

Sustainable Green Composites from Nanostructured Bioplastic and Natural Fiber: Advanced Materials for Next generation of Automotive

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ABSTRACT

Stiffness-toughness heat deflection temperature (HDT) balanced biocomposites were fabricated in this work through structuring novel biodegradable blends. Starting from partially miscible polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT), nano-structured PBS/PBAT blends underwent reactive extrusion in the presence of free radicals. The processed nano-blends exhibited full compatibility with PBAT droplets dispersed at a nanoscale (droplet diameter was <100 nm). Resulting from the nanoscale dispersion of PBAT, the PBS/PBAT nano-blends exhibited super-toughness with a high melt strength. Further incorporation of agriculture residues, being miscanthus fiber and its derivative biocarbon, into the nano-blends significantly improved their modulus by a factor of 3 times, as well as the HDT. The miscanthus fiber derivative biocarbon performed better in improving the thermal-mechanical properties of the matrix, resulting from its micro-size and better thermal stability. The nano-blends and micro/macro-sustainable filler reinforcements provided a synergistic effect of nano-toughness and micro and macro-reinforcements. New-generation hierarchical biocomposites with excellent mechanical strength and processability have been prepared, which is expected to promote the application of biocomposites in different industrial sectors.

INTRODUCTION

Biocomposites, or green composites, have garnered global researchers' attention for decades, both in academic and industrial sectors, due to their benefits in improving the thermal-mechanical performance of plastics, reducing carbon footprints, and promoting our society towards a sustainable circular economy [1]. Despite enormous benefits, fabrication of stiffness-toughness balanced biocomposites with stronger interfacial actions between the polymeric matrix and sustainable fillers, such as natural fiber, is still a main challenge for researchers. Chemical modification of sustainable fillers to remove their hydrophilic hydroxyl groups is essential in improvement of polymer-filler adhesion. Those modifications, including alkaline treatment, silane-treatment, free radical grafting, and maleated coupling agents, etc., exhibited their efficiency in improvement of the mechanical properties of the biocomposites [2]. Another route for preparation of high toughness or high melt strength bio-polymeric matrices is the incorporation of large amounts of natural fiber fillers, which has been developed in last decade. Various kinds of matrices, such as PHBV/PBAT (45/55) [3], PBS/PBAT (60/40) [4], PHBV/PBAT/epoxidized natural rubber blends [5], and PBAT [6], have been developed in our group to fabricate stiffness-toughness balanced biocomposites.

Nano-structured bioplastic, or nano-blends, are quite new but effective routes to obtain high performance polymer blends. Through dispersion of one phase (the toughening phase) at the nanoscale (< 100 nm), the toughness or elongation at break of a brittle matrix can be significantly improved without a large sacrifice in matrix stiffness [7]. Such a method has been used in a previous study in our group to modify the flexibility of polylactide [8]. However, achieving the nano-dispersion of one phase in polymer blends is quite a challenging task and is almost impossible in a customary blending, due to the surface tension disparity between different polymers and a lack

of interfacial adhesion. Through ex-situ block copolymerization [9], in-situ reactive blending [10], and high shear processing [11], nano-blends have been realized and reported. Starting from partially miscible PBS and PBAT, nano-structured PBS/PBAT blends were successfully prepared via reactive extrusion with free radicals in this research work.

The novel biodegradable polymer nano-blends prepared by in-situ reactive extrusion technology showed super-toughness and high melt-strength, which can take up large amounts of biomass fillers. Micro-sized biocarbon and macro-sized natural miscanthus fibers were introduced into the nano-blends to prepare hierarchical green composites with stiffness-toughness-HDT balanced properties, as shown in Fig. 1; the structure - properties relationship was evaluated in this work.

