DEGRADATION OF CELLULOSE / HEMP BIOCOMPOSITES UNDER VARIOUS PROCESSING AND HYDROTHERMAL ENVIRONMENTS

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Abstract

The aim of this paper is to isolate the mechanisms by which a unidirectional biodegradable composite degrades in the presence of moisture. Cellulose Acetate Butyrate, a biodegradable thermoplastic polymer, was reinforced with oriented hemp fibers. Basic material properties were quantified, as was the reduction of these properties as a function of water uptake. The mechanism by which the composite degrades was found to be primarily the swelling of the fibers which reduced the mechanical interlock between the individual fibrils that make up each fiber, as evidenced by the regaining of a majority of the composite's stiffness after re-drying under vacuum. Two common surface treatments, acrylonitrile and silane, are also evaluated, with silane showing improved results. Finally, basic trends of material properties as a function of processing conditions are found, revealing better properties with pressures lower than 1.5 MPa and as low a temperature as required to ensure polymer flow.

1 Introduction

Natural fiber reinforced polymer composites ("biocomposites") are gaining attention as a viable alternative to glass fiber reinforced composites, especially as secondary-structure components in the automotive and aerospace industries where weight is of importance [1]. Current applications generally use non-biodegradable petroleum resins, which are not as environmentally-advantageous as biodegradable polymers. However, biodegradable polymers are notorious for susceptibility to degradation in wet environments [2], thus limiting their possible applications to interior, non-primary structures.

The goal of this research is to take an all natural biocomposite previously studied by others [3] and identify the mechanisms by which it degrades due to moisture. In addition, two surface treatments that have shown success with other biocomposites [4] are evaluated, as is the effect of processing conditions. From this, further work can be tailored towards the development and optimization of all-natural biocomposites that can be used as primary structural components while retaining their end-of-life biodegradable capacity.

2 Experimental

2.1 Materials

Powdered cellulose acetate butyrate (CABP-381-20) was obtained through Eastman Chemical Company, Kingsport, TN, USA. 'Uncut' primary hemp fibers were obtained through Hempline Inc. (now operating as Stemergy), Delaware, Ontario, Canada. Acrylonitrile, Dicumyl Peroxide (DCP) and Aminopropyltriethoxy-silane ("silane") were obtained through Sigma Aldrich, St. Louis, MO, USA.

2.2 Fiber Orientation

The fibers used were received as a large bundle of loose, randomly aligned fibers. To isolate the effect of the fibers on the composite properties, these loose fibers needed to be aligned. To accomplish this, a window-frame compression mold was fitted with two springs laid on their sides, one on either side of the frame (See Fig. 1). The fibers were then strung, one at a time, across the opening and between the coils of the spring, until the frame was filled.
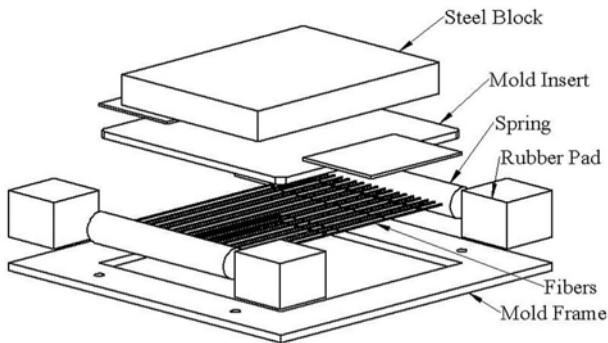
Fig. 1. Compression mold setup showing fiber orientation.

2.3 Compression Molding

The steel mold consisted of two main parts – a window-frame with inner dimensions of 101.6 mm x 101.6 mm x 3 mm, and an insert designed to fit securely inside. Steel blocks were placed on top of the insert so as to make contact with the upper hotpress platen before the springs, ensuring that the heat and pressure be applied to the composite rather than the springs. This was then placed on a steel plate, with Teflon peel plies placed on either side of the composite area. Lastly, dense rubber pads were placed on the frame so as to apply a small amount of pressure to it, holding it against the Teflon and reducing the amount of flash on the finished composite.

When the fibers are pushed down into the mold during forming, the high viscosity of the polymer prevents them from being completely encased. This results in a layer of polymer with exposed fibers held on the top. In an effort to completely encase the fibers in the center of the polymer, the polymer had to be pressed in two layers – one for beneath the fibers, one for above. Because the fibers were initially pushed down into the first layer, that layer had to be thicker than the second. The first layer consisted of 6 grams of polymer, and the second consisted of 4 grams.

