Influence of Glass Fibers on the Processability and Mechanical Properties of PP Homopolymer for Fused Filament Fabrication (FFF)

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Abstract. Polypropylene (PP) has been used very little as additive manufacturing material so far. Commercial filaments often consist of copolymers or blends and thus do not achieve the mechanical stability of PP homopolymers. Therefore, the topic of this work is the investigation of PP homopolymers and their glass fiber (GF) reinforced compounds regarding the processability in the fused filament fabrication (FFF) process and the mechanical properties of printed parts. A PP homopolymer was used as neat material and as compounds with 10 or 20 wt% of short or long GF. All materials were extruded into filaments and printed using FFF. The mechanical properties of the printed samples were compared to injection-molded ones. The study showed that filaments with a suitable mean diameter could be produced from all compounds. Good printability was demonstrated for neat PP and the short GF reinforced compounds. Concerning mechanical properties, an excellent welding quality of the neat material led to strength and stiffness in the range of the injection-molded reference. A slightly lower welding quality and the presence of pores in the GF reinforced parts resulted in lower mechanical values. Overall, the work showed a high potential of PP homopolymer compounds regarding processability and mechanical properties.

INTRODUCTION

Polypropylene (PP) is a versatile and abundant polymer and has many applications in various industries. Its advantages include chemical resistance, the ability to vary properties over a wide range and excellent price-performance ratio. In terms of processing, there are several possibilities to obtain products through injection molding, extrusion, blow-extrusion, or other well-known technologies.[1] However, when it comes to additive manufacturing, PP is not a well-established material. This is due to the high crystallinity of PP, which leads to severe material shrinkage during printing. In addition, PP is a non-polar material with no functional groups, resulting in low adhesion to most surfaces. Based on these properties, the print quality of PP, especially in the fused filament fabrication (FFF) process, has been low and other materials such as PLA or ABS have been preferred.[2] Nevertheless, the attractive properties of PP are driving the filament and 3D printing research for these polymers.

Currently, there are a handful of PP filaments on the market, usually based on blends or copolymers. On one hand, this can improve printability by reducing shrinkage. On the other hand, the mechanical and thermal properties suffer from the polymer modifications. In literature, some publications deal with filament extrusion and FFF printing of PP [2-10] and very few also investigate glass fiber (GF) reinforced PP[11, 12]. However, in general, the understanding of PP as

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a 3D printing material is still poor. Therefore, in this work a PP homopolymer with and without GF is investigated in terms of processability in filament extrusion and FFF and mechanical properties compared to injection-molded PP.

MATERIALS AND METHODS

The materials used were Lyondellbasell's PP homopolymer Moplen HF501 from and two different types of GF. The first type is a long fiber (L) grade from the company ECTA with an average fiber length of 3.5 mm and a diameter of 10 µm. The second is the short fiber (S) material MF7982 from Lanxess with an average length of 210 µm and a diameter of 14 µm. Both fibers were E-glass fibers with silane sizing.

Five compounds were produced from the raw materials using a Coperion ZSK26 twin-screw extruder with a temperature profile of 160 °C (first heating zone) to 210 °C (die) and a screw speed of 300 rpm:

- Neat PP (PP-Neat)
- PP+10wt% short GF (PP-10S)
- PP+20wt% short GF (PP-20S)
- PP+10wt% long GF (PP-10L)
- PP+20wt% long GF (PP-20L)

The compounds were used for a filament extrusion process on a Collin filament extrusion line, containing a single-screw extruder with a 3 mm nozzle, a cooling bath, a laser-based measurement of the filament diameter, a pulling and a winding unit. The extruder temperature and the pulling speed were adjusted to achieve a filament diameter of 1.75 mm. In the next step, the filaments were printed using a Raise 3D Pro2 printer. A general investigation of the printability of the different filaments was performed. Several printing parameters were adjusted to achieve good print quality. For mechanical characterization, tensile bars were printed with an infill amount of 100% and an infill pattern of lines with ±45° direction. The five materials were not only printed but also injection molded to compare these samples with the printed ones. The injection molding was done on an Arburg 470 H100-170 using a die temperature of 210 °C, a mold temperature of 30 °C, an injection speed of 50 cm^3/s and a pressure of 1200 bar.

