Rheological properties of powder blend for extrusion of ceramic-polymer filament used in 3D printing

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Abstract. The article presents the results of comparative studies of the rheological properties of the ceramic polymer blend of polylactide (PLA) filled with 50 %vol alumina to evaluate the possibility of obtaining extruded filament for 3D printing.

Fused deposition modeling (FDM) is one of the cheapest and available layer-by-layer techniques in the additive manufacturing domain [1]. Being printed out, the objects are ready for work right away without further processing. Although polymers are the main materials the technology works with, the latest trends include ceramics as well in the list of prospective materials [2–4]. Today, several scientific groups are conducting research on obtaining ceramic objects by FDM through developing ceramic-polymer filaments [2–6]. There are various methods for making filament for 3D printing, such as single-screw extrusion, twin-screw extrusion, chemical solvent method, etc. Single-screw extrusion is one of the cost-effective methods of obtaining raw materials, which consists of an inexpensive extruder and a winding unit. The raw materials prepared by extrusion must have acceptable rheological properties to avoid obstructions in the nozzle causing and prevent defects during printing.

The current work aims to study the rheological properties of the polymer compositions based on PLA filled with ceramic powder and to establish their optimal processing temperature for extrusion during FDM.

The study objects in this work are commercially available PLA powder sized $d_{50}=35 \mu m$ and a ceramic-polymer blend of PLA and 50 %vol. alumina with particle size $d_{50}=38 \mu m$ mixed in 1:1 ratio volume.

Rheology tests were performed on a rotational rheometer MARS (Thermo Fisher Scientific Inc., USA) with a “plane-plane” working unit geometry (diameter 20 mm, 1 mm offset). According to the recommended temperature range for the materials, the measurements were taken in the range 200-220$^\circ C$ for the PLA and 200-240$^\circ C$ the PLA-alumina blend.

Testing conditions were the following:

1. Frequency dependence of the dynamic modulus components at a deformation amplitude of 1% (the deformation frequency was varied from 0.1 Hz to 100 Hz).

2. Creep tests at a constant load of 10, 100 and 500 Pa for an unfilled PLA with subsequent removal of the load (recovery stage).

3. Dependence of viscosity on shear rate (the shear rate range was increased stepwise from 0.001 to 10 $s^{-1}$ with holding at each stage for 30 s).
The study of the filled PLA showed that rheological properties differ markedly from those of the unfilled PLA. Table 1 and figure 1b present viscoelastic behavior of the filled PLA composition in the form of frequency dependences. In contrast to the unfilled PLA (figure 1a), the frequency curves intersect at 60 s⁻¹, above which elastic deformations predominate.

**Table 1. Viscoelastic behavior of the filled PLA.**

| Temperature, °C | $\tan \delta G'$ | $\tan \delta G''$ | $\omega_{crossover},$ s⁻¹ | $G_{crossover},$ Pa |
|----------------|------------------|------------------|---------------------|---------------------|
| 200            | 1.25             | 0.75             | 55                  | 114.2 × 10⁴         |
| 220            | 1.06             | 0.82             | 86                  | 94.3 × 10⁴          |
| 240            | 1.18             | 0.68             | 150                 | 108.3 × 10⁴         |

The crossover point at 200°C corresponds to modulus values $8.75 \times 10^4$ Pa, while for the unfilled PLA it was found to be $14.5 \times 10^4$ Pa. Above this value, the elastic component of the dynamic modulus prevails over the loss modulus, which indicates that the elasticity of the material becomes dominant.

Figure 2 shows graphs of the dependence of viscosity on shear stress for unfilled (a) and filled with 50 vol.% Al₂O₃ (b) polylactide at different temperatures.

As the temperature rises, the values of the modulus are expected to decrease, and the crossover point shifts to the region of higher angular frequencies. Moreover, under stationary shear conditions (figure 2b), the filled PLA behaves like a Newtonian liquid with a viscosity of $1.5 \times 10^4$ Pa·s at 200 °C, which is approximately 15 times higher than the viscosity of the unfilled sample. Such an increase in viscosity is due to the presence of a filler and the adsorption of polymer macromolecules on it.

To explain the dependence of viscosity on shear stress for both the unfilled and filled PLA at different temperatures, studies were additionally carried out using differential scanning calorimetry and thermogravimetric analysis. Thermogravimetric analysis was performed on a TGA/DSC3 + machine (Mettler Toledo, Switzerland) with an HSS2 sensor. The tests were carried out in a heating mode at a constant rate of 10 K/min, in the range from 25 to 1000 °C, in an air atmosphere, with a flow rate of 50 ml/min.

The results (figure 3) showed that the filler shifts the destruction temperature to higher temperatures (358°C compared to 320°C for the unfilled PLA).

The study of thermal transitions between the unfilled and filled PLA was carried out on a DSC3 + device (Mettler Toledo, Switzerland), with a liquid nitrogen cooling system, HSS9 + sensor. The
results showed that the filled sample noticeably differs in properties from the pure PLA: crystallinity is suppressed, and the glass transition temperature shifts to higher temperatures ($T_{\text{vit}} = 101-108^\circ\text{C}$).

![Figure 2](image1.png)

**Figure 2.** Shear stress versus viscosity plot for the unfilled (a) and filled (b) PLA at different temperatures.

![Figure 3](image2.png)

**Figure 3.** Thermogravimetric curve of the filled and unfilled PLA.

Overall, it was found that the rheological properties of the filled PLA are acceptable for the production of filament by extrusion. It behaves as a Newtonian viscoelastic liquid with viscosity much higher than that of unfilled PLA. This fact along with decreases angle coefficients of frequency dependencies of the elastic and loss modulus indicates the formation of a sufficiently strong structure in the composite. Further research will be aimed at increasing the content of the ceramic component in the mixture, obtaining filaments by extrusion and three-dimensional printing of products from them.

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