After the fibers were strung across the window-frame and the first layer of polymer distributed evenly, the insert (with Teflon and steel blocks) was placed on top and the entire mold placed in the hotpress at 195 ºC for 10 minutes to reach thermal equilibrium with the press. It was then pressed at approximately 0.5 MPa for 10 minutes, removed and allowed to cool 10 minutes. The steel blocks and insert were removed, and the second layer of polymer applied. Then the insert and blocks were placed back on top, the mold placed back into the hotpress for 10 minutes to reach equilibrium, pressed at approximately 0.5 MPa for 10 minutes,

and finally taken out and allowed to cool under ambient conditions of 22 ºC and approximately 30% relative humidity for at least 30 minutes.

After cooling, the composite tile was removed from the mold and specimens cut from it using a wet saw. Each finished specimen measured approximately 80mm x 9mm x 0.9mm, and had a fiber volume content of approximately 18%.

Unreinforced polymer specimens were made exactly as above, except both layers consisted of 6 grams of polymer.

2.4 Testing Matrix

2.4.1 Material Properties

The ultimate strengths and moduli of elasticity of the biocomposite and neat polymer were obtained through tension tests, following ASTM D-3039.

2.4.2 Degradation Due to Moisture Uptake

Specimens of both the biocomposite and neat polymer were immersed in water, and the change in material properties as a function of water uptake (measured as a percentage mass gain) was recorded.

2.4.3 Degradation Mechanism

It was assumed that the mechanism by which the composite could lose stiffness in the presence of water could be one of two options. The first is swelling of the fibers, causing the individual fibrils within each fiber to separate and lose the mechanical interlock that gave the fiber its stiffness. This mechanism would be at least partially reversible by re-drying the fibers, thus putting those fibrils back into contact with each other. The second possibility is that the bond between the fiber and the polymer is degraded, which would be a permanent loss. To test which mechanism governs, tension data was compared between specimens that were never immersed, specimens that were immersed for a week, and specimens that were immersed a week and then dried under vacuum at ambient temperature for 24 hours.

2.4.4 Long Term Degradation

Specimens were allowed to stay immersed in water and tension tested at 2 and 4 week intervals.

2.4.5 Surface Treatment

Two chemical fiber surface treatments that have showed promise in other studies were evaluated: acrylonitrile and silane. Specimens of each surface treatment were tested dry and after immersion in water for 5 days.

2.4.5.1 Acrylonitrile

A solution was made of 3% acrylonitrile, 0.5% DCP, and 96.5% ethanol (all %weight) and stirred in a covered beaker for 3 hours. The fibers were oriented in the mold, and the mold placed in the solution and allowed to soak for 15 minutes. The fibers were then drained and allowed to dry under the hood for 30 minutes, then dried under vacuum overnight at ambient temperature and compression molded as normal.

2.4.5.2 Silane

A solution of 1% silane was made in 99% deionized water and ethanol (1:1, all %volume) and allowed to hydrolyze for 2 hours, at which point glacial acetic acid was used to bring the pH of the solution to 4. This required 50mL of acid added to 500mL of solution. The fibers were oriented in the mold, and the mold placed in the solution and allowed to soak for one hour. The fibers were then drained and allowed to dry under the hood for 2 hours, then vacuum dried for 8 hours at ambient temperature and compression molded as normal.

2.4.6 Processing Effects

To evaluate the effect of different processing temperatures and pressures, the above method of compression molding was followed exactly with the exception of changing the hotpress temperature and pressure. The Temperature/Pressure combinations used were 180 ℃ / 1.0 MPa, 180 ℃/ 1.5 MPa, 210 ℃ / 1.0 MPa, and 210 ℃ / 1.5 MPa.

