

Adarsh Chaturvedi, Lalit Ranakoti, Pawan Kumar Rakesh*, Niraj Kumar Mishra

National Institute of Technology Uttarakhand, Mechanical Engineering Department, Srinagar – 246174, India

*Corresponding author: E-mail: pawanrakesh@nituk.ac.in

Received (Otrzymano) 22.03.2021

EXPERIMENTAL INVESTIGATIONS ON MECHANICAL PROPERTIES OF WALNUT SHELL AND PINE NEEDLE ASH POLYLACTIC ACID BIOCOPOMPOSITES

Biocomposites consisting of polylactic acid reinforced with 2 to 8 wt.% walnut shell and pine needle ash fillers were fabricated by the microwave heating technique. The mechanical properties such as tensile strength, flexural strength, impact strength, Vickers hardness, and sliding wear behavior of the produced biocomposites were examined. The tensile strength declined by 11.62% with a reinforcement of 8 wt.% pine needle ash (PNA) in the PLA matrix as compared to the neat PLA matrix. The flexural strength also dropped by 3.09% with the reinforcement of 8 wt.% PNA in the PLA matrix compared to the neat PLA. It was found that the impact energy was enhanced by 77.27 and 66.67% with the reinforcement of 8 wt.% PNA and WN fillers in the PLA matrix, respectively. The Vickers hardness also improved by 14.54 and 10.35% with the reinforcement of 8 wt.% PNA and WN fillers in the PLA matrix, respectively. In addition, the weight loss due to sliding wear was improved by 95.86 and 94.52% with the reinforcement of 8 wt.% WN and PNA fillers in the PLA matrix as compared to the neat PLA matrix, respectively. The drilling forces (thrust force and torque) were additionally recorded during the drilling process of the PNA and WN filled PLA based biocomposites.

Keywords: biocomposites, walnut shell, pine needle ash, polylactic acid, mechanical properties

INTRODUCTION

Sustainable materials are among of the foremost priorities in product development due to environmental degradation, the concern about greenhouse gases, and non-biodegradable plastic waste [1-3]. A biodegradable polymer, particularly polylactic acid (PLA), has shown excellent potential as a matrix material owing to its superior physical, mechanical, and thermal properties [4-7]. Moreover, PLA forms an intermolecular bond with bio-reinforcement materials, leading to the fabrication of durable biocomposites [8-11]. In the last decade, researchers have used a PLA matrix reinforced with several natural fibers such as hemp, basalt, sisal, and sugar beet to make biocomposites. For instance, a PLA matrix reinforced with 10 wt.% kenaf and okra natural fibers increased the stiffness and Young's modulus of the biocomposites [7]. PLA based biocomposites with up to 30 wt.% kenaf fiber enhanced the tensile strength and tensile modulus, and a further addition of 10 wt.% kenaf fiber resulted in a reduction in the tensile strength [10]. PLA/oil seed fiber biocomposites with a fiber loading greater than 20 wt.% reduced the mechanical properties [6]. PLA reinforced with various natural fibers exhibited superior mechanical properties to pure PLA, and their mechanical properties depend on the types of fillers and manufacturing processes [12-16]. Sosa et al. [17] studied the microwave energy assisted manufacturing and repair of carbon-reinforced nano-

composites and found that microwave produced composites exhibited a 40% greater bond strength relative to composites bonded by conventional heating.

In addition, rice husk was used as the filler material for a PLA matrix, which enhanced the thermal properties of PLA; however, it reduced the elongation at break [9]. The hybridization of various fillers like cassava powder, pineapple powder, wood powder, and pineapple ash in the PLA matrix improved the mechanical properties [18-26]. Singh et al. [27] carried out a feasibility study on the microwave processing of polylactic acid reinforced sisal fiber composites and suggested that microwave energy offers a feasible solution for green composite fabrication. Bajpai et al. [28] produced natural fiber reinforced composites using microwave energy and found that microwave manufacturing provides a higher bond strength as compared to adhesive bonding.

Based upon the existing literature, it was revealed that most of the composites had been fabricated via the hand layup technique, as well as injection molding and compression molding machines. Nevertheless, very limited research work has been reported on the fabrication of polylactic acid based biocomposites via the microwave heating technique. Therefore, continuous improvement in the fabrication of polylactic acid reinforced with natural fillers is needed to explore their

various applications such as food packaging, automotive interior parts, and household items. In the present study, polylactic acid based biocomposites reinforced with walnut shell (WN) and pine needle ash (PNA) were fabricated via the microwave heating process, and their mechanical properties, as well as sliding wear were examined. In addition, the thrust force and torque were analyzed during the drilling process to study the drilling behavior of the PLA biocomposites.

