaw Cycles				
	0	2	5	8	12
MOR (MPa)	38.93	37.57^{NS}	36.71^{S}	35.98^{S}	35.39^{S}
MOE (GPa)	3.37	2.94^{S}	2.74^{S}	2.68^{S}	2.71^{S}

[1] 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.

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 3.1 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 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 5 W cycles) had a significant impact upon the flexural properties of the composites compared to the unexposed control. Flexural properties of the composites exposed to 5 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.



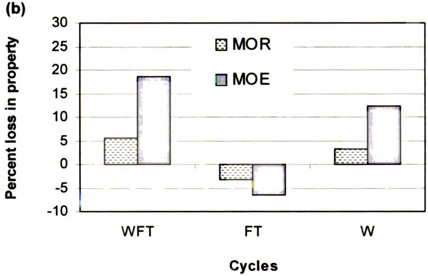


Figure 3.1 The effect of each freeze-thaw cycle portion on the loss of flexural properties of rigid PVC filled with 100 phr wood flour: (a) maple and (b) pine.

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).
FT cycle includes freezing and thawing only (without water soak).
The cycle length for WFT, W, and FT cycles was kept constant at 5 cycles.

Rigid PVC filled with 100 phr of pine flour showed a slightly different trend than that observed with maple flour (figure 3.1). Compared to the unexposed control, both the flexural strength and stiffness of the composites filled with pine flour increased after exposure to 5 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 5 water only (W) cycles was statistically the same as that of 5 full freeze-thaw (WFT) cycles. For the loss in MOR, however, 5 water only cycles produced significantly different results compared to 5 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 approximately 3.5% in flexural strength was observed in this study with exposure to 5 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 approximately 24.5% in flexural strength was observed after 5 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 (figure 3.2) 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 (figure 3.2a) 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 the 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 5 full freeze-thaw cycles with water, freezing and thawing (figure 3.2b). There are also intact fibers that are indicative of holes in the other half of the broken sample where the fibers used to be bound. These holes and intact fibers are evidence of loss in bonding between the fibers and the matrix for the composites exposed to 5 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 5 water only (W) cycles (figure 3.2c) bears a striking resemblance to that of 5 full freeze-thaw

(WFT) cycles (figure 3.2b). As seen with 5 full freeze-thaw cycles (figure 3.2b), 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.

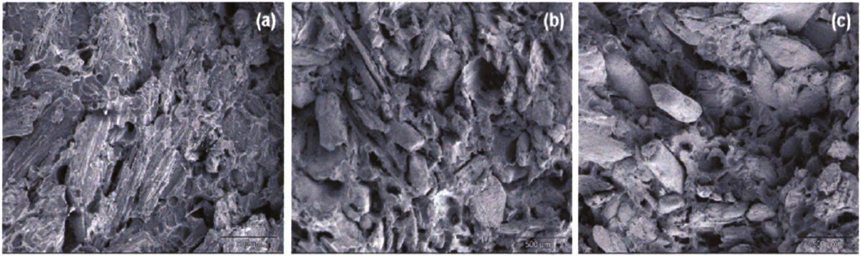


Figure 3.2 SEM micrographs of rigid PVC filled with 100 phr maple wood flour: (a) unexposed control, (b) sample exposed to five full freeze-thaw cycles (water, freezing, and thawing), and (c) sample exposed to five water-only cycles (W cycles without freezing).

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 5 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 2 freeze-thaw cycles, regardless of wood species. However, maple flour filled rigid PVC composites showed a significant loss in flexural strength after 2 full freeze-thaw cycles, whereas it took 5 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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Chapter 4

DURABILITY OF WOOD FLOUR-PLASTIC COMPOSITES EXPOSED TO ACCELERATED FREEZE-THAW CYCLING

PART II. HIGH DENSITY POLYETHYLENE MATRIX

This chapter is slightly modified from *Journal of Applied Polymer Science*. In submission as of February 2005. It is co-authored by J.M. Pilarski[1] and L.M. Matuana[1].

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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.

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 lose 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

Due to 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 (MFI) of 0.49 g/10min and density of 0.9 g/cm^3. The 0.425mm (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 approximately 48 hours before processing to remove moisture. The TPW104 lubricant from Struktol® Company (Stow, OH) was used to reduce friction between components and equipment, which eased processing. This lubricant is a blend of an aliphatic carboxylic acid salts and mono and diamides.

Compounding and Extrusion of Composites

A 10 liter 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 a 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, 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 hours, and (iii) thawing for 24 hours. 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 (approximately 21°C). Samples were weighed every 24 hours until the weight gain was less than 1%, which implied that the sample had reached its EMC. A General Electric 0.38 cubic meter (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 (RH).

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 Corporation 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, 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 samples were oven dried at 105°C for 24 hours, 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 minutes 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 4.1. 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 to their unexposed counterparts (control samples). The greater flexural property loss in maple flour filled HDPE composites compared to 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 4.1). However, the composites with pine flour were higher density and therefore less porous than those with maple flour. This made pine samples less sensitive to the damage caused by freeze-thaw exposure. Higher density WPCs absorb less moisture (17), which is the primary cause of mechanical property loss. As expected, composites with pine wood flour reached the equilibrium moisture content faster and subsequently gained less moisture per cycle (3.1 wt.% vs. 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.

Table 4.1 Changes in the physical and mechanical properties in HDPE composites before and after exposure to freeze-thaw cycling.

