



Moisture diffusion and its impact on uniaxial tensile response of biobased composites

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ARTICLE INFO

Article history:

Received 8 July 2011

Received in revised form 11 November 2011

Accepted 30 November 2011

Available online 8 December 2011

Keywords:

A. Fabrics/textiles

A. Laminates

B. Environmental degradation

B. Mechanical properties

Biobased

ABSTRACT

Biobased composites made from biopolymers and plant-based fibers are being evaluated for construction applications as replacements for wood or petroleum-based composites and plastics. The biobased composites studied here have been demonstrated to rapidly biodegrade in anaerobic conditions to methane thereby reducing construction-related landfill waste and producing a useful end product, namely fuel for energy or a feedstock to grow more biopolymer. To be a useful in construction, susceptibility to moisture and eventual moisture resistance is necessary. Diffusion properties and mechanical properties are characterized in various moisture and temperature conditions for hemp/cellulose acetate and hemp/poly(β -hydroxybutyrate) composites. The composites were observed to follow Fick's 2nd law of diffusion. The tensile moduli of elasticity were found to decrease with full moisture saturation while the ductility increased and the ultimate strength did not change significantly. Measured diffusion coefficients are compared to petroleum-based and other biobased composites.

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1. Introduction

The construction practices and materials used in today's building industry leave an alarmingly significant ecological footprint. In 2003, the building industry generated 170 million tons of construction and demolition debris. An estimated 52% of that debris was disposed of in landfills [1]. Wood, drywall, and plastic comprise 30–50% of construction and demolition debris [2]. These materials are recalcitrant in landfills and potentially can be replaced by bio-based composite materials.

Significant research has been conducted in recent years on bio-based composites (e.g., summaries in [3–5]). Limited attention has been given to potential construction applications of these materials (e.g., summary in [6]). The biobased composites researched here are intended for construction applications. They are made from renewable resources that biodegrade in an anaerobic environment after their useful service life thereby reducing construction-related waste. Two biobased composites are the focus of studies presented here, both made from plant fibers, namely hemp fiber fabric. Two different biopolymers are investigated as the matrix material: cellulose acetate, a biopolymer derived from plants, and poly(β -hydroxybutyrate) (PHB), a type of polyhydroxyalkanoate biopolymer derived by bacterial fermentation.

This paper focuses on the rate of moisture absorption and the effects of moisture absorption on mechanical properties of hemp/cellulose acetate and hemp/PHB biobased composites. The motivation for this research is that these composites have been shown to have mechanical properties comparable to engineered wood [6], and in the case of hemp/PHB composites have the potential for a closed-loop life-cycle [7]. To be used in the construction industry, the biobased composites must be resistant to weathering and, in particular, to moisture.

To determine the rate of moisture absorption, balanced 8-ply laminates of the two biobased composites studied here were subjected to a humid environment. The diffusion of moisture into the composites exposed to three different temperatures was measured and compared to predictions based on Fick's 2nd law. Further comparisons are made to other biobased and synthetic fiber-reinforced polymeric composites. To determine how moisture affects the mechanical behavior of the biobased composites, the uniaxial tensile responses of specimens that were unsaturated, saturated, and saturated followed by drying are compared. The impact of saturation temperature on mechanical performance is also investigated.

2. Background

Although considerable moisture-related research has been conducted on natural fiber composites using synthetic matrix materials such as polyethylene or polypropylene, relatively few studies have been conducted on completely biobased composites. Alvarez et al.

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measured moisture absorption of fibers, matrix material and composites of short sisal fiber reinforced MaterBi-Y material (derived from cellulose and starch) with varying fiber volume fractions and conditioned at varying humidity [8]. The moisture absorption of the composite did not vary significantly from that of the matrix alone due to the high moisture absorption of the starch in the matrix. When tested in flexure, the modulus decreased with moisture absorption for both the matrix and the composite [9]. Alam et al. measured moisture absorption in jute fabric/Biopol(poly(β -hydroxybutyrate)-co-poly(β -hydroxyvalerate) or PHBV) composites and found that moisture absorbed by the composites was greater than that for the pure matrix [10].

3. Materials and methods

3.1. Materials and sample preparation

The cellulose acetate plastic matrix is made from 70 wt.% cellulose acetate powder (Sigma Aldrich cellulose acetate, 39.7% acetyl, average Mn 50,000) plasticized by 30 wt.% triethyl citrate 99+%, FCC (Sigma Aldrich). The PHB matrix is made from pellets (Biomer P226) that are a PHB blended with a proprietary citric acid plasticizer. The hemp fabric used in the composites is 100% hemp linen (Hemp Traders, Product CT-L5, 5.8 oz., plain weave, 45 yarns in the warp direction, 42 yarns in the weft direction). The hemp fiber had been water retted then boiled in a solution of sodium hydroxide to remove the lignin from the fiber. The fiber was then combed, spun into yarn, and woven into a fabric. The fabric was further bleached lightly with hydrogen peroxide.

The plasticized cellulose acetate powder and the PHB pellets were first made into thin films of roughly 25–30 g of material per film using a hot press. The films were then layered with single plies of fabric to form 8-ply composite plates. A pressure of 1.4 MPa was applied for the hemp/CA composites and 0.25 MPa for the hemp/PHB composites. Lower pressure was used for the hemp/PHB composites because the PHB has a lower melt viscosity than cellulose acetate. Test specimens were cut from the plates using a band saw.

3.2. Measuring diffusion in biobased composites

The diffusion coefficient and Arrhenius constant of the two biobased composites at three different temperatures were determined through experiments and the application of Fick's 2nd law of diffusion [11,12]. Fick's 2nd law of diffusion has been observed to apply to biopolymer-natural fiber composites [9] and petrochemical polymer-natural fiber composites (e.g., [13,14]), but has not yet been reported for the biobased composites studied here.

To determine the diffusion coefficient for the hemp/PHB and the hemp/cellulose acetate composites, a composite plate made from eight layers of hemp was fabricated with each matrix material. Thin, rectangular specimens (25.4 mm \times 50.8 mm) were cut from the plate and conditioned in an environmental chamber at 100%

relative humidity (RH). A description of the specimens used for measurements and testing is given in Table 1. The average thicknesses of the hemp/cellulose and hemp/PHB specimens were 2.87 mm and 3.05 mm, respectively. Volume fractions for each plate were measured using a dissolution method [15]. Because the diffusion coefficients for the biobased composites were assumed to be dependent on the temperature, the rate of moisture diffusion was determined for each composite at 30 °C, 40 °C, and 50 °C.

