IMPACT OF CORNCOB FILLER ON PHB-PLA COMPOSITE FILAMENTS FOR 3D PRINTING

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ABSTRACT

Due to its capacity to replicate complicated shapes and geometries while maintaining outstanding mechanical qualities, three-dimensional (3D) printing has become a popular method for quick prototype development and manufacture. The current study discusses the potential for using an agricultural residue as filler to ultimately promote environmental sustainability. This is achieved by creating low-cost value for a highly underutilised biomass in bio-polymer composite filament manufacturing, in-line with the drive for improved biomaterials as Canada anticipates banning single use non-degradable plastics. As a first attempt, a manufacturing procedure is developed for producing affordable polyhydroxybutyrate (PHB) - polylactic acid (PLA) / corncob (PHB-PLA/corncob) composite filaments for 3D printers. The samples for conducting the tests were made by blending generic PHB and PLA pellets in the percentage ratio of 55%:45% (PHB:PLA) w/w and subsequently corncob powder of average particle diameter of 20 µm was added as a filler at varying weight percentages of 0%, 2%, 4%, 6% and 8% w/w. The composite mix was extruded using a Filabot single screw extruder to produce a fused filament for 3D-printing of a consistent diameter of 2.85 mm. These filaments were tested under tensile loading until fracture to establish its tensile properties. The corncob filler powder as well as the fractured surfaces of the composite filaments was examined under a scanning electron microscope (SEM). Tensile strength of the filament exhibited a gradual decline with increase in filler loading while the tensile modulus showed a visible increase trend of up to 20% for 6% wt.% of corncob powder filler when compared to the pure polymer composite without filler (0 wt.% corncob). Scanning electron micrographs of the filler powder showed non-crystalline sheet shapes while the fractured surface showed good improvement in filler-matrix bonding and stiffness as filler loading is increased, with best results seen at 6 wt.% filler loading. The results show this is a promising composite filament material for 3D printers.

1. INTRODUCTION

Biocomposites, are often referred to as eco-composites as they are composed of materials made from blending a biopolymer with natural filler. The percentage of lignin, cellulose and hemicellulose in natural fillers directly contributes to the filler-matrix bonding as well as particle dispersion in the resultant composite formed from adding lignocellulose natural fillers to a biopolymer matrix. Recently, biopolymers have been mixed with natural fillers like eggshell [1], wood pith, rice husks, palm kernel shell, banana fiber, coconut shell and others to improve biodegradability and address one of the biggest shortfalls of conventional synthetic plastics [2,3].

Polyhydroxybutyrate (PHB) and polylactic acid (PLA) are a known class of biodegradable polymers [4,5]. Corncob is an abundant agricultural residue that is produced in large volumes in both the temperate and tropical regions of the world yet highly underutilized. Corncobs have proven to have huge scientific prospects due to its reasonable amount of natural complex organic polymers, high abundance and availability. They are often used as heating fuel for cooking or left in the fields to decay. Although corncobs in recent times have been used to produce edible fungi, energy generation and other similar bio-synthesis processes that requires complex equipment, high energy, and manpower [6], there has not been a meaningful improvement in the level of utility for corncob as huge amounts are still being wasted. However, in order to reduce the cost of PHB and improve its properties for industrial applications, it is usually blended with other biopolymers such as PLA and/or bio-fillers.

Three-dimensional (3D) printing, often referred to as rapid prototyping is a recent trend in manufacturing where pre-designed models are formed by joining multiple layers of the melted filament typically made from mostly polymer thermoplastic material. Currently, the automobile industry has largely adopted the use of fused filament fabrication (3D printing) for the manufacturing of numerous automobile parts especially ones used in developing the car interior as well as in restoring classic automobiles by printing missing parts [7]. The 3D printer filaments are made through a hot extrusion process. For instance, a *Filabot* is a single screw desktop extruder designed to produce filaments specifically for 3D printers.

