

# Enhanced Thermal and Mechanical Properties of Sapodilla/PLA Biocomposites Using Filament Extrusion 3D Printing

Nalaeram Sivaram R<sup>1</sup>, Senthil Muthu Kumar Thiagamani<sup>1,2,3\*</sup>, Hossein Ebrahimnezhad-Khaljiri<sup>4</sup>, Jeyanthi Subramaniam<sup>5</sup>, Senthilkumar Krishnasamy<sup>6</sup>, Chandrasekar Muthukumar<sup>7</sup>, Mai Nguyen Tran Thanh<sup>8</sup>, Anish Khan<sup>9</sup>

<sup>1</sup>Department of Mechanical Engineering, Kalasalingam Academy of Research and Education, Anand Nagar, Krishnankoil 626126, Tamil Nadu, India.

<sup>2</sup>Department of Mechanical Engineering, INTI International University, Persiaran Perdana BBN, Putra Nilai, 71800 Nilai, Negeri Sembilan, Malaysia.

<sup>3</sup>Centre for Advanced Composite Materials (CACM) Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Johor, Malaysia.

<sup>4</sup>Department of Materials Science and Engineering, Faculty of Engineering, University of Zanjan, Zanjan, Iran.

<sup>5</sup>School of Mechanical Engineering, Vellore Institute of Technology, Kelambakkam - Vandalur Rd, Rajan Nagar, Chennai 600127, Tamil Nadu, India

<sup>6</sup>Department of Mechanical Engineering, PSG Institute of Technology and Applied Research, Neelambur 641062, Coimbatore, Tamil Nadu, India

<sup>7</sup>Department of Aeronautical Engineering, Hindustan Institute of Science and Technology, Padur, Kelambakkam 603103, Chennai, Tamil Nadu, India

<sup>8</sup>Department of Transportation Construction, Faculty of Civil Engineering, Nha Trang University, 02 Nguyen Dinh Chieu St, Nha Trang City, Khanh Hoa Province, Vietnam

<sup>9</sup>Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah, Saudi Arabia

Corresponding Author Email ID: [tsmkumar@klu.ac.in](mailto:tsmkumar@klu.ac.in); Mobile Number: +91-9442394350

## Abstract

The large-scale use of non-biodegradable materials, mainly comprising plastics, has raised serious environmental concerns for their viable alternatives. However, most of the biocomposites, including PLA-based matrix material, exhibit shortcomings in mechanical and thermal properties, thus posing serious barriers to their applications. Dealing with such challenges, the present work is related to the additive manufacture of biocomposites using Poly (lactic) acid (PLA) reinforced with sapodilla seed shell particulates through an FDM technique. PLA was mixed with different concentrations of SSS fillers such as 5, 10, 15, 20, and 25 wt.%. PLA and SSS were extruded into filaments used for 3D printing. The experimental results

reported an improvement in tensile and flexural strength; in particular, the composites showed tensile and flexural strengths around 25.5 MPa and 49.46 MPa, respectively, which is an increase of about 51.25% and 27.6% as compared to the PLA matrix. However, the addition of SSS fillers did not have any significant influence on impact energy absorption. Thermal stability was checked using TGA, while its char residue increased from 1.15% to 2.59% in the composites, compared to pure PLA at 0.64%. These results clearly indicate that sapodilla seed shell fillers can overcome the inherent weaknesses of PLA, offering a promising solution toward lightweight and environmentally sustainable applications in additive manufacturing, such as biodegradable packaging materials and lightweight automotive interior components.

**Keywords:** Biopolymer; Natural filler; 3D Printing; Mechanical properties; thermal characterization

## 1. Introduction

Despite the fact that the collection of 3D printable materials has recently expanded dramatically, their number remains restricted, and their development continues to be one of the primary impediments to future improvements in 3D printing applications [1]. Amorphous polymers are the main materials used in the classic fused deposition method (FDM) of 3D printing. These materials include poly(lactic acid) (PLA), polyamide 6, polycarbonate, and acrylonitrile butadiene styrene (ABS) [2,3]. The field of composite product design and production is seeing a surge in interest due to recent developments in 3D printed composite materials. The addition of natural fillers to the printable polymer matrix gives the resultant materials unique physicochemical properties, enabling the production of 3D printed composites with improved properties and performances [4].

