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Characterization of poly-hydroxybutyrate films and hemp fiber reinforced composites exposed to accelerated weathering

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ABSTRACT

Renewable biobased polymers and composites have been shown to have suitable initial specific strength and stiffness for use in commercial applications. However, the long-term performance of these materials under variable environmental conditions is largely unknown. Accelerated weathering testing is performed on poly-hydroxybutyrate (PHB) biopolymer films and PHB-hemp fiber reinforced composites. Simulated weathering conditions include exposure to cyclic ultra-violet (UV) light, heat, water spray, and elevated relative humidity. Two distinct weathering procedures are performed, one with cyclic elevated relative humidity and one without. Changes in the mechanical properties of ultimate stress, ultimate strain, and modulus of elasticity, as well as mass, cross-sectional area, molecular weight, and color are reported. It was found that neat PHB polymer films exhibit increased elastic modulus and decreased ultimate strength and strain with weathering exposure, while PHB-hemp fiber composites exhibit decreased ultimate strength and elastic modulus. Both the films and composites experienced mass loss and increased fading with weathering exposure. The molecular weight of the PHB polymer decreased steadily with increasing weathering. The observed changes in physical and mechanical properties are attributed to photo-oxidation and hydrolytic degradation of the PHB bio-polyester and cyclic hygro-thermal expansion and contraction of the natural reinforcing fibers.

1. Introduction

The construction and building industry is a large consumer of raw materials and producer of industrial waste. For example, worldwide construction consumes approximately 10–20% of global energy [1] and 25% of all harvested wood [2]. While some construction materials are recycled after their removal from service, most are landfilled. In the U.S. it is estimated that 60% of annual construction and demolition (C&D) waste (96 million tons) is sent to landfills [3] and represents approximately 40% of all U.S. landfill volume [4]. A subset of C&D waste comprised primarily of structural and non-structural wood, plastics, and drywall (25% or roughly 38 million tons) can potentially be replaced with engineered biobased composite materials that are made from rapidly renewable resources and are anaerobically biodegradable.

Engineered biobased composites made from naturally derived polymers and fibers show great promise as replacements for many traditional construction materials due to their relatively high strength and stiffness, low environmental impact, and inherent renewability. However, the long-term stability of these composites when exposed to in-situ environmental conditions is a concern, owing primarily to their susceptibility to moisture and temperature induced degradation. This susceptibility presents a major hurdle for biobased composites that must be understood and addressed before they can gain acceptance in industry.

In this research, PHB polymer films and PHB-hemp fabric biobased composites are subjected to two accelerated weathering procedures. The objectives of this research are to (1) quantify changes in the physical, mechanical, and visual properties of biopolymer films and composites resulting from weathering exposure, (2) identify degradation mechanisms resulting from weathering exposure, and (3) associate changes in film and composite properties with the identified degradation mechanisms. Changes in physical, mechanical, and visual properties are monitored throughout the weathering tests and are used as indicators of material deterioration.

2. Background

Biobased composites can be broadly categorized as partially biobased (natural polymer/synthetic fiber or synthetic polymer/

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natural fiber) and fully biobased (natural polymer and fiber) [5]. The focus of this research is fully biobased composites made from the microbially synthesized polyester poly-hydroxybutyrate (PHB) and natural fiber fabrics. These composites are expected to require less energy to produce than synthetics [6] and biodegrade anaerobically [7] both to reduce construction related landfill waste and produce a degradation end product, namely fuel for energy or a renewable feedstock to cultivate more biopolymer [8]. Therefore the current paradigm of linear, or cradle-to-grave, construction (i.e., raw materials to built systems to waste materials) can be replaced by a closed-loop model [9].

While the eventual biodegradation of biobased composites is necessary to realize a closed-loop life cycle, in-service resistance to degradation must be maintained for the composites to be useful as engineering materials. Most biobased composites are vulnerable to hygrothermal loads due to the general incompatibility between hydrophilic reinforcing fibers and hydrophobic binding matrices, as is the case with the PHB-natural fiber reinforced composites investigated herein [10]. While weathering and hygrothermal impacts on partially biobased composites, particularly composites made from traditional thermoplastic or thermoset polymers and natural fiber reinforcement (e.g., wood plastic composites), have been studied extensively, the effect of weathering on fully biobased composites has received less attention. In general, environmental exposure has been linked to mechanical property degradation, dimensional instability, and fading [11]. Full spectrum weathering of biobased composites, including photodegradation from environmental UV radiation, has been shown to exacerbate damage induced by hygrothermal effects alone [12–14].

