Carbon fibre-graphene composite polylactic acid (PLA) material for COVID shield frame

Kohlenstofffaser-Graphen-Polylactid (PLA)-Verbundwerkstoff als COVID-Schutzrahmen

E.P. Mohammed Basheer¹, K. Marimuthu¹

Challenges in the development of carbon fibre and graphene reinforced composite polylactic acid material is reserved in this research. A screw extrusion process is used to blend the carbon fibre particle (1 wt.%) and graphene (1 wt.%) with polylactic acid pellets (98 wt.%) to extrude and draw a continuous composite polylactic acid wire. The size of the wire drawn is 1.75 mm and it is found uniform in shape. Through electron microscope, the dispersion of carbon fibre and graphene in the polylactic acid material is confirmed with good bonding. Subsequently, the presence of carbon fibre and graphene reinforcement in polylactic acid material is confirmed through the x-ray diffraction peaks. The composite polylactic acid material developed through screw extrusion is to build a mechanical test sample. The strength of composite polylactic acid material is 31 MPa and 3D printed composite polylactic acid material is 63 MPa. The density of the composite material is found increased in 3D printed material than the raw polylactic acid material. With valid mechanical and thermal properties of composite polylactic acid material, a commercial product is developed. An autoclavable COVID-19 face shield is designed and developed through Fused filament fabrication 3D printer and the same was implemented.

Keywords: Composite / polylactic acid / COVID face shield / 3D printing / properties

Schlüsselwörter: Verbundwerkstoff / Polylactid / COVID-Gesichtsschutz / 3D-Druck / Eigenschaften

1 Introduction

In the last two decades of day-to-day life, the use of plastic components has been increased. So, these plastic materials have directly affected the environment. To avoid this issue, the manufacturing industries are looking for biodegradable plastic materials. That way, in present days, most of the plastic industries are using biodegradable (polylactic acid (PLA), polyglycolic acid (PGA), polyhydroxy butyrate (PHB), polycaprolactone (PCL), etc.) based plastic materials in the form of fillet, pellets, powders or liquid resins. In order to produce various engineering components, plastic production industries are seeking suitable manufacturing method. On the other hand, in present day, 3D printing technology also has grown up rapidly. Fused filament fabrication (FFF) is a method of fabricating structures from three dimensional (3D) models that are used in additive manufacturing (AM) [1–4].

¹ Research Scholar Advanced Manufacturing Technology, Coimbatore Institute of Technology, Anna University, Tamil Nadu, India

Corresponding author: E.P. Mohammed Basheer, Research Scholar Advanced Manufacturing Technology, Coimbatore Institute of Technology, Anna University, Tamil Nadu, India, E-Mail: epmohdbasheer@gmail.com
In order to improve the mechanical property of polylactic acid printed composites, micro or nano-ceramic powders were added. [5]. For that reason, hydroxyapatite (HA) powders with a mean particle size of 90 nm to 1 micron have commonly used [6]. The mechanical properties of the synthetic scaffolds were investigated using tensile, compression and flexural (tree point bending) tests, and it was discovered that the use of polylactic acid-hydroxyapatite composite enhanced the mechanical strength of the scaffolds, allowing them to withstand up to 10 MPa mechanical strength without deformation or failure of mechanical property. These 3D-printed biodegradable, eco-friendly structures had good mechanical properties. Several process parameters such as nozzle and platform temperature, printing speed and orientation, layer deposition height, raster angle, infill pattern, and so on have a significant impact on the mechanical characteristics of 3D printed materials generated by Fused filament fabrication during the printing process [5–7]. Polylactic acid is a potential thermoplastic for 3D printing because of its lower glass transition temperature (Tg = 60 ºC–65 ºC) and melting point (Tm = 173 ºC–178 ºC), reduced coefficient of thermal expansion, and non-adherence to the printing surface [8, 9]. However, its applicability is limited because of its low thermal stability, high rate of deterioration during processing, brittle character, low toughness, moisture sensitivity, and significantly greater cost than conventional polyolefin [10–12].