Due to the extensive use of non-biodegradable materials, notably plastics, the globe is currently experiencing a number of environmental problems [5]. In this regard, over the recent years, research on developing bio-composites has gained more attention owing to their lightweight, sturdy, and environmentally friendly nature. Further, there is a larger need to turn agricultural/crop residues and wastes into marketable commodities [6]. Many such waste materials from agricultural products such as banana [7,8], tamarind [9–12], rice [13], corn [14], egg, coffee [15–17], tea, beans [18], coconut [19], cashew [20] and other agricultural weeds [21,22] have been turned in to reinforcing fillers in composite applications. Other than agro-wastes animal wastes have also been used for instance sheep wool [23], fish scale [24] etc.

**Table 4.** The TGA/DTG data of SSS filler reinforced PLA biocomposites

Specimen	TGA/DTG			
	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	D <sub>w</sub> (%/min)	Y <sub>c</sub> (%)
PLA	284.01	370.55	26.28	0.64
SSS5-PLA	284.13	370.58	27.31	1.15
SSS10-PLA	284.14	370.48	24.04	2.06
SSS15-PLA	284.12	369.02	25.23	2.08
SSS20-PLA	284.04	369.22	24.63	2.59
SSS25-PLA	284.00	370.77	22.94	2.22

#### 4. Conclusions

With FDM 3D printing, there is a significant improvement in the properties of the obtained composites by incorporating SSS fillers into the PLA matrix. The important results obtained are:

- Tensile strength showed an increase of about 51% by addition of 15 wt.% SSS filler and reached 25.5 MPa against pure PLA.
- Its tensile modulus increased by 17.6% with the maximum value of 1.47 GPa at 10 wt.% SSS filler.
- The percentage improvement in flexural strength was 27.6%, thus giving a value of 49.46 MPa at 15 wt.% SSS filler.
- The tensile and flexural properties both improved with increasing filler content up to 15 wt.% and then decreased but still remained above the values for pure PLA.
- There is no impressive enhancement in absorption energy by the addition of SSS fillers.
- The thermal analysis showed different thermal stability, and the filled onset decomposition temperature and T<sub>max</sub> obtained with various filler contents.
- An increase in char residue from 0.64%, for pure PLA, up to 2.59% was recorded in the composites, indicating a better thermal stability for some composite filler concentrations.

The obtained results showed that with the addition of SSS fillers, PLA was able to improve some of its properties successfully, and because of this fact, they can be pursued as one of the potential ways for the development of lightweight and sustainable lighter-weight materials for additive manufacturing applications.

## Acknowledgement

The authors thank the management of Kalasalingam Academy of Research and Education for providing facilities to carry out this research.

## Data Availability

Not applicable

## Conflicts of Interest

The authors declare no conflicts of interest.

## Author credit statement

**Nalaeram Sivaram R, Senthil Muthu Kumar Thiagamani:** Conceptualization, Methodology, Data curation, Writing – original draft; **Jeyanthi Subramaniam:** Testing and characterization; **Hossein Ebrahimnezhad-Khaljiri, Senthilkumar Krishnasamy, Chandrasekar Muthukumar, Thanh Nguyen Tran Mai, Anish Khan:** Writing – review & editing.