Before conditioning in the moisture chamber, each specimen was dried in an oven at 70 °C until all initial moisture was removed. The dry mass, m_D , of each specimen was measured. Immediately following the dry mass measurement, the specimens were placed in the environmental chamber, and the moisture content for each specimen was determined by measuring the mass, m , of each specimen periodically until saturation was reached. When specimens were removed from the chamber for measurement, they were placed into a sealed bag to limit moisture loss and removed only to take measurements. Before measurement of the specimen mass, the moisture on the surface of each specimen was removed. Upon completion of mass measurements, the specimens were returned to the environmental chamber. Measurements were completed more frequently at the beginning of the test because of the high initial rate of change of mass that occurs. The conditioning was terminated upon reaching saturation as demonstrated by a plateau on the moisture content vs. square root of time graph (Fig. 1).

The moisture content was plotted against the square root of time. The maximum moisture content, M_m , and diffusion coefficient, D , were then determined from the graph using the solution to Fick's second law for a semi-infinite solid (Fig. 1). The plotted experimental data was then compared to the behavior predicted by Fick's second law for a thin-sheet. Details are given in [15].

The percent of moisture uptake, M , was calculated for each mass measurement as follows:

$$M_j = \frac{m_j - m_D}{m_D} \times 100 \quad (1)$$

where m is the mass of the specimen, the subscript j refers the j th measurement, and the subscript D refers to the dry state prior to conditioning.

3.3. Measuring the impact of diffused moisture on composite tensile response

To determine how moisture affects the mechanical properties of the hemp/cellulose acetate and hemp/PHB composites, tensile specimens were conditioned in environmental chambers at 30 °C and 100% relative humidity (RH) and then tested to failure in uniaxial tension. Although biobased composite behavior was expected to change when specimens were saturated, it was not known if saturation would damage the biobased composite permanently. Therefore, the tensile behavior of saturated biobased composite specimens was compared both to control specimens that were

Table 1
Test specimens.

Specimen description			Conditioning	
Matrix	Fiber	Avg. thickness (mm)	Temperature (°C)	Relative humidity (%)
Cellulose acetate	Hemp fabric	2.83	30	100
Cellulose acetate	Hemp fabric	2.91	40	100
Cellulose acetate	Hemp fabric	2.83	50	100
PHB	Hemp fabric	3.09	30	100
PHB	Hemp fabric	3.03	40	100
PHB	Hemp fabric	3.06	50	100

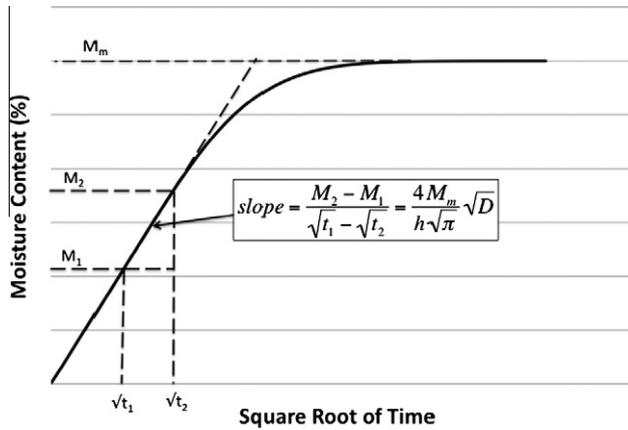


Fig. 1. Graph of Fickian diffusion (adapted from [25]).

conditioned at room temperature and humidity (roughly 21 °C and 20% RH) and to specimens that were saturated as described above and then allowed to re-equilibrate to room conditions.

A composite plate was made from eight layers of hemp and each matrix type. Nine tensile specimens, in dog-bone shape per ASTM D638 [16], were cut from each plate. Three control specimens were sealed in a plastic bag and stored in the laboratory to prevent significant change in moisture content. Six specimens were placed in an environmental chamber and were conditioned at 100% RH and 30 °C until saturated. The change in specimen mass was measured on a regular basis to determine the moisture uptake and to identify when the specimens became saturated. Specimens were assumed to be saturated when the specimen mass stopped increasing, which corresponds to when the moisture content vs. the square root of time graph levels off. Moisture conditioning was terminated immediately upon saturation before any loss in mass was measured.

Upon saturation, all six specimens were removed from the environmental chamber. Three tensile specimens were tested immediately while saturated. The control specimens were tested at the same time as the saturated specimens. The remaining three saturated specimens were allowed to dry, at room temperature and humidity (21 °C and 20% RH), to reach moisture levels similar to the unconditioned specimens prior to testing.

The tensile specimens were tested according to ASTM D638 [16] wherein they were instrumented with an extensometer along a 50 mm gage length and loaded uniaxially at 5 mm/min. All specimens were loaded parallel to the warp yarns of the hemp fabric. After the cross-sectional area was measured, the testing was performed on an MTS 858 table-top tester with a capacity of 14.7 kN. The mechanical wedge grips, flat with saw tooth profile, were separated a distance of 115 mm. The MTS load cell measured the applied load. The extensometer measured the longitudinal deformation. Testing was stopped after failure (tensile rupture) of the specimen.

3.4. Measuring the impact of saturation temperature on uniaxial tensile response of saturated composites

To determine if the expected changes in rate of diffusion and maximum moisture content with varying conditioning temperature would impact the mechanical tensile properties of saturated composites, additional 8-layer composite plates were manufactured with each type of matrix material. Nine dog-bone shaped tensile specimens per ASTM D638 [16] were cut from the plates. Three specimens were conditioned at 100% RH in separate chambers held at 30 °C, 40 °C, and 50 °C over a period of 9–40 days until

saturated. The change in specimen mass was measured periodically, as described in Section 3.1, to determine the moisture content and to identify when the specimens were saturated.

Upon saturation, specimens were removed from their environmental chambers and placed in a plastic bag to prevent moisture loss before testing. All specimens were tested within 1 h of being removed from the moisture chamber and placed in a sealed plastic bag, and no significant difference in specimen mass was measured during this interval. The tensile specimens were tested according to ASTM D638 [16] as described in Section 3.3.