Flexural and Physical Properties	**Composites with maple flour[1]**		**Composites with pine flour[1]**	
	0 (control)	15 cycles	0 (control)	15 cycles
MOR (MPa)	20.73^{A} ± 2.26	16.31^{B} ± 1.40	24.68^{C} ± 1.04	23.47^{D} ± 0.51
MOE (GPa)	1.63^{A} ± 0.33	0.83^{B} ± 0.11	2.21^{C} ± 1.04	1.38^{D} ± 0.07
Density (g/cm^3)	0.89^{A} ± 0.03	0.90^{A} ± 0.02	0.99^{B} ± 0.003	1.01^{B} ± 0.02

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

Porosimetry

Porosimetry was conducted for quantitative evaluation of the porosity in the samples before and after 15 freeze-thaw exposures. Figure 4.1 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 to 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.

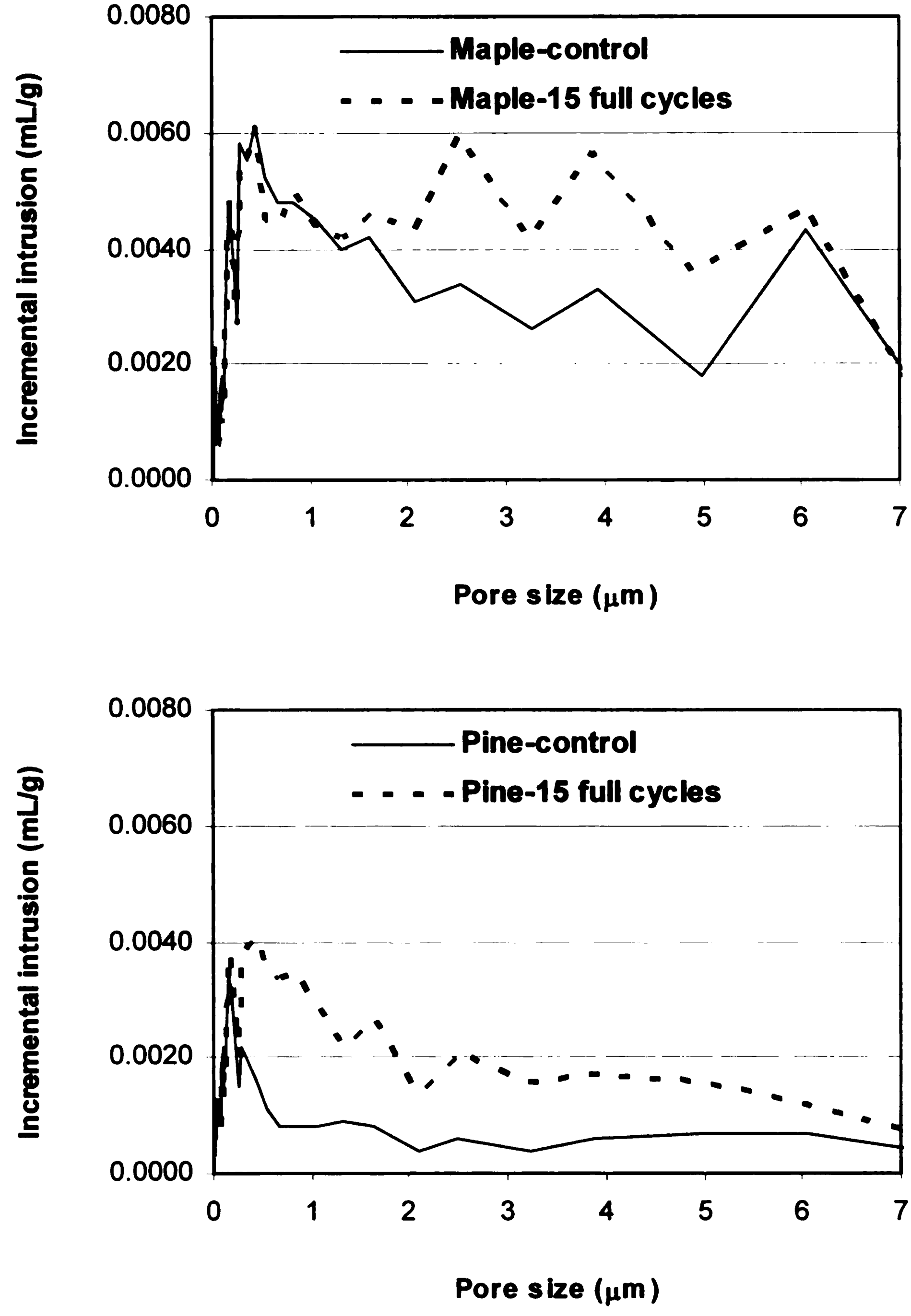

Figure 4.1 The effect of freeze-thaw cycling on porosity: (a) maple-HDPE composites and (b) pine-HDPE composites.

Scanning Electron Micrographs

Scanning Electron Microscopy (SEM) was used to evaluate the interfacial adhesion between the matrix and fibers in order to determine to 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 4.2 support the finding of our porosity investigation (Figure 4.1). The unexposed sample showed a considerable amount of fiber and matrix breakage with very little intact material on the surface (Figure 4.2a) 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 4.2b 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 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).

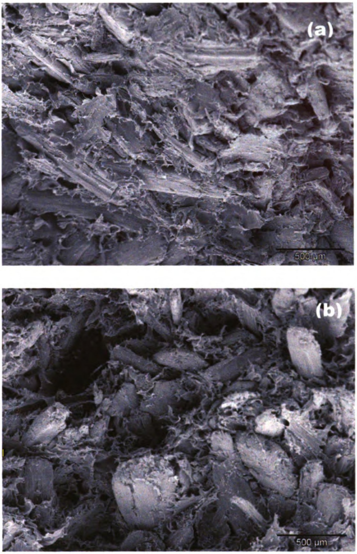

Figure 4.2 SEM micrographs of HDPE filled with maple wood flour: (a) unexposed control and (b) sample exposed to 15 freeze-thaw cycles (WFT including water, freezing and thawing).