## References

- [1] Razali M S, Khimeche K, Melouki R, Boudjellal A, Vroman I, Alix S and Ramdani N 2022 Preparation and properties enhancement of poly(lactic acid)/calcined-seashell biocomposites for 3D printing applications *J Appl Polym Sci* **139** 51591
- [2] Suteja J, Firmanto H, Soesanti A and Christian C 2022 Properties investigation of 3D printed continuous pineapple leaf fiber-reinforced PLA composite *Journal of Thermoplastic Composite Materials* **35** 2052–61
- [3] Lohar D V., Nikalje A M and Damle P G 2022 Development and testing of hybrid green polymer composite (HGPC) filaments of PLA reinforced with waste bio fillers *Mater Today Proc* **62** 818–24
- [4] Scaffaro R, Citarrella M C, Catania A and Settanni L 2022 Green composites based on biodegradable polymers and anchovy (*Engraulis Encrasicolus*) waste suitable for 3D printing applications *Compos Sci Technol* **230** 109768
- [5] Senthil Muthu Kumar T, Rajini N, Obi Reddy K, Varada Rajulu A, Siengchin S and Ayrilmis N 2018 All-cellulose composite films with cellulose matrix and Napier grass cellulose fibril fillers *Int J Biol Macromol* **112** 1310-1315
- [6] Anandharaja M, Kumar T S M, Senthilkumar K, Ilyas R A, Arpitha G R and Chandrasekar M 2023 A review on the impact of bio-fillers on thermal and mechanical properties of the polymer composites *AIP Conference Proceedings* **2492** 040022 (American Institute of Physics Inc.)

- [7] T S M K, N R, A A, Siengchin S, A V R and Ayrilmis N 2019 Development and Analysis of Completely Biodegradable Cellulose/Banana Peel Powder Composite Films *Journal of Natural Fibers* **18** 151–160
- [8] Senthil Muthu Kumar T, Rajini N, Siengchin S, Varada Rajulu A and Ayrilmis N 2019 Influence of Musa acuminata bio-filler on the thermal, mechanical and visco-elastic behavior of poly (propylene) carbonate biocomposites *International Journal of Polymer Analysis and Characterization* **24** 439–46
- [9] Indira Devi M P, Nallamuthu N, Rajini N, Senthil Muthu Kumar T, Siengchin S, Varada Rajulu A and Ayrilmis N 2019 Biodegradable poly(propylene) carbonate using in-situ generated CuNPs coated Tamarindus indica filler for biomedical applications *Mater Today Commun* **19** 106-113
- [10] M.P. I D, N. N, N. R, T. S M K, Siengchin S, A. V R and N. H 2019 Antimicrobial properties of poly(propylene) carbonate/Ag nanoparticle-modified tamarind seed polysaccharide with composite films *Ionics (Kiel)* **25** 3461–71
- [11] Kumar T S M, Chandrasekar M, Senthilkumar K, Ilyas R A, Sapuan S M, Hariram N, Rajulu A V, Rajini N and Siengchin S 2021 Characterization, Thermal and Antimicrobial Properties of Hybrid Cellulose Nanocomposite Films with in-Situ Generated Copper Nanoparticles in Tamarindus indica Nut Powder *J Polym Environ* **29** 1134–42
- [12] Senthil Muthu Kumar T, Rajini N, Jawaid M, Varada Rajulu A and Winowlin Jappes J T 2018 Preparation and Properties of Cellulose/Tamarind Nut Powder Green Composites: (Green composite using agricultural waste reinforcement) *Journal of Natural Fibers* **15** 11-20
- [13] Thiruganasambanthan T, Thiagamani S M K, Santulli C, Krishnasamy S and Muthukumar C 2022 Preparation of Sodium Alginate/Rice starch blend polymer film for soil moisture sensing *Mater Today Proc* **64** 352–6
- [14] Sari N H, Setyawan P D, Thiagamani S M K, Suteja, Tamimi R, Rangappa S M and Siengchin S 2022 Evaluation of mechanical, thermal and morphological properties of corn husk modified pumice powder reinforced polyester composites *Polym Compos* **43** 1763–71
- [15] Kumar T S M, Rajini N, Huafeng T, Rajulu A V, Ayrilmis N and Siengchin S 2019 Improved mechanical and thermal properties of spent coffee bean particulate reinforced poly(propylene carbonate) composites *Particulate Science and Technology* **37** 639–46
- [16] Muthu Kumar S T, Yorseng K, Siengchin S, Ayrilmis N and Rajulu V A 2019 Mechanical and thermal properties of spent coffee bean filler/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) biocomposites: Effect of recycling *Process Safety and Environmental Protection* **124** 187–95
- [17] Thiagamani S M K, Nagarajan R, Jawaid M, Anumakonda V and Siengchin S 2017 Utilization of chemically treated municipal solid waste (spent coffee bean powder) as reinforcement in cellulose matrix for packaging applications *Waste Management* **69** 445-454

