Preparation and characterization of poly(lactic acid)/boehmite alumina composites for additive manufacturing

L Lendvai1 and I Fekete1

1 Széchenyi István University, Audi Hungaria Faculty of Vehicle Engineering, Department of Materials Science and Engineering, Győr, Hungary

E-mail: lendvai.laszlo@sze.hu

Abstract. The purpose of this work is to investigate the suitability of boehmite alumina (BA) reinforced poly(lactic acid) (PLA) for additive manufacturing with the fused filament fabrication method. PLA filaments with 0-10 wt.% BA content were produced via melt compounding using a twin-screw extruder. Dumbbell-shaped and prismatic specimens were manufactured then by feeding the prepared filaments into a desktop 3D printer. Mechanical, morphological and melt flow properties of the developed samples were determined. The addition of BA decreased the melt flow rate of PLA, however not so much that it would have hindered its suitability for 3D printing. With increasing BA content both the strength and the stiffness of the samples increased slightly at constant deformability and toughness. Scanning electron microscopic images revealed a homogenous dispersion of BA particles within the PLA matrix, although remaining agglomerates were also observed.

1. Introduction

Additive manufacturing (AM) – generally referred to as 3D printing – is a rapidly developing technology that received a significant amount of scientific interest over the last two decades. AM technologies are based on the principle of building products through a layer-by-layer process and offer numerous advantages, including reduced production time and cost and the opportunity to fabricate complex objects that would be otherwise impossible. Numerous AM techniques have been developed up until now, each of them operating on different principles [1]. Additive manufacturing can be used either to fabricate parts directly or to prepare molds for common polymer processing technologies, such as injection molding. This latter is a cost efficient way to produce low series of 3D objects [2].

The most widespread methods of AM are the fused deposition modeling (FDM) and the fused filament fabrication (FFF). These similar technologies use filaments of polymers (or metals with low melting temperature) for the printing process. The only difference lies within the heating of the building chamber: while FDM machines are generally applied with temperature control in the build chamber, the FFF ones are mostly non-industrial equipment without this feature. Due to their low cost in use and maintenance both are widely used for biomedical applications, in the aerospace and automotive industry and recently in the everyday life as well [3]. Various commodity and engineering plastics (e.g. polystyrene, polyamide 6, polyethylene terephthalate) are suitable for FDM and FFF printing, however the most common ones are acrylonitrile butadiene styrene and poly(lactic acid) (PLA).

In recent years there has been an increasing interest in the development of bio-based and biodegradable polymers due to the persistently escalating petroleum consumption [4, 5]. PLA is...
considered as one of the most promising candidates. It is a semi-crystalline thermoplastic polyester that can be prepared from renewable resources and it is also biodegradable. Considering its mechanical properties, PLA could substitute petrochemical polymers in the packaging, agricultural and automotive industry and it is excellent for biomedical applications as well due to its biocompatibility. Generally, PLA exhibits a high enough strength and stiffness to substitute common petrol-based plastics such as polystyrene or polyethylene terephthalate. However, because of its low rate of crystallization from melt it can become quite amorphous when exposed to rapid cooling [6].

A considerable amount of literature has been published on the development of PLA-based polymer blends and composites with enhanced properties in order to increase its range of applications [7]. A widely used method to improve the mechanical properties of PLA is to reinforce it with suitable micro- or nanofillers (graphene, cellulose, layered silicates, etc.). Previous studies have reported that the incorporation of such reinforcing particles does not only improve the mechanical properties of PLA, but also beneficially affects its processability when printing it with FDM and FFF [8].

Among these micro- and nanofillers used as reinforcement, an aluminum oxyhydroxide, namely boehmite alumina (BA) is one of the most promising candidate due to its relatively low price and availability in large industrial scales. In the past decade a number of researchers have sought to determine the effects of BA on the properties of various polymers [9], including PP [10] and PLA [11]. The incorporation of BA particles is reported to improve the mechanical properties, the thermal stability and the flame resistance of the polymer matrix as well.

So far, no previous study has investigated the possibility of using BA reinforced PLA composite filaments for FDM or FFF printing. The aim of this present work is to produce PLA/BA composites with a BA content up to 10 wt.% and to validate their suitability for FFF printing applications. The effect of BA as reinforcement on the melt flow rate, the mechanical and morphological properties of 3D printed objects are presented and evaluated in this paper.

