Proceedings of the Canadian Society for Mechanical Engineering International Congress 2021
CSME Congress 2021
June 27-30, 2021, Charlottetown, PE, Canada

Towards Circular Manufacturing: Repurposing Eggshell Waste as Filler for Poly Lactic Acid Feedstock for 3D printing

Jean-Philippe Leclair[1], Newton Borges[2], Duncan Cree[2*], Lucas A. Hof[1*]
[1]Department of Mechanical Engineering, École de technologie supérieure, Montréal, Canada
[2]Department of Mechanical Engineering, University of Saskatchewan, Saskatoon, Canada
[*] duncan.cree@usask.ca, [*] lucas.hof@etsmtl.ca

Abstract— White eggshell (WES) waste was crushed into a fine powder (32 µm) and used as filler in poly lactic acid (PLA), a plant-based polymer, to enhance its mechanical properties such as its flexural strength and modulus. Pure PLA is a relatively brittle material that could benefit extra ductility to broaden its usage opportunities. Therefore, the influence of WES on this characteristic was also observed. Samples containing 5, 10 or 20% (w/w), respectively of WES were compared to samples containing the same proportions of limestone (LS) and to samples of pure PLA in flexural tests following ASTM D790-17. The observed mechanical properties were successfully improved using WES as filler when compared to LS or to pure PLA samples. Considering flexural strength and modulus, an approximate optimal point of 5% (w/w) WES could be determined by analyzing the data. Further, selected fractured samples were observed on a Scanning Electron Microscope (SEM) (Hitachi TM3000) to characterize and correlate the distribution of filler particles in the PLA matrix to these improvements. The SEM also allowed to characterize the fractures qualitatively on ductility compared to pure PLA. It could be concluded that the samples containing filler particles are more ductile than pure PLA. It was also possible to conclude that samples containing the highest filler content (i.e. 20%), regardless of the filler type, exhibited the most textured fracture surfaces thus indicating a more ductile fracture mode.

Keywords - Circular economy; sustainable materials; biopolymers; bio-fillers; additive manufacturing

I. INTRODUCTION

Today's leading societies seem to be on the path of never-ending expansion, similar to the Universe. However, in contrast to the Universe which may be infinite, earth's resources are finite. In order to keep up with the increasing demand for highly personalized new products, and to minimize waste, our linear economy model has to be re-thought to shift towards a circular economy.

The concept of circular economy, which was introduced decades ago, proposes a sharp contrast to our actual linear economy model but still lacks tools allowing it to thrive [1]. The fundamental goal of a circular economy is to close the material loop across the full supply chain. It is a very ambitious goal that requires drastic changes at many levels of this chain, from design to recycling strategies. Nowadays, the fundamentals of this concept begin to be well defined, and this circular approach is slowly gaining in popularity among industries. A good example is the growing popularity of additive manufacturing (AM) [2,3], a very promising technology to support a transition towards a more circular manufacturing model [4,5,6]. AM regroups very agile manufacturing techniques, able to deal with complex shapes and multiple materials. This set of techniques inherently maximizes the buy-to-fly ratio and virtually eliminates the need for tooling, making it very lean when compared to more traditional subtractive manufacturing processes.

In order to unleash the full potential of circular economy models, more technologies have to be developed and adopted. To drive long-term improvements in industrial trends and philosophies, a sum of many incremental steps will be required to generate profound change. Using a waste element generated by a process as a value-added raw material of an unrelated process fits well within such circular approach. Research in the aim of developing new sustainable and high-performing materials for three-dimensional (3D) printing has gained in interest in the last years [7,8]. More effort must be deployed towards this goal as there is still a lot of room for improvement. Repurposing chicken eggshells as a filler for polymers is an excellent opportunity to consume this widely available form of waste. A review [9] about the production/availability of eggshell waste and its possible usage as a sustainable biological filler for polymers in different fabrication processes such as hot pressing, injection molding, compression molding and film casting has already been conducted, showing its potential. However, a study exploring the possible use of this filler in feedstock materials for 3D printing such as poly lactic acid (PLA) is still lacking.

In this contribution, we investigate the use of organic waste, such as chicken eggshells, as a filler to enhance the mechanical

properties of 3D printed PLA flexure test samples. As a first step, the mechanical properties that will be evaluated quantitatively are flexural strength and flexural modulus. Flexure testing was chosen because of the semi-brittle behavior of the PLA material. The change in the ductile-brittle failure mode will also be observed using the Scanning Electron Microscope (SEM) and discussed qualitatively.