- [18] Muthusamy A R, Thiagamani S M K, Krishnasamy S, Muthukumar C, Rangappa S M and Siengchin S 2022 Lignocellulosic microfibrils from *Phaseolus lunatus* and *Vigna radiata* biomass: characterization and properties *Biomass Convers Biorefin* <https://doi.org/10.1007/s13399-022-03428-7>
- [19] Senthil Muthu Kumar T, Senthilkumar K, Chandrasekar M, Rajini N, Siengchin S and Varada Rajulu A 2019 Characterization, thermal and dynamic mechanical properties of poly(propylene carbonate) lignocellulosic *Cocos nucifera* shell particulate biocomposites *Mater Res Express* **6** 096426
- [20] Rajendran M, Ramanathan R, Shanmugavel R, Senthil Andavan G T and Thiagamani S M K 2024 Utilization of cashew nutshell biomass as eco-friendly sound-emitting pyrotechnic formulation to reduce sulfur usage in fireworks *Biomass Convers Biorefin* **14** 12921–12931
- [21] Ramalingam K, Thiagamani S M K, Pulikkalparambil H, Muthukumar C, Krishnasamy S, Siengchin S, Alosaimi A M, Hussein M A and Rangappa S M 2022 Novel Cellulosic Natural Fibers from *Abelmoschus Ficulneus* Weed: Extraction and Characterization for Potential Application in Polymer Composites *J Polym Environ* **31** 1323–1334
- [22] Ajithram A, Winowlin Jappes J T, Muthu Kumar T S, Rajini N, Rajulu A V, Rangappa S M and Siengchin S 2020 Water hyacinth for biocomposites—an overview *Biofibers and Biopolymers for Biocomposites: Synthesis, Characterization and Properties* 171–9
- [23] Manivannan J, Rajesh S, Mayandi K, Abuthakeer S S, Ravichandran M, Kumar T S M, Sanjay M R and Siengchin S 2022 A novel and prediction approach of sheep wool reinforced polyester composites: Surface qualities and hybrid modeling *Polym Compos* **43** 5274–90
- [24] Joseph Arockiam A, Rajesh S, Karthikeyan S, Thiagamani S M K, Padmanabhan R G, Hashem M, Fouad H and Ansari A 2023 Mechanical and thermal characterization of additive manufactured fish scale powder reinforced PLA biocomposites *Mater Res Express* **10** 075504
- [25] Zanini N, Carneiro E, Menezes L, Barud H and Mulinari D 2021 Palm fibers residues from agro-industries as reinforcement in biopolymer filaments for 3D-printed scaffolds *Fibers and Polymers* **22** 2689–99
- [26] Ohaeri O and Cree D 2022 Development and Characterization of PHB-PLA/Corn cob Composite for Fused Filament Fabrication *Journal of Composites Science* **6** 249
- [27] Pavon C, Aldas M, Samper M D, Motoc D L, Ferrandiz S and López-Martínez J 2022 Mechanical, Dynamic-Mechanical, Thermal and Decomposition Behavior of 3D-Printed PLA Reinforced with CaCO<sub>3</sub> Fillers from Natural Resources *Polymers (Basel)* **14** 2646
- [28] Olam M and Tosun N 2022 3D-printed polylactide/hydroxyapatite/titania composite filaments *Mater Chem Phys* **276** 125267
- [29] Ahmad N D, Kusmono, Wildan M W and Herianto 2023 Preparation and properties of cellulose nanocrystals-reinforced Poly (lactic acid) composite filaments for 3D printing applications *Results in Engineering* **17** 100842

