Soy-based Bailing Twine with High Digestibility – Further Development
-Mid-term Report -

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1. Research Overview and Objectives

The goal of this research is to develop the formulations and processing conditions of PLA/soyhull twine and compare its properties with those of PLA/soymeal twine to identify the most suitable soy material and conditions for twine production.

2. Completed Work

Materials

Luminy® PLA (LX175) pellets were purchased from Filabot company. Soyhull (SH) powder was kindly provided by Northern Crops Institute, North Dakota State University. Calcium carbonate ($CaCO_3$) and 3-(Trimethoxysilyl)propyl methacrylate ($C_{10}H_{20}O_5Si$) were purchased from Ambeed company. The average particle size of $CaCO_3$ is ~ 3.8 μm according to its scanning electron microscope (SEM) image. Epoxidized soybean oil (ESO) was purchased from Spectrum Chemical Manufacturing Corp. All the chemicals were in the analytical grade and were used without further purification.

Preparation of PLA/SH/$CaCO_3$ biocomposites

Ultrafine soyhull powder was prepared by co-milling SH with a small amount of rigid ultrafine $CaCO_3$ powder, which acts as an abrasive to improve the milling efficiency. Briefly, the as-obtained coarse soyhull particles and ultrafine $CaCO_3$ were ground together using a commercial grinder (CGOLDENWALL CAN 923D) for 3 h. The ratio between soyhull and $CaCO_3$ was varied. The milled powder was sieved (400 mesh, 37 μm) and named as SHCaX, where X represents the weight ratio between soyhull and $CaCO_3$.

Preparation of PLA/SH/$CaCO_3$ biocomposites

PLA/SHCa biocomposites were prepared by twin screw extrusion. Briefly, SHCa and PLA were first dried in a vacuum oven in order to eliminate moisture. The PLA pellets were then mixed with SHCaX, ESO (as a plasticizer), and $C_{10}H_{20}O_5Si$ (as a silane coupling agent) using a kitchen mixer (HOWORK SM-1518Z) for 30 min. The mixtures were stored in zip lock bags for 24 h to achieve equilibrium. The final mixture was compounded and extruded into filaments or ribbons using a co-rotating twin-screw extruder (HAAKE PolyLab) operating at a 50-rpm screw speed. The temperatures of the extruder were all set at 160°C (from the feeder zone to the die). The as-obtained filaments were twisted to form baling twine/rope (3-strand, 8-thread, Z-lay, lay length 10.5 mm) with Schacht Incredible Rope Machine (WS6201). The formulations for all the biocomposite samples prepared in this work are shown in Table 1.

Table 1 Formulations of PLA/SHCa biocomposite samples. ESO and $C_{10}H_{20}O_5Si$ were added in phr - parts per one hundred resin (i.e., the base PLA/SHCa formulation).

Samples	PLA (wt %)	SHCa (wt %)	ESO (phr)	$C_{10}H_{20}O_5Si$ (phr)
PLA	100	0	7.5	0
PLA/SHCa10	90	10	7.5	2.5
PLA/SHCa20	80	20	7.5	2.5
PLA/SHCa30	70	30	7.5	2.5

Characterization of SHCa

Particle sizes

Particle sizes of SHCa were studied using a field-emission scanning electron microscope (SEM, JSM-7600F, JEOL, Japan). An accelerating voltage of 15 kV was used to obtain SEM images. The average sizes of SHCa were measured using ImageJ (ij153-win-java8) software.

Soyhull contents

The soyhull content of SHCa was determined using a hydrochloric acid titration method because the reaction between hydrochloric acid and calcium carbonate to form carbon dioxide. Briefly, the weight of SHCa was measured before excessive hydrochloric acid solution (1 mol/L) was added dropwise. The weight change (i.e., the weight of generated carbon dioxide) was recorded and the soyhull content was determined using the following equation:

$$C_{SH}\ (\%) = \frac{W_{SHCa} - W_{CO_2} \times \frac{100}{44}}{W_{SHCa}} \times 100$$

where C_{SH} (%) represents the content of soyhull in SHCa, W_{SHCa} (g) is the weight of SHCa for reaction, and W_{CO_2} (g) is the weight change of the system.