This preliminary study was to assess the quality and properties of the filaments produced by the *Filabot* extruder. The research investigated the effect of corncob filler loadings on tensile properties of the PHB-PLA/corncob composite filaments. Scanning electron microscopy (SEM) was used to observe the fractured surface morphology of the filaments. The results showed the composite filaments could be marketed as a more environmentally friendly option to consumers for potential use in 3D printing of parts and components.

2. METHODOLOGY

2.1 Materials

Pelletized PHB with an average diameter of 0.45 mm were purchased from Delta Scientific Laboratory Products, Mississauga, Ontario while pelletized PLA of average diameter of 0.5 mm was received from Jamplast Inc, Missouri, USA. Corncobs were obtained from Ross Welford Farm, Maymont, Saskatchewan. The corncobs are a Pioneer variety P7213R grown for direct grazing by cattle and seeded on a black soil zone.

2.2 Filler preparation

Corncobs were harvested by hand, and the corncob powder was prepared according to a published modified procedure [8]. The corncobs were oven dried in the lab for 24 hours at a temperature of 105 ^{o}C. A custom made hammer mill was used to initially crush the corncobs into smaller chunks after which a grinding mill was further used to reduce the samples into fine aggregates. The powders were sieved using a 20 µm sieve to obtain the particle size required for this study. The filler particle density and particle size were equally evaluated using a gas pycnometer (Accupyc 1340) and a particle size analyzer (Malvern Mastersizer Hydro 2000 S), respectively.

2.3 PHB-PLA/corncob composite preparation

To make the 3D printer biocomposite filaments, the matrix was composed of PHB and PLA pellets in a ratio of 55 % to 45 %, while the corncob powder fillers were added in different varying batches of 0 %, 2 %, 4 %, 6 % and 8 % weight/weight. The constituents were thoroughly mixed together and dried at a temperature of 80 °C for 1 hour before blending in a Filabot extruder (Figure 1) which was set at a temperature of 180 °C. This is in consideration of the melting points of PHB and PLA which are between 150 ^{o}C to 180 ^{o}C as well the degradation temperature which is above 185 ^{o}C for both biopolymers. The filaments were extruded to a diameter of about 2.85 mm and controlled using a digital fila-measure device for monitoring the filament diameter. The diameter of the filament was intermittently adjusted using the Filabot spooler speed control and the Filabot extruder speed control to maintain consistency and uniformity of the filament diameter.

2.4 Tensile testing

Tensile testing was performed on PHB-PLA/corncob composite filaments following the guidance of ASTM standard A931-18 [9] using a Mark-10 force tester as shown in Figure 2. Bollard grips were used, and this entails wrapping the two ends of the filaments around the component posts of the two different bollards and securing the tip with a component vice grip mechanism. The test was conducted at room temperature with a test specimen of 50 cm length and a 20 cm gauge length at a crosshead speed of 5 mm/min. Values for tensile force and elongation at fracture were generated as an average of triplicate runs.

