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Properties for PIM Feedstocks Used in Fused Filament Fabrication

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Abstract

Fused filament fabrication (FFF) is one of the most commonly used polymer-based additive manufacturing techniques. FFF could be used to shape parts with PIM feedstocks instead of injection moulding and after debinding and sintering obtain solid parts with complex geometry. Currently used PIM feedstocks do not necessarily meet the requirements of the majority of FFF machines available in the market, which rely on the use of flexible filaments. In this paper, the specific properties needed by the FFF feedstock materials are discussed. Different feedstocks with 316L steel powder at 55 vol.-% were characterized (viscosity and mechanical properties) and tested regarding the printability using a conventional FFF machine. Out of these experiments the most important requirements for printable PIM feedstocks are deduced.

Introduction

Thermoplastic-based Fused Filament Fabrication (FFF) is one of the most widely used additive manufacturing techniques in the world. The main reasons of its increasing popularity and use have been its reliability, safe and simple fabrication process, low cost and the availability of a variety of thermoplastic filaments [1].

In FFF, the printing material is heated until melts or softens and then it is extruded from a nozzle on a substrate to build a structure in a layer-by-layer manner. The extrudate solidifies when its temperature decreases due to air convection and heat conductivity to the previous layers [2]. Materials that can be processed by FFF must be melt-processable; that is they must flow when heated without applying any significant shear. Conventional FFF machines are basically ram extruders, with the ram being the printing material in the shape of a filament. The filament is first pulled by a driving wheel and then is pushed by the same wheel into a liquefier and a nozzle. Therefore, sufficient mechanical strength is required for the filament to retain its shape after being forced through the drive wheels, so it can transfer the force provided by these wheels forward into the liquefier. The force that is generated by the motors must be transferred to the filament via the wheels and then into the liquefier. This transfer of force can be altered by a number of factors. First, the motors must generate sufficient force. Next, the wheels must have enough friction with the filament to transfer the force from the wheels to the filament. At the same time, the filament must be strong enough to avoid shearing due to the friction from the wheels. Finally, the filament must not buckle between the drive wheels and the entrance to the liquefier. That is, the force transferred from the drive wheels to the filament should be efficiently transferred into the centre of the liquefier in the direction of the melt flow, with minimal loss due to filament buckling and compression [3]. In addition to these requirements the filament should also be flexible enough so that it can be spooled, that way the filament can be easily stored in a compact place and fed in a more or less continuous fashion into the liquefier.

Many unfilled or lightly filled thermoplastics fit all these mechanical requirements. Some examples of unfilled materials commercially available for FFF include: acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), acrylonitrile styrene acrylate (ASA), polyamide 12 (PA12), polycarbonate (PC), polyphenylsulfone (PPSU), polyetherimide (PEI) and some blends of the previously mentioned polymers [4]. Some examples of composite materials commercially available for FFF include: ABS reinforced with carbon fibres, PLA with stainless steel and iron powders [5] and PLA with copper, brass, bronze, bamboo fibres and recycled wood fibres [6]. Other materials used in FFF reported in the literature include: soft thermoplastic elastomers (STPE) [3]; nylon with 30 or 40 vol.-% iron particles [1]; ABS filled with copper or iron at fill rates from 10 to 40 wt.-% [7; 8]; and nylon filled with 5 to 10 vol.-% alumina powder [9]. All of the filled materials reported in the literature have a powder content below the level needed for the part to be sinterable, which is approximately (50 vol.-%). One of the reasons why the powder content reported in the literature remains below 50 vol.-% is that as the powder content increases, the filaments become very brittle and their melt viscosity increases substantially; therefore the mechanical properties of the filament required for ram extrusion are not met.

The aim of our research is to produce filaments for the manufacturing of solid metal parts with complex geometry, by a process called Shaping, Debinding and Sintering (SDS) (Figure 1). The shaping step can be done by injection moulding or by additive manufacturing techniques, like FFF. Debinding consists of the removal of the polymeric material that binds together the loose metallic powder during the shaping step. Debinding can be achieved thermally or by using solvents. And finally sintering is done to fuse together the loose powder and obtain a solid metallic part.