II. EXPERIMENTAL PROCEDURES

A. *Raw Materials for 3D printing*

Poly Lactic Acid (PLA):

In this study we used PLA, Prime Natural 4043D procured from Jamplast Inc, Ellisville, MO, USA as biopolymer. They were received in pellet form.

Filler materials:

The filler materials were calcium carbonate, mineral limestone (LS) obtained from Imasco Minerals Inc., Surrey, BC, Canada. It was received in white powder form. White eggshell (WES) waste was sourced from Burnbrae farms, which is an egg-breaking plant in Ontario, Canada.

B. *Eggshell and limestone filler preparation and composite material production*

The eggshell fillers were prepared by first rinsing them with hot water to remove remaining egg white from the eggshell. They were later coarse crushed and dried. The coarse particles (< 10 mm) were further ball milled into a powder, rinsed with water to remove any eggshell membrane remnants and dried. Both, the mineral limestone and eggshell based calcium carbonate powders were sifted through a 32 μm sieve.

Composite material preparation:

Composites were made with PLA bio-resin along with fillers of LS and WES in weight concentrations of 5, 10 and 20 % (w/w), respectively. The PLA filler composites were processed in a twin-screw extruder (SHJ-35, Nanjing Yougteng Chemical Equipment Co. Ltd., Jiangsu, China) - a melt blending method - at a temperature of 175°C. The final product was in the form of pellets. Pure PLA, PLA/LS and PLA/WES composites in pellet form were dried at 80°C for 12 hours prior to making the 3D filament.

3-D printing filament preparation:

In a next step, the composite material pellets were used to make 3D printing filaments with a "Filabot" single screw extruder [10]. The following Filabot parameters were used: 1) the temperature was set to 200°C for PLA material as per the guidelines laid down in the Filabot manual, and 2) the fan speed was set to 100%. The "Filameasure", an in-line filament measurement device was continuously monitored to keep the filament cross-sectional diameter close to the required 2.85 mm. The spooling speed was controlled to maintain the filament diameter within ± 0.1 mm of the targeted nominal diameter. The length of the filaments for each batch were based on the individual weights of the required flexural samples. Fig. 1 presents a schematic of the "circular" material flow and its preparation, and the printing process.

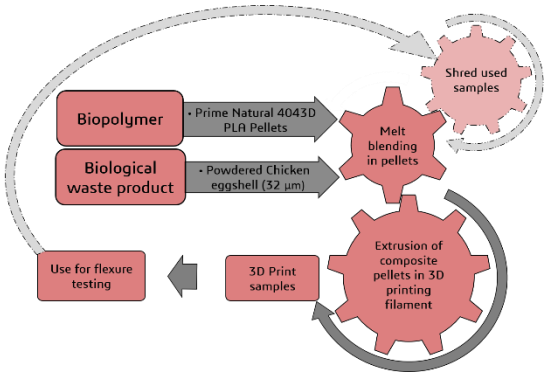


Figure 1. Solid lines: Schematic representation of the process flow for sample preparation and testing in this study. Dotted lines: Insight of next recommended step of closing the material loop by reusing test samples as raw material.

C. *Fused filament fabrication 3D printing process settings*

All the test specimens were produced by 3D printing using the Ultimaker 3 (Ultimaker) printer along with the open-source Cura slicing and preparation print software version 4.0.0 [11]. The Ultimaker 3 works on the fused filament fabrication (FFF) principle [12]. It has dual-extrusion print heads with an automatic nozzle lifting system and interchangeable print cores. The print core BB is used for support material such as water soluble PVA (polyvinyl alcohol) but was not required in this study. Hence, only one print head was used. The print core head AA was interchanged with a print core head CC red (ruby cone) having a 0.6 mm diameter nozzle which is specially designed to handle wear-resistant composite materials.

The flexure test specimen geometries as per ASTM D790-17 were drafted in AutoDesk Inventor and saved in stereolithographic (stl) format. The *stl* file was imported and processed by the software Cura 4.0.0. A *gcode* file was created by Cura from the *stl* file, which was subsequently fed to the Ultimaker 3D printer. The 3D printing specimen flexural sample size was 127.0 mm x 12.7 mm x 3.2 mm (l x w x t) mm^3. Table 1 presents the parameters used for 3D printing of the flexural specimens. In order to find the best printing conditions for the developed bio-composite feedstock, four different liquefier (nozzle) temperatures were chosen around the standard 3D printing working point for pure PLA filaments (180-200 °C). As well, four different printing speeds were defined around the standard recommended printing speed (typically 50 mm/s).

