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Bioplastics
The Synthesis And Tensile Strength Of Bioplastic Film Of Guyana's Saccharum Officinarum L. (Sugarcane) Bagasse

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***Abstract*—There is a vast range of applications that demand the use of plastic materials. This coupled with the environmental impact of plastic production merits the importance of bioplastic production from agro-waste sources. The temporary acetylation of cellulose-rich biomass using trifluroacetic acid (TFA) produces plastic films with a wide range of mechanical properties comparable to engineered polymers produced from fossil fuel resources. Sugarcane bagasse was pre-treated using an alkali/bleaching matrix to remove hemicellulose and lignin fractions, which reduces kinks and failure of plastic films. IR results found that reflux treatment of biomass with 16% NaOH followed by 2% sodium chlorite solution resulted in a 70% and 80% decrease in peaks responsible for hemicellulose and lignin content, respectively. Pre-treated biomass was acetylated using TFA, which produced plastic films after 6-9 days. There was a 100% conversion of raw material to plastic film with an ultimate tensile strength of 31.56 MPa. Depending on the application, the ultimate tensile strength of this plastic film is similar to the low-density polyethylene (LDPE) based plastic products like squeezable bottles (e.g. honey and mustard), polyurethane (PU), soft rubbers and elastomers (BR) and silicones (PDMS). Bioplastic material resulting from sugarcane bagasse possesses the tensile strength required to compete with other engineered polymers in the market.**

Keywords—bioplastic; sugarcane bagasse; tensile strength.

INTRODUCTION

The continuous search for plastics manufactured from renewable sources is one of the most researched areas of late. In fact, the motivation for renewable plastics has been driven because of concerns with global warming, surging energy demands, and the depletion of fossil based resources [2]. Reference [2] carefully documented the search for bioplastics beyond the limited scope of natural polymers and focused on the biomass conversion in bio refineries and the chemical carbon fixation to produce highly tailored polymers. Their review focused on outlining research articles looking at “green monomer” from bio refineries and “renewable oils” that can potentially be used to manufacture sustainable polymers.

Sugarcane bagasse (SCB) contains about 40-50% cellulose followed by about 25-35% hemicellulose and the rest is mostly lignin of 18-24% [3]. The hemicellulose component is mainly xylose, arabinose, galactose and mannose. In this study, the husk of bagasse will be pre-treated to remove the hemicellulose and lignin fractions before acidic digestion using triflouroacetic acid (TFA). The pre-treatment is done with the aim of producing plastic film with relative tensile strength since lignin and hemicellulose fractions are known to contribute to kinks and failure.

LITERATURE REVIEW

Reference [1] investigated the direct transformation of edible vegetable wastes into bioplastics. The results produced from the wastes of cocoa pod husk, rice hulls, parsley and spinach stems with varying mechanical properties. The method employed was digestion with triflouroactic acid (TFA), casting and evaporation. In this way amorphous cellulose-based plastics were synthesized. It was observed that the color and transparency of the plastic films were indicative of the raw material used.

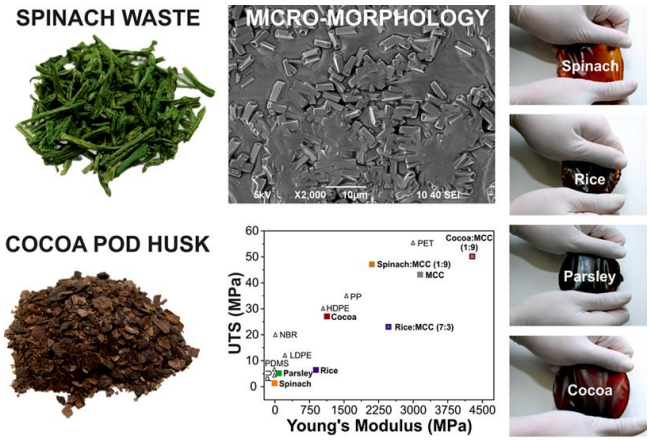

Fig. 1. The range of plastic films produced

Filter paper was used as the reference material in this study as it has about 97% cellulose. Illker and team produced amorphous cellulose plastic films from pure cellulose by treatment with TFA solution. After 3 days of aging cellulose plastics were casted. Dried films are trifluoroacetylated immediately after their formation and evaporation of TFA. However, this esterification was found to be temporary as it was spontaneously reversed in the presence of water or in humid atmosphere after 1-2 days.

EXPERIMENTAL

Materials

Whatman #1 filter paper (97% cellulose), 80% sodium chlorite flakes (Mol. wt. 90.44 g/mol,), potassium bromide, sodium hydroxide pellets (Mol. wt. 40.01 g/mol, > 98 %), and acetic acid (Mol. wt. 60.05 g/mol, > 99.7 %) were all sourced from amazon; trifluoroacetic Acid (TFA) (Mol. wt. 114.02 g/mol, > 99 %) was purchased from Sigma Aldrich USA.