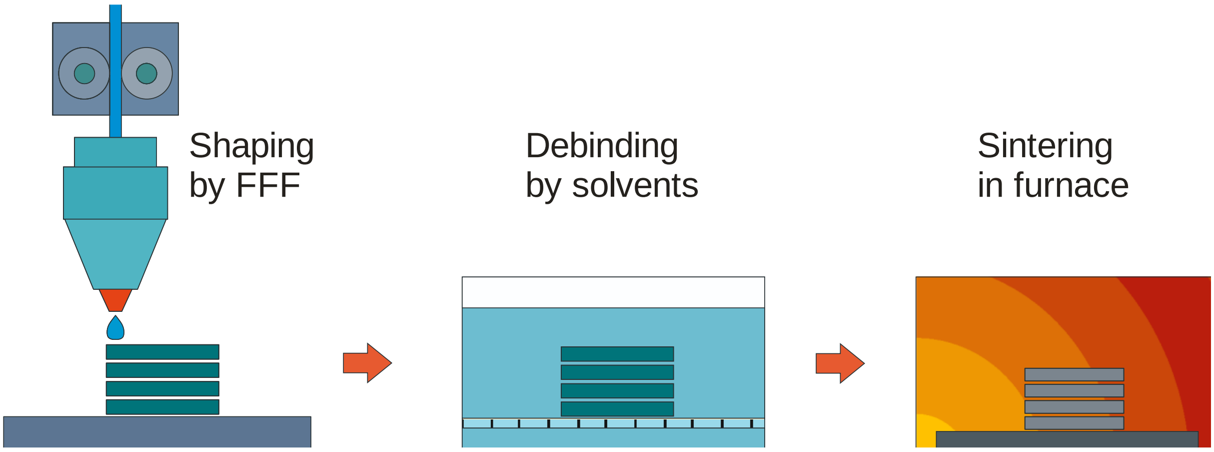

Figure 1. Schematic representation of the SDS process

In this article, two highly filled polymer systems with 55 vol.-% that are capable of being printed in conventional FFF machines are presented. The mechanical properties and viscosity of these printable highly filled composites are compared to other highly filled composites that are not printable, as well as to unfilled polymers that are printable.

Materials and Methods

As it is the case with feedstock material used in powder injection moulding, the feedstock material for FFF is composed of a polymeric binder system and filler particles. The binder system has three components: the main binder component, the backbone polymer and a compatibilizer. In this paper the main binder component was a type of soft and flexible Thermoplastic Elastomer- TPE (Kraiburg TPE GmbH & Co. KG, Germany). For the backbone three different types of polyolefins were used (Borealis AG, Austria and BYK Chemie GmbH, Germany). Two types of compatibilizers with different chemical composition were used (Merck Schuchardt OHG, Germany and BYK Chemie GmbH, Germany). The filler particles in these feedstock materials were 316L (Epson-Atmix Corporation, Japan). In total 4 feedstock materials were prepared. The exact composition of the feedstock will be kept confidential; however a qualitative description of the prepared feedstocks is shown in Table 1. In addition to feedstock materials, two commercially-available unfilled filaments were tested: Black ABS and Orange PLA (Prirevo, Wels, Austria).

Table 1. Description of materials prepared and investigated.

Material	Main binder	Backbone	Backbone content †	Compatibilizer	Filler powder at 55 vol.-%
Feedstock 1 (FS01)	TPE	Polyolefin 1	**	Type 1	316L
Feedstock 2 (FS02)	TPE	Polyolefin 2	**	Type 1	316L
Feedstock 3 (FS03)	TPE	Polyolefin 3	**	Type 2	316L
Feedstock 4 (FS04)	TPE	Polyolefin 3	***	Type 2	316L
Unfilled black ABS (ABS)	ABS	None	None	None	None
Unfilled orange PLA (PLA)	PLA	None	None	None	None

† Relative backbone content identified by number of *

Feedstocks were compounded in a kneader with counter rotating rollers (Plasti-Corder PL 2000, Brabender GmbH & Co. KG, Germany). Kneader temperature was 200 °C and the total kneading time was 30 minutes. After compounding the feedstocks were grinded in a cutting mill with a sieve with square perforations of 4 mm in length (Retsch SM200, Retsch GmbH, Germany).

