

PP in 3D Printing – Technical and Economic Aspects

IONEL DANUT SAVU¹, SORIN VASILE SAVU¹, DALIA SIMION¹, NICUȘOR-ALIN SÎRBU^{2*},
MIRELA CIORNEI³, SORIN AUREL RATIU^{4*}

¹University of Craiova, 13th A.I. Cuza Str., 200585, Craiova, Romania

²NRDI for Welding and Material Testing, 30th Mihai Viteazu Str., 300222, Timișoara, Romania, ISIM Timișoara,

³Territorial Labor Inspectorate of MH / Inspectoratul Teritorial de Muncă MH, 3rd Carol I Str., 220099, Drobeta Tr. Severin, România

⁴Polytechnic University of Timisoara, Faculty Engineering of Hunedoara, 5 Revolutiei Str., Hunedoara, 331128, Romania

FDM is 3D printing technology using mainly PLA and ABS as filament materials. PP has close characteristics to PLA and, due to that, is a potential material for for deposition. Paper aims to analyse the behaviour of PP during heating cycle specific to 3D printing process. Macroscopic and microscopic analysis of the deposited strings have been performed. They revealed less stiffness of the PP deposition comparing to PLA, which is due to the lower viscosity of PP. DSC Thermal analysis has been done at it revealed a 30% higher heat flux in PP comparing to PLA and that increases its fluidity. It was recorded a difference between the elongation viscosity of the PP filament and the PP deposited by FDM process. After 5s the deposited PP proves higher values for the elongation viscosity. Dynamic shear rheology measurements the was applied on samples deformed under 210 kN at 190°C. It has been found that the PP requires lower storage energy and that means that it has a lower viscosity for the entire range of applied frequencies. In the same time, the complex viscosities prove different behavior. To improve the control of the deposition shape, it is necessary to reduce the extrusion temperature with 4-5%. That leads to economy in power consumption.

Keywords: PP filament, DSC analysis, dynamic shear rheology measurement, storage modulus, complex viscosity, elongation viscosity

FDM 3D printing is technology often applied for rapid erection of different types of products, from prototypes (single primary product) to production (not mass, but limited) [1- 4]. The named technology uses polymers or metals, in different shapes (filament, powder, pool, etc.), to generate layer over layer until the shape and the dimensions of the piece to be produced are reached [2-4]. The additive process is, generally, regulated by EN ISO/ASTM 52900:

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3D technology is continuously finding new application in various domains and the literature of the last decade gave the measure of the 3D technology's importance [2, 5 6]. Zapciu [7] reported the design and prototyping of several 3D-printable mechanisms which are designed to be pneumatically actuated, as a potentially cheaper and more widely accessible alternative to existing solutions. He produced the prototypes from thermoplastic materials using Fused Deposition Modeling (FDM). Motomanca [8] concluded that the 3D scanning permits the fabrication of digital which can be lately 3D-printed. The 3D printing allows rapid fabrication of duplicates starting from a prototype with acceptable size accuracy. The results of Fabian [9] showed that the MED610 biocompatible material is a good choice for 3D printing of specific medical devices dedicated to surgery. The method which he applied brought added value to the secondary cleft surgery, by increasing the volumetric precision of the bone-graft and, more, the increasing of its density. Tarnita [5] used the 3D technology and high-performance composite powder to produce physical prototypes of orthopaedic implants and complex functional prosthetic systems. She applied the prototypes in „in vitro” experimental tests, obtaining important improvements in prosthetics.

In parallel with the development of new applications, research on the improvements of the materials to be added has been conducted. The most used consumables are ABS and PLA, but PETG, PP, Nylon, Carbon fiber, ASA and even PE cpuld be used. Dimonie [10] considers that starch presents good potential to be used in polymer technology, and the FDM method of 3D printing is appropriate to involve starch based-compounds as deposited material. Trhlíková [11] used the step transient method to evaluate the properties of different types of PLA and PP and ABS materials from 3D printing fillaments, and she determined all the required parameters using a fractal heat transfer model. Vasilescu [6]