Yield of SHCa

The yield of SHCa was calculated using the following equation:

$$Yield\ (\%) = \frac{W_{SHCa}}{W_{SH} + W_{Ca}} \times 100$$

where *Yield* (%) represents the yield of ultrafine SHCa, W_{SHCa} (g) is the weight of as-obtained SHCa, W_{SH} (g) is the weight of the soyhull for co-milling, and W_{Ca} (g) is the weight of the $CaCO_3$ for co-milling.

Thermogravimetric analysis (TGA)

The thermal properties of SHCa were investigated using a thermogravimetric analyzer (TGA, TGA-Q500, TA Instruments, USA). The samples (~5 mg) were heated in a platinum crucible from 25°C to 800°C at a ramp rate of 10°C /min under continuous nitrogen flow (50 ml/min).

Characterization of PLA/SH/$CaCO_3$ biocomposites

Rheology

The rheological behavior of PLA/SH/$CaCO_3$ biocomposites was tested by a TA ARES G2 rheometer at 180°C in dynamic oscillation mode with a 25 mm parallel plate geometry. The linear viscoelastic region was first determined by sweeping from 0.1 to 600%. The analysis for frequency sweep was carried out in the range of 0.1~100 rad·s^{-1} with a fixed strain of 0.1% to ensure a linear viscoelastic region during the test.

3. Progress of work and results to date

Characteristics of the ultrafine SHCa

SEM images of the particles and their size distribution are presented in Fig. 1. The average particle size decreases after $CaCO_3$ is incorporated into the systems, i.e., from ~ 18.7 μm for pure SH to ~ 7.8 μm for SHCa4 and ~ 4.6 μm for SHCa2. This is because the rigid $CaCO_3$ particles can enhance the shearing force and friction for the soyhulls. However, the average particle size of SHCa1 (~ 6.9 μm) is higher than that of SHCa2 (~ 4.6 μm). This may be attributed to the weakened shearing process with limited soyhulls and agglomerated $CaCO_3$ when an excessive amount of $CaCO_3$ is incorporated into the systems.

Table 2 shows the yield of SHCa. The pure SH control sample only exhibits a yield of 9.1%, indicating the difficulty of grinding soyhull into ultrafine powder. The yield of SHCa increases after the incorporation of $CaCO_3$, confirming $CaCO_3$'s effect on improving the milling efficiency of soyhull. This is because the rigid ultrafine $CaCO_3$ powder can act as an abrasive grinding agent. Especially, SHCa2 has the highest yield of 91.8%, which is significantly higher than that of pure SH (9.1%). However, excessive $CaCO_3$ has a negative effect on SHCa1 yield (53.6%), which is confirmed by the SEM results in Fig. 1. This is most likely due to $CaCO_3$ agglomeration and the limited amount of soyhulls, both of which reduce the strength of grinding action on soyhull. Table 2 also shows the soyhull contents of SHCa4, SHCa2, and SHCa1 after 3-hour milling, which are nearly identical to their start contents, implying a homogeneous mixture of the soyhull and $CaCO_3$ powders.