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 to 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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Chapter 5

SUMMARY OF FINDINGS

The use of accelerated laboratory testing has shown that extruded wood-plastic composites are all susceptible to freeze-thaw actions, although to varying degrees. Composite compositions were varied with different wood contents, wood species, plastic types, and additives. Regardless of the formulation, significant property loss was observed for all composite formulations. Some formulations took slightly longer to reach this level of property loss, but property loss is inevitable for all WPCs studied. Significant effects were seen after as few as 2 freeze-thaw cycles for some composites. Generally, the stiffness was affected to a greater extent than the strength. However, there has not been any conclusive link as to what has caused the MOE to be affected more than the MOR.

Work with both PVC and HDPE composites have shown that the density of the composites remain stable throughout the freeze-thaw exposure. The dimensional stability is also relatively well intact as was shown for PVC. There were some dimensional increases, likely from the exposure to water, but these were relatively low compared to other materials, such as solid wood or other wood-based composites. The water portion has also been attributed as the main cause of flexural property loss. This was only tested for PVC composites with maple and pine wood flour, but likely extends to HDPE composites because the composites have behaved similarly in other ways.

Scanning electron microscopy (SEM) has shown that the exposure to freeze-thaw cycling increases microscopic cracking. PVC composites filled with 100 phr (~46 wt.%) maple wood flour and HDPE composites with 50% maple wood flour were examined since they displayed greater flexural property losses compared the pine filled composites. The full cycle exposure and water-only exposure appeared the same in SEM images for both polymers, which further confirms that the water portion is attributable for the majority of flexural property losses. The control samples showed thorough adhesion between the wood and polymer, however, after exposure it appears that the water had penetrated the samples and caused a loss of bonding between the wood and polymer.

Porosity testing on HDPE composites further confirmed that there was a loss of bonding between the wood flour and polymer matrix in freeze-thaw exposed composites. Porosity testing on both maple and pine filled composites exhibited more and larger pores forming after freeze-thaw exposure. This increased porosity is likely a result of decreased bonding, which in turn decreases the flexural properties. The flexural properties decrease from increased porosity because the polymer matrix can no longer transfer the applied load to the wood component, which provides the structural strength.

Generally, the maple filled composite were more susceptible to freeze-thaw cycling than the pine filled composites for both HDPE and PVC composites. This could be a result of the wood fibers behaving differently during processing. Chemical variations between the wood species could result in different abilities to form bonds with the polymers. The 50% maple-HDPE composites and the

100 phr maple-PVC composites both had lower densities than their pine counterparts. Lower density materials are well known to have lower mechanical (flexural) properties, so this could be a reason for their poorer performance. The lower density also likely leaves more points of entry from moisture to be absorbed into the WPC.

The interaction between the different wood flour species and polymer matrices are not currently understood. HDPE composite with 50% maple wood flour lost 21% of their strength and 49% of their stiffness after 15 freeze-thaw cycles. PVC composites with 100phr of maple wood flour lost 15% of their strength and 30% of their stiffness after exposure to 12 full freeze-thaw cycles. A plateau trend was observed for PVC where the majority of the property loss was observed after 5 freeze-thaw cycles, so these values are likely representative of most of the property loss that will occur in PVC composites.

Future Work

The effect of exposure to freeze-thaw cycling had not been previously evaluated for WPCs before this study. The results have clearly shown that WPCs are susceptible to freeze-thaw cycling and are likely susceptible to other environments as well. Consequently, exposures to all types of environments need to be assessed for wood-plastic composites.

Maple and pine wood fibers exhibited different physical and mechanical properties when used in the exact same formulation. Consequently, an analysis of how wood species affects bonding within the composite would be beneficial.

Perhaps there is a chemical difference between species that could enhance bonding between the wood and plastic. Chemical modification has been proven to be effective at enhancing bonding, but maybe a wood species could be found that would improve the properties without further modification.

WPCs are also currently made with varying wood contents. This work had a limited range of wood contents because of the need to gain a basic understanding of freeze-thaw effects. The testing of freeze-thaw durability for HDPE composites with wood contents other than 50% and PVC composites with more than 100 phr (~46 wt.%) wood contents could be beneficial. The lower wood contents for PVC have been shown to have improved freeze-thaw resistance and might be a solution to the detrimental effects found in HDPE composites. Additionally, the PVC composites have shown improved freeze-thaw resistance compared to HDPE composites, but this may be different at higher wood contents and if additives were used in the HDPE composites. Coupling agents are often used with HDPE, and future should include this additive.

Further optimization of WPC formulations is definitely needed to decisively prove what can enhance freeze-thaw resistance. There are a variety of other polymers, wood species, wood sizes, and countless additives that can be incorporated into WPCs. Perhaps there is some phenomenon that occurs during the processing of some of these other components that could enhance the freeze-thaw resistance. This study only provided introductory information that WPCs are susceptible to freeze-thaw effects and there is a lot of work yet to be done on determining a formulation that is resistant to these freeze-thaw actions.

