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PREDICTING FREEZE-THAW DETERIORATION IN WOOD-POLYMER COMPOSITES

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Abstract
Natural fiber-reinforced polymers are currently used in a variety of low- to high-performance applications in the automotive, packaging, and construction industries. Previous studies have demonstrated that natural fibers (e.g., flax, hemp) exhibit good tensile mechanical properties and have positive environmental and economic attributes such as low cost, rapid renewability, and worldwide availability. However, natural fibers are inherently susceptible moisture-induced changes in physical and mechanical properties, which can be unfavorable for in-service use. This study illustrates how a micromechanics-based modelling approach can be used to help facilitate durability design and mitigate the deleterious effects of freeze-thaw deterioration in wood-plastic composites (WPCs). The model described in this study predicts the critical fiber volume fraction (V_{fcrit}) at which damage to the composite will occur under certain environmental conditions for different WPC formulations of hardwood and softwood fiber reinforcement and polymer matrix types. As expected, the results show that V_{fcrit} increases (a positive result) as anticipated *in situ* moisture content decreases. In addition, results suggest that fiber packing distribution directly influences V_{fcrit} and that V_{fcrit} increases as the mechanical properties of the polymer matrix increase. In sum, the study demonstrates how predictive modeling can be applied during the design phase to ensure the durability of WPCs.

Keywords:
Wood polymer composites; freeze-thaw durability; mechanics; analytical modeling

1 INTRODUCTION

The future market for natural fiber composites (NFC) is expected to grow due to continued environmental, social, and political pressure for alternatives to petroleum-based materials [Väisänen 2016]. In 2015, the global NFC market was over $3.5 billion, and wood fiber composites comprised over 60% of the market [Grand View Research 2016]. Wood fiber, a byproduct of the timber industry and a biorenewable resource, is used in the manufacture of wood polymer composites (WPCs). Wood fiber reinforcement adds strength and stiffness while the polymer matrix transfers the applied load throughout the composite [Niska 2008]. WPCs exhibit consistent mechanical properties without the natural flaws found in dimensional lumber. In addition, WPCs are lightweight and can be formed into many different shapes and cross-sections using different processing techniques [Dai 2014]. The construction and automotive sectors are the main consumers of WPCs for applications, such as interior or exterior car parts, and decking, fencing, or siding materials for construction [Grand View Research 2016].

1.1 WPC Constituents

Many polymers have been used for WPCs, including biopolymers, recycled plastics, and synthetics [Najafi 2013, Niska 2008, Srubar 2013]. Polymers are typically selected for construction applications for their hydrophobic nature and good mechanical properties [Dai 2014, Niska 2008]. For this reason, the synthetic polymer matrices selected for investigation in this study are high-density polyethylene (HDPE), polypropylene (PP), and rigid polyvinyl chloride (PVC).

Wood fiber in WPCs is either considered a softwood or hardwood [Niska 2008, Dickson 2014]. Softwood species harvested for construction are typically from temperate conifer forests in Scandinavia, North America, New Zealand, Japan, and the United Kingdom [Dickson 2014]. Although softwoods constitute a majority of the global commercial timber market, some hardwood species are used for construction applications [Dickson 2014, McKenzie 2007]. Hardwood species are typically from northern temperate forests in Europe and North America or tropical rain forests in Malaysia and Indonesia. In most cases, hardwoods are physically harder and denser and have correspondingly higher strength and stiffness when compared to softwoods. Hardwoods, however, typically have slower growth rates than softwoods [Dickson 2014].

Due to their use in structural applications, douglas-fir, larch, spruce, and pine were selected as the softwood species, and teak, iroko, keuring, and greenheart were selected as the hardwood species for wood fiber reinforcement in this study

1.2 Effect of Environmental Aggressors on WPCs

Although wood fiber is a low-cost biorenewable filler with high mechanical properties, the chemistry of wood fiber contains molecular groups that have an affinity for water molecules. Absorbed moisture negatively affects the bonding of the chemical constituents in wood and reduces the mechanical properties of the fiber [Niska 2008]. In addition, the associated fiber particle volume increase with moisture absorption (due to swelling), which results in matrix cracking and subsequent loss of composite mechanical properties [Srubar 2013]. This deterioration mechanism is exacerbated in freezing conditions when the absorbed water freezes and expands [Srubar 2015]. Freeze-thaw deterioration is a common cause for repair and replacement of construction materials [Pilarski 2005].

