

# **BIOCARBON PRODUCED FROM AGRICULTURAL, INDUSTRIAL, FORESTRY, AND FOOD WASTE: PERFORMANCE EVALUATION OF BIOCARBON-REINFORCED POLYPROPYLENE BIOCOMPOSITES**

*Arturo U. Rodriguez<sup>1,§</sup>, Neelima Tripathi<sup>1,2</sup>, Amar K. Mohanty<sup>1,2,\*</sup> and Manjusri Misra<sup>1,2,\*</sup>*

*<sup>1</sup>Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, University of Guelph, Guelph, N1G 2W1 Ontario, Canada*

*<sup>2</sup>School of Engineering, Thornborough Building, University of Guelph, Guelph, N1G 2W1 Ontario, Canada*

*<sup>§</sup>Presenting author: [rarturo@uoguelph.ca](mailto:rarturo@uoguelph.ca)*

*<sup>\*</sup>Corresponding authors: [mmisra@uoguelph.ca](mailto:mmisra@uoguelph.ca) (M. Misra); [mohanty@uoguelph.ca](mailto:mohanty@uoguelph.ca) (A. Mohanty)*

## **Abstract**

We engineered advanced biocarbon through pyrolysis of forestry waste (wood chips), agricultural waste (corn cob), energy crops (Miscanthus grass), proteinaceous material (chicken feather) and food waste (crab shell and shrimp shell). The developed sustainable fillers on reinforcement with polypropylene (PP) result in the development of light-weight biocomposites. Through reactive extrusion followed by injection molding the test samples were made for their performance evaluations. The biocarbon developed in the range of 500-600 °C present functionality over carbon surface unlike those made at > 900 °C pyrolysis temperature. High temperature biocarbon (~ 900 °C) showed improved interfacial adhesion towards polypropylene (which is a hydrophobic plastic). Biocomposites manufactured with high temperature-made biocarbon exhibited higher modulus as compared to low-temperature made counterpart. Again, the use of maleated-g-polypropylene (MA-g-PP) helped in improving the overall performance of the developed biocomposites. The particle size reduction of biocarbon has a profound effect on the performance of the resulting composites. The combination of particle size reduction with the maleated coupling agent has a dramatic bonding effect thus on the performance of the resulting biocomposites. The developed biocomposites with 27 wt.% sustainable biocarbon fillers showed density of ~ 1 g/cm<sup>3</sup> making those quite lighter as compared to mineral-filled counterparts. Such light biocomposites from waste resources show significant potential in the development of light-weight auto-parts.

## **Keywords**

Polypropylene, biocarbon, maleic anhydride grafted polypropylene, mechanical and thermal properties of polypropylene composites

## Introduction

Polypropylene reinforced with mineral fillers and fibers are composites commonly used in the automotive industry. Mineral talc and glass fibers are used to improve the stiffness as well as thermal properties like the heat deflection temperature and thermal-dimensional stability. Many polypropylene-based composites are manufactured by two-step processing, i.e., melt-extrusion followed by injection molding. This combined technology is simple and cost-effective and allows the production of materials with intricated shapes [1].

In general, the properties of these composites are governed by several factors related to the fillers/fibers and matrix properties. The most evident change in properties occurs due to the particle morphology (surface area, particle size, and aspect ratio), the filler/fiber load and distribution/arrangement within the composite, the modulus of the particles, and the chemistry of the surfaces (fillers and matrix). All these parameters result in complex systems which govern inter-particle distance as well as the interactions at the interface filler-matrix [2].

