SUSTAINABLE COMPOSITES FROM BIOBASED ENGINEERING THERMOPLASTIC AND BIOBASED FILLER FOR AUTOMOTIVE PARTS

Maisyn Picard[1,2]*, Suman Thakur*[1,2]*, Manjusri Misra*[1,2]*, Deborah F. Mielewski*[3]*,*
Amar K. Mohanty[3]
[1]*Bioproducts Discovery and Development Centre, University of Guelph, Guelph, ON, CA*
[2]*School of Engineering, University of Guelph, Guelph, ON, CA.*
[3]*Research and Innovation Center, Ford Motor Company, Dearborn, MI, USA.*

Abstract

The average life span for a car in the United States has been approximated just over 15 years. Some of the materials could be recycled but what happens to the plastic components. Much of this material is sent to landfill where it accumulates and becomes a loss of resources. Composites car parts manufactured with bioplastic and biofillers offer an alternative to petroleum products which are not regenerated after use. The combination of partially biobased poly(trimethylene terephthalate) and biocarbon at 20 weight percentage (wt.%) were used in injection molding to make sustainable composites for car interiors. Many favorable characteristics of peanut hull biocarbon including a low ash content at 4 %, high thermal stability over 300 °C, and higher graphitization content suggested its potential as a replacement to petroleum-based carbon black. The fabricated composites resulted in a successful product with 48 wt.% biocontent and a modulus which outperformed even the neat polymers. This work created a fundamental basis for the use of peanut hull biocarbon and its potential success in automotive composites applications.

Introduction

Food industry waste generate large volumes of materials each year which are often used as animal feed or landfilled. Some food wastes can be used as animal feed but there are challenges with the nutritional value of some feedstock materials [1]. However, there have been many efforts recently to convert waste residues into useable filler for polymer composites [2]–[4].

The food industry waste of interest in this work are peanut hulls, the outer most wood layer which encases the peanut. The shells are removed prior to peanut processing. There is no current use for these peanut hulls as they are currently spread back onto the fields after harvest is complete. The production of peanuts world-wide was over 45 million metric tons in 2017 [5], and since peanut hulls are about 25 wt.% of peanuts, the accumulating waste products are in ample quantity.

The challenge with using waste residues into polymer composites is odour during processing and limited thermal stability [6], [7]. To overcome these challenges materials can be pyrolyzed. The thermal conversion process is referred to as pyrolysis which requires heating the material to higher temperature to form a carbonaceous material. The carbon-based material, referred to as biocarbon is one of three by-products. The other bio-products are syngas and bio-oil [8] but are of lesser interest in this work. Biocarbon characteristics are impacted by the pyrolysis temperature, residence time, presence/absence of oxygen, heating rate, moisture content and type of biomass [9]–[12]. Biocarbon with high modulus, greater number of surface functionalities or high strength are favourable.

Biocarbon has been combined with many polymers such as engineering thermoplastics polyesters [13]–[15] like polyamides [16], commodity plastics [3] like polypropylene [17]. Engineering thermoplastic polyesters include polymers such a poly(trimethylene terephthalate) (PTT), poly(ethylene terephthalate), and poly(butylene terephthalate) [18]. The synthesis of PTT requires condensation reaction of 1,3-propanediol (PDO) and terephthalic acid. Dupont chemical company has created a method to synthesize PDO from renewable sources and reduce the greenhouse gas emission by 40 % for that component of PTT [19]. The increased biocontent suggests it potential adaptation in composites manufacturing as an alternative to strictly petroleum-based plastics.

This paper focuses renewable materials for automotive composites from PTT and peanut hull biocarbon. Although in the preliminary stages of investigation the fabrication of composites highlights the potential to development automotive composites via circular economic approach to safeguard resources and the environment.

Materials and Methods

Peanut hulls, grown in Southern Ontario, Canada, are a wood biomass on the outside of the peanut. The peanuts are planted in late May and harvested mid-September. The peanut grown in the ground as shown in Figure 1a and the hull (Figure 1b) protects the peanuts during the growing season.

