



REINFORCEMENT EFFECTIVENESS ON MECHANICAL PERFORMANCES OF COMPOSITES OBTAINED BY POWDER BED FUSION

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ABSTRACT

New material formulations to be used in Additive Manufacturing machines are one of the major interests in this fast growing field. The possibility to tune functional and mechanical properties, by the addition of reinforcements to a polymeric matrix, is hindered by the low provisional capability of the additive manufactured composite. The inherent anisotropy of layer manufacturing combines with mechanisms of filler dispersion and of filler/matrix adhesion in a complex scenario. The paper entails a critical evaluation of mechanical properties measured for several polymeric composites produced by Powder Bed Fusion, in the perspective of provisional models commonly accepted for composite materials. The models are reviewed versus experimental and literature data. The provisional effectiveness is generally good, except for the case of nanometric or surface treated fillers, or of specific anisotropic microstructures obtained by layer manufacturing.

Keywords: Additive Manufacturing, Polymeric Composite, Mechanical Properties, Powder Bed Fusion

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1. INTRODUCTION

A limitation of additive manufactured components is the difference in mechanical properties of fabricated parts from conventional products. In powder bed fusion technique (PBF), mechanical properties of the part are influenced by many factors such as: powders, process parameters, part orientation, and post-processing. Yet, the main determining factor for mechanical properties is the powder material [1]. Besides, one of the main obstacles to widespread adoption of Additive Manufacturing (AM) techniques is the limited range of

materials, particularly polymeric, that can be processed. The limitation is due to the complex thermal chemistries and consolidation phenomena of polymers.

Polymeric materials suitable for PBF are mainly limited to polyamide (PA), Polystyrene (PS) and polycarbonate (PC) based powders. The move towards AM has necessitated increasing research into the processing of supplementary formulations such as polymeric matrix composites.

Advances in materials for AM over the last 25 years fall generally into the following categories:

- The improvement in the intrinsic properties of base materials;
- The development and commercialization of new materials (such as EOS GmbH's PAEK and PEEK);
- The development of composites with new and improved properties (i.e. the addition of ceramic or metallic powders into SL resins or FDM filaments)[2, 3].

Typically, parts obtained by powder bed fusion cannot replace the equivalents produced by injection moulding, because of a substantial gap in the achievable mechanical performances [4].

As said, a key advance on the side of materials for direct manufacturing is the incorporation of additives and reinforcements to polymer matrixes, in order to enhance the mechanical properties of resulting parts [3]. Among all marketable RP techniques, the most interesting for the production of composites are powder bed fusion processes, which allow to combine thermoplastics with various fill materials.

The binding mechanism involved in PBF is Liquid Phase Sintering (LPS) that is the most common method used for consolidating a composite [5]. Some common composite formulations used for direct parts manufacturing are:

- Polycaprolactone/hydroxyapatite (PCL/HA), where HA is added to PCL for enhancing its strength and biocompatibility [6];
- Polyether ether ketone (PEEK) and HA [7];
- PE and HA [8];
- PA and nano-clay [9];
- HA-filled HDPE powder [10].

In the field of rapid tooling, for layer fabrication of moulds interesting composite formulations are [11]:

- copper-filled PA [12, 13];
- aluminium-filled PA (DuraForm AF) and glass-filled PA (DuraForm GF) [14, 15];
- Al_2O_3 -PS composite [16];
- Short carbon-fiber (0.2–0.4 mm) reinforced acrylonitrile-butadiene-styrene (ABS) [17].

In addition, several studies address the use of micro- and nano-sized inorganic fillers [2]: glass beads; SiC; hydroxyapatite; various clays; SiO_2 ; Al_2O_3 .

In additive fabrication, reinforcements are more often particles rather than fibres, since the latter give problems against the formation of a smooth surface [5].

At present, the polymers used in PBF technology are primarily semi-crystalline. Thermoplastic amorphous polymers (PC, PS, ABS) show low consolidation shrinkage in the PBF process but their high melting viscosity determines a low sintering rate during the process. On the contrary, semi-crystalline polymers show a higher sintering rate due to the

low melt viscosity: PA-based powders are the most commonly used semi-crystalline polymer materials for SLS [18].