4. Experimental results

4.1. Diffusion behavior and diffusion coefficients

The experimental results for the hemp/cellulose acetate and hemp/PHB at the three temperatures are plotted along with the predicted relationship for Fickian diffusion (solid line) in Fig. 2a–c and d–f, respectively. Fickian behavior predicted the initial moisture absorption well for both composite materials. The experimental behavior became non-Fickian as time increased. The maximum moisture content was between 11% and 12% for the hemp/cellulose acetate and between 7% and 8.5% for the hemp/PHB. This difference is attributed primarily to the hydrophilicity of the cellulose acetate and both the hydrophobicity and high crystallinity relative to cellulose acetate of the PHB [17,18]. The hydrophilic hemp fibers absorbed moisture in both composites. The steeper slopes of the hemp/cellulose acetate graphs indicate the faster rate of moisture diffusion and higher diffusion coefficient as compared to the hemp/PHB composites.

The average coefficient of diffusion, D , for each specimen was determined from the maximum percent of moisture uptake, M_m , the initial slope of the line of the moisture content vs. square root of time graphs (labeled in Fig. 1) and the specimen thickness, h , with the following equation:

$$D = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (2)$$

The average diffusion coefficient, D , measures the rate of moisture diffusion through all faces of the specimen and is specific to the specimen. For comparison to other materials, the one-dimensional diffusion coefficient in the direction of thickness, D_x , is calculated. For one-dimensional flow in a finite specimen (such as those that tested and reported herein) the diffusion coefficient for the material, D_x , is derived by relating the diffusion through the large faces to that through all sides, assuming that diffusion rates are equal through all sides:

$$D_x = \frac{D}{(1 + h/l + h/w)^2} \quad (3)$$

Because the natural fibers are hydrophilic and are exposed at the edges, the rate of moisture flow through edges will likely be higher than that through the faces. Thus the one-dimensional diffusion coefficient described by Eq. (3) is expected to overestimate the actual rate of diffusion through the faces of these biobased composite specimens leading to conservative results when evaluating moisture resistance of these biobased composites.

The average data from three measurements for each material-temperature combination as well as the resulting diffusion coefficients, D (Eq. (2)), and diffusion coefficients for one-dimensional flow, D_x (Eq. (3)), are given in Table 2. The diffusion coefficients and maximum moisture content for the hemp/cellulose acetate were higher than for the hemp/PHB, which is attributed to the cellulose acetate matrix being hydrophilic and PHB being both hydrophobic and more crystalline than the cellulose acetate. The

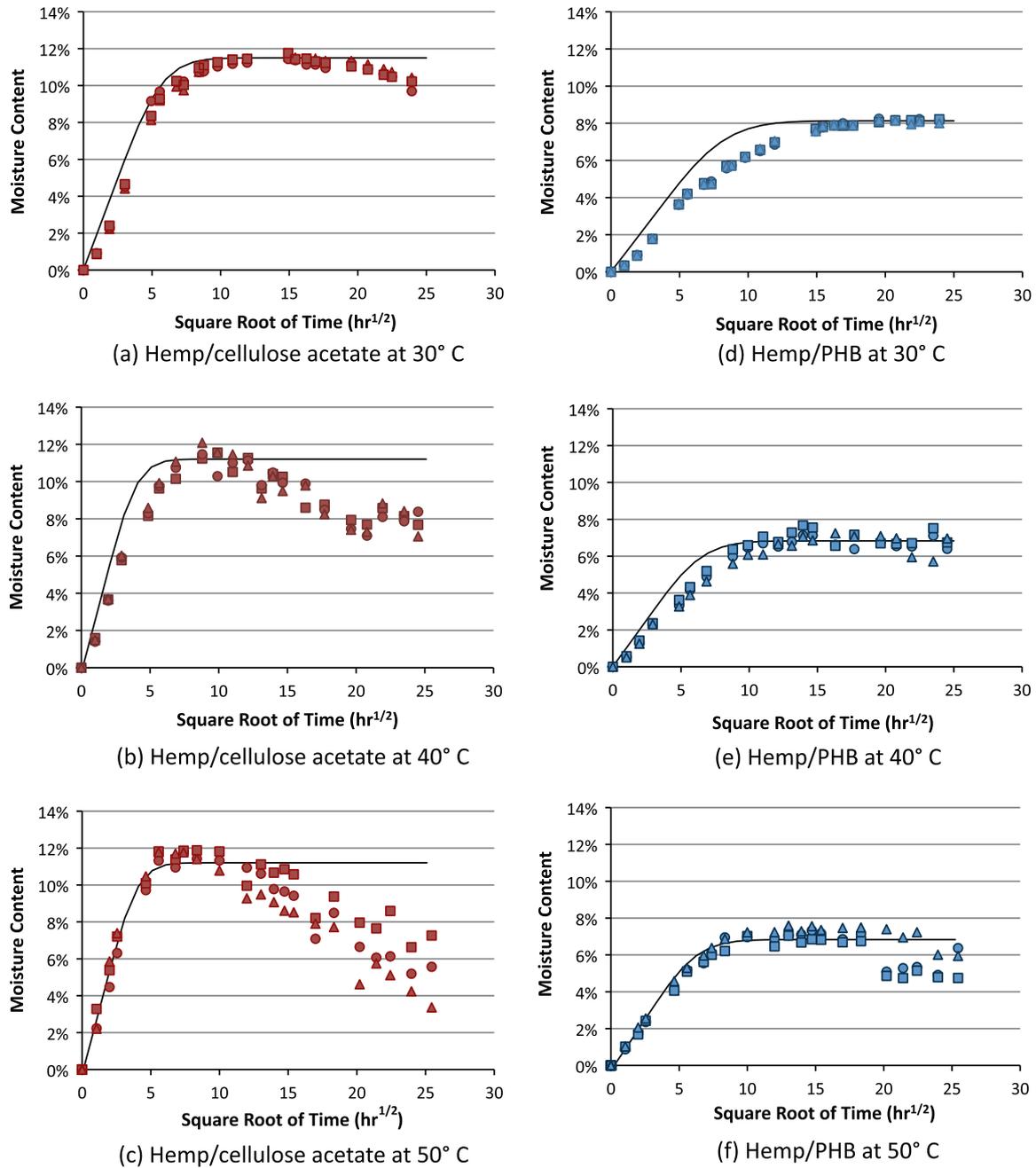


Fig. 2. Moisture measurements of (a–c) hemp/cellulose acetate composite specimens, and (d–f) hemp/PHB composite specimens at 3 different temperatures. Each marker geometry represents one of the three specimens used for measurements per material/temperature combination.

