

## Mechanical Performance and Moisture Absorption of Various Natural Fiber Reinforced Thermoplastic Composites

Nicole-Lee M. Robertson,<sup>1</sup> John A. Nychka,<sup>1</sup> Kirill Alemaskin,<sup>2</sup> John D. Wolodko<sup>2</sup>

<sup>1</sup>Department of Chemical & Materials Engineering, University of Alberta, 7th Floor, ECERF, 9107-116 Street, Edmonton, Alberta, Canada T6G 2V4

<sup>2</sup>Alberta Innovates, Technology Futures, Advanced Materials Group, 250 Karl Clark Road, Edmonton, Alberta, Canada T6N 1E4

Correspondence to: J. D. Wolodko (E-mail: john.wolodko@albertainnovates.ca)

**ABSTRACT:** Natural fibers are seeing increased use in composite applications due to their reduced cost, low density, and environmental benefits (more sustainable and lower carbon footprint). Although many natural fiber systems have been examined over the last decade, there have been relatively few studies which have compared a variety of fiber types and processing methods directly in the same experimental set. In this study, natural fiber composites made from low density polyethylene (LDPE) and a variety of Canadian based fiber feedstocks were examined including hemp bast, flax bast, chemically pulped wood, wood chips, wheat straw, and mechanically pulped triticale. The effect of fiber type, fiber fraction and maleic anhydride polyethylene (MAPE) coupling agent on the mechanical properties and long-term moisture absorption behavior was quantified. In general, addition of natural fiber to LDPE results in an increase in modulus (stiffness) with a corresponding loss of material elongation and impact toughness. Of the fiber types tested, composites made from chemically pulped wood had the best mechanical properties and the least moisture absorption. However, the use of MAPE coupling agent was found to significantly increase the mechanical performance and reduce moisture absorption for all other natural fiber types. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

**KEYWORDS:** cellulose and other wood products; composites; degradation; thermoplastics; mechanical properties

Received 15 December 2012; accepted 24 February 2013; published online 00 Month 2013

DOI: 10.1002/app.39237

### INTRODUCTION

Over the past decade, there has been an increased awareness and demand for greener, more sustainable materials and products. Natural fiber reinforced composites, one type of biocomposites, are a viable material option in an effort to help close the carbon cycle and manufacture greener plastic parts. Biocomposites are composed of two or more distinct materials, with at least one being biologically derived, which are combined to yield a new material with improved performance over the original components. The advantages of using natural fibers, as opposed to synthetic fibers, are lower cost, sustainability (renewable), biodegradability (end of life), and their relatively low density. Potential applications of biocomposites span transportation (light weight parts) to low cost construction materials.<sup>1,2</sup> Applications have already been realized by the automotive sector, and various market segments continue to look for innovative ways to utilize biocomposites.<sup>3</sup> A unique aspect of natural fiber composites is the fact that they can be produced using a variety of plant feed stocks from around the world. Competitive advantage can be achieved only by assessing the cost-benefit of

various source materials grown both globally and locally. Although there is significant potential for these materials, the widespread use of natural fiber composites has yet to be realized due to a number of drawbacks including lower mechanical properties (compared to synthetic fiber composites), and an affinity for absorbing moisture.

Both the mechanical and moisture absorption properties of natural fiber thermoplastic composites have been extensively investigated over the past decade.<sup>1–16</sup> This body of knowledge has included the characterization of a wide range of natural fiber types including: wood, hemp, jute, flax, cotton, wheat straw, pineapple leaf, bagasse, henequen, rice husks and straw, reed fibers and recycled paper. In these previous studies, however, moisture absorption is often only characterized over a relatively short period of time (less than 60 days or 1500 h). There is limited long-term absorption data available for most natural fiber types.

Although the vast majority of research has focused on characterizing individual fiber feedstocks, only a few studies have

directly compared the performance of a wide range of fiber types and processing conditions under equivalent experimental conditions (i.e., same matrix and compounding conditions). Xu et al.<sup>6</sup> studied the mechanical, thermal, and moisture absorption characteristics of polyvinyl chloride composites compounded with bagasse, rice straw, rice husk, and pine fiber along with an impact modifier at one fiber fraction (30% by weight). The authors found that tensile strength did not vary with fiber type but impact properties varied with impact modifier and fiber type. Yao et al.<sup>11</sup> investigated the mechanical and crystallization properties of virgin and recycled high density polyethylene reinforced with a number of rice plant byproducts including husks, leaves, straw stems and whole straw, as well as wood fiber at two fiber fractions (30 and 50% by weight).

Another factor which has been shown to be important for both mechanical and moisture absorption properties in natural fiber composites is the interfacial bonding between the fiber and matrix. In most natural fiber composites, a weak bond typically exists between the fiber and matrix due to the incompatible nature of most thermoplastics (hydrophobic) and natural fibers (hydrophilic). Improvements in mechanical properties have been shown by utilizing fiber surface treatments and coupling agents.<sup>14–19</sup> For example, maleic anhydride (MA), a common coupling agent, increases the degree of interfacial adhesion between the matrix and the natural fiber by grafting to the thermoplastic matrix polymer. MA acts by covalently bonding to hydroxyl groups available on the surface of the natural fibers.<sup>7,14,15</sup>

The aim of the current study is to evaluate the effect of fiber type on the mechanical properties and long-term moisture absorption characteristics of a thermoplastic composite made from a single matrix material (low density polyethylene with and without maleic anhydride) and a variety of fiber feedstocks grown in a Canadian setting.

## EXPERIMENTAL

### Materials

Six (6) fiber types, including hemp bast, flax bast, wood chips, chemically pulped wood, wheat straw, and mechanically pulped triticale, were tested in this investigation. Fibers were supplied and processed at Alberta Innovates Technology Future's (AITF) lab facilities in Edmonton, Canada. Fiber processing methods varied depending on fiber type, and included retting, decortication, chopping, milling, mechanical pulping (refining) and/or wet chemical pulping. A summary of processing conditions for each fiber type is shown in Table I. As shown in Figure 1, there was a clear difference in physical morphology and geometry between the fiber types after processing (prior to composite manufacturing). The macro photographs demonstrate the general appearance and clumping tendency of a small sample (<1 cm<sup>3</sup>). The inset pictures are optical microscope silhouettes using bright field reflected light (Zeiss Axio Imager M2) that demonstrate the typical ranges in fiber diameter (note that these are not representative of actual fiber length distributions).

The matrix material used in this study was low density polyethylene (LDPE) supplied from AT Plastics (AT418). The maleic

**Table I.** Processing Methods Used for the Fiber Types Tested

Feedstock	Fiber processing method
Hemp bast fiber	Decorticated, milled and pelletized
Flax bast fiber	Retted and milled
Wood pulp (spruce)	Chemically pulped and milled
Wood chips (spruce)	Chopped and milled
Wheat straw	Chopped and milled
Triticale pulp	Chopped and mechanical pulped

anhydride polyethylene (MAPE) coupling agent was supplied from DuPont (Fusabond MB265D).

### Composite Manufacturing

Composites were manufactured by compounding low density polyethylene (LDPE) with the six available fiber types. Two series of materials were produced in this study: (1) a comprehensive set of specimens at four fiber weight fractions (10, 20, 30, and 40% fiber by weight), and (2) a limited set of specimens with coupling agent at one fiber weight fraction (30 wt % fiber, 5 wt % MAPE, and 65 wt % LDPE by weight). Specimens were also manufactured from the virgin LDPE (unreinforced) for baseline comparison.