TABLE 1. Printing parameters of the flexural test specimens

Liquefier temperature	190, 200, 210, 220	°C
Printing speed	20, 40, 60, 80	mm/s
Nozzle diameter	0.6	mm
Layer height	0.1	mm
Wall thickness	1	mm
Infill density	100	%
Infill pattern	Longitudinal lines	N/A
Fan speed	100	%
Build plate temperature	60	°C

D. Flexure testing of 3D printed specimens

Test specimens were tested according to the ASTM D790-17 – Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials [13]. The flexural tests were performed on an Instron 1137 universal testing machine (Model 3366). A load cell of 10 kN, a three-point flexure test fixture and a support span of 57 mm was used. The grips were displaced at a rate of 1.5 mm/min (crosshead speed) to cause the flexure. Fig. 2 shows typical test specimens used for this research, while Fig. 3 shows a flexural sample in the test fixture. Three specimens for each composite were tested.

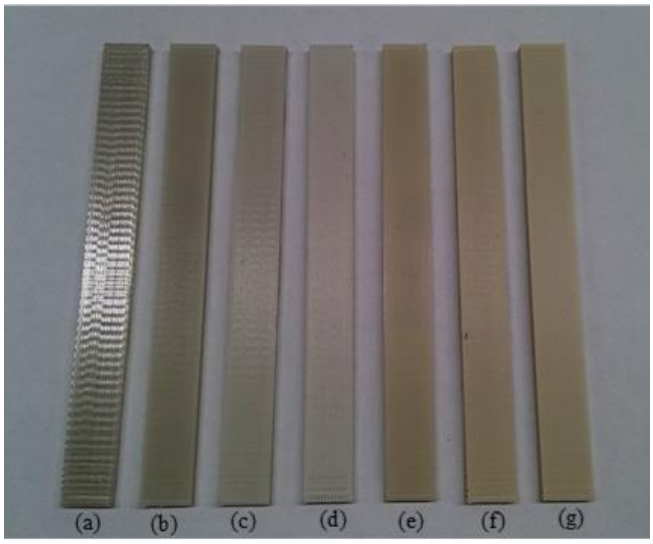


Figure 2. Typical 3D printed flexural specimens (a) pure PLA, (b) 5% (w/w) LS, (c) 10% (w/w) LS, (d) 20% (w/w) LS, (e) 5% (w/w) WES, (f) 10% (w/w) WES and (g) 20% (w/w) WES.

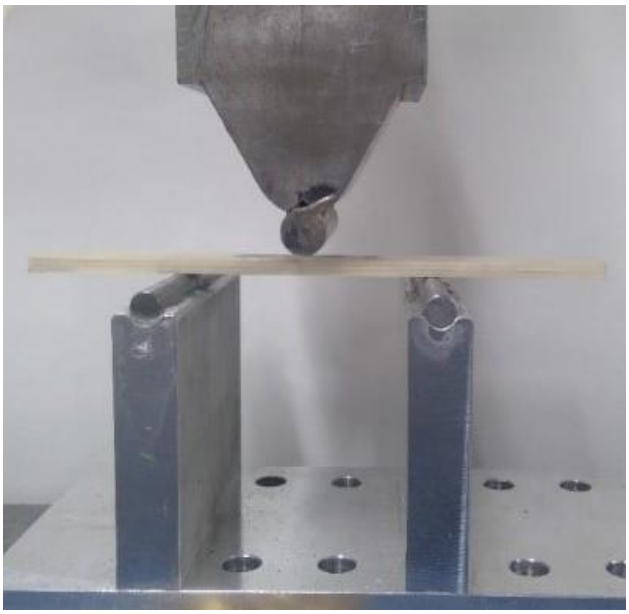


Figure 3. Flexural three-point bending setup following ASTM D790-17 standard used in this study.