Previous research by the authors have shown that the deleterious effects of freeze-thaw deterioration can be mitigated using predictive modeling. Simulating the response of WPCs to environmental stresses can be used to select appropriate fiber reinforcement, matrix materials, and the proportions of each. Previous experimental studies have also shown that an increase in the fiber content of the WPC worsens deterioration due to both moisture absorption and freezing [Srubar 2013, Pilarski 2005]. Findings suggest the existence of a maximum threshold for fiber volume fractions that will not cause damage high humidity, wet, or frost conditions. The micromechanics-based model used in this study predicts this threshold, or critical fiber volume fraction, at which freeze-thaw damage occurs.

2 METHODS

The model described herein predicts the mechanical response of WPCs subjected to freeze-thaw conditions. The authors previously developed and validated this model using eleven experimental WPC formulations from five separate studies. As a summary, this model [Srubar 2015] uses Hill's generalized self-consistent method for composites [Hill 1965], Lame's solution [Caré 2008], and cylindrical pressure vessel mechanics [Timoshenko 1956]. For different fiber packing arrangements and wood fiber species, the model calculates the critical fiber volume fraction at which frozen expanded moisture causes permanent loss of mechanical properties due to matrix cracking. The model problem, illustrated in Fig. 1, is analogous to the corrosion-induced deterioration of reinforced concrete that is caused by expansive rust products [Caré 2008].

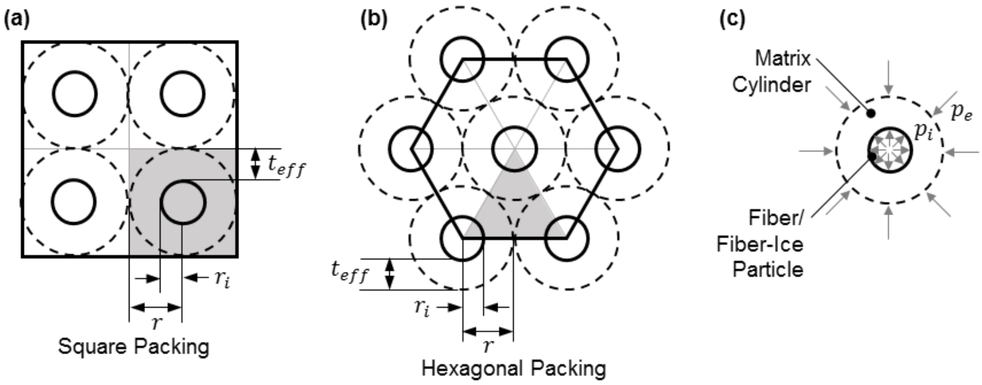

Fig. 44 : Illustration of model problem. This study considers (a) square and (b) hexagonal fiber packing arrangements. The effective thickness (t_{eff}) of the matrix cylinder is the difference between the outer radius (r) and the inner radius (r_i). Part (c) shows the external pressure (p_e) caused by atmospheric pressure (1.0 MPa) counteracting the internal pressure (p_i) caused by the expanding fiber/fiber-ice particle due to absorbed then frozen moisture

2.1 Model Assumptions

The following assumptions were made to formulate the analytical freeze-thaw deterioration model:

1. The wood fiber reinforcement is isotropic, axisymmetric, has uniform particle size and shape, and is evenly dispersed and longitudinally aligned.
2. The wood fiber particles are compressed during processing, removing all voids resulting in a particle comprised only of wood cell wall material.
3. The wood fiber particle expands due to moisture absorption and subsequent freezing. Wood cell walls are known to absorb moisture until they reach a fiber saturation point (FSP), which has been well documented as 28-32% by weight. The composite is considered fully saturated when the wood fiber reinforcement reaches 30% moisture content by weight. The internal pressure experienced by the polymer matrix cylinder is only due to moisture absorption from an oven dry state and subsequent complete freezing from a liquid to solid state. The effects of mechanical coupling are assumed negligible in comparison.
4. The polymer matrix material is hydrophobic, isotropic, and linear elastic.
5. A polymer matrix cylinder surrounds each fiber/fiber-ice particle with uniform thickness and is treated as a thick-walled cylinder in which ideal pressure vessel mechanics apply.
6. The external pressure from surrounding fiber/fiber-ice particles and matrix cylinders is assumed negligible.
7. The rate of freezing and freeze-thaw cycling are not considered in this model formulation. It is assumed that the initial freeze causes significant mechanical property loss compared to subsequent freeze-thaw cycles.

2.2 Model Formulation and Input Parameters

In order to observe the difference in assumed fiber distribution within the composite, square and hexagonal packing was considered, as shown in Fig. 1a and 1b, respectively. Packing influences the fiber volume fraction (V_f) and effective thickness (t_{eff}) where d_f is the diameter of the fiber reinforcement. For example, the maximum fiber volume fraction for square and hexagonal packing is $\frac{\pi}{4}$ and $\frac{\pi}{2\sqrt{3}}$, respectively. The matrix cylinder, shown in Fig. 1c, for each packing arrangement is an equivalent hollow cylinder that surrounds the fiber or fiber-ice particle with an effective thickness (t_{eff}). For square and hexagonal packing arrangements, the effective thickness (t_{eff}) is described by the following expressions:

Square Packing: $$t_{eff} = \frac{1}{2}\left[\sqrt{\frac{\pi}{V_f}}\frac{d_f}{2} - d_f\right] \quad (1)$$

Hexagonal Packing: $$t_{eff} = \frac{1}{2}\left[\sqrt{\frac{\pi}{2V_f}}\frac{d_f}{3^{\frac{1}{4}}} - d_f\right] \quad (2)$$

When the maximum tensile stress in the matrix cylinder (σ_θ) equals or exceeds the tensile strength of the polymer matrix material (σ_m), cracking is considered to have occurred. To account for uncertainty, the proposed model used a tolerance of 0.05 to equate σ_θ and σ_m. Since radial and tangential moisture induced swelling are known to dominate, the longitudinal direction is considered negligible. The mechanical properties for the polymer matrix materials used in this study are provided in Table 1.

Table 22: Mechanical properties of common polymer matrices for wood fiber composites [Niska 2008]

Polymer Matrix	Modulus of Elasticity (E_m) (MPa)	Tensile Strength (σ_m) (MPa)
High-density polyethylene (HDPE)	700	18
Polypropylene (PP)	1300	37
Rigid polyvinyl chloride (PVC)	3500	75

The maximum tensile stress in the polymer (σ_θ) is described by the following expression:

$$\sigma_\theta = \frac{2\, p_i\, r_i^2 - p_e(r^2 + r_i^2)}{r^2 - r_i^2} \quad (3)$$

Where the parameters (p_e, p_i, r_i, r) are illustrated in Fig. 1c. The geometry of the hollow matrix cylinder is defined by the inner radius (r_i) and the outer radius (r). The external pressure (p_e) is considered equal to atmosphere pressure (0.1 MPa), and the internal pressure (p_i) is described by the following expression:

$$p_i = (r_z - r_f)\left(\frac{t_{eff}}{E_m} + \frac{r_z}{E_z}\right)^{-1} \quad (4)$$

The radius of the fiber particle (r_f) and the radius of the fiber-ice particle (r_z) are determined by assuming the particles have circular cross-sectional areas described by the following expressions:

Fiber: $$A_f = \frac{\pi}{4}\, d_f^2 \left[1 - \frac{d_l}{(d_l + 2t_{cw})^2}\right] \quad (5)$$