Methodology

Pre-treatment of raw material

The quantity of raw material used for the preparation of the plastic film was 4-5 grams. The sugarcane bagasse was pre-treated to remove the lignin and hemicellulose fractions using alkaline and bleaching treatments with sodium hydroxide and a sodium chlorite/acetate buffer solutions, respectively. That is, alkaline and bleaching treatments were performed based on accepted and previously published methods [4].

Briefly, approximately four (4) grams of the raw material was heated via refluxed at around 85 °C for 4 hours with 4%, 8% and 16% (w/v) sodium hydroxide solution (200 mL). The fibers were continuously washed with distilled water. The alkali treated material was then bleached via heating in reflux for 2-4 hours at around 130 °C in 200 mL (1:1 v/v) of 2%, 4% and 8% solution of sodium chlorite and acetate buffer (27 g of sodium hydroxide and 75 mL acetic acid diluted to 1 L). The reaction was left to cool to room temperature then washed with excess distilled water. Three samples of SCB were treated with 4% sodium hydroxide after which each was then bleached using 2%, 4% and 8% sodium chlorite. This was repeated for the samples treated with 8% and 16% NaOH. Hence, there were a total of nine (9) samples. The design of alkali and subsequent bleaching treatments along with material yield are summarized in Table 1.

Table 2. Pre-treatment Stages

Raw Material	NaOH Treatment (%)	$NaClO_2$ Treatment (%)	Final Weight (g)
SCB1	4	2	1.90
SCB2		4	1.80
SCB3		8	1.95
SCB4	8	2	1.72
SCB5		4	1.60
SCB6		8	2.40
SCB7	16	2	1.60
SCB8		4	1.62
SCB9		8	1.63

Preparation of Films

Pre-treated material was left open overnight in a fume hood to be dried. The dried material was placed into a 50 mL glass bottle and 30 mL of triflouroacetic acid (TFA) solution was added, maintaining a concentration of solids at 3%. As can be appreciated, the different macro structural arrangements of the different components, as well as surface area would influence the time needed for cellulosic dissolution via the added TFA. Table 2 shows the reaction time for the SCB and filter paper samples.

Table 1. Reaction Time

Raw Material	Time (days)
Filter Paper	6-7
Sugarcane Bagasse	9-10

After exposure to the TFA, the films were produced from the suspension. The suspension was decanted onto recrystallization petri dishes and left in the fume hood for evaporation of excess TFA until dried plastic films were formed.

RESULTS/DISCUSSION

Characterization of Pre-treated Material

The pre-treatment was done primarily to reduce as much of the hemicellulose and lignin fractions from the biomass. These two compounds are second to cellulose in terms of the chemical composition of the SCB. Removing them will increase the access to the cellulose fibers in the material allowing for better fiber-

matrix adhesion to form plastic films with better mechanical properties [5]. It should be noted that the optimization of the pre-treatment was not performed in this study as in Yue's work [6].

The alkali treatment of the fibers involves the removal of surface impurities, the swelling of the crystalline region and the alkalization of the peripheral hydroxyl groups. The common trend in the observations is that there is a gradual decrease of hemicellulose and lignin from the raw materials. Further, bleaching with sodium chlorite causes an oxidative fragmentation of the lignin and some part of the lignin dissolves out as lignin chloride [7]. Reference [7] focused primarily on fibers originating from coconut coir, however, it is reasonable to assume the same explanation is valid for the sugarcane bagasse fibers used in this study.

Table 3. Reduction of Hemicellulose and Lignin from SCB

Sugarcane Bagasse	Transmission (AU) at Peaks of Interest		
	1740 cm^{-1}	1650 cm^{-1}	1240 cm^{-1}
Raw SCB	34.56	28.71	36.26
SCB1	20.33	14.35	17.76
SCB2	35.71	27.58	41.14
SCB3	21.47	16.04	23.97
SCB4	12.20	10.41	18.20
SCB5	14.87	12.10	16.43
SCB6	25.80	19.00	19.39
SCB7	32.53	24.35	26.49
SCB8	37.61	30.26	37.21
SCB9	10.41	6.58	7.02

Note. Sample SCB9 resulted in the most significant decrease in lignin and hemicellulose content, which corresponds to the pre-treatment conditions of 16% NaOH and 8% $NaClO_2$.