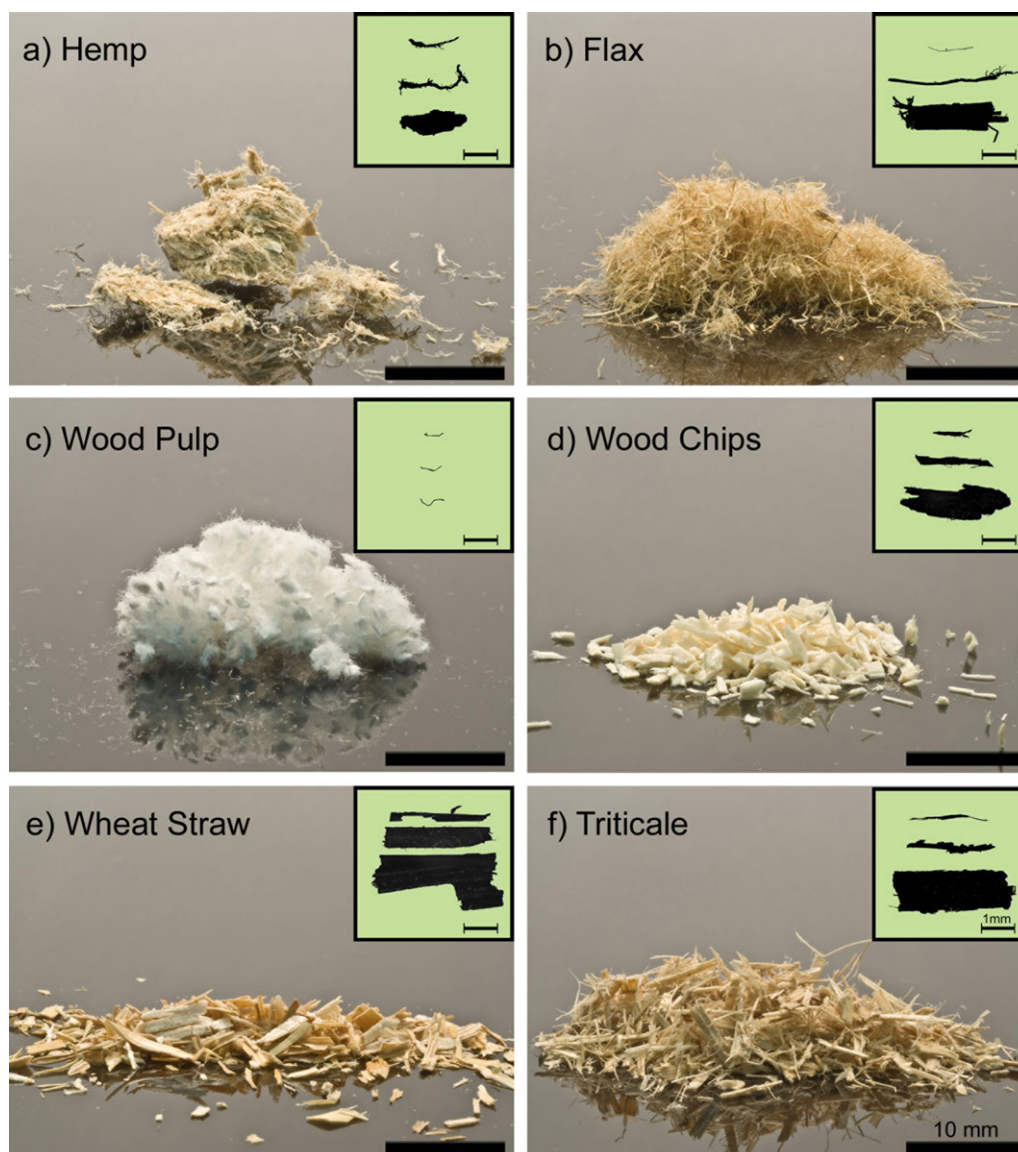
Because of the differences in consistency for the various fiber types, two methods of compounding were used in this study: (1) a twin screw co-rotating extruder (Haake Rheomix PTW 24/40) was used for hemp bast, wood chips, wheat straw, and triticale mechanical pulp, and (2) a batch mixer (Haake PolyLab OS 3000) was used for flax bast and wood pulp. Batch mixing was necessary for the latter since the fibers could not be fed into the extruder at a constant rate. Both compounding methods provide equivalent material forms and properties,<sup>20</sup> however, the extruder is the preferred method as it is a fast, continuous process compared to batch mixing. Initial feeding difficulties encountered for hemp bast were overcome by pre-pelletization using an Amandus Kahl pelletizer (3/8" die).

Once the fiber and polymer were compounded into pellets, material test specimens were injection molded (Battenfeld 100 injection molding system) into both flat bars and tensile "dog-bone" specimens, as per ASTM D790-10 and ASTM D638-10 Type 1, respectively (tensile gage section: 50 mm long by 13-mm wide; thickness: 3.2 ± 0.4 mm). The flat bars were used to make notched Charpy impact test specimens, as per ISO 179 (width: 10.16 ± 0.05 mm; thickness: 3.2 ± 0.4 mm; distance to notch between 61.0 and 63.5mm).

A physical comparison of the final compounded materials is shown in Figure 2 (images taken from the grip section of the tensile specimens). It can be seen that the various fiber types and fiber loadings (weight fractions) produce a significant variation in observed color and texture. This can be attributed to differences in original feedstock color, and to potential color changes as a result of thermal effects during compounding and injection molding.

### Mechanical Testing

Monotonic tensile tests were conducted as per ASTM D638 using an Instron 4032C load frame (5 kN load cell). Tests were



**Figure 1.** Macro photographs and bright field optical micrographs of each fiber type after processing. Macro images illustrate the distribution of fiber diameter and length (inset micrographs are fiber silhouettes demonstrating the typical range in fiber diameter). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

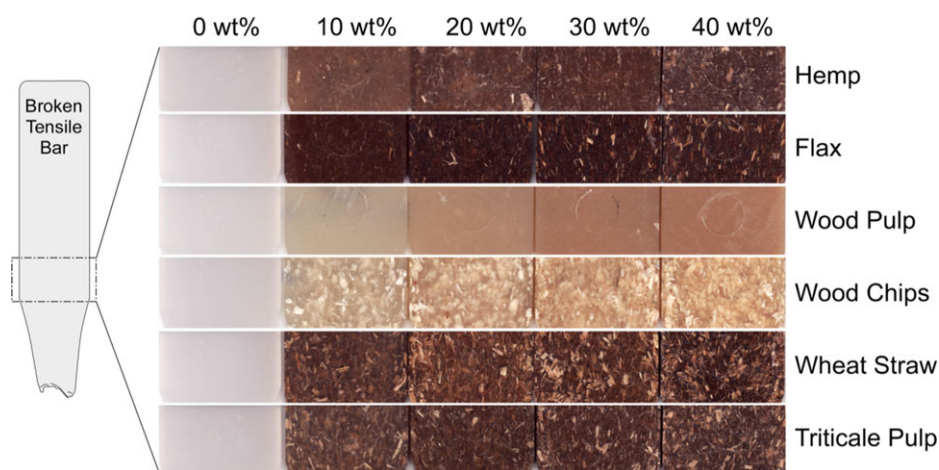
conducted under strain control at a rate of 5 mm/min. Strain measurements were derived from using both a clip-on extensometer (up to 8% strain) and the cross-head displacement (beyond 8% strain). The tensile modulus was determined from the stress-strain curve using the secant method (between stress levels of 0 and 5 MPa), while the tensile strength was taken to be the stress at maximum load. Percent elongation (%El) was determined as the strain reading at break. In addition to tensile tests, Charpy impact tests were also performed as per ISO 179. All specimens were preconditioned for 48 h at constant conditions (23°C and 50% relative humidity) prior to testing. A minimum of five specimens were conducted for each tensile and Charpy impact test.

After testing, fracture surfaces from tensile tests were imaged using a Hitachi S-3000N scanning electron microscope (SEM)

at accelerating voltage 20 kV with a tungsten filament. Fracture surfaces were gold coated prior to imaging using an Edwards S150 Sputter Coater.