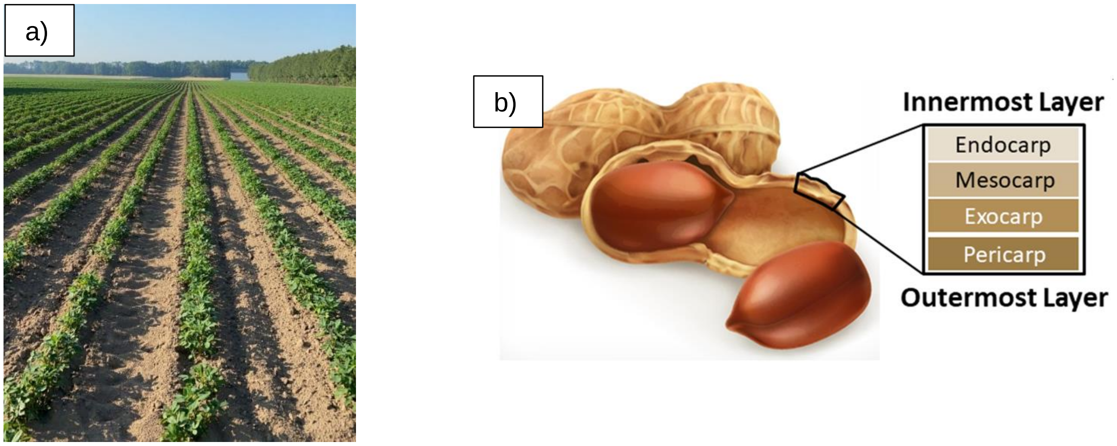

Figure 1: a) peanut field in Southern Ontario July 2020 captured by author, and b) peanut structure from literature [13].

The hulls were milled (6000 rpm through 1 mm sieve) and dried prior to pyrolysis in a tube furnace (heating rate 7 °C/minute, to 500 °C with 15 mins residence time). Pyrolysis was completed in nitrogen atmosphere to reduce the formation of ash during the process. Ash is an unfavourable product when processing composites. The experimental set-up is displayed in Figure 2.

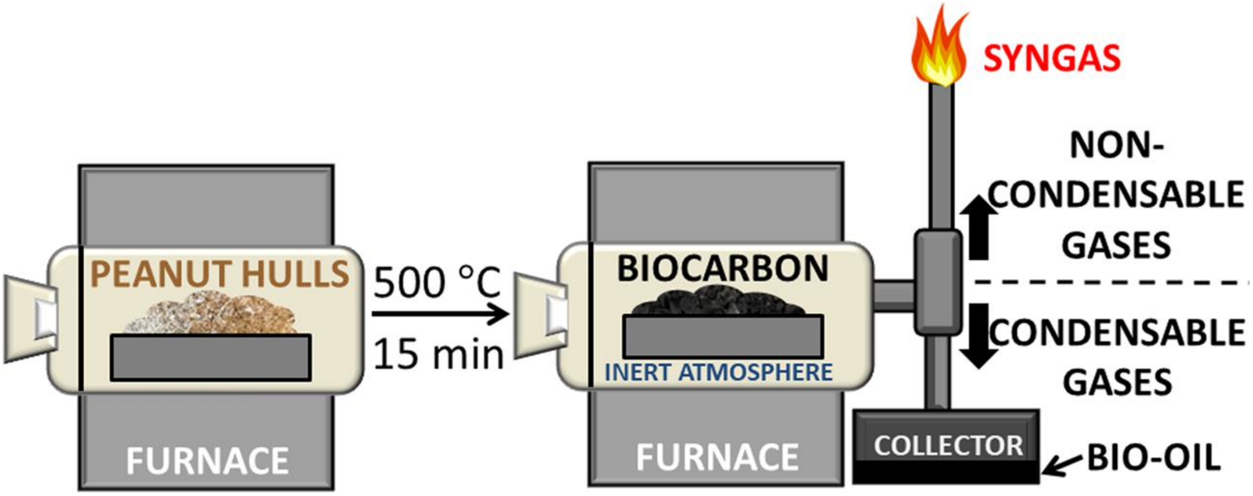

Figure 2: Pyrolysis set up for biocarbon production in an inert atmosphere [13].

Samples were ball milled at 300 rpm for 1 hour. For composite fabrication, both poly(trimethylene terephthalate) (PTT) from Dupont and peanut hull biocarbon were dried prior to processing. Samples were prepared on a twin-screw extruder (DSM, Netherlands) with a co-rotating screw configuration. Processing conditions included 250 °C melt temperature, 40 °C mold temperature, 2 minutes residence mix time and 100 rpm screw speed. The injection molded samples followed size constraints of ASTM stands. The ASTM standard samples were tested on a universal tester (Instron, USA) in accordance with D790 and D638 for flexural and tensile tests, respectfully. Due to the nature of the sample and time of testing requirements, tensile samples were tested at a rate of 5 mm/min.

The pyrolysis process undoubtedly released volatile material during the heating process. To analyze these gases, samples were placed in a thermogravimetric (TGA)-FTIR analyzer. A TGA5500 machine (TA Instruments, USA) heated 10 mg sample of peanut hulls to 550 °C (at a rate of 20 °C/min) since this was just above the pyrolysis temperature.

