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Material and process optimisation for 3D printing of polypropylene-based compounds

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Introduction

Among all the 3D printing techniques for polymers, Fused Deposition Modelling (FDM) is the most used and the most developed in the global production system. Frequently, the limiting factor for additive manufacturing is the poor variety of available materials [1]. The main issue is that there is still the absence of a deep knowledge of the specific properties that a material should have to be 3D printable.

The driving force of this work has been to develop a deeper knowledge about polypropylene (PP), one of the most studied and commercialised polymers in the world, focusing on the features that it must have to be suitable for FDM. The reasons why pure PP is difficult to process with FDM technology and must be modified with other polymers and/or fillers are directly connected with its volumetric shrinkage and inadequate rheological behaviour.

Volumetric shrinkage and the severe warpage that it can induce on the printed object are well-known and studied problems of all semi-crystalline thermoplastics, and most of all of PP. In order to decrease crystallinity and, hence, minimize volumetric shrinkage related problems PP can easily and successfully blended or copolymerised with other polymers, [2].

Concerning rheology, deeply understand the rheological characteristics of a polymer is mandatory for assessing its processability through FDM. First of all, pure PP has a typical Newtonian behaviour at low shear rates, with a well-developed plateau reaching the zero-frequency value. This is a problem when this condition occurs in the process, e.g. during the not printing extruder movements or when it temporarily stops, so that the absence of a yield stress behaviour cause material oozing. Another zero-shear condition is when the material is deposited. In this case, a high value of yield stress together with a strong shear thinning behaviour would assure the material to maintain its shape without drooping [3].

In the first part of this work different grades of PP and PP-based compounds have been studied, investigating their thermal and rheological properties related to FDM. In the second part, three different fillers have been added to PP in order to assess the morphology and the mechanical properties of 3D printed specimen. PP COPO 12 (ISPLEN PB 170 G2M - MFI=12) has been melt-compounded with 30 wt% of Talc HTP1 grade (IMI Fabi Spa), 30 wt% of Calcium Carbonate OMYACARB 1T-AV grade (OMYA) and 3 wt% of a nano-filler, Cloisite 20 (BYK), in a co-rotating twin-screw extruder Process 11 (Thermo Fisher Scientific). Next 1.0 Advanced filament making machine (3Devo) has been used to produce a filament with a nominal diameter of 1.75 mm in order to feed Roboze One 3D printer.

Results and discussion

In order to have a screening of rheological behaviour of different PP grades, characterized by different MFI or by the presence of another polymer or a filler, viscosity curves at 260°C (set as 3D printer extruder temperature) of all selected material were obtained (Figure 1). As far as unfilled PP materials is concerned, PP HOMO 12 (ISPLEN PP 070 G2M) shows a typical homopolymer-like behaviour, with a Newtonian plateau in the low frequency range, which evolves in a shear thinning behaviour as the frequency increases. As expected, PP HOMO 0.3 (PP PPH 1060), characterized by a lower MFI, exhibits higher viscosity values than PP HOMO 12 and a more evident shear thinning behaviour.

The introduction of talc particles significantly modifies the rheological behaviour of PP; in fact, PP HOMO TALC (Axtroplen TC4 - 40 wt%Talc) does not show the Newtonian plateau at low frequencies, and a well-pronounced yield stress can be observed in the low frequency range. This behaviour can be attributed to the establishment of strong interactions between PP chains and the well-dispersed talc particles. The presence of a second polymer in the matrix (PP COPO 12) leads to the appearance of a yield stress behaviour in the low frequency range. Finally, coupling the talc and the second polymer effects, PP COPO TALC (PP COPO 12 + 20 wt%Talc compounded with co-rotating twin-screw extruder LEISTRITZ ZSE 18 HP) a pronounced yield stress at low frequencies is obtained, followed by a shear thinning behaviour.

Differential Scanning Calorimetry (DSC) analyses have been performed to evaluate the Melting Enthalpy (ΔH_m), which is correlated with the volumetric shrinkage of the material. The effect on ΔH_m of adding talc is the most evident result. In fact, the introduction of the fillers causes a reduction of the shrinkage of the material. It has been found that the two formulations with the inorganic filler have the lowest ΔH_m. By adding talc to PP COPO 12, ΔH_m

value decreases by 23% with respect to that of the neat polymer.