III. RESULTS AND DISCUSSION

Flexural strength of the test specimens prepared with varying printing speeds and liquefier temperatures were evaluated (Table 1) and the most promising results are presented below. There were a total of seven combinations of liquefier temperature and print speeds which were decided upon to be 3D printed (190, 200, 210 and 220°C keeping print speed constant at 60 mm/s and 20, 40, 60 and 80 mm/s keeping the liquefier temperature constant at 200°C). Within these seven combinations, there were seven types of PLA/composites to be printed (Pure PLA, PLA with 5, 10, and 20% (w/w) of LS and PLA with 5, 10, and 20% (w/w) of WES). In total, there were 147 test specimens (7x7x3 nos.) printed to measure their average flexural strength and flexural modulus. From the data, it was observed that the optimal results for flexural strength and flexural modulus were obtained by setting printing parameters to 200°C for the liquefier temperature and 60 mm/s for the print speed. The results obtained by using this combination of parameters were therefore validated as most concluding and are presented in Table 2 and in Fig. 4 for flexural strength and in Table 3 and in Fig. 5 for flexural modulus.

TABLE 2. Flexural strength results obtained using a liquefier temperature of 200°C and a printing speed of 60 mm/s

	Flexural Strength (MPa)			**Standard Deviation (MPa)**		
Filler	**5% (w/w)**	**10% (w/w)**	**20% (w/w)**	**5% (w/w)**	**10% (w/w)**	**20% (w/w)**
LS	98.34	98.41	85.77	1.61	1.36	3.79
WES	102.66	87.82	78.82	1.66	1.96	3.92
Pure PLA	91.75	91.75	91.75	0.49	0.49	0.49

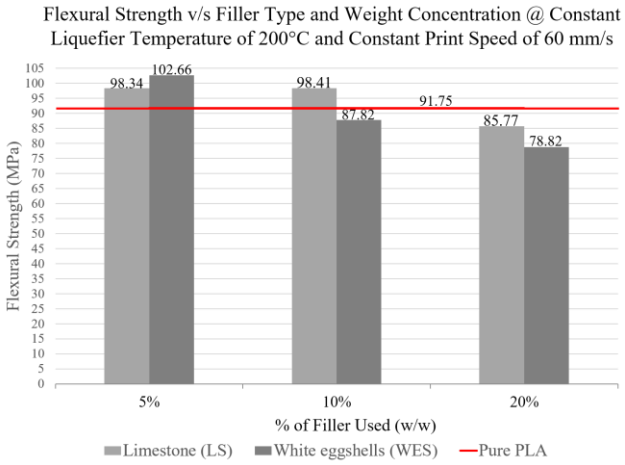


Figure 4. Graph of flexural strength v/s filler type and concentration % (w/w) for samples printed using a liquefier temperature of 200°C and a printing speed of 60 mm/s.

From the bar diagram presented in Fig.4, the flexural strength (MPa) of the specimens printed with the best combination of parameters are plotted against varying concentrations (5, 10, 20% (w/w)) of either LS or WES filler while keeping the liquefier temperature at 200°C and the printing speed at 60 mm/s. The results obtained for pure PLA printed samples using the same parameters are displayed as a horizontal reference line in order to facilitate benchmarking with

the other results, which are presented side-by-side on the graph. The results suggest that the optimum flexural strength was obtained when 5% WES was added. Adding up to 10% LS also improves flexural strength when compared to pure PLA.

Pure PLA displayed a flexural strength of 91.75 MPa, PLA with 5% LS gives an intermediate result of 98.3 MPa while the highest strength was shown by PLA with 5% WES achieving a strength of 102.65 MPa. However, increasing the filler weight concentration to 10% for WES or 20% for LS, the composites resulted in a lower strength when compared to pure PLA. Similarly, the flexural strength of LS and WES composites containing 20% (w/w) fillers reduced. It can therefore be concluded that the optimal weight concentration percentage of WES is close to 5%, surpassing pure PLA by about 12% when considering flexural strength. For the case of LS, the optimal weight concentration is around 10%, surpassing pure PLA by about 7% when considering flexural strength.

The following results, which are presented numerically in Table 3 and plotted in Fig.5, show the flexural modulus of the specimens. In contrast with flexural strength, the flexural modulus increases with increase in filler weight percentages of 5, 10 and 20% when compared to pure PLA material. The PLA composites containing the most WES fillers (i.e. 20%) showed slightly more resistance towards flexural deformation and hence improved stiffness than compared to composites containing the same concentration of LS filler. When considering flexural modulus, the optimal weight percentage of filler is clearly not the same as when considering flexural strength, in fact the filler content should be much higher.

