Mechanical properties of sandwich products obtained by 3D printing from PLA-PLA/Al_2O_3

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Abstract: The mechanical properties of samples made by 3D printing from poly(lactic acid) (PLA) and PLA filled with 20, 40, 60 and 80 wt% PLA/Al_2O_3 (85/15) was evaluated. Addition of PLA/Al_2O_3 improved mechanical properties of PLA. Tensile strength increased by approx. 19%, tensile modulus by 27%, compression modulus by approx. 42%, flexural modulus by 70%, impact strength by 20% and hardness by approx. 14% compared with pure PLA.

Keywords: 3D printing, PLA, aluminium oxide.

Właściwości mechaniczne wyrobów typu *sandwich* otrzymanych metodą druku 3D z PLA-PLA/Al_2O_3

Streszczenie: Zbadano właściwości mechaniczne kształtek wykonanych metodą druku 3D z poli(kwasu mlekowego) (PLA) napełnionego 20, 40, 60 i 80% mas. PLA/Al_2O_3 (85/15). Wytrzymałość na rozciąganie zwiększyła się o ok. 19%, moduł sprężystości przy rozciąganiu o 27%, moduł przy ściskaniu o ok. 42%, moduł sprężystości przy zginaniu o 70%, udarność o 20%, a twardość o ok. 14% w porównaniu z czystym PLA.

Słowa kluczowe: druk 3D, PLA, tlenek glinu.

In recent days, industries have been working hard to meet customer demands and compete effectively on the market daily. Industries that introduce new technological products, will occupy, and sustain in the market in near future. This time reductions and technological innovations are possible only because of modern manufacturing technology. In continuation of modern manufacturing technologies, Additive Manufacturing (AM) is a promising technology for new product developments. AM technology produces the parts directly from the computer-Aided Design (CAD) model into physical components. This additive manufacturing is classified into seven categories as per ASTM standards. In additive technologies, the Fusion Deposition Modelling (FDM) uses the plastic wires as feedstock materials (e.g., PLA, ABS, polyamides, etc.), melts these materials in the heated nozzle, and deposits it over the bed as per the given input until the object is completed. The strength of fabricated parts is a critical factor that influences the use of FDM technology. If the strength of fabricated parts is equal to that of manufactured conventionally, they can be directly used as functional parts, which will grow the servicing industries. The strength of the fabricated parts can be increased by optimising the control parameter and changing the material.

In the recent past, thermoplastics were used for a variety of applications, such as automobile applications, dashboards, packaging trays, headliners, doors, and interior decoration [1]. From the variety of thermoplastics, polylactic acid (PLA) is most used because of its biodegradability and excellent mechanical properties [2]. Even though the fabricated parts' strength is satisfactory, it is not equal to that of the manufactured conventionally parts. In additive manufacturing, a single print cannot meet the functional requirements as conventional manufactured parts. This can be improved by engineering the existing materials' properties by optimising the machine parameters and developing composite materials by adding fillers or fibres along with the feedstock materials. Most used fillers are wood fibres [3, 4], carbon fibres [5, 6], ceramics [7–9], and metal particles [10, 11]. The strength of the fabricated parts cannot be obtained completely by optimising the control parameters; therefore, additional material strength can be introduced by making the reinforcement with the existing materials [12].

The PLA/Al_2O_3 fabrication at high temperatures improves the mechanical properties and develops good bonding between the layers [13]. Microwave post-processing of PLA and Al_2O_3 samples increased rather than decreased porosity [14]. The addition of PLA/Mg (4 wt%)

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is best suited for the improvement of mechanical properties with reduced porosity. The porosities in the filaments can be reduced by allowing them to twin while extruding them [15]. The nozzle diameter also influences the porosity; the porosity can be reduced by increasing the nozzle diameter of the printer, but an increased nozzle diameter leads to changes in the roughness of the printed parts [16, 17]. The PLA/stabilized zirconia reinforcement contains more voids than the PLA/Al_2O_3 due to this tensile strength drastically reduced. The flexural strength of the PLA/Al_2O_3 composites depends on the defects and flaws in the printed specimens [18]. Ceramics ($CaCO_3$, 30-micron size) added to PLA reduce the elastic modulus while improving the polymer matrix strengths [19]. Because of the uniform dispersion, PLA/titanium (5% to 20% by volume) increases tensile and compressive strengths up to 10% by volume addition of titanium, which also increases impact strength over pure PLA. On the other hand, addition of titanium to PLA, reduces crystallinity and thermal stability [20]. PLA/ZnO (1 wt%) reinforcement used for biosensor development improves the mechanical properties significantly. It improves the antimicrobial, magnetic, optical, and thermal properties of the thermoplastics [21].

