# ENVIRONMENTAL EFFECTS ON THE PROPERTIES OF COMMERCIAL BIOPOLYMER PRODUCTS

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# Abstract

Trends towards sustainability have increased interest in biodegradable plastics. The effect of environmental factors such as UV radiation, humidity, and temperature on the properties of 7 biopolymers used in serviceware including bagasse, fiber pulp, wheatstraw and polylactic acid were analyzed. The properties of biopolymers were comparable to synthetic plastics in the as received condition, but deteriorate significantly with exposure to water and UV radiation. Improvements may be needed before biopolymers are effective replacements for traditional plastics.

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## Introduction

Biodegradable polymers, specifically from renewable resources, are being examined for replacement of synthetic plastics. The most common ASTM definition of biodegradable polymers states that a degradable polymer is one in which "degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae" [1]. Biodegradable polymers may be converted back into carbon dioxide after their use [2]. With this ability, biopolymers that are produced by renewable resources may create a "carbon neutral" life cycle in which the net amount of carbon dioxide released into the environment remains relatively constant [2]. A variety of renewable biopolymers are produced by plants such as cellulose, starch, and protein [3]. Agro-polymers, typically starch and bagasse, are being examined for their sustainable nature due to vast agricultural resources available for use [4]. The resources used in the production of renewable biopolymers are continually replenished which becomes advantageous over traditional plastics for sustainability [2]. Typical commercial biopolymers are polylactic acid (PLA), polyhydroxyalkanoates (PHA), starches, and bagasse. Some applications for PHAs range from stiff packaging to flexible coatings [2]. PLA can be used for flexible packaging or drinking cups as well as similar applications to polypropylene (PP) and polystyrene (PS) [5, 6]. Applications for starches reside mainly with food packaging [7]. Where starch products are known for their highly hydrophilic nature, current applications are limited.

When comparing the mechanical properties for synthetic and biodegradable plastics, there is a wide range of values for the strength of both classes of materials, but generally synthetic plastics are stronger than biodegradable plastics [4]. The degradation period for synthetic plastics may last up to 450 years in a landfill whereas some biodegradable polymers, starch and bagasse composites, may degrade within a few months [8]. The degradation behavior of the most common biopolymer, PLA, has been studied extensively. PLA can degrade in compost by microorganisms which discharge esterase, protease, or lipase [5]. Biodegradable polymers can, with slight improvements, be comparable to their synthetic counterparts in many applications. The drawbacks with biopolymers may be reduction in strength after use in certain environments or limitation on available data. Many renewable biopolymers, when introduced to moist or humid environments, may exhibit reduced mechanical properties [8]. Hydrophilic biopolymers tend to degrade quickly and drastically decline in strength while exposed to humid environments [8, 9]. Even though biopolymers gained increasing amounts of attention, the data on the mechanical behavior during use is limited, and service conditions are not understood [3, 8, 9]. Many manufacturers do not provide information on the change in properties of the product during or after use [10, 11, 12, 13]. Therefore, the objectives of this research were to identify some emerging commercial products in serviceware and to determine their as-received mechanical property values. Also, the effects of ultraviolet (UV) radiation, humidity and water exposure were analyzed according to the changes in the mechanical properties of the samples. Finally, the properties after long-term use were examined since plastics may be used for longterm applications. In order to achieve these objectives, several commercial biopolymers were obtained from manufacturers including Pactiv, ECO Products, Be Green Packaging, and Earth To-Go. The biopolymer samples were subjected to a variety of standard ASTM test procedures.

# **Objectives**

The overall objectives of this MQP are to:

- Identify and select emerging commercial products in serviceware
- Determine mechanical and thermal properties of these products
- Analyze effect of environment on biopolymer's properties
- Determine temporal changes in properties

## Procedure

A variety of serviceware items were collected from manufacturers, providing an overall selection of seven different biodegradable plastics: bagasse, a bagasse bamboo blend, polylactic acid (PLA), wheatstraw, fiber pulp, potato starch, and a bamboo bulrush wheatstraw blend. Polystyrene was obtained to use as a control.

The mechanical properties were tested according to ASTM D882-10 using an Instron 4201 machine at a strain rate of 1mm/min until fracture. The plastic samples were cut using a Xacto knife and an acrylic template from the center portions of the product along the direction of maximum orientation. At least three samples were used in each test in order to obtain an average value and runs which deviated more than 10% from the average value were rejected.

In order to examine the effect of UV radiation on mechanical behavior, samples were irradiated with UV light using a UVP Tansilluminator for a period of 15 min at a wavelength of 360 nm (the equivalent of 90 days outdoor exposure). The samples were then subjected to the tensile testing in the manner described previously to determine the change in properties from photo-degradation.

In order to study the effects of moisture on the properties, samples were tested according to ASTM D7191-10. The samples were placed in a water bath for 24hr. They were then removed from the water and blotted dry before being placed in a desiccator for 72hr. The samples were then tensile tested as before to determine their change in properties. Additionally, samples were tested according to ASTM D570-98 to determine density and water absorption along with the mass lost during water exposure. The effects of moisture on tensile properties were further examined with tensile samples by submerging in distilled water at 20°C for 24hr. The samples were removed from water, blotted dry, and tested immediately.

In order to determine the long term changes in mechanical properties, the samples were subjected to accelerated aging. They were placed in a Cole-Parmer oven at an average temperature of 100°C. After 3 weeks, the samples were removed, allowed to cool to room temperature, and tensile tested in the manner above to determine the resultant change in properties. The temperature-time equivalence based on the Arrhenius equation was used to estimate the properties over time [14]:

$$t_2 = t_1 \exp\left[\frac{Q}{8.314} \left(\frac{1}{298} - \frac{1}{373}\right)\right] \tag{1}$$

The equivalent time ( $t_2$ ) at room temperature corresponding to 3 weeks ( $t_1$ ) at 100°C was calculated to be roughly 6 months using an activation energy Q of 26200 J/mol [15].

The thermal degradation behavior was examined by using a Texas Instruments TGA 2950. These tests were used to determine the mass loss in a sample with respect to temperature. The samples were heated to 600°C at a rate of 10°C per minute.

# This MQP report is presented in the form of two technical papers:

K. Buffum, H. Pacheco, and S. Shivkumar, "Environmental Effects on the Properties of Commercial Biopolymer Products" accepted for publication in ANTEC Proceedings 2013; accepted for Presentation at the Annual Society of Plastic Engineers Conference, Cincinnati, OH, April 22-24, 2013.

K. Buffum, H. Pacheco, and S. Shivkumar, "Environmental Effects on the Properties of Commercial Biopolymer Products" *Journal of Polymer Research* (2013) submitted for publication.

The papers are attached in the following sections.

Paper 1

K. Buffum, H. Pacheco, and S. Shivkumar, "Environmental Effects on the Properties of Commercial Biopolymer Products" accepted for publication in ANTEC Proceedings 2013; accepted for Presentation at the Annual Society of Plastic Engineers Conference, Cincinnati, OH, April 22-24, 2013.

# TENSILE PROPERTY CHANGES IN COMMERCIAL BIOPOLYMER PRODUCTS BASED ON ENVIRONMENTAL CONDITIONS

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#### Abstract

The current trend towards sustainability has created new interest in biodegradable plastics. While many investigations have examined the behavior of biodegradable plastics, the changes in properties that may occur during use have not been fully developed. The mechanical properties of seven types of biodegradable plastics were analyzed. In addition, the properties of polystyrene (PS) used in similar applications were examined. The effects of UV exposure, humidity and accelerated aging on the mechanical properties were studied. In general, the strength of several biopolymers was less than that of PS. Polylactic acid and wheatstraw had a higher strength than PS. The properties of biodegradable plastics deteriorated significantly upon exposure to UV radiation and humidity. Accelerated aging data indicates that after 6 months under ambient conditions, the biodegradable plastics also have a reduction in strength and modulus. Additional improvements may be necessary to resist environmental effects so that biopolymers can be effective replacements for traditional plastics.

#### Introduction

Biodegradable plastics are currently being explored for a variety of commercial applications, such as films for agricultural use and food packaging. Biodegradable plastics produced from renewable sources are gaining attention due to their ecological sustainability [1]. There are both benefits and drawbacks to using biodegradable plastics over commercial plastics. Plastics produced by renewable resources are advantageous over commercial plastics produced by

petroleum, since petroleum based plastics take longer to degrade in the environment. Plants produce a variety of renewable biodegradable polymers such as cellulose, starch and protein [2]. Agro-polymers are being examined for their sustainable nature due to the large amount of agricultural resources available for use. These types of biodegradable plastics may lack mechanical strength but can degrade quickly, and with added plasticizers they may have comparable mechanical stability to typical commercial thermoplastics [3]. Biopolymers and synthetic plastics can be reinforced with a variety of biological fibers to produce biocomposites. Many biocomposites have been evaluated to be ecologically sustainable with comparable mechanical properties to commercial plastics. For example, bamboo and bagasse are produced from renewable resources. Bamboo is comprised of cellulose, lignin, and hemicellulose, and reportedly has a high tensile strength due to the alternating wide and narrow lamella [4]. The mechanical strength for bagasse fibers is lower than that of bamboo [5]. Bagasse is a by-product of crushed sugarcane stalk [6]. A drawback with biocomposites is that they are engineered with chemically derived products developed from renewable sources, rather than direct application of naturally occurring materials such as plant based plastics. The transition from commercial plastics to sustainable biodegradable plastics should reduce the burden of managing solid waste.