#### Moisture Absorption Characterization

Long term water immersion tests were conducted on composite samples over a period of 11,515 h (or 68.5 weeks) in a reverse osmosis water bath at  $22.5 \pm 0.5^\circ\text{C}$ . The water was drained and replaced every 7 days to minimize the chance of microbial attack. Specimens were cut from injection molded bars to dimensions  $16.0 \text{ mm} (\pm 2.0 \text{ mm}) \times 12.4 \text{ mm} (\pm 1.0 \text{ mm}) \times 3.1 \text{ mm} (\pm 0.04 \text{ mm})$ , then were dried for 24 h at  $60^\circ\text{C}$  prior to immersion. Five specimens for each fiber weight fraction and fiber type were submerged in the water bath. At the designated time interval, each specimen was removed from the water, wiped of excess surface water with paper towel and then



**Figure 2.** Physical appearance of manufactured composites by fiber type and fiber loading taken from end tabs of broken tensile bars (all 0 wt % images are of the same virgin LDPE control specimen). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

weighed three times each before being resubmerged. Measurements were taken on a Sartorius LA 3105 four point balance. Moisture absorption was calculated as shown in eq. (1):

$$M = \frac{m_t - m_i}{m_i} \times 100 \quad (1)$$

where  $M$  is the percentage mass gain of the specimen,  $m_i$  is the initial mass of the specimen after drying, and  $m_t$  is the mass of the specimen at the given time interval. Data was reported as the average and standard deviation of five specimens within each set.

## RESULTS AND DISCUSSION

### Mechanical Behavior

The stress–strain response of LDPE reinforced with various fiber types and fiber loadings (no coupling agent) is shown in Figure 3. In general, the trends show that as the fiber content increases, there is a noticeable change in stress–strain response. For all fiber types, there is a definitive increase in elastic modulus and a significant decrease in elongation at failure with increasing fiber fraction. Changes in tensile strength (stress at failure), however, is seen to vary depending on fiber type. Of all the fiber types tested, wood pulp displays the most unique stress–strain curve with large variations in modulus and tensile strength with increasing weight fraction.

A comparison between fiber types can be better seen by separately plotting the trends for modulus, strength, and elongation, as shown in Figure 4. In addition, results from the Charpy impact tests are also provided in this figure.

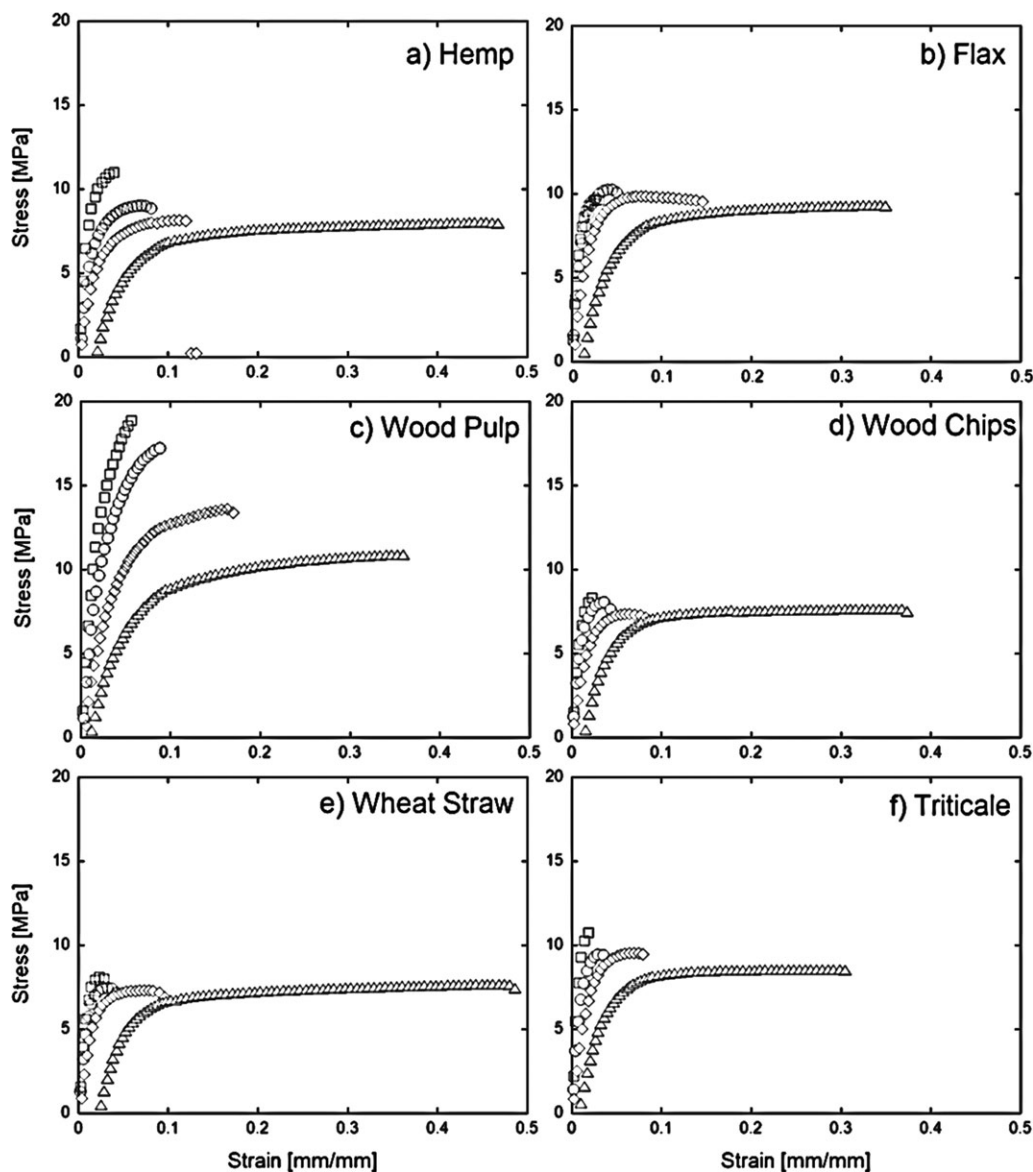
Referring to Figure 4(a), the modulus (stiffness) is seen to significantly increase with increasing fiber weight fraction for all fiber types. At lower fiber fractions (10 and 20 wt %), there is relatively little difference between fiber types, however, at higher fiber fractions, there is more variation. At 40% weight fraction, flax bast and triticale pulp composites had the highest modulus (1.43 and 1.45 GPa, respectively), while the wood chips and wheat straw composites had the lowest (1.13 and 1.07 GPa,

respectively). Compared to the modulus of virgin LDPE (0.110 GPa), the addition of 40% natural fiber by weight results in a minimum increase in modulus of approximately eight times.

As shown in Figure 4(b), all composites tested also showed a general increase in tensile strength with increasing fiber content. The extent of this increase, however, was found to depend on fiber type. Composites made from wood pulp showed the most significant increase in strength. As the content of wood pulp was increased to 40% by weight, there was a corresponding increase in tensile strength to approximately 19 MPa (twice the strength of the virgin LDPE). The remaining fiber types also showed a slight increase in strength with increasing fiber content, but not to the same extent as the wood pulp composites. Compared to the strength of the virgin (unreinforced) LDPE, some fibers types (including wood pulp, flax bast, hemp bast, and triticale pulp) were shown to strengthen the polymer, while the addition of others (wood chips and wheat straw) were shown to slightly decrease the strength.

The Charpy impact strength of the various composites is shown in Figure 4(c). An increase in fiber loading results in decreased impact strength converging to a range of approximately 6–9 kJ/m<sup>2</sup>. The impact results demonstrate that the fibers are responsible for the increased brittle response, and that this response is not dependent on the fiber type. However, it can be noted that at the rate which they converge on this point is different from one fiber to the next, perhaps based on the intrinsic nature of the fibers. Unfortunately, in this study, full characterization of the fiber lengths and diameters was not undertaken.