The industry, however, is continuously looking for sustainability in its operations, including incorporating more sustainable materials. Thus, a current trend in composites manufacture is to reduce the associated carbon footprint by using more sustainable materials, including plastics, fillers, and fibers.[3]

Particulate biocarbon is a promising bio-based substitute for mineral fillers as well as carbon blacks in many practical and high-performance applications [4, 5]. The use of this material is also aimed at reducing the overall weight of the final composites owing to its comparatively lower density [5]. The hydrophilicity of common bio-fillers is comparatively its main drawback. However, it has been proved that biocarbon is extraordinarily hydrophobic compared to traditional bio-fillers such as wood flour or natural fibers, etc., due to the intrinsic phenomenon of removal of hydroxyl and other polar groups occurring during pyrolysis of biomass. Furthermore, the hydrophilicity of biocarbon can be reduced by increasing the temperature of the pyrolysis of biocarbons [6]. Another important property of biocarbon is the ash content which depends on the source of biomass from which it is derived. The pyrolysis temperature dramatically reduces most of the differences found in the original raw materials yielding elemental carbon showing different ratios of amorphous to graphitic structures [7]. However, the ash content remains, and the relative yield increases with the increasing temperature of pyrolysis. Wood-based biocarbon for instance will present less ash content with respect to grass-derived biocarbons (miscanthus or switch grass-based biocarbons) [8-10]. Since biocarbon tends to keep the original shape of the basic pyrolyzed material, the particle size can be further controlled by using a simultaneous mechanical milling and sieving process. This process can lead even to the nano-scale size. However, since the particle size reduction of biocarbon is a “top-down” process, the production of particles is currently a relatively challenging task, as the size of biocarbons produced from biomass tends to present relatively large standard deviations [11]. Therefore, more dedicated research and analyses are required with respect to the effects of the properties of the different biocarbons on the overall performance of the composites.

This work focuses on the evaluation of biocarbon-reinforced polypropylene composites. The biocarbon was synthesized from different biomass sources, mostly waste biomass. The waste obtained from various sources was pyrolyzed at various temperatures, and the change in mechanical properties of the biocarbon was obtained.

## Materials

Different sources (forestry waste (wood chips), agricultural waste (corn cob), energy crops (Miscanthus fibers [12]), proteinaceous material (chicken feather) and food waste (crab shell and shrimp shell) of biocarbon [13] were used in this study to prepare composites at a fixed load of 27 wt.%. Talc and carbon black were used to compare with the biocarbons. The fillers used for this comparative study are listed in Table 1.

Miscanthus, wood, and chicken feather biocarbons were provided by Competitive Green Technologies (Leamington ON, Canada). For these pyrolyzed biocarbons, a continuous pyrolyzer Metamag Inc. unit (London, ON, Canada) was used. The biochar obtained was hammer milled and passed in a 1/64 (~ 0.4 mm) screen. Further was ball milled by the same company in a D-type ball mill from Petterson Inc. (Toronto ON, Canada). The milling media consisted of ceramic balls with diameters from 3/4 to 1/4 inch at 300 rpm.

Corn cob and shrimp shell biocarbons were produced and ball milled *in situ* in our laboratory using a unit GLO-Gero type pyrolyzer (Germany) and a planetary ball milling Pulverisette 5, Laval Lab Inc. (Canada) by using ceramic milling media and ceramic jars.

The polymer used to manufacture the composites was a homopolymer polypropylene (PP) from Pinnacle Polymers (Garyville, LA, USA) grade 1120H. The coupling agent, the maleic anhydride grafted polypropylene (MA-g-PP) grade Fusabond® 353P was from DuPont (Wilmington, DE, USA). Mineral talc and carbon black were used to fabricate similar composites and to compare them with biocarbon. The carbon black used was from Asbury® carbons code 5501 (US), and the talc JetFine 500 was from Imerys® talc (USA).