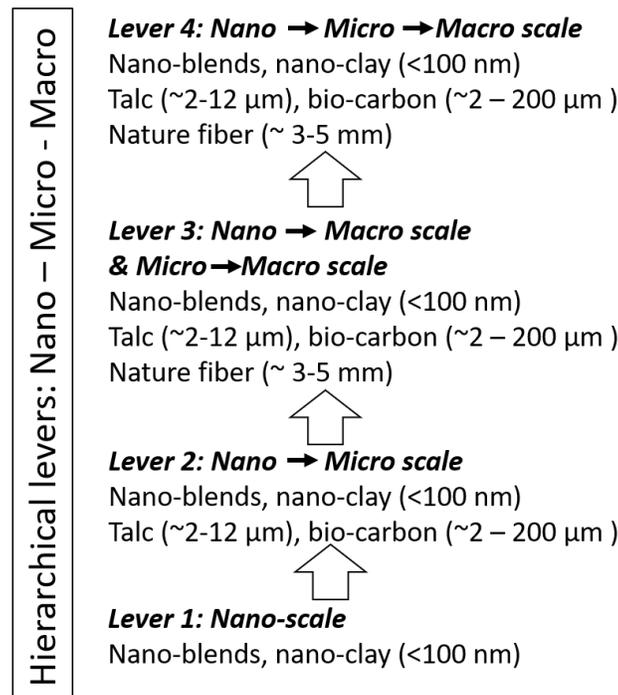


Figure 1. Various approaches to hierarchical level reinforcements of the biocomposites (Redrawn from Ref [7]).

MATERIALS AND CHARACTERIZATION

Materials and sample processing

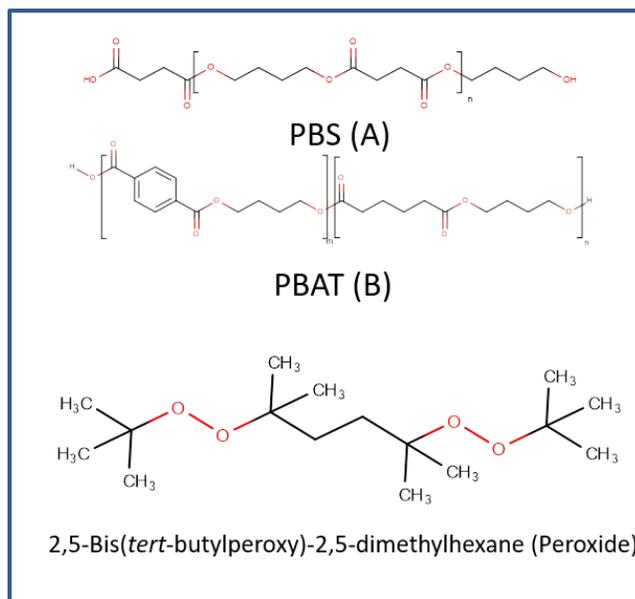


Figure 2. Chemical structures of the biodegradable polymers and peroxide used in this work.

Polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT) were purchased from Xinjiang Blueridge Tunhe Chemical Industry Co., Ltd with brand name Tunhe Th803s and Tunhe Th801t. Peroxide (2,5-bis(tert-butylperoxy)-2,5-dimethylhexane) was used as a free radical initiator, purchased from Sigma-Aldrich, Canada. The chemical structures of the biodegradable polymers and peroxide are drawn in Fig. 2. Chopped 2 mm fiber harvested in southern Ontario, Canada and supplied by Competitive Green Technologies (Lamington, ON, Canada) was used as natural fiber fillers. The biocarbon was pyrolyzed from miscanthus fiber at 650 °C and ball milled for 2 hours through use of vertical pyrolysis equipment in an N₂ atmosphere. The green composites were produced using a two-feeder extrusion system (Leistritz Micro-27, Germany) through one-step extrusion at 180 °C. The pellets were injection molded into standard samples for mechanical

and HDT characterization through use of an micro-injection molding system (Micro-15, DSM, Netherland) at 180 °C for 1 min.

Morphology observation

The nano-structure characterization of the biodegradable blends was performed through transmission electron microscopy (TEM) with an ultra-thin sample (70 nm). The instrument used was a JEOL JEM-1200 Ex II, with an accelerating voltage of 80 kV in operation.