Ice: $$A_i = A_f\, s_x\, \frac{m_c}{m_{FSP}}\, (1 + e_i)^{2/3} \quad (6)$$

Fiber-Ice: $$A_z = A_f + A_i \quad (7)$$

The diameter of the of the fiber particle (d_f) is determined by the mesh size of the wood fiber. For the proposed model, 20 mesh wood fiber was considered which has an average particle diameter of 853 µm. The diameter of the fiber cell lumen (d_l), the fiber cell wall thickness (t_{cw}), and average moisture expansion coefficient (s_x) depend on the wood specie and are provided in Table 2. The increased variability in fiber geometry for softwood species is due to the change in anatomical dimensions between the earlywood and latewood cells which are a seasonal characteristic of softwoods [Hannrup 2001, Hannrup 2004].

Table 23: Fiber geometry and average shrinkage by wood specie [Ross 2010].

Average Shrinkage (s_x) (%)			
Hardwoods [Ververis 2004, Redman 2016]			
(d_l = 6.59 µm ± 2.75, t_{cw} = 4.42 µm ± 0.57)			
Teak	Iroko	Keruing	Greenheart
4.2	3.3	8.1	9.2
Softwoods [Hannrup 2001, Hannrup 2004]			
(d_l = 19.88 µm ± 5.60, t_{cw} = 4.38 µm ± 1.08)			
Douglas Fir	Larch	Spruce	Pine
5.9	6.8	5.7	5.6

The moisture content of the fiber (m_c) ranges from 0% (oven dry) to 30%, the moisture content at the fiber saturation point (m_{FSP}) is 30%, and the volumetric expansion of ice (e_i) is 8.7% [Lide 2004, Srubar 2015]. The elastic modulus of the matrix (E_m) for common polymers matrix materials is provided in Tab. 1. The elastic modulus of the fiber-ice particle (E_z) is described by the following rule of mixtures expression:

$$E_z = \nu_f\, E_f + \upsilon_i\, E_i \quad (8)$$

The volume fractions of the fiber and ice are $\nu_f = A_f/A_z$ and $\nu_f = A_i/A_z$, respectively. The elastic modulus of ice (E_i) is 8000 ± 500 MPa [Mellor 1983, Srubar 2015], and the transverse elastic modulus of the fiber is described by the following expression:

$$E_f = E_T\left[1 - \frac{m_c}{m_{FSP}}\left(\frac{\rho_w}{\rho_{cw} + \rho_w}\right)\right] \quad (9)$$

The density of water (ρ_w) is well known to be 1.0 g/cm³. The transverse elastic modulus of a wood cell wall (E_T) and the density of a wood cell wall (ρ_{cw}) have been experimentally quantified as 4540 ± 605 MPa [Jager 2011] and 1.5 g/cm³ [Siau 1984, Stamm 1929], respectively. Previous studies have shown similar mechanical properties and cell wall densities between hardwoods and softwoods [Dai 2014, Stamm 1929].

Uncertainty in mechanical and physical properties was incorporated using a stochastic (Monte Carlo) approach. The averages and standard deviations of modeling parameters were used to sample a normally distributed value for each simulation. The number of simulations ($n = 10{,}000$) used for this study ensured consistent results while minimizing computational effort [Srubar 2015].

3 RESULTS AND DISCUSSION

The results from the model simulations are shown in Figs. 2, 3, and 4. As previously discussed, the model was previously validated using experimental results from the literature [Srubar 2015]. Given a certain moisture content of the composite, the critical fiber volume fraction (V_{fcrit}) is the corresponding fiber volume fraction (V_f) at which matrix cracking occurs ($\sigma_\theta = \sigma_m$). At 10% moisture content, Figs. 2a, 3a, and 4a show V_{fcrit} for different species of wood fiber arranged in square and hexagonal packing formations with HDPE, PP, and PVC polymer matrices, respectively. At 30% moisture content, Figs. 2b, 3b, and 4b show V_{fcrit} for different species of wood fiber arranged in square and hexagonal packing formations with HDPE, PP, and PVC polymer matrices, respectively. The results from this study provide more conservative predictions for V_{fcrit} since parameters such as improved interfacial adhesion between the fiber and polymer matrix were not considered.