Characterization of the biocarbon samples and fracture surface of the composites was completed with a scanning electron microscope (Phemon, Netherlands) at 15 kV. Additional spectroscopic analysis included Fourier's Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy. The FTIR spectroscope was implemented to determine the surfaces functionalities on the biocarbon and the impact of pyrolysis on such groups. FTIR spectra were obtained over a range from 4000 to 400 cm^{-1}. The Raman spectroscopic analysis was performed with at 1 mW laser power with 50 times zoom over a 50 µm slit. The spectra ranged from 2000 cm^{-1} down to 800 cm^{-1}.

Results and Discussion

Peanut hulls are a cellulosic mass which has been found to have elemental ranges for carbon, hydrogen, oxygen and nitrogen of 50 - 70, 6 - 8, 12 - 38 and 0.5 - 2 % [20]–[22]. However, once pyrolyzed at 500 °C, the carbon content increases substantially whereas there are reductions in oxygen and hydrogen contents. Novak et al. found that the 500 C peanut hull biocarbon had a carbon content of 82 %, hydrogen at 3 %, oxygen at 3 % and nitrogen at 3 % [21]. Further physicochemical analysis found that peanut hull biocarbon pyrolyzed at 500 °C possessed an ash content of 4.8%. This value was comparable to that of peanut hulls alone that had an ash content of 4 % [13].

The SEM images of the peanut hulls (Figure 3a) and the peanut hull biocarbon (Figure 3b) show that the sheet-like surface morphology was maintained during the pyrolysis process. The large surface area exposed of on the filler, results in a greater or improved adhesion between filler and the matrix material [17]. A successfully filler-matrix interface is able to dissipate forces evenly throughout the material and improve the mechanical performance [6].

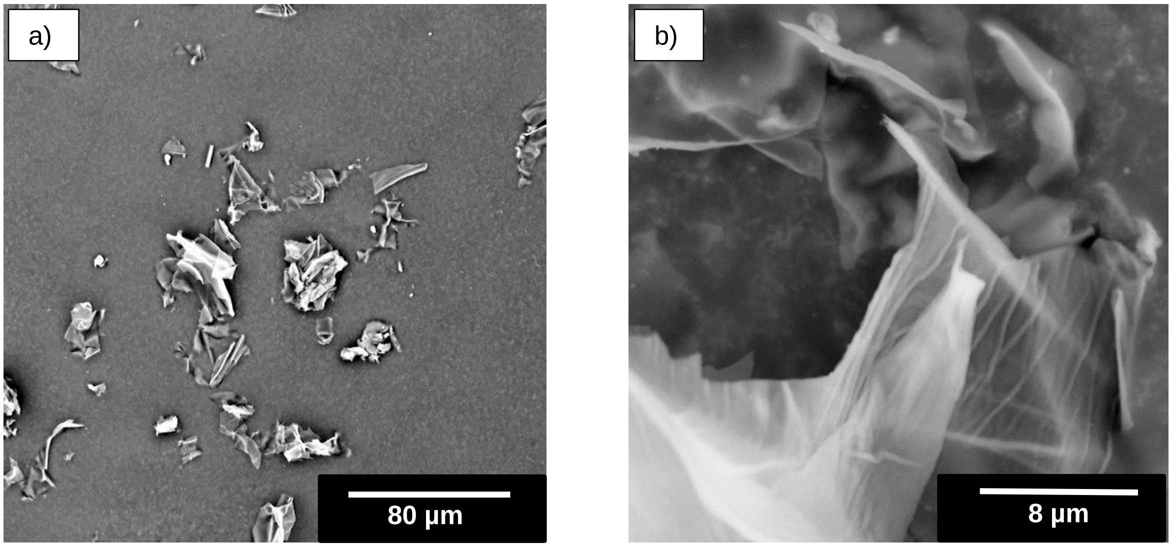

Figure 3: SEM images of a) milled peanut hulls at 1000x, b) peanut hull biocarbon pyrolyzed at 500 °C at 10000x.

The Raman spectra of peanut hulls (Figure 4a) display that there is a higher graphitized carbon content than disordered content based on the variation in height of peaks. The deconvoluted peaks are used to identify the general structure on the surface of the peanut hulls [7], [13]. The graphitization peak is centered at 1588 cm^{-1} and the disordered peak centered at 1352 cm^{-1} noted, respectively, as the pink and blue curves below. The disordered peak D' has been associated with sp^3 orbital in amorphous carbons [23], [24] and has been found located in other biocarbon sources. When looking a Raman spectrum, the ratio of the intensity of D bands to G bands can be compared as a quick means for comparison. The I_D/I_G peaks ratio was 0.66 which was comparable to palm kernel shells [25] and walnut shell [26] pyrolyzed at similar temperature. A ratio of less than one confirms that there was more graphitic than disorder carbon on the surface of the samples.