Rheological characterization

The melt strength of the blends and composites were characterized by shear and extensional rheology using a SER fixture installed on a stress-controlled rheometer (Anton Paar MCR320, Germany) at 180 °C. Disk samples with a diameter of 15 mm was used for shear viscosity characterization. Standard rectangular samples with dimensions of 12 x 10 x 0.6 mm and an extension rate of 0.5 s⁻¹ were used for extensional rheological testing.

Mechanical characterization

Mechanical performance (tensile, flexure and notched impact strength) was characterized through use of a universal mechanical machine (Instron 3328) and a TMI instrument according to ASTM D638, D790 and D256. 5 specimens were tested for each sample to get the mean value and standard deviations.

Heat deflection temperature (HDT)

The HDT was tested with a dynamic mechanical analysis (DMA Q 800, TA, US) at a heating rate of 2 °C/min. The temperature at which a deformation of 250 μm happened was recorded as the HDT of the composites. Prior to the thermal - mechanical testing, all the samples were conditioned at 23 °C and 50% humidity for 48 hr.

RESULTS AND DISCUSSION

Morphology of PBS/PBAT Nano-blend

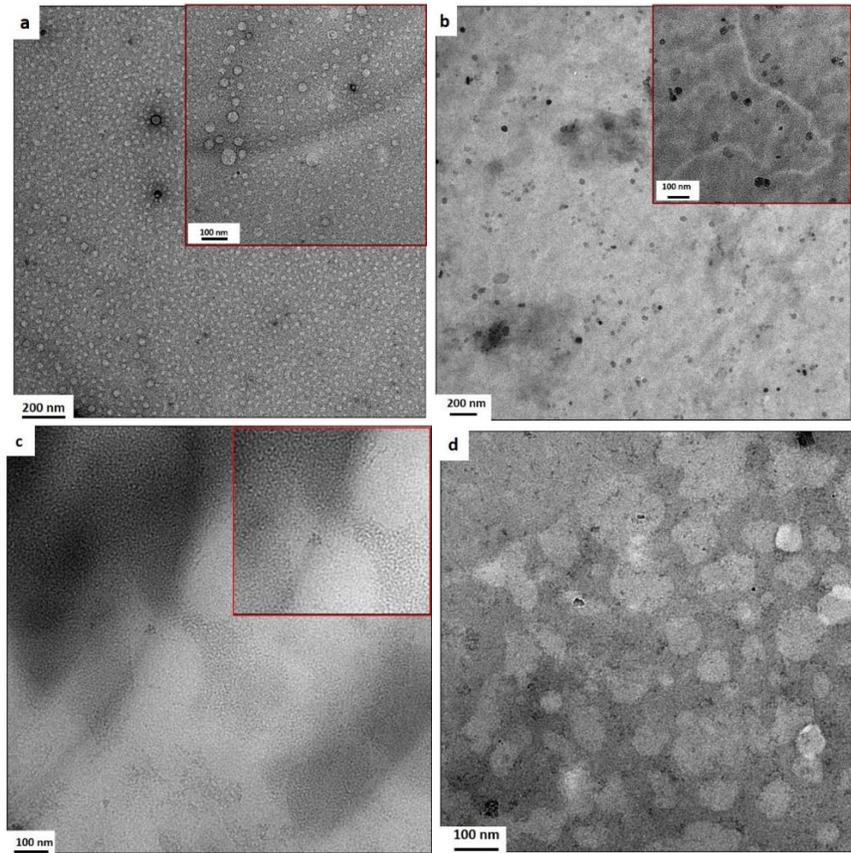


Figure 3. Transmission electron micrographs of the nano-structured PBS/PBAT binary blend: (a) PBS/PBAT (95/5); (b) PBS/PBAT (90/10); (c) PBS/PBAT (85/15); (d) PBS/PBAT (80/20). All samples were extruded with 0.02 phr free radicals [12].