Reinforcing effectiveness that can be achieved in parts obtained by AM is still a point of debate in scientific literature, where results are not unanimous. Often the reported values refer to comparisons between a specific composite obtained by PBF and the equivalent formulation processed by injection molding. Also, some uncertainty derives from different approaches in measuring and discussing the mechanical performances, which happen to be represented in terms of various of the following characteristics: flexural strength, flexural modulus, tensile strength, tensile modulus or material response to dynamic stress.

As an example, Goodridge et al. report a research on the mechanical performance of carbon nanofibre/PA12 composite expressed as a visco elastic answer to dynamic load [2]. While the dynamic analysis helps to describe the performance of scaffolds or biomechanical devices, the little PMC components produced by AM (usual maximum dimension smaller than 300 mm) are mostly used under static or quasi-static loading.

Powder material characteristics and fabrication parameters determine the mechanical properties and appearance of the components: reinforcing nanoparticles tend to agglomerate; inorganic fillers may have absorbance (0.5) value lower than of the organic matrix (0.9) [16]; the process parameters optimized for the unfilled material may differ from those optimized for the filled powder. For such reasons, the evaluation of reinforcing effectiveness involves the comparison of the maximum tensile strength of both unfilled and filled material that may be produced with different process parameters.

The target of this paper is to evaluate the reinforcing effectiveness, in terms of increase of mechanical performances, in composites manufactured by PBF techniques. Both literature and experimental data are analysed and contrasted with provisional models for property variation versus filler type/percentage in the field of composites.

2. MATERIALS AND METHODS

This paper addresses several composites produced by PBF and evaluates the mechanical performances in terms of tensile strength, as compared to that of the unfilled material. Literature data is collected and added to original experimental figures, in order to refer the study to a significant amount of data to check the validity of commonly accepted provisional models on. The whole dataset considered in the study is reported in Table 1.

As to experimental tests, cylindrical tensile specimens are produced with an EOS machine, following the specifications of ASTM D638-08 (2008): diameter and length of narrow section are 6 and 65mm, respectively. Three material formulations are used:

- unfilled Polyamide 12 (PA 2200);
- 30% alumium-filled Polyamide 12 (Alumide) [19];
- 30% alumina-filled Polyamide 12.

Each formulation is evaluated as built with specifically optimized parameters, which are therefore not the same for the three materials. The latter is a key point, in order to test the each process/material system in the optimal configuration.

Tensile tests are performed by using an Instron 4468 machine with self-centring equipment. A testing speed of 1 mm/min is adopted, which ensures values of strain rate below $2.7 \times 10^{-3} \text{ s}^{-1}$. Such a low strain rate is representative of the worst working conditions for polymers, because it promotes viscous behaviour. Specimens are produced with different orientations: for X and Y groups the specimen axis lays on the worktable, parallel to the

recoater speed vector and to its perpendicular direction, respectively; in Z group specimen axis is parallel to the growth direction (Figure 1).

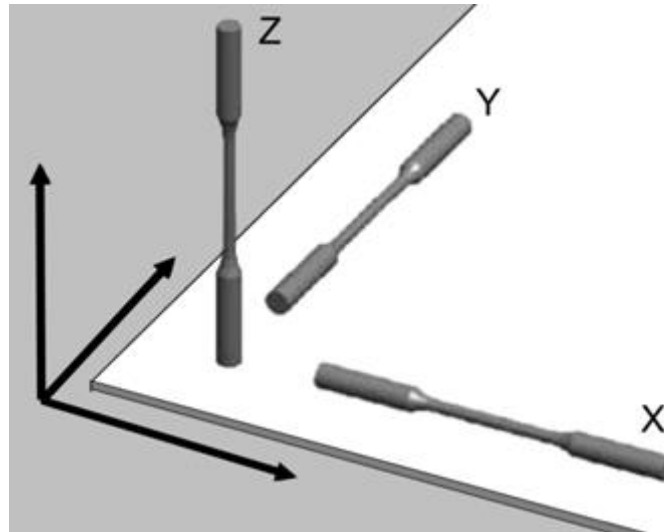


Figure 1 orientation of the specimens used for the experimental tests

Some authors report that the ratio between tensile strength of an inorganic filled composite and that of the matrix alone is comparatively insensitive to the polymer type or to its adhesion to the particles. Tensile strength would thus depend only on the volume fraction of particles [20]. This may be explained by particles debonding in the necking region, occurring with both weak and strong adhesion.