TABLE 3. Flexural modulus results obtained using a liquefier temperature of 200°C and a printing speed of 60 mm/s

	Flexural Modulus (GPa)			**Standard Deviation (GPa)**		
Filler	**5% (w/w)**	**10% (w/w)**	**20% (w/w)**	**5% (w/w)**	**10% (w/w)**	**20% (w/w)**
LS	4.17	4.22	4.35	0.03	0.11	0.13
WES	4.29	4.89	4.96	0.12	0.09	0.11
Pure PLA	3.59	3.59	3.59	0.06	0.06	0.06

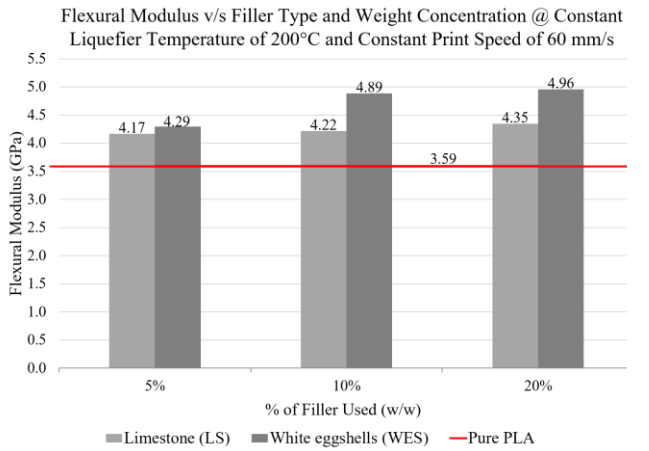


Figure 5. Graph of flexural modulus v/s filler type and concentration % (w/w) for samples printed using a liquefier temperature of 200°C and a printing speed of 60 mm/s.

From the bar diagram presented in Fig.5, the flexural modulus (GPa) of the specimens printed with the best combination of parameters are plotted against varying concentrations (5, 10, 20% (w/w)) of either LS or WES filler while keeping the liquefier temperature at 200°C and the printing speed at 60 mm/s. The results obtained for pure printed PLA samples using the same parameters as the composites are displayed as a horizontal reference line in order to facilitate benchmarking with the other results, which are presented side-by-side on the graph.

The results suggest that the optimum flexural modulus was obtained when 20% WES and 20% LS were added as fillers which improved this property significantly when compared to pure PLA. It follows that the flexural modulus increased on addition of LS or WES, respectively compared to the pure PLA samples. For example, pure PLA displayed a flexural modulus of 3.59 GPa, PLA with 20% LS had an intermediate result of 4.35 GPa while the highest modulus achieved was shown with PLA containing 20% WES and resulted in a modulus of 4.96 GPa.

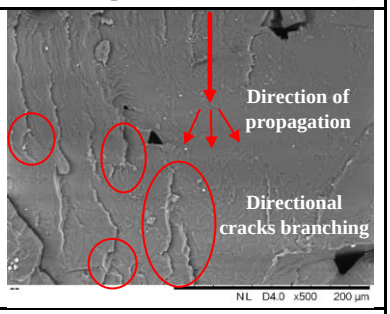
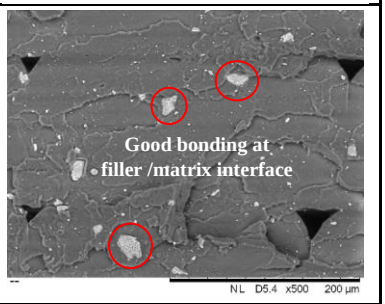
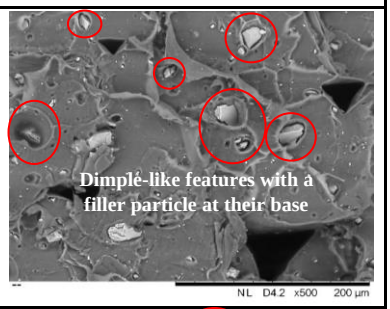
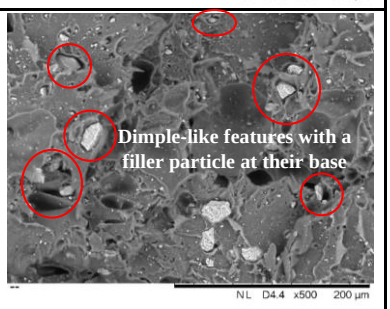
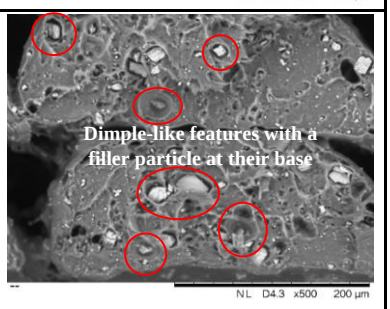
The flexural strength of composites containing 10% and 20% WES fillers reduced drastically when compared to pure PLA and PLA with 10% to 20% LS fillers. In contrast to flexural strength, the flexural modulus increased with increase in filler weight percentage of 5, 10 and 20% when compared to pure PLA. This observation can be explained by the much higher flexural modulus of the calcium-based fillers used in this study when compared to PLA. It can also be observed that PLA composites containing WES showed more resistance towards flexural deflection and hence improved stiffness when compared to composites containing LS fillers.