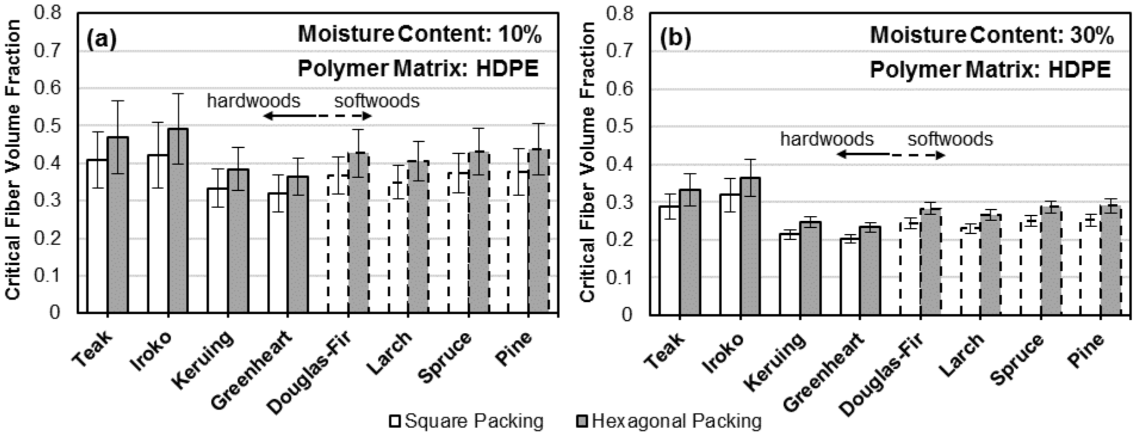

Fig. 45: Critical fiber volume fraction (V_{fcrit}) at (a) 10% and (b) 30% moisture contents for composites with hardwood and softwood fiber reinforcement and a HDPE polymer matrix

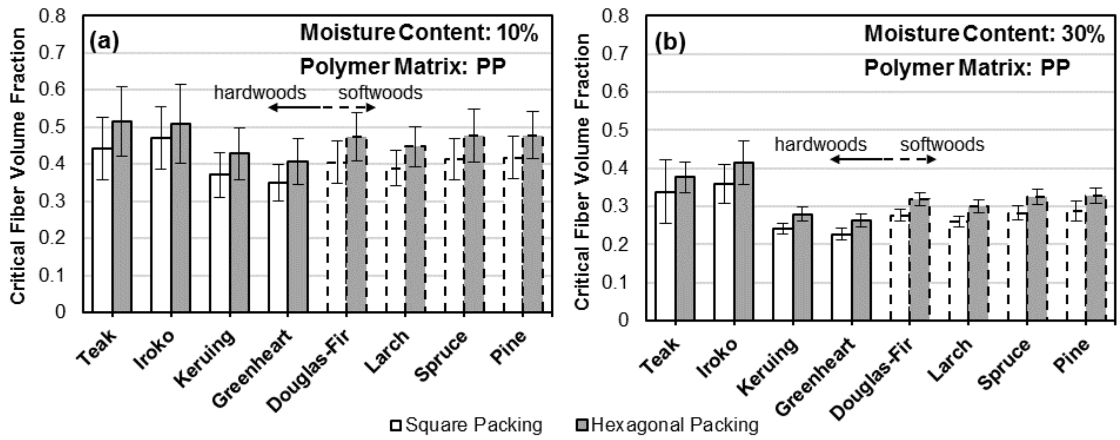

Fig. 46: Critical fiber volume fraction (V_{fcrit}) at (a) 10% and (b) 30% moisture contents for composites with hardwood and softwood fiber reinforcement and a PP polymer matrix