According to the analysis of the number of surveys, polylactic acid (PLA) is considered a good substitute for varieties of other plastics because of its biodegradability. This can be produced from natural materials such as molasses, sugar beets, and corn [22, 23]. It can be easily processed and used for a variety of applications in the fields of food packaging industries, disposable bottle manufacturing, medical applications, automobiles, electronics, and unmanned vehicles [24–26]. Aluminium oxide (Al_2O_3) is chosen as a reinforcement particle, which is a good and compatible material with PLA that increases strength and decreases porosity. Furthermore, the FDM method is a simple technology to use, inexpensive, and able to process various materials [27–29]. According to the reviews, it can be noted that the addition of fillers to PLA improve the strength of the printed parts.

Therefore, this work is focused on investigating the new method of additive manufacturing by making the sandwich 3D printing of pure PLA and Al_2O_3 reinforced PLA.

EXPERIMENTAL PART

Materials

The industry-grade PLA was purchased from Sun Polymers (Coimbatore, India) with a density of 1.24 g/cm^3. NICE chemicals LTD (Coimbatore, India) provided the aluminium oxide (Al_2O_3) particles of 150 mesh industry grade with a purity of 99.4 wt% (water soluble matters of 0.5 wt%, sulphate of 0.05 wt% maximum, and iron 0.02 wt% maximum). Before using aluminium oxide was dried up to remove moisture.

PLA/Al_2O_3 filaments preparation

For the preparation of PLA/Al_2O_3 (15 wt% Al_2O_3) filament, a single screw extruder was used. The pellets were melted using three heating zones (185°C, 140°C, and 130°C) and an extruder die diameter of 1.75 mm. The filament was double extruded at a rate of 22.5 mm/s, to improve reinforcement dispersity. Initially, for the continuous and smooth extrusion of reinforced filaments, 1 wt% of surfactant (wax) was added with the pellets.

Sandwich sample preparation

The samples were prepared by printing alternating layers of PLA (five layers) and PLA-PLA/Al_2O_3 (four layers). The samples were marked as shown in Table 1.

T a b l e 1. Samples designations for printing

Sample	S1	S2	S3	S4	S5	S6
PLA	100	80	60	40	20	0
PLA/Al_2O_3	0	20	40	60	80	100

A Flash Forge Creator-3 Pro twin-screw extruder (Zhejiang, China) with a double nozzle and an FDM printer was used to prepare the samples. The filaments were placed in individual nozzles. In one nozzle, PLA was held at 215°C and in the other, the reinforced PLA/Al_2O_3 was held at 235°C. The bed temperature was maintained at 60°C to reduce bed separation. The layer thickness used was 0.12 mm, the overlap was 30%, the number of layers was 3 and the filling density was 100%.

Methods

DSC 200 F33 differential scanning calorimeter (Netzsch, Selb, Germany) was used to determine the thermal properties. The analysis was performed in the temperature range from 20°C to 300°C at a heating rate of 20°C/min, a cooling rate of 10°C/min, and a reheating rate of 10°C/min. The cold crystallization temperature (T_{cc}), melting point (T_m), and glass transition temperature (T_g) were measured. Surface morphological data were analysed according to ASTM E1508 using a field emission scanning electron microscope (FESEM) equipped with an EDX device (Ametek, Berwyn, PA, USA) at an accelerating voltage of 15 kV. Tensile strength was measured using a FIE UNITEK-9450 universal testing machine (Ichalkaranji, Maharashatra, India) at a load of 5 KN and a head speed of 1 mm/min. Tensile strength and elastic modulus were tested. Instron 4482 machine (Ulm, Germany) was used to determine the flexural properties. Tests were performed at room temperature with a head speed of 5 mm/min, up to 5% deformation, according to ASTM D790. Samples with dimensions of 127 × 13 × 3.2 mm were used. All samples were printed with the same layer thickness and number of layers