Table 1. Fillers used for the preparation of specimens

Filler	Properties, Size, Source, Company	Acronyms used for powder sample
<i>Synthetic fillers</i>		
Mineral Talc	<i>JetFine 500 Imerys®, 5 microns</i>	TC
Carbon black	Asbury®5501, 500 nanometers	CB
<i>Biocarbons</i>		
Miscanthus biocarbon (Energy grasses)	900°C Less than 300 microns Produced by hammer mill and passed through a mesh of 1/64 inch,	MBC900
Miscanthus biocarbon	900°C (Same as above) + Ball milled 1 hour	MBC900-1
Miscanthus biocarbon	600°C Less than 300 microns Produced by hammer mill and passed through a mesh of 1/64 inch, Competitive Green Technologies, Leamington, ON, Canada	MBC600
Miscanthus biocarbon	600°C(same as above)+ Ball milled 1 hour	MBC600-1
Miscanthus biocarbon	600°C(same as above)+ Ball milled 24 hour	MBC600-24
Wood waste chips (Forestry waste)	600°C 1 hour ball milled	WCB600
Shrimp shell biocarbon (Food waste)	600°C <i>1 hour ball milled</i>	SSB600
Chicken feather (poultry, protein waste)	500°C 1 hour ball milled	CFB500
Corn cob biocarbon (Agricultural waste)	500°C 1 hour ball milled	CCB500

## Methods

Composites were prepared in a 15-cc micro twin screws extruder from X-plore Instruments B.V. (Sittard, the Netherlands), having a screws length of 150 mm and an aspect ratio of 18. The compounding was performed at 100 rpm and 190°C with a residence time of 2 min. The mold temperature was 30°C, and the average pressure and holding time were 10 bar and 20 sec, respectively. The filler and the coupling agent (MA-g-PP) were kept constant at 27 wt% and 3 wt%. Table 2 shows the composition of the manufactured composites.

*Table 2. Composition of composites manufactured*

ID	Polypropylene (Wt.%)	Filler (Wt. %)	MA-g-PP (Wt. %)	
<b>PP-TC</b>	73	27	----	Figure 1
<b>PP-CB</b>	73		----	
<b>PP-MBC900</b>	73		----	
<b>PP-MBC900-1</b>	73		----	
<b>PP-MBC600</b>	73		----	Figure 2
<b>PP-MBC600-MA</b>	70		3	
<b>PP-MBC600-1</b>	73		----	
<b>PP-MBC600-1-MA</b>	70		3	
<b>PP-MBC600-24</b>	73		----	
<b>PP-MBC600-24-MA</b>	70		3	
<b>PP-CFB500-1</b>	73		----	Figure 3
<b>PP-CFB500-1-MA</b>	70		3	
<b>PP-WCB600-1</b>	73		----	
<b>PP-WCB600-1-MA</b>	70		3	
<b>PP-CCB500-1</b>	73		----	
<b>PP-CCB500-1-MA</b>	70		3	
<b>PP-SS600-1</b>	73		----	
<b>PP-SS600-1-MA</b>	70		3	

## Characterization

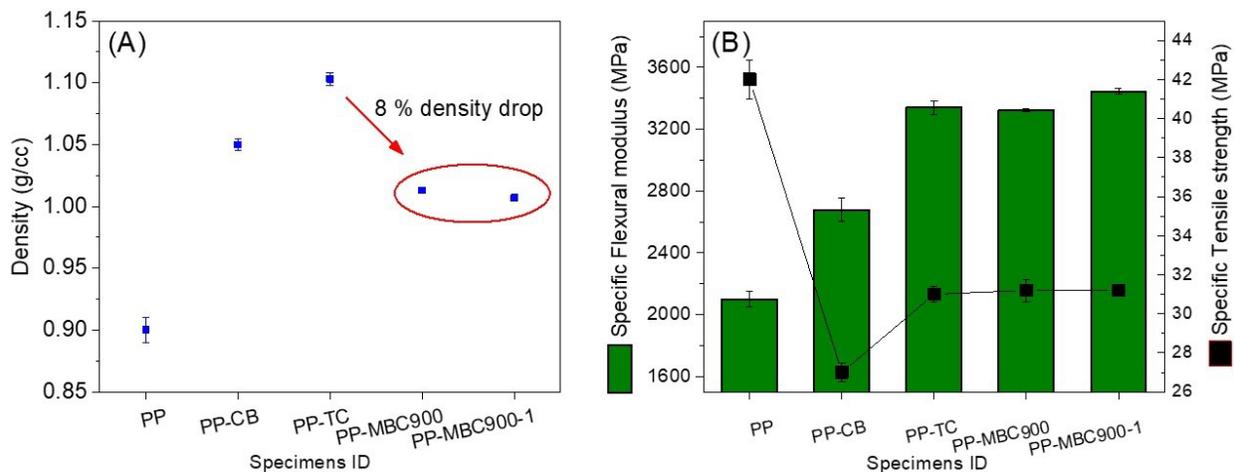
The tensile and flexural tests were performed in a universal testing machine from Instron (UTS-3382, Norwood, MA, USA). Tensile testing bars type IV for these tests were manufactured accordingly to ASTM D638. Flexural specimens were manufactured and tested according to ASTM D790. Specimens for the unnotched Izod impact strength were fabricated and tested by following the ASTM D 4812 standard. A unit ZwickRoell impact tester (Germany) was used for measuring impact strengths.