For the elongation at break [Figure 4(d)], there is a significant drop in failure strain with increasing fiber fraction for all fibers tested. Similar to modulus, however, there does not seem to be a significant difference between the performance of various fiber types. The elongation dropped from a range of 30–47% strain for 10 wt % fiber to only 2–6% strain at 40 wt % fiber. At 10 wt %, hemp bast and wheat straw composites had higher strains at failure relative to flax, wood chip and triticale pulp composites (although there was a higher statistical variation at lower fractions).



**Figure 3.** Representative stress–strain curves for hemp bast, flax bast, wood pulp, wood chips, wheat straw and triticale pulp at 10 wt % ( $\Delta$ ), 20 wt % ( $\diamond$ ), 30 wt % ( $\circ$ ) and 40 wt % ( $\square$ ).

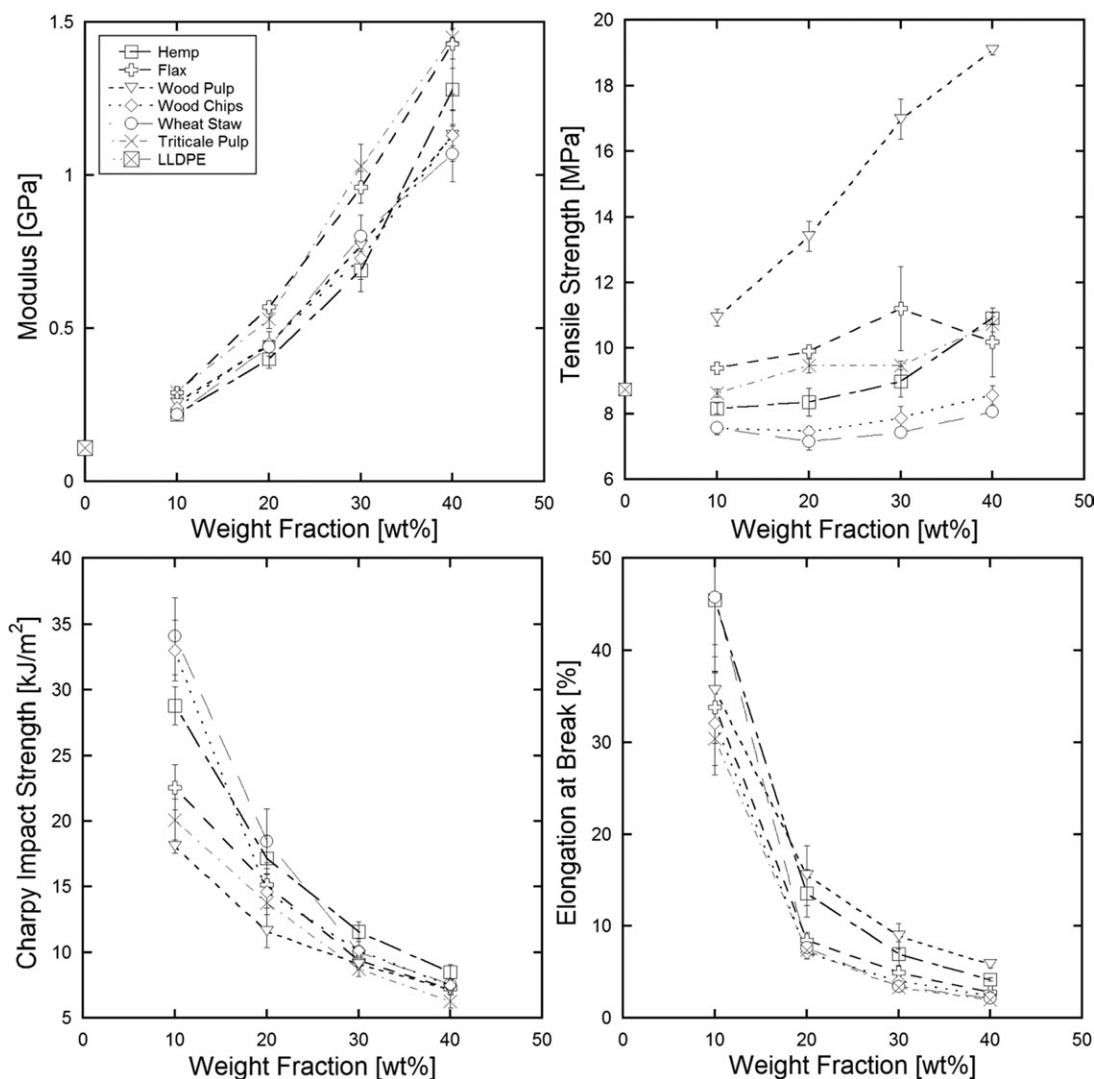
It should also be noted that the data for LDPE is not plotted for the elongation and impact strength. For virgin LDPE, the elongation was found to be 136% strain [and was off the plotted scale in Figure 4(c)]. Similarly, the LDPE samples did not break during Charpy impact testing indicating a very high toughness beyond the capacity of the machine. The observed trends in elongation and toughness show that reinforcing LDPE with natural fibers is a major drawback in applications where elongation and toughness are critical.

To further understand the mechanical behavior observed, representative SEM images of the tensile fracture surfaces were taken for all fiber types, as shown in Figures 5 and 6. In general, the failure surfaces for all natural fiber composites, except for wood pulp, show quite complex and rough fracture surface features (i.e., a large range of particle sizes can be clearly observed in these fractographs). It can be seen that

the failure mechanisms include fiber fracture/splintering, fiber pull-out and debonding, and localized matrix fracture (between fibers).

Conversely, for the wood pulp composite [Figure 6(a)], the fracture surface is smoother and has a more uniform fiber distribution compared to the other fiber types. Additionally, the pulping process has created a much more uniform fiber size distribution (no large particles). Finally, the virgin LDPE fracture surface [as shown in Figure 5(a)] has a ductile failure surface with uniformly distributed micro-cracks.

These comparative observations clearly show why the composites made from chemically pulped wood have improved strengthening over the other fiber types. Overall, increased strength is achieved by utilizing fiber structures with large aspect ratios and uniform sizes [Figure 1(c)], and ensuring that



