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Microstructural origin of physical and mechanical properties of polyamide 12 processed by laser sintering

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ABSTRACT

The microstructure and properties of plastic parts made by laser sintering are known to be affected by a number of process and material parameters, whose influences are not totally elucidated yet. This study addresses the influence of the energy supplied to the powder on the microstructure and on the physical properties of sintered parts. Two different polyamide 12 powders were used. The energy density, which is derived from the laser characteristics, was shown to have a great impact on the residual porosity and on the amount of nascent particles in parts.

The study of the pore size and of the porosity distribution was carried out by X-ray tomography. It is shown that the particles size distribution and the crystallisation temperature are the key parameters in the porosity formation. Finally, the influence of the microstructure and crystalline features on the mechanical properties of sintered parts is discussed.

1. Introduction

In laser sintering (LS), parts are made in an additive way directly from 3D computer aided design data (CAD), without the need for tooling. Laser sintering produces parts by using a laser to selectively sinter areas of successive layers of a material in a powder form (polymers, metals and ceramics). Semi-crystalline polymers (predominantly Nylon 12 and 11) are currently sintered successfully with superior mechanical properties than amorphous polymers [1,2]. This technology was originally known as rapid prototyping (RP) since the properties of the parts produced were generally only suitable for prototyping. However, the technology of laser sintering from polymer powders has evolved to the point where it has become a viable manufacturing technique [3]. Applications are still limited though, partly due to the low mechanical properties which prevent the final parts from being functional in demanding applications.

It is well known that parts made by laser sintering have poor elongational or ductile properties, and this phenomenon is partially due to the residual porosity [1]. As LS is a process in which powder particles are fused or sintered together by heat supplied by a laser, the part density strongly depends on the energy density provided by the laser, i.e. the amount of energy per surface unit, as well as on several other process parameters like the different preheating temperatures of the powder bed [4,5]. These parameters greatly influence the mechanical behaviour of the produced parts [6,7].

Practically, to be used in laser sintering process, polymers have to present very particular properties [8]. The "processing window" between the melting and crystallisation temperatures has to be as wide as possible. Thus the crystallisation occurs sufficiently slowly to prevent part warpage during the building process. A high enthalpy of fusion is also preferable to avoid melting of powder particles due to heat conduction in the vicinity of the particles targeted by the laser. In addition, during laser sintering, a narrow melting temperature range in combination with a low melt viscosity are required to achieve the necessary

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level of fluidity very quickly without inputting excessive energy [9]. The need for these particular properties explains why PA12 is the most commonly used polymer in laser sintering [10]. However, to customise the properties of PA12 for this process, powders can be produced by different routes. For example, some powders are obtained by precipitation in ethanol at high temperature and pressure, by using different monomers during the synthesis, or by annealing at a temperature near the crystallisation temperature in water [9,11]. The objective is always the same, i.e. to increase the processing window and to increase the enthalpy of fusion of the polymer.

The morphology and the granulometry of the powder are well known to be crucial parameters in laser sintering [2]. In fact these properties have an impact on the powder bed density and on the powder flowability. The flowability of the powder is a critical point because the powder has to be spread uniformly at high temperature and with a thickness of about 100 μm. So to increase their density and flowability, the powders dedicated to LS have a specific granulometry and a good sphericity [9]. Moreover, flowability agents are usually added, especially silica.

This paper presents physical and mechanical characterizations of two polyamide 12 powders, specifically commercialised for LS, and of parts built under different sintering conditions. The difference in the degree of porosity and the pores morphology between the different parts was studied, as well as their microstructure in terms of crystal weight fraction, spherulite size, nascent particles content, and their mechanical properties. The role of the powder and polymer characteristics in the porosity formation during the process is pointed out, and the relationships between processing parameters, microstructure and mechanical properties are discussed.

2. Materials and process

2.1. Polyamide 12 powders

The laser sintering materials investigated in this work were Duraform PA®, supplied by 3D Systems, USA and Innov PA 1550® supplied by Exceltec, France. The powder median particle size d_{50} is 60 μm for Duraform PA, with a significant quantity of particles around 8 μm diameter, and 43 μm for Innov PA. The Innov PA powder particles are more regular and spherical than Duraform PA ones, as shown in Fig. 1. Measurements of powders apparent density were carried out according to ASTM D 1895-96 and were 0.50 and 0.43 g/cm^3 for Innov PA and Duraform PA respectively. The molecular weights were measured by SEC in a 95/5 (vol %) dichloromethane/trifluoroacetic anhydride solution and are gathered in Table 1. Both powders contain less than 1% of silica to improve their flowability, which is an important property in the laser sintering process.

Table 1
Molecular weights of PA12 from the two powders.

Powder	Mn (g/mol)	Mw (g/mol)	IP
Duraform PA	16190	75053	4.64
Innov PA	18080	129196	7.15

2.2. The selective laser sintering

The different steps of the laser sintering (LS) process are illustrated in Fig. 2. A laser beam is used as a heat source for scanning and fusing powder grains in predetermined sizes and shapes of layers. The geometry of the scanned layers corresponds to the various cross sections of the CAD model file of the object. After the first layer is scanned, a second layer of loose powder is deposited from one of the two feeds tanks to the top of the build tank, and the process is repeated from bottom to top until the object is complete.

During sintering, many process parameters play an important role like part build orientation, feed/build tanks temperatures, layer thickness, laser power or laser scan spacing. The supplied energy density ($E\rho$) is a measure of the amount of energy supplied to the particles per unit area of the powder bed surface. It is a function of four of the laser features: laser power (P), laser scan spacing (S), laser beam displacement velocity (v) and laser radius (r). According to Beaman et al. [4] the energy density provided by the laser to the powder bed can be written as:

$$E\rho = \frac{P}{\pi r^2}\frac{2r}{v}\frac{2r}{s} \quad (1)$$

With P expressed in Watt, r in cm, v in cm s^{-1} and s in cm, the supplied energy density $E\rho$ is then given in J cm^{-2}.

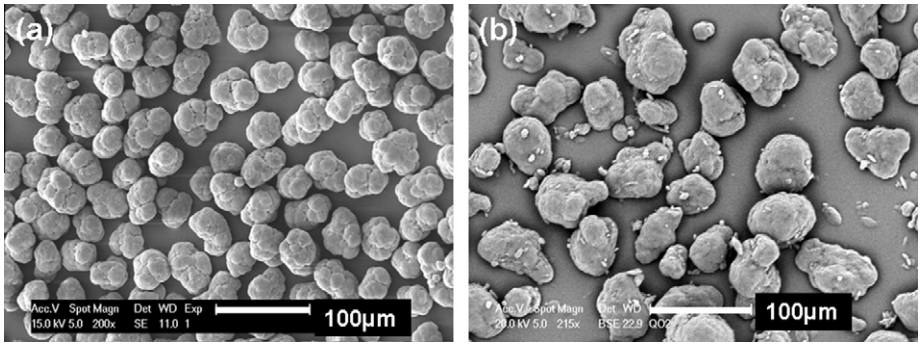

Fig. 1. Scanning electron microscopy observation of (a) Innov PA powder and (b) Duraform PA powder.