Processing of Polypropylene by Material Extrusion Additive Manufacturing

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ABSTRACT

Material extrusion additive manufacturing, also known as fused deposition modeling (FDM™) or fused filament fabrication (FFF), is one of the simplest and most economical additive manufacturing technologies. The feedstocks used in FFF are filaments, and numerous thermoplastic filaments are commercially available. However, polypropylene (PP) was only recently added to the list, due to some difficulties encountered during FFF. Polypropylene is a semi-crystalline thermoplastic, which undergoes a drastic volume contraction when cooling down from the printing temperature; this contraction can lead to detachment from the build platform and warpage of the printed specimen. To prevent detachment from the build platform, appropriate surfaces and processing conditions are needed. On the other hand, to prevent warpage, the reduction of the crystallinity and the preparation of blends, copolymers, or particulate composites can be used.

Keywords: polypropylene, additive manufacturing, extrusion, filament, composite

1 INTRODUCTION

Additive manufacturing (AM) has come to revolutionize the way products are made. New complex geometries in small batches are possible to be produced by AM. According to ISO/ASTM 59000, there are seven types of AM categories. Three categories can be used to shape thermoplastic materials, Material Extrusion (MEX), Powder Bed Fusion (PBF) and Material Jetting (MJT). Among these three categories, MEX is one of the most utilized since the equipment and the feedstock materials are inexpensive. Other common names of MEX include fused deposition modelling (FDM™), fused layer modelling (FLM), and fused filament fabrication (FFF).

MEX consists of selectively dispensing material through an orifice in the shape of continuous strands that are deposited adjacent to each other to form a layer of a three-dimensional object [1]. The most common feedstock materials for MEX are thermoplastic filaments. Still, a similar principle can be used to extrude molten thermoplastic pellets, slurries or viscous resins [2].

Numerous thermoplastic filaments commercially available have been successfully processed via MEX, including polypropylene (PP). PP is a versatile commodity plastic with good mechanical properties, recyclability, good chemical resistance and inertness. Therefore, producing parts of PP by MEX is attractive for many professional and hobby users. Examples of possible applications for PP specimens shaped by MEX include microreactors for the medical and chemical industry [3], custom-made chemical-resistant laboratory tools [4], orthoses [5] and implants [6]. However, MEX-processing of PP can be challenging [7]. In this paper, some recommendations are provided to prevent warpage and improve the dimensional stability of PP parts produced by MEX.

2 PP ISSUES IN MEX

2.1 Filament Production

PP is usually melt processed by extrusion into sheets, films, pipes and fibres. Therefore, producing high-quality filaments usable in MEX machines is not a big problem. The low water absorption of PP means there is no need to pre-dry pellets before extrusion. PP filaments for MEX can be produced using single-screw extruders and the corresponding downstream equipment, which include a haul-off unit, cooling device, measuring device to monitor filament dimensions and a winding unit [8]. It is crucial to monitor and actively control the dimensions and ovality of the filament to prevent flow variations during the extrusion process in a MEX machine, which can lead to porosity, rough surfaces or dimensional variations [1].

2.2 Build Platform Adhesion

After the filament is prepared, the first challenge to process PP in MEX is to select a suitable build platform. It was observed that PP does not adhere to traditional build platform materials such as glass or polyimide films. This lack of adhesion occurs since PP lacks surface functional groups and has a low polarity and low surface energy. The most common way to ensure adhesion is to use a PP surface, but this can lead to welding to the building surface, leading to damage when removing the part from the build platform. One possible way is to use ultra-high molecular weight polyethylene (UHMWPE) as a build platform, increase the platform temperature to 80 °C and the extrusion temperature to 230 °C. The interfacial tension can be decreased to provide a stronger adhesion during printing, but not welding, using this approach. However, to avoid premature detachment from the build platform due to shrinkage upon cooling, a rough UHMWPE surface is preferred to increase mechanical interlocking [9].