Smith's model [21] describes the effect of rigid filler particles on fracture stress of the composite, under the assumption that all particles debond from the matrix prior to fracture, so that the crack grows through a plane weakened by the appearing pores. As a result, the strength of the composite is proportional to the cross section of the matrix. Therefore, under the hypothesis of a cubic array of spherical particles, the tensile strength may be expressed as:

$$\sigma_c = \sigma_m(1 - \beta V^{2/3})$$

Where:

β = shape factor, equal to 1.21 for spheroidal fillers, to 1 for cubic particles

σ_m = tensile strength of the matrix;

σ_c = tensile strength of the composites;

V = volumetric concentration of the filler.

If particle distribution is instead random, the tensile strength of the composite may be expressed as:

$$\sigma_c = \sigma_m \frac{1 - V^{1/3}}{\sqrt{1 + V^{1/3} + V^{2/3}}} e^{\sqrt{3} \left[\arctan\left(\frac{1+2V^{1/3}}{\sqrt{3}}\right) - \frac{\pi}{6} \right]}$$

Smith's model is applied to the dataset in Table 1 and experimental/foreseen values of tensile strength are used to assess the provisional efficacy.

Rupture surfaces of the specimens are observed by SEM, in order to verify the failure mechanisms assumed in the model.

3. RESULTS AND DISCUSSION

Both literature and experimental data allow to affirm that, even if fillers ensure a significant increase of the slope in the elastic area of the stress-strain curve, quite frequently they are associated with a sensible decrease of the tensile strength (Table 1).

Table 1 Experimental (^{exp}) and literature data for the tensile strength of composites obtained by PBF and of the unfilled matrix [MPa].

Composite formulation	Matrix tensile strength	Composite tensile strength	Filler wt%
Montmorillonite/PA12 [22]	38	47	3,00%
SiC/PA12 [23]	46	31	50,00%
SiC/PA12 [23]	46	5	50% vol
Rectorite/PA12[24]	45	49	2,50%
Rectorite/PA12[24]	45	51	5,00%
Treated nano Al ₂ O ₃ /PS[16]	10	31	5,00%
Untreated nano Al ₂ O ₃ /PS[16]	10	10	5,00%
dissolution–precipitation nano SiO ₂ /PA12[25]	38	46	3,00%
mechanically mixed nano SiO ₂ /PA12[25]	38	39	3,00%
Y stabilised zirconia/PA6[26]	50	24	5,00%
Hectorite clay/PA6[26]	50	25	5,00%
uncoated glass beads/PA12[27]	53	52	10,00%
uncoated glass beads/PA12[27]	53	52	20,00%
uncoated glass beads/PA12[27]	53	48	30,00%
uncoated glass beads/PA12[27]	53	41	40,00%
treated glass beads/PA12[27]	53	54	10,00%
treated glass beads/PA12[27]	53	55	20,00%
treated glass beads/PA12[27]	53	52	30,00%
treated glass beads/PA12[27]	53	52	40,00
Al ₂ O ₃ /PA12 X direction (^{exp})	34	24	30,00%
Al ₂ O ₃ /PA12 Y direction (^{exp})	34	23	30,00%
Al ₂ O ₃ /PA12 Z direction (^{exp})	44	18	30,00%
Al/PA12 X direction (^{exp})	34	33	30,00%
Al/PA12 Y direction (^{exp})	34	34	30,00%
Al/PA12 Z direction (^{exp})	44	32	30,00%

Particularly in the case of layerwise manufacturing, fillers can cause effects that are neglected by many researchers, detrimental to the reliability of composite parts produced by