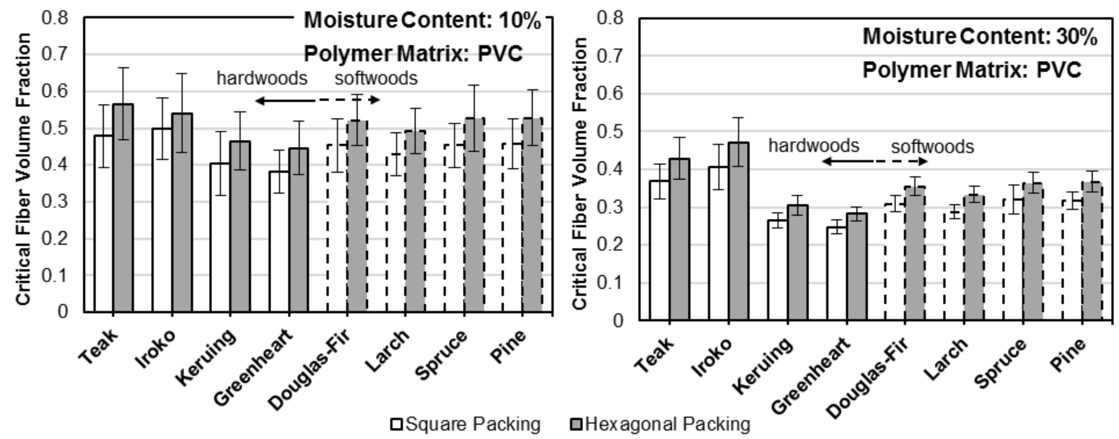

Fig. 47: Critical fiber volume fraction (V_{fcrit}) at (a) 10% and (b) 30% moisture contents for composites with hardwood and softwood fiber reinforcement and a HDPE polymer matrix

As expected, the V_{fcrit} is lower for fully saturated (30% moisture content) compared to partially saturated (10% moisture content) for all formulations. This trend is due to the presence of addition moisture in the wood fiber which causes additional internal pressure from increased radial expansion upon freezing. It is observed that an increased V_{fcrit} results in higher variation, evident by the error bars, which may be attributed to the uncertainty associated with the wood fiber parameters compared to the constant threshold values associated with the polymer matrix. The hardwood species teak and iroko have a higher V_{fcrit} at fully saturated moisture conditions which may correspond an inherent resistance to swelling, as evident by the lower shrinkage parameters compared to the other wood species.

The fiber packing arrangement is shown to influence V_{fcrit}. Independent of the formulation, square packing results in composites with a lower V_{fcrit} than hexagonal packing for both 10% and 30% moisture conditions. For 30% moisture content, however, the difference in V_{fcrit} between square and hexagonal packing is less than that for 10% moisture content. The influence of fiber packing arrangement suggests that processing techniques will affect the mechanical response of WPCs to freeze-thaw conditions and is therefore an important design consideration.

The type of polymer matrix has an observable effect on V_{fcrit}. As the mechanical properties of the polymer matrix increase, V_{fcrit} also increases. In order to increase the amount of fiber in the composite for a certain environmental condition, one design consideration is to use a polymer matrix with increased mechanical properties. In humid environments (Figs. 1b, 2b, and 3b), for example, PVC would allow for a high fiber volume fraction. However, in dry environments (Figs. 1a, 2a, and 3a), HDPE would allow for a comparably high fiber volume fraction. In this way, the results from the model simulations can be used to inform WPC design (e.g., select polymer types) for different environmental conditions.

4 SUMMARY

This study described and applied a micromechanics-based analytical model to predict the response of WPCs to humid and freezing environmental conditions. The critical fiber volume fraction (V_{fcrit}) was computed as a parameter to assess when damage occurs for different WPC formulations of wood fiber specie and polymer matrix types. Results showed that V_{fcrit} decreases as moisture content increases, the fiber packing arrangement influences V_{fcrit}, and V_{fcrit} increases as the mechanical properties of the polymer matrix increase. The study illustrated how model simulations for different WPC formulations can be used to inform design considerations (i.e., fiber loading) for different environmental scenarios.

5 ACKNOWLEDGMENTS

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