The major peaks found on FTIR spectra the peanut hulls and peanut hull biocarbon are displayed in Figure 4b. The broad peak which is centered at 3300 cm^{-1} is associated with O-H side groups of the samples [27]. The peaks located around 1633 cm^{-1} and 1250 cm^{-1} are associated with lignin content of peanut hulls [27]. Hemicellulosic peaks at 1730 cm^{-1} were attributed to C=O stretching [28]. The peak at 1030 cm^{-1} was associated with the C-OH stretching of cellulose and hemicellulose [29]. Other lignocellulosic associated peaks were found at 2921 cm^{-1} from the methylene and methyl groups [28]. The loss in intensity or removal of peaks after pyrolysis was from the evolution of volatile components during the heating process [30].

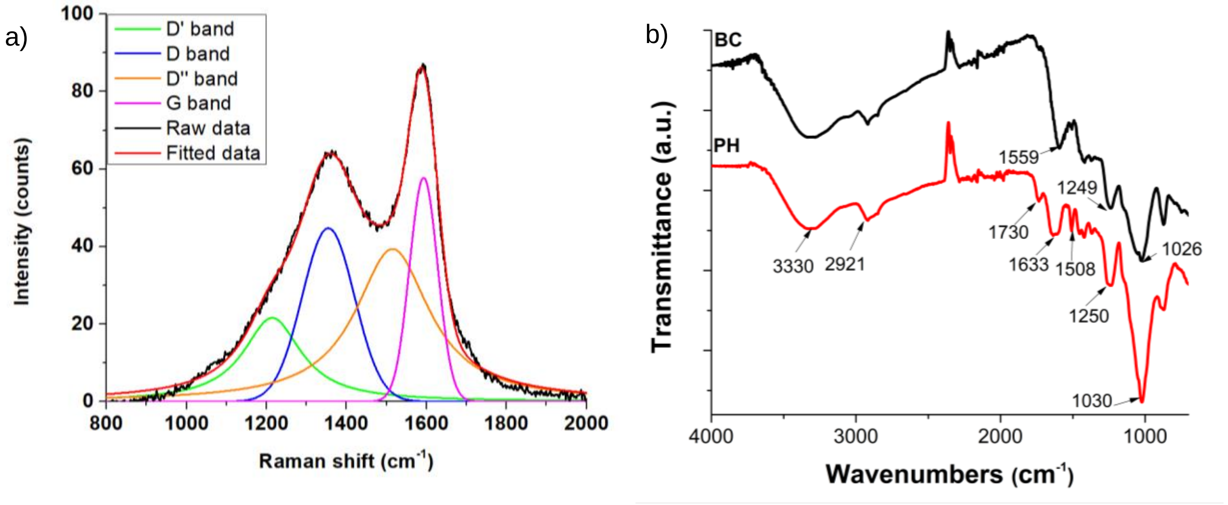

Figure 4: a) Raman spectra for 500 °C peanut hull biocarbon, b) FITR of peanut hulls (PH) and biocarbon (BC) obtained from literature [13].

The evolution of gases from pyrolysis process was studied via TGA-FTIR analysis (Figure 5). Water was identified between 3400 to 4000 cm^{-1} from the O-H stretching. From 2700 - 3000 cm^{-1} hydrocarbons were released and identified from C-H stretching. Carbon dioxide volatiles were identified from 2250-2400 cm^{-1} for C=O stretching and at 586-726 cm^{-1} C=O bending. The carbon monoxide released during pyrolysis was identified by the peak from 2000-2250 cm^{-1} which corresponded to C-O stretching. Carbonyl and ether groups were identified at 1650-1900 cm^{-1} and 1000-1450 cm^{-1}, respectfully .