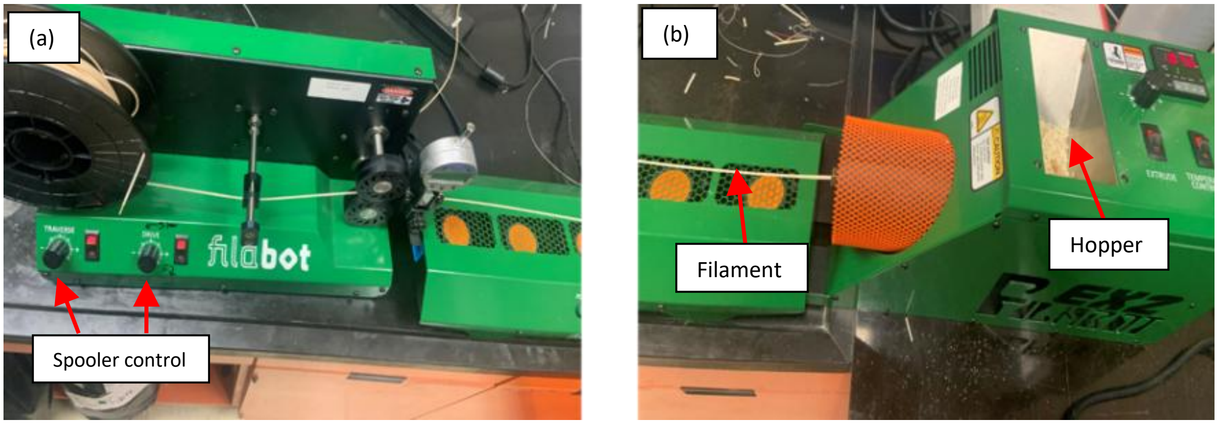


Figure 1. Filament extrusion apparatus (a) Filabot spooler (b) Filabot extruder.

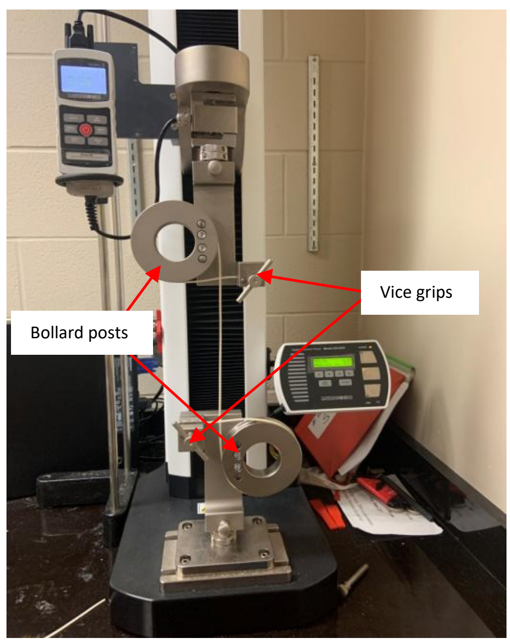


Figure 2. Tensile testing of PHB-PLA/corncob composite filament.

2.5 Microstructural examination

The fractured surfaces of the filaments were viewed using a scanning electron microscope (SEM) (HITACHI SU6600) operated at 2kV. The specimens were sputter coated with gold (Au) to improve conductivity and minimize electron charging.

3. RESULT AND DISCUSSION

3.1 Particle analysis

A Malvern Mastersizer (Hydro 2000S) dispersion unit particle analyzer with the capacity of processing particle size range of between 0.05 µm to 600 µm as well as helium gas pycnometer (Micrometrics Accupyc 1340) were used in performing these tests. Table 1 presents results of the average triplicates of the particle attributes of the corncob filler material used in this study.

Table 1. Corncob filler particle analysis

	Equipment Used	**Average**
Particle size (SMD in µm)	Malvern mastersizer (Hydro 2000 S)	25.42 (± 0.035)
Particle density (g/cm^3)	Gas pycnometer (Micrometrics Accupyc 1340)	2.91 (± 0.11)

Under typical room conditions, a scanning electron micrograph of corncob powder morphology (Figure 3) demonstrates visible aggregation dominated by thin sheets and slender shapes possibly due to the grinding preparation process. A similar study found that the morphology of corncob powder without heating has particle aggregation dominated by sheet shapes [10]. Also, the powder particles were found to be generally non-crystalline, compact, fine and moderately dense in nature [10,11].