PBF. In the material formulation, quite often filler quantity is expressed in terms of weight percentage. Yet, what is decisive to reinforcing mechanisms is instead the volume distribution and the amount of surface area of fill particles. Many of the figures in Table 1 can be better understood after a conversion of the filler quantity into a volume percentage. It becomes evident that the reinforcing mechanism is effective almost exclusively under two circumstances: in the case of nano reinforcements or in that of high adhesion between the matrix and the filler, where the interface bond is stronger than the matrix itself. Otherwise, the filler is ineffective on or even detrimental to tensile strength. This result is clear in Figure 2, where stress-strain curves of unfilled PA12 are compared to those of the same material, when filled with Aluminium or Alumina particles. A strong detriment in the mechanical response is observed as a consequence of the filler addition, irrespective of specimen orientation.

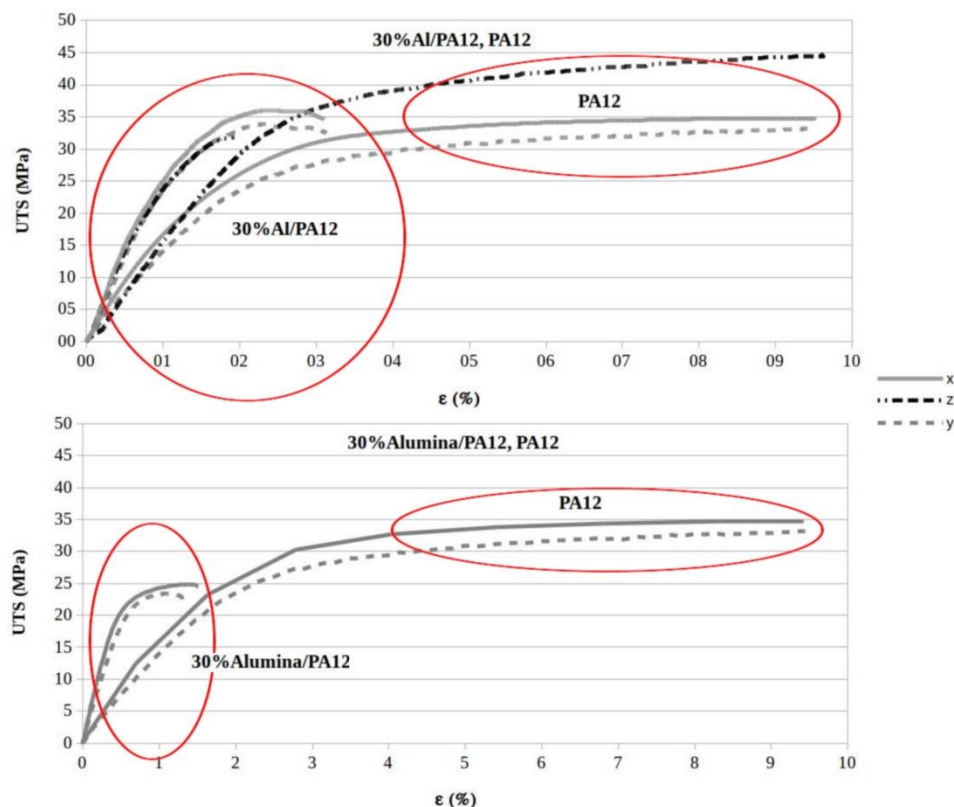


Figure 2 Top: comparison between stress-strain curves of 30%wt Al/PA12 and unfilled PA12, for X, Y and Z specimens. Bottom: comparison between stress-strain curves of 30%wt Al_2O_3 /PA12 and unfilled PA12, for X and Y specimens.

Smith's model was formulated for polymer matrix composites produced by traditional technologies, but in this paper it is applied to the data in Table I. Percent deviation is calculated as the spread between the foreseen and the experimental value, divided by the experimental value. The results are graphed in Figure 3: white/black bars are obtained with the expressions for random/cubic array distributions, respectively. Quite often the model for random distribution overestimates the composite strength, whereas the expression for the cubic array results in an underrate. Overall, the results for random distribution show a closer compliance to experimental data, with a very good provisional efficacy in at least half of the considered experiments, where the percent deviation is lower than 20%. In five additional cases the deviation remains inferior to 30%, which is still an extremely valuable result. The model loses provisional efficacy if the reinforcement has nano-dimensions [23,26].