The properties of the compounds were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was done at a Netzsch 209 F1 Libra at a heating rate of 10 °C/min up to a temperature of 1000°C in a nitrogen atmosphere to determine the GF content. DSC was measured using a Mettler Toledo DSC 1 between -25 and 225 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. Melting points, as well as crystallinity, were determined. In addition, fiber length analysis was done for both the as-received fibers and the fibers after compounding. After pyrolysis of the compounds at 650 °C, the fibers were dispersed in a solution of 1 l water, 0.15 ml silane, 0.4 ml glycerin and 0.15 ml acetic acid. Microscopic images were taken, and the fiber length was analyzed via ImageJ. The filaments were characterized in terms of diameter and ovality using laser gauge. Porosity and roughness were also evaluated. Tensile properties were measured according to DIN ISO 527 at a Zwick universal testing machine. The injection-molded bars had standard 1A geometry. For the printed bars, shortened bars with a measuring length of 80 mm and the standard cross-section were used. The preliminary tests showed that the results of both bars are comparable. Testing speed was 1 mm/min to determine Young's modulus and 50 mm/min afterward. The fracture surfaces were investigated by scanning electron microscopy (SEM) on a Zeiss Ultra plus SEM.

RESULTS AND DISCUSSION

Compound Properties

The properties of the five compounds are given in Table 1. Compounding was successful and the fiber amounts of 10 and 20 wt% were achieved. The fiber length was reduced around 8% during processing from 210 µm to 192 µm for the short fibers. A higher decrease of 83% fiber length was seen for the long fibers from 3500 µm to 608 µm. The fiber length of compounds with 10 and 20 wt% was in the same range. The GF did not significantly influence the melting temperature and degree of crystallinity. They were 165 ± 2°C and 43 ± 1%, respectively.

TABLE 1. Properties of the different compounds.

Compound	Amount GF / wt%	Amount GF / vol%	Fiber length / µm	Tm / °C	Crystallinity / %
PP-Neat	0	0	-	167.3 ± 0.7	43.1 ± 1.2
PP-10S	10.6	3.9	193 ± 96	166.3 ± 0.3	42.9 ± 2.7
PP-20S	20.1	8.0	192 ± 88	165.6 ± 1.2	42.3 ± 0.2
PP-10L	9.6	3.5	605 ± 345	164.2 ± 1.1	42.6 ± 2.1
PP-20L	19.8	7.9	642 ± 400	163.6 ± 0.1	44.2 ± 0.2

Filament properties

Filament extrusion was done with all compounds. The parameters were adjusted to produce filaments with an average diameter of 1.75 mm. The extruder speed and filament pulling speed were equal for all compounds with 50 rpm and 12-12.5 m/min. Different temperature profiles were tested to achieve suitable filament properties. PP-Neat and short fiber reinforced PP could be processed with barrel and die temperatures of 190-195°C. For the long fiber reinforced grades, higher temperatures of 200-205°C were necessary due to higher viscosity. The filament properties are given in Table 2. The average aim diameter of 1.75 ± 0.1 mm was achieved with all materials. However, there is some ovality for all filaments (value 0 would be perfectly round) that is getting more severe for the long fiber reinforced grades. Furthermore, the porosity and shape were investigated. PP-Neat showed a very smooth surface, while porosity was an issue. Large pores could be detected in the middle of the filament resulting from fast cooling and shrinkage of the filament. Only smaller and noticeably fewer pores were observed for the reinforced filaments. The high modulus of the fibers reduced shrinkage and therefore pores. However, those filaments had a rough surface. Again, the issues were higher with long fibers. As the average length of these fibers is around 35% of the filament diameter and some fibers are even longer, the arrangement of the fibers inside the filament is crtical. Especially the stretching from 3 mm at the die to the final diameter of 1.75 mm causes the penetration of the initially smooth surface by GF.

These trials were the first ones to show the feasibility of filament extrusion. In the future, a systematic study is aimed to further improve the filament quality.

TABLE 2. Properties of the different filaments.

Filament material	Diameter	Ovality	Porosity and shape
PP-Neat	1.74 ± 0.05	1.19 ± 0.71	Smooth surface, high porosity
PP-10S	1.69 ± 0.05	1.49 ± 0.85	Slight roughness, low porosity
PP-20S	1.72 ± 0.06	1.30 ± 0.79	Slight roughness, low porosity
PP-10L	1.74 ± 0.11	2.05 ± 1.39	Severe roughness, low porosity
PP-20L	1.77 ± 0.12	1.97 ± 1.59	Severe roughness, low porosity

Part properties

Printing trials were carried out with the produced filaments. It was shown that PP-Neat, as well as the short fiber filaments PP-10S and PP-20S, could be printed successfully. The printing speed was 45 mm/s, the bed temperature 110 °C and the nozzle temperature 210 °C. A layer thickness of 0.25 mm was used. The long fiber filaments PP-10L and PP-20L could not be continuously conveyed through the Bowden tube because of their high roughness and ovality.