Table 2
Diffusion coefficients.

Material	Temp. (°C)	<i>h</i> (mm)	<i>M</i> ₂ (%)	<i>M</i> ₁ (%)	$\sqrt{t_2}$ (\sqrt{h})	$\sqrt{t_1}$ (\sqrt{h})	<i>M</i> _m (%)	<i>D</i> (mm ² /s)	<i>D</i> _x (mm ² /s)
Hemp/cellulose acetate	30	2.83	4.53	2.31	3.02	1.90	11.50	1.30E–05	1.12E–05
Hemp/cellulose acetate	40	2.91	3.66	1.49	1.95	1.00	11.20	1.91E–05	1.63E–05
Hemp/cellulose acetate	50	2.83	5.24	2.58	1.99	1.05	11.20	2.76E–05	2.37E–05
Hemp/PHB	30	3.09	3.64	1.78	4.94	3.02	8.13	7.33E–06	6.20E–06
Hemp/PHB	40	3.03	2.33	1.33	2.92	1.95	6.83	1.13E–05	9.57E–06
Hemp/PHB	50	3.06	2.44	1.83	2.55	1.99	6.83	1.35E–05	1.14E–05

diffusion coefficients for both materials increased with increasing temperature because, at higher temperatures, water molecules contact the surface of the specimen at increased rates leading to

increased rates of diffusion. Maximum moisture content was observed to be independent of the conditioning temperature for these materials and the range of conditioning temperatures considered.

4.2. Impact of temperature on diffusion

After reaching saturation, the hemp/cellulose acetate composites and the hemp/PHB composites at 40 °C and 50 °C, respectively, began to lose mass. Loos et al. explained this phenomenon for polyester-E-glass composites by suggesting that, as moisture was absorbed, microcracks formed in the matrix due to hygrothermal stresses brought about by differential moisture expansion of the matrix and fibers [19]. As the specimens saturated, they were all observed to swell (thickness increases noted in Section 4.3) and the specimen color darkened due to moisture absorption. Upon cracking, matrix particles were observed to have crumbled from the specimens. Cracking and flaking were evident through visual inspection for both the hemp/cellulose acetate and hemp/PHB composites and were most pronounced at the higher temperatures. Hydrolytic degradation of both the cellulose acetate matrix and the PHB matrix is another possible cause for polymer decomposition and eventual mass loss [20,21].

With the cellulose acetate composites, after the maximum moisture content was reached, portions of the specimens began to lighten in color as crazing occurred in the matrix followed by flaking off of the matrix exposing the lighter colored fibers. The surface texture of the hemp/cellulose acetate composites roughened in comparison to the unconditioned composite and this roughening is attributed to fiber swelling (as observed through composite swelling), hydrolysis, crazing, and flaking of the matrix material.

When the hemp/PHB composites saturated at 50 °C were removed from the moisture chamber for mass measurements, the surface was covered by a slippery paste, which, when allowed to dry dried to a powder. For these composites, some of the matrix was likely lost when the specimens were blotted to remove moisture from the surface prior to mass measurement. The loss of matrix particles likely occurred throughout the duration of the conditioning, but was most pronounced once the maximum moisture content had been reached. Prior to reaching the maximum moisture content, moisture was being absorbed so quickly that the any loss of mass was not apparent through mass measurement. Less paste was observed on the specimens conditioned at 30 °C and 40 °C, which suggests that higher temperatures will cause more material degradation for PHB composites.

The diffusion measurements showed that the diffusion coefficients for the biobased composite materials increased with increasing temperature. The diffusion coefficients for petroleum-derived composites also increase with increases in temperature (e.g. Table 3) and have been shown to increase according to the Arrhenius equation:

$$D = D_0 e^{-C/T} \quad (4)$$

where D is the diffusion coefficient, T is the temperature at which diffusion is occurring, and D_0 and C are referred to as the Arrhenius coefficients [22]. By taking the natural log of each side of Eq. (4), the natural log of D is shown to have a linear relationship with the inverse of the temperature:

$$\ln D = \ln D_0 - C(1/T) \quad (5)$$

From Eq. (5), the Arrhenius coefficients, D_0 and C , can be determined from the experimentally determined diffusion coefficient, D , at temperature, T , by plotting $\ln D$ versus $1/T$ (Fig. 3) and performing a linear regression. If the correlation is strong, the relationship between diffusion coefficient and temperature can be modeled by the Arrhenius equation, as is the case with the biobased composites studied here (Fig. 3).

The Arrhenius coefficients for the biobased composites tested here are tabulated in Table 4 and compared to those of other composite materials in Section 5.1.

4.3. Impact of diffused moisture on uniaxial tensile response

At testing, the average apparent moisture content in the tensile specimens that were saturated then allowed to dry as compared to the mass prior to conditioning was 0.26% higher for the hemp/PHB specimens and 0.21% lower for the hemp/cellulose acetate specimens. Additionally, after conditioning, the biobased composites had a permanent change in thickness, which in this case is the dimension normal to the planes of fabric, of 7.7% and 3.1% for the hemp/cellulose acetate and the hemp/PHB composites, respectively.

The stress–strain behaviors for the hemp/cellulose acetate and hemp/PHB composites with various conditioning are shown in Figs. 4 and 5, respectively. Upon saturation, initial stiffness decreased by 75% and 29% for the hemp/cellulose acetate and hemp/PHB composites, respectively (Table 5). After some yielding and nearly plastic straining, stiffening occurs for the saturated and the saturated-then-dried specimens. The stress–strain behavior upon drying of saturated specimens did not return to that of the unconditioned state despite being at roughly the same moisture content and temperature. Therefore, saturation can be assumed to have caused permanent damage to both biobased composites. While some increase in stiffness was evident upon drying for the hemp/cellulose acetate composites, very little was observed for the hemp/PHB composite.

The mechanical properties from these tension tests are summarized in Table 5. In general, moisture conditioning of the hemp/cellulose acetate composites showed a larger change in properties than moisture conditioning of the hemp/PHB composites. Yet, upon drying, the hemp/cellulose acetate properties recovered more than the hemp/PHB properties. The strength of the composites was the least affected mechanical property. While the strength degradation by 16% for the hemp/cellulose acetate was most severe when saturated, the hemp/PHB composite was observed to increase in strength by 8% upon saturation (Table 5). After saturation and then drying, the strength of the hemp/PHB composite reduced with respect to both the “unconditioned” and “saturated” strengths (Table 5).