EXPERIMENTAL METHODS

Fabrication techniques

The matrix material was polylactic acid (3052 D) purchased from M/s Natur-Tec India Pvt. Ltd., Chennai. It was received in the form of pellets. The physical properties of the PLA are as follows: specific gravity – 1.1-1.5, melting temperature – 140-210°C, melt flow index – 4-22 g/10 min [29]. Pine needle ash and walnut shell in the form of powder were used. The pine tree needles were collected from the local forest in the state of Uttarakhand, India. The needles were washed with water to remove the dust and then burned entirely in an oven. The pine needle ash was ground to form a powder and sieved as a 350 micron grain size. In a previous study [23], the author conducted an XRF test of PNA to determine its chemical composition, as shown in Table 1. Light microscope micrographs of both the biocomposites and SEM micrographs of the pine needle ash are shown in Figure 1.

Table 1. Chemical composition of pine needle ash [23]

Elements	C	Mg	Si	S	K	Ca	Fe
Weight [%]	92.99	0.91	0.75	0.53	1.75	2.68	0.39

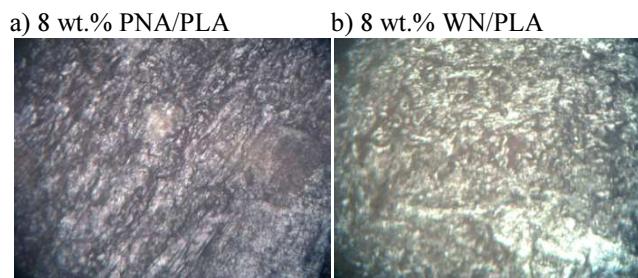


Fig. 1. Light microscope micrographs of biocomposites (a,b), SEM micrograph of pine needle ash (c)

The walnut powder was made from walnut shells, which were also collected from the local market. They were washed and dried, ground and sieved to obtain a grain size of 350 microns. The walnut shell powder was used directly for composite fabrication without burning.

The fabrication process was carried out via microwave heating, as shown in Figure 2. First, a mold was made from a galvanized iron sheet of the size 150 × 150 mm × 4 mm. The PLA pellets were mixed with either filler from 2 to 8 wt.% in the required proportion and kept inside a microwave oven at the temperature of 175°C for 45 minutes. The melting of PLA formed a nonhomogeneous mixture with the reinforcement. The microwave oven was then shut down and the mixture was left to cure. Finally, the mold was taken out of the microwave oven and the biocomposite samples were prepared. Separate samples, namely, PNA/PLA biocomposites and WN/PLA biocomposites were fabricated, as shown in Table 2.

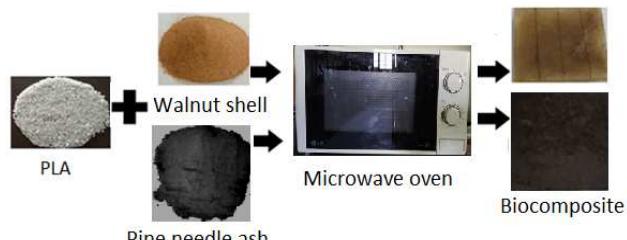


Fig. 2. Steps for biocomposite fabrication in microwave oven

TABLE 2. Thrust force and torque of WN and PNA reinforced PLA biocomposites

No.	Biocomposites [wt.%]	Thrust force [N]	Torque [Nm]
1	PLA 100%	70	0.12
2	PLA 98% -PNA 2%	71	0.11
3	PLA 96%-PNA 4%	80	0.12
4	PLA 94%-PNA 6%	84	0.13
5	PLA 92%-PNA 8%	93	0.14
6	PLA 98%-WN 2%	60	0.10
7	PLA 96%-WN 4%	66	0.11
8	PLA 94%-WN 6%	75	0.12
9	PLA 92%-WN 8%	76	0.12