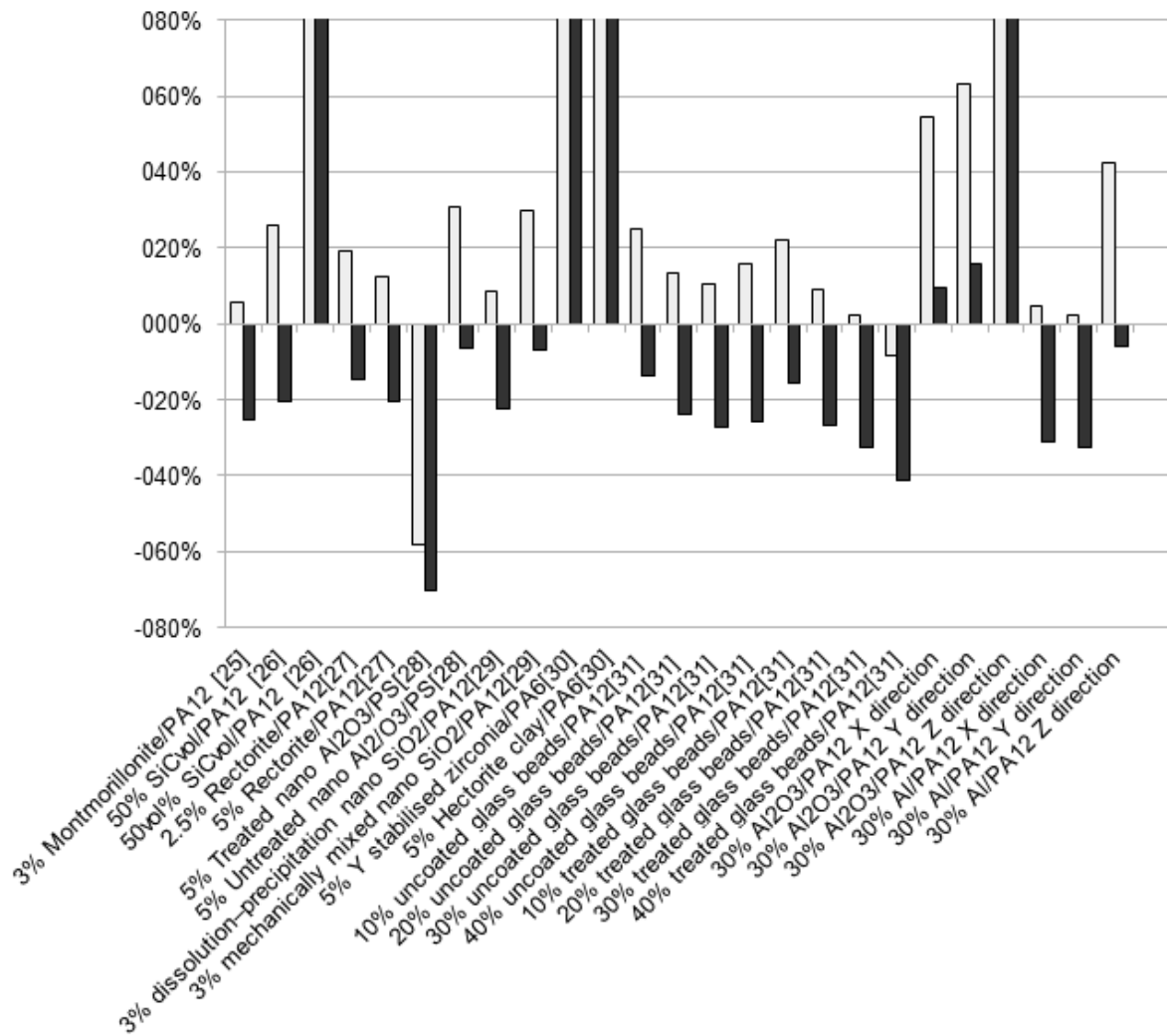


Figure 3 Percent deviation between tensile strength foreseen by Smith's model and experimental. White bars refer to the formulation for random distribution, black ones to that for a cubic array of spherical reinforcement.