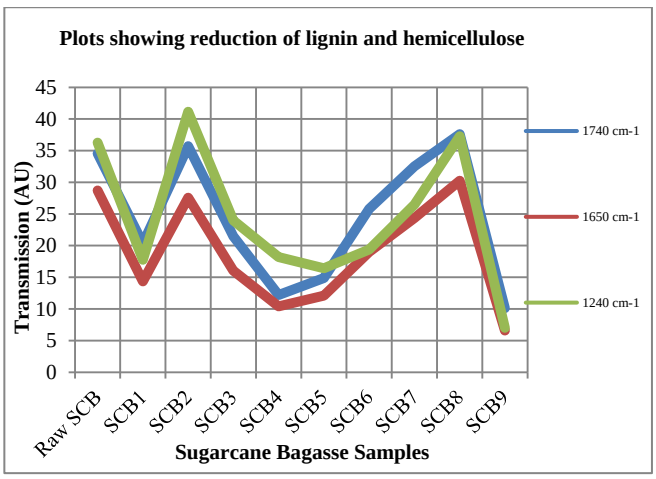

Fig. 2. Intensity of peaks for all SCB samples

Note. Reference can be made to Table 1 to observe the extent of cleaning as a result of the various combinations of alkali/bleaching pre-treatment conditions used for the SCB samples.

Note. The decrease in the intensities of the peaks is translated in term of Arbitrary Units (AU) on the y-axis.

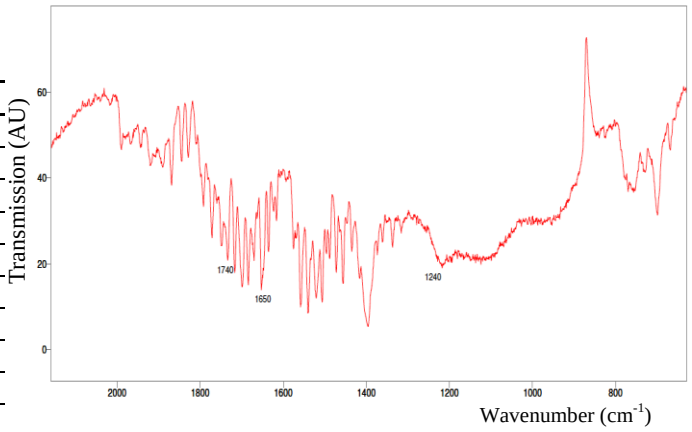

Fig. 3. IR spectrum of raw sugarcane bagasse

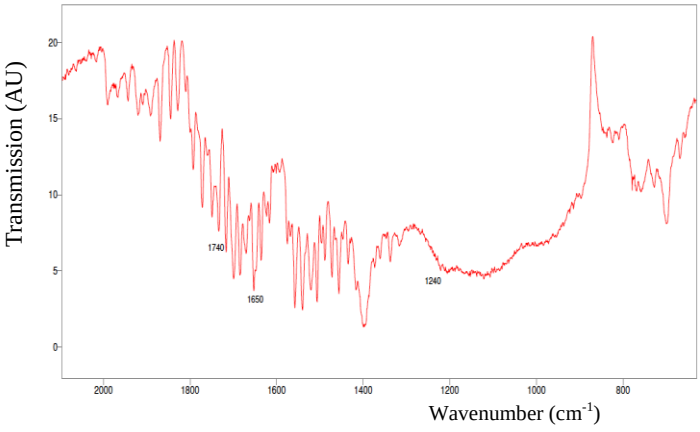

Fig. 4. IR spectrum of treated sugarcane bagasse

Sugarcane bagasse contains about 40-50% cellulose followed by about 25-35% hemicellulose and the rest is mostly lignin of 18-24% [3]. The hemicellulose component is mainly xylose, arabinose,

galactose and mannose. FTIR analysis shows the reduction of hemicellulose and lignin fractions through analysis of their functional groups. There are some peaks specific to sugarcane bagasse but still around the wavelengths characteristic of hemicellulose and lignin. The peak at 1240 cm^{-1} corresponds to C-O stretching vibration of aryl group in lignin and at 1640 cm^{-1} corresponds to C=C stretching vibrations of aromatic rings in lignin. The C=O stretching vibrations of carboxylic groups of hemicellulose and lignin is around 1740 cm-1. Reference [3] report a similar correspondence, however, the peaks were at 1252 cm^{-1} and 1511 cm^{-1} and 1738 cm^{-1}, respectively. These subtle differences can simply be shifts in the spectra due to external vibrations. Sample SCB9 resulted in the most significant reduction of hemicellulose and lignin by about 70.6% and 80.6%, respectively.

Fig. 5. Raw biomass and bioplastic film of SCB

Note. Bioplastic films produced from the sugarcane bagasse

Mechanical Properties

The mechanical properties are summarized in Table 3. The values reported in this communication are significantly greater than those reported by [1]. It can be reasoned that this was due to the more significant cellulosic content and stronger, harder nature of the biomass in this study compared to the softer cocoa leaves, parsley and spinach biomass [1].