Characterization of biocomposites

Specimens of the size 150 mm × 15 mm × 4 mm were prepared for the tensile test, and the testing was carried out on a HEICO (New Delhi) HL-590 computerized universal testing machine (UTM) according to the ASTM D 3039 standard at the crosshead speed of 2 mm/min. Flexural testing was done following the ASTM D 790-07 standard and specimen dimensions of 125 mm × 12.7 mm × 3.2 mm. The ISO 179 unnotched Charpy standard was followed for the impact test carried out on an AIT-300D Fasne Test Equipment Pvt Ltd (Maharashtra) impact tester machine. The specimen

dimensions of the impact test were 55 mm × 10 mm × 4 mm. The Vickers hardness test was performed in compliance with the ASTM E92 standard. The weight loss due to wear was calculated in accordance with ASTM G-99-17. A polished specimen was loaded on a TR-20 LE Ducom pin-on-disc machine with a disk hardness of 75 HRC and a track diameter of 100 mm. The weight loss was calculated by the difference in the values of the initial and final weight of the sample. The average values of three samples in each test were taken. Neat PLA samples were also prepared and tested.

RESULTS AND DISCUSSION

Tensile strength

The tensile strength of the walnut shell and pine needle ash PLA biocomposites is shown in Figure 3. The tensile strength of neat PLA was 78.6 MPa. The tensile strength of the 2 wt.% of WN and PNA reinforced PLA biocomposites was 55.54 MPa and 60.82 MPa, respectively.

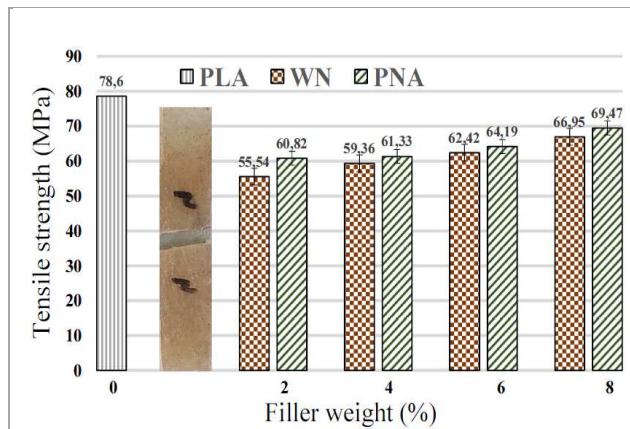


Fig. 3. Tensile strength of biocomposites with different wt.% of fillers

These results indicate a slight decrease with the reinforcement as compared with the neat PLA, which may be due to improper bonding with the PLA matrix. However, it was observed that a further addition of WN and PNA fillers to the PLA matrix improved the tensile strength of the biocomposites compared to the 2 wt.% reinforcement. With the addition of 8 wt.% PNA fillers to the PLA matrix, the tensile strength rose back up to 69.47 MPa and similar trends were also observed in the WN reinforced biocomposites, i.e. 66.95 MPa. Among these fillers, an increase in the tensile strength of the PNA/PLA biocomposites was reported as compared with WN/PLA, owing to the presence of hard particles of SiO_2 , Al_2O_3 , Fe_2O_3 , and others in PNA. SEM micrographs of the failed tensile specimens of the 8 wt.% PNA and WN filled PLA based biocomposites are shown in Figure 4. The experimental results are in good agreement with the previous findings of Yussuf et al. [8].