Overall, the flexural strength of PLA decreased when the composites contained more than 5% (w/w) of WES or more than 10% (w/w) LS. As the weight percent increases from 5% to 10% and 20%, the number of filler particles increase respectively as well. At a low filler contents, the fillers may be more dispersed in the PLA matrix. The filler/matrix bonding interactions and compatibility will be reviewed in a further study. The eggshell membrane contained on the WES may or may not have a positive influence on these properties.

Table 4 presents the SEM (Hitachi TM300) images of fractured test specimens infused with different weight percentage concentrations of filler particles. The images presented are 1) a pure PLA sample, 2) samples containing 5% (w/w) WES and LS, respectively and finally, 3) PLA / 20% (w/w) WES and LS, respectively. In the images captured, the surfaces exhibit increasingly textured features as the filler content increases. Further, the distribution of filler particles seems homogenous and the bonding at the filler/matrix interface looks adequate as there is no apparent void between the constituents.

All images presented include comments about the notable details that can be observed. This presents evidence of a clear progression from brittle fracture to a more ductile failure mode as the weight percentage of filler concentration increased.

TABLE 4. SEM captures including comments and observations for selected samples (Pure PLA, 5% (w/w) WES, 5% (w/w) LS, 20% (w/w) WES and 20% (w/w) LS)

Comments and observations	SEM Capture (Hitachi TM3000)
Pure PLA Traces of filler. Brittle fracture features : Not much texture. Presence of directional cracks branching following the direction of propagation.	
5% WES Homogeneous distribution of filler. Signs of increasing ductility: Marginal increase of randomly oriented texture marks. No signs of debonding at the filler / matrix interface can be observed.	
5% LS Homogeneous distribution of filler. Signs of increasing ductility: Marginal increase of randomly oriented texture marks. Appearance of randomly oriented dimple-like features indicating plastic deformation. Most of the features have a filler particle at their base.	
20% WES Homogeneous distribution of filler. Signs of increasing ductility: Significant increase of randomly oriented texture marks. Increase of randomly oriented dimple-like features indicating plastic deformation. Most of the features have a filler particle at their base.	
20% LS Homogeneous distribution of filler. Signs of increasing ductility: Significant increase of randomly oriented texture marks. Increase of randomly oriented dimple-like features indicating plastic deformation. Most of the features have a filler particle at their base.	

IV. Conclusion

In this research, the influence on flexural properties and ductility of two different fillers, LS and WES, in 3D printed PLA flexural specimens were compared with each other as well as with samples printed with pure PLA. The weight concentration of both types of fillers were 5, 10 and 20%. The samples were tested in a three-point bend test setup following ASTM790-17 specifications and the most promising results were graphed and compared. The influence on the ductility of the weight percentage concentration of filler particles in the PLA matrix was also analyzed by SEM. At first, tests were conducted to determine optimal printing parameters for the flexural test specimens by varying the printing speed from 20 to 80 mm/s and the liquefier temperature from 190 to 220°C. The best experimental results were obtained with a print speed of 60 mm/s and a liquefier temperature of 200°C. Therefore, the results for the samples that have been printed using these settings were presented in this article. The following conclusions can be drawn from the results and observations:

Natural fillers in 3D printed PLA can significantly improve flexural properties such as flexural strength and flexural modulus.

From experimental results, it was shown that the optimal weight percentage, with regards to flexural strength, is ~5% for WES and ~10% for LS.