## Results and Discussion

### (I) Effect of high temperature (900 °C) pyrolyzed Miscanthus biocarbon on polypropylene composites

Comparisons of PP reinforced with Miscanthus biocarbon (MB) with particulate fillers such as carbon black and talc composites were carried out. As a rule, incorporation of fillers (27 %) results in a decrement of strength and increment of the moduli (tensile and flexural). The tensile modulus is usually similar to or slightly higher than the flexural modulus. The increase of the moduli is required when the filler is incorporated, despite the reduction of the elongation properties. Figure 1 (A) shows the density of the biocarbon reinforced composites compared to talc and carbon black reinforced composites, and Figure 1 (B) shows the specific flexural modulus and the specific tensile strength.

The properties of the composites are strongly dependent on the morphology of the fillers. Among all composites, carbon black showed the lowest specific tensile strength and specific flexural modulus. Talc and Miscanthus biocarbon composites showed similar specific flexural modulus and specific tensile strength (density of composites is shown in Figure 1(A)). The particle size and aspect ratio of biocarbons play a significant role in the performance of the composites [14, 15]. Figure 1 (B) shows Miscanthus biocarbon composites (of different particle sizes) pyrolyzed at 900°C. In one of the composites, biocarbon was passed through a mesh of 1/64 inch (PP-MBC900), and the other was further ball milled for an hour (PP-MBC900-1). A slight increment in the flexural modulus was observed after the biocarbon particle size reduction and homogenization. The high performance of high temperature pyrolyzed biocarbon PP composites can be attributed to the lack of polar functional groups or the increased hydrophobicity of biocarbon. The lack of functional groups can generally render better compatibility at the interface PP-Biocarbon.

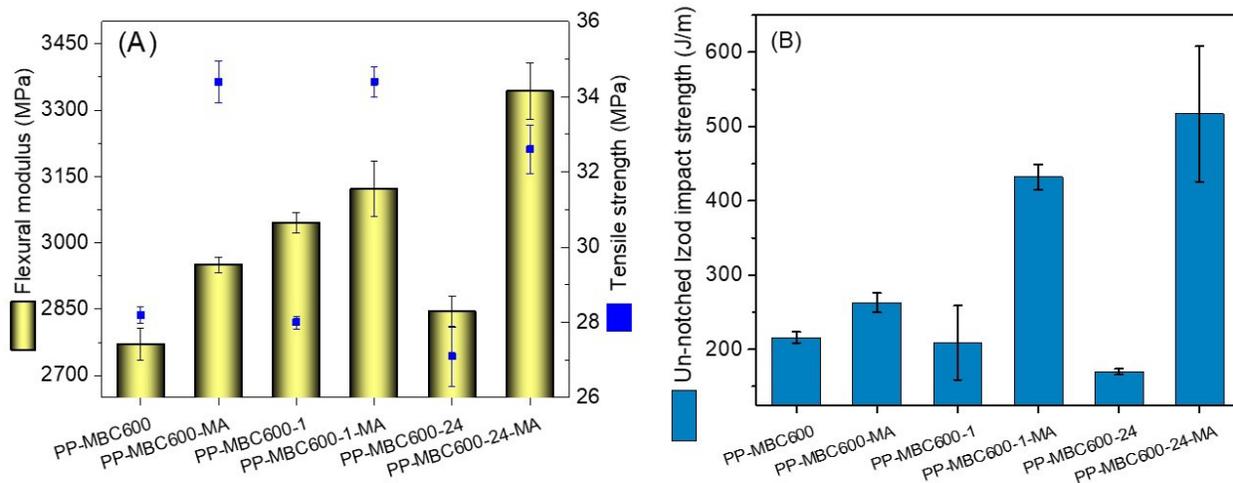


**Figure 1.** Comparison of PP composites with conventional and high-temperature pyrolyzed Miscanthus biocarbon properties: (A) densities; (B) specific flexural modulus and tensile strength.