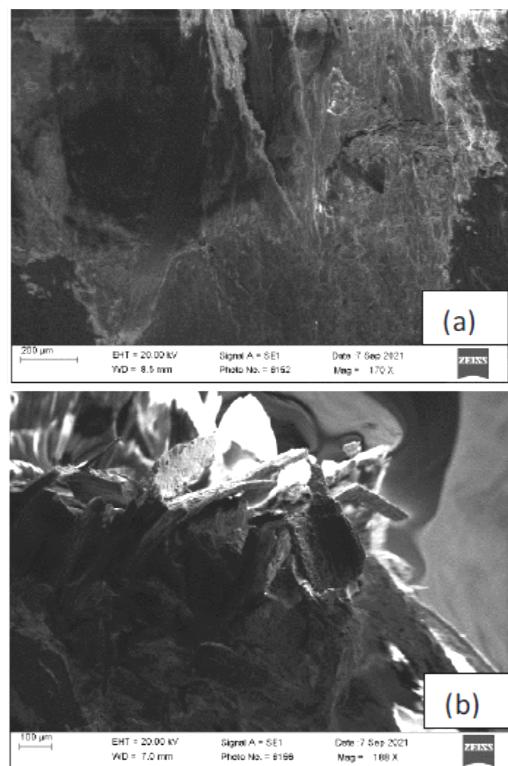


Fig. 4. SEM micrographs of failed tensile samples: a) 8 wt.% PNA, b) 8 wt.% WN

Flexural strength

The flexural strength of the pure PLA was found to be 106.5 ± 0.083 MPa. The flexural strength decreased by 3.5 and 40.16% with the addition of reinforcement of 2 wt.% PNA and 2 wt.% WN fillers, respectively, to the PLA matrix. In contrast, the addition of 8 wt.% PNA fillers to the PLA matrix resulted in an enhanced flexural strength by 3.09%. As far as the effect of the reinforcement is concerned, it is evident from Figure 5 that the 8 wt.% PNA filler loading gives a higher flexural strength, i.e. 109.9 MPa, than the WN filler loading, i.e. 87.29 MPa, which can be attributed to the improved stress transfer and enhanced bonding of the PNA filler with the PLA matrix [12]. SEM micrographs of the failed flexural specimens of the 8 wt.% PNA and WN filled PLA based biocomposites are shown in Figure 6.

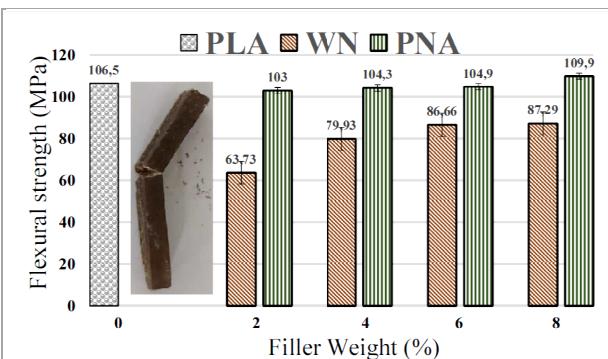


Fig. 5. Flexural strength of biocomposites with different wt.% of fillers

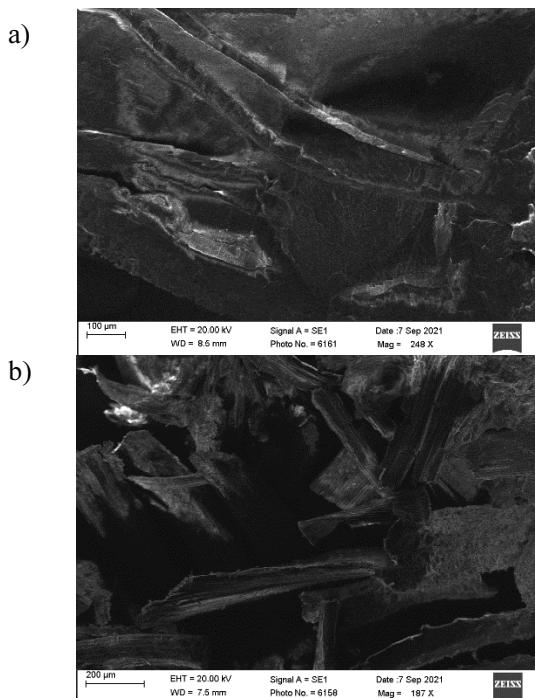


Fig. 6. SEM micrographs of failed flexural specimens: a) 8 wt.% PNA, b) 8 wt.% WN

Impact strength

The effect of the filler loading on the impact energy of the PLA biocomposites is shown in Figure 7. The incorporation of fillers into the matrix generally increases the stiffness, which results in enhancement of the energy-absorbing capability [6]. The impact energy of the neat PLA biocomposites was 1.5 ± 0.075 J. The impact energy of the PLA biocomposites was enhanced with the addition of both fillers. The maximum impact energy was obtained at an 8 wt.% filler loading, i.e. 4.5 and 6.6 J for both fillers. It was observed that the impact energy was enhanced by 77.27% regarding the PNA reinforced biocomposites and 66.67% for the WN reinforced biocomposites compared with the neat PLA matrix. The experimental results are in good agreement with the findings of Juntuek et al. [10].