- [30] Sivaram R N, Kumar Thiagamani S M, P S, M S, Surya Narayana B Y, Ebrahimnezhad-Khaljiri H, M M, Rangappa S M and Siengchin S 2023 Isolation and characterization of agro-waste biomass sapodilla seeds as reinforcement in potential polymer composite applications *Heliyon* e17760
- [31] Guo Y, Byambasuren K, Liu X, Wang X, Qiu S, Gao Y and Wang Z 2021 Extraction, Purification, and Characterization of Insoluble Dietary Fiber from Oat Bran *Transactions of Tianjin University* **27** 385–93
- [32] Leng E, Zhang Y, Peng Y, Gong X, Mao M, Li X and Yu Y 2018 In situ structural changes of crystalline and amorphous cellulose during slow pyrolysis at low temperatures *Fuel* **216** 313–21
- [33] Lee C M, Kubicki J D, Fan B, Zhong L, Jarvis M C and Kim S H 2015 Hydrogen-Bonding Network and OH Stretch Vibration of Cellulose: Comparison of Computational Modeling with Polarized IR and SFG Spectra *Journal of Physical Chemistry B* **119** 15138–49
- [34] Maleki A, Gharibi S, Valadi K and Taheri-Ledari R 2020 Pumice-modified cellulose fiber: An environmentally benign solid state hybrid catalytic system for the synthesis of 2,4,5-triarylimidazole derivatives *Journal of Physics and Chemistry of Solids* **142** 109443
- [35] Chouhan A P S, Husain A and Mukherjee S 2020 Thermogravimetric Analysis of Pinus Wood for Kinetic Analysis by Using Coats and Redfern Method *Journal of Physics: Conference Series* vol 1531 (IOP Publishing Ltd)
- [36] Zhang F, Sun Y, Li J, Su H, Zhu Z, Yan B, Cheng Z and Chen G 2022 Pyrolysis of 3D printed polylactic acid waste: A kinetic study via TG-FTIR/GC-MS analysis *J Anal Appl Pyrolysis* **166** 105631
- [37] Qu P, Gao Y, Wu G-F and Zhang L-P 2010 Nanocomposites of Poly(lactic acid) reinforced with cellulose nanofibrils, *Bioresources. (2010)* **5** 1811–1823
- [38] Shameli K, Bin Ahmad M, Md Zin Wan Yunus W, Azowa Ibrahim N, Abdul rahman russy, Jokar M and Darroudi M 2010 Silver/poly (lactic acid) nanocomposites: preparation, characterization, and antibacterial activity *International Journal of Nanomedicine* **5** 573–579
- [39] Zhao B, Zhang Y and Ren H 2020 Effects of microcrystalline cellulose surface modification on the mechanical and thermal properties of polylactic acid composite films *Plastics, Rubber and Composites* **49** 450–5
- [40] Torres-Hernández Y G, Ortega-Díaz G M, Téllez-Jurado L, Castrejón-Jiménez N S, Altamirano-Torres A, García-Pérez B E and Balmori-Ramírez H 2018 Biological compatibility of a polylactic acid composite reinforced with natural chitosan obtained from shrimp waste *Materials* **11** 1465
- [41] Zorah M, Mustapa I R, Daud N, Nahida J H, Sudin N A S, Majhool A A and Mahmoudi E 2020 Improvement thermomechanical properties of polylactic acid via titania nanofillers reinforcement *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* **70** 97–111