There are many different types of biodegradable plastics that are commercially available. Aliphatic polyesters have relatively good mechanical and thermal degradation properties for many household products [1]. These polymers can be easily processed and degrade with exposure to certain enzymes. Polylactic acid (PLA) is the principle polyester that has become widely accepted. Lactic acid can be produced through starch fermentation; then, by polycondensation of the lactic acid, PLA is formed [7]. High molecular weight PLA has recently been produced with improved structural properties and, under humid environments, it can last longer without degrading than regular PLA [1]. Pure starch polymers tend to degrade quickly under high moisture environments, though it is shown that a mixture of starch and vinyl alcohols provide more stability [2]. An important type of starch that has gathered attention is thermoplastic starch (TPS). This plastic is made from renewable sources and is cost comparable to commercial thermoplastics. The only drawback is that TPS is brittle. Plasticizers such as water or glycol can be added for a flexible structure [3]. Different variations of polyhydroxybutyrates (PHBs) have been developed since they can attain similar physical and mechanical properties to current commercial plastics. Typically, the elastic modulus (E) and tensile strength (TS) of P(3HB) are comparable to those of polypropylene (PP). However, the elongation of PP is reported to be higher than the elongation of P(3HB) [8]. The flexibility of the material can be improved when hydroxyvalerates (3HVs) are added as plasticizers. The main application for P(3HB-co-3HV) is commercial packaging. A general comparison of current trends shows that some commodity plastics (PP, PVC) have an elastic modulus within the range of 1-2.5 GPa, whereas some biodegradable plastics (PLA, PHB) have an elastic modulus around 3-4 GPa [3]. When comparing the mechanical properties for synthetic and biodegradable plastics, there is a wide range of values for the strength of materials. In general, synthetic thermoplastics are stronger than biodegradable plastics [3]. Other than manufacturer's specifications, there is no significant data on the changes in mechanical properties during storage and use. There are many potential applications for biodegradable plastics to replace commercial synthetic plastics, such as agricultural and compostable packaging, where the plastic may be exposed to harsh environmental conditions [9]. An understanding of the behavior of bioplastics under these

conditions is desirable, as in these plastics environmental conditions are analogous to degradation conditions [10]. The purpose of this work is to evaluate environmental effects on the mechanical properties of seven different biodegradable plastics. The biodegradable plastics chosen were bagasse, a bagasse bamboo blend, polylactic acid, wheatstraw (a composite of lignin, hemicellulose, and cellulose [11]), fiber pulp (recycled paper fiber [12]), potato starch (a potato based resin [13]), and a bamboo bulrush (a composite of neutral and acid detergent fiber, hemicellulose, cellulose, lignin and ash [14]) wheatstraw blend. Most of the polymers chosen are relatively new to the commercial field of biodegradable plastics.

#### **Materials and Methods**

Specifically for the purpose of testing, a variety of serviceware items were collected from manufacturers, providing an overall selection of seven different biodegradable plastics (Table 1). Samples of the following plastics were tested: bagasse, a bagasse bamboo blend, polylactic acid (PLA), wheatstraw, fiber pulp, potato starch, and a bamboo bulrush wheatstraw blend. The bagasse, PLA, wheatstraw and fiber pulp were provided by the manufacturer in the form of clamshell containers while the bagasse bamboo blend, potato starch and bamboo bulrush wheatstraw blend were provided in the form of plates. Polystyrene was obtained from a commercial manufacturer in the form of a clamshell and evaluated under similar conditions to the bioplastics. Illustrations of how the samples were obtained for testing can be found in Fig. 1.

	Base	Commercial Name	Supplier
	Polymer(s)		
Α	Bagasse	Sugarcane Clamshells	ECO Products, Boulder, CO 80301
В	Bagasse,	Earth Choice Bagasse	Pactiv,
	Bamboo	Blend Tableware	Lake Forest, IL 60045
С	Bagasse,	Be Green Light Line	Be Green Packaging, Santa Barbara,
	Bamboo,	Plates	CA 93101
	Wheatstraw		
D	Fiber Pulp	Earth Choice Fiber	Pactiv
		Blend Hingeware	
Е	PLA	Clear Clamshells	ECO Products
F	PS	ClearView SmartLock	Pactiv
G	Potato	TaterWare	Earth To-Go, Sunriver, OR 97707
	Starch		
Η	Wheatstraw	Be Green Light Line	Be Green Packaging
		Clamshells	

Table 1. Summary of the materials used in this study including commercial name, base polymers, supplier, and the letter designation used in figures and tables.

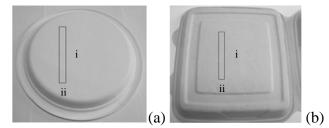


Figure 1. Photographs of the as-received products. Samples B, C, and G (Table 1) were obtained as plates (a). Samples A, D, E, F, and H were obtained as clamshells (b). The location and orientation of the samples cut from the plates and clamshells are indicated. The length of the cut sample (i) was 100mm and the width (ii) was 13mm. The plates and clamshells typically had a thickness of 0.6mm.

The mechanical properties were tested according to ASTM D882-10. The plastic samples were cut as shown in Fig. 1 using a Xacto knife and an acrylic template. Samples were generally cut along the direction of maximum orientation (Fig. 1). At least three and up to eight samples were used in each test in order to obtain an average value.

Tensile testing was performed using an Instron 4201 machine. As the samples had an average thickness of 0.6mm, cardboard strips were attached to each end with superglue on both sides to increase the gripping capabilities of the machine. An additional cardboard piece was used to support the samples as they were loaded into the machine to prevent them from fracturing prematurely. The samples were tested at a strain rate of 1mm/min until fracture. Sample runs which deviated more than 10% from the average value were rejected from the analysis.

In order to examine the effect of UV radiation on mechanical behavior, samples were irradiated with UV light using a UVP Tansilluminator for a period of 15 min at a wavelength of 360 nm. The samples were then subjected to the tensile testing in the manner described previously to determine the change in properties from photo-degradation. A 15 min treatment corresponds to approximately 0.249 years or 89.7 days of outdoor exposure.

In order to study the effects of moisture on the properties, samples were tested according to ASTM D7191-10. The samples were placed in a water bath for 24hr. They were then removed from the water and blotted dry before being placed in a desiccator for 72hr. The samples were then tensile tested as before to determine their change in properties.

In order to determine the long term changes in mechanical properties, accelerated aging was performed on the samples. They were placed in a Cole-Parmer oven at an average temperature of 100°C for 3 weeks. Then, the samples were removed, allowed to cool to room temperature, and tensile tested in the manner above to determine the resultant change in properties. The temperature-time equivalence based on the Arrhenius equation was used to estimate the properties at long times [14]:

$$t_2 = t_1 \exp\left[\frac{Q}{8.314} \left(\frac{1}{298} - \frac{1}{373}\right)\right]$$
(1)

The equivalent time (t<sub>2</sub>) at room temperature corresponding to 3 weeks (t<sub>1</sub>) at 100°C was calculated. An activation energy Q of 26200 J/mol was used in the above equation [16]. In general, t<sub>2</sub> was on the order of 6 months. Thus, the degradation properties after 6 months at room temperature can be simulated by aging the plastics for 3 weeks at 100°C.

#### **Results and Discussion**

A wide variety of biodegradable serviceware is now available in stores, with nationwide chain stores usually selling at least one brand. These newer materials generally exhibit similar properties to their polystyrene counterparts before being subjected to service conditions for extended periods as shown in Fig. 2. Data in Fig. 2 were chosen to represent the average elastic modulus and tensile strength (TS) for each material. It can be seen in the figure that some of the biopolymer materials have a greater strength than polystyrene (F). Polylactic acid (E) had the greatest tensile strength of all the as-received materials. A full summary of the results of tension tests performed can be found in Table 2. In general, most of the biopolymers tested were brittle; the best, wheatstraw, only provided 2.6% elongation. Along with this, wheatstraw provides a significant strength advantage over polystyrene with a TS of 36.2 MPa. Fiber pulp and potato starch products, however, proved to be particularly weak with TS of only about 4.6 MPa and 6.7 MPa, respectively. This result is in agreement with other investigations that have shown that starch-based thermoplastics are particularly weak with a yield strength of about 3 MPa when compared with traditional thermoplastics [17].