2. Experimental

2.1. Materials

An extrusion grade PLA (2003D) of high molecular weight ($M_n = \sim 100\ 500$ g/mol, $M_w = \sim 180\ 500$ g/mol [12]) obtained from NatureWorks LLC (Minnetonka, MN, USA) was used as polymer matrix. It has a melting temperature of $\sim 170$ °C and a D-isomer content of $\sim 4\%$. As reinforcement Disperal® 40 grade BA of Sasol GmbH (Hamburg, Germany) was applied. This specific type has an Al$_2$O$_3$ content of 80 m\%, an average particle agglomerate size of 35 μm, and a surface area of 100 m$^2$/g. The list of abbreviations and formulations of the prepared samples are listed in Table 1.

| Sample code | PLA (wt.%) | BA (wt.%) |
|-------------|------------|-----------|
| PLA         | 100        | -         |
| PLA_2.5BA   | 97.5       | 2.5       |
| PLA_5BA     | 95         | 5         |
| PLA_10BA    | 90         | 10        |

2.2. Preparation of the filaments

The PLA and the BA powder were dried at 80 °C for 4 hours prior to processing. Melt compounding of the components was performed using a co-rotating twin-screw extruder (LTE 20-44, Labtech Engineering Co., Ltd., Samutprakan, Thailand) with intermeshing screws (diameter of 20 mm, L/D ratio of 40). The temperature of the heating zones from feed hopper to die end was set to 155 °C, 160 °C, 160 °C, 165 °C, 165 °C, 170 °C, 170 °C, 175 °C, 180 °C, 185 °C and 185 °C, respectively. The screw speed was 30 rpm, the diameter of the die was 2 mm. In this way, neat PLA and BA-reinforced PLA composite filaments with a diameter of 1.75 ± 0.08 mm were produced.
2.3. Printing of the filaments by fused filament fabrication

The filaments prepared by extrusion were used to manufacture dumbbell-shaped specimens (type: 3 according to EN ISO 8256) for tensile tests and prismatic specimens (80 mm x 10 mm x 4 mm) for impact tests (Figure 1). Samples were prepared with a Creality CR-10 FFF machine. A linear infill with horizontal processing direction and raster angle (±45°) between the layers was used. The printing temperature was 210 °C, the nozzle diameter was 0.4 mm and the temperature of the building platform was set to 40 °C. The layer height was 0.2 mm and the filling rate was 100% for all samples.

![Figure 1. The dumbbell-shaped and the prismatic specimen’s orientation on the building platform](image)

Computed tomographic (CT) analysis was performed on the 3D printed samples in order to exclude the possible defects presence. It was also determined, that the average porosity of the 3D printed samples was approximately 0.18%.

2.4. Measurements and characterization

The measure of melt flow rate (MFR) was conducted using an apparatus Ceast 7026.000 (Ceast S.p.A., Pianezza, Italy). The applied load was 2.16 kg, the temperature of the cylinder was set to 210 °C.

Tensile mechanical properties, i.e., yield strength, elongation at break and Young’s modulus were determined with an Instron® 3344 (Instron Ltd., Norwood, USA) universal tensile testing machine equipped with a 2 kN force sensor. The tests were carried out at a crosshead speed of 5 mm/min. The results reported in here are the averages of five parallel measurements.

The Charpy impact toughness was measured on a Ceast 6545 (Ceast S.p.A., Pianezza, Italy) pendulum-type testing machine equipped with an impact hammer of 2 J. The specimens were unnotched, rectangular bars. The results reported are the averages of five parallel measurements.

A scanning electron microscope (SEM) Hitachi S-3400N (Hitachi Ltd., Tokyo, Japan) with an acceleration voltage of 10 kV was used to investigate the fracture surfaces of the 3D printed samples at various magnifications. The surfaces of the samples were coated by a gold layer in a Quorum Technologies SC7620 high-vacuum sputter coater (Quorum Technologies Ltd, Laughton, UK).