The properties of the printed tensile bars of PP-Neat, PP-10S and PP-20S were compared with injection-molded samples of the same material. The results are given in Fig. 1. Additionally, in Fig. 2, the fracture surfaces of the tensile bars are shown to identify the difference in fracture behavior. It can be seen that Young's modulus increased with higher amounts of GF. For injection-molded samples, an increase of 128% was reached, while the increase was only 41% with printed samples. One possible reason is that the fiber orientation in printed tensile bars is ±45° for almost every fiber. In injection molding, the amount of fibers in tensile direction was higher to reinforce the PP matrix more

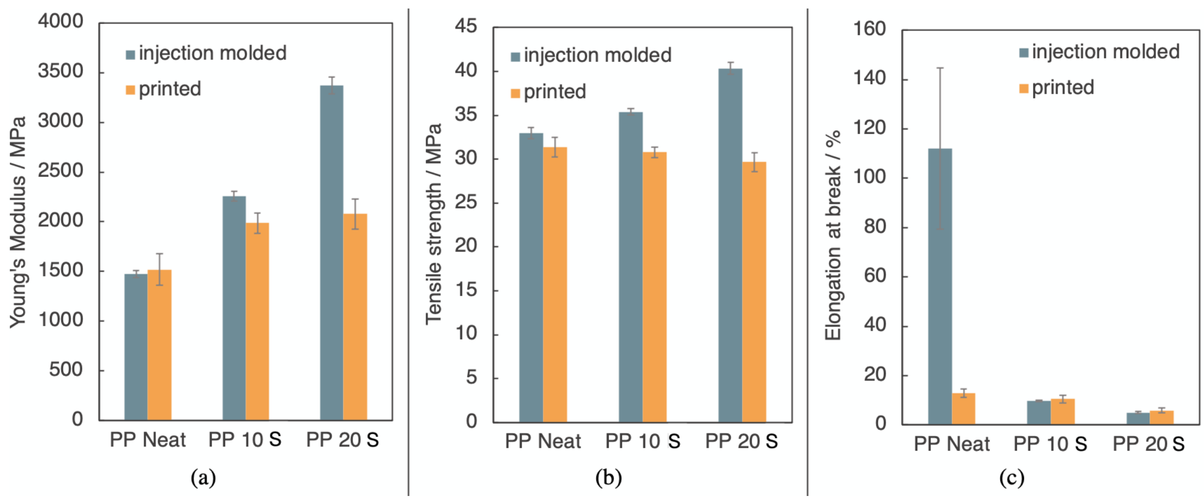

FIGURE 1. Results of tensile tests for injection molded and printed samples. (a) Young's modulus, (b) tensile strength, (c) elongation at break.