The TEM images of PBS/PBAT nano-blends with various composition ratios are shown in Fig. 3. With the introduction of small amounts of free radicals, the micro-phase separated PBS/PBAT blends have been transferred into nano-blends with PBAT dispersed at the nanoscale, which is independent of PBS/PBAT composition ratios. The mean diameter of PBAT in the PBS/PBAT (80/20) blends is approximately 80 nm, indicating the successful preparation of nano-blends via the versatile and economic reactive extrusion technology. The formation of nano-blends resulted from the synthesis of PBS-PBAT copolymers initiated by free radicals in reactive extrusion. This

has been confirmed through atomic force microscopy (AFM) shown in Fig. 4 and Fourier-transform infrared spectroscopy (FTIR) characterizations in our published studies [12]. A surrounding phase outside of PBAT is visible in the AFM images, which corresponds to the formed PBS-PBAT copolymers since its modulus value is between PBS and PBAT. The nano-structuring endows the prepared blends super-toughness with a notched impact strength higher than 530 J/m, making it suitable for incorporation of high amounts of fillers.

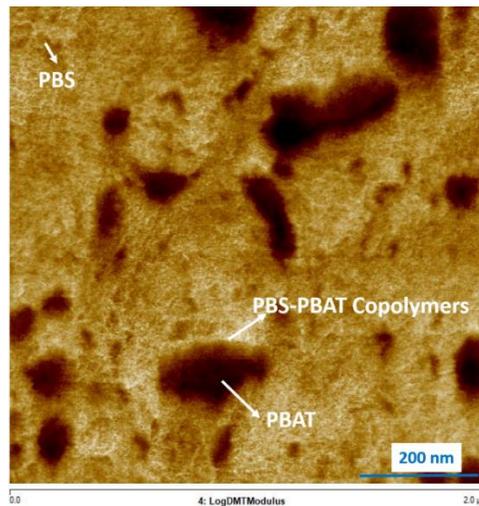


Figure 4. The atomic force microscopy (AFM) image of PBS/PBAT nano-blend.

Melt strength of PBS/PBAT Nano-blend and its composites

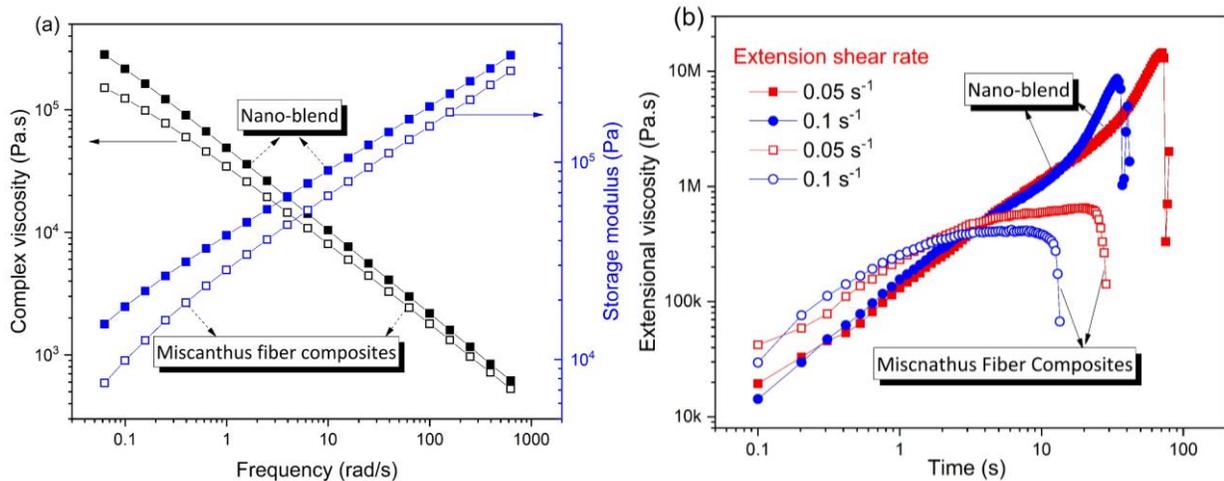


Figure 5. Rheological characterization of the nano-blends and their composites: (a) dependence of storage modulus and shear viscosity on frequency; (b) dependence of extensional viscosity on time at a different extension shear rate.