*email: alin_sirbu@yahoo.com, asirbu@isim.ro; sorin.ratiu@fih.upt.ro

reported specific deviations of the obtained dimensions from the design, due to thermal expansion and contraction of the used material. Other results [12-16] showed that the semi-crystalline polymers present similar deformation behaviour (yielding, strain softening or hardening) as mainly of the amorphous polymers. Each modification influences the polymer behaviour during the 3D printing process. The deformation behaviour is significantly influenced by the crystallinity and by the lamellar thickness, according to Van Erp [12]. He reported in its Master thesis that a higher degree of crystallinity and an increase of lamellar thickness produce an important increasing of the yield stress. Jeřábek [17] analysed the ways of loading of a polymeric material used in engineering applications and he concluded that material is multiaxial loaded and beside tensile loads the compressive stresses proved to be dominant. The polymer he used was the PP and he obtained a linear correlation between the equivalent stress and the mean stress for different test temperatures. The results of Gleiter [18] showed that at low temperatures plastic deformation occurs by slip only, which is different from the high temperatures where the deformation processes are thermally activated. Séguéla [19] and Wilhelm [20] and Hirsch [21] and Boyd [22] reported that the crystallographic processes are active at any strain level, since the melting recrystallization is limited to the post-yield in conjunction with the chain unfolding (being more a result of chain unfolding than a mechanism of the plastic deformation). Hirsch [21] estimated the contribution of the crystalline part of the PP to its plastic flow. The flowing of the PP during the welding process and its behaviour in electric applications were reported by Chinnadurai [23], Chi [24] and Cicic [25]. Both of them revealed a decrease in plasticity during heating and cooling cycles. Such behavior was confirmed by Maries [26], Bolocan [27], Savu [28,29] and Rapa [30], the last confirming, also, that the melt viscosity is given as the ratio of shear stress to shear rate. All the reported results confirm various modifications of the characteristics of PP after a thermal cycle consisting of heating plus cooling, even if the polymeric material is a composite [31]. That means that using of PP filaments involves specific issues during the additive process. Analysis of those issues is required, if decide to replace the „classic” materials dedicated to 3D printing that are PLA and ABS. Also, information regarding the economic aspects of the introduction of PP as filler material is important to be known.

Starting with these, the paper presents comparative analysis of using the ABS and the PLA on the one hand and the PP on the other hand. The technical comparison regards the modifications of crystallization and the flowing parameters. The economic analysis regards the comparison between the involved costs for the two situations. Before any comparison is important to remind the characteristics of PP:

- It has 60-70% crystallinity degree
- Its density is 900-1000 kg/m³
- Melt Flow Index (2.16 kg/230⁰C) acc. to ASTM D1238: 8 g/10min
- Tensile Strength / Elongation at Yield acc. to ASTM D638: 25 N/mm² / 20 %
- Charpy Notched Impact Strength (at -20⁰C) acc. to DIN 53453: 7.2 mJ/mm²
- Flexural Modulus (1% SECANT) acc. to ASTM D790: 1130 MPa
- Rockwell Hardness acc. to ASTM D785: 87 R-Scale
- Heat Distortion Temperature (Load 0.45 N/mm²) acc. to ASTM D 648: 92 ⁰C.

Regarding the use in 3D printing, the filament is pushed by specific feeder to the heating nozzle and, subsequently, to the melting area. That means that the filament should have appropriate stiffness to allow the feeder to push it without deformation which could block the filament into the nozzle. In the same time, the filament material should have good strength in order to give to the product appropriate mechanical resistance. The filament material should have as low as possible density, in order to have high length for a specific quantity of material and for a specific diameter. Last but not least, the filament material should have low price, because an important component of the product’s price is related to the filament’s price. Table 1 presents few characteristics of the PP, ABS and PLA materials, characteristics which are relevant for the use in the 3D printing process.

Table 1
COMPARISON OF THE MAIN CHARACTERISTICS

	PP	ABS	PLA
Mechanical properties and characteristics			
Yield stress [Unit] ([MPa])	1 (32)	1,25 (40)	2,00 (64)
Stiffness [Unit]	1	1,25	1,85
Lifetime [Unit]	1	0.9	0.45
Max temperature in service [Unit] (°C)	1 (100)	0.95 (95)	0.5 (0.5)
Physical properties and characteristics			
Specific mass [Unit] ([g/cm ³])	1 (0.9)	1.17 (1.05)	1.40 (1.25)
Coefficient of Thermal Expansion [Unit] ([µm/m/°C])	1 (150)	0.6 (90)	0.45 (67)
Economic aspect			
Average price [Unit] (EUR)	1 (80)	0.25 (20)	0.25 (20)

It can be observed in Table 1 that the strength of PP is lower than the strength of ABS and PLA, but PP compensates the difference by longer lifetime. The stiffness of PP is similarly lower, but PP compensates the named difference by lower specific mass and that means that for the same quantity of material and for the same diameter, the PP filament is longer. Economically speaking, the PP filament is 4 times more expensive than ABS or PLA.

Experimental part

Materials and equipment

To evaluate the behaviour of PP during a thermal cycle which is specific to the 3D printing, it was used filament of RA130E which is a high molecular weight polypropylene random copolymer (PP-R) compound, produced by extrusion of heated granules composed of polypropylene homopolymer, manufactured and delivered by Borealis Polyolefine GmbH. RA130E had a melt flow rate (MFR) around 0.3 g / 10 min (ISO 1133, at 230°C). In the same time commercial PLA filament was used in the same conditions as reference. The both filaments were used to erect specific pieces by 3D printing, using Da Vinci 2.0 printer.