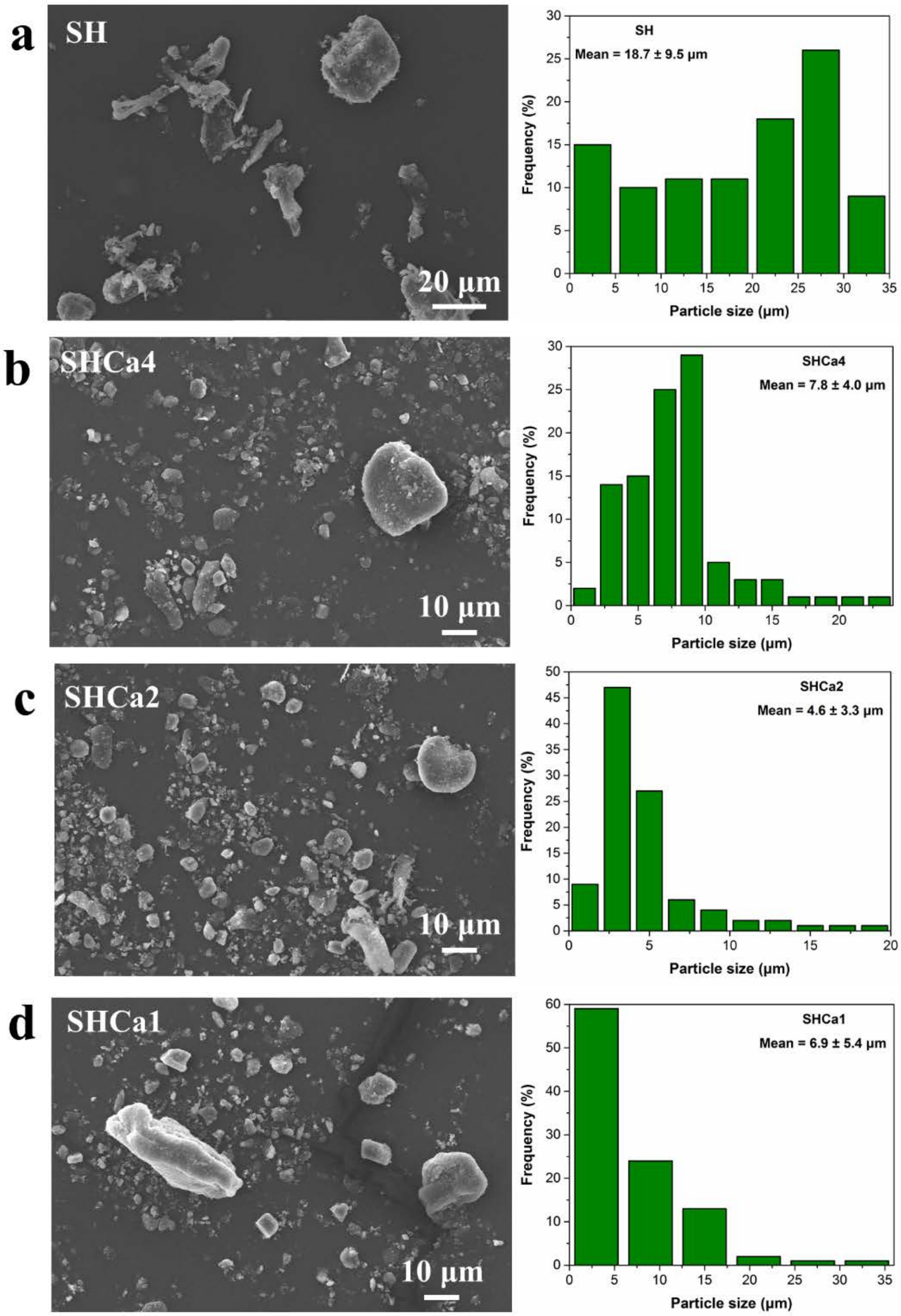

Fig. 1 The SEM images and size distributions of SH (a), SHCa4 (b), SHCa2 (c), and SHCa1 (d).

Table 2 The yield and size of the powder with ultrafine milling

Samples	Average size (μm)	Yield (%)	Soyhull contents (%)
SH	18.7 ± 9.5	9.1	100
SHCa4	7.8 ± 4.0	63.7	80.9
SHCa2	4.6 ± 3.3	91.8	67.2
SHCa1	6.9 ± 5.4	53.6	48.7

Fig. 2 shows the thermogravimetric (TGA) and derivative thermogravimetric (DTG) curves of SHCa2 in nitrogen from 25°C to 800°C. It is noted that soyhull loses its weight at the beginning of the test, which is quite different from $CaCO_3$. Two major stages of weight loss can be identified from the curves of SHCa2. The first occurs at ~292°C and the second at ~660°C (corresponding to the two DTG peaks), which are associated with the thermal decomposition of soyhull and $CaCO_3$, respectively.

The above results show that ultrafine soyhull powders can be prepared by co-milling with $CaCO_3$. SHCa2 was further utilized for PLA/SH/$CaCO_3$ biocomposites preparation unless otherwise mentioned.