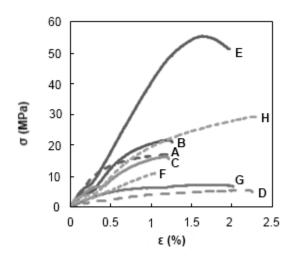


Figure 2. Sample stress strain curves for the as-received materials. The legend coincides with the designations in Table 1.

Table 2. Summary of the material properties for the data plotted in Fig. 1. E-elastic modulus, YS-yield strength, TS-tensile strength, % Elong.-% elongation.

Type E (GPa)	YS (MPa)	TS (MPa)	% Elong.
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Α	3.8±0.2	8.9±4.3	12.6±8.9	1.5±0.6
В	3.0±0.2	6.3±1.4	21.8±1.1	1.4±0.2
С	3.7±0.2	6.2±0.3	18.9±2.7	$1.2\pm0.0$
D	0.5±0.1	$1.7\pm0.4$	4.6±0.7	2.1±0.2
Е	4.3±0	$7.0\pm0.4$	58.0±5.7	$2.4{\pm}0.5$
F	1.1±0.3	3.7±1.0	11.8±1.3	1.5±0.4
G	1.1±0.1	$5.5 \pm 0.9$	6.7±0.6	1.7±0.3
Н	4.6±1.6	4.3±0.2	36.2±6.0	2.6±0.3

An examination of the data in Table 2 indicates that most of the biodegradable plastics exhibit properties generally similar to synthetic plastics. For example, the modulus of polylactic acid (PLA) has been reported to be 2.8 GPa by Verbeek and Bier and 4.3 GPa in the present investigation [3]. This compares well with the elastic modulus (E) for polystyrene from the clamshell which was calculated to be 1.1 GPa.

Ultraviolet (UV) exposure had a drastic effect on the properties of most materials. A full summary of results can be found in Table 3 and a comparative graph in Fig. 3. In Fig. 3, it can be seen that after the UV exposure, the strengths of all the materials is affected significantly. The majority of the materials also have higher percent elongation than the polystyrene after the exposure. Wheatstraw, polylactic acid, the bagasse bamboo blend, and potato starch proved especially vulnerable, with at least an 80% decrease in E and a minimum decrease of 78% in TS. UV radiation may have initiated the hydrolysis of the ester groups in PLA as well as increased the rate of degradation. After UV treatment, the mechanical properties of PLA may decrease by approximately 50%, which is comparable to the calculated data [18]. All of the biodegradable materials except fiber pulp were affected significantly more than the polystyrene. Overall, the UV radiation caused significant reduction in the properties of the biomaterials while having less of an effect on polystyrene.

Туре	E (GPa)	YS (MPa)	TS (MPa)	% Elong.
А	0.9±0.2	2.8±1.9	6.6±0.5	1.6±0.2
В	0.6±0.1	1.5±0.3	4.2±0.8	1.3±0.2
С	$0.8\pm0$	0.8±0.2	3.6±0.2	$1.0\pm0.0$
D	$0.4\pm0.0$	$1.1\pm0.2$	3.7±0.8	1.9±0.3
Е	$0.7 \pm 0.0$	3.5±1.6	6.8±1.4	1.6±0.1
F	$0.7 \pm 0.2$	$2.6\pm0.4$	$10.5 \pm 5.1$	$1.4\pm0.8$
G	$0.2\pm0.0$	$1.2\pm0.2$	1.5±0.3	$1.9\pm0.2$
Н	0.6±0.1	1.2±0.3	5.5±1.6	$2.2\pm0.2$

Table 3. Material properties in tension after 15 min UV of exposure. E-elastic modulus, YS-yield strength, TS-tensile strength, % Elong.-% elongation.

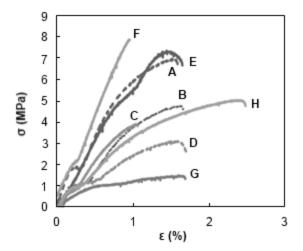


Figure 3. Sample stress strain curves after 15 minutes of UV radiation. The legend coincides with the designations in Table 1.

Exposure to humidity also had a dramatic effect on the mechanical properties (Fig. 4), summarized in Table 4. Again, the biodegradable materials were affected more than polystyrene. Here it can be seen that polystyrene has a greater strength than all the biomaterials along with having a greater E than all but the bamboo bagasse blend. In general, the effect of humidity was not as drastic as that of the UV radiation. However, the humidity took a particular toll on the E of bagasse causing an 85% decrease and on the TS of the bagasse bulrush wheatstraw blend causing an 80% decrease. Bagasse may contain different levels of hydrophobic lignin and water soluble hemicellulose [19]. The bagasse sample used may have more hemicellulose components which may result in a decrease of the mechanical properties. Starch based polymers also exhibit hydrophilic characteristics. The mechanical strength of starch polymers drastically decrease after exposure to humidity as reported by Tang and Alavi [20]. Overall, the humidity increases the ductility of the materials possibly due to water absorption and swelling, such as what occurs with polyvinyl alcohol [20].

Table 4. Material properties in tension after 24hr in a 100% humidity environment. E-elastic modulus, YS-yield strength, TS-tensile strength, % Elong.-% elongation. Material E was not tested due to the lack of samples.

Туре	E (GPa)	YS (MPa)	TS (MPa)	% Elong.
А	0.6±0.1	1.7±0.4	4.2±0.6	1.9±0.5
В	$0.8 \pm 0.0$	2.0±0.7	4.9±0.4	$2.4{\pm}0.4$
С	0.5±0.1	1.6±0.6	3.7±0.5	1.6±0.2
D	$0.4{\pm}0.1$	1.6±0.2	3.6±0.7	2.6±0.6
Е				
F	0.8±0.1	2.4±0.0	$13.0 \pm 1.3$	2.5±0.4
G	$0.2 \pm 0.0$	1.7±0.1	$1.7\pm0.1$	1.5±0.4
Н	1.2±0.5	1.2±0.2	$8.4{\pm}1.8$	2.9±0.4

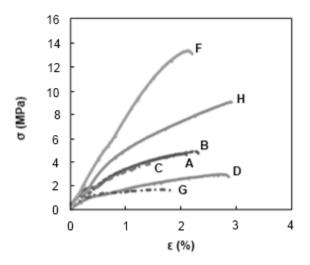


Figure 4. Sample stress strain curves after 24hrs at 100% humidity. The legend coincides with the designations in Table 1.

The accelerated aging data indicated that over a six month period, most of the biodegradable plastic products undergo a significant reduction in strength as shown in Fig. 5 and Table 5. It can be seen that aging does not significantly affect the percent elongation, since most materials already have low ductility. However, the majority of the biomaterials have lower strengths than in their as-received condition. Due to aging, the bagasse bamboo blend's E dropped from 3 GPa to 0.8 GPa and the TS from 21.8 MPa to 5.7 MPa while the bamboo bulrush wheatstraw blend's E dropped from 3.7 GPa to 0.7 GPa and the TS from 18.9 MPa to 2.7 MPa. On the other hand, the modulus and strength of polystyrene increased. This decrease in strength in biopolymers may be caused by chain scission, which shortens the molecules in the material [21]. Random scission and/or chain-end scission may occur during the aging process [21]. Overall, the bioplastics tested were more susceptible to aging than the polystyrene.

Table 5. Material properties in tension after 3 weeks in a 100°C environment. E-elastic modulus, YS-yield strength, TS-tensile strength, % Elong.-% elongation. Materials E and G were not tested due to the lack of samples.

Туре	E (GPa)	YS (MPa)	TS (MPa)	% Elong.
А	5.0±0.8	5.0±0	30.5±10.2	1.2±0.5
В	$0.8\pm0.1$	2.3±0.7	5.7±0.4	$1.4{\pm}0.0$
С	$0.7 \pm 0.0$	1.3±0.0	2.7±0.5	0.6±0.1
D	$3.5 \pm 0.6$	$14.8 \pm 1.5$	$20.4 \pm 2.8$	1.4±0.3
Е				
F	4.2±0.5	10.6±0	13.5±4.4	0.39±0.13
G				

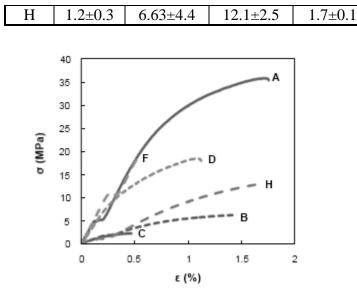


Figure 5. Sample stress strain curves after accelerated aging at 100°C for three weeks corresponding to six months. The legend coincides with the designations in Table 1.