- [42] Chu Z, Zhao T, Li L, Fan J and Qin Y 2017 Characterization of antimicrobial poly (lactic acid)/nano-composite films with silver and zinc oxide nanoparticles *Materials* **10** 659
- [43] Lu J, Wang T and Drzal L T 2008 Preparation and properties of microfibrillated cellulose polyvinyl alcohol composite materials *Compos Part A Appl Sci Manuf* **39** 738–46
- [44] Qi X M, Liu S Y, Chu F B, Pang S, Liang Y R, Guan Y, Peng F and Sun R C 2016 Preparation and characterization of blended films from quaternized hemicelluloses and carboxymethyl cellulose *Materials* **9** 4
- [45] Punia Bangar S, Sharma N, Kaur H, Kaur M, Sandhu K S, Maqsood S and Ozogul F 2022 A review of Sapodilla (*Manilkara zapota*) in human nutrition, health, and industrial applications *Trends Food Sci Technol* **127** 319–34
- [46] Ikumapayi O M, Akinlabi E T, Majumdar J D and Akinlabi S A 2020 Applications of coconut shell ash/particles in modern manufacturing: a case study of friction stir processing *Modern Manufacturing Processes* (Elsevier) pp 69–95
- [47] Mosaddegh E 2013 Ultrasonic-assisted preparation of nano eggshell powder: A novel catalyst in green and high efficient synthesis of 2-aminochromenes *Ultrason Sonochem* **20** 1436–41
- [48] Devi M, Barbhuiya M H, Das B, Bhuyan B and Dhar S S 2020 Modified mesoporous graphitic carbon nitride: A novel high-performance heterogeneous base catalyst for transesterification reaction *Sustain Energy Fuels* **4** 3537–45
- [49] Kalpana V N, Kataru B A S, Sravani N, Vigneshwari T, Panneerselvam A and Devi Rajeswari V 2018 Biosynthesis of zinc oxide nanoparticles using culture filtrates of *Aspergillus niger*: Antimicrobial textiles and dye degradation studies *OpenNano* **3** 48–55
- [50] Compeán-Jasso M E, Ruiz F, Martínez J R and Herrera-Gómez A 2008 Magnetic properties of magnetite nanoparticles synthesized by forced hydrolysis *Mater Lett* **62** 4248–50
- [51] Shen W, Wu W, Liu C, Wang Z and Huang Z 2020 Achieving a high thermal conductivity for segregated BN/PLA composites via hydrogen bonding regulation through cellulose network *Polym Adv Technol* **31** 1911–20
- [52] Devi L U, Bhagawan S S and Thomas S 1997 Mechanical properties of pineapple leaf fiber-reinforced polyester composites *J Appl Polym Sci* **64** 1739–48
- [53] Nasri K, Loranger É and Toubal L 2023 Effect of cellulose and lignin content on the mechanical properties and drop-weight impact damage of injection-molded polypropylene-flax and-pine fiber composites *J Compos Mater* **57** 3347-3364
- [54] Siraj S, Al-Marzouqi A H, Iqbal M Z and Ahmed W 2022 Impact of micro silica filler particle size on mechanical properties of polymeric based composite material *Polymers (Basel)* **14** 4830



- [55] Abdullah R M, Aziz S B, Mamand S M, Hassan A Q, Hussein S A and Kadir M F Z 2019 Reducing the crystallite size of spherulites in PEO-based polymer nanocomposites mediated by carbon nanodots and Ag nanoparticles *Nanomaterials* **9** 874
- [56] Anwer M A S, Naguib H E, Celzard A and Fierro V 2015 Development and Characterization of PLA-Based Bio Composites *ASME International Mechanical Engineering Congress and Exposition, Proceedings (IMECE)* **14** IMECE2014-39261, V014T11A026; 7 pages
- [57] Lezak E, Kulinski Z, Masirek R, Piorowska E, Pracella M and Gadzinowska K 2008 Mechanical and Thermal Properties of Green Polylactide Composites with Natural Fillers *Macromolecular Bioscience* **8** 1190–200
- [58] Kuan H T N, Tan M Y, Shen Y and Yahya M Y 2021 Mechanical properties of particulate organic natural filler-reinforced polymer composite: A review *Composites and Advanced Materials* **30** 26349833211007504
- [59] Satsum A, Busayaporn W, Rungswang W, Soontaranon S, Thumanu K and Wanapu C 2022 Structural and mechanical properties of biodegradable poly (lactic acid) and pectin composites: using bionucleating agent to improve crystallization behavior *Polym J* **54** 921–30
- [60] Rozman H D, Ismail H, Jaffri R M, Aminullah A and Mohd Ishak Z A 1998 Polyethylene-oil palm frond composites-a preliminary study on mechanical properties *Int J Polym Mater* **39** 161–72
- [61] Cheremisinoff N P 1996 THERMAL ANALYSIS *Polymer Characterization* 17–24
- [62] Richardson M J 1989 Thermal Analysis *Comprehensive Polymer Science and Supplements* 867–901
- [63] Xiang S, Feng L, Bian X, Li G and Chen X 2020 Evaluation of PLA content in PLA/PBAT blends using TGA *Polym Test* **81** 106211