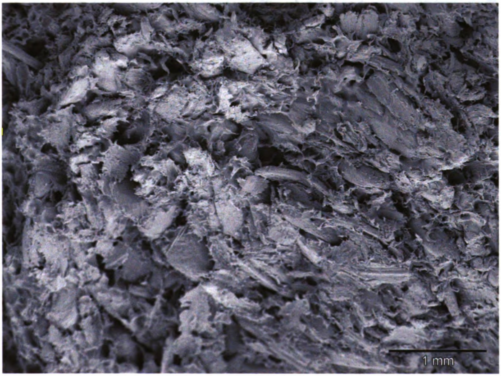
APPENDIX

This appendix contains additional scanning electron microscopy (SEM) images that were taken of 100 phr (~46%) PVC and 50% HDPE composites filled with both maple and pine wood flour. SEM images were displayed in the text for maple filled composites because they showed a greater loss in flexural strength and stiffness than pine filled composites. The greater flexural property loss meant that the maple composites' SEM images more clearly displayed the effects of freeze-thaw cycling. These images include controls, full (water-freeze-thaw) cycle exposures, water-only exposures (with no freezing), and freeze-thaw only exposures (with no water submersion). These are abbreviated as control, FT only, W only, and WFT. The SEM images will be grouped by composite and exposure type and in order of increasing magnifications (25x and 50x).

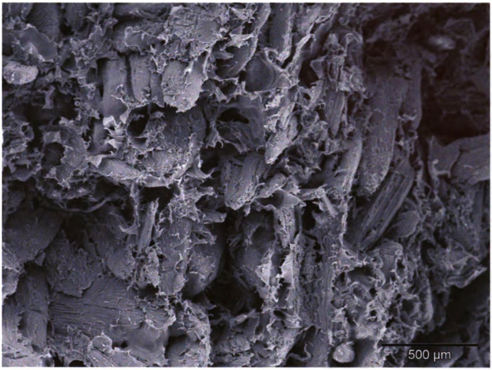
The HDPE composites' SEM images are shown first. These images include the effects of freeze-thaw cycle portions, which were previously only investigated for PVC composites. There are also additional control and 15 WFT images, as well as SEM images of pine that were not used in the journal article.

Next are the PVC images. The first two sets of SEM images are for PVC composites made as part of the study to examine the effects of wood content. These images were taken to show similarities between the two different groups of PVC samples that were made for the work in chapter 3. The last set of images show the effects of the freeze-thaw cycling and freeze-thaw cycle portions after 5 exposures on PVC-wood flour composites, for both maple and pine composites.

Control maple-HDPE composites at 25x resolution.

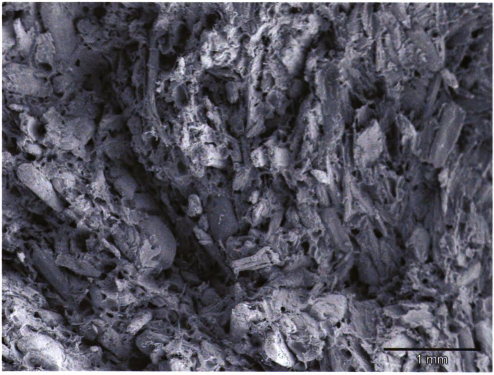


Control maple-HDPE composite at 50x resolution.

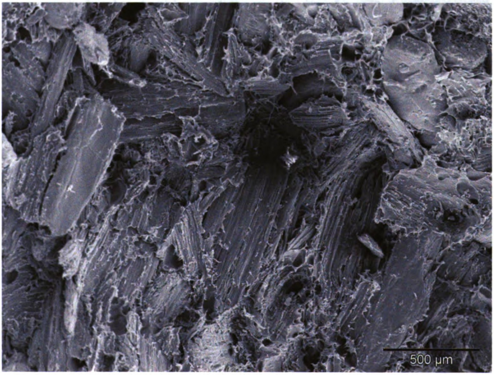


15 FT only maple-HDPE composite at 25x.

15 FT only maple-HDPE composite at 25x resolution (cont'd).

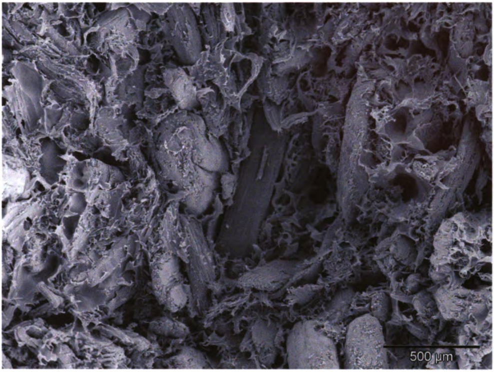


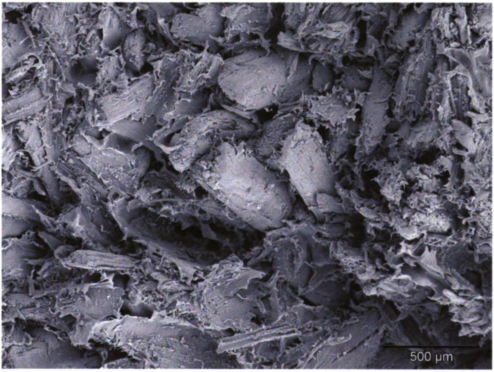
15 FT only maple-HDPE composite at 50x resolution shared few similarities.



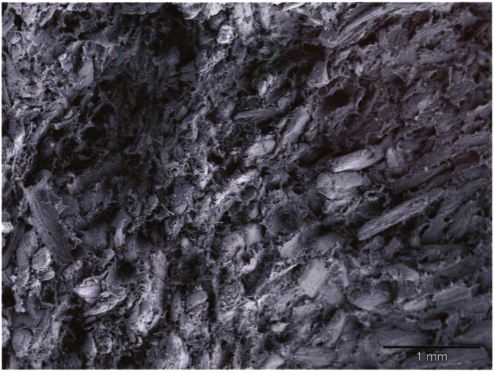
15 W only maple-HDPE composites at 25x resolution.