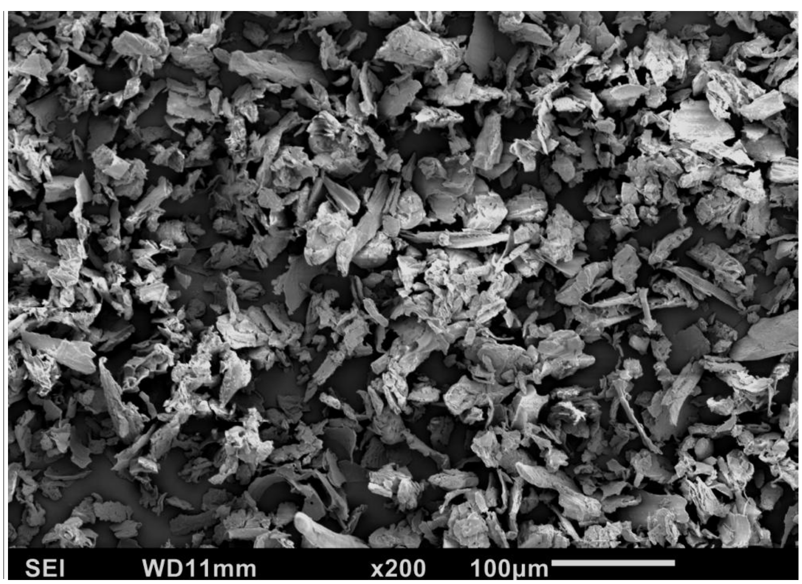


Figure 3. Scanning electron micrograph of corncob powder

3.1 Tensile properties

The effect of corncob filler loading on the tensile strength and tensile modulus of the composite filaments are presented in Figure 4 and Figure 5.