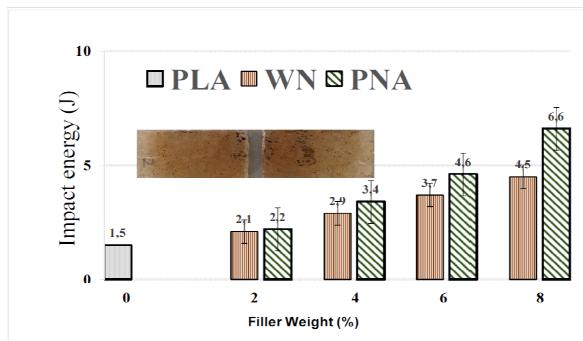


Fig. 7. Impact energy of biocomposites with different wt.% of fillers

Vickers hardness

The effect of the filler loading on the Vickers hardness is shown in Figure 8. The Vickers hardness of the

PLA was 30.5 HV. The addition of filler to the PLA matrix increased the Vickers hardness values. During the test, the indenter is supposed to come into contact with the filler particles, which have more tenacity than the PLA matrix, resulting in a higher Vickers hardness value. The maximum Vickers hardness values at 8 wt.% PNA and WN filler loading were 35.69 and 34.02 HV, respectively. The PNA reinforced PLA composites exhibit higher hardness due to the hard particles of the PNA fillers compared to the WN fillers. Three readings were taken on each sample.

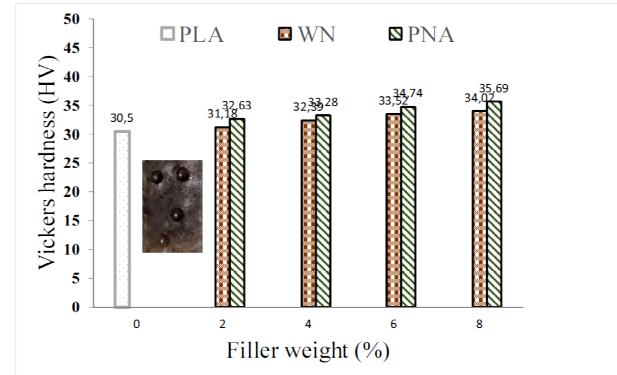


Fig. 8. Vickers hardness of biocomposites with different wt.% of fillers

Weight loss due to sliding wear

Sliding wear tests were carried out on the pin-on-disc test rig at the load of 20 kN and speed of 600 rpm. It was observed that the PLA matrix becomes heated due to the increase in temperature between the specimen and the steel disc, causing softening of the PLA, which starts flowing in a semi-solid form, as shown in Figure 9. Particles detach from the specimen, which are considered as the weight loss due to sliding wear.

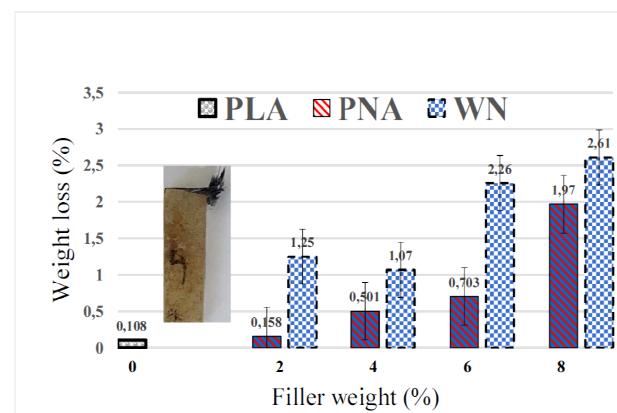


Fig. 9. Weight loss due to sliding wear for biocomposites with different wt.% of fillers

From Figure 9, the minimum weight loss [%] was observed for pure PLA, and the maximum wear rate was observed for the 8 wt.% WN filled PLA based biocomposites. The WN filled PLA biocomposites exhibited a higher weight loss than the PNA/PLA biocomposites under all loading conditions. The pine needles

were burnt at high temperature (300°C), and then the pine needle ash was used for reinforcement, whereas, the walnut shell powder was directly used (without burning) in the PLA matrix. Nonetheless, the PNA particles have higher strength and hardness as compared to the walnut shell. Therefore, the WN filled PLA biocomposites experienced a greater weight loss compared to the PNA filled PLA biocomposites, which may be due to improper bonding between the WN filler particles and the PLA matrix. The SEM micrographs of the sliding wear surfaces of the 8 wt.% PNA and WN filled PLA based biocomposites are shown in Figure 10.