When use in 3D printing, the melted material is forced to cross a narrow section which is specific to the active nozzle of the printer [32] (figure 1). That means that a modification of the pressure is acting on the material. In this case it is important to know how the modification of the pressure influences the shear stress and the viscoelasticity during the 3D printing process.

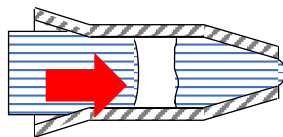


Fig. 1. Modification of the melt filament section in 2 stages

Macroscopic analysis

Compared to the extruded and deposited PLA filament, the deposited PP seems to be less viscous, even if the melting points are almost similar. PLA shows stiffness and direction, while PP is soft and difficult to control (figure 2). As deposited material, the PLA's strings show similar melting, they keep linear direction (according to the printer movement), while the PP's strings show areas of "over-melting" heating (figure 3). Solutions to increase the control could be the decreasing of the extrusion temperature or the doping of the PP to increase its stiffness.

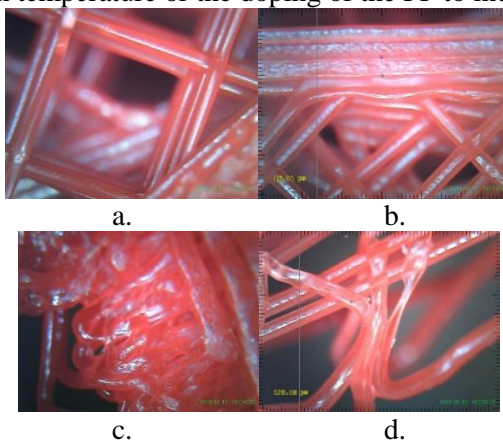


Fig. 2. Extruded PLA(a,b) and PP(c,d) at 188°C

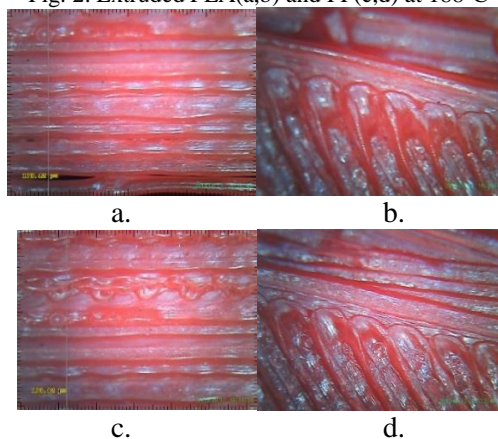


Fig. 3. Deposited strings of PLA(a,b) and PP(c,d) at 188°C

Thermal analysis

The filament material and the deposited material were analysed by using Differential scanning calorimetry (DSC, STARe DSC822e). It was evaluated the melting and the evolution of the crystallization process. The measurements were performed in the range of 25-190°C with a 10 °C/min heating and cooling cycle.

The observed behaviour of the PP can be evaluated by analysing the heat flow and the heat flux during thermal analysis. PP proved crystallization reaction according to the curves presented in figure 4. The curve moved its pick when modified the cooling rate: the increasing of the cooling rate from 12°C/min to double (24°C/min) decreased the temperature of the pick from 122.3°C to 117.2°C. In the same time, a decreasing of the heat flow with about 10% (figure 4)

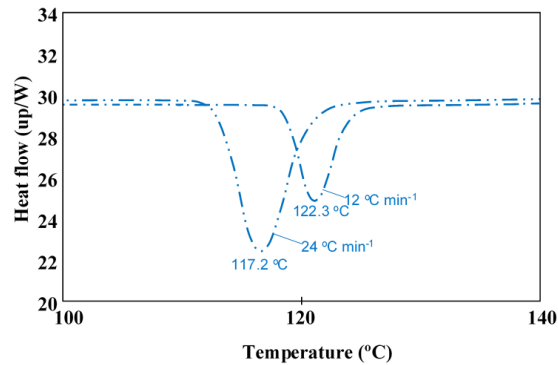


Fig. 4. Crystallization curve of PP

When compare to PLA the heat flux within PP proves about 15% higher heat flux in the filament and 30% higher in the deposited material (figure 5). That explains the difference between the viscosity of the two materials at the same temperature.