Coronavirus (COVID-19) pandemic is a challenging healthcare system worldwide today. It was declared as international “public-health emergency” by the World Health Organization (WHO) by the end of January 2020. Personal protective equipment (PPE) is critical for healthcare professionals (HCWs) who are treating COVID-19 patients. There is currently no common standard for protecting the face and eyes from biological risks, as seen by the wide range of public health care guidelines [13–15]. Face shields, in combination with supplementary personal protective equipment (goggles and mouth/nose mask), have been proven to lower the risk of inhalational exposure, particularly when conducting activities involving aerosol production [16]. Many workers (e.g., medical, dental, and veterinary employees) wear face shields to protect their faces from splashes, sprays, or the spatter of body fluids. Face shields, on the other hand, should be used in conjunction with other protective equipment and are classified as adjunctive personal protective equipments. [17]. Face shields are used differently depending on the situation, but the World Health Organization has called for an increase in their manufacturing due to the critical use of personal protective equipments in the population during the pandemic [18].

The frame (foam or plastic material-based) and the transparent protective visor shield are the two basic components of a face shield (visor) (mostly transparent plastic or acrylic glass material). Additional components, such as elastic bands (frame-head holder), face contact softening materials (sponge, foam, rubber, etc.), and clips for securing the transparent shield to the frame, can be provided [19, 20].

Research on composite polylactic acid material is one of the challenging processes. One of the major issues is reinforcement of carbon fibre and graphene material in the raw polylactic acid material. One of the predominant process found from the literature is mechanical screw extrusion process to develop composite polylactic acid material. Thus, an attempt is made to develop carbon fibre-graphene reinforced composite polylactic acid material for additive manufacturing. As a secondary phase, the mechanical testing of composite polylactic acid material and additive built samples for properties is evaluated. Finally, the above analysis is further verified by the observations of scanning electron microscopy (SEM) images, x-ray diffraction (XRD) and differential scanning calorimetry (DSC) from developed material. Further the qualified material is used to develop COVID-19 shield through composite polylactic acid material for commercialization.

### 2 Materials and methodology

In this paper, the polylactic acid material is used to modify with two different additives such as carbon fibre and graphene material to increase the strength of the material. The polylactic acid pallets (2 mm in size), the carbon fibre (150 μm) and graphene (90 μm) are used as major sources for composite polylactic acid wire extrusion. The reinforcement of graphene (1 wt.%) and carbon fibre (1 wt.%) are mixed through screw extrusion process. Mixture of
polylactic acid, graphene and carbon fibre are fed into the machine through hopper. The rotational speed of the screw (100 min\(^{-1}\)) leads the mixture material towards the extrusion nozzle. Further it starts to fuse at a maximum temperature of 190 °C and a wire is drawn as an end product to a dimension of 1.75 mm.

The composite wire extruded is evaluated for mechanical testing and metallurgical characterisation techniques. The dimension of composite wire is measured through scanning electron microscope and the reinforcement (graphene and carbon fibre) is confirmed through electron imaging. The wire tensile strength and density of the composite polylactic acid material is evaluated for discussion.

To study the printability of composite polylactic acid material, RAISE 3D, fused filament fabrication 3D Printing machine is used to print the test sample coupons. The service temperature for the proposed material design is 180 °C and the maximum temperature of the fusion bed is not to exceed 60 °C. The build plate temperature is 60 °C with a printing speed of 60 mm/s. Following are the 3D printing details used: hatch direction-rectilinear, nozzle diameter- 0.4 mm, print layer resolution-200 microns, print speed- 60 mm/s and infill-100 % to build a test coupon. Besides comparing the properties of composite polylactic acid material, the pure polylactic acid material is also used to develop coupons with same process conditions. Further, the mechanical qualified composite material is suggested to develop a frame for COVID shield.