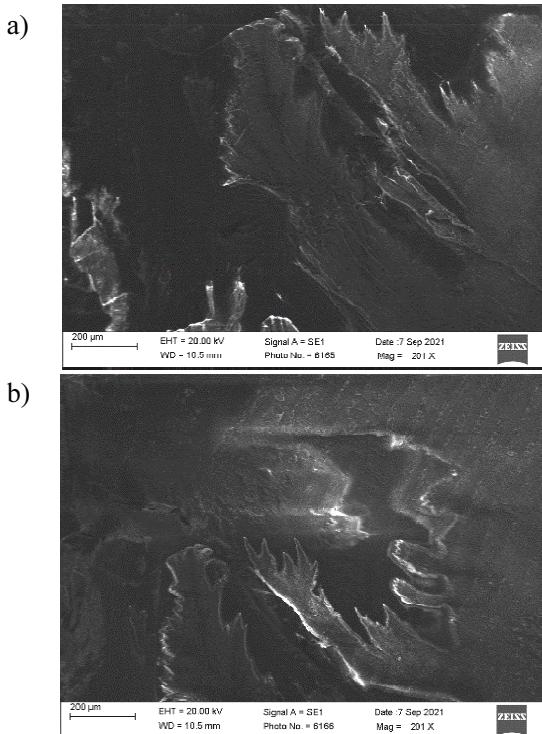


Fig. 10. SEM micrographs of sliding wear surface: a) 8 wt.% PNA, b) 8 wt.% WN

Drilling of biocomposites

The drilling behaviors of the walnut shell and pine needle ash PLA biocomposites are shown in Figure 11. The drilling parameters of the spindle speed of 800 rpm, and feed rate of 0.09 mm/revolution with the twist drill geometry were considered. The values of thrust force amounting to 76 N and torque equaling 0.12 Nm were recorded via a Kistler Dynamometer (9272) for the 8 wt.% WN filler PLA biocomposites. It was observed that the variation in the thrust force is due to the cutting dissimilarity of the walnut shells in the PLA biocomposites. The hard particles of the walnut shell came into contact with the drill geometry, resulting in variation in the thrust forces. A spiral chip was formed during the drilling process due to plastic deformation of the PLA biocomposites, as shown in Figure 12. The thrust force and torque values for the different compositions containing walnut shell and pine needle ash filler are shown in Table 2. Similarly, the highest

values of thrust force of 93 N and torque of 0.14 Nm were recorded for the 8 wt.% PNA filled PLA biocomposites. A total of nine samples were drilled at a constant spindle speed and feed rate.

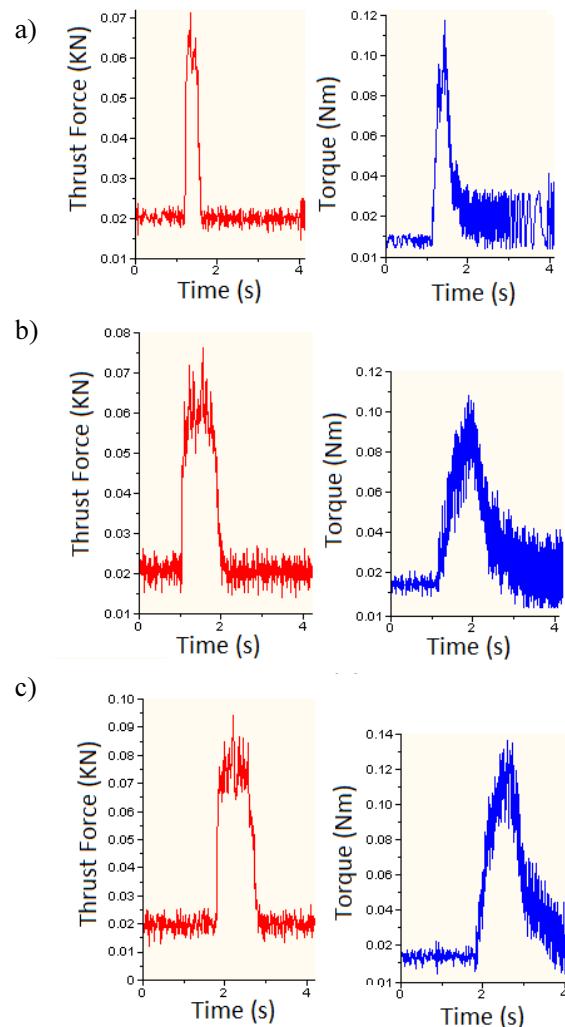


Fig. 11. Typical drilling forces with twist drill geometry (spindle speed 800 rpm, feed rate 0.09 mm/revolution): a) neat PLA, b) WN filled, c) PNA filled biocomposites