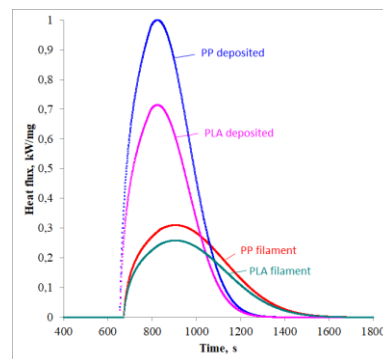


Fig. 5. Heat flux for the filament and for the deposited material

For FMD process a higher viscosity (in the range that permits a correct deposition) gives better results regarding the shape of the erected product. More, by applying an analysis of the elongation viscosity of PP, it can be observed a slight difference between the curve recorded before the melting of the filament and the curve of the deposited material, in the range of 1...5 s (figure 6). Below 1 s and after 5 s the differences between the two curves increase, especially in long periods of testing.

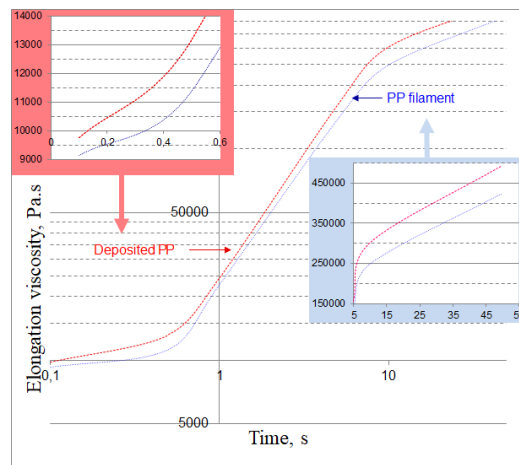
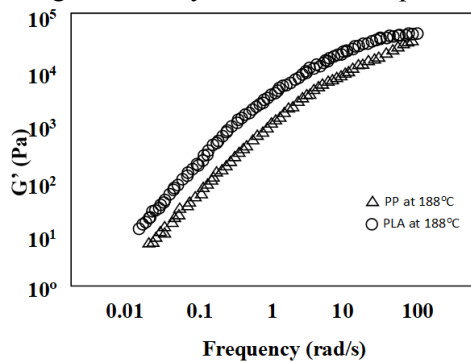
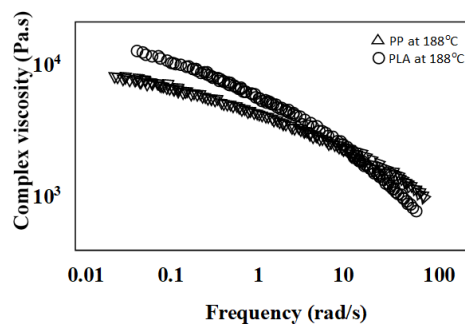


Fig. 6. Elongation viscosity at 188°C

To better understand the behaviour of PP, when pass through the extrusion nozzle, dynamic shear rheology measurements. The test has been applied on samples deformed under 210 kN at 190°C. It was the plate/plate version and the used frequencies range was 0.01 to 100 rad/s. From the test resulted information regarding the storage modulus and the complex viscosity of the both polymers in deposited status (figure 7 a and b). Comparing the storage modulus of the two polymers, in deposited conditions (so, after the melting during printing process), it can be observed that the PP requires lower storage energy and that means that it has a lower viscosity for the entire range of frequencies. In the same time, the complex viscosities prove different behavior. Up to frequency of 10 rad/s, the PLA keeps a higher viscosity, and between 10...100 rad/s the situation is changed. PP shows a lower decreasing of the viscosity from 0.01...100 rad/s than PLA. That means a higher stability of the PP's complex viscosity.



a.



b.

Fig. 7. The storage modulus and the complex viscosity at 188°C

Based on the obtained results it was considered that to improve the control of the deposition shape, it is necessary to reduce the extrusion temperature. A decreasing with 5%, from 210°C to 200°C, improved the behaviour of the PP filament. The specific string deposition became almost similar to the deposition of PLA (figure 8).

An advantage of that measure is the economy in power consumption.



Fig. 8. Deposition shape in lower extrusion temperature

Conclusions

Concluding on the obtained results, it can be considered that PP can be used as filament material for deposition, but it has lower behaviour in 3D printing comparing to the PLA, due to its high viscosity, which reduces the possibility to control the edges of the deposited shapes. The heat flux in PP is 30% higher than in PLA and that increases its fluidity. There is a difference between the elongation viscosity of the PP filament and the PP deposited by FDM process. After 5s the deposited PP proves higher values for the elongation viscosity. 5...7 s means exactly the time of crossing the nozzle and in that range of time the molten PP becomes more fluid than in the range of 1...5 s.

A possibility to improve the control of the deposition shape is to reduce the extrusion temperature and that brings other advantage, which is the decreasing of the power consumption. Anyway, the cost of PP is 4 times higher than the

cost of PLA and it keeps PLA advantage against PP.

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