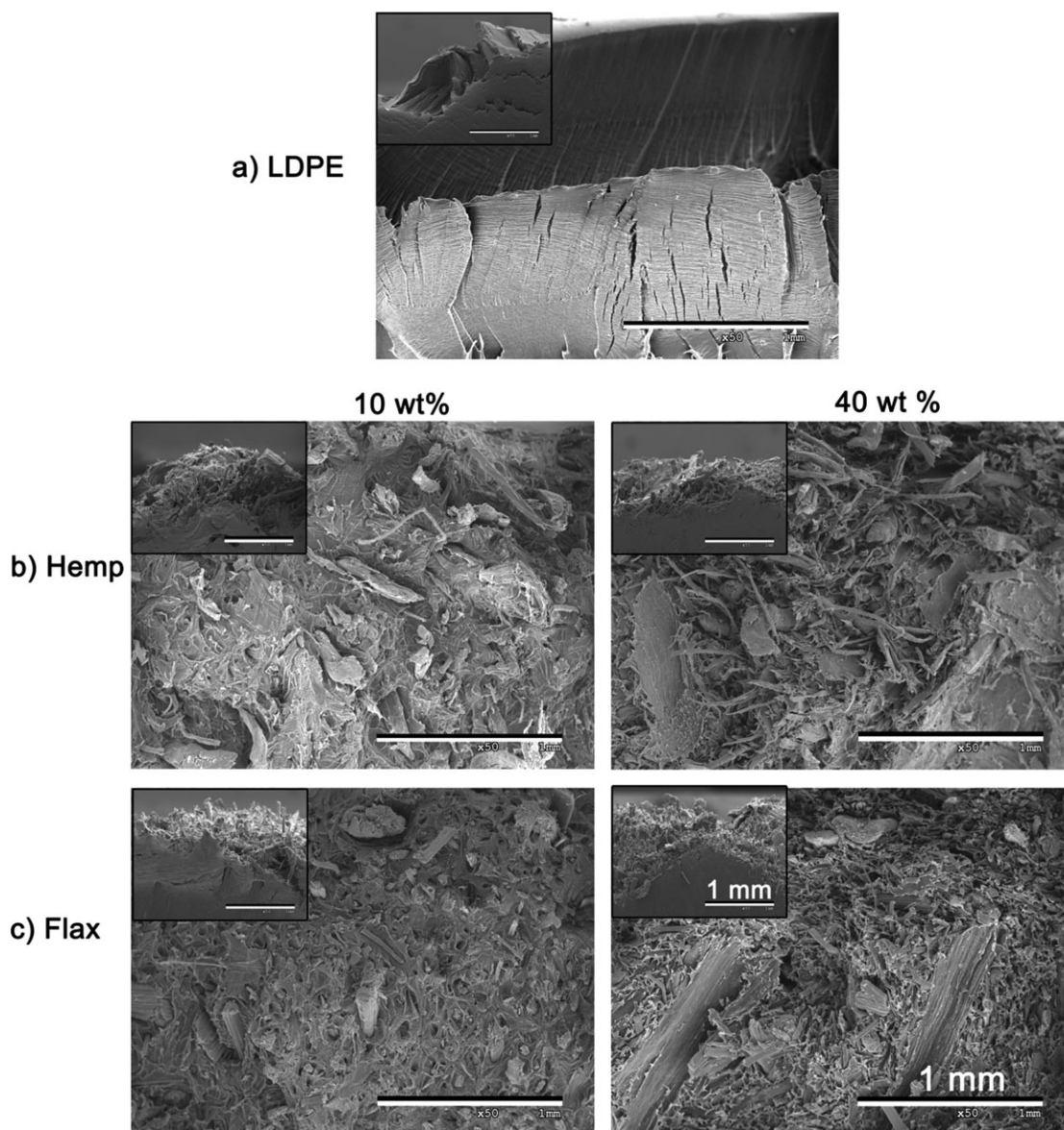
**Figure 4.** Mechanical properties of various natural fiber reinforced LDPE composites over a range of fiber fractions: (a) tensile modulus, (b) tensile strength, (c) Charpy impact, and (d) elongation at break.

these fibers are uniformly distributed throughout the composite structure [Figure 6(a)]. Furthermore, chemically pulped wood has a highly purified cellulose structure relative to the other fibers which provides for increased fiber strength (in general, most chemical pulps are greater than 80% cellulose). The homogenous composite structure (with high strength fibers) as shown by both the uniform color distribution observed in Figure 2, and the uniform fiber distribution on the fracture surface in Figure 6 owe to the improved mechanical performance. It is interesting to note, however, that the improved performance of wood pulp composites in terms of tensile strength does not translate to an increase in elongation or toughness; the latter properties may be more dependent on bulk properties rather than factors which govern localized effects (such as fiber size distribution). For the other fiber types (hemp bast, flax bast, wood chips, wheat straw, and triticale pulp), strength could possibly be increased by reducing the range of particle sizes and increasing the effective fiber aspect ratio.

#### Characterization of Long Term Moisture Absorption

The long-term moisture absorption behavior of LDPE reinforced with various natural fiber types is shown in Figures 7 and 8. All the natural fiber composites tested experienced various levels of water uptake over a period of 11,515 h (68 weeks or approximately 16 months). The rate and magnitude of absorption was found to be a function of both fiber type and fiber weight fraction. Tests conducted on virgin LDPE samples showed negligible moisture gain during this period (<0.4%). As a result, all moisture absorption in the composite samples was attributed to the natural fibers themselves.

In general, increased fiber content resulted in an increase in moisture absorption. At 10 wt % fiber fraction, all fiber types absorbed similar amounts of water (approximately 2% mass gain at 16 months), while at the other fiber fractions, there was a significant difference between fiber types. At 40 wt % fiber fraction, the wood pulp composite had the lowest overall

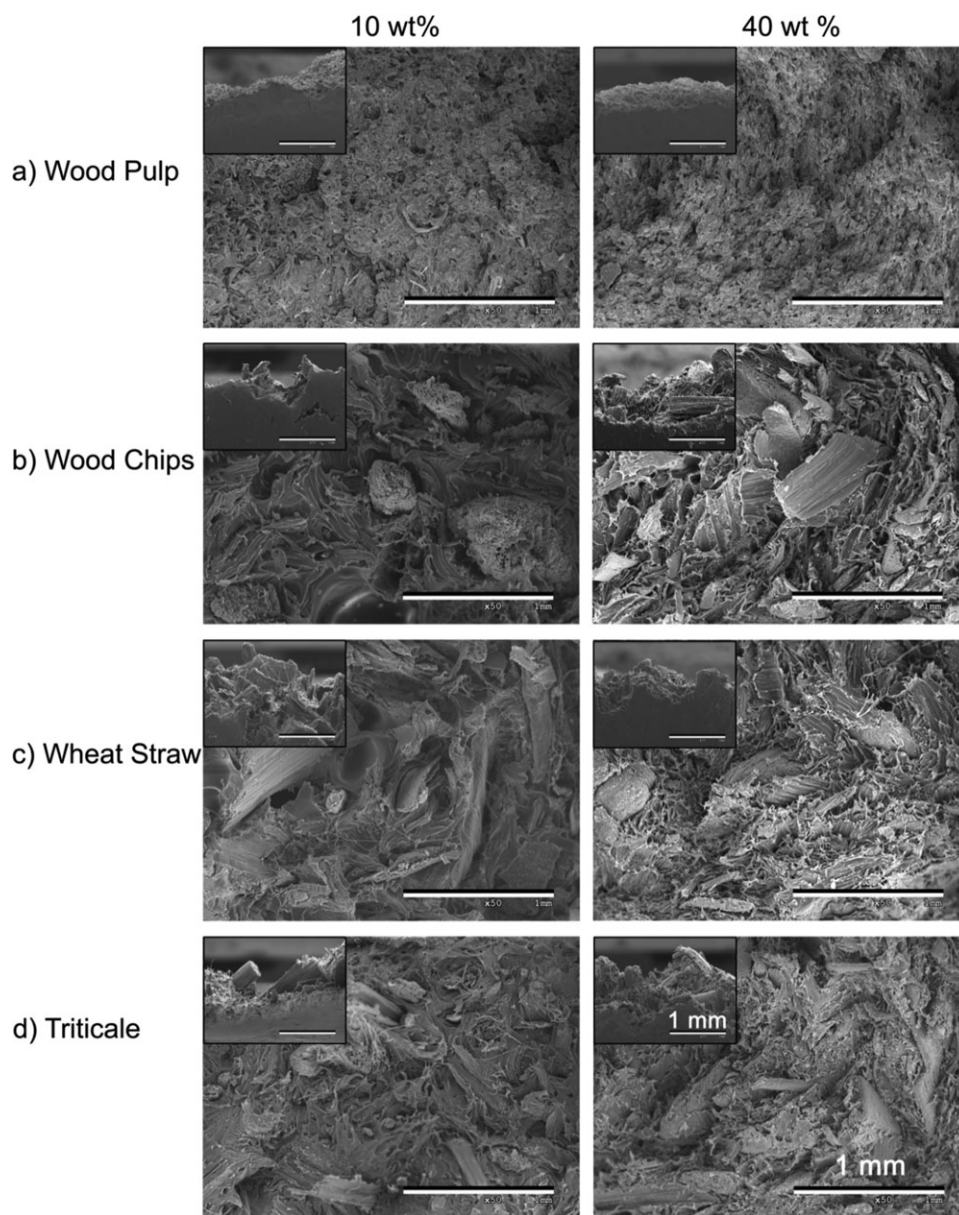


**Figure 5.** Secondary electron Scanning Electron Microscope (SEM) fractographs of failed tensile specimens: (a) Virgin LDPE (no reinforcement), (b) Hemp bast and (c) Flax bast, for 10 wt % (left column) and 40 wt % (right column). Inset images are perpendicular to the fracture surface.

moisture gain at 6.3%, while all other fiber types absorbed between 11.1 and 13.5% water (Figure 7). This discrepancy can be attributed to the observed differences in fiber geometries and size distribution. As shown in Figure 1(c), chemically pulped wood fiber is very fine (small diameter) and has a more uniform size distribution compared to the other fiber types. As shown in Figure 6(a), the wood pulp composite's microstructure is also quite homogenous (evenly distributed fibers) and shows good fiber-matrix bonding. These factors contribute to the reduction in moisture uptake by limiting transport pathways between contacting fibers, and at the fiber-matrix interface. Conversely, all other fiber types had a wider range of fiber sizes with noted larger particles (see the inset images in Figure 1). The larger fibers tend to have natural internal pathways for water transport (lumen) which most likely contributed to this increase in observed moisture absorption.