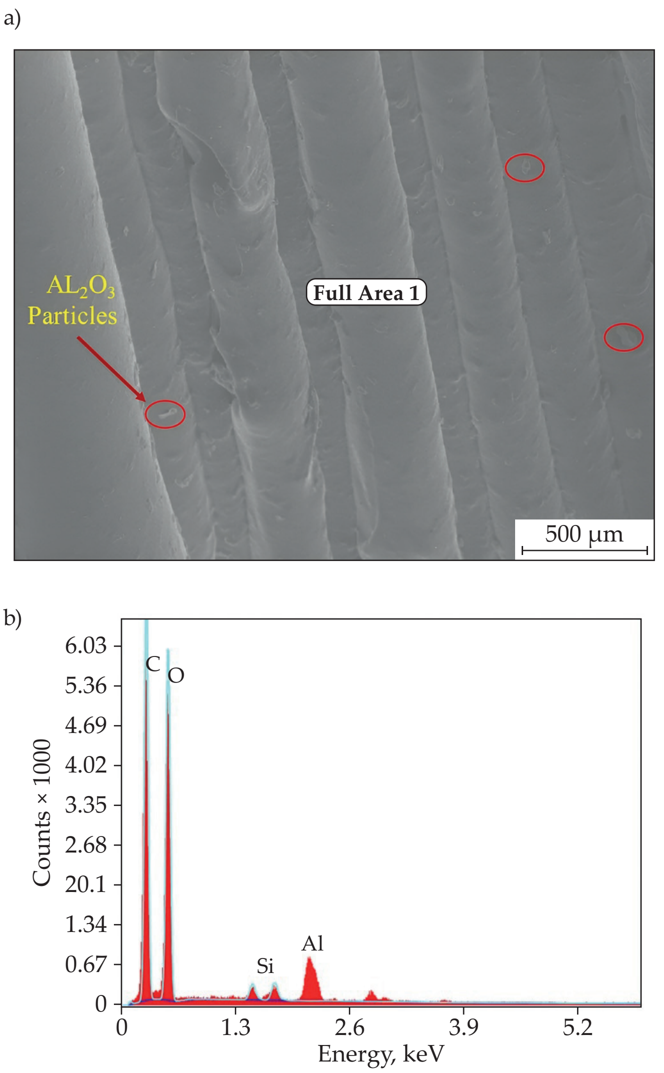

Fig. 1. FESEM images of PLA-PLA/Al_2O_3 (a), EDX analysis (b)