Generally, all hemp/cellulose acetate specimens failed by brittle fiber rupture. Prior to failure, the conditioned specimens displayed more warning of the impending failure with 108% and 77% increase in strain at failure for the saturated and saturated then dried specimens, respectively (Table 5). The relatively short fibers protruding from the fracture surface, as shown in Fig. 6a, show that the unconditioned composite failed by fiber rupture. This failure was sudden, marked by a loud bang with no visual warning (such as cracking) prior to failure. The hemp/cellulose acetate composites that were saturated-then-dried, failed by fiber rupture with slight fiber pull-out (Fig. 6b). Microcracking was visually observed during testing which coincided with the plateau region on the stress–strain graph (at a tensile strain of 0.008 mm/mm and beyond in Fig. 4). Just before failure, a few pops were heard that could be associated with fiber rupture. The saturated hemp/cellulose acetate composite showed the most significant fiber pull-out followed by fiber rupture (Fig. 6c). Failure in the saturated specimens was a slow process in which a white band first spread across the specimen, followed by a slow separation of the two pieces of the specimen. The slightly more ductile failure mode for the saturated specimens while noticed visually was not apparent from the stress–strain response (Fig. 4).

The failure mode for the unconditioned hemp/PHB specimens was largely fiber fracture with slight fiber pull-out (Fig. 7a). Tiny horizontal cracks formed on the surface of the specimen (observed

Table 3
Diffusion coefficients and maximum moisture contents for various FRP composites.

Material	Conditioning temperature (°C)	Moisture condition	M_m (%)	D_x (mm ² /s)
Hemp(40%)/cellulose acetate	30	100% RH	11.50	1.12E–05
	40	100% RH	11.20	1.63E–05
	50	100% RH	11.20	2.37E–05
Hemp(40%)/PHB	30	100% RH	8.13	6.20E–06
	40	100% RH	6.83	9.57E–06
	50	100% RH	6.83	1.14E–05
E-glass/polyester [19]	32	100% RH	3.60	6.00E–07
	50	100% RH	4.00	1.80E–06
	65	100% RH	3.50	3.40E–06
	30	60% RH	1.25	4.30E–06
	30	40% RH	0.65	6.90E–06
	23	Immersed in water	3.50	5.10E–07
	50	Immersed in water	3.75	2.10E–06
Rice Hulls(40%)/HDPE [13]	23	Immersed in water	7	3.96E–07
Rice Hulls(55%)/HDPE [13]	23	Immersed in water	12	4.50E–07
Rice Hulls(65%)/HDPE [13]	23	Immersed in water	18	8.42E–07
Sisal(15%)/MaterBi-Y [9]	5	Immersed in water	18.2	3.00E–06
	25	Immersed in water	21.6	5.00E–06
	60	Immersed in water	39.3	2.20E–05
	25	Immersed in water	5.5	6.25E–07
Coir(30%)/LDPE [14]	45	Immersed in water	6.5	7.56E–07
	75	Immersed in water	7.0	1.03E–06

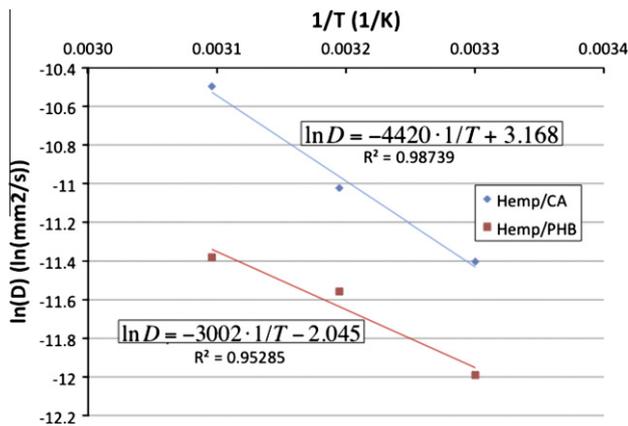


Fig. 3. Temperature-dependency of diffusion and Arrhenius rate-law relationships.

at a strain of roughly 0.02–0.03 mm/mm) prior to failure. Again prior to ultimate failure, the conditioned specimens displayed more warning of the impending failure with a 70% and 33% increase in strain at failure for the saturated and saturated then dried specimens, respectively (Table 5). The saturated then dried specimens showed more prominent horizontal cracking corresponding to the plateau region of the stress–strain graph (observed at a strain of roughly 0.015 mm/mm). The failure mode for these

specimens was a combination of fiber pull-out and rupture (Fig. 7b). The visually observed fiber pull-out corresponds to the rapid reduction in stiffness prior to the brittle failure as shown by the stress–strain response (Fig. 5). The saturated specimens also showed horizontal cracking and a combination of fiber pull-out and rupture (Fig. 7c). Flaking of the surface layer of the matrix was observed near the fracture surface.

4.4. Impact of saturation temperature on uniaxial tensile response of saturated composites

The tensile stress–strain behavior for saturated hemp/cellulose acetate and hemp/PHB specimens are shown in Figs. 8 and 9, respectively. From the graphs, it is clear that little variation exists in the tensile response of the specimens conditioned at different temperatures. The behavior shown in these figures can be assumed to result from saturation, not elevated temperatures. Thus, while elevated temperature affects the rate of diffusion, it does not cause more significant damage. Despite the measured loss in mass for the hemp/cellulose acetate composites conditioned at 40 °C and 50 °C, the stress–strain behavior is similar to the specimens conditioned at 30 °C. Variation in failure mode with conditioning temperature was not observed for either material; all tested specimens failed by fiber pull-out.

Table 4
Arrhenius constants for composites.