A comparison of properties of bagasse bamboo blend and polystyrene can be seen in Fig. 6. Polystyrene, in general, is not affected significantly by UV exposure and humidity. The E, TS, and ductility are essentially similar to the values obtained in the as-received samples. Polystyrene, however, was significantly affected by accelerated aging. The modulus increased to 4.2 GPa from an initial value of 1.1 GPa. Similarly TS increased to 13.5 MPa from 11.8 MPa. These results suggest a potential crosslinking effect during degradation [21]. On the other hand, the blend material exhibited a drastic decrease in strength under all conditions, which is a trend displayed in almost all of the biopolymers. However, fiber pulp seemed relatively immune to changes in strength from ultraviolet or humidity exposure. Thus, in general, the bioplastics may experience a lessening in strength during use that does not occur in traditional materials such as polystyrene.

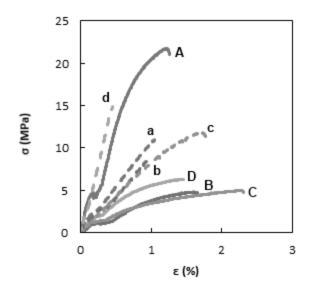


Figure 6. A direct comparison of the properties of bagasse bamboo blend (solid lines) and polystyrene (dashed lines). A-as-received, B-after 15 min UV exposure, C-after 24hr in a 100% humidity environment, D-after 3 weeks accelerated aging at 100°C.

The tested biodegradable products can generally be classified into three groups: cellulose containing, polylactic acid based, and starch based. It can be seen that the starch based materials are most affected by the environmental conditions while the cellulosic materials are least affected. For example, wheatstraw, which is a starch based polymer, undergoes an 85% decrease in tensile strength under UV light while the bagasse, a cellulosic, only undergoes a 48% decrease. The results are similar under 100% humidity conditions with the bagasse having a 67% decrease while the wheatstraw has a 77% decrease. Similar results on the loss of properties in starch under humid conditions have been reported previously [17] However, additives can be used to overcome any shortcomings in starch based plastics. Therefore, it is necessary for these biomaterials to be improved to be viable substitutes for synthetic plastics.

#### Conclusions

Biodegradable serviceware is currently being considered as a viable alternative to traditional plastics. Seven biodegradable plastics were tested and found to have generally similar properties to polystyrene in the as-received condition. Some biopolymers exhibited higher strength and over half of the materials exhibited a higher percent elongation than polystyrene. The biodegradable plastics, however, may be more sensitive to humidity and UV exposure compared to traditional plastics. After 6 months, the strength of most biodegradable plastics can be expected to decrease significantly, while that of polystyrene does not change appreciably. Under service conditions, it is possible for the biopolymer materials' properties to change, and this behavior should be taken under consideration during the design process, particularly when the material will be subjected to extended periods of moisture exposure.

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#### Paper 2

K. Buffum, H. Pacheco, and S. Shivkumar, "Environmental Effects on the Properties of Commercial Biopolymer Products" *Journal of Polymer Research* (2013) submitted for publication.

#### **Environmental Effects on the Properties of Commercial Biopolymer Products**

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#### Abstract

The current trend towards sustainability has created new interest in biodegradable plastics. While many investigations have examined the behavior of biodegradable plastics, the changes in properties that may occur during use have not been fully developed. The mechanical properties of seven types of biodegradable plastics were analyzed. In addition, the properties of polystyrene (PS) used in similar applications were examined. The effects of UV exposure, humidity, and accelerated aging on the mechanical properties were studied. In general, the strength of several biopolymers was less than that of PS with the exceptions of polylactic acid and wheatstraw. The properties of the biopolymers generally deteriorated significantly upon exposure to UV radiation and humidity, with polylactic acid, wheatstraw, potato starch, and the bamboo bulrush wheatstraw blend being affected the most. Accelerated aging data indicate that after 6 months under ambient conditions, the potato starch, wheatstraw, and bamboo bulrush wheatstraw blend have a reduction in strength and modulus. Thermal analysis displayed a general weight loss curve for all samples tested, with the exception of potato starch. The major weight loss region occurred over a temperature range of 250-400 degrees Celsius with weight loss values of approximately 69-97%. Additional improvements may be necessary to resist environmental effects so that biopolymers can be effective replacements for traditional plastics.

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Keywords: biopolymers, biodegradable, PLA, starch, bagasse

#### **1. Introduction**

Biodegradable polymers, specifically from renewable resources, are being examined for replacement of synthetic plastics. The most common ASTM definition of biodegradable polymers states that a degradable polymer is one in which "degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae" [1]. Biodegradable polymers may be converted back into carbon dioxide after their use [2]. With this ability, biopolymers that are produced by renewable resources may create a "carbon neutral" life cycle in which the net amount of carbon dioxide released into the environment remains relatively constant [2]. A variety of renewable biopolymers are produced by plants such as cellulose, starch, and protein [3]. Agro-polymers, typically starch and bagasse, are being examined for their sustainable nature due to vast agricultural resources available for use [4]. The resources used in the production of renewable biopolymers are continually replenished which becomes advantageous over traditional plastics for sustainability [2]. Typical commercial biopolymers are polylactic acid (PLA), polyhydroxyalkanoates (PHA), starches, and bagasse. Some applications for PHAs range from stiff packaging to flexible coatings [2]. PLA can be used for flexible packaging or drinking cups as well as similar applications to polypropylene (PP) and polystyrene (PS) [5, 6]. Applications for starches reside mainly with food packaging [7]. Where starch products are known for their highly hydrophilic nature, current applications are limited.

When comparing the mechanical properties for synthetic and biodegradable plastics, there is a wide range of values for the strength of materials. In general, synthetic thermoplastics are stronger than biodegradable plastics [4]. Specifically, polyhydroxybutyrate, P(3HB), has mechanical properties similar to polypropylene with the exception of its elongation at breaking as 6% [2]. Some biodegradable polymers are quite brittle, such as thermoplastic starch. To improve ductility, plasticizers can add more flexibility to the structure [4]. The degradation period for synthetic plastics may last up to 450 years in a landfill whereas some biodegradable polymers, starch and bagasse composites, may degrade within a few months [8]. The degradation behavior of the most common biopolymer, PLA, has been studied extensively. The degradation rate for PLA may be reduced by changing the extent of its hydrophilic property or its crystallinity [9]. PLA can degrade in compost by microorganisms which discharge esterase, protease, or lipase [5]. Biodegradable polymers can, with slight improvements, be comparable to their synthetic counterparts in many applications. The drawbacks with biopolymers may be reduction in strength after use in certain environments or limitation on available data. Many renewable biopolymers, when introduced to moist or humid environments, may exhibit reduced mechanical properties [8]. Hydrophilic biopolymers tend to degrade quickly and drastically decline in strength while exposed to humid environments [8, 9]. Even though biopolymers gained increasing amounts of attention, the data on the mechanical behavior during use is limited, and service conditions are not understood [3, 8, 9]. Many manufacturers do not provide information on the changes in properties of the product during or after use [10, 11, 12, 13]. Consequently, the objectives of this research were to obtain as-received mechanical property values comparable to traditional plastics and to analyze the effects of ultraviolet (UV) radiation

and water exposure on the mechanical properties of commercial biopolymers. In order to achieve these objectives, several sample biopolymers were obtained from manufacturers and subjected to standard ASTM test procedures.

#### 2. Materials and Methods

Specifically for the purpose of testing, a variety of serviceware items were collected from manufacturers, providing an overall selection of seven different biodegradable plastics (Table 1). Samples of the following plastics were tested: bagasse, a bagasse bamboo blend, polylactic acid (PLA), wheatstraw, fiber pulp, potato starch, and a bamboo bulrush wheatstraw blend. The bagasse, PLA, wheatstraw and fiber pulp were provided by the manufacturer in the form of clamshell containers while the bagasse bamboo blend, potato starch and bamboo bulrush wheatstraw blend were provided in the form of plates. Polystyrene was obtained from a commercial manufacturer in the form of a clamshell and evaluated under similar conditions to the bioplastics as a means of comparing their properties to existing materials.

The mechanical properties were tested according to ASTM D882-10. The plastic samples were cut using a Xacto knife and an acrylic template from the center portions of the product (see Table 1). Samples were generally cut along the direction of maximum orientation. At least three and up to eleven samples were used in each test in order to obtain an average value. Tensile testing was performed using an Instron 4201 machine. The samples were tested at a strain rate of 1mm/min until fracture. Sample runs which deviated more than 10% from the average value were rejected from the analysis.

In order to examine the effect of UV radiation on mechanical behavior, samples were irradiated with UV light using a UVP Tansilluminator for a period of 15 min at a wavelength of 360 nm. The samples were then subjected to the tensile testing in the manner described previously to determine the change in properties from photo-degradation. A 15 min treatment corresponds to approximately 0.25 years or 90 days of outdoor exposure.