The melt strength of PBS/PBAT (80/20) nano-blend and its miscanthus fiber composites (20 wt% miscanthus fiber) was characterized by shear and extensional rheological studies, as shown in Fig. 5. Fig. 5a showed the shear viscosity and modulus of the nano-blend and its miscanthus fiber composites. The viscosity and modulus decreased slightly with the addition of 20% miscanthus fiber, resulting from wall-slip effects of the natural fibers [13]. The obvious shear thinning of the biocomposites resulted from chain disentanglement under the shearing process, revealing that the strong chain entanglement formed in PBS/PBAT nano-blends still existed in the presence of fillers. The strong chain entanglement ensures a high melt strength of the biocomposites, which can also be shown by the extensional viscosities (Fig. 5b). Similar to shear viscosity, the extensional viscosity of biocomposites was reduced compared to that of the nano-blend. However, the biocomposites exhibited very high extensional viscosity of $\sim 10^5$ Pa.s. Furthermore, the viscosity increased with increasing extensional time, indicating that the melt can withstand stretch shaping during real processing.

Thermal-mechanical Properties

The effects of miscanthus fiber and its derivative biocarbon on the tensile and flexural modulus/strength of the nano-blend is shown in Fig. 6. The modulus of the nano-blend is quite low with a value of 460 MPa, which can be significantly improved by the addition of miscanthus fibers. A 3-fold improvement of tensile modulus was achieved with 20% miscanthus fiber addition. More interesting is that the modulus can be further improved by the miscanthus fiber derivate biocarbon, as shown in Fig. 6. The tensile modulus was improved to 1500 MPa with 20% biocarbon, higher than that of the miscanthus fiber biocomposites. Not only the modulus, but the strength can be

improved with the addition of biocarbon compared to that of natural fibers. The more significant enhancement effect of biocarbon mainly results from: (1) the smaller biocarbon size; the macro-size miscanthus fiber is decreased to micro-scale biocarbon after pyrolysis; (2) the strong thermal stability of the biocarbon; (3) the higher modulus of biocarbon itself, compared to that of miscanthus fiber. Due to the super-toughness of the blends, resulting from the nanostructures (impact strength of ~ 680 J/m), the biocomposites with 20% miscanthus fiber showed a high toughness, with an impact strength around 168 J/m.