Referring to Figure 7, there was a significant increase in absorption rate and total mass gain for hemp bast, flax bast, wheat straw and triticale pulp composites at 40 wt % versus 30 wt % fiber fractions. As the fiber loading is increased, there is a greater probability for fiber-to-fiber contact. The jump in moisture absorption observed between 30 and 40 wt % fiber fractions is most likely due to this increased fiber interaction and connectivity, resulting in greater moisture transport (percolation effect). As this connectivity is a random effect, this may also explain the larger variation in mass gain measurements (error bars) observed for these fibers at the 40 wt % fiber fraction.

For the majority of natural fiber composites, with the exception of wood pulp, equilibrium was not reached until 12 months of immersion testing. Some variations such as 30 wt % Flax Fiber, 30 wt % Wood Chips, 20 wt % Wheat Straw and 30 wt %



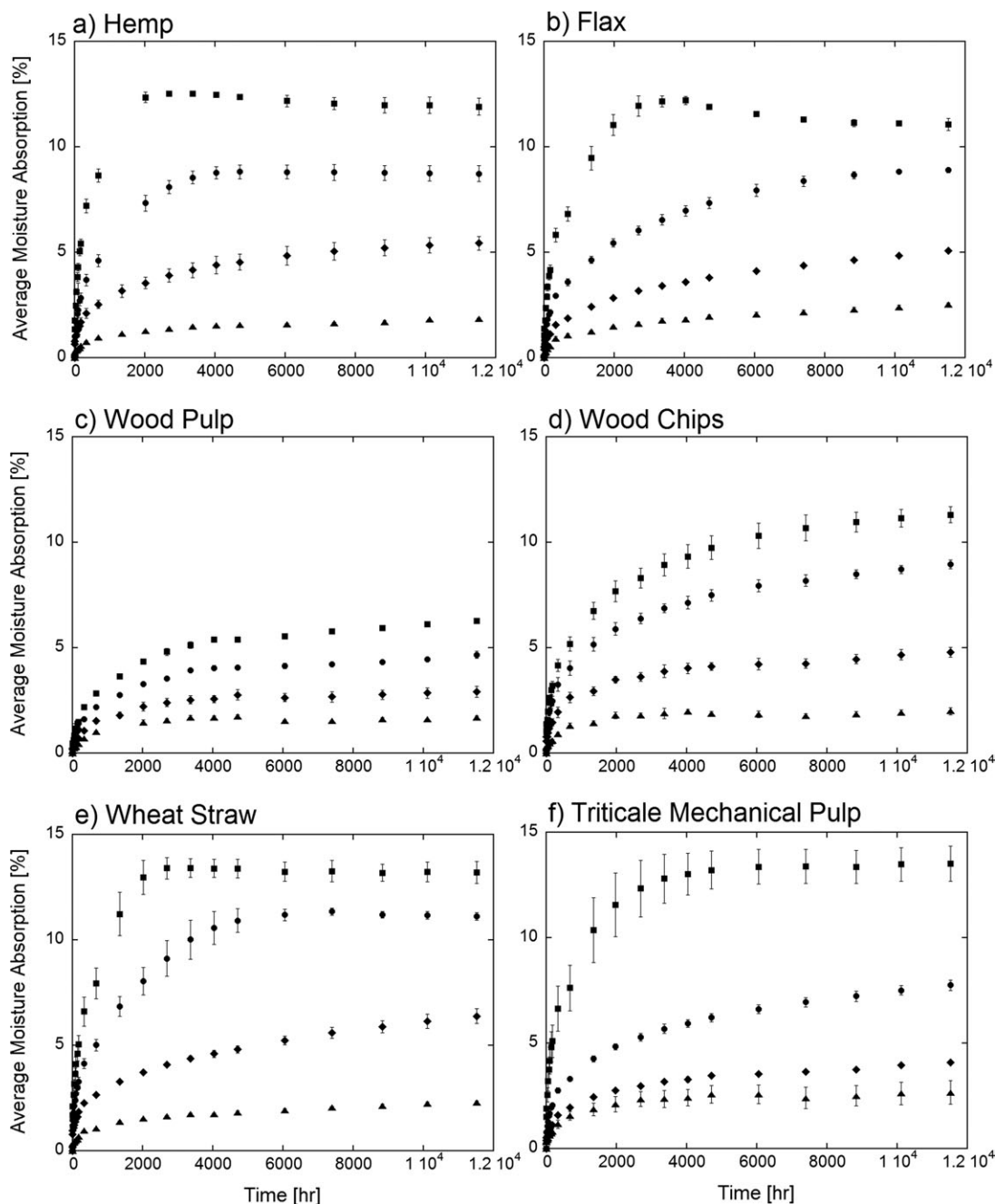
**Figure 6.** Secondary electron Scanning Electron Microscope (SEM) fractographs of failed tensile specimens: (a) wood pulp, (b) wood chips, (c) wheat straw, and (d) triticale pulp, for 10 wt % (left column) and 40 wt % (right column). Inset images are perpendicular to the fracture surface.

Triticale even after 16 months of immersion have still not reached equilibrium. Both hemp bast and flax bast fiber composites at 40 wt % fiber fraction experienced a plateau and subsequent mass loss at approximately 4000 h (24 weeks). Mass loss was also observed for the majority of natural fiber composites coupons after being oven dried after 16 months of immersion testing, as shown in Table II. This loss in mass supports the theory that fibers appear to be degrading during immersion testing as a result of dissolution of fiber constituents (the LDPE matrix material shows no long-term mass gain or loss when immersed in water). There is a correlation that an increase in fiber weight percent correlates to an increase in the mass lost by the coupons, with the exception of wood based composites.

#### Effect of Coupling Agent

The mechanical properties of natural fiber reinforced LDPE with a maleic anhydride polyethylene (MAPE) coupling agent are shown in Figure 9. The benefit of using a coupling agent is seen to depend on the property of interest, as well as the fiber type. Overall, the addition of MAPE resulted in a general increase in modulus, tensile strength and elongation (ductility) for all fiber types. However, the effect of coupling agent on Charpy impact strength was mixed, as two of the six fiber types showed a decrease in average impact properties with the addition of MAPE. The addition of MAPE is assumed to increase the interfacial bonding between the natural fiber and thermoplastic matrix. This results in an increased load transfer





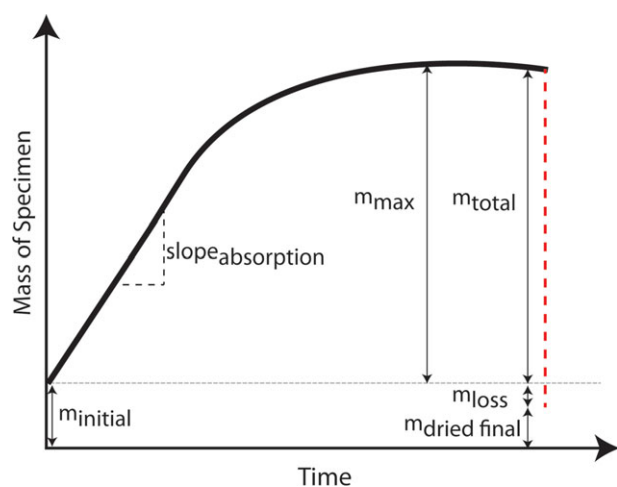
**Figure 7.** Average moisture absorption versus immersion time in water for fiber types: (a) hemp bast, (b) flax bast, (c) wood pulp (d) wood chips (e) wheat straw, and (f) triticale pulp at 10 wt % (▲), 20wt % (◆), 30 wt % (●), and 40 wt % (■). Error bars indicate  $\pm$  one standard deviation.

efficiency which is reflected in the general improvement of mechanical properties.