In comparison to pure PLA, there was an increase of ~12% in strength on testing the 5% (w/w) WES samples and an increase of ~7% in strength on testing the 10% (w/w) LS composite samples.

As more filler is added to the PLA, the flexural modulus increased but the flexural strength significantly decreased past the optimal point as reported above.

In comparison to pure PLA, there was an increase of ~38% in modulus for composite samples containing 20% (w/w) WES and an increase of ~21% in modulus for composite samples with 20% (w/w) LS filler.

From the SEM observations, it was shown that natural fillers in 3D printed PLA have a direct impact on the fractured face texture. This points to a more ductile failure mode than for pure PLA samples which exhibited typical brittle failure characteristics.

The 3D printed PLA samples can be sufficiently strengthened by adding up to 5% (w/w) of WES and up to 10% (w/w) of LS. Although filler weight percentages above these values tend to benefit the flexural modulus and ductility, they negatively impact the flexural strength. For next steps, it is recommended that the studied tests will be pursued to determine a more accurate optimal value of WES filler for PLA and to further investigate the influence of the filler particle distribution on changes of mechanical properties.

Another study will be conducted on tests for recyclability of the developed organic waste-composite material. In such study, fractured samples could be re-used as base material for extruding new filament and the degradation of mechanical properties of the material being recycled and reused over varying life cycles will be explored.

ACKNOWLEDGMENT

The authors would like to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) under the Discovery Grant (RGPIN-2020-06701 and RGPIN-2019-05973).

REFERENCES

[1] United Nations, "The future is now Science for achieving sustainable development" Global sustainable develoment report, pp. 46–118, 2019.

[2] H. Kim *et al*., "A look at the challenges and opportunities of 3D printing," *Comput. Graph. Forum*, vol. 5, no. 1, p. 35, 2016.

[3] C. Ziemian, M. Sharma, and S. Ziemi, "Anisotropic Mechanical Properties of ABS Parts Fabricated by Fused Deposition Modelling," *Mech. Eng.*, no. February 2018, 2012, doi: 10.5772/34233.

[4] M. Sauerwein, E. Doubrovski, R. Balkenende, and C. Bakker, "Exploring the potential of additive manufacturing for product design in a circular economy," *J. Clean. Prod.*, vol. 226, pp. 1138–1149, 2019, doi: 10.1016/j.jclepro.2019.04.108.

[5] M. Sauerwein, C.A. Bakker, and A.R. Balkenende, "Additive manufacturing for circular product design: a literature review from a design perspective," *Prod. Lifetimes Environ. 2017 - Conf. Proc.*, no. 2012, pp. 358–364, 2017, doi: 10.3233/978-1-61499-820-4-358.

[6] Y. Tang, K. Mak, and Y. F. Zhao, "A framework to reduce product environmental impact through design optimization for additive manufacturing," *J. Clean. Prod.*, vol. 137, pp. 1560–1572, 2016, doi: 10.1016/j.jclepro.2016.06.037.

[7] Y. Tang, K. Mak, and Y. F. Zhao, "A framework to reduce product environmental impact through design optimization for additive manufacturing," *J. Clean. Prod.*, vol. 137, pp. 1560–1572, 2016, doi: 10.1016/j.jclepro.2016.06.037.

[8] A. van Wijk and I. van Wijk, *3D printing with biomaterials: Towards a sustainable and circular economy*. 2015.

[9] S. Owuamanam and D. Cree, "Progress of Bio-Calcium Carbonate Waste Eggshell and Seashell Fillers in Polymer Composites: A Review," *J. Compos. Sci.*, vol. 4, no. 2, p. 70, 2020, doi: 10.3390/jcs4020070.

[10] "Filabot EX2 filament extruder" [Online]. Available: https://www.filabot.com/products/filabot-original-ex2. (Accessed Jan. 01, 2021)

[11] "Ultimaker 3" [Online]. Available: https://ultimaker.com/3d-printers/ultimaker-3. (Accessed Jan. 01, 2021)

[12] M. Rafiee, R. D. Farahani, and D. Therriault, "Multi-Material 3D and 4D Printing: A Survey," *Adv. Sci.*, vol. 7, no. 12, pp. 1–26, 2020, doi: 10.1002/advs.201902307.

[13] ASTM INTERNATIONAL, "Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. D790," *Annu. B. ASTM Stand.*, pp. 1–12, 2017, doi: 10.1520/D0790-17.2.