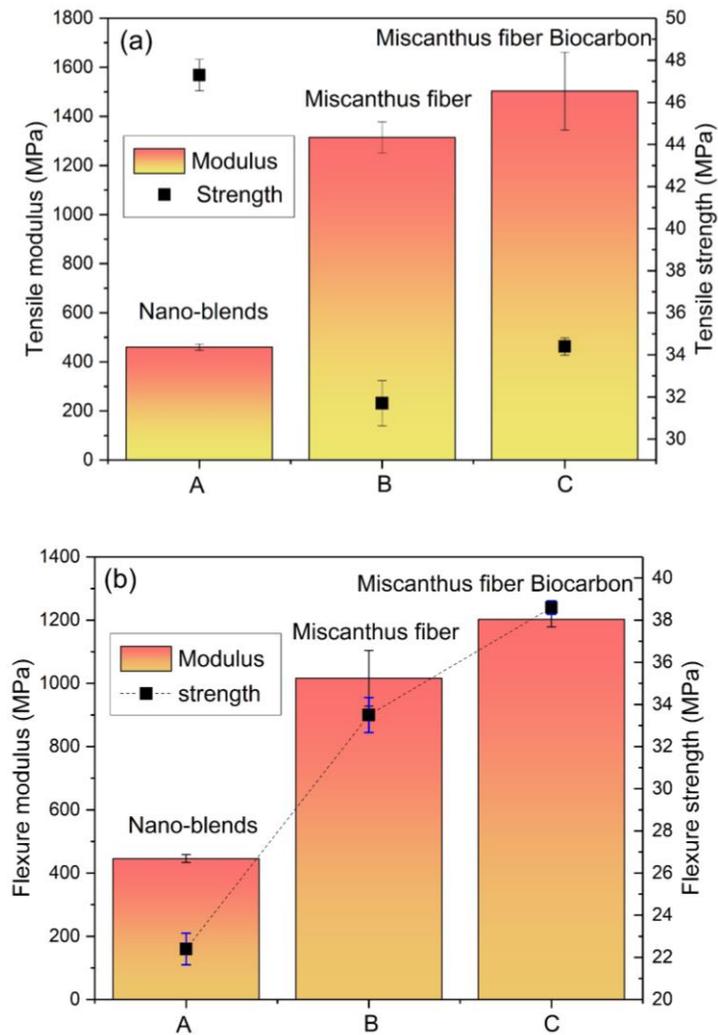


Figure 6. The mechanical performance of the nano-blends and its biocomposites: (a) tensile modulus and strength; (b) flexure modulus and strength. Samples: A – PBS/PBAT (80/20) nano-blend; B - 20% Miscanthus fiber biocomposites; C – 20% biocarbon.

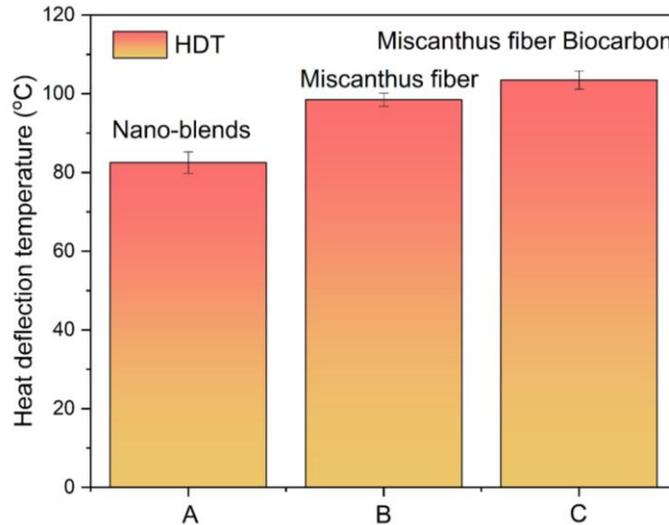


Figure 7. The heat deflection temperature of the nano-blends and its biocomposites. Samples: A – PBS/PBAT (80/20) nano-blend; B - 20% Miscanthus fiber biocomposites; C – 20% biocarbon.

Not only modulus and strength, but the heat deflection temperature (HDT) of the biocomposites was improved through addition of biocarbon, compared to that of miscanthus fiber biocomposites, as shown in Fig. 7. It is well known that the HDT is closely related to the flexure modulus of materials, with a higher modulus normally corresponding to a higher HDT [3]. The current study showed that biocarbon is better in improving the thermal-mechanical performance of the bioplastics, compared to their original biomass fillers. Such a strategy (converting the biomass filler into biocarbon via pyrolysis) can solve the problems present through usage of natural fibers, being that it cannot be processed at high temperatures because of the thermal decomposition of hemi-cellulose, cellulose and lignin in the natural fibers, without sacrificing the reinforcement of natural fibers.

CONCLUSIONS

Hierarchical biocomposites prepared from biodegradable nano-blends, micro-sized sustainable biocarbon and macro-sized miscanthus fiber exhibited excellent stiffness-toughness-heat deflection temperature balanced properties, are expected to be used in different industrial sectors. The biocomposites hold great potential to promote our society towards a more sustainable circular economy, which is significantly important for our daily life. Structuring hierarchical reinforcement from nano to micro and macro is important to create a new generation of multifunctional biocomposites for different applications, as proposed by us decades ago.