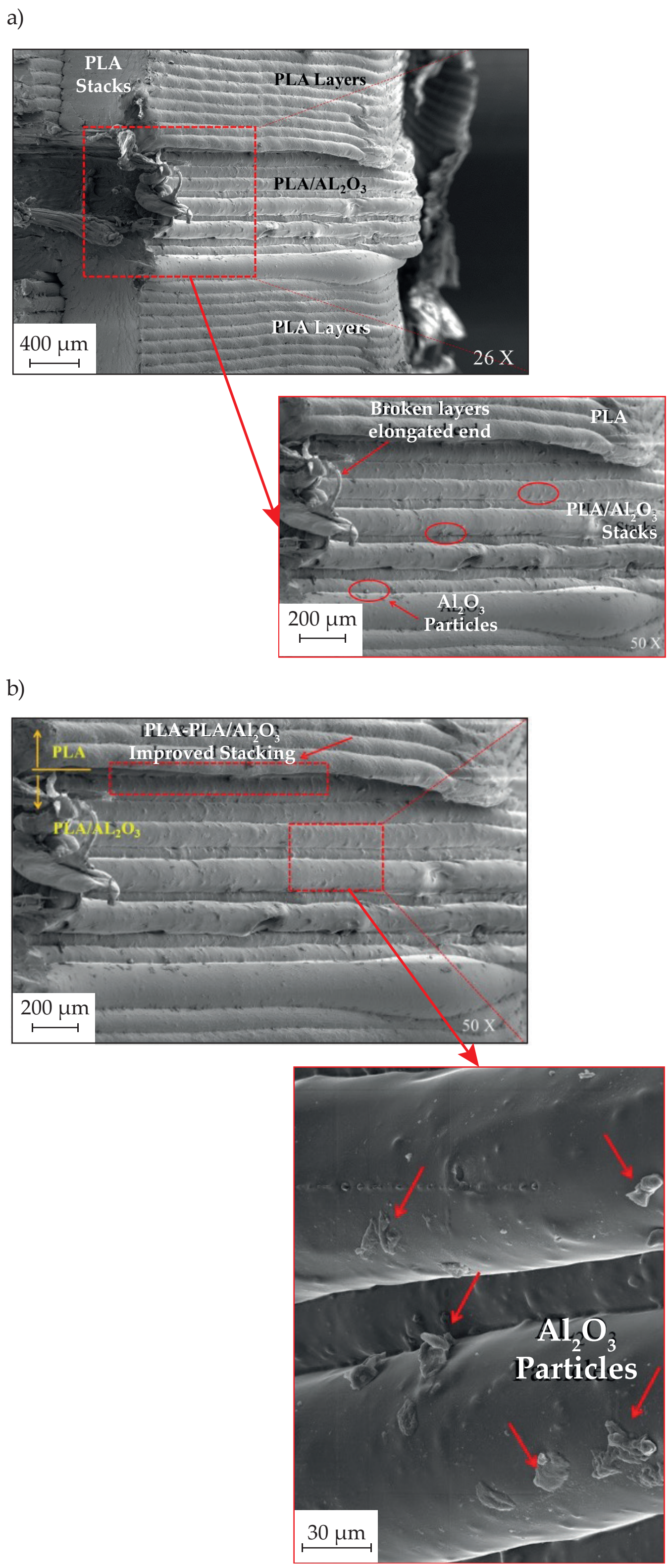

Fig. 2. FESEM images: a) PLA, b) PLA/Al_2O_3

[30]. The FIE UNITEK-9450 universal testing machine (Ichalkaranji, Maharashatra, India) was used to analyze the compressive strength. Tests were carried out in accordance with ASTM D695. Cylindrical samples with a diameter of 12.7 mm and a thickness of 25.4 mm were used. Impact strength was assessed using the Charpy V-notch method in accordance with the ASTM D6110 standard, using an impact hammer from pendulum impact tester (AIT-300-N, Chennai, India). Due to anisotropy, all impact strength test samples were printed in the horizontal direction (X-Y). Shore D hardness tester was used (Mitutoyo Yuzuki, Hiroshima, Japan). The tests were carried out in accordance with the ASTM D2240 standard.

RESULTS AND DISCUSSION

Morphology

The morphological surface of the PLA-PLA/Al_2O_3-reinforced sandwiches was examined by field emission scanning electron microscopy (FESEM) and the corresponding image is shown in Figure 1. Al_2O_3 particles are evenly dispersed in the PLA due to the double extrusion (Fig. 1a). The particles are clearly visible on the outer boundary of the reinforcing layers. Figure 1b shows the elemental contribution to PLA-PLA/Al_2O_3. The proportion of C, O, Al, and Si is 48.54, 50.20, 0.78 and 0.48 wt%, respectively. It is clear from Fig. 2 that the bonding between PLA and the reinforcement has improved. Due to the sandwich effect,

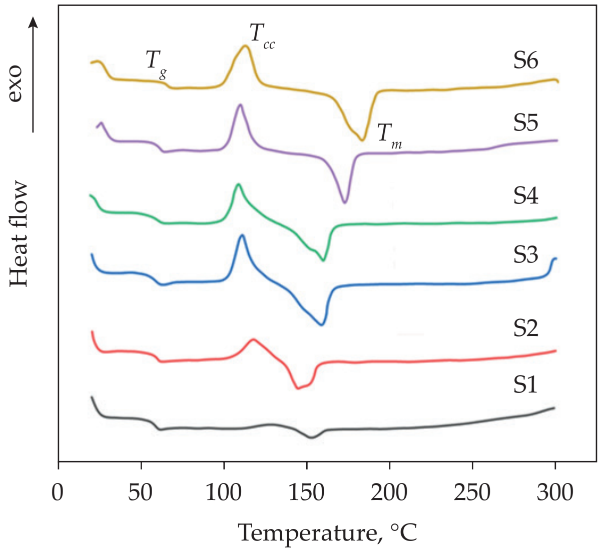

Fig. 3. DSC curves of the samples

the layers bonded well to each other and the number of voids between the layers was drastically reduced.

Thermal properties

The temperatures T_m, T_{cc} and T_g obtained from the DSC curves are shown in Fig. 3 and Table 2. The addition of 80 wt% PLA/Al_2O_3 increased the T_g from 56.9°C to 61.8°C due to molecular interactions. The reinforcement also reduces the mobility and flexibility of the PLA chains. The addition reinforcement increased the melting point temperature of PLA from 151.1°C to 174.4°C. The cold crystalline temperature clearly demonstrated the effect of the reinforcement on the crystallinity of PLA. The T_{cc} of reinforced sandwiches was lower than pure PLA. The T_{cc} of sandwiched reinforcement decreased from 118.1°C to 110.3°C. The reduction of T_{cc} indicated that the addition of reinforcement strengthens PLA.