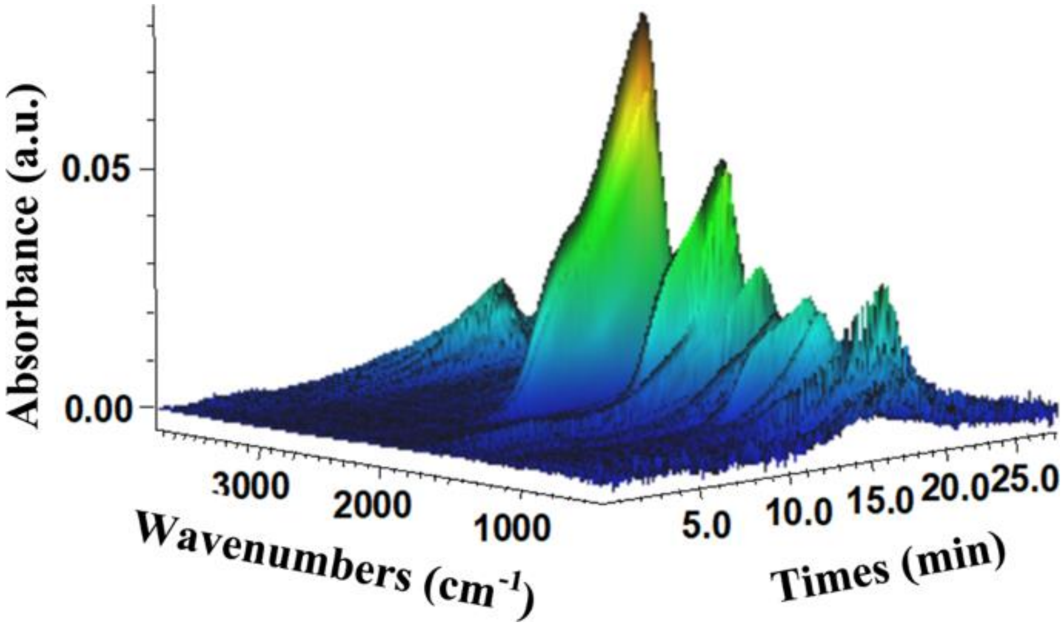

Figure 5: TGA-FTIR analysis of peanut hulls heated to 550 °C [13].

The addition of biocarbon with partially biobased PTT increased the biocontent to 48 wt.% which is greater than the current market solutions with petroleum-based polymer and carbon black. Biocarbon had the advantage of having no odour as compared to other natural fillers [6], [7], it can be obtained at little to no cost [31], and is much more thermally stable than other natural fillers with a maximal degradation temperature at 350 °C [13]. The benefits were accompanied by the improved flexural and tensile moduli (Figure 6). Unfortunately, there was a decrease in impact strength with the addition of biocarbon. The biocarbon like added stress concentration factors within the matrix and reduced the stress dissipation of the impact [15], [32]. This can be improved through the addition of a compatibilizer or through use of a polymer with higher bonding affinity to biocarbon.

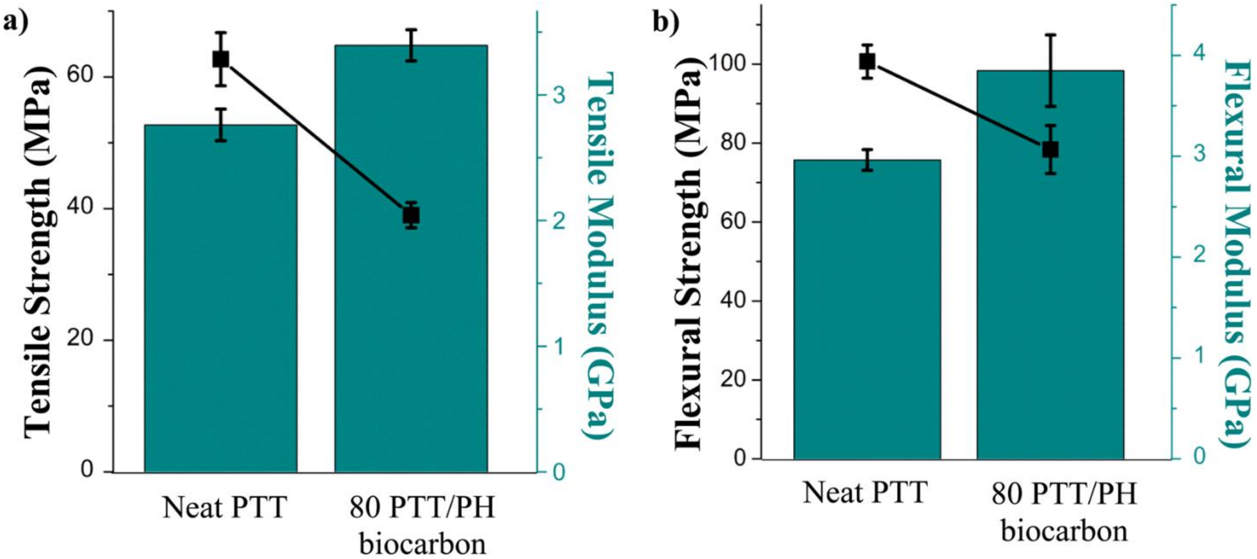

Figure 6: a) tensile properties of 80 PTT/20 peanut hull biocarbon and b) flexural properties for 80 PTT/20 peanut hull biocarbon [13].

The SEM analysis of neat polymer fracture surface (Figure 7a) and composites (Figure 7b). The highlighted ridges in the neat PTT are representative of a brittle facture surface. The addition of biocarbon exhibited similar characteristics as confirmed by the reduction in impact strength. However, there was also accumulation of biocarbon as noted in the red circle below. The processing of this material was challenging due to thermal expansion of the samples. Further processing modifications may also improve the dispersion of the biocarbon as well as the overall mechanical performance.