3 Results and Discussion

3.1 Mechanical Properties

Table 1. Mechanical Properties

	Ultimate Strength (MPa)	Secondary Stiffness E (MPa)
Polymer	16	1949
Fibers	364	-
Composite	69	5702

3.2 Degradation Due to Moisture Uptake

Moisture uptake appeared to have no affect on the ultimate strength of unreinforced polymer, but did reduce the ultimate strength of the composite by about 10% after a 5% increase in mass. For the same mass increase, the stiffness of the composite reduced by 50%, while the polymer only reduced by 20%.
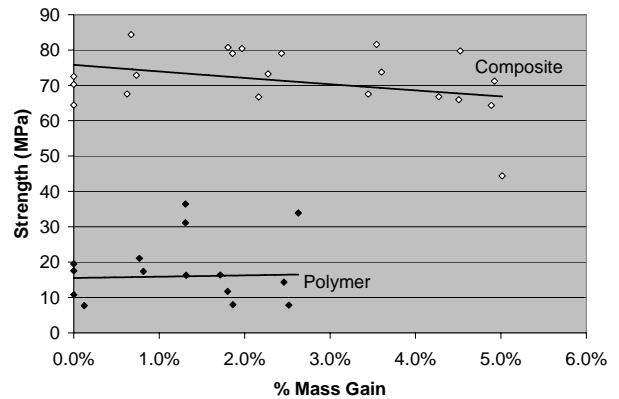

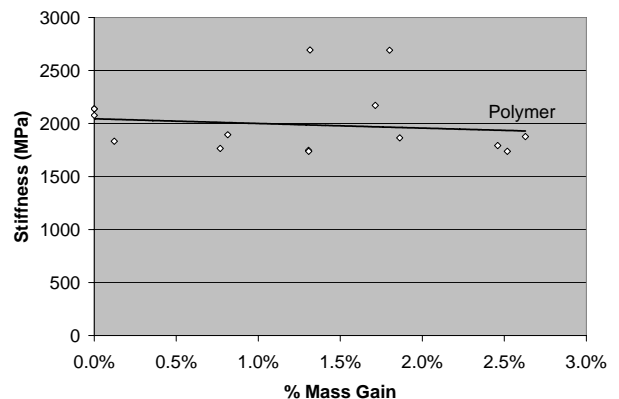Fig. 2. Tensile strength as function of water uptake

Fig. 3.   Stiffness of unreinforced polymer as function of water uptake
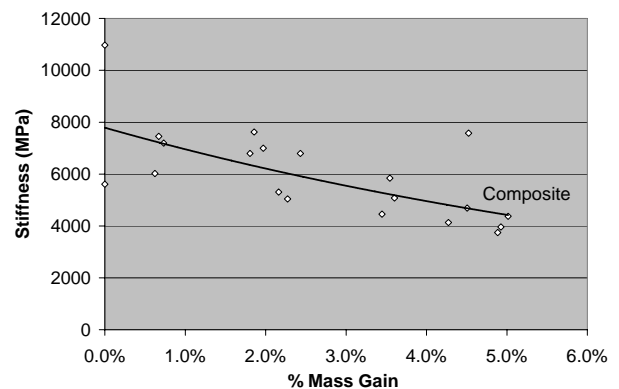

Fig. 4. Stiffness of composite as function of water uptake

3.3 Degradation Mechanism
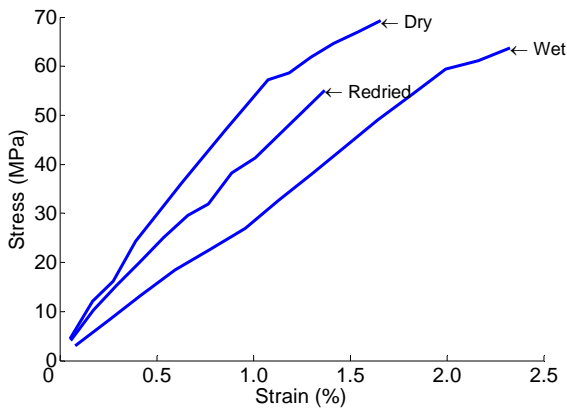

Fig. 5. Typical stress-strain response showing partial stiffness recovery after drying degraded composite

Table 2. Degradation Mechanism Data

	Strength (MPa)	E (MPa)
Dry	71.8	5463
Wet	65.3 *(-9%)*	3043 *(-44%)*
Redried	55.4 *(-23%)*	4623 *(-15%)*

As can be seen above, re-drying the degraded composite results in a recovery of most of the lost stiffness. Re-drying also results in a dramatically reduced tensile strength, likely due to microcracking caused by the sudden removal of moisture under vacuum.

3.4 Long Term Degradation

At the time of submission, long term degradation study was still ongoing.