T a b l e 2. Effect of PLA/AL_2O_3 on thermal properties of PLA

Sample	T_g, °C	T_{cc}, °C	T_m, °C
Pure PLA	56.9	–	151.1
20 wt% PLA/Al_2O_3	57.8	118.1	151.9
40 wt% PLA/Al_2O_3	58.5	110.9	158.9
60 wt% PLA/Al_2O_3	59.7	108.7	160.4
80 wt% PLA/Al_2O_3	60.8	109.9	172.5
PLA/Al_2O_3	61.8	110.3	174.4

Mechanical properties

The mechanical properties are shown in Figs. 4–9. The tensile strength increases in the order S6<S4<S1<S3<S2<S5. PLA has a strength of 29 MPa, while the strength of PLA/Al_2O_3 (S5) is 35 MPa, which is an increase of 19% compared to PLA and 28% compared to PLA/Al_2O_3 (S6). Moreover, the addition of 80 wt% PLA/Al_2O_3 (S5) reduced the voids, which resulted in greater interaction between the layers. In the case of S6, crack propagation was observed over the entire sample surface. While PLA placed between PLA/PLA/Al_2O_3 layers stops crack propagation, which can result in high tensile strength of sandwich samples. The presence of layers containing PLA/Al_2O_3 reduced the compressive strength. In Fig. 5, PLA deforms more than other samples. PLA/Al_2O_3 layers strengthen the system and prevent the layers from slipping, thus reducing buckling. Moreover, flexural strength does not change up to 60 wt% PLA/Al_2O_3 and then decreases. The results are shown in Fig. 4.

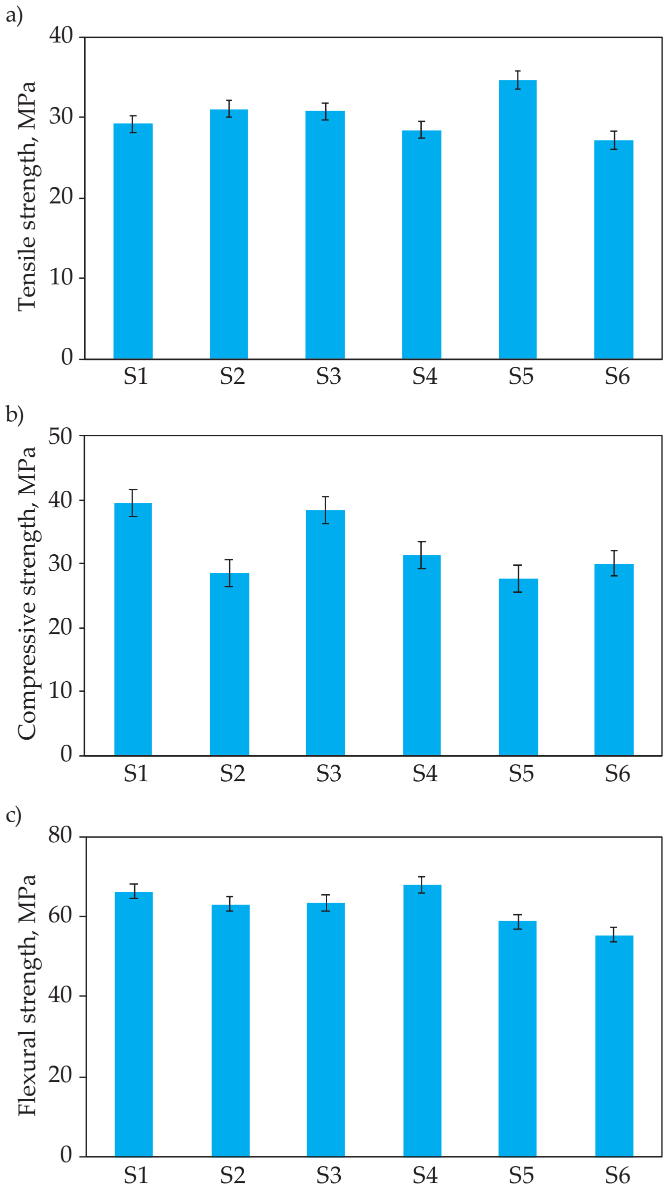

Fig.4. Mechanical properties: a) tensile strength, b) compressive strength, c) flexural strength

The Young's modulus for samples S4 and S6 was 27% and 54% higher than that of PLA, respectively (Fig. 6a). This confirms the change in fracture properties to brittle. The compression modulus reached a maximum of 665 MPa for a sample containing 40% PLA/Al_2O_3 (S3), which was almost 42% higher than for pure PLA (Fig. 6b). Further increasing the reinforcement reduced the modulus.