Material	Conditioning method	D_0 (mm ² /s)	C (K)
Hemp/cellulose acetate	Humidity	23.8	4420
Hemp/PHB	Humidity	0.13	3002
Sisal(15%)/MaterBi-Y [9]	Immersion in water	14.42	3870
Graphite/epoxy (Fiberite T300/1034) [22]	Humidity	2.28	5554
Graphite/epoxy (Fiberite T300/1034) [25]	Humidity	0.44	5058
Graphite/epoxy (Hercules AS/3501–5) [22]	Humidity	6.51	5722
Graphite/epoxy (Hercules AS/3501–5) [26]	Humidity	0.44	4768
Graphite/epoxy (Hercules AS/3501–5) [27]	Humidity	28.8	6445
Graphite/epoxy (Narmco T300/5208) [22]	Humidity	0.57	4993
Graphite/epoxy (Narmco T300/5208) [28]	Humidity	0.41	5231
Graphite/epoxy (Fiberite T300/1034) [22]	Immersion in water	16.3	6211
Graphite/epoxy (Hercules AS/3501–5) [22]	Immersion in water	768	7218
Graphite/epoxy (Narmco T300/5208) [22]	Immersion in water	132	6750

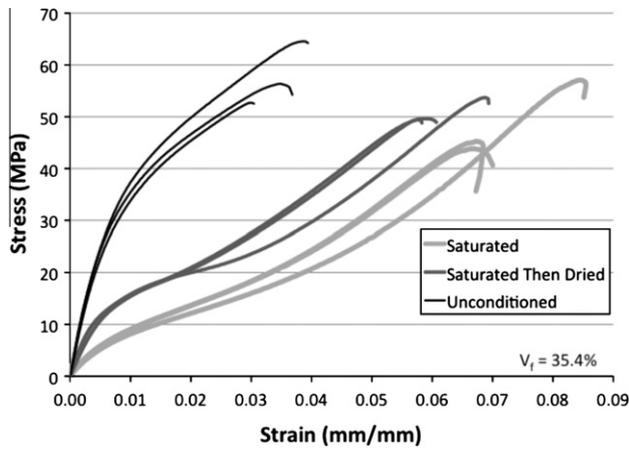


Fig. 4. Stress–strain behavior of conditioned and unconditioned hemp/cellulose acetate composites.

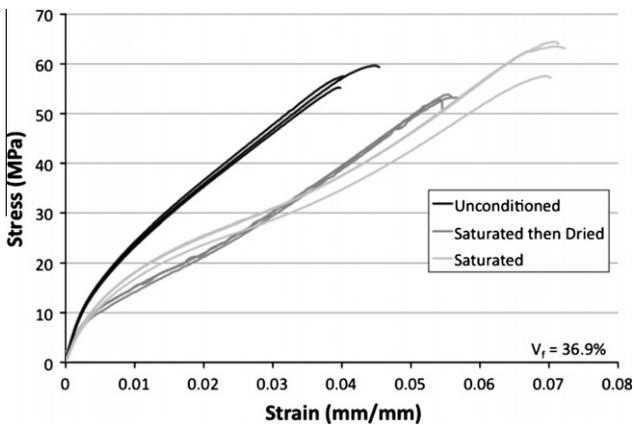


Fig. 5. Stress–strain behavior of conditioned and unconditioned hemp/PHB composites.

5. Discussion

5.1. Comparison of diffusion coefficients to other composite materials and wood products

To determine how the rates of diffusion for the biobased composites compare to other materials, the materials must be conditioned in the same manner (at the same temperature and moisture condition) as the rate of diffusion is dependent on the concentration of moisture at the surface of the material. Most of the diffusion data for natural fiber composites reported in the literature was measured as the composites were immersed in water. Therefore, only qualitative and not direct comparisons can be

made between immersed materials and those studied here (conditioned at 100% RH).

Table 3 shows the unidirectional diffusion coefficients for other composites made with both natural and synthetic fibers. As compared to the fully synthetic fiber composite of E-glass/Polyester, which was also conditioned to 100% RH, the rate of diffusion for the biobased composites was higher given their use of hydrophilic natural fibers.

The diffusion coefficients for the biobased composites studied here are comparable to the other natural fiber composites tabulated in Table 3 if the difference in conditioning is considered. That is, the hydrophobic matrices (PHB, HDPE, Polyester, and LDPE) help to reduce maximum moisture content and diffusion rate for natural fiber composites when conditioned in a similar manner compared to those with hydrophilic matrices (Cellulose Acetate, MaterBi-Y). The diffusion in the PHB composite is faster than in the HDPE and LDPE composites in most part because the form of fiber in the PHB composite is a fabric, which was exposed at the edges and could act to funnel moisture into the composite as opposed to the short fibers that were used in the LDPE and HDPE composites. As discussed in Section 4.1, anisotropic diffusion properties were not measured or considered in the determination of D_x , leading to an overestimation of the diffusion coefficient. Both the hemp/PHB and the hemp/cellulose acetate composites absorbed less moisture than the Sisal/MaterBi-Y composites, which is the only other completely biobased composite shown in Table 3. The high moisture absorption in the Sisal/MaterBi-Y was attributed to the hydrophilic starch-based matrix.

The diffusion coefficient for wood is in the range of 0.00001 – 0.0001 mm^2/s^2 [23]. The moisture content is about 12% for dry wood and greater than 20% for green wood [24]. The diffusion coefficients and moisture content for engineered wood products would likely be lower than for wood because in engineered wood, the wood is usually mixed with hydrophobic polymer matrices to form the products. Thus, the biobased composites studied here have diffusion properties comparable wood and most likely higher than engineered wood products.

The Arrhenius coefficients for the biobased composites tested here are compared to the Arrhenius coefficients for other synthetic and natural fiber composites in Table 4. The measured and computed coefficients for the biobased composites fall within the range of coefficients for other composites. The wide range of coefficients that were found by other researchers for the same material tested in different laboratories shows the extreme variation that is possible when determining these values. Such large variations suggest that either the relationship between diffusion and temperature fluctuates widely with material or that implementation of experimental methods may be inconsistent.

5.2. Damage mechanisms from diffused moisture impacting tensile properties

Changes in the mechanical properties of the biobased composites may be attributed to a number of factors including plasticiza-

Table 5
Summary of mechanical properties of moisture-conditioned composites.