*(II) Effect of particle size of low temperature (600 °C) pyrolyzed Miscanthus biocarbon on PP composites and effect of maleic anhydride grafted polypropylene (MA-g-PP)*

Figure 2 shows polypropylene composites manufactured with 27 wt% Miscanthus biocarbon (MBC) produced at 600 °C, followed by sieving using a 1/64-inch screen (abbreviated as MBC600). Further, this biocarbon was ball milled for 1 hour (MBC600-1) and 24 hours (MBC600-24), as shown in Table 1. The density of these three biocarbon samples were similar to PP-MBC900. These three biocarbons were used to prepare PP composites and were then reinforced with a commercial source of maleic anhydride grafted polypropylene (MA-g-PP) to generate compatibilized composites termed as PP-MBC600-MA, PP-MBC600-1-MA, and PP-MBC600-24-MA (Table 2).

The interfacial adhesion of low-temperature biocarbon (600°C) and the PP can be considerably improved by using the coupling agent (MA-g-PP). The flexural modulus and the tensile strength (PP-MBC600, PP-MBC600-1 and PP-MBC600-24) improved when the coupling agent (MA-g-PP) was added. The larger surface area of the biocarbon after 24h ball milling produced a drastic reduction in the performance in uncompatibilized composites (PP-MBC600-24), which, however, in the presence of the coupling agent showed the best performance. The effect of the compatibilizer can be seen in the impact strength properties of the composites (Figure 2 (B)). As the surface area increased due to the milling of the Miscanthus biocarbon, the reduction in flexural modulus and tensile strength were observed in the case of the uncompatibilized composites, while compatibilized composites showed significant improvement in flexural modulus.



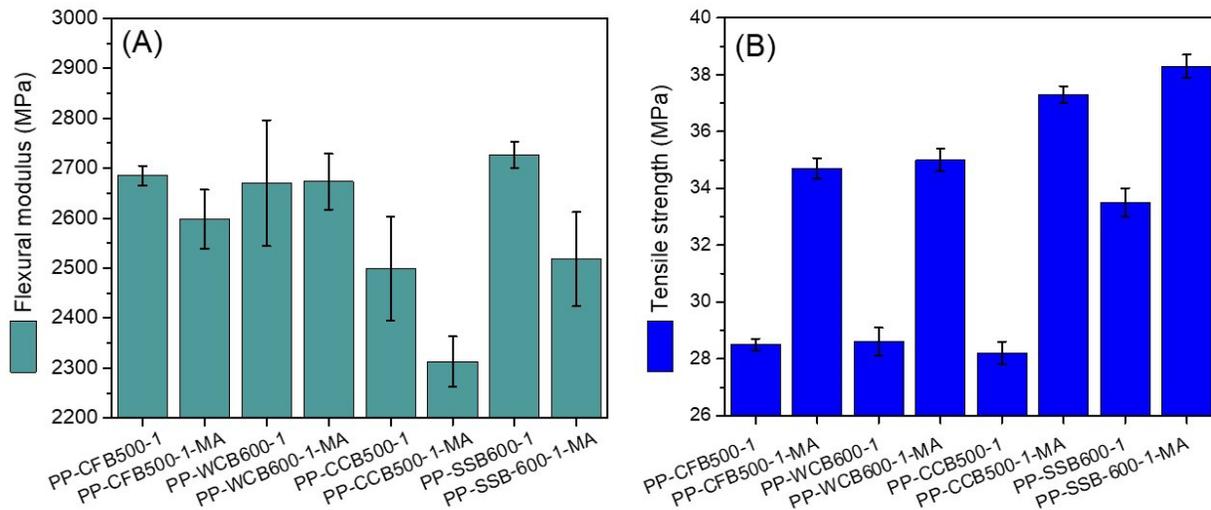
**Figure 2.** Effect of compatibilization of PP composites with low-temperature pyrolyzed Miscanthus biocarbon of different particle size: (A) flexural modulus and tensile strength; (B) unnotched Izod impact strength.