The MAPE coupling agent had the greatest effect on the tensile strength for all fiber types except wood pulp. The most significant improvement occurred for the wheat straw composites which saw an increase in tensile strength of approximately two times. For the wood pulp composites, the increase in properties relative to the other fiber types was quite minimal. It should be noted that the wood pulp composites (without coupling agent) already had a significantly higher strength than composites

made from the other fiber types [Figure 4(b)]. This suggests that interfacial bonding between the fiber and matrix in wood pulp composites may already be quite good, and that there is no benefit derived in adding a MAPE coupling agent.

In terms of moisture absorption, the addition of MAPE resulted in a general decrease in moisture uptake for all fiber types, as shown in Figure 10. Overall, the most significant impact was seen for hemp bast, flax bast, wood chips, and wheat straw. This finding implies that the increase in bonding between the fiber and matrix (as a result of adding MAPE) may reduce



**Figure 8.** Generalized schematic of change in mass due to moisture absorption for all natural fiber composites tested. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

moisture transport through interfacial pathways. For the wood pulp composites, however, the reduction in moisture absorption was found to be minimal when MAPE coupling agent was used.

This lack of improvement is similar to that found for the mechanical properties, and reiterates that the interfacial bonding in wood pulp composites may already be quite good (i.e., the use of MAPE may not be necessary).

## CONCLUSIONS

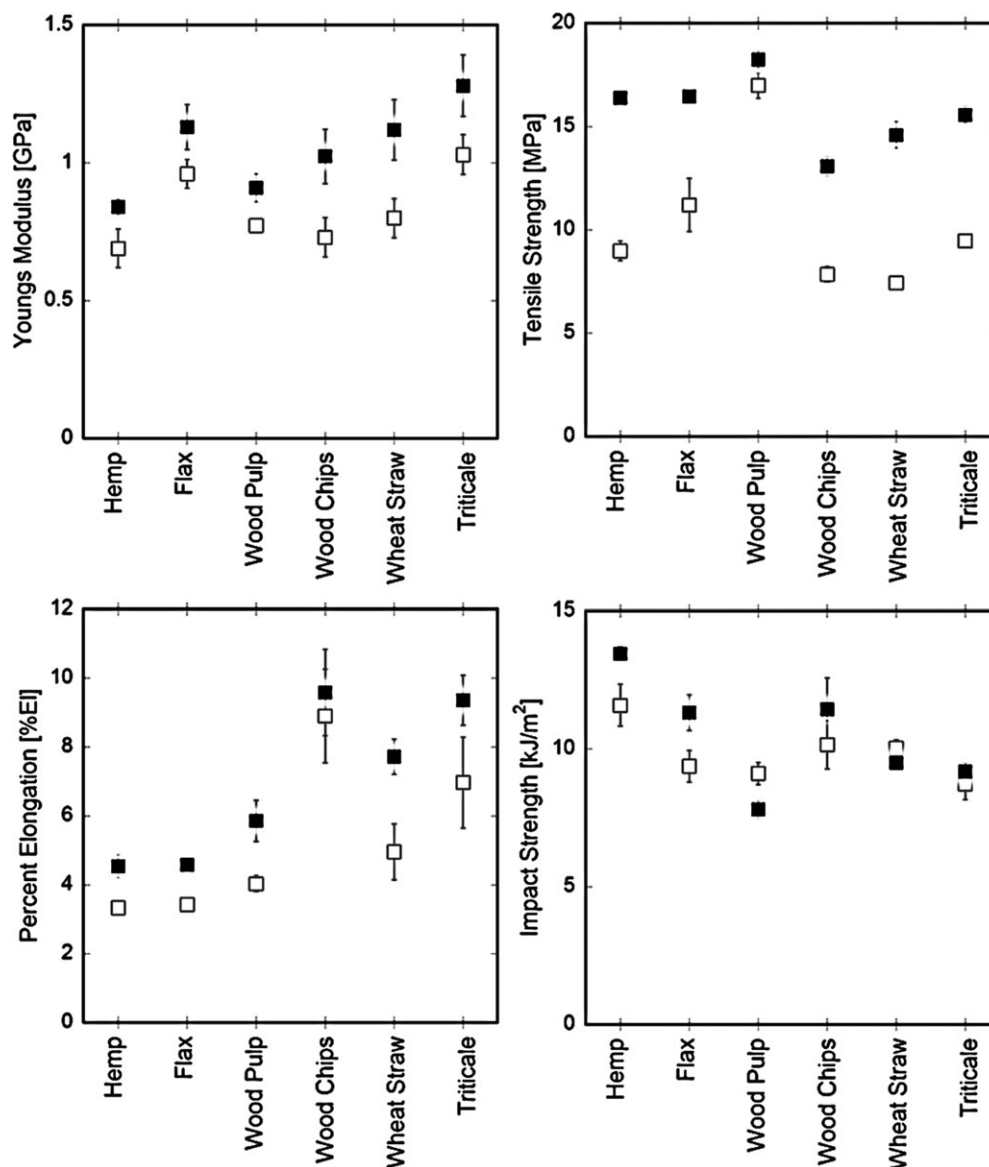
Natural fiber composites made from low density polyethylene (LDPE) and a variety of Canadian based fiber feedstocks (including hemp bast, flax bast, chemically pulped wood, wood chips, wheat straw, and mechanically pulped triticale) were manufactured and tested. In this study, the effect of fiber type, fiber fraction and maleic anhydride polyethylene (MAPE) coupling agent on the mechanical properties and long-term moisture absorption behavior was quantified.

In general, fiber type and fiber fraction were both shown to affect the mechanical properties, moisture absorption characteristics and effectiveness of the MAPE coupling agent for the range of natural fiber composites tested. In terms of mechanical properties, an increase in fiber content resulted in a composite with increased elastic modulus but reduced elongation and Charpy impact strength. Tensile strength was shown to vary depending on fiber type and fraction.