15 W only maple-HDPE composites at 50x resolution.

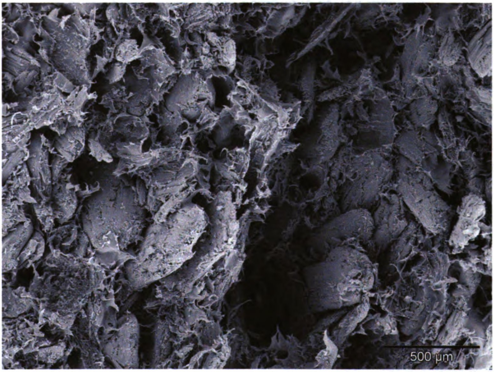




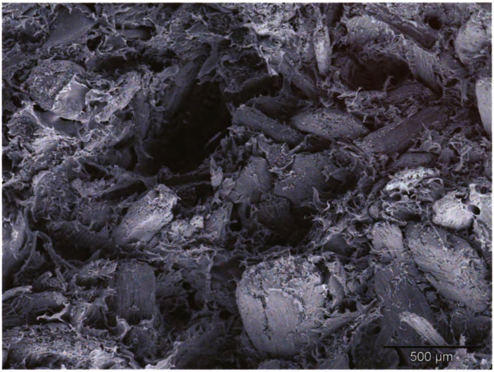
15 WFT exposures at 25x for a maple-HDPE composite.



15 WFT exposures at 50x for maple-HDPE composites.

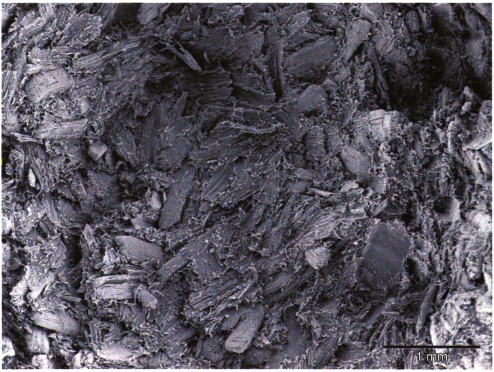


15 WFT resolutions at 50x for maple-HDPE composites (cont'd).

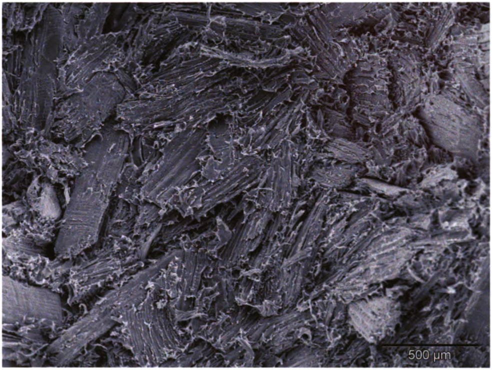


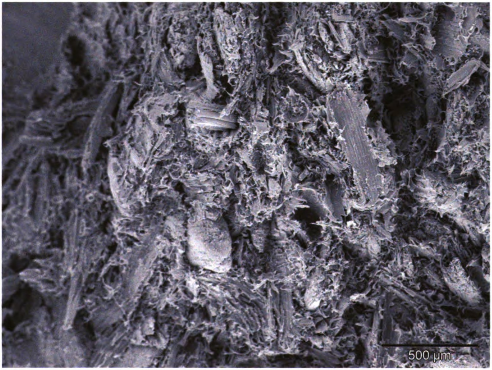
HDPE-pine composites were similar to their maple counterparts.

Control for an HDPE-pine composite at 25x resolution.



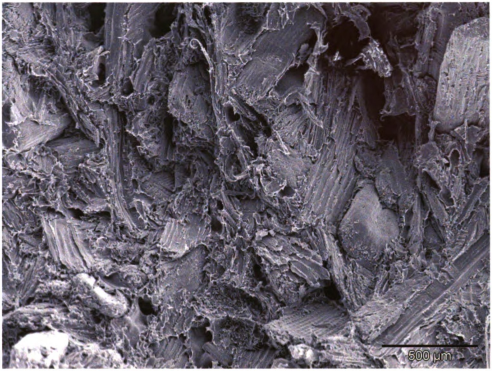
Control for HDPE-pine composites at 50x resolution.

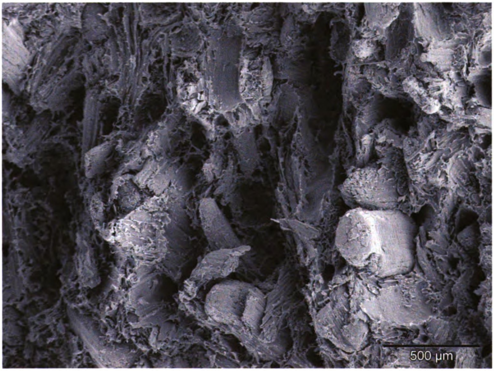




HDPE-pine composites exposed to 15 WFT cycles at 25x.

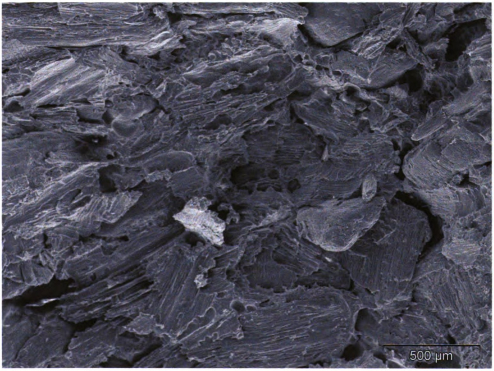
15 WFT exposed HDPE-pine composite at 50x. Fibers left their imprint, but were no longer bonded to the polymer matrix.