Table 4. Mechanical Properties of SCB Bioplastic

Sample	Ultimate Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation (%)
97% Cellulose	73.92	1029.16	8.21
Sugarcane Bagasse	31.56	173.23	23.59

The tensile strength and modulus of the filter paper based plastic is superior to the SCB because of the high purity of cellulosic content (97%) that enables better dispersion during casting and homogenous mixing. It was clear that the SCB plastic film could withstand a relatively high strain compared to other engineered polymers. Therefore, it has the potential to stretch and be ductile.

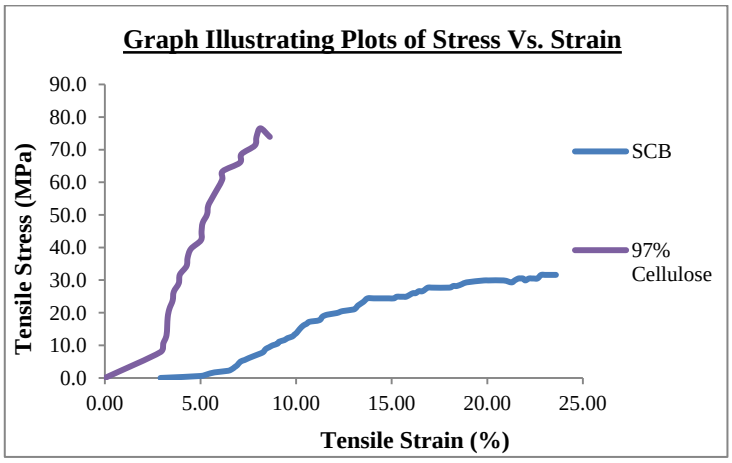

Fig. 6. Tensile strength of SCB and filter paper

The environmentally unfriendly phthalates that are present in engineered polymers is responsible for ductility but are absent in the SCB plastic film in this study. Nonetheless, the plastic film show similar characteristics to the low-density polyethylene (LDPE) based plastic products like the squeezable bottles, e.g. honey and mustard), polyurethane (PU), soft rubbers and elastomers (BR) and silicones (PDMS).

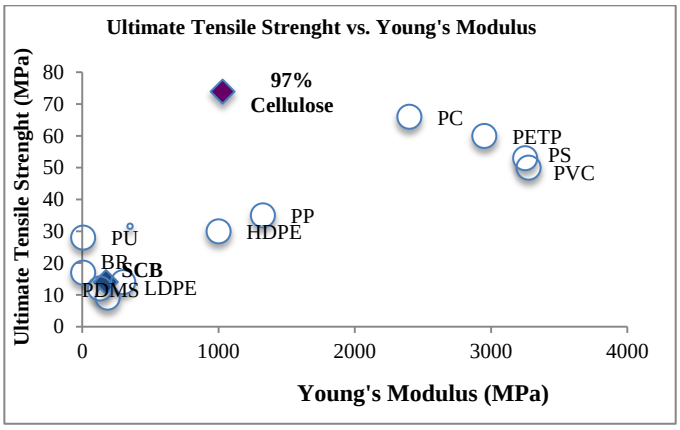

Fig. 7. Ultimate tensile strength and Young's Modulus

It was observed that, depending on the application, the ultimate tensile strength of the plastic film is in the region of the low-density polyethylene (LDPE) based plastic products like the squeezable bottles (e.g. honey and mustard), polyurethane (PU), soft rubbers and elastomers (BR) and silicones (PDMS) as evident in Figure 6. Therefore, the plastic film in this study has the potential to perform similar functions as those established. It should be noted that this film has the potential to be tuned to desired mechanical properties. Hence, it has the potential to attain characteristics of those engineered polymers with higher Young's Modulus values such as the HDPE, PP and even PVC. However, this is beyond the scope of this study.

CONCLUSION

Sugarcane bagasse was cleaned from 70% and 80% hemicellulose and lignin using 16% NaOH and 2% $NaClO_2$ solutions, respectively. Bioplastic films were produced after 6-9 days of aging in trifluoroacetic acid (TFA). Films had a tensile strength of 31.56 MPa. Bioplastic film can be readily produced via temporary acetylation with TFA from cellulose rich biomass.

RECOMMENDATIONS

The thermal stability via thermo gravimetric analysis of the plastic films should be performed to determine elongation properties at break point. Furthermore, the mechanical properties of other abundant cellulose rich biomass should be investigated in the future. And finally, it would be interesting to investigate whether these bioplastic films from cellulose rich biomass can be tuned to meet desired mechanical properties for specific applications.

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