3 Results and discussion

3.1 Development of composite (carbon fibre + graphene + polylactic acid) material for additive manufacturing

The composite polylactic acid (carbon fibre + graphene + polylactic acid) material is developed through the screw extrusion process in the form of wire. Screw extruder is used to develop a modified wire with different input materials, Figure 1. The polylactic acid reel material in the form of pellets, and reinforcement materials in micron are used to develop composite polylactic acid reel material in the form of wire drawing for additive manufacturing. The polylactic acid pallets (2 mm in size), the carbon fibre (150 μm in size) and graphene (90 μm in size) are fed on the hopper in a defined quantity. In this paper, in 98 % of polylactic acid material, additives such as carbon fibre (1 wt.%) and graphene (1 wt.%) are used. It has to be noted that, in the production of dense polylactic acid wire, the velocity of the screw extruder should be varying from inlet to outlet. In this system, the material inlet hopper takes pellet/fibre materials that lead at a velocity of 35 mm/s and develop to a maximum of 155 mm/s. The variation in velocity influences in extrusion temperature and it was found varying from hopper inlet to wire drawn orifice (nozzle). In addition, the extrusion barrel is also subjected to a convective heat transformation through a band heater placed around the system. The function of a band heater is to fuse the pellet and supports to blend reinforcement uniformly. Heating band is maintained to a maximum temperature of 230 °C and the same is found dissipated to a minimum temperature of 28 °C on extrusion of composite polylactic acid wire reel. From the extrusion, the diameter of the continuous (carbon fibre and graphene reinforced polylactic acid material) wire has been maintained to a uniform diameter of 1.75 mm, Figure 2.

3.2 Metallurgical analysis and mechanical properties evaluation

To discuss in detail, the modified polylactic acid material developed in the form of composite material is subjected to microscopic imaging, x-ray diffraction analysis, differential scanning calorimetry (DSC) analysis, thermogravimetric (TG) analysis and mechanical testing on hybrid polylactic acid material. The physical structure and the diameter of the carbon fibre + graphene reinforced polylactic acid material is observed through scanning electron microscope to confirm the morphological structure, Figure 3. The diameter of the wire is found uniform throughout the extrusion. It has been understood that the mechanical mixing of carbon fibre + graphene reinforced polylactic acid material through screw extrusion process has produced a uniform composite polylactic acid wire. The distribution of carbon fibre and graphene in the extruded wire is studied in detail through high resolution electron imaging. Mechanical extrusion
process has been recommended as a suitable process to impregnate the carbon fibre and graphene material. Electron imaging has proved the presence of graphene and carbon fibre as a reinforcement in the polylactic acid matrix, Figure 4. Carbon fibre reinforced in the polylactic acid material is found strongly impregnated with matrix material. Subsequently, the graphene material is also confirmed to be distributed uniformed. The carbon fibre dispersed in the polylactic acid material is a random orientation that increases the strength of the material. In addition to electron image analysis, the metallurgical quality and the mechanical properties of the developed hybrid polylactic acid material is evaluated for further discussion. To study the metallurgical quality of the carbon fibre + graphene reinforced polylactic acid material, the x-ray diffraction (XRD) analysis is used, Figure 5. In general, the x-ray diffraction pattern for polylactic acid material has been reported with wide space and no available peaks [21]. However, the addition of graphene and carbon fibre in polylactic acid material has modified the pattern of the peak. It has wide peak for polylactic acid material and a broad peak for graphene structure.

From the differential scanning calorimetry analysis, the material transition temperatures are clearly noticed for both pure polylactic acid and composite polylactic acid material. Pure polylactic acid does not have any detailed crystalline changes, Figure 6. However, the polylactic acid with graphene and carbon fibre has eloquent changes due to added elements. The first stage (glass transition) is found at 65.6 °C, second stage (crystalline transition) at
116 °C and the third stage (melting point) is at 364 °C. With standard formula for percentage of crystalline, it has been understood that 3 % of element found in composite polylactic acid material is crystal. Similarly, from thermogravimetric (TG) analysis, residual for pure polylactic acid material is 43.27 % at 398.6 °C and is found less as 8.81 % for same temperature in composite polylactic acid material are identified, Figure 7.

**Figure 2.** Photo image of hybrid (carbon fibre + graphene + polylactic acid) material.

**Figure 3.** Electron image to confirm the physical structure of hybrid (carbon fibre + graphene + polylactic acid) material.