3. Results and Discussion

3.1. Melt flow rate

The MFR of the neat PLA and its composites at various concentration of BA are represented in Figure 2. During FFF-based 3D printing the suitable materials are highly limited depending on their melt viscosity. If the viscosity is lower than the optimal, then the material is not able to provide structural support. However, when it is too high, then the extrusion may fail because of the molten polymer getting stuck within the nozzle [13]. Measuring the MFR of a polymer can be helpful to predict its processing behaviour as it is inversely proportional to the viscosity. Based on the literature [14] the printing of a
material with lower than 1 g/10 min MFR might fail due to its high viscosity. According to the results listed in Figure 1 the addition of BA particles definitely influences the melt flow rate of PLA. The MFR value of neat PLA (8 g/10 min) dropped when 2.5 wt.% BA was added (to 5.8 g/10 min). This is most probably due to the rigid BA particles hampering the motion of polymer chains. With further BA incorporated, the MFR decreased steadily, bottoming at 5 g/10 min at 10 wt.% BA content. These results refer to the suitability of the developed PLA/BA composites for FFF-based printing even at maximum (10 wt.%) BA loading.

![Figure 2. The melt flow rate (MFR) of neat PLA and its composites with various (0-10 wt.%) BA content](image)

3.2. Tensile mechanical properties

The characteristic stress-strain curves of the 3D printed PLA specimens containing 0-10 wt.% BA are shown in Figure 3. It can be clearly seen, that the tensile properties of PLA and the PLA/BA composites are close. The neat PLA sample without BA reinforcement exhibited a brittle behavior. Fracture occurred without a necking phenomenon. Even though the presence of rigid fillers – such as BA – tend to cause polymers to show a more brittle behavior, in here, mainly due to the poor initial toughness of PLA only a slight embrittlement can be observed.

![Figure 3. Stress-strain curves of the 3D printed PLA specimens containing 0-10 wt.% BA](image)

The tensile mechanical properties of the samples are listed in Table 2. According to the results, there was a slight improvement in yield strength with increasing BA content (from ~48 MPa to ~50 MPa), albeit only within the deviation range. The rise of Young’s modulus as a function of BA concentration was more remarkable. The value measured for the sample PLA_10BA (~1.45 GPa) is relatively 20% higher than that of parent PLA (~1.23 GPa). Interestingly, the modulus values described in the literature
for this specific PLA grade are significantly higher (2-3 GPa). A potential explanation for this discrepancy can be the different processing techniques applied for the sample preparation (extrusion, compression moulding, injection moulding, etc.). One must also consider that prior to processing with those conventional techniques, PLA is usually dried. However, due to the relatively long period of sample manufacturing with FFF printing, the filament could regain its moisture content during the process easily, therefore the drying of PLA is mostly neglected. As PLA is highly sensitive to moisture (even a small amount of water can hydrolyze PLA in its molten state), the lack of drying may be the reason behind this drop measured in the Young’s modulus. Regarding the deformability it can be concluded, that the presence of BA does not affect it. All the samples showed an elongation at break of about 5.3%.

| Sample code | Yield strength (MPa) | Young’s modulus (GPa) | Elongation at break (%) |
|-------------|----------------------|-----------------------|------------------------|
| PLA         | 48.0 ± 2.1           | 1.23 ± 0.06           | 5.3 ± 0.7              |
| PLA_2.5BA   | 48.7 ± 2.0           | 1.35 ± 0.05           | 5.4 ± 0.7              |
| PLA_5BA     | 50.0 ± 1.3           | 1.37 ± 0.05           | 5.2 ± 0.2              |
| PLA_10BA    | 50.2 ± 1.7           | 1.45 ± 0.05           | 5.2 ± 0.7              |

Mean ± standard deviation

3.3. Impact test results

Figure 4 displays the impact strength of the prepared samples as a function of BA content. Based on the results it can be concluded that the incorporation of BA particles does not affect the toughness of PLA. All the samples exhibited an impact strength of about 12 kJ/m². This is in good agreement with the tensile test results. Recall, that PLA is a polymer of low toughness in itself. Thus, the presence of rigid BA particles does not cause the PLA to embrittle even more.

![Impact strength graph](image)

**Figure 4.** Charpy impact strength of the 3D printed neat PLA and the PLA/BA composite specimens containing various amount (0-10 wt.%) of BA