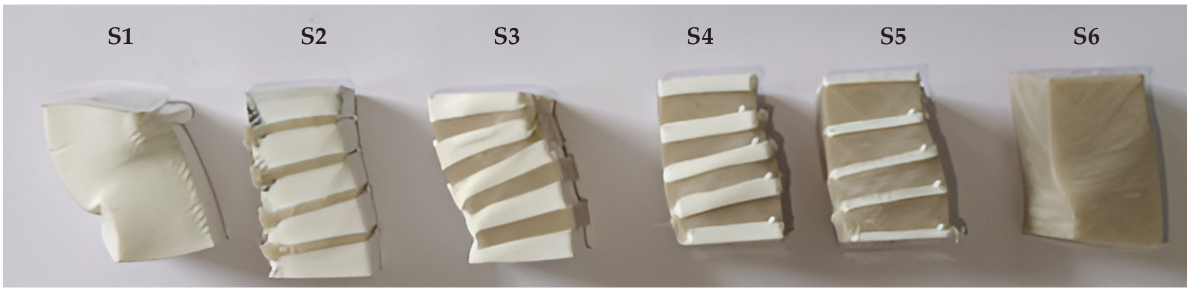

Fig. 5. The samples after compression test

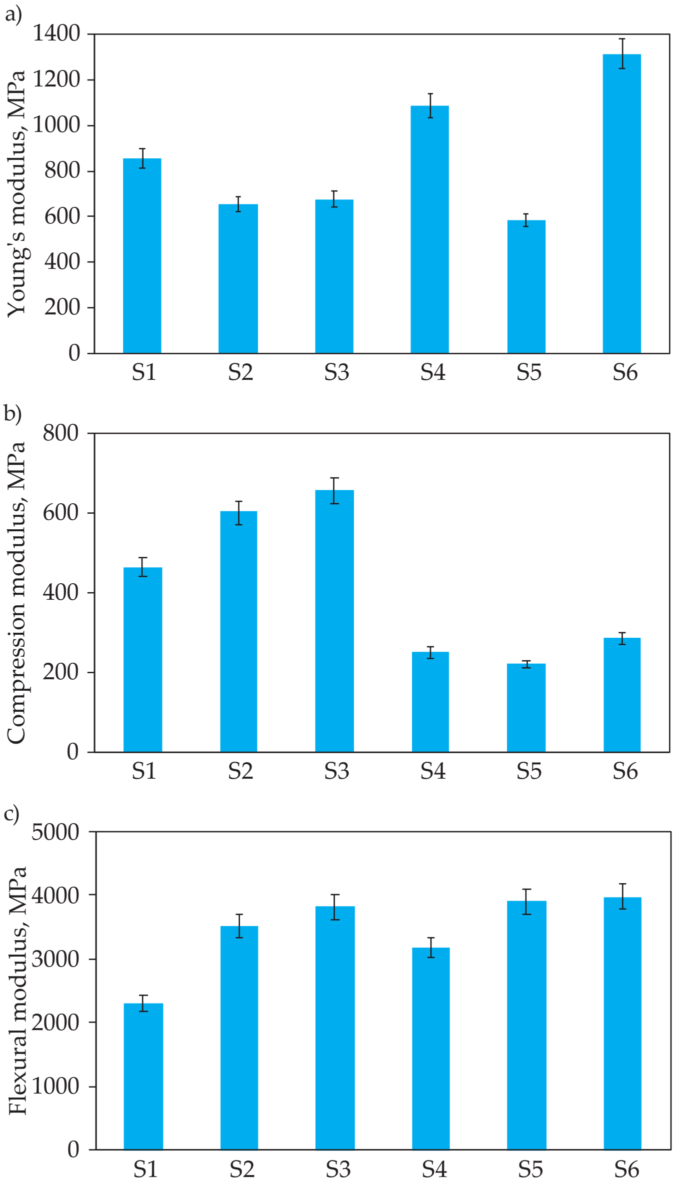

Fig. 6. Mechanical properties: a) Young's modulus, b) compression modulus, c) flexural modulus

It is clear from Fig. 6c that addition of PLA/Al_2O_3 improved PLA flexural modulus. The modulus increases with increasing PLA/Al_2O_3 content from 2.3 to 3.9 GPa (by 52 to 72%). The exception was the sample containing 60 wt% Al_2O_3 (S4), for which the modulus improvement was 37.5% only. The addition of reinforcement increases the bonding between the layers, therefore reducing delamination and increasing flexural modulus. From the FESEM analysis, the improved bonding between the PLA and the reinforcements can be seen, which is the cause of the modulus improvement and reduced flexibility.