In order to study the effects of moisture on the properties, samples were tested according to ASTM D7191-10. The samples were placed in a water bath for 24hr. They were then removed from the water and blotted dry before being placed in a desiccator for 72hr. The samples were then tensile tested as before to determine their change in properties.

Additionally, samples were tested according to ASTM D570-98 to determine density and water absorption along with the mass lost during water exposure.

The effects of moisture on tensile properties were examined with tensile samples by submerging in distilled water at 20°C for 24hr. the samples were removed from water, blotted dry, and tested immediately.

In order to determine the long term changes in mechanical properties, accelerated aging was performed on the samples. They were placed in a Cole-Parmer oven at an average temperature of 100°C for 3 weeks. Then, the samples were removed, allowed to cool to room temperature, and tensile tested in the manner above to determine the resultant change in

properties. The temperature-time equivalence based on the Arrhenius equation was used to estimate the properties at long times [14]:

$$t_2 = t_1 \exp\left[\frac{Q}{8.314} \left(\frac{1}{298} - \frac{1}{373}\right)\right] \tag{1}$$

The equivalent time ( $t_2$ ) at room temperature corresponding to 3 weeks ( $t_1$ ) at 100°C was calculated. An activation energy Q of 26200 J/mol was used in the above equation [15]. In general,  $t_2$  was on the order of 6 months. Thus, the degradation properties after 6 months at room temperature can be simulated by aging the plastics for 3 weeks at 100°C.

The thermal degradation behavior was examined by using a Texas Instruments TGA 2950. These tests were used to determine the mass loss in a sample with respect to temperature. Initial samples were heated to 600°C at a rate of 10°C per minute.

#### 3. Results and Discussion

#### 3.1 As Received Properties

A wide variety of biodegradable serviceware is now available in stores, with nationwide chain stores usually selling at least one brand. An examination of the data in Table 2 indicates that most of the biodegradable plastics exhibit properties generally similar to synthetic plastics. For example, the modulus of polylactic acid (PLA) has been reported to be 2.8 GPa by Verbeek and Bier and 5.3 GPa in the present investigation [4]. This compares well with the elastic modulus (E) for polystyrene from the clamshell which was calculated to be 0.9 GPa.

While all of the biopolymers tested except potato starch experience yielding, some have more a prominent region II than others. PLA (E), the bamboo bulrush wheatstraw blend (C), and wheatstraw (H) have the most visible region II with wheatstraw having the most clear and consistent region. This region runs from occurs from between around 0.1-0.3 percent elongation.

It can be seen in Fig. 1 that some of the biopolymers (E, H) can even have a greater strength than polystyrene (F). Polylactic acid (E) had the greatest tensile strength of all the as-received materials (56.8 MPa). It also exhibited slight signs of necking, the only material to do so. Additionally, wheatstraw (H) also has a much higher tensile strength (39.8 MPa) than PS (10.3 MPa). Fiber pulp, bagasse, bagasse bamboo blend, and potato starch products, however, proved to be particularly weak with strengths less than 6 MPa. This result is in agreement with other investigations which have shown that starch-based thermoplastics are particularly weak with a yield strength of about 3 MPa and a tensile strength of 10 MPa when compared with traditional thermoplastics which have a tensile strength in the range of 25-80MPa [4, 16, 17]. In general, most of the biopolymers tested were brittle; the best, wheatstraw, only provided 2.6% elongation.

In general, most of the biopolymers had densities between 0.5 g/cm<sup>3</sup> (bamboo bulrush wheatstraw blend, fiber pulp) and 1.3 g/cm<sup>3</sup> (PLA). By comparison, the density of most traditional commodity thermoplastics in between 0.9 g/cm<sup>3</sup> and 2 g/cm<sup>3</sup> [17]. Thus, the specific modulus in the biopolymers tested was between 83.4 m\*kg (potato starch) and 628.9 m\*kg (wheatstraw). Similarly the specific strength ranged between 0.5 m\*kg (potato starch) and 6.8

m\*kg (wheatstraw). Even though they may have low strengths, the specific moduli and specific strengths of the biopolymers are comparable to traditional plastics because of their low density. The low density may also facilitate a reduction in transportation and handling costs.

#### 3.2 Effect of Ultraviolet Exposure

Ultraviolet (UV) radiation generally has been known to reduce the strength of some plastics [18]. UV exposure had a drastic effect on the properties of most biopolymers. A full summary of results can be found in Table 3 and a comparative graph in Fig. 2. It can be seen that after the UV exposure, the strengths most of the biopolymers decreased significantly while PS was not affected. Wheatstraw and PLA proved especially vulnerable, with at least a 78% decrease in E and a minimum decrease of 84% in TS. This effect of UV on mechanical properties has been most studied in respect to PLA, with very little information available in the literature about the other biopolymers tested, as they are fairly new to the market. UV radiation may have initiated the hydrolysis of the ester groups in PLA as well as increased the rate of degradation [18]. After UV treatment, the mechanical properties of PLA may decrease by approximately 50%, which is comparable to the calculated data [7]. All of the biodegradable materials, except bagasse, were affected significantly more than the polystyrene. Additionally, the region II in all the biopolymers that exhibited yielding became now more prominent, covering a range of 0.3% elongation. Wheatstraw's region II spanned a range from about 0.2-0.5 percent elongation. There was a marginal increase in the ductility of the biopolymers. Overall, the UV radiation caused a significant reduction in the properties of the biopolymers while having a negligible effect on polystyrene. This indicates that biopolymer products, when exposed to sunlight, may lose properties.

#### 3.3 Effects of Humidity and Moisture

Exposure to humidity also had a dramatic effect on the mechanical properties of the biopolymers (Fig. 3), summarized in Table 4. Again, the effect on polystyrene was negligible. In general, the effect of humidity was not as drastic as that of the UV radiation. However, the humidity took a particular toll on the PLA causing an 83% decrease in E and an 80% decrease in TS. It also no longer has a yield strength. This could be due to the hydrolysis of the ester linkages in the molecules [18]. Bagasse and wheatstraw have the most prominent region II after the humidity exposure. Bagasse may contain different levels of hydrophobic lignin and water soluble hemicellulose [8]. The bagasse sample used may have more hemicellulose components which may result in a decrease of the mechanical properties. Starch based polymers also exhibit hydrophilic characteristics. The strength of starch polymers is known to drastically decrease after exposure to humidity due to plasticization caused by moisture as reported by Tang and Alavi [6]. Overall, the humidity increased the ductility, possibly due to water absorption and swelling of most biopolymers [6].

Complete immersion of the biopolymer products in water lead to significant swelling and absorption. The amount of water absorption ranged from 0 to 100% (fiber pulp). PLA, PS, and

potato starch were not much affected by their immersion in water. All of the materials did not experience much mass loss indicating that there was significant hydrolysis.

To examine the effect of water on the samples further, they were immersed in water for 24hrs before being tensile tested without desiccation, simply being blotted dry before mounting. This testing showed a drastic decrease in the tensile properties of all the biodegradable materials without having any significant effect on the polystyrene. The polymers all experienced at least a 42% decrease in tensile strength. Full results can be seen in Table 5 and Fig. 4, where PS dominance in wet environments can be clearly seen. For example, fiber pulp no longer exhibits a yield strength and its TS decreased from 5.4 to 1.4 MPa. All the biopolymers have a TS under 8.4 MPa. However, most experience an increase in ductility. This overall loss of properties during moisture and humidity exposure indicates that some of these biopolymers are not the best choice for containing beverages or soups for more than short periods of time.

#### 3.4 Effect of Aging

The long term exposure to ambient conditions is generally tested by accelerated aging. The thermal degradation at high temperature can represent the changes occurring over longer periods at room temperature. Over a six month period of exposure to ambient conditions, half of the biodegradable plastic products undergo a significant reduction in strength as shown in Fig. 5 and Table 6. Wheatstraw's E dropped from 3.7 GPa to 1.6 GPa and the TS from 39.8 MPa to 9.0 MPa while the bamboo bulrush wheatstraw blend's E dropped from 1.3 GPa to 0.7 GPa and the TS from 6.9 MPa to 2.3 MPa. The PLA was extremely affected, curling up so that the samples could not be tested post aging. This may be caused by the recovery of residual stresses created in the thermoforming process [17]. The relaxation time for PLA was calculated using the Williams-Landel Ferry equation and a glass transition 60°C temperature of as reported by Lim et al to be 8.4hr at 100°C [18, 19]. On the other hand, the modulus and strength of polystyrene increased. Additionally, fiber pulp and bagasse underwent drastic increases in strength and elastic modulus and the bagasse bamboo had a slight increase in these properties. After aging, fiber pulp is the strongest material with a TS of 20 MPa, an increase from its original TS of 5.4 MPa and no longer exhibits a yield strength. This could be due to either thermally induced crosslinking or the evaporation of plasticizers in the material [20, 21]. Potato starch on the other hand, now exhibits a yield strength after aging that was not present before. The decrease in strength in biopolymers may be caused by chain scission, which shortens the molecules in the material [20]. Random scission and/or chain-end scission may occur during the aging process [20]. Bagasse, the bamboo bulrush wheatstraw blend, wheatstraw, and PS only display a one in three change of retaining a yield strength after aging. This could also have been caused by thermally induced crosslinking, which would reduce the chain flexibility [20]. Biopolymers display a range of responses when undergoing accelerated aging.