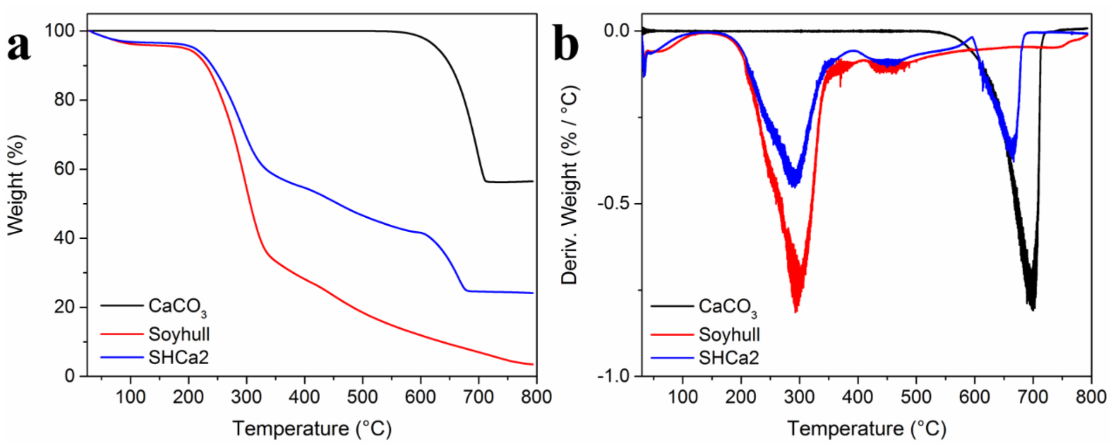

Fig. 2 Thermogravimetric (a) and derivative thermogravimetric (b) curves of SHCa2.

Characteristics of the PLA/SH/$CaCO_3$ *biocomposites*

The rheology of the extruded PLA/SH/$CaCO_3$ ribbons was studied in the linear viscoelastic region as it provides some key information for processing. Fig. 3a shows the complex viscosity η* of the samples as a function of shear strain, which defines the linear elastic region of the samples. Based on the results, frequency sweep tests were performed on the samples at 0.1% shear strain. As shown in Fig. 3b & 3c, the storage modulus (G') and loss modulus (G'') of all the samples increase with the angular frequency (ω), showing a good agreement with the linear viscoelastic theory. G', G'', and η^* all increase with the increasing content of SHCa due to the reinforcement effect of the powders. These results indicate uniform dispersion of the powders in PLA and strong interactions between the polymer and the powders.