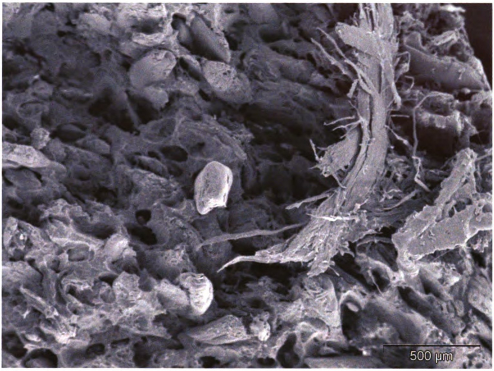


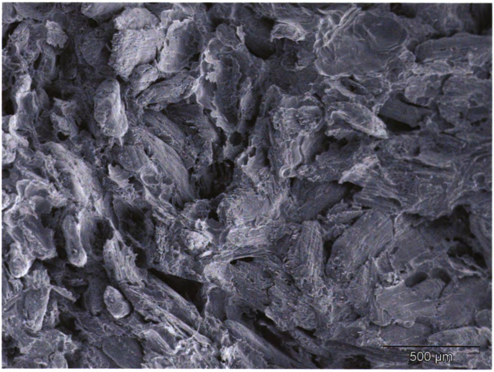
Control 100 phr maple PVC composite from varied wood content study at 25x.

Control 100 phr maple PVC composite from varied wood content study at 50x.

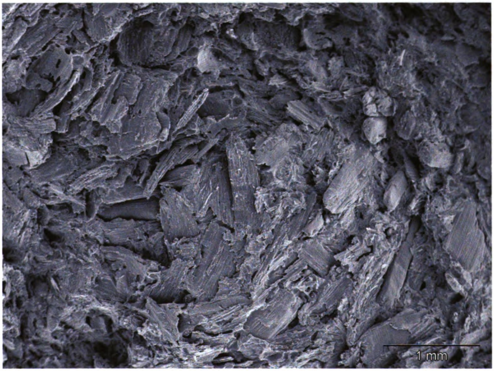


Control 100 phr maple PVC composite from varied wood content study at 50x (cont'd). The strand on the right of the top image shows a torn apart fiber.

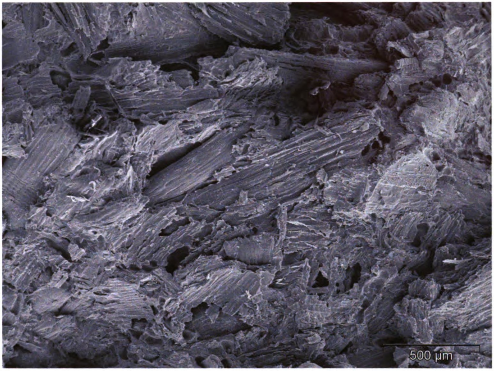




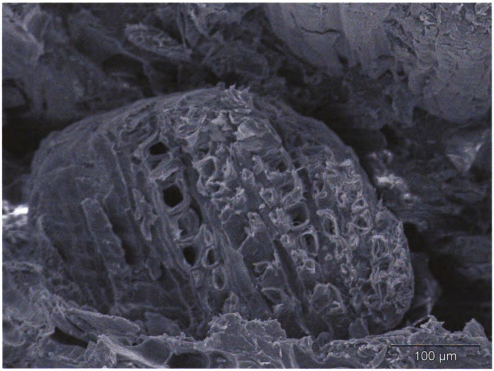
Control 100 phr pine PVC composite from the varied wood content study at 25x.



Control 100 phr pine PVC composite from the varied wood content study at 50x.

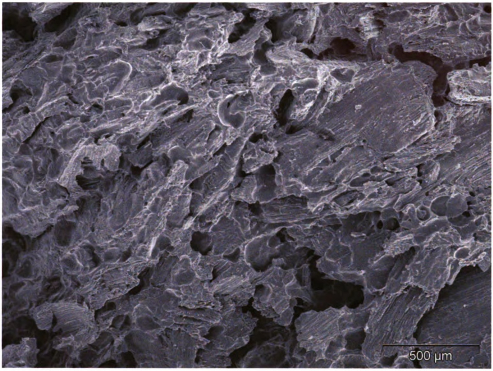


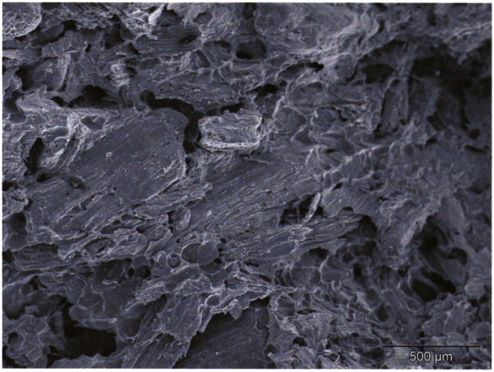
A 230x magnification image of the wood in a control 100 phr pine-PVC composite.



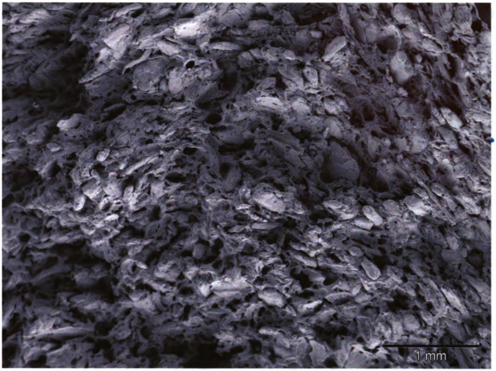
The rest of the SEM images are from the cycling effect study.