A comparison of properties of wheatstraw and polystyrene can be seen in Fig. 6. Polystyrene, in general, is not affected significantly by UV exposure and humidity. The E, TS, and ductility are essentially similar to the values obtained in the as-received samples. Polystyrene, however, was significantly affected by accelerated aging. The modulus increased to 3.3 GPa from an initial value of 0.9 GPa. Similarly TS increased to 12.4 MPa from 10.3 MPa. These results suggest a potential crosslinking effect during degradation [20]. On the other hand, the wheatstraw exhibited a drastic decrease in strength under all conditions, which is a trend displayed in almost all of the biopolymers. However, fiber pulp, bagasse, and the bagasse bamboo blend seemed relatively immune to changes in strength from ultraviolet or humidity exposure. Thus, in general, the bioplastics may experience a lessening in strength during use that does not occur in traditional materials such as polystyrene.

The tested biodegradable products can generally be classified into three groups: cellulose containing, polylactic acid based, and starch based. It can be seen that the starch based materials are most affected by the environmental conditions while the cellulosic materials are least affected. For example, wheatstraw, which is a starch based polymer, undergoes an 85% decrease in tensile strength under UV light while the bagasse, a cellulosic, ha a 7% increase in strength. The results are similar under 100% humidity conditions, with the bagasse having a 26% decrease while the wheatstraw has a 77% decrease. Similar results on the loss of properties in starch under humid conditions have been reported previously [4] However, additives can be used to overcome any shortcomings in starch based plastics. Therefore, it is necessary for these biomaterials to be improved to be viable substitutes for synthetic plastics.

#### 3.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) shows a general trend throughout the samples tested. Depicted in Fig. 7, there are three degradation regions. The first and last regions, from approximately 0-250°C and 420-600°C, are the general degradation regions for the material. The middle region, from approximately 250-420°C, with the decreasing slope line, is the main degradation for the biopolymer sample. For all the samples except for potato starch, there was only one main degradation peak whereas the potato starch sample had two peaks. The degradation peaks occur when the biopolymer main chains are broken. Since potato starch tends to degrade quickly, plasticizers may have been added to the tested sample. One of the two degradation peaks could be attributed to the degradation of the plasticizer and the other one to main degradation of potato starch. The peak temperatures and their corresponding weight loss, in percent, are listed under Table 7. The sample weight loss during the main degradation reaction ranges from 69-97%.

#### 4. Conclusions

Biodegradable serviceware is currently being considered as a viable alternative to traditional plastics. Seven biodegradable plastics were tested and found to have generally similar properties to polystyrene in the as-received condition. Some biopolymers exhibited higher strength and half of the materials exhibited a higher percent elongation than polystyrene. The biodegradable plastics, however, may be more sensitive to humidity and UV exposure compared

to traditional plastics. After 6 months, the strength of some biodegradable plastics can be expected to decrease significantly, while that of polystyrene and other biopolymers increases, with the strength of bagasse and fiber pulp increasing drastically. Under service conditions, it is possible for the biopolymer materials' properties to change, and this behavior should be taken under consideration during the design process, particularly when the material will be subjected to extended periods of moisture exposure.

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## List of Tables

Table 1: Summary of the polymers used in this study including commercial name, base polymers and supplier. A photograph indicating the as received products is also included. The numbers in parenthesis in column 3 correspond to the dimensions (mm) of the product in the as received condition. X: location of the sample for mechanical testing. The labeling system defined in this table will be used in all subsequent figures and tables.

Table 2: As received densities and tensile properties. E-elastic modulus, YS-yield strength, TS-tensile strength, %Elong-percent elongation, SS-specific strength, SE-specific modulus.

Table 3: Biopolymer properties in tension after 15min of UV Exposure. E-elastic modulus, YS-yield strength, TS-tensile strength, %Elong-percent elongation.

Table 4: Biopolymer properties after 24 hours in a 100% humidity environment. E-elastic modulus, YS-yield strength, TS-tensile strength, %Elong-percent elongation.

Table 5: Tensile properties measured after complete immersion in water for 24 hours. The data were obtained immediately after removal from water (after blotting the sample dry). E-elastic modulus, YS-yield strength, TS-tensile strength, %Elong-percent elongation. The increase in mass after removal from the water is also shown.

Table 6: Tensile properties measured after accelerated aging (100°C for 3 weeks) to simulate room temperature changes in properties after 6 months.. E-elastic modulus, YS-yield strength, TS-tensile strength, %Elong-percent elongation. No PLA data due to sample deformation.

Table 7: Data from the TGA analysis. The temperatures and weight loss after the primary reaction is shown.

## **List of Figures**

Figure 1: Stress strain curves in the as-received condition. The legend coincides with the designation in Table 1.

Figure 2: Stress strain curves after 15 minutes of UV exposure. The legend coincides with the designation in Table 1.

Figure 3: Stress strain curves after complete immersion in water for 24 hours. The legend coincides with the designation in Table 1.

Figure 4: Stress strain curves after 24 hours in water, tested while still wet. The legend coincides with the designation in Table 1.

Figure 5: Stress strain curves after accelerated aging for 3 weeks at 100°C to simulate the change in properties at room temperature after 6 months. The legend coincides with the designation in Table 1.

Figure 6: A direct comparison of the properties of wheatstraw and polystyrene. Wheatstraw: Aas received, B-after UV exposure, C-after humidity exposure, D-after accelerated aging. Polystyrene: A´-as received, B´-after UV exposure, C´-after humidity exposure, D´-after accelerated aging.

Figure 7: TGA curves as a heating rate of 10°C/min. The legend coincides with the designation in Table 1.

	Base Polymer	Commercial Name	Supplier	Photo
A	Bagasse	Sugarcane Clamshells (229x229x76)	ECO Products, Boulder, CO 80301	x
В	Bagasse, Bamboo	Earth Choice Bagasse Blend Tableware (254)	<i>Pactiv</i> , Lake Forest, IL 60045	
С	Bagasse, Bamboo, Wheatstraw	Be Green Light Line Plates (267)	<i>Be Green Packaging</i> , Santa Barbara, CA 93101	X
D	Fiber Pulp	Earth Choice Fiber Blend Hingeware (198x198x76)	Pactiv	X
E	PLA	Clear Clamshells (203x203x76)	ECO Products	X
F	PS	ClearView SmartLock (203x203x76)	Pactiv	X 2 CONTRACTOR X 2 CONTRACTOR 1 CONTRACT
G	Potato Starch	TaterWare (152)	<i>Earth To-Go</i> , Sunriver, OR 97707	
Н	Wheatstraw	Be Green Light Line Clamshells (254x254x76)	Be Green Packaging	x

Sample	Density	Е	TS	YS	%Elong	TS/p	Ε/ρ
_	$(g/cm^3)$	(GPa)	(MPa)	(MPa)	_	(m*kg)	(m*kg)
Bagasse	0.6±0	$0.7 \pm 0.4$	5.4±1.8	1.0±0.6	1.4±0.6	0.9	119
Bagasse	0.6±0	0.7±0.1	4.3±1.8	2.1±1.6	1.1±0.2	0.7	119
Bamboo							
Blend							
Bamboo	$0.5\pm0$	1.3±0.9	6.9±6.3	3.4±2.9	0.8±0.3	1.4	102
Bulrush							
Wheatstraw							
Blend							
Fiber Pulp	$0.5 \pm 0$	$0.7{\pm}0.1$	$5.4\pm0.3$	$1.5\pm0.7$	$2.0\pm0.2$	1.1	142.8
Polylactic	1.3±0	5.3±1.9	$56.8 \pm 5.8$	6.3±0.5	2.4±0.5	4.5	415.7
Acid							
Polystyrene	0.9±0.3	0.9±0.3	10.3±0.9	2.7±0.8	1.5±0.3	1.2	102
Potato	1.1±0.1	0.9±0.5	5.9±3.2		1.7±0.3	0.5	83.4
Starch							
Wheatstraw	0.6±0	3.7±0.5	39.8±1.6	5.0±1.1	2.6±0.3	6.8	628.9