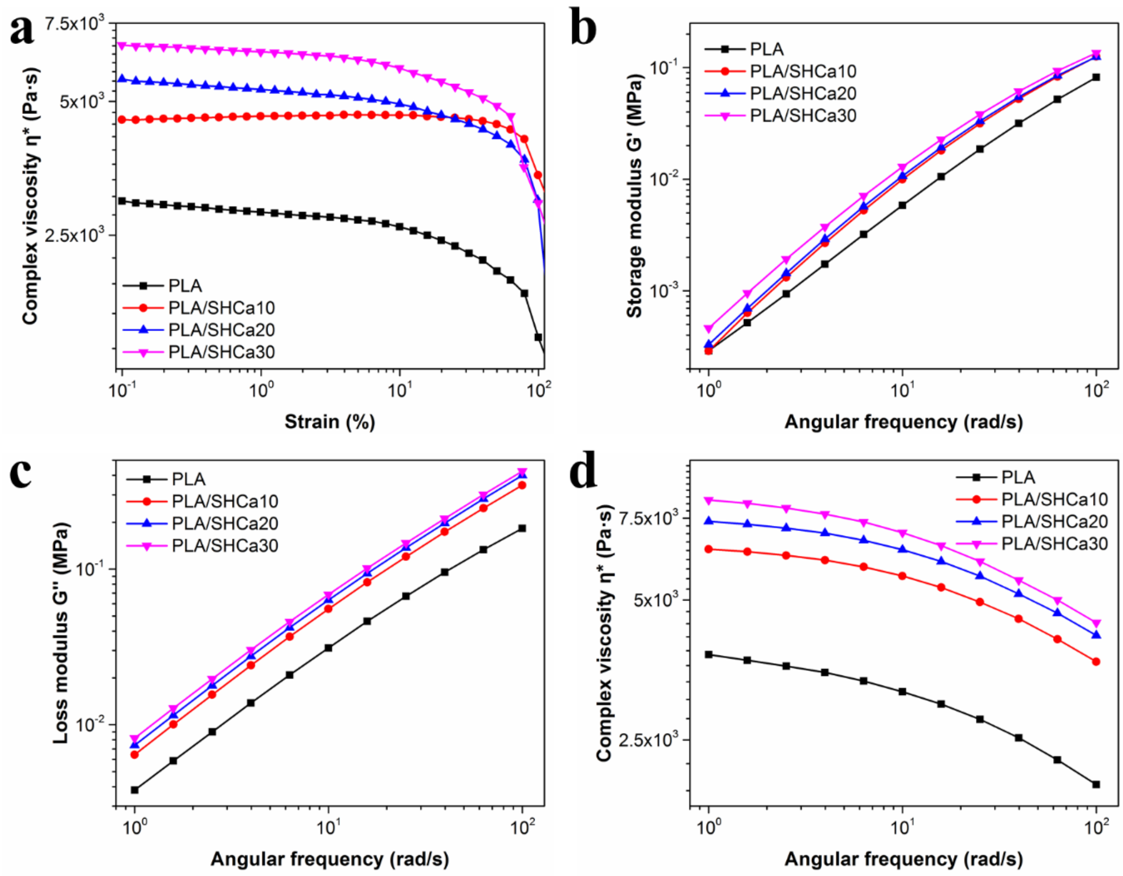

Fig. 3 (a) Strain sweep test results showing the linear viscoelastic regions of the samples. Storage modulus (b), loss modulus (c), and complex viscosity (d) of samples measured using frequency sweep tests.

Fig. 4 shows the filaments extruded using four PLA/SHCa formulations and baling twines made by manually twisting the filaments together.

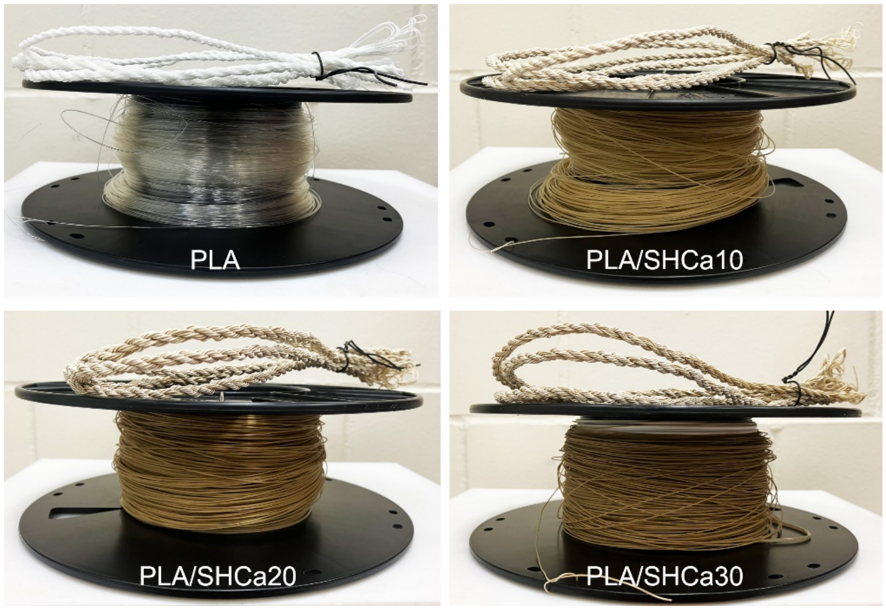

Fig. 4 Extruded filaments and their twisted baling twines made from different PLA/SHCa formulations.

4. Work to Be Completed

We plan to prepare more twine samples with higher soyhull contents. All the samples will be evaluated for their performance in terms of mechanical properties, UV resistance, digestibility, and other properties. Digestibility tests on the existing samples will start in December, followed by more future formulations.

5. Other relevant information

We don't expect major hurdles in this research.

6. Summary

We have successfully prepared PLA/soyhull based bailing twines in the first half of the project by exploring the grinding and extrusion conditions. Some initial sample properties have been investigated. We will expand the formulation in the remaining period and carry out more systematic property characterizations. We expect to obtain a good understanding of the fabrication and performance of the new soy-based twine products at the end of the project.