Filaments were prepared using a high pressure capillary rheometer (Rheograph 2002, Göttfert Werkstoff-Prüfmaschinen GmbH, Germany). A round capillary with a diameter of 2 mm and length of 20 mm was used. Extrusion temperature was set at 185 °C and the piston speed was 0.5 mm/s. At the exit of the die a Teflon conveyor belt was placed to pull the filament as it was extruded. At the same time filaments were produced, the apparent viscosity was measured at the apparent shear rate of 113 s^{-1}. At least three repetitions were performed per filament.

The mechanical properties of filaments were tested in a material tensile testing machine with pneumatic grips (Zwick Z001 2.5 kN load cell, Zwick GmbH & Co. KG, Germany). The pneumatic pressure was 3 bar for feedstocks, 9 bar for PLA and 4 bar for ABS. Measurements were performed at 23 °C and 50 % r.h. Gauge length was set at 75 mm. In order to measure the apparent secant modulus an extension rate of 1 mm/min was used, afterwards the rate was increased to 10 mm/min until the sample broke to estimate the elongation at break. The apparent secant modulus was estimated between 0.05 % and 0.25 % extension. At least 5 repetitions were performed per type of filament.

Printing trials were performed on a HAGE 3Dp-A2 FFF machine at Hage Sondermaschinenbau GmbH & Co KG, Austria. Solvent debinding and sintering was performed at OBE GmbH & Co. KG, Germany. Solvent debinding was used to remove the main binder component (TPE) and the backbone component (Polyolefin) was removed thermally during the first stages of sintering. The actual processing parameters represent industrial knowhow, so they will be kept confidential in this paper.

Results and discussion

The material properties investigated are summarized in Figure 2. Three properties are shown in Figure 2, the apparent viscosity measured during filament preparation, the secant modulus and the strain at break for the filaments. These three properties may be able to provide enough information to determine if a filament is printable or not.

By looking at Figure 2, it can be seen that there is not a unique combination of these three properties (η, E, ε_{br}) that lead to printability. It can be seen that non-printable materials have a viscosity between 1900 and 840 Pa·s, modulus between 150 and 100 MPa, and strain at break around 10%. On the other hand, printable materials have viscosity between 2360 and 50 Pa·s, modulus between 2700 and 415 MPa, and strain at break between 50 and 3 %. What can be concluded is that in order to have printable filaments, they should have preferably a medium viscosity (~1000 Pa s) and medium to high secant modulus (400 to 2700 MPa). If filaments have high enough modulus then the viscosity could be high and the elongation at break low. This information may indicate that the strain at break is not so crucial if the filaments have high enough modulus, like is the case of ABS filaments.