Sample	E (GPa)	TS (MPa)	YS (MPa)	%Elong
Bagasse	0.9±0.1	$5.8 \pm 0.8$	1.6±0.6	1.5±0.4
Bagasse	$0.6\pm0.1$	3.3±0.6	1.1±0	1.3±0.3
Bamboo				
Blend				
Bamboo	$0.4\pm0.2$	3.3±0.2	0.8±0.2	1.2±0.3
Bulrush				
Wheatstraw				
Blend				
Fiber Pulp	$0.5 \pm 0.1$	$3.8 \pm 0.9$	$1.2\pm0.2$	1.9±0.3
Polylactic	$0.8\pm0$	$8.1 \pm 2.0$	2.9±0.9	$1.6\pm0.1$
Acid				
Polystyrene	0.9±0.3	10.8±3.7	2.2±0.4	1.5±0.7
Potato Starch	0.3±0	2.2±0.4		1.9±0.3
Wheatstraw	0.8±0.3	6.1±1.8	1.2±0.2	1.9±0.6

Sample	E (GPa)	TS (MPa)	YS (MPa)	%Elong
Bagasse	0.5±0.1	4.0±0.6	1.4±0.6	1.9±0.5
Bagasse	0.6±0	4.2±0.3	1.3±0	2.3±0.3
Bamboo				
Blend				
Bamboo	0.5±0.1	3.5±0.5	1.3±0.5	1.6±0.2
Bulrush				
Wheatstraw				
Blend				
Fiber Pulp	0.5±0.2	3.4±0.8	1.6±0.2	2.6±0.6
Polylactic	0.9±0.2	$11.2 \pm 1.8$		1.8±0.3
Acid				
Polystyrene	1.0±0.3	$11.8 \pm 1.9$	2.4±0.2	2.0±0.7
Potato Starch	0.4±0	2.6±0.2		1.5±0.4
Wheatstraw	2.0±1.5	9.1±2.0	1.3±0.2	2.8±0.3

Sample	E (GPa)	TS (MPa)	YS (MPa)	%Elong	% increase
					in mass
Bagasse	$0.2 \pm 0.1$	$1.9\pm0.5$	$1.0\pm0.3$	2.3±0.7	64.4±1.8
Bagasse	$0.5\pm0.2$	$2.5 \pm 0.8$	1.1±0.2	$1.6\pm0.8$	52.5±3.6
Bamboo					
Blend					
Bamboo	0.5±0.1	2.6±0.6	0.9±0.1	1.3±0.4	62.1±2.5
Bulrush					
Wheatstraw					
Blend					
Fiber Pulp	0.1±0	1.4±0		3.1±0.1	99.8±4.3
Polylactic	1.1±0.2	8.4±4.2	2.0±0.9	1.7±0.2	-0.1±0.2
Acid					
Polystyrene	1.0±0	10.8±0.6	1.8±0	1.4±0.1	-0.7±1.7
Potato Starch	0.5±0.1	2.7±0.2	1.3±0.3	1.9±0.1	1.8±0.2
Wheatstraw	0.2±0.1	2.3±0.5	1.2±0	3.0±0.3	73.0±1.0

Table	6
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Sample	E (GPa)	TS (MPa)	YS (MPa)	%Elong
Bagasse	3.3±1.7	18.5±13.2	5.0±0	1.1±0.5
Bagasse	$0.8\pm0$	5.4±0.4	1.8±0.2	1.4±0
Bamboo				
Blend				
Bamboo	0.7±0.1	2.3±0.1	1.25±0	0.5±0
Bulrush				
Wheatstraw				
Blend				
Fiber Pulp	3.7±0.2	20.3±2.3		1.4±0.3
Polylactic				
Acid				
Polystyrene	3.3±0.7	12.4±3.7	8.6±0	0.4±0.1
Potato Starch	0.5±0.1	2.4±0.3	1.2±0.2	0.9±0
Wheatstraw	1.6±0.4	9.0±0.4	0.8±0	1.4±0.2

Sample Name	Start Temp (°C)	Peak Temp ( <sup>o</sup> C)	End Temp (°C)	Weight Loss during Reaction (%)
Bagasse	290	388	417	79
Double Blend	287	377	409	81
Triple Blend	247	393	440	70
Fiber Pulp	253	381	416	73
PLA	308	391	406	97
Potato Starch	277	340	364	79
(2 peaks)	400	498	525	
Wheat Straw	249	383	414	69