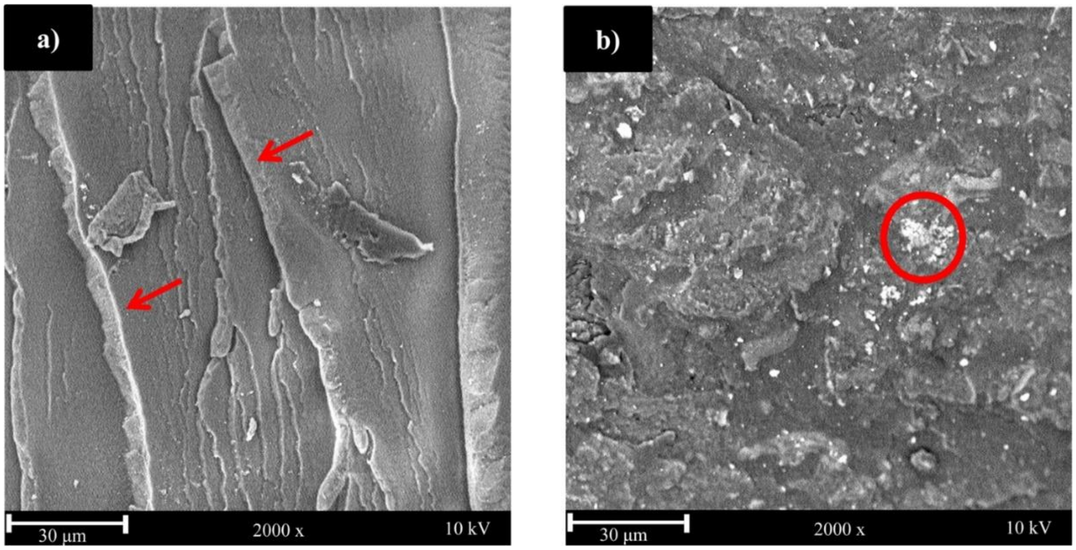

Figure 7: SEM images of impact fracture surface for a) neat PTT and b) peanut hull biocarbon composites [13].

Next Steps

The next part of this work focuses on further modifications to the biocarbon. Samples of peanut hull biocarbon were pyrolyzed at 900 °C with a modified pyrolysis procedure. Higher temperature samples were produced in large GLO carbolite furnace to increase the quantity of biocarbon produced. Initial analysis was performed via Raman to determine the relative amounts of graphic and disordered carbon content (Figure 8). The higher temperature biocarbon exhibited an I_D/I_G ratio of 1.05 suggesting a greater amount of disordered carbon present than graphitized carbon.

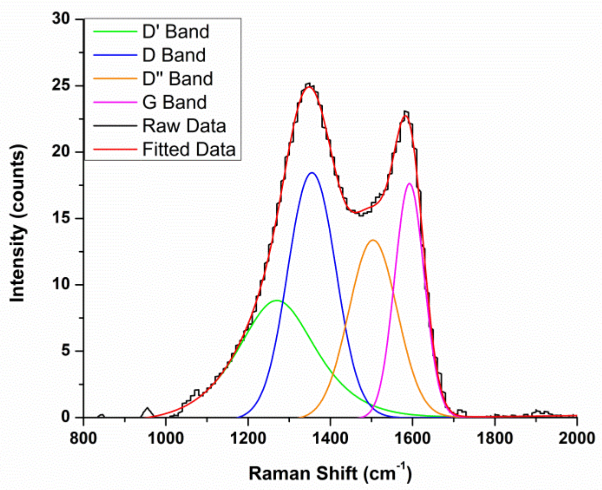

Figure 8: Peanut hull biocarbon pyrolyzed at 900 °C

A preliminary set of composites were made with 900 °C peanut hull biocarbon. The flexural and tensile moduli were 3.15 GPa and 2.45 GPa, respectfully. The flexural strength was 58 MPa and the tensile strength was 32 MPa which were similar or less than that of the 500 °C samples. The next steps would be to compatibilize the system to improve the filler-matrix interphase since only the flexural modulus experienced improvements over the 500 °C biocarbon.

Summary

Overall, this work highlighted the first time use of low temperate pyrolyzed peanut hulls in composites applications. The peanut hulls obtained from a food processing industry, were pyrolyzed at 500 °C to generate a high carbon content material. Thermal and chemical analysis found that peanut hull biocarbon offer exceptional thermal stability and low ash content which would benefit biocomposites fabrication. Peanut hull biocarbon was combined at 20 wt.% with partially biobased engineering thermoplastic poly(trimethylene terephthalate). The composites experienced enhanced flexural and tensile moduli but losses in other properties. This work laid the foundation for future work with peanut hull biocarbon and the potential to optimize the process and product. The next steps of this work would be to optimize the biocarbon content to make easier processability or adjust the pyrolysis temperature to improve the surface functionalities which directly related to the adhesion between filler and matrix. Further works may also arise in the adaptation of peanut hull biocarbon composites in additive manufacturing technologies.