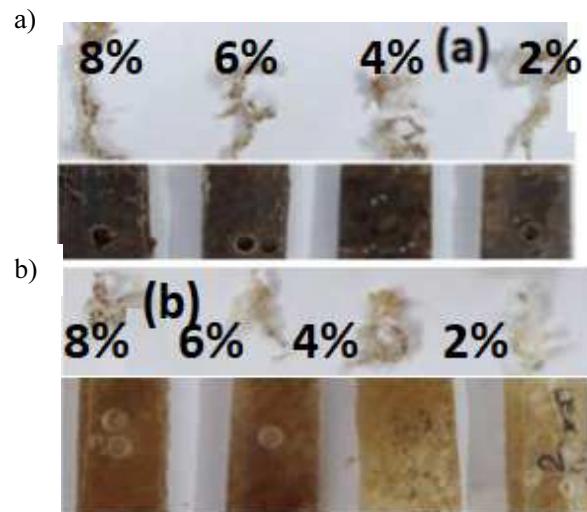


Fig. 12. Chip formation during drilling of biocomposites: a) PNA/PLA, b) WN/PLA

CONCLUSIONS

Walnut shell and pine needle ash filler polylactic acid biocomposites were fabricated via the microwave heating process, and the key findings are as follows:

- PLA reinforced with pine needle ash and walnut shell fillers exhibited a decline in the tensile and flexural strength compared to the neat PLA matrix.
- The impact strength and Vickers hardness were significantly enhanced with the addition of both the fillers to the PLA matrix.
- The sliding wear resistance of the pine needle ash/polylactic acid biocomposites was superior to that of the walnut shell reinforced biocomposites.
- Superior drilling forces (thrust force and torque) were recorded for the pine needle ash reinforced biocomposites as compared to the walnut shell reinforced biocomposites.

From the present investigation, it was concluded that the fabricated biocomposites might be useful for food packaging applications, which are fully biodegradable and eco-friendly.

Acknowledgements

The authors would like to express their gratitude to the Design Innovation Center (DIC), the Ministry of Education (MoE), the Government of India, and TEQIP-III, NIT UK, for providing support for this work.