**Table II.** Average Ratios of Mass Gained and Lost Compared to Initial Mass, Where  $n = 4$

Fiber type	$W_f$ (wt %)	$m_{total}/m_{initial}$ (%)	$m_{loss}/m_{total}$ (%)	$m_{loss}/m_{initial}$ (%)
Hemp fiber	10	$2.1 \pm 0.1$	$12.4 \pm 1.1$	$0.3 \pm 0.0$
	20	$6.5 \pm 0.4$	$9.0 \pm 2.1$	$0.6 \pm 0.2$
	30	$9.5 \pm 0.3$	$7.6 \pm 2.1$	$0.7 \pm 0.2$
	40 <sup>a</sup>	$14.4 \pm 0.4$	$17.2 \pm 5.0$	$2.5 \pm 0.8$
Flax fiber	10	$2.9 \pm 0.1$	$12.4 \pm 0.8$	$0.4 \pm 0.0$
	20	$5.7 \pm 0.1$	$12.1 \pm 0.4$	$0.7 \pm 0.0$
	30	$9.7 \pm 0.1$	$8.4 \pm 0.7$	$0.8 \pm 0.1$
	40 <sup>a</sup>	$13.2 \pm 0.4$	$16.3 \pm 4.1$	$2.2 \pm 0.6$
Wood pulp	10	$1.7 \pm 0.1$	$3.5 \pm 0.9$	$0.1 \pm 0.0$
	20	$3.2 \pm 0.4$	$9.6 \pm 0.9$	$0.3 \pm 0.1$
	30	$5.0 \pm 0.3$	$7.2 \pm 4.9$	$0.4 \pm 0.3$
	40	$6.5 \pm 0.1$	$3.9 \pm 0.4$	$0.3 \pm 0.0$
Wood chips	10	$2.3 \pm 0.2$	$12.3 \pm 1.3$	$0.3 \pm 0.0$
	20	$5.2 \pm 0.2$	$6.5 \pm 1.0$	$0.3 \pm 0.0$
	30	$9.3 \pm 0.3$	$4.4 \pm 0.6$	$0.4 \pm 0.1$
	40	$11.8 \pm 0.5$	$4.2 \pm 0.4$	$0.5 \pm 0.1$
Wheat straw	10	$2.6 \pm 0.1$	$11.8 \pm 0.6$	$0.3 \pm 0.0$
	20	$7.1 \pm 0.3$	$11.3 \pm 0.6$	$0.8 \pm 0.0$
	30	$12.6 \pm 0.3$	$11.7 \pm 1.7$	$1.5 \pm 0.3$
	40	$15.9 \pm 0.9$	$16.6 \pm 0.1$	$2.6 \pm 0.3$
Triticale	10	$3.1 \pm 0.6$	$11.1 \pm 0.9$	$0.3 \pm 0.0$
	20	$4.5 \pm 0.1$	$10.2 \pm 0.4$	$0.5 \pm 0.0$
	30	$8.4 \pm 0.3$	$7.7 \pm 1.3$	$0.6 \pm 0.1$
	40	$14.9 \pm 3.1$	$7.7 \pm 15.9$	$1.5 \pm 2.5$
Control (LDPE only)	0	$-0.1 \pm 0.1$	$145.8 \pm 116.6$	$-0.1 \pm 0.0$

<sup>a</sup>Sample size is 5.



**Figure 9.** Comparative mechanical properties of various natural fiber composites reinforced at 30 wt % without (□) and with (■) MAPE coupling agent. Error bars: + one standard deviation.

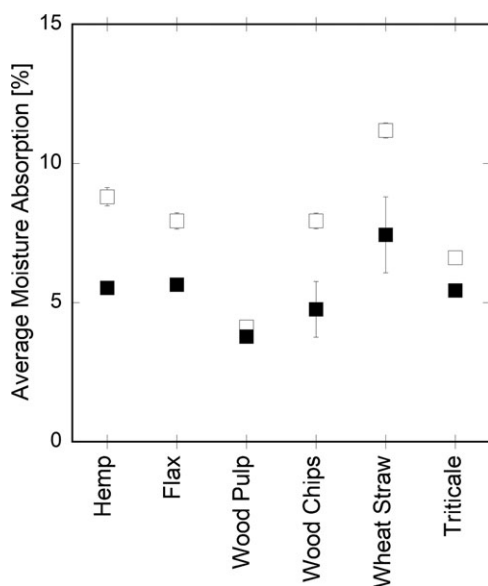
Similarly for moisture absorption, an increase in fiber fraction resulted in an overall increase in total water uptake. The majority of the natural fiber composites took 12 months to reach equilibrium moisture content (saturation). Composites made with high fractions of hemp bast and flax bast fibers (40% by weight) experienced a plateau in the absorption curves and subsequent mass loss after approximately 4000 h (24 weeks) due to possible degradation of the fiber. After 16 months of immersion specimens were oven dried, the majority of natural fiber composites experienced a mass loss. An increase in fiber fraction resulted in an increase in mass loss, suggesting fiber degradation due to dissolution during long term immersion testing.

Of the fiber types tested, composites made from chemically pulped wood had the best mechanical properties and the least moisture absorption. For all other natural fiber types, the use of MAPE coupling agent was found to significantly increase the mechanical

performance and reduce moisture absorption. The effectiveness of the MAPE coupling agent, however, was dependent on the particular fiber type, and was shown to have a minimal effect on the wood pulp composites. Overall, this suggests that fiber morphology, fiber distribution and, in particular, fiber–matrix interfacial properties all play an important role in both the mechanical and moisture absorption behavior of these composites. Further work will be required to better understand the relative influence and specific mechanisms of each of these factors.

#### ACKNOWLEDGMENTS

This study was funded by Alberta Innovates—Bio Solutions (2010F074R). The authors would like to thank Lisa Sopkow (AITF) for her technical assistance with manufacturing, testing, and microscopy, and the staff of the Forest Products Business Unit (AITF) for their help in fiber processing.



**Figure 10.** Comparison of moisture absorption after 6050 h (36 weeks) for natural fiber composites (at 30 wt %) without (□) and with (■) MAPE coupling agent. Error bars:  $\pm$  one standard deviation.

## REFERENCES

- John, M. J.; Thomas, S. *Carbohydr. Polym.* **2008**, *71*, 343.
- Mehta, G.; Mohanty, A. K.; Thayer, K.; Misra, M.; Drzal, L. T. *J. Polym. Environ.* **2005**, *13*, 169.
- Ashori, A. *Bioresour. Technol.* **2008**, *99*, 4661.
- Bavan, D. S.; Kumar, G. C. M. *J. Reinf. Plast. Compos.* **2010**, *29*, 3600.
- Chollakup, R.; Tantatherdtam, R.; Ujjin, S.; Sriroth, K. *J. Appl. Polym. Sci.* **2011**, *119*, 1952.
- Xu, Y.; Wu, Q.; Lei, Y.; Yao, F.; Zhang, Q. *J. Polym. Environ.* **2008**, *16*, 250.
- Kim, S. J.; Moon, J. B.; Kim, G. H.; Ha, C. S. *Polym. Test.* **2008**, *27*, 801.
- Pan, M.-Z.; Zhou, D.-G.; Deng, J.; Zhang, S. Y. *J. Appl. Polym. Sci.* **2009**, *114*, 3049.
- Bourmaud, A.; Pimbert, S. *Compos. Part A Appl. Sci. Manufact.* **2008**, *39*, 1444.
- Chand N., Fahim, M. In *Tribology of Natural Fiber Polymer Composites*; Limited, W. P., Ed.; CRC Press LLC: Boca Raton, FL, **2008**; Chapter 1.
- Yao, F.; Wu, Q. L.; Lei, Y.; Xu, Y. J. *Ind. Crops Prod.* **2008**, *28*, 63.
- Tajvidi, M.; Takemura, A. *J. Polym. Environ.* **2010**, *18*, 500.
- Salmah, H.; Faisal, A. *Polym. Plast. Technol. Eng.* **2010**, *49*, 672.
- Mohanty, A. K.; Misra, M.; Drzal, L. T. *Compos. Interfaces* **2001**, *8*, 313.
- Faruk, O.; Bledzki, A. K.; Fink, H.-P.; Sain, M. *Prog. Polym. Sci.* **2012**, *37*, 1552.
- Shinoj, S.; Panigrahi, S.; Visvanathan, R. *J. Appl. Polym. Sci.* **2010**, *117*, 1064.
- Chang, S. Y.; Ismail, H.; Ahsan, Q. *Bioresources* **2012**, *7*, 1594.
- Mohanty, A. K.; Drzal, L. T.; Misra, M. *J. Adhes. Sci. Technol.* **2002**, *16*, 999.
- Rachini, A.; Mougin, G.; Delalande, S.; Charneau, J. Y.; Barres, C.; Fleury, E. *Polym. Degrad. Stab.* **2012**, *97*, 1988.
- Wolodko, J.; Vidmar, J.; Slaski, J.; Chute, W.; Alemaskin, K.; Perras, T.; Bell, K.; Fotouh, A.: **2010**, p 77.