3.5 Surface Treatment

Table 4. Surface treatment effects

	Strength (MPa)	E (MPa)
Unmodified		
Dry	69.07	5702
Wet	59.97	2812
Degradation	*-13.2%*	*-50.7%*
Silane Treated		
Dry	57.0	6727
Wet	54.1	4525
Degradation	*-5.2%*	*-32.7%*
Acrylonitrile Treated		
Dry	69.6	7170
Wet	68.0	3314
Degradation	*-2.2%*	*-53.8%*

Both surface treatments showed promise for reducing degradation of the ultimate tensile strength of the composite, but silane was the only one of the two to reduce degradation of the stiffness as well.

3.6 Processing Effects

Only three of the four Temperature / Pressure combinations were successfully fabricated. The fourth, at 210 ºC and 1.5 MPa, had too low a viscosity and flowed out between the window-frame mold and Teflon sheet. The trend of data favoring lower temperatures and pressures beneath 1.5 MPa suggests that this fourth combination would have yielded poor results. It is also worth noting that the specimens pressed at 210 ºC and 1.0 MPa had an abundant number of voids, to the extent that the tested specimens were positively buoyant with a specific gravity of 0.9 while all other specimens were negatively buoyant with a specific gravity of around 1.2.

Table 5. Processing Effects

Temp / Press (ºC / MPa)	Strength (MPa)	E (MPa)
195 / 0.5	69.1	5702
180 / 1.0	84.2 *(22%)*	6816 *(20%)*
180 / 1.5	75.2 *(9%)*	6125 *(7%)*
210 / 1.0	38.3 *(-45%)*	2729 *(-43%)*

180 ºC platens pressed at 1.0 MPa appears to be more towards the optimum processing conditions than the 195 ºC at 0.5 MPa that was used for the rest of this study. Going lower than 180 ºC would require higher pressures in order for the powdered polymer to melt and bind to itself – indeed, at 180 ºC and 1.0 MPa there was a good amount of un-formed polymer. However, these results suggest that a higher pressure could cause a reduction in properties.

Table 6 shows what effect the processing conditions had on degradation due to moisture, with the samples pressed at 180 ºC showing an increase in strength after moisture uptake.

Table 6. Processing effects on degradation due to moisture uptake

	Strength (MPa)	E (MPa)
195 / 0.5		
Dry	69.1	5702
Wet	60.0	2812
Degradation	-13.2%	-50.7%
180 / 1.0		
Dry	84.2	6816
Wet	89.4	2932
Degradation	6.2%	-57.0%
180 / 1.5		
Dry	75.2	6125
Wet	89.5	3410
Degradation	19.0%	-44.3%
210 / 1.0		
Dry	38.3	3264
Wet	35.4	2729
Degradation	-7.5%	-16.4%

4 Conclusions

These results show promise for bringing biodegradable polymers to a point where they can be used as primary structures, even in wet environments.

With a fiber volume fraction of around 18%, the composites tested in this study attained a maximum moisture uptake of around 4.5% of the dry mass after one week of immersion in water, which caused a 13% reduction in tensile strength and a 50% reduction in stiffness.

The mechanism by which the stiffness is reduced is largely a swelling of the fibers which causes the individual fibrils within to separate, as evidenced by the partial recovery of stiffness upon re-drying the composite.

Both silane and acrylonitrile surface treatments showed promise for reducing the degradation of tensile strength due to moisture uptake, limiting it to 5% and 2% loss, respectively, compared with 13% loss for the unmodified composite. Only silane was able to reduce degradation of the stiffness as well, limiting it to a 33% loss compared with 51% for the unmodified composite.

Keeping the platen temperature low while still ensuring adequate polymer melt and flow at pressures beneath 1.5 MPa appears to be ideal.

Further study is needed to optimize this composite system for primary structural applications. In addition, any surface treatments should be evaluated for their effect on the overall biodegradability of the composite.

References

[1] Baillie C. (editor). "*Green composites: polymer composites and the environment*". 1st edition, Woodhead Publishing, 2004.

[2] Netravali N. "Composites Get Greener". *Materials Today*, Vol. 6, No. 4, pp 22-29, 2003.

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[4] Mehta G., Drzal L., Mohanty A., Misra M. "Effect of fiber surface treatment on the properties of biocomposites from nonwoven industrial hemp fiber mats and unsaturated polyester resin". *Journal of Applied Polymer Science*, Vol. 99, pp 1055-1068.

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