*(III) Effect of compatibilization on mechanical properties of biocarbons (low temperature pyrolyzed) from sources such as CFB (chicken feather biocarbon), WCB (wood waste chips biocarbon), CCB (corn cob biocarbon), SSB (shrimp shell biocarbon)*

Biocarbon was obtained from different sources such as forest residue (wood waste chips), agricultural residue (corn cob), proteinaceous industrial residues (chicken feather), and residues from the food industry (crab and shrimp shells). A comparison among different biocarbon fillers for polypropylene produced at similar temperatures (500 and 600°C) was performed.

Chicken feather biocarbon (CFB500), wood chips derived biocarbon (WCB600), corn cob (CCB500), and shrimp shell (SSB600) were all produced at 500 and 600°C with a further 1 h ball milled and compounded with and without MA-g-PP (Figure 3).

The reduction of the flexural modulus was observed in all biocarbon samples when the coupling agent was added (Figure 3 (A)). The improvement of the tensile strength (Figure 3 (B)) from uncompatibilized to compatibilized composites is almost constant despite the biocarbon source, which occurs from 28 MPa to 35 MPa on average with more than 20% increment in all cases. The maximum tensile strength obtained was for shrimp shell compatibilized with MA-g-PP, which was even slightly higher compared to the neat PP.



**Figure 3.** Effect of compatibilization on flexural modulus and tensile strength of biocarbons from sources such as CFB (chicken feather biocarbon), WCB (wood waste chips biocarbon), CCB (corn cob biocarbon), SSB (shrimp shell biocarbon).

## Conclusions

- *High-temperature biocarbon (~900°C) improves interfacial adhesion towards polypropylene (a hydrophobic plastic), resulting in higher modulus.*
- *After reducing the particle size of 1/64 inch high temperature biocarbon (900°C) by using 1 h of ball milling, a slight difference in the overall properties of the polypropylene composites was observed.*
- *A low interfacial adhesion was observed for low temperature pyrolyzed biocarbon (pyrolyzed at 500 and 600°C). However, by adding a maleated coupling agent, the performance of the polypropylene composites improved dramatically.*
- *The particle size reduction of low temperature biocarbon has a significant effect on the properties of composites. The larger area exposed gives rise to a more significant repulsion between the hydrophobic and hydrophilic phases. Thus, the combination of particle size reduction with the maleated coupling agent has a dramatic bonding effect on the composites. Size reduction of low temperature biocarbon has to be accompanied by maleated coupling agents.*
- *Biocarbon particles are by nature irregular. The use of mechanical techniques to reduce the particle size or make such particles more uniform tends to make them more uniform or tend to be spherical. The performance of the composites will then respond to such morphological change. The extreme scenario of a spherical-like nanoparticle is shown by the testing of carbon black. Talc presents a lamellar or layered morphology. The extreme scenario will be graphene (a single atomic layer morphology).*

## Acknowledgements

The authors would like to thank the following for their financial support to carry out this research: (i) the Ontario Research Fund, Research Excellence Program; Round 9 (ORF-RE09) Ontario Ministry of Economic Development, Job Creation and Trade (Project Nos. 053970 and 054345); (ii) the Ontario Agri-Food Innovation Alliance – Bioeconomy for Industrial Uses Research Program (Project Nos. 030331 and 030332); (iii) the Natural Sciences and Engineering Research Council (NSERC), Canada Discovery Grants (Project No. 401111) and (iv) the Natural Sciences and Engineering Research Council of Canada (NSERC), - Collaborative Research and Development Grants (CRD) Project No. 401637 with the partner industries Prism Farms Limited and Competitive Green Technologies, Lamington, Ontario, Canada to carry out this research.