Conditioning	Strength		Young's modulus		Strain at failure	
	(MPa)	% Change	(MPa)	% Change	%	% Change
<i>Hemp/PHB</i>						
Unconditioned	57.5 ± 2.2	–	4340 ± 160	–	4.2 ± 0.3	–
Saturated–dried	53.3 ± 2.5	–7	3730 ± 200	–23	5.6 ± 0.1	33
Saturated	61.8 ± 3.7	8	3420 ± 150	–29	7.1 ± 0.1	70
<i>Hemp/cellulose acetate</i>						
Unconditioned	57.9 ± 6.1	–	5990 ± 350	–	3.6 ± 0.5	–
Saturated–dried	50.9 ± 2.4	–12	3230 ± 570	–46	6.3 ± 0.6	77
Saturated	48.7 ± 7.3	–16	1490 ± 70	–75	7.4 ± 1.0	108

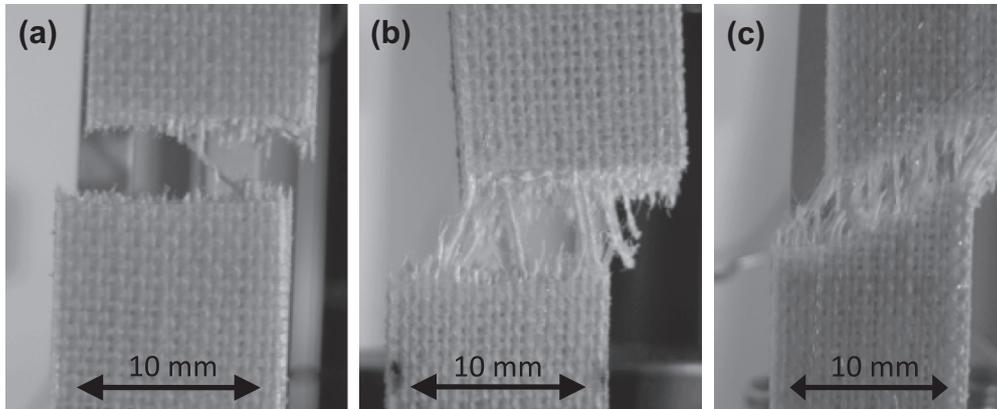


Fig. 6. Failure of (a) unconditioned hemp/cellulose acetate composite by fiber rupture, (b) saturated then dried hemp/cellulose acetate composite by fiber pullout then rupture, and (c) saturated hemp/cellulose acetate composite by fiber pullout then rupture.

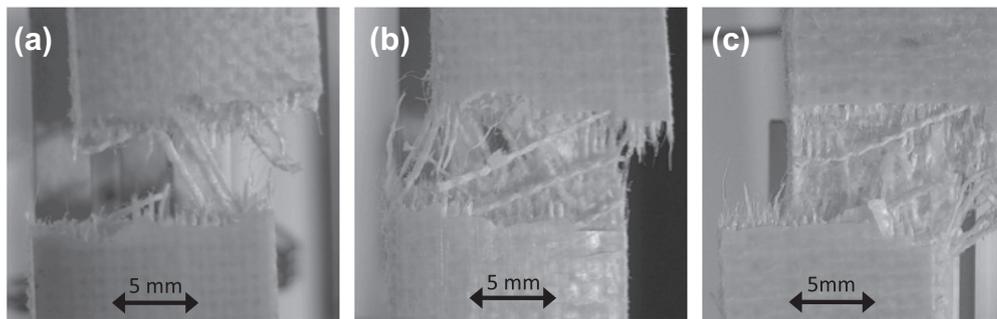


Fig. 7. Failure of (a) unconditioned hemp/PHB composite by fiber rupture, (b) saturated then dried hemp/PHB composite by fiber pullout and rupture, and (c) saturated hemp/PHB composite by fiber pullout and rupture.

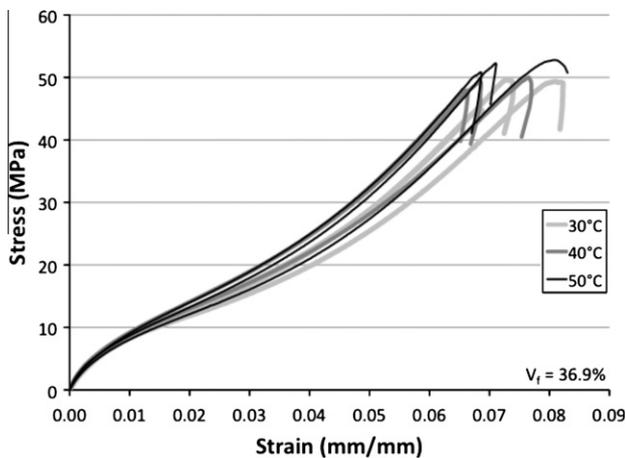


Fig. 8. Tensile response of hemp/cellulose acetate composites saturated at three temperatures.

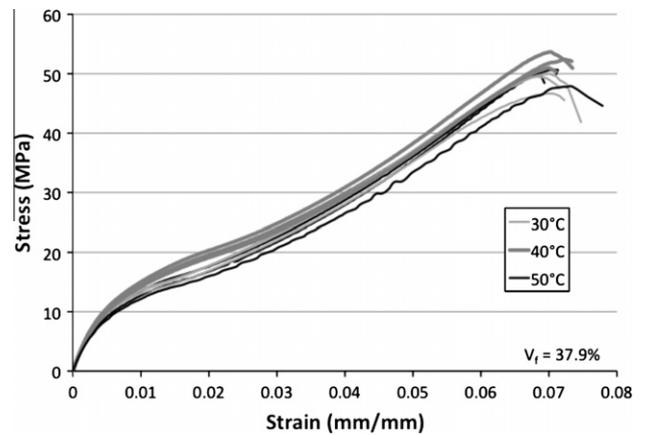


Fig. 9. Tensile response of hemp/PHB composites saturated at three temperatures.

tion and hydrolysis of the matrix, plasticization of the cellulose and lignin in the fibers, degradation of the fiber–matrix interface, and matrix cracking. Water can act as a plasticizer as moisture enters both the matrix and the fiber. The material stiffness is lowered as plasticizers penetrate the space between the polymer chains and push the chains apart effectively lowering the glass transition temperature for the plastic and making it softer. Additionally, moisture penetration may have led to hydrolytic decomposition of the matrix material as well as deterioration of the fiber–matrix interface thus lowering the fiber–matrix interfacial shear strength. Finally, due to dimensional stability issues upon absorption of moisture,

the composite cracked leading to matrix flaking and mass loss (as evidenced by the apparent lowering of moisture content after saturation in Fig. 2). The damaged cross-sections would behave differently than the un-damaged cross-sections, again lowering stiffness.

From a comparison of the stress–strain behavior, it is observed that although the hemp fabric absorbed moisture in both composites, the hemp modulus did not decrease. The slope of the stress–strain response just prior to failure was relatively similar for all materials (Figs. 4 and 5). Because the stiffness of the conditioned composites after cracking and crazing (i.e., the plateau region) was similar to the secondary stiffness (post-matrix yielding) for

the unconditioned specimens, it is believed that the hemp fiber in the saturated composite was not plasticized.