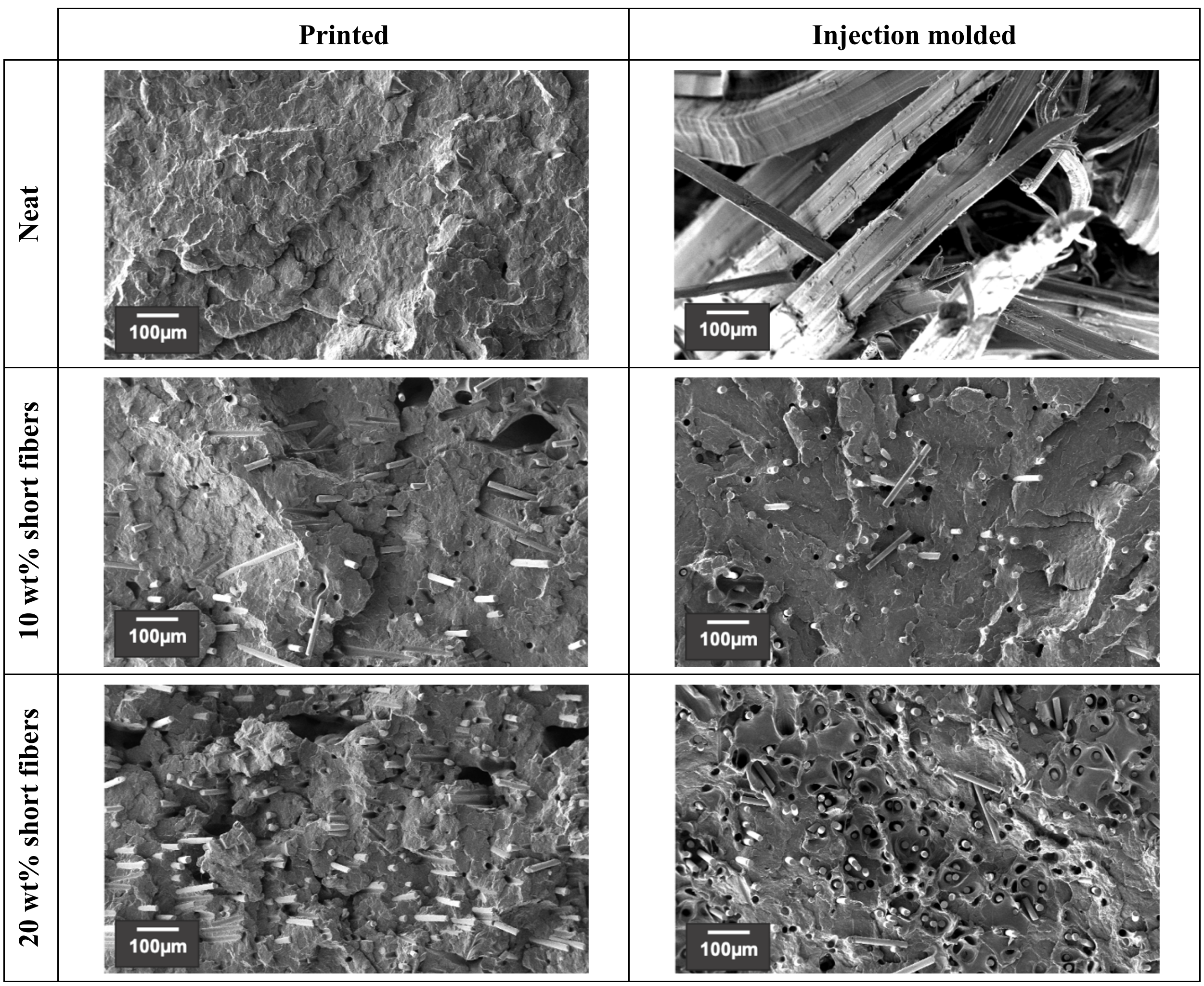

FIGURE 2. SEM of the fracture surface of printed tensile bars in comparison to injection molded ones.

efficiently. Looking at the tensile strength, an increase of up to 22% for injection molded bars was visible. In contrast, a decrease of 10% in tensile strength was observed in printed samples, which was mainly caused by pores between single strands or layers. A remarkable result was the excellent printing quality of PP-Neat with a very few pores. This led to a similar value in modulus and strength for printed and injection molded PP-Neat. As all materials were printed with 210 °C nozzle temperature, the flowability of PP-Neat was higher than of GF reinforced PP. Therefore PP-neat tensile bars showed a significantly lower porosity and better welding than the PP-10S and PP-20S samples.

The investigation of elongation at break showed that ductile deformation did only happen for injection-molded PP-Neat. The elongation at break of printed PP was 89% lower in comparison. Possible reasons include pre-orientation of the chains during printing, leading to a lower deformation capability, or changes in crystallinity. This needs to be investigated in more detail. All fiber-reinforced materials showed an elongation at break of 5-12%, which is due to limited deformation by the fibers. The values of the injection molded samples and the printed samples were similar, although the printed parts suffered from porosity.

CONCLUSION

This work investigated the influence of different GF types and amounts on the processability of PP homopolymer in the FFF process chain and the resulting mechanical properties compared to injection molded samples. Two GF types were used, which had a length of about 200 µm (short fibers) and about 600 µm (long fibers) after compounding. The fibers were used in amounts of 10 and 20 wt%. It was shown that suitable filament quality and a diameter of 1.75 ± 0.1 mm were achieved with PP-Neat and short fiber reinforced PP. Long fibers caused excessive roughness of the filament and therefore continuous printing was not possible. The print quality of PP-Neat was very good and resulted in comparable stiffness and strength to injection-molded samples. In the case of the fiber-reinforced materials, lower mechanical values were obtained in the printed parts due to porosity, lower welding quality and less favorable fiber orientation. In terms of porosity and welding an increase of printing temperature could guide to an improvement. In the future, a detailed investigation of the influence of the processing parameters is required to improve the quality of the filament and the parts.

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