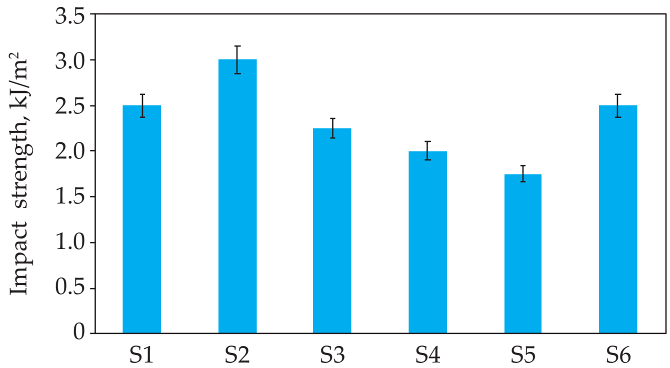

Fig. 7. Impact strength of PLA, PLA-PLA/Al_2O_3 and PLA/Al_2O_3

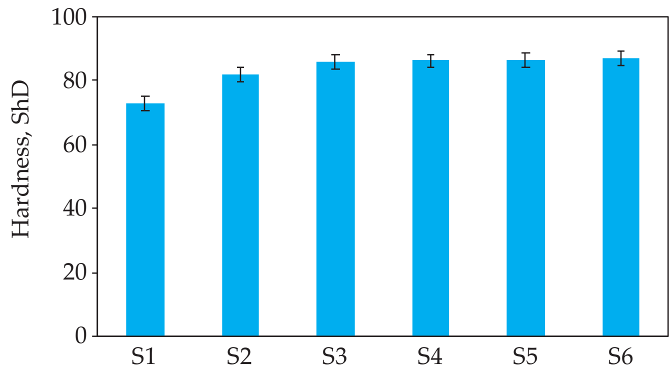

Fig. 8. Shore-D hardness of samples

The addition of PLA/Al_2O_3 decreased the impact strength of investigated samples (Fig. 7). The exception was the sample containing 20 wt% PLA/Al_2O_3 (S2), for which the impact strength increased by 20%. PLA/Al_2O_3 (S6) and PLA did not differ in impact strength. PLA with 20 wt% PLA/Al_2O_3 provided the best bond between layers. Bigger addition of PLA/Al_2O_3 reduces the impact strength due to the voids between the outer coatings and the filler layers. This is visible in FESEM micrographs (Fig. 2).

The hardness of PLA (Fig. 8) increased with the addition of PLA/Al_2O_3, which is consistent with the literature data [31]. At 40 wt% PLA/Al_2O_3, the hardness was 86 ShD (19% more than PLA). Further addition had no effect on this parameter.

CONCLUSIONS

The influence of PLA/Al_2O_3 content on the mechanical properties of PLA-PLA/Al_2O_3 samples obtained by 3D-FDM printing was examined. A perfect connection was created between the PLA and PLA/Al_2O_3 reinforcing layers, which resulted in increased tensile and flexural strength as well as hardness and reduced compressive deformation. At the same time, the compressive and flexural modulus increased by 40% and 70%, respectively, compared to PLA. Moreover, the impact strength with 20% reinforcement was 20% higher.

REFERENCE

[1] Cantrell. J.T., Rohde S., Damiani D. *et al*.: *Rapid Prototyping Journal* **2017**, *23(4)*, 811. https://doi.org/10.1108/RPJ-03-2016-0042

[2] Serra T., Planell J.A., Navarro M.: *Acta Biomaterialia* **2013**, *9(3)*, 5521. https://doi.org/10.1016/j.actbio.2012.10.041

[3] Yang. T.-C., Yeh C.-H.: *Polymers* **2020**, *12(6)*, 1334. https://doi.org/10.3390/polym12061334

[4] Huang Y., Löschke S., Proust G.: *Composites Part C: Open Access* **2021**, *5*, 100140. https://doi.org/10.1016/j.jcomc.2021.100140

[5] Ansari A.A., Kamil M.: *International Journal of Lightweight Materials and Manufacture* **2022**, *5(3)*, 369. https://doi.org/10.1016/j.ijlmm.2022.04.006

[6] Calignano F., Lorusso M., Roppolo I. *et al*.: *Machines* **2020**, *8(3)*, 52. https://doi.org/10.3390/machines8030052

[7] Hedjazi L., Guessasma S., Belhabib S. *et al*.: *Polymers* **2022**, *14(14)*, 2924. https://doi.org/10.3390/polym14142924

[8] Singh R., Kumar R., Singh I.: *Journal of Thermoplastic Composite Materials* **2021**, *34(8)*, 1103. https://doi.org/10.1177/0892705719864623