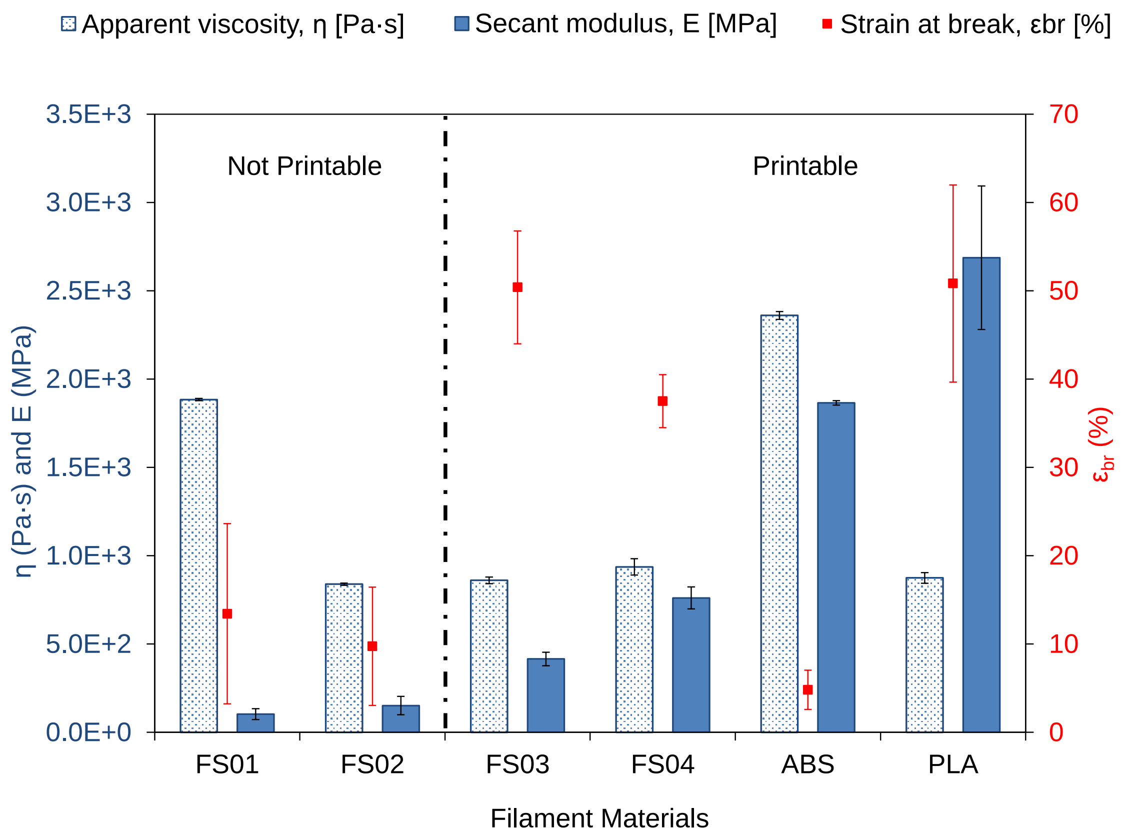

Figure 2. Viscosity and mechanical properties of printable and not printable filaments.

Figure 3a shows printed parts done with the highly filled filaments FS03 and FS04. Figure 3b, shows a green part printed by FFF and a finished part after solvent debinding and sintering. The linear shrinkage from printed part to sintered part is 15 %, which is in agreement with the amount of polymer that was removed (45 vol.-%). These parts are the first demonstrators printed with 316L stainless steel. In the future feedstock with other metals like NdFeB alloys will be investigated to print permanent magnets with complex geometry [10].

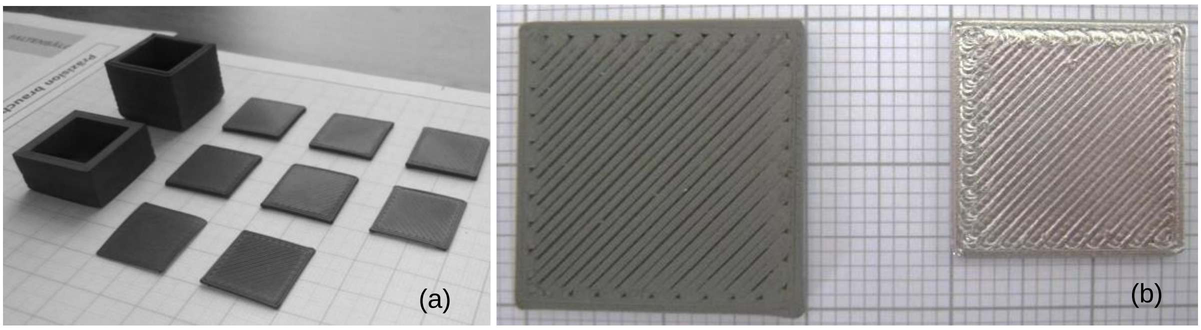

Figure 3. (a) Printed parts produced with feedstock materials FS03 and FS04; (b) greenpart shaped by FFF and final part after debinding and sintering.

Conclusions

Four distinct highly filled composite materials (feedstock) have been prepared with 55 vol.-% of 316L stainless steel. These feedstock materials were formed into filaments to be used in a traditional FFF machine. Two of them were non-printable, while two were printable. The viscosity and the mechanical properties of the filaments were measured and compared to unfilled commercial filaments of ABS and PLA. It was observed that in order to have printable filaments, they should have a medium viscosity (~1000 Pa·s), medium modulus (~800 MPa) and medium strain at break (~40 %). The strain at break is not so crucial if the filaments have high enough modulus and low viscosity. The printable feedstock materials were also capable of being debound and sintered to obtain solid parts of stainless steel with a linear shrinkage of approximately 15 %.

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