Fiber pull-out was evident from the long fibers protruding at the failure surfaces of both composites after saturation (Figs. 6 and 7). The fiber pull-out is believed to be evidence of a weakened fiber–matrix interface. While the unconditioned specimens tended to fail at one cross-section perpendicular to loading with all fibers failing in the same plane, the weak fiber–matrix interface of the saturated specimens failed allowing the fibers to rupture at their weakest location above or below the fracture surface. Thus longer fibers protruded from the fracture surface. Slightly lower strengths would result if the fibers failed at their weakest location rather than in one cross-section.

The strength of the hemp/PHB composite increased slightly (8%) upon saturation. The maintaining of strength could be the result of a temporarily improved fiber–matrix interface from differential moisture swelling. The behavior of the saturated then dried specimen is evidence that moisture penetrated and weakened the fiber–matrix interface of the hemp/PHB composites causing large reductions in stiffness. However, if the yarn swelled significantly upon absorption of moisture and exerted pressure on the surrounding unplasticized PHB matrix, that could have resulted in increased mechanical interaction through friction leading to a slightly higher material strength, despite potential chemical bond/interface deterioration. Given that the thickness of the specimens was permanently increased after saturation and drying, it can be assumed that swelling fibers permanently changed the position of the matrix. Upon drying, the fiber swelling was reduced leaving a weakened fiber–matrix interface. Thus, a strength reduction (and no stiffness recovery) was found for the saturated then dried hemp/PHB composite.

When the hemp/PHB composite absorbed moisture, the initial modulus of elasticity decreased by 29%. Upon drying, only a slight rebound (increase) in modulus was measured. Because the rebound was so small and the PHB matrix is known to be both hydrophobic and have high crystallinity, it can be deduced that the PHB matrix absorbed only small amounts of moisture and was not plasticized by the water. In contrast to the hemp/PHB, the modulus of the hemp/cellulose acetate rebounded somewhat upon drying. As moisture entered the hydrophilic cellulose acetate, it plasticized the polymer and lowered the stiffness. Upon moisture desorption, the cellulose acetate stiffness increased. The permanent degradation of the moduli for both materials is attributed to irreversible damage caused by matrix cracking.

The change in the shape of the stress–strain graph for both composites from a bi-linear response in the unconditioned state to a tri-linear response in the saturated and saturated-then-dried states is likely due to matrix crack propagation through the thickness of the conditioned specimens. While tiny cracks were observed at the matrix surface prior to testing, more significant horizontal cracks began to appear on the specimen surfaces as the plateau region was forming (beginning at about 0.1% strain). Given that cracking was already present at the start of loading, a stress concentration at the tip of a crack would cause a crack to propagate. Many cracks along the length of the composite propagated at approximately the same stress causing significant straining over a relatively small increase in stress. Once the cracks formed, the fibers bridging across the cracks were reengaged and the stiffness of the conditioned composites again increased prior to failure.

6. Summary and conclusions

The rate of moisture diffusion into two biobased composites materials and how that moisture affects composite mechanical behavior has been investigated. Specifically, cellulose acetate and

PHB biopolymer matrices with hemp fabric reinforcement were studied. The diffusion and tensile properties were measured for these biobased composites conditioned in a moisture chamber at 100% relative humidity at three different temperatures.

The diffusion coefficients, calculated using Fick's Law, for both biobased composites were comparable to wood and other biobased composites and higher than the coefficients for synthetic composites. The cellulose in the hemp fiber is hydrophilic and absorbs a significant amount of water similar to the cellulose in wood, but in contrast to synthetic fibers such as glass. The hemp/cellulose acetate composite absorbed 40–60% more moisture than the hemp/PHB composite. This observation is attributed to the cellulose acetate itself being hydrophilic whereas PHB is both hydrophobic and more crystalline than cellulose acetate. The rate of diffusion for both materials was found to increase with increasing temperature. The behavior was found to be Fickian until near saturation at which point there was some material loss, which is attributed primarily to damage from the swelling of the natural fibers.

To determine the effects of moisture on mechanical behavior, specimens conditioned by saturation and by saturation followed by drying were tested in tension and compared to unconditioned specimens tested in tension. The hemp/cellulose acetate composites were more affected by moisture absorption than the hemp/PHB composites. The initial moduli of elasticity decreased upon saturation by 75% and 29% for the hemp/cellulose acetate and hemp/PHB composites, respectively. Strain at failure increased by 70% for the hemp/PHB and 108% for the hemp/cellulose acetate. The strength properties degraded by 16% for the hemp/cellulose acetate and increased by 8% for the hemp/PHB composite. The absorption of moisture likely plasticized the cellulose acetate (possibly leading to hydrolytic decomposition) and also weakened its interfacial bond to the fibers resulting in degraded mechanical properties. In the PHB composite, there was less damage to the PHB itself when saturated but still a loss of composite stiffness attributed to changes in interfacial bond and fiber swelling. The strength increase for the hemp/PHB composite may have been the result of increased fiber–matrix interaction due to differential moisture swelling: the fiber swelled while the matrix did not, thus increasing the mechanical bond and frictional resistance when saturated.

To determine if saturation may cause permanent damage to the biobased composites, specimens were saturated and then allowed to dry in the unconditioned environment prior to tensile testing. Upon drying some of the lost properties were recovered, but permanent damage was apparent, as the stress–strain behavior did not return to the unconditioned behavior. The strength of the hemp/PHB composites decreased by 14% upon drying from the saturated state. Permanent damage was attributed to damage to the interface from the moist-dry cycle and cracking or crazing of the matrices due to stresses from fiber swelling.

The mechanical properties of biobased composites conditioned to full saturation at different temperatures were compared and the temperature within the conditioning chamber was found to have no effect on tensile behavior.

The degradation of mechanical properties upon introduction to humid environments limits the potential applications of these biobased composites. For these biobased composites to be used widely within the construction industry, the original motivation for the study, they must be protected from moisture for example through sealants and/or fiber treatments. Due to its hydrophobic behavior, the PHB matrix will likely be more suitable for use in humid environments than the cellulose acetate matrix. The results of this research are currently being used to guide the optimal design of new composites for both moisture-resistant in-service performance as well as rapid anaerobic biodegradation out-of-service [7].

Acknowledgments

This research was funded in part by the Woods Institute for the Environment at Stanford University as well as the California EPA (Grant No. 07T3451). The opinions expressed in this paper are those of the authors and do not necessarily represent the opinions of any of the sponsors.

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