[9] Kremzer M., Tomiczek B., Matula G. *et al*.: *Materials* **2023**, *16(15)*, 5473. https://doi.org/10.3390/ma16155473

[10] Vakharia V.S., Kuentz L., Salem A. *et al*.: *Polymers* **2021**, *13(20)*, 3545. https://doi.org/10.3390/polym13203545

[11] Bulanda K., Oleksy M., Oliwa R. *et al*.: *Advances in Manufacturing Science and Technology* **2020**, *44(1)*, 15. https://doi.org/10.2478/amst-2019-0003

[12] Huang S.H., Liu P., Mokasdar A, Hou L.: *The International Journal of Advanced Manufacturing Technology* **2013**, *67*, 1191. https://doi.org/10.1007/s00170-012-4558-5

[13] Prathumwan R., Subannajui K.: *RSC Advances* **2020**, *54(10)*, 32301. https://doi.org/10.1039/D0RA01515F

[14] Zhenhua H. Shifei Z. Canhui L.: *Processing and Application of Ceramics* **2020**, *14(2)*,128. https://doi.org/10.2298/PAC2002128H

[15] Pascual-González C., Thompson C., de la Vega J. *et al*.: *Rapid Prototyping Journal* **2022**, *28(5)*, 884. https://doi.org/10.1108/RPJ-06-2021-0152

[16] Caminero M.Á., Romero Gutiérrez A., Chacón J.M. et al.: *Rapid Prototyping Journal* **2022**, *28(10)*, 2004. https://doi.org/10.1108/RPJ-01-2022-0023

[17] Armstrong C.D., Todd N., Alsharhan A.T. *et al*.: *Advanced Materials Technologies* **2021**, *6(1)*, 2000829. https://doi.org/10.1002/admt.202000829

[18] Choudhary N., Sharma V., Kumar P.: *Journal of Vinyl and Additive Technology* **2021**, *27(3)*, 612. https://doi.org/10.1002/vnl.21837

[19] Donate R., Monzón M., Alemán-Domínguez M.E. *et al*.: *Journal of Biomedical Materials Research Part B: Applied Biomaterials* **2023**, *111(2)*, 429. https://doi.org/10.1002/jbm.b.35162

[20] Lee J., Lee H., Cheon K.-H. *et al*.: *Additive Manufacturing* **2019**, *30*, 100883. https://doi.org/10.1016/j.addma.2019.100883

[21] Kumar R., Singh R., Singh M. *et al*.: *Journal of Thermoplastic Composite Materials* **2022**, *35(6)*, 799. https://doi.org/10.1177/0892705720925119

[22] Pang X., Zhuang X., Tang Z. *et al*.: *Biotechnology Journal* **2010**, *5(11)*, 1125. https://doi.org/10.1002/biot.201000135

[23] Joseph T.M., Kallingal A., Suresh A.M. *et al*.: *The International Journal of Advanced Manufacturing Technology* **2023**, *125(3–4)*, 1015. https://doi.org/10.1007/s00170-022-10795-y

[24] Meng X., Bocharova V., Tekinalp H. *et al*.: *Materials and Design* **2018**, *139*, 188. https://doi.org/10.1016/j.matdes.2017.11.012

[25] Bulanda K., Oleksy M., Oliwa R. *et al*.: *Polimery* **2020**, *65(6)*, 430. https://doi.org/10.14314/polimery.2020.6.2

[26] Papageorgiou K., Theochari S., Milioris K.: *Polimery* **2023**, *68(6)*, 317. https://doi.org/10.14314/polimery.2023.6.2

[27] Wang X., Jiang M., Zhou Z. *et al*.: *Composites Part B: Engineering* **2017** *110*, 442. https://doi.org/10.1016/j.compositesb.2016.11.034

[28] Ninan N., Joseph B., Visalakshan R.M. *et al*.: *Materials Advances* **2021**, *2(20)*, 6620. https://doi.org/10.1039/D1MA00444A

[29] Jose J., Sultan S., Kalarikkal N. *et al*.: *RSC Advances* **2020**, *10(62)*, 37928. https://doi.org/10.1039/D0RA08295C

[30] Bharath H.S., Bonthu D., Gururaja S. *et al*.: *Composite Structures* **2021**, *263*, 113732. https://doi.org/10.1016/j.compstruct.2021.113732

[31] Bulanda K., Oleksy M., Oliwa R. *et al*.: *Polymers* **2021**, *13(15)*, 2455. https://doi.org/10.3390/polym13152455

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