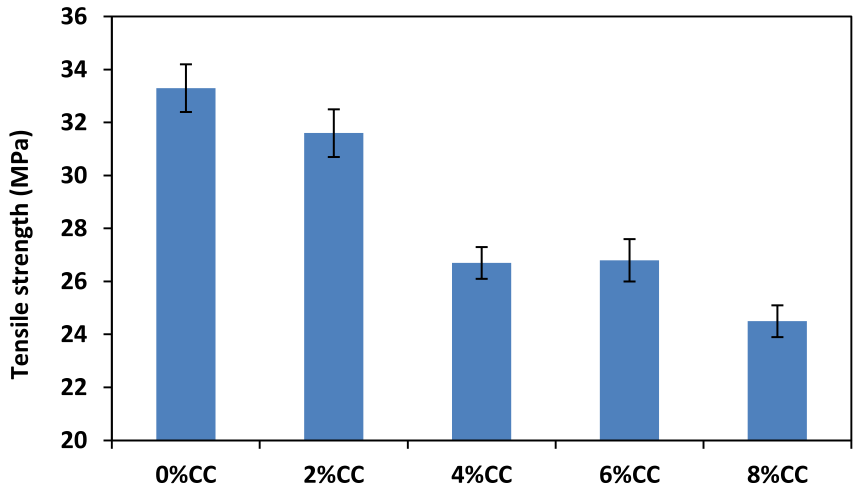


Figure 4. Effect of filler loading on tensile strength

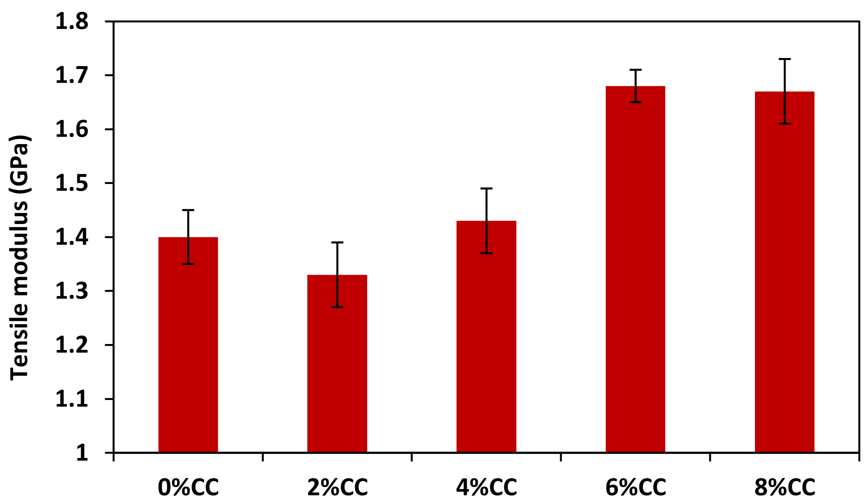


Figure 5. Effect of filler loading on tensile modulus

Similar studies have estimated the tensile strength and tensile modulus of injection molded dog-bone samples [12] of pure PLA to be about 53 MPa and 3.6 GPa, respectively [13] while those for injection molded dog-bone samples of pure PHB are about 40 MPa and 3 GPa, respectively [14]. This shows that both the tensile strength and tensile modulus values for 3D printing filament samples (Figure 4 and 5) are generally lower than that of injection molded dog-bone samples due to the smaller test surface area of the filaments. However, the data generated from testing the 3D printing filaments would be very significant in terms of developing a procedure for thin layer and intrinsic shapes manufacturing where 3D printing of parts is often employed.

From Figure 4 the tensile strength significantly decreased by up to a total of 26.4 % as filler loading was increased. Also, the tensile modulus of the samples containing 6 wt.% corncob (CC) filler powder was found to be 20 % higher than that of samples containing 0 wt.% corncob filler possibly due to the integration of an optimum amount of corncob filler which bonded efficiently with the matrix phase. These trends are in agreement with similar studies performed for injection molded dog-bone samples of both PLA/corncob composites [15] as well as polypropylene/clay composites [16]. Also, additional corncob filler visibly enhanced the tensile modulus by 20 % with the best value recorded at 6 wt.% of corncob filler.

3.2 Regression equations

Both properties studied demonstrated a fourth order polynomial response to filler loading increase throughout the filler loading range investigated. All results acquired in this study were evaluated by statistical trend-line analysis using Microsoft Office Excel 365. Regression equations for predicting how the filler loading would likely affect the composite filament tensile properties were generated. The following regression equations (equation 1.0 and 2.0) were established to define these parameters evaluated as corncob filler loadings increased from 0 wt.% to 8 wt.%.

Tensile strength:

$$T_s = -0.0406 f^4 + 0.6583 f^3 - 3.2125 f^2 + 3.2667 f + 33.3 \qquad (R^2 = 1) \qquad (1)$$

Tensile modulus:

$$T_m = -0.001 f^4 + 0.0118 f^3 - 0.0209 f^2 - 0.0321 f + 1.4 \qquad (R^2 = 1) \qquad (2)$$

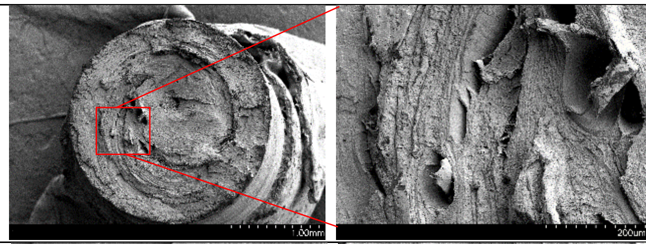
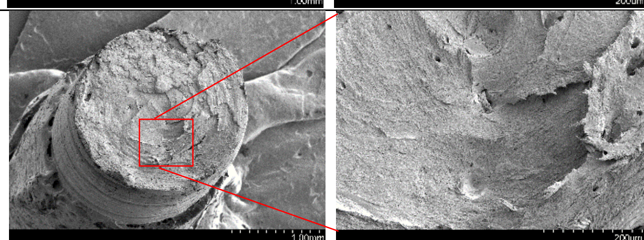
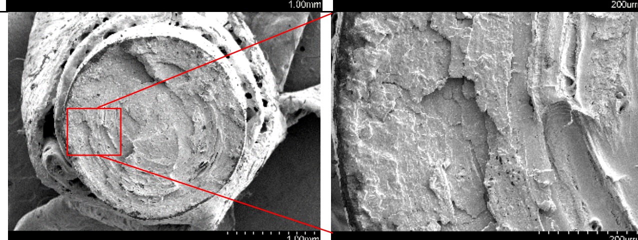
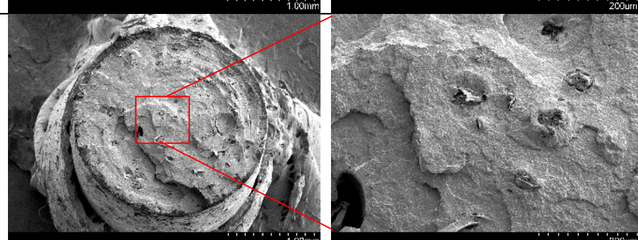
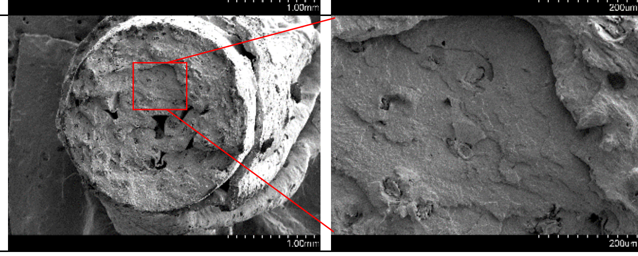
where f is the filler loading in wt.% and R^2 is the statistical coefficient of determination (goodness of fit).