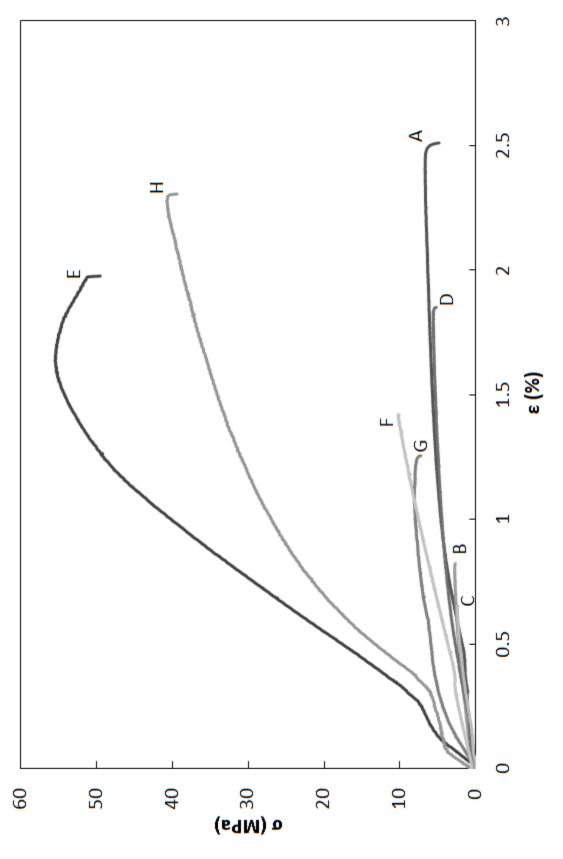


Fig. 1

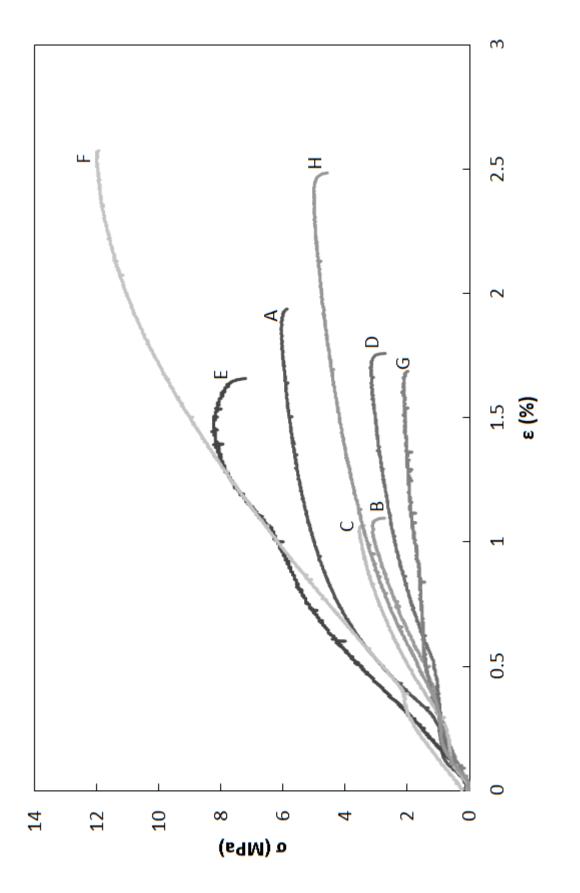


Fig. 2

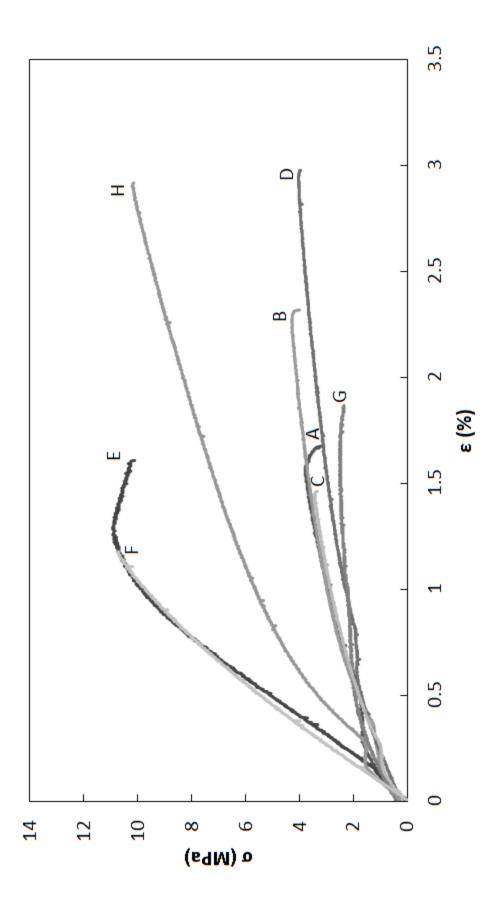
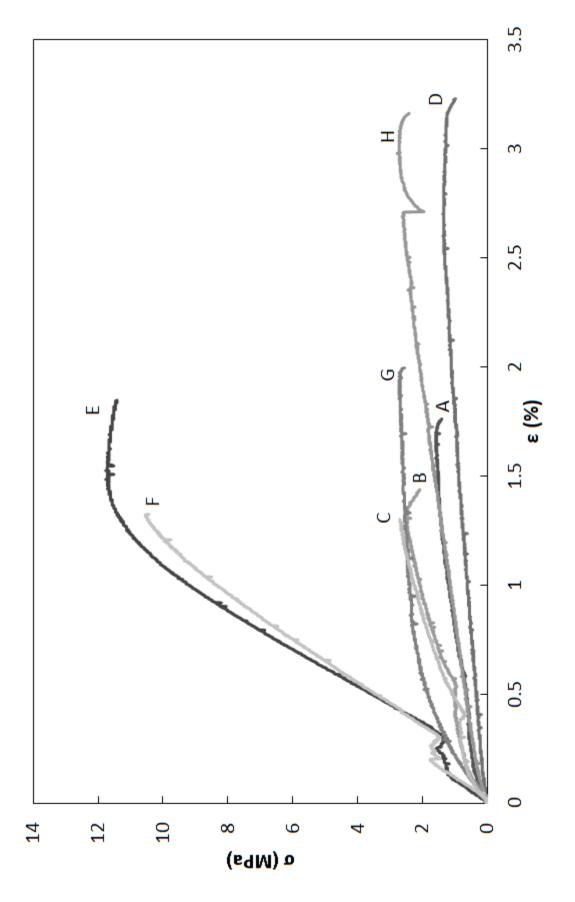


Fig. 3



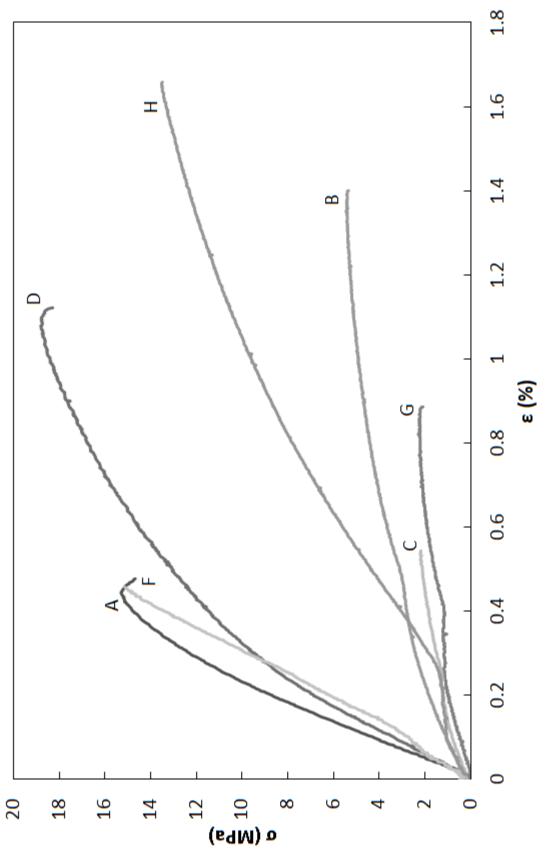


Fig. 5

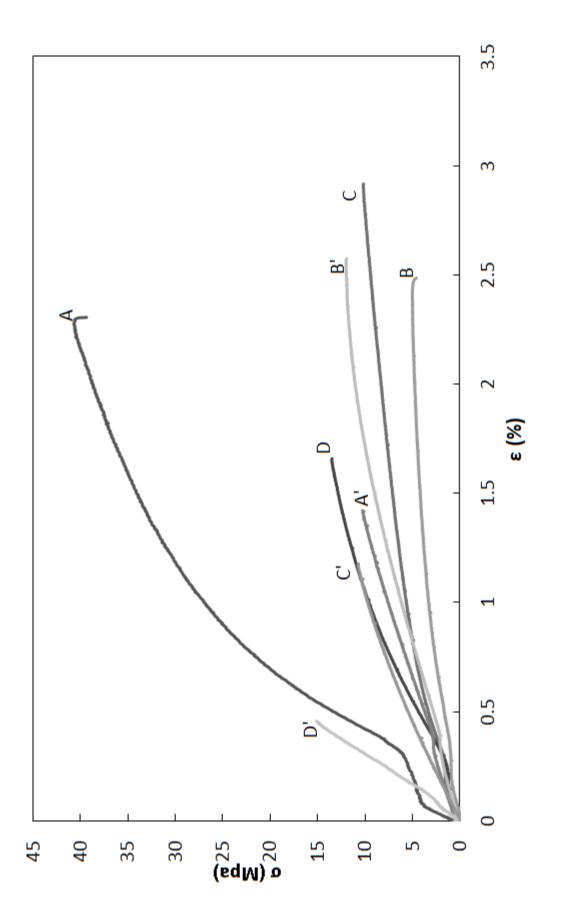


Fig. 6

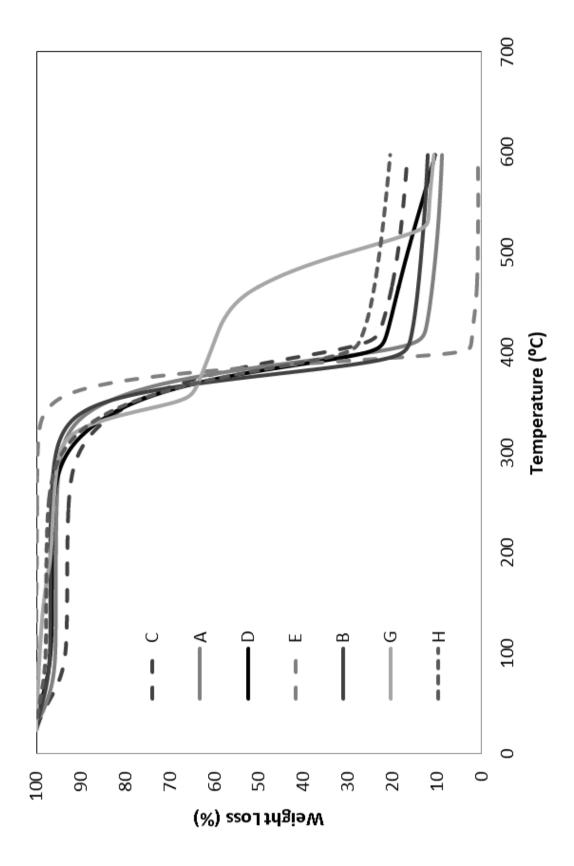


Fig. 7

## **Overall Conclusions for the MQP**

The results of this project indicate that the use of biopolymers in serviceware is expanding. The properties of biopolymers can be comparable to those of synthetic plastics in the as received condition where E is within the range of 0.7-5.3GPa and TS is within the range of 4.3-56.8MPa. However, biopolymers are highly susceptible to UV radiation, humidity, and moisture, all of which cause significant property reduction. For example, under UV conditions the TS of wheatstraw dropped from 39.8 MPa to 6.1 MPa whereas the TS under humidity exposure was reduced to 9.1 MPa and the TS when exposed to moisture reduced to 2.3 MPa. Generally, where biopolymers exhibited a decline in strength, PS did not. In addition, most biopolymers absorbed a significant amount of water when exposed to moisture, with fiber pulp nearly doubling in weight. Furthermore, biopolymers tend to experience property changes over time, exhibiting a significant reduction after six months. For instance, the TS of wheatstraw, starting from 39.8 MPa, reduced to 9.0 MPa. Thermogravimetric analysis displayed a general trend where many biopolymers exhibited a 69-81% weight loss at a temperature range of approximately 380-400°C. Since several anecdotal descriptions of the drawbacks for biopolymers have been documented, improvements in the properties of biopolymers may be necessary in order to expand their applications [6, 18]. Methods for enhancing resistance to the effects of UV radiation, humidity, and moisture for these biopolymers should be examined. In the future, biopolymer applications may create a more sustainable option than current commercial synthetic plastics.

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# Appendix

All experimental data obtained from Mechanical and TGA testing is attached in zip files.

Mechanical Testing

- Text files explaining the included data.
- Instron output files for all test runs under all conditions.
- Table of density, moisture absorption and mass loss data from the tests in accordance to ASTM D570-98.
- Graphs including curves for all runs used to calculated tensile properties under all conditions. Sample thickness values can be found in the calculations for each curve.
- A photograph of the PLA samples post accelerated aging.

TGA Testing

- Excel files containing data values and graphs.
- Text files obtained from the TGA machine.