Nowadays, there are also commercial material plates with undisclosed compositions that provide sufficient adhesion. The recommendation is to print the first layer at 80 °C, then cool down the build platform to room temperature to build the successive layers. Finally, to remove the printed part, it is recommended to heat up the build platform between 100 and 110 °C to be able to easily remove the part. This is because adhesion between the deposited filament and the build platform is greatly dependent on temperature, as has been reported in the literature [10].

Additional structures may be needed to ensure proper adhesion to the build platform depending on the specimen geometry and orientation on the build platform. Brims are examples of these structures. Brims are additional layers of material that extend beyond the perimeter of the printed specimen to increase the area in contact with the build platform [1]. This additional material prevents detachment from the platform and provides stability, as thin parts are built up in the vertical direction, shown in Figure 1 for a curved PP specimen and a wipe tower.

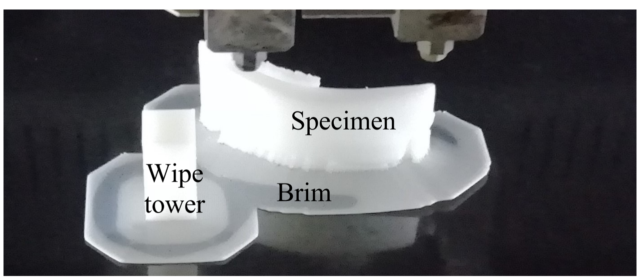

Figure 1: Brim to enhance adhesion to the build platform.

2.3 Shrinkage and Warpage

During MEX, thermoplastic materials are heated up to a temperature where they can flow, extruded, and be deposited as strands. When the polymer solidifies after extrusion, the volume of the polymeric sample, including the free volume between the polymeric chains and their vibrational volume, decreases as long as the temperature is above the glass transition temperature (T_g). The molecular rearrangement results in material shrinkage, which is different for amorphous and semicrystalline polymers. Amorphous polymers like ABS exhibit a linear weakly developed decrease of specific volume until its T_g is surpassed during cooling. Semicrystalline polymers like PP, however, reveal a drastic change in specific volume in the crystallisation region (T_c), as the formed crystalline structures are significantly denser than the amorphous structures in the melt state. The higher the degree of crystallinity is, the higher is the shrinkage. This drastic shrinkage complicates the MEX processing of semicrystalline thermoplastics, since warpage can occur [7].

Warpage occurs when a specimen shrinks differently at various positions. There is an anisotropic strand deposition during the MEX process when laying the perimeter and the infill of each layer. Polymeric chains are oriented in the extrusion direction that is constantly changing, and the thermal loading severely fluctuates depending on the position of the strand in the specimen. The thermal gradient during MEX varies for each strand because the polymer is extruded above its melting temperature and deposited on a build platform at a lower temperature. The heat of the extruded material is transferred to the build platform and the previously deposited strands. The previously deposited strands are reheated before they can cool down to the ambient temperature. The reheating leads to recrystallization, even when the temperature is below T_c, a phenomenon referred to as cold crystallization. All these crystalization and recrystallization processes lead to the release and accumulation of thermal stresses. The highest accumulation of stresses generally occurs at the first layers since they are the farthest from the extruder, and due to the poor thermal conductivity of polymers, they cannot be reheated to a temperature where the stresses can be released [11]. These stresses can eventually detach the specimen from the build platform or severely warp the printed specimen (Figure 2).

Figure 2: Warpage and detachment of PP during MEX.

The MEX process has many parameters that can be adjusted. The selection of the appropriate MEX parameters is crucial to prevent warpage and obtain good mechanical properties with PP. The first step is to design geometries that are less prone to warpage. For example, dense cylindrical specimens warp less than cubic specimens. Cubic specimens warp considerably at the corners due to strong contractile force pulling toward the cube's center. Also, thin-walled hollow specimens tend to warp more compared to dense specimens regardless if they were cubes or cylinders. These deformations have been attributed to the higher residual stresses in the hollow parts due to higher cooling rates [12]. Therefore, designing specimens with round corners and not completely hollow can help reduce the warpage of PP specimens. However, more important is the temperature gradient between the deposited strands and the surrounding environment. Thus, using a lower nozzle temperature, higher deposition speeds, depositing short stacking lengths, and increasing the layer thickness can help minimize PP specimens' warpage [13, 14].