3.4. Morphology

Figure 5 reveals SEM images of the impact fracture surfaces of the 3D printed PLA and PLA/BA specimens. According to Figure 5/a the neat PLA has a rigid, homogenous fracture surface. This is in good accordance with the results of the mechanical tests. Those samples containing BA show a rigid fracture surface as well, however, with BA agglomerates of 10-30 µm also included. The presence of agglomerates refers to the fact that the decomposition of BA particle bundles during melt compounding was imperfect. Even though these agglomerates on the micrographs do not seem to be the starting points of the crack propagations during the failure of the sample, they still can act as failure sites. This might be the reason for the marginal enhancement observed in the strength.
At higher magnification (Figure 6) it can be clearly seen that besides the agglomerates, the PLA/BA composites also contain BA particles dispersed individually (or as much smaller bundles). The dispersion of these small particles seems homogenous within the polymer matrix. This refers to a partial disintegration of the boehmite alumina agglomerates. One should consider, however, that the morphology of the fracture surface does not necessarily correspond with that of the bulk, still this is generally accepted in the literature.
4. Conclusions
This study has shown that PLA/BA composites are generally suitable for 3D printing with an FFF equipment. In order to demonstrate this, filaments with 0-10 wt.% BA reinforcement were produced by melt compounding. The melt flow rate analyses substantiated the assumption that these newly developed materials can be processed with FFF technology. Specimens for the mechanical and morphological tests were 3D printed out of these filaments.

According to the mechanical test results the PLA/BA composites outperformed neat PLA in Young’s modulus and there was also a slight improvement in yield strength. The elongation and impact strength was, however, not affected, all the results were within deviation range. The SEM images revealed a fine dispersion of BA particles in the PLA matrix, although remaining agglomerates were observed as well.

Acknowledgements
The research was carried out as part of the EFOP-3.6.2-16-2017-00016 project in the framework of the New Széchenyi Plan. The project was also supported by the Ministry of Human Capacities through the project NTP-NFTÓ-19.

References
[1] Ngo T D, Kashani A, Imbalzano G, Nguyen K T Q and Hui D 2018 Additive manufacturing (3D printing): A review of materials, methods, applications and challenges Composites Part B 143 172–96
[2] Tábi T, Kovács N K, Sajó I E, Czigány T, Hajba S and Kovács J G 2016 Comparison of thermal, mechanical and thermomechanical properties of poly(lactic acid) injection-molded into epoxy-based rapid prototyped (PolyJet) and conventional steel mold J. Therm. Anal. Calorim. 123 349–61
[3] Liu Z, Wang Y, Wu B, Cui C, Guo Y and Yan C 2019 A critical review of fused deposition modeling 3D printing technology in manufacturing polylactic acid parts Int. J. Adv. Manuf. Tech. 102 2877–89
[4] Singh T, Gangil B, Patnaik A, Biswas D and Fekete G 2019 Agriculture waste reinforced corn starch-based biocomposites: effect of rice husk/walnut shell on physicomechanical, biodegradable and thermal properties Mater. Res. Express 6 045702
[5] Singh T, Pruncu C I, Gangil B, Singh V and Fekete G 2020 Comparative performance assessment of pineapple and Kevlar fibers based friction composites J. Mater. Res. Technol. 9 1491–9
[6] Garlotta D 2001 A literature review of poly(lactic acid) J. Polym. Environ. 9 63–84
[7] Lendvai L and Brenn D 2020 Mechanical, morphological and thermal characterization of compatibilized poly(lactic acid)/thermoplastic starch blends Acta Technica Jaurinensis 13 1–13
[8] Coppola B, Cappetti N, Di Maio L, Scarfato P and Incarnato L 2018 3D Printing of PLA/clay nanocomposites: influence of printing temperature on printed samples properties Materials 11 1947
[9] Karger-Kocsis J and Lendvai L 2018 Polymer/boehmite nanocomposites: A review J. Appl. Polym. Sci. 135 45573
[10] Lendvai L 2020 Water-assisted production of polypropylene/boehmite composites Period. Polyttech., Mech. Eng. 64 128–35
[11] Das K, Ray S S, Chapple S and Wesley-Smith J 2013 Mechanical, thermal, and fire properties of biodegradable polylactide/boehmite alumina composites Ind. Eng. Chem. Res. 52 6083–91
[12] Kmetty A, Litauszki K and Reti D 2018 Characterization of different chemical blowing agents and their applicability to produce poly(lactic acid) foams by extrusion Appl. Sci. 8 1960
[13] Wang X, Jiang M, Zhou Z, Gou J and Hui D 2017 3D printing of polymer matrix composites: A review and prospective Composites, Part B 110 442–58
[14] Cataldi A, Rigotti D, Nguyen V D H and Pegoretti A 2018 Polyvinyl alcohol reinforced with crystalline nanocellulose for 3D printing application Mater. Today Commun. 15 236–44