Acknowledgements

The authors would like to thank the following for their financial support: i) Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA)/University of Guelph – Bioeconomy for Industrial Uses Research Program (Project # 030332); ii) Natural Sciences and Engineering Research Council (NSERC), Canada Discovery Grants Project # 400320 and 401111; iii) the Ontario Research Fund, Research Excellence Program; Round-7 (ORF-RE07) from the Ontario Ministry of Research, Innovation and Science (MRIS) (Project # 052644 and 052665). A special thanks to Picard Foods Partnership (795 Old Hwy 24, Waterford, Ontario) and Dupont, USA for their donation of the peanut hull samples and biobased PTT samples respectively to carry out this research .

Bibliography

[1] A. C. Gowman, M. C. Picard, L. Lim, M. Misra, and A. K. Mohanty, “Fruit Waste Valorization for Biodegradable Biocomposite Applications: A Review,” *BioResources*, vol. 14, no. 4, 2019.

[2] E. G. Ertane, A. Dorner-Reisel, O. Baran, T. Welzel, V. Matner, and S. Svoboda, “Processing and Wear Behaviour of 3D Printed PLA Reinforced with Biogenic Carbon,” *Adv. Tribol.*, vol. 2018, no. 1763182, pp. 1–11, 2018.

[3] T. Wang, A. Rodriguez-Uribe, M. Misra, and A. K. Mohanty, “Sustainable Carbonaceous Biofiller from Miscanthus: Size Reduction, Characterization, and Potential Bio-composites Applications,” *BioResources*, vol. 13, no. 2, pp. 3720–3739, 2018.

[4] Y. Shao, C. Guizani, P. Grosseau, D. Chaussy, and D. Beneventi, “Use of lignocellulosic materials and 3D printing for the development of structured monolithic carbon materials,” *Compos. Part B Eng.*, vol. 149, no. March, pp. 206–215, 2018.

[5] American Peanut Council, “The Peanut Industry,” 2018. [Online]. Available: https://www.peanutsusa.com/about-apc/the-peanut-industry.html.

[6] M. C. Picard, A. Rodriguez-Uribe, M. Thimmanagari, M. Misra, and A. K. Mohanty, “Sustainable biocomposites from poly(butylene succinate) and apple pomace: A study on compatibilization performance,” *Waste and Biomass Valorization*, vol. 0, no. 0, p. 0, Mar. 2019.

[7] Z. Li, C. Reimer, M. C. Picard, M. Misra, and A. K. Mohanty, “Characterization of Chicken Feather Biocarbon for Use in Sustainable Biocomposites,” *Front. Mater.*, 2020.

[8] A. K. Mohanty, S. Vivekanandhan, J.-M. Pin, and M. Misra, “Composites from renewable and sustainable resources: Challenges and innovations,” *Science (80-.).*, vol. 362, no. 6414, pp. 536–542, 2018.

[9] S. Arnold, A. Rodriguez-Uribe, M. Misra, and A. K. Mohanty, “Slow pyrolysis of bio-oil and studies on chemical and physical properties of the resulting new bio-carbon,” *J. Clean. Prod.*, vol. 172, pp. 2748–2758, 2016.

[10] S. Al Arni, “Comparison of slow and fast pyrolysis for converting biomass into fuel,” *Renew. Energy*, vol. 124, pp. 197–201, 2018.

[11] I. Major, J.-M. Pin, E. Behazin, A. Rodriguez-Uribe, M. Misra, and A. Mohanty, “Graphitization of Miscanthus grass biocarbon enhanced by in situ generated FeCo nanoparticles,” *Green Chem.*, vol. 20, p. 2269, 2018.

[12] R. Z. Vigouroux, “Pyrolysis of biomass,” 2017.

[13] M. Picard, S. Thukur, M. Misra, D. F. Mielewski, and A. K. Mohanty, “Biocarbon from peanut hulls and their green composites with biobased poly(trimethylene terephthalate) (PTT),” *Sci. Rep.*, vol. 10, p. 3310, 2020.

[14] V. Nagarajan, A. K. Mohanty, and M. Misra, “Biocomposites with Size-Fractionated Biocarbon: Influence of the Microstructure on Macroscopic Properties,” *ACS Omega*, vol. 1, no. 4, pp. 636–647, Oct. 2016.

[15] B. P. Chang, A. K. Mohanty, and M. Misra, “Sustainable biocarbon as an alternative of traditional fillers for poly(butylene terephthalate)-based composites: Thermo-oxidative aging and durability,” *J. Appl. Polym. Sci.*, vol. 136, no. 27, pp. 1–14, 2019.