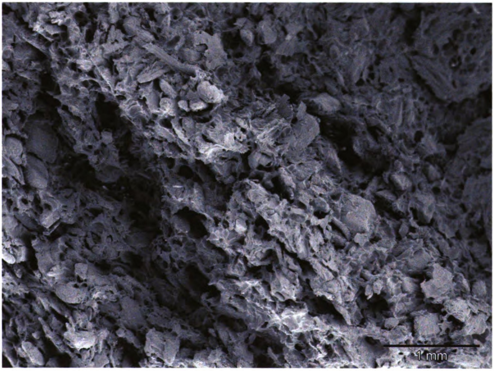
Control 100 phr maple-PVC composites at 50x.





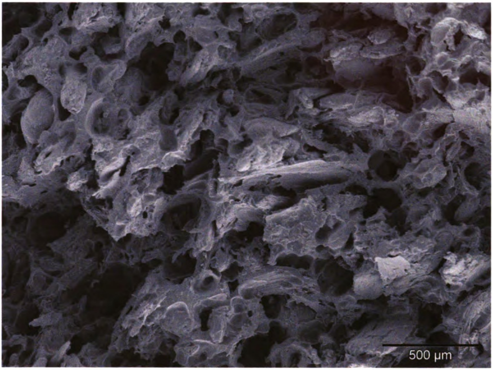
100 phr maple-PVC composites exposed to 5 FT only cycles at 25x resolution.

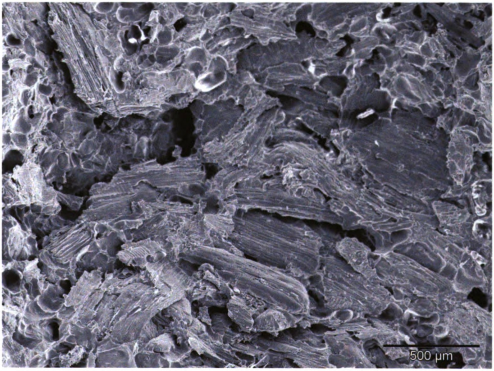




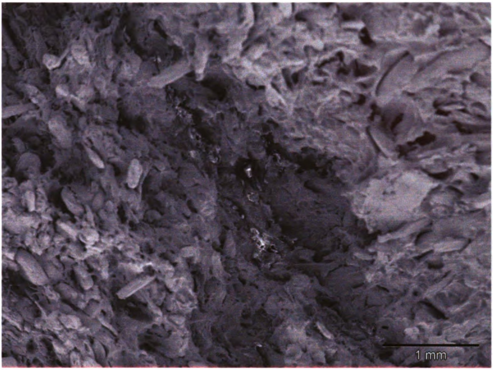
50x resolution images of 100 phr maple-PVC composites after 5 FT only cycles.

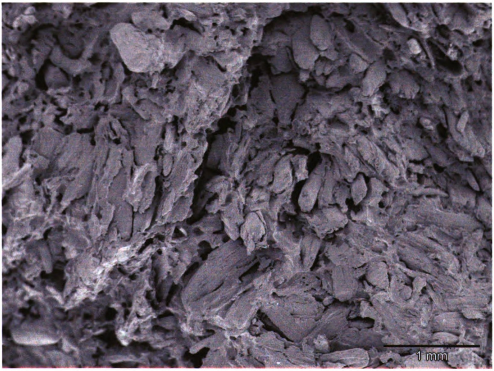
As with their HDPE counterparts there were few similarities in these images.



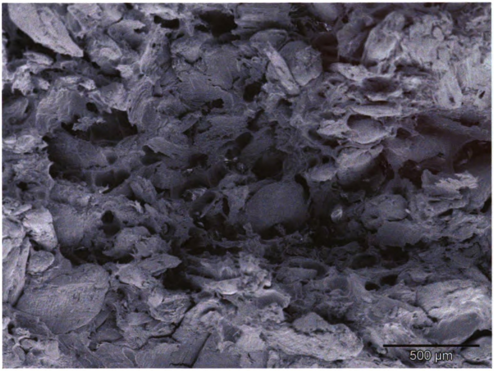


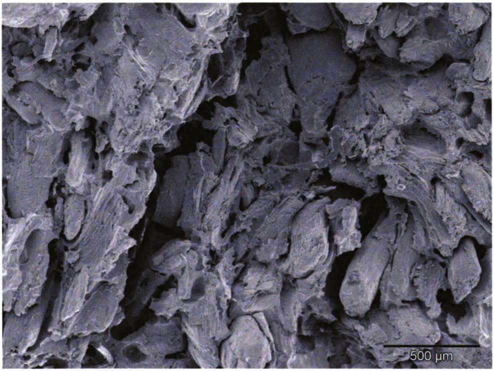
5 W only cycles of 100 phr maple-PVC composites at 25x.