3. Materials and methods

3.1. Materials and sample preparation

Pelletized PHB polymer, an isotactic aliphatic polyester synthesized by bacteria as a carbon storage mechanism, was obtained from Biomer® (P226). The PHB polymer was reported to be 98% pure after microbial extraction and then blended with an unreported amount of nontoxic nucleating agents and plasticizers by the manufacturer to improve melt processing [15]. The reported tensile modulus of P226 is 1750 MPa, elongation at break is 6%, and ultimate tensile strength is 24 MPa [16]. Bidirectional woven hemp fabric supplied by Hemp Traders© (CT-L5 5.8 oz hemp linen) was used as reinforcing in the biobased composites. The hemp was water retted, boiled in a sodium hydroxide solution, then combed, spun, and woven into a fabric by the manufacturer. No further fiber treatments were used in this study.

The pelletized PHB was processed using a Brabender Plasti-Corder® extruder operated at 25 rpm with a heating profile ranging from 160 °C at the hopper to 150 °C at the die. A 25.4 mm wide tape die was used to extrude 1 mm thick films which were then cut into tensile specimens consistent with ASTM D638 [17]. Extruded PHB polymer tapes were also combined with woven hemp fabric via compression molding on a 267 kN PHI® hot press to produce 8-ply PHB-hemp composite sheets with a nominal thickness of 3.5 mm and fiber volume fraction of 40%. The composites were pressed at 207 kPa while both top and bottom heating platens were maintained at 180 °C. Tensile specimens were cut from the resulting composite sheets using a band saw. Details regarding testing designations, materials, and manufacturing processes for the film and composite tensile specimens are provided in Table 1. All specimens were conditioned at 65% relative humidity and 25 °C for 48 h prior to testing.

Table 1
Specimen testing designations, material composition, and manufacturing processes.

Specimen designation	Material	Manufacturing process	Test procedure	Total specimens	Specimens/test
P1-F	PHB film	Extrusion	P1	27	3
P2-F	PHB film	Extrusion	P2	27	3
P1-C	PHB-hemp composite	Extrusion/hot pressing	P1	27	3
P2-C	PHB-hemp composite	Extrusion/hot pressing	P2	27	3

3.2. Weathering methods

Two weathering procedures, referred to as P1 and P2, were used to simulate accelerated UV radiation and temperature fluctuations with and without moisture. Specimen designations provided in Table 1 specify the weathering procedure followed by the material type, where -F corresponds to Films and -C corresponds to Composites. Details for each procedure are summarized in Table 2. The testing procedures applied in this study are modeled after ASTM standards G151 and G155 [18,19] and similar tests implemented by Podgorski [20] and Mehta [12].

Procedure P1 cycles 340 nm UV light (UV-A spectrum) at an irradiance of 0.85 W/m^2 for 150 min dry followed by 30 min with direct water spray. The light phase is followed by a dark condensation phase at 90% relative humidity for 1440 min. Procedure P2 is designed to subject specimens to the same UV and thermal exposure as P1 but eliminate variable moisture by removing the direct water spray and condensation cycles.

PHB film and PHB-hemp composite specimens were subjected to 74 cycles of each procedure, for total weathering times of 1998 and 384 h for procedures P1 and P2, respectively. Mass, cross-sectional dimensions, color, and uniaxial tensile mechanical properties were measured at approximately eight equal intervals throughout testing (i.e., every 250 h for P1 and every 48 h for P2) as described more fully in Section 3.3. The test results from each procedure were compared on the basis of a UV exposure cycle, which is defined as the number of complete UV cycles a specimen is subjected to between testing intervals.

Both accelerated weathering procedures were implemented using an Atlas Ci3000 + Xenon Weather-Ometer® with a xenon arc light source. When combined with the supplied Type "S"/Borosilicate filter the system creates a UV spectrum which closely resembles that of peak natural sunlight [21].

3.3. Material characterization methods

Mass and cross-sectional dimensions were measured using a standard balance and micrometer, respectively. Specimens were wiped lightly prior to massing to remove surface moisture. Each reported cross-sectional area is the average of three equally spaced measurements along the 50.8 mm tensile gage section of the specimen. Relative changes in specimen density were calculated by dividing the change in mass by the change in cross-sectional area.

Table 2
Accelerated weathering test procedure details; IRR ≡ irradiance at 340 nm, CHT ≡ chamber temperature; RH ≡ relative humidity.

Procedure	Phase	Light source	IRR (W/m^2)	CHT (°C)	RH (%)	Duration (min)	Water spray
P1	1	Xenon	0.85	60	60	150	Off
	2	Arc	0.85	25	0	30	On
	3		0	45	90	1440	Off
P2	1	Xenon	0.85	60	60	180	Off
	2	Arc	0	45	60	131	Off