In this study, macro-sized miscanthus fiber and its derivative biocarbon are used as reinforcement for the biodegradable PBS/PBAT nano-blends. The addition of these sustainable fillers can further improve the stiffness and heat deflection temperature of the bio-matrix. Biocarbon performs better compared to its original source, miscanthus fiber, mainly resulting from the smaller particle size, higher modulus and better thermal stability of the biocarbon itself. Due to the high melt-strength and super-toughness of the bio-blends, the prepared biocomposites also exhibited a high melt strength (high extensional viscosity) and good toughness (notched impact strength of ~ 170 J/m). The study also revealed that biocarbon can be a good solution to solve the issue that natural fiber cannot be processed at high temperature, while simultaneously maintain the enhancement effect that fibers have in biocomposites.

ACKNOWLEDGEMENT

The financial support from the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA)/University of Guelph - Bioeconomy for Industrial Uses Research Program (Project # 030361 and 030486); the Ontario Ministry of Economic Development, Job Creation and Trade, Ontario Research Fund – Research Excellency, ORF-RE09-078 (Project # 053970 and 054345)

and the Natural Sciences and Engineering Research Council (NSERC), Canada Discovery Grants (Project # 400320) are gratefully acknowledged. A special thanks to Competitive Green Technologies, Lamington, Ontario, Canada for providing *Miscanthus* fiber samples.

REFERENCE

- [1] Mohanty AK, Vivekanandhan S, Pin J-M, Misra M. Composites from renewable and sustainable resources: Challenges and innovations. *Science*. 2018;362:536-42.
- [2] Kabir MM, Wang H, Lau KT, Cardona F. Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview. *Composites Part B: Engineering*. 2012;43:2883-92.
- [3] Nagarajan V, Mohanty AK, Misra M. Sustainable green composites: Value addition to agricultural residues and perennial grasses. *ACS Sustainable Chemistry & Engineering*. 2013;1:325-33.
- [4] Muthuraj R, Misra M, Mohanty AK. Biocomposite consisting of miscanthus fiber and biodegradable binary blend matrix: compatibilization and performance evaluation. *RSC advances*. 2017;7:27538-48.
- [5] Zhang K, Misra M, Mohanty AK. Toughened sustainable green composites from poly (3-hydroxybutyrate-co-3-hydroxyvalerate) based ternary blends and miscanthus biofiber. *ACS Sustainable Chemistry & Engineering*. 2014;2:2345-54.
- [6] Torres S, Navia R, Campbell Murdy R, Cooke P, Misra M, Mohanty AK. Green composites from residual microalgae biomass and poly (butylene adipate-co-terephthalate): processing and plasticization. *ACS Sustainable Chemistry & Engineering*. 2015;3:614-24.

- [7] Mohanty AK, Bhardwaj R. Nanostructure Controlled Bioplastics in the Design and Engineering of sustainable multifunctional green materials. 2009.
- [8] Bhardwaj R, Mohanty AK. Modification of Brittle Polylactide by Novel Hyperbranched polymer based nanostructure. *Biomacromolecules*. 2007;8:2476-84.
- [9] Ruzette A-V, Leibler L. Block copolymers in tomorrow's plastics. *Nature materials*. 2005;4:19-31.
- [10] Hu G-H, Cartier H, Plummer C. Reactive extrusion: toward nanoblends. *Macromolecules*. 1999;32:4713-8.
- [11] Hiroshi Shimizu YL, Akira Kaito, and, Sano H. Formation of Nanostructured PVDF/PA11 Blends Using High-Shear Processing. *Macromolecules*. 2005;38:7880-3.
- [12] Wu F, Misra M, Mohanty AK. Novel tunable super-tough materials from biodegradable polymer blends: nano-structuring through reactive extrusion. *RSC Advances*. 2019;9:2836-47.
- [13] Wu F, Misra M, Mohanty AK. Sustainable Green Composites from Biodegradable Plastics Blend and Natural Fibre with Balanced Performance: Synergy of Nano-structured Blend and Reactive Extrusion. *Composites Science and Technology*. 2020;In press.