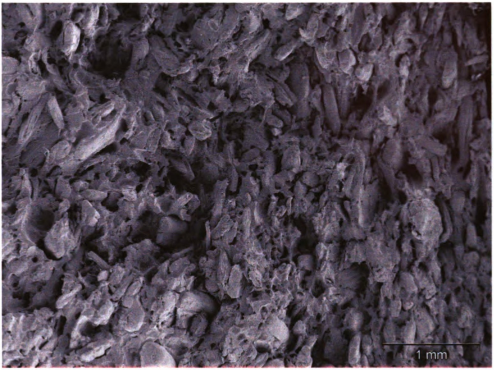


5 W only cycles of 100 phr maple-PVC composites at 50x resolution.

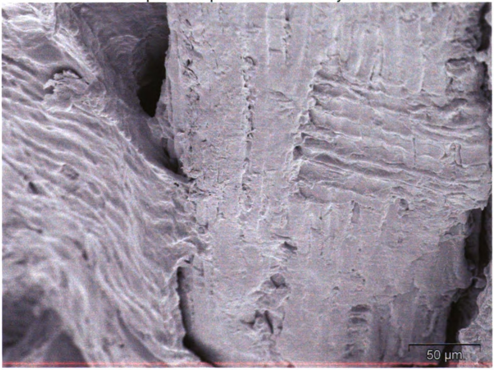




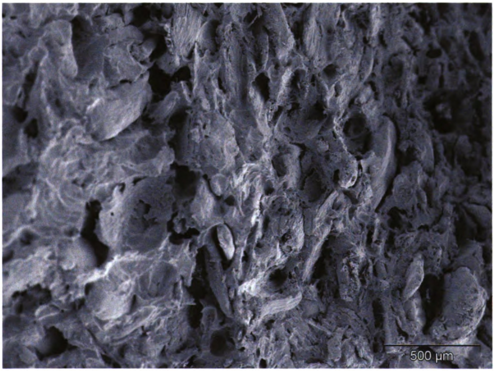
A 100 phr maple-PVC composite exposed to 5 WFT cycles at 25x.



A 370x image of a degraded maple wood fiber in a 100 phr maple-PVC composite exposed to 5 WFT cycles.

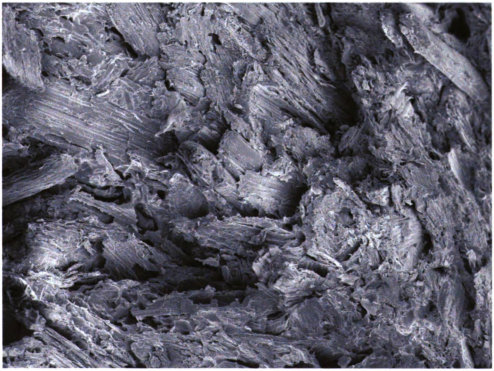


100 phr maple-PVC composites exposed to 5 WFT cycles at 50x resolution.

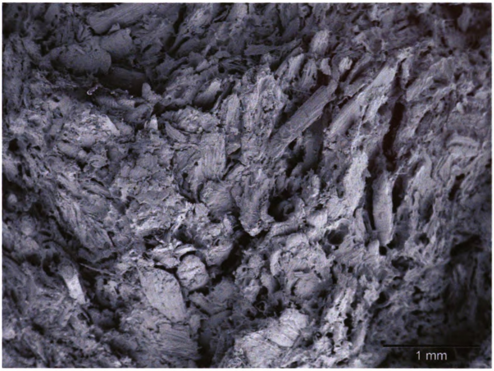


A control 100 phr pine-PVC composite at 25x resolution.

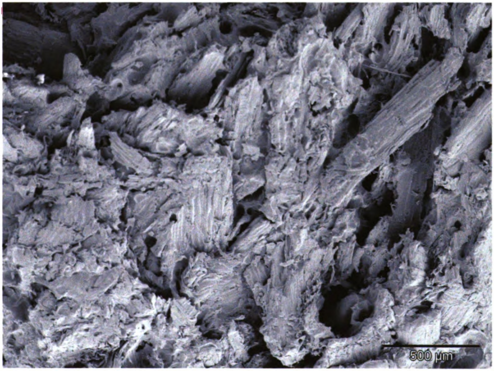
A control 100 phr pine-PVC composite at 50x.



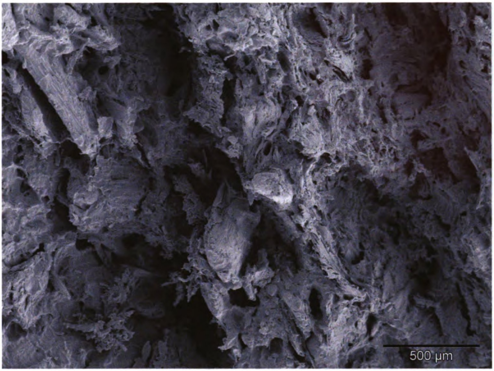
A 100 phr pine-PVC composite after 5 FT only cycles at 25x.

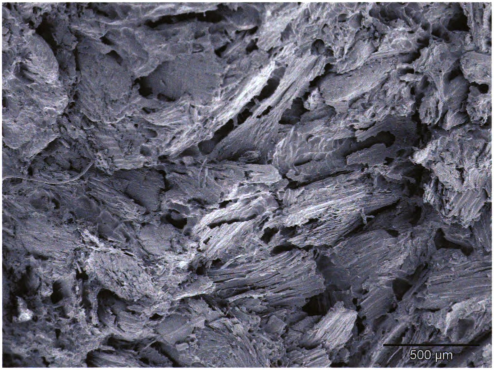


A 100 phr pine-PVC composite after 5 FT only cycles at 50x.

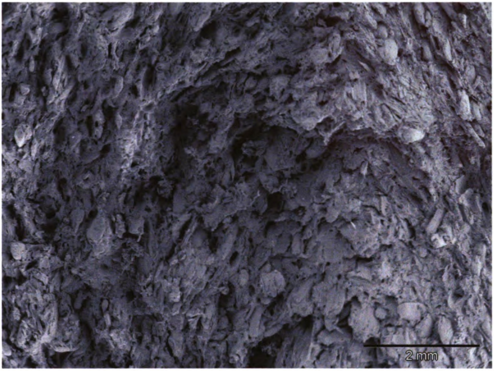


100 phr pine-PVC composites after 5 FT only cycles at 50x (cont'd).





A 100 phr pine-PVC composite at 15x resolution after 5 W only cycles.



A 100 phr pine-PVC composite after 5 W only cycles at 25x resolution.

A 100 phr pine-PVC composite after 5 W only cycles at 50x resolution.

A 100 phr pine-PVC composite after 5 WFT cycles at 25x.

100 phr pine-PVC composites after 5 WFT cycles at 50x resolution.