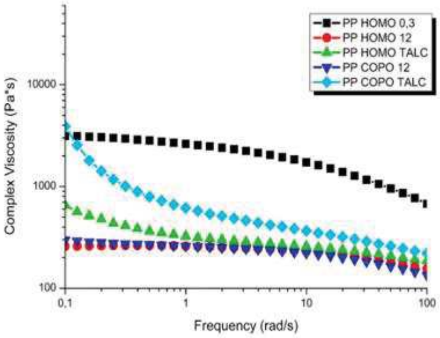

Figure 1 – Rheological analysis (260°C) of different PP grades.

After evaluating the characteristics that PP must have to be 3D printed, three composites containing different inorganic fillers have been produced. Due to its rheological behaviour characterized by the presence of yield stress in the low frequency range, PP COPO 12 has been chosen as a matrix for the composites.

Rheological analysis demonstrated a yield stress behaviour for all systems, with different values of viscosity and yield stress depending on the type and aspect ratio of the fillers.

DSC characterization shown a decrease in ΔH_m of all composites compared to neat PP COPO 12. Among the considered formulations, the system containing 30wt.% of Calcium Carbonate showed the highest decrease of ΔH_m value compared to PP COPO 12 (-27%) whereas for the materials containing 30 wt% of Talc and 3 wt% of nano-filler ΔH_m decrease by 20 and 4%, respectively.

Filament fabrication is a fundamental step for 3D printing, that is a continuous process that cannot undergo interruptions due to, for example, an irregularity in the filament. A filament suitable for FDM must have the following characteristics: constant diameter equal to 1.75 mm; round shape; smooth surface with low roughness. In order to optimize the processing conditions for achieving a regular filament, the filament fabrication has gone through a series of steps that involved the change of the three main parameters of the filament extruder: temperature profile, screw speed and percentage of cooling operation of the fans. Before proceeding with the 3D printing process, the filaments were analysed using SEM images.

As for the filament making, parameters optimisation trials have been carried out for 3D printing process. The parameters were chosen after observing the printed parts by evaluating compliance with geometric tolerances, the ability to reproduce details and the presence of distortions or defects. In Figure 2 details from bottom, top and section part of the 3D printed specimen (ISO 527A-5A) are reported. Printing quality increases from the bottom to the top part. In the lower part the layers are clearly visible, probably because of the rapid solidification of the first layers deposited on the raft. At variance, the top layers are deposited on layers at a higher temperature and therefore the spaces between the adjacent filaments are filled. It is possible to notice the detachment of the outermost perimeter from the innermost one. This defect was resolved by proceeding from the bottom upwards until reaching the last layer which is completely full.

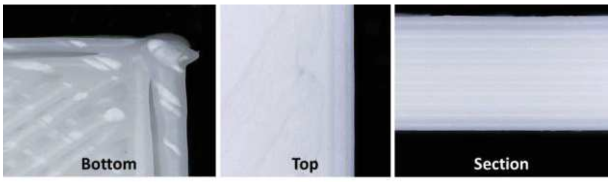

Figure 2 – Optical micrographs of PP+30 wt% Calcium Carbonate specimen for tensile tests.

The tensile behaviour is clearly influenced by the type of embedded filler. In particular, the mechanical tests carried out on PP+30 wt% Talc revealed the highest elastic modulus value (1387±77 MPa). PP+30 wt% Calcium Carbonate showed the highest value of elongation at break (49±20 %). PP+3 wt% Cloisite 20 finally presents the highest maximum tensile stress value (21±0.4 MPa).

Conclusions

PP-based compounds suitable for FDM technique have been formulated and optimised. The main features affecting FDM processability have been identified and their achievement has been investigated through thermal and rheological analysis. Furthermore, the right parameters of the filament making and 3D printing processes have been optimised.

To overcome the high volumetric shrinkage of PP, the enthalpy of the material must be minimized. A successful solution is the addition of an inorganic filler. A non-Newtonian behaviour at low shear rates, showing a strong shear thinning effect, and a yield stress behaviour at low frequencies are fundamental at the temperature used in the FDM technique. Once again, the presence of inorganic filler has been found to be a good solution.

It is therefore possible to 3D print PP-based composites with talc, calcium carbonate and nano-filler Cloisite 20. Mechanical tests showed that it is possible to obtain 3D printed materials both characterized by a high stiffness and with an appreciable elongation at break.

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