REFERENCES

- [1] Gandini A., Lacerda T.M., Carvalho A.J., Trovatti E., Progress of polymers from renewable resources: furans, vegetable oils, and polysaccharides, *Chemical Reviews* 2016, 116(3), 1637-1669.
- [2] Yu T., Ren J., Li S., Yuan H., Li Y., Effect of fiber surface-treatments on the properties of poly (lactic acid)/ramie composites, *Composites Part A: Applied Science and Manufacturing* 2010, 41(4), 499-505.
- [3] Koronis G., Silva A., Fontul M., Green composites: A review of adequate materials for automotive applications, *Composites Part B: Engineering* 2013, 44(1), 120-127.
- [4] Hitesh S., Ujendra K., Singh I., Misra J.P., Pawan R., Introduction to green composites, [In:] *Processing of Green Composites*, Springer, Singapore 2019, 1-13.
- [5] Finkenstadt V.L., Liu C.K., Evangelista R., Liu L., Cermak S.C., Hojilla-Evangelista M., Willett J.L., Poly (lactic acid)-green composites using oilseed coproducts as fillers, *Industrial Crops and Products* 2007, 26(1), 36-43.
- [6] Ibrahim N.A., Yunus W.M.Z.W., Othman M., Abdan K., Hadithon K.A., Poly(lactic acid)(PLA)-reinforced kenaf bast fiber composites: the effect of triacetin, *Journal of Reinforced Plastics and Composites* 2010, 29(7), 1099-1111.
- [7] Ranakoti L., Gupta M., Rakesh P., Analysis of mechanical and tribological behavior of wood flour filled glass fiber reinforced epoxy composite, *Materials Research Express* 2019, 6(8), 085327.
- [8] Yussuf A.A., Massoumi I., Hassan A., Comparison of poly-lactic acid/kenaf and polylactic acid/rice husk composites: the influence of the natural fibers on the mechanical, thermal and biodegradability properties, *Journal of Polymers and the Environment* 2010, 18(3), 422-429.
- [9] Sis A.L.M., Ibrahim N.A., Yunus W.M.Z.W., Effect of (3-aminopropyl) trimethoxysilane on mechanical properties of PLA/PBAT blend reinforced kenaf fiber, *Iranian Polymer Journal* 2013, 22(2), 101-108.
- [10] Juntuek P., Ruksakulpiwat C., Chumsamrong P., Ruksakulpiwat Y., Mechanical properties of polylactic acid and natural rubber blend using calcium carbonate and vetiver grass fiber as filler, *Advanced Materials Research* 2011, 410, 59-62.
- [11] Guna V., Ilangoan M., Ananthaprasad M.G., Reddy N., Hybrid biocomposites, *Polymer Composites* 2018, 39, E30-E54.
- [12] Fortunati E., Puglia D., Monti M., Santulli C., Maniruzzaman M., Foresti M.L., Kenny J.M., Okra (*Abelmoschus esculentus*) fibre-based PLA composites: mechanical behaviour and biodegradation, *Journal of Polymers and the Environment* 2013, 21(3), 726-737.
- [13] Way C., Wu D.Y., Cram D., Dean K., Palombo E., Processing stability and biodegradation of polylactic acid (PLA) composites reinforced with cotton linters or maple hardwood fibres, *Journal of Polymers and the Environment* 2013, 21(1), 54-70.
- [14] Song Y., Liu J., Chen S., Zheng Y., Ruan S., Bin Y., Mechanical properties of poly (lactic acid)/hemp fiber composites prepared with a novel method, *Journal of Polymers and the Environment* 2013, 21(4), 1117-1127.
- [15] Asaithambi B., Ganesan G., Kumar S.A., Bio-composites: Development and mechanical characterization of banana/sisal fibre reinforced polylactic acid (PLA) hybrid composites, *Fibers and Polymers* 2014, 15(4), 847-854.
- [16] Kuciel S., Mazur K., Hebdz M., The influence of wood and basalt fibres on mechanical, thermal and hydrothermal properties of PLA composites, *Journal of Polymers and the Environment* 2020, 1-12.
- [17] Sosa E.D., Worthy E.S., Darlington T.K., Microwave-assisted manufacturing and repair of carbon-reinforced nanocomposites, *Journal of Composites* 2016, Article ID 7058649.
- [18] Bayart M., Gauvin F., Foruzanmehr M.R., Elkoun S., Robert M., Mechanical and moisture absorption characterization of PLA composites reinforced with nano-coated flax fibers, *Fibers and Polymers* 2017, 18(7), 1288-1295.
- [19] Bhattacharjee S., Bajwa D.S., Feasibility of reprocessing natural fiber filled poly(lactic acid) composites: an in-depth investigation, *Advances in Materials Science and Engineering* 2017, 1-10.
- [20] Zaaba N.F., Ismail H., A review on peanut shell powder reinforced polymer composites, *Polymer-Plastics Technology and Materials* 2019, 58(4), 349-365.
- [21] Awal A., Rana M., Sain M., Thermorheological and mechanical properties of cellulose reinforced PLA biocomposites, *Mechanics of Materials* 2015, 80, 87-95.
- [22] Battegazzore D., Alongi J., Frache A., Poly(lactic acid)-based composites containing natural fillers: thermal, mechanical and barrier properties, *Journal of Polymers and the Environment* 2014, 22(1), 88-98.
- [23] Gupta M.K., Rakesh P.K., Characterization of pine needle ash particulates reinforced surface composite fabricated by friction stir process, *Mater. Res. Express* 2019, 6(2019), 046539.
- [24] Gairola S., Gairola S., Sharma H., Rakesh P.K., Impact behavior of pine needle fiber/pistachio shell filler based epoxy composite, *Journal of Physics: Conference Series* 2019, 1240, 012096, 1-7.

- [25] Pokhriyal M., Prasad L., Rakesh P.K., Raturi H.P., Influence of fibre loading on physical and mechanical properties of Himalayan nettle fabric reinforced polyester composite, Materials Today: Proceedings 2018, 5(9), 16973-16982.
- [26] Ranakoti L., Rakesh P.K., Physio-mechanical characterization of tasar silk waste/jute fiber hybrid composite, Journal of Composites Communications 2020, DOI: 10.1016/j.coco.2020.100526.
- [27] Singh I., Bajpai P.K., Malik D., Sharma A.K., Kumar P., Feasibility study on microwave joining of green composites, Akademeia 2011, 1(1), ea0101.
- [28] Bajpai P.K., Singh I., Madaan J., Joining of natural fiber reinforced composites using microwave energy, experimental and finite element study, Materials and Design 2012, 35, 596-02.
- [29] Pantani R., Volpe V., Titomanlio G., Foam injection molding of poly (lactic acid) with environmentally friendly physical blowing agents, J. Mater. Process. Technol. 2014, 214(12), 3098-3107.