**Figure 4.** Electron image to confirm the presence of graphene and carbon fibre in a PA matrix of hybrid material.

**Figure 5.** XRD Peak of hybrid material; polylactic acid with carbon fibre and graphene reinforcement.

**Figure 6.** DSC peak for pure polylactic acid material and hybrid polylactic acid material developed through screw extrusion process.
Comparatively, the basic mechanical properties of the composite polylactic acid material is studied and reported here. The density of the composite polylactic acid material is recorded with a maximum density of 1.3 g/cm³ through the test following Archimedes principle. The actual density of pure polylactic acid material is 1.24 g/cm³, the addition of graphene and carbon fibre in the pure polylactic acid material has increased the density. Consecutively, the strength of the composite wire is 48 MPa and the pure polylactic acid material has 65 MPa. It has been understood that the rate of displacement in the composite polylactic acid wire is found reduced. Reduction in displacement is less due to the impregnation of hard materials under thin section. This may not be consistently retained over printed material.

3.3 Mechanical and thermal properties of 3D printed composite polylactic acid material

Further, the material has been evaluated for mechanical properties to justify and qualify the graphene-carbon fibre reinforced polylactic acid material for additive manufacturing. The ultimate service temperature is 52 °C with thermal expansion coefficient of 57.5 μm/m °C. The addition of carbon fibre and graphene has tremendously supported to reduce the expansion of polylactic acid material from 68 μm/m °C to 57.5 μm/m °C. The deformability of pure polylactic acid may lead to plastic shear on any load applications. The reinforcement of hard particles and/or any fibres may support to distributed load eventually. In addition, the mechanical strength of the material will also be increased. To study the mechanical properties of newly developed composite polylactic acid material, the test coupons are developed through fused filament fabrication method (FFF) following the ASTM standards for dimensions. The 3D printing machine used to print tensile test coupons for mechanical testing and future product developments, Figure 8. Test coupons are made with pure polylactic acid material and composite polylactic acid material at same process condition to compare and discuss. The test coupons used for universal testing machine to read the strength of polylactic acid material are developed following the ASTM D638 standard, Figure 9. The results are plotted in the form of graph. Result revealed that the comparison of the strength of developed polylactic acid wire and 3D printed material which is confirmed with the standard material, Figures 10, 11. The strength of the 3D printed material (63 MPa) is found increased two times of composite polylactic acid wire material (31 MPa). Subsequently, the strength of
the composite material (31 MPa) has significant
difference and found better than the raw polylactic acid material (26 MPa). From the results, it can be
clearly shown that tensile property is strongly de-
depend on the variation of raster angle (45°/45°) as well as build orientation. A substantial change in
3D printed material is due to the bonding of materi-
al and increase in bulk properties. It has been evi-
dently proved that the density of printed material is high for both raw polylactic acid and composite polylactic acid materials. The difference in the den-
sity of raw polylactic acid material and composite polylactic acid material developed for the proposed research. Therefore, the composite polylactic acid material developed through screw extrusion process
has substantially increased properties with respect to mechanical and thermal conditions. Hence it has
been recommended to implement in commercial product.

3.4 COVID face shield product development with composite polylactic acid material

The composite polylactic acid material in the com-

bination of graphene and carbon fibre as reinforce-
ment is used to develop a shield frame for face mask. The carbon fibre-graphene reinforced composite polylactic acid filament material has been used to develop a face shield product through 3D printing process, following the fusion bed method. Initially, the product model is developed in the CAD software and the data is stored in the form of ‘.stl’ for processing. The designs are made with proper legs to fuse on bed and for easy handling at the end of printing, Figure 12. The newly devel-
oped composite polylactic acid material has been
replaced (due its biodegradability) for the COVID shield frame developed through ABS material. It has
highly supported to meet the demand in shield frame production during the pandemic situation. The COVID face shield frame product developed through composite polylactic acid is found less in weight and safe to use in real time application. As a result, the products are produced in number of counts and commercialized to market.

Figure 9. Photo image of CNT reinforced polylactic acid material (i) as built sample and (ii) fractured sample after mechanical testing.

Figure 10. Strength of raw polylactic acid and hybrid polylactic acid (PLA–G–CF) material under tensile load.

Figure 11. Difference in density of raw polylactic acid material and hybrid polylactic acid (PLA–G–CF) material before and after 3D built process.
4 Conclusions

Investigation has been performed to develop carbon fibre and graphene reinforced composite polylactic acid material for real time application. The following points are identified as a major confession to recommend the findings of the research proposed.

- The composite polylactic acid material has been successfully developed through screw extrusion process. It is confirmed that the composite polylactic acid wire has substantial metallurgical quality with uniform distribution of carbon fibre and graphene.