These regression equations are similar to those developed for the effect of moisture content on *Dikanuts*, a lignocellulosic biomaterial with similar properties [17].

3.3 Microstructure

Table 2 presents the SEM images of the fractured filament samples at varying weight percentage concentration of filler particles. From the micrographs, the distributions of particles were largely homogenous with a reasonable bonding at the filler/matrix interface. The particles tended to fracture rather than pull out of the matrix. Void spaces were not observed at bonding sites of the constituents which indicates the corncob particles had a good bonding with the polymer matrix. The images generally show an obvious effect of corncob filler on the fractured surface, directly indicating a relationship with the mode of fracture at the various filler loading percentages.

Table 2: Fractured surface analysis

Composite composition	SEM Micrographs	Observations and comments
PHB(55%)/PLA(45%)		No filler. Very ductile fractured surface, indicating an elastic tear with very poor stiffness.
PHB(55%)/PLA(45%) + 2%CC w/w		Smooth and largely ductile, indicating ductile fracture and slightly improved stiffness
PHB(55%)/PLA(45%) + 4%CC w/w		Homogenuity in filler dispersion. Good bonding at filler-matrix interface. Optimum stiffness.
PHB(55%)/PLA(45%) + 6%CC w/w		Slight agglomeration. Presence of dimples indicating good stress propation within the matrix during tensile loading.
PHB(55%)/PLA(45%) + 8%CC w/w		Few cleavage facets and dimples indicating improved stiffness before fracture.

4. CONCLUSION

At the end of this research, PHB-PLA/corncob composite filament for 3D printing applications was developed to enhance the capabilities of the individual matrix materials alone. The composite was characterized to establish the effect of filler particle loading on the properties of the resultant bio-composite filament. The evaluated tensile modulus has shown remarkable improvement as filler loading was increased up to 6 wt.%. The pure PHB-PLA composite with no filler displayed the highest value for tensile strength. Although tensile strength reduced with increase in filler loading, a good performance in tensile modulus showed an optimum improvement in stiffness and stress transmission through the matrix material before fracture. This was observed at the 6 wt.% filler loading formulation. Hence, the mechanical properties of 3D printed parts will be improved using this formulation. It is therefore clear that although tensile strength showed a decline, tensile modulus was slightly enhanced as filler loading was increased. The fractured surfaces indicate that corncob powder contributed to reducing porosity within the composite filaments. Similarly, the filler particles influenced the failure mode of composite materials under tensile loading. The pure PHB-PLA composite showed mainly cleavage features, while the addition of fillers increased the manifestation of rougher fracture facets as well as dimples. This indicates that the introduced corncob powder filler bonded well with the matrix material and largely improved stiffness and stress propagation until slight agglomeration became visible at 8 wt.%. Further research on this composite should include additional tensile, flexural, and Charpy impact testing of 3D printed PHB-PLA/corncob composite samples following ASTM D638-14, D790-17, D6110-18 standards respectively. This would generate substantial results and provide a greater understanding of the properties of this composite, particularly when 3D printed.

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