3 PP MODIFICATIONS FOR MEX

It is essential to mention that sometimes adjusting the MEX processing parameters is not enough to obtain specimens with good dimensional stability and mechanical performance; therefore, researchers have modified PP by making copolymers, blends or particulate composites.

3.1 Co-polymers and Blends

Reducing the crystallinity of PP can be accomplished at the molecular level by changing the molecular mass or incorporating co-monomers [7]. For example, adding ethylene monomers can lead to very soft PP, while adding cyclic olefins can increase the stiffness of PP by internal cross-linking. Many of the commercially available filaments are based on random ethylene-propylene copolymers. Depending on the amount of copolymer added, the degree of crystallinity and observed warpage are reduced. However, filaments could become highly flexible to the extent that they cannot be extruded in filament-based MEX machines. Also, ethylene co-monomers lower the heat deflection and melt temperatures; therefore, limiting their applications compared to PP homopolymers [15].

Another way to reduce the crystallinity of PP is to blend it with amorphous polyolefins, hydrocarbon resins, UHMWPE, and polyamide. Blending can be done by melt compounding or directly at reactors leading to nanostructured blends. Blending has been shown to reduce warpage, increase the interlayer adhesion and improve the mechanical properties compared to PP homopolymers [15].

3.2 Particulate Composites

In recent years, numerous studies have investigated incorporating particles into PP to improve different properties of feedstocks for MEX. Fillers affect the rheological, mechanical, and thermal properties of PP. Therefore, they affect the dimensional stability of MEX-produced specimens. Examples of fillers investigated include mineral fibres, glass fibres and bubbles, talc particles, cellulose nanofibrils, hemp fibres, volcanic ash particles, harekeke fibres and rice husk [7, 16, 17].

One beneficial aspect for increasing the dimensional stability of MEX-produced specimens is that fillers can decrease the crystallization rate, and it has been observed that a slower crystallization rate leads to reduced warpage [18]. Fillers also hinder volumetric changes due to temperature changes and therefore reduce shrinkage and warpage [19] (Figure 3).

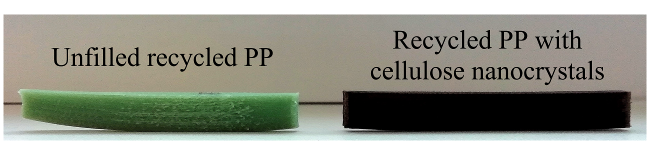

Figure 2: Warpage reduction due to fillers in recycled PP

The content of fillers also affects the warpage. It was observed with numerous fillers that as the content increases the warpage is reduced, as long as the particles can be homogeneously distributed in the matrix [7]. Once fillers agglomerated, the warpage increased, and the mechanical properties decreased [20].

The proper distribution of fillers in PP depends on the surface chemistry of the particles and the processing methods used to prepare the composites; therefore, care should be taken to ensure the right chemistry is on the particle's surface or in the PP. For example, using a small fraction of maleic anhydride grafted PP in a heterophasic PP copolymer was observed to help disperse volcanic ash, glass spheres, mineral fibres, cellulose and carbon fibres [7, 8, 19]. Equally important is the use of compounding equipment that provides enough dispersive and distributing mixing. Examples of such equipment are internal mixers (a.k.a kneaders) and co-rotating twin-screw extruders. Finally, the selection of the processing conditions should be taken care of to prevent damage to the fillers, such as fibre length reduction and breakage of glass bubbles, because shape and size affect the rheological, mechanical and warpage behaviour of PP compounds [19, 21, 22].

4 CONCLUSIONS

Polypropylene (PP) is a very versatile thermoplastic with numerous applications. Further applications could be found for PP in combination with additive manufacturing technologies, such as material extrusion (MEX). The semicrystalline nature of PP can lead to poor dimensional stability during MEX processing. Strategies for improving the dimensional stability of PP specimens produced by MEX include selecting appropriate processing parameters and modifying PP by making copolymers, blends, or particulate composites.

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