## References

1. Michael Tolinski. Additives for Polyolefins: getting the most out of polypropylene, polyethylene and TPO. Second Edition (2015). Chadds Ford, PA, USA.
2. Leif Jilken, Goran Malhammar, Ragner Selden. The effect of mineral fillers on impact and tensile properties of polypropylene. Polymer Testing, 10(1991) 329-344. DOI: [https://doi.org/10.1016/0142-9418\(91\)90011-L](https://doi.org/10.1016/0142-9418(91)90011-L).

3. Mohanty, A.K., Vivekanandhan, S., Pin, J.M. and Misra, M., 2018. Composites from renewable and sustainable resources: Challenges and innovations. *Science*, 362(6414), pp.536-542.
4. Mohanty A., Misra., M., Rodriguez-Urbe A., Vivekanandhan S. Hybrid sustainable composites and methods of making and using thereof. US9809702B2. 2017.
5. Mohanty A., Misra., Bali A., Rodriguez-Urbe A. Renewable replacements for carbon black in composites and methods of making and using thereof. US20170107334A1. 2019.
6. Behazin E., Misra M., Mohanty A. Sustainable biocarbon from pyrolyzed perennial grasses and their effects on impact modified polypropylene biocomposites. 2017. *Composites Part B: Engineering*, 118 (2017) 116-124. DOI: <https://doi.org/10.1016/j.compositesb.2017.03.003>.
7. Ian Major, Jean-Mathieu Pin, Ehsan Behazin, Arturo Rodriguez-Urbe, Manjusri Misra, Amar Mohanty. Graphitization of *Miscanthus* grass biocarbon enhanced by *in situ* generated FeCo nanoparticles. *Green Chem.*, 2018, **20**, 2269-2278. DOI: [10.1039/C7GC03457A](https://doi.org/10.1039/C7GC03457A)
8. Kloss S, Zehetner F, Dellantonio A, Hamid R, Ottner F, Liedtke V, Schwanninger M, Gerzabek M, Soja G. Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. *J Environ Qual*. 2012 Jul-Aug; 41(4):990-1000.
9. Behazin E, Ogunsona E, Rodriguez-Urbe A, Mohanty A, Misra M, Anyia A. 2016. Mechanical, chemical, and physical properties of wood and perennial grass biochars for possible composite application. *Bioresources* 11, 1334–1348.
10. Suliman W, Harsh J, Abu-Lail N, Fortuna A, Dallmeyer I, Garcia-Perez M. 2016. Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties. *Biomass Bioenergy* 84, 37–48.
11. Wang T., Rodriguez-Urbe A., M. Misra, A Mohanty. 2018. Sustainable carbonaceous biofillers from miscanthus: size reduction, characterization, and potential bio-composites applications. *BioResources* 13(2) 3720-3739.
12. Ogunsona, E.O., Misra, M. and Mohanty, A.K., 2017. Sustainable biocomposites from biobased polyamide 6, 10 and biocarbon from pyrolyzed miscanthus fibers. *Journal of Applied Polymer Science*, 134(4).
13. Chang, B.P., Rodriguez-Urbe, A., Mohanty, A.K. and Misra, M., 2021. A comprehensive review of renewable and sustainable biosourced carbon through pyrolysis in biocomposites uses: Current development and future opportunity. *Renewable and Sustainable Energy Reviews*, 152, p.111666.
14. Codou, A., Misra, M. and Mohanty, A.K., 2018. Sustainable biocarbon reinforced nylon 6/polypropylene compatibilized blends: Effect of particle size and morphology on performance of the biocomposites. *Composites Part A: Applied Science and Manufacturing*, 112, pp.1-10.
15. Nagarajan, V., Mohanty, A.K. and Misra, M., 2016. Biocomposites with size-fractionated biocarbon: influence of the microstructure on macroscopic properties. *ACS omega*, 1(4), pp.636-647.