- Metallurgical quality of composite polylactic acid in terms of crystalline changes has detailed transition and pure polylactic acid is inferior to the developed one. The residual mass of pure polylactic acid is the maximum of 47 % and 8.81 % in composite polylactic acid due to reinforcement of carbon and graphene material.

- The density of pure polylactic acid material and composite polylactic acid material are in marginal difference (0.06 g/cm²) and the strength found is a minimum of 31 MPa in composite polylactic acid compared to pure polylactic acid material. On other hand, the 3D printed material found is a maximum of 63 MPa in composite polylactic acid material.

- From the validated composite polylactic acid material, a positive report has been recommended to develop a commercial product. A COVID face shield frame has been developed through fused bed method in place of acrylonitrile-butadiene-styrene process-based shield frame and the same has been implemented.

5 References

[1] T.J. Horn, O.L.A. Harrysson, Sci. Prog. 2012, 95, 255.
[2] N. Guo, M.C. Leu, Front. Mech. Eng. 2013, 8, 215.
[3] M. Vaezi, H. Seitz, S. Yang, Int. J. Adv. Manuf. Technol. 2013, 67, 1721.
[4] M.A. Imran, K.K. Singam, S.P. Jani, S. Uppalpati, Mater. Today: Proc. 2021.
[5] R. Siakeng, Jawaid, M. Ariffin, H. Sapuan, S.M. Asim, M. Saba, Polym. Compos. 2019, 40, 446.
[6] K.V. Niaza, F.S. Senatov, S.D. Kaloshkin, A.V. Maksimkin, D.I. Chukov, J. Phys. Conf. Ser. 2016, 741.
[7] V.E. Kuznetsov, A.N. Solonin, O.D. Urzhumtsev, R. Schilling, A.G. Tavitov, Polymer 2018;10(3):313.
[8] I. Chiulan, A. Frone, C. Brandabur, D. Panaitescu, Bioeng. 2017 5:2.
[9] M.A. Cuiffo, J. Snyder, A. Elliott, M. Romero, N. Kannan, G.P. Halada, Appl. Sci. 2017, 7, 579
[10] O. Gordobil, I. Egüés, R. Llano-Ponte, J. Labidi, Polym. Degrad. Stab. 2014, 108, 330.
[11] V. Mimini, E. Sykacek, S.N.A. Hashim, J. Holzweber, H. Hettegger, K. Fackler, J. Wood Chem. Technol. 2019, 39, 14.
[12] S.P. Jani, A.S. Kumar, M.A. Khan, S. Sajith, A. Saravanan, J. Nat. Fibers 2019.
[13] WHO, Rational Use of Personal Protective Equipment for Coronavirus Disease (Covid-19): Interim Guidance, 27 February 2020; World Health Organization: Geneva, Switzerland. 2020.
[14] R.J. Roberge, J. Occup. Environ. Hyg. 2016, 13, 235.
[15] ANSI/ISEA Z87.1-2015. American National Standard for Occupational and Educational Personal Eye and Face Protection Devices. Available online: https://safetyequipment.org/
product/ansiisea-z87-1-2015/ (accessed on 3 April 2020)

[16] W.G. Lindsley, J.D. Noti, F.M. Blachere, J.V. Szalajda, D.E. Beezhold, *J. Occup. Environ. Hyg.* **2014**, *11*, 509.

[17] P. Zhou, Z. Huang, Y. Xiao, X. Huang, G. Fan, *Infect. Control. Hosp. Epidemiol.* **2020**, *1*.

[18] S. Feng, C. Shen, N. Xia, W. Song, M. Fan, B.J. Cowling, *Lancet Respir. Med.* **2020**.

[19] H.K. Celik, O. Kose, M.E. Ulmeanu, A.E. Rennie, T.N. Abram, I. Akinci, *Int. J. Bioprint.* **2020**, *6*.

[20] L. Talikwa, *Managing Inf. Control.* **2002**, *2*, 3.

[21] Z. Viskadourakis, G. Perrakis, E. Symeou, J. Giapintzakis, G. Kenanakis, *Appl. Phys. A: 2019*, *125*, 159.

Received in final form: August 7th 2021