[16] E. O. Ogunsona, M. Misra, and A. K. Mohanty, “Sustainable biocomposites from biobased polyamide 6 , 10 and biocarbon from pyrolyzed miscanthus fibers,” *J. Appl. Polym. Sci.*, vol. 44221, pp. 1–11, 2017.

[17] A. Codou, M. Misra, and A. K. Mohanty, “Sustainable biocarbon reinforced nylon 6/polypropylene compatibilized blends: Effect of particle size and morphology on performance of the biocomposites,” *Compos. Part A Appl. Sci. Manuf.*, vol. 112, no. January, pp. 1–10, 2018.

[18] E. V. Diederichs, M. C. Picard, B. P. Chang, M. Misra, D. F. Mielewski, and A. K. Mohanty, “Strategy to improve printability of renewable resource based engineering plastic tailored for FDM applications,” *ACS Omega*, pp. 1–11, 2019.

[19] J. V. Kurian, “A new polymer platform for the future - Sorona® from corn derived 1,3-propanediol,” *J. Polym. Environ.*, vol. 13, no. 2, pp. 159–167, 2005.

[20] J. W. Lee, B. Hawkins, M. K. Kidder, B. R. Evans, A. C. Buchanan, and D. Day, “Characterization of biochars produced from peanut hulls and pine wood with different pyrolysis conditions,” *Bioresour. Bioprocess.*, vol. 3, no. 1, 2016.

[21] J. M. Novak *et al.*, “Characterization of Designer Biochar Produced at Different Temperatures and Their Effects on Loamy Sand,” *Ann. Environ. Sci.*, vol. 3, pp. 195–206, 2009.

[22] J. M. Jarvis, A. M. McKenna, R. N. Hilten, K. C. Das, R. P. Rodgers, and A. G. Marshall, “Characterization of pine pellet and peanut hull pyrolysis bio-oils by negative-ion electrospray ionization fourier transform ion cyclotron resonance mass spectrometry,” *Energy and Fuels*, vol. 26, no. 6, pp. 3810–3815, 2012.

[23] J. Schwan, S. Ulrich, V. Batori, H. Ehrhardt, and S. R. P. Silvia, “Raman Spectroscopy on amorphous carbon films,” *J. Appl. Phys.*, vol. 80, no. 1, pp. 440–447, 1996.

[24] R. E. Shroder and R. J. Nemanich, “Analysis ofthe composite structures in diamond thin films by Raman spectroscopy,” *Phys. Rev. B*, vol. 41, no. 6, pp. 3738–3745, 1990.

[25] Z. Ma *et al.*, “Evolution of the chemical composition, functional group, pore structure and crystallographic structure of bio-char from palm kernel shell pyrolysis under different temperatures,” *J. Anal. Appl. Pyrolysis*, vol. 127, no. 38, pp. 350–359, 2017.

[26] F. N. D. Mukome, X. Zhang, L. C. R. Silva, J. Six, and S. J. Parikh, “Use of Chemical and Physical Characteristics To Investigate Trends in Biochar Feedstocks,” *J. Agric. Food Chem.*, vol. 61, pp. 2196–2204, 2013.

[27] Z. Zhong, Q. Yang, X. Li, K. Luo, Y. Liu, and G. Zeng, “Preparation of peanut hull-based activated carbon by microwave-induced phosphoric acid activation and its application in Remazol Brilliant Blue R adsorption,” *Ind. Crop. Prod.*, vol. 37, no. 1, pp. 178–185, 2012.

[28] A. Tasar, S., Kaya, F., and Ozer, “Biosorption of lead (II) ions from aqueous solution by peanut shells : Equilibrium , thermodynamic and kinetic studies,” *J. Environ. Chem. Eng.*, vol. 2, pp. 1018–1026, 2014.

[29] Y. Liu, X. Sun, and B. Li, “Adsorption of Hg2+ and Cd2+ by ethylenediamine modified peanut shells,” *Carbohydr. Polym.*, vol. 81, no. 2, pp. 335–339, 2010.

[30] M. A. Zazycki, M. Godinho, D. Perondi, E. L. Foletto, G. C. Collazzo, and G. L. Dotto, “New biochar from pecan nutshells as an alternative adsorbent for removing reactive red 141 from aqueous solutions,” *J. Clean. Prod.*, vol. 171, pp. 57–65, 2018.

[31] T. Balint, B. P. Chang, A. K. Mohanty, and M. Misra, “Underutilized Agricultural Co-Product as a Sustainable Biofiller for Polyamide 6,6: Effect of Carbonizatoin Temperature,” *Molecules*, vol. 25, no. 1455, pp. 1–19, 2020.

[32] E. Behazin, M. Misra, and A. K. Mohanty, “Compatibilization of toughened polypropylene/biocarbon biocomposites: A full factorial design optimization of mechanical properties,” *Polym. Test.*, vol. 61, pp. 364–372, 2017.