As regards the model compliance to our experimental results, high deviations are observed in 4 of the 6 setups. SEM observation of failure mechanisms is very helpful for understanding such divergence. SEM images of the rupture surface of 30%wtAl/PA12 (Figure 4) shows very clearly that the failure mechanism assumed by Smith concerns only a step of the crack propagation through the entire specimen section. For these samples, crack propagation may be split into 3 stages: I) crack initiation; II) crack propagation with local necking; III) crack propagation through a matrix layer. As fully detailed in [14], for these composites PBF results in a bedding phenomenon of the reinforcing particles. If the energy required for the crack to grow is evaluated, during the second stage two antagonist mechanisms coexist. The crack propagates easily, with low energy required for the new crack surface, along the weak interface between the matrix and fillers. Concurrently, necking associated with high strain occurs between two subsequent particles, up to the creation of new rupture areas with high energy consumption. In the last step, instead, the crack propagates through the matrix without coming across any reinforcement. As a result, the composite fails rapidly and a ductile-to-brittle transition is observed.

The drop in fracture strain is caused by the transition from a ductile to quasi-brittle fracture [28].

The result has been described before also for parts produced by traditional processes: it may be observed that if a polymer yields with necking, an increase in filler content leads to fracture during neck propagation, to quasi-brittle fracture during formation of a neck [20].

For this reason, the mechanical performances of many composites obtained by PBF are similar to those of components produced using the unfilled matrix, with an even lower resistant section.

It becomes evident that an increase in the mechanical performances could be achieved through an extension of stage II. This may be obtained by a surface treatment of the filler, in order to obtain a greater interface strength, or by an enlargement of the interface area (through a decrease of filler dimensions). Both situations fall outside the application domain of Smith's model.

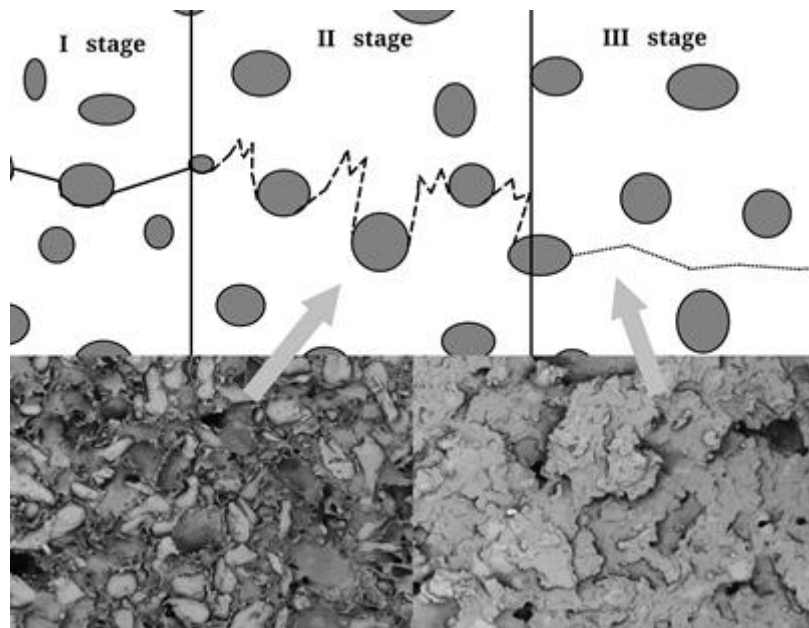


Figure 4 Crack propagation observed on the rupture surface of a 30%wt Al/PA12 composite, Z specimen

4. CONCLUSIONS

The addition of reinforcing particles to a polymer matrix manufactured by PBF, even if advantageous for stiffness, can be highly detrimental to tensile strength. In the absence of a surface treatment or of nanometric dimensions, fillers can have the only effect of diminishing the resistant section, as foreseen by Smith's model. Anisotropic microstructures built in the material during the additive process can add complexity to the system, by the modification of the failure modes.

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