European Polymer Journal 75 (2016) 163–174

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Characterization of polyamide powders for determination of laser sintering processability

Leander Verbelen [a,*], Sasan Dadbakhsh [b], Michael Van den Eynde [a], Jean-Pierre Kruth [b], Bart Goderis [c], Peter Van Puyvelde [a]

[a] KU Leuven – University of Leuven, Department of Chemical Engineering, Leuven, Belgium
[b] KU Leuven – University of Leuven, Department of Mechanical Engineering, Leuven, Belgium
[c] KU Leuven – University of Leuven, Department of Chemistry, Leuven, Belgium

ARTICLE INFO

Article history:
Received 21 October 2015
Received in revised form 30 November 2015
Accepted 20 December 2015
Available online 21 December 2015

Keywords:
Laser sintering
Polyamide
Powder flow
Melt rheology
Polymer crystallization

ABSTRACT

With the increasing use of laser sintering for the production of end-use parts, there is considerable interest in developing new and improved polymer materials for this technique. Due to the complexity of the process, however, materials are subject to very specific requirements in order to be easy processable. To gain a better understanding of these material requirements, this study investigates the currently most widely used material family: polyamides. Four commercial polyamide sintering grades, including two polyamide-12 grades, one polyamide-11 and one polyamide-6 grade, are characterized, using a new screening approach that encompasses all material properties essential for laser sintering. These include powder characteristics, melt flow, and solidification behavior of the polymer. The study reveals several particular characteristics of polyamides that explain the current popularity of this material family for laser sintering, and may be used as a guideline for finding new materials for the process.

1. Introduction

Laser sintering is a form of Additive Manufacturing in which parts are built layer-by-layer by selectively fusing powdered material [1,2]. Upon deposition, a powder layer is preheated, which is then followed by the fusion of selected regions that are heated by a laser. Subsequently, another layer of powder is spread, and the procedure is repeated until the entire part or set of parts is fabricated. The additive nature of this process enables increased part complexity, low volume production and even completely customized products [3].

In contrast to other Additive Manufacturing technologies, laser sintering allows the processing of almost any material that consolidates upon heating, including polymers, metals and even ceramics [4,5]. Additionally, parts produced by laser sintering can reach material properties that are close to those obtained by other manufacturing processes, such as injection molding [6,7]. In practice, however, this is not currently the case, as many materials show limited processability or result in inferior parts. The focus of this study will therefore be on the processability of polymer materials in laser sintering, with emphasis on the polyamide family.

* Corresponding author at: Celestijnenlaan 200F, 3001 Leuven, Belgium.
E-mail address: leander.verbelen@cit.kuleuven.be (L. Verbelen).

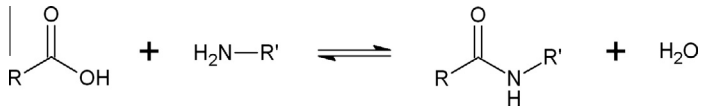
http://dx.doi.org/10.1016/j.eurpolymj.2015.12.014
0014-3057/

2. Polymers and laser sintering

2.1. Laser sintering of polyamide

As polyamides are currently the most widely used polymers for laser sintering, most of the published work has focused on these materials, including mainly polyamide-12 (PA12) in pure or reinforced form [7–18], but also polyamide-11 (PA11) [7,19–22] and polyamide-6 (PA6) [23,24]. Work on other polymers is limited, but mainly considers polystyrene [25–27], polycarbonate [28–30] and various polyaryletherketones [8,31,32].

In general, polyamides are a family of polymers in which repeating units are linked by amide groups. Characteristic for polyamide formation, is the condensation reaction of an amine and an acid [33]:



where R and R' are alkyl group chains. The polycondensation of polyamides is an equilibrium reaction and unless chain stabilizers are added, chains remain reactive and new equilibria can be formed, depending on environmental conditions such as temperature and humidity [33,34]. Especially in the molten state these reactions readily occur, but also in the solid state reactions are possible [35].

During laser sintering, the polyamide material is kept at elevated temperatures for long times, under a dry nitrogen purge. Therefore, the molecular weight increases through postcondensation reactions, and this has important consequences for both processing and recycling of the material. Many authors investigate these changes in molecular weight of sinter polyamides using either the melt flow rate (MFR) [36–43], solution viscosity [37], melt rheology [37,41,44], or gel permeation chromatography (GPC) [39,44].

2.2. Material requirements for laser sintering

There are several factors that may prevent successful processing of a polymer in laser sintering [7,45–47]. This section gives an overview of these factors and ways to evaluate them through experimental techniques.

2.2.1. Powder properties

The first step in a laser sintering cycle is the deposition of a powder layer on the build area. These layers typically have a thickness of 100–150 μm, which limits the maximum applicable particle size. Moreover, the powder should have good flowability in order to allow consistent deposition of thin, homogeneous layers of powder, with high packing density [7,45]. In principle, good powder flow is attained when interparticle adhesion and friction are low. Therefore, smooth particles with high sphericity are preferable for laser sintering, while flow enhancing additives such as silicas are often added to further enhance powder flow [7,8,18].

Several methods exist to measure powder flow [48,49], and several have been used to investigate flowability of sinter powders [50–52]. However, parameters obtained for powder flow are highly dependent on the measurement method. This means that there is not always a direct link between the measured parameters and the actual flowability in the sintering process. Recently, however, a new powder flow-measuring device was introduced by our group that uses a deposition technique similar to the one used in laser sintering machines [53].

2.2.2. Melting and coalescence

Next to the deposition of powder layers, proper fusion of powder particles is crucial in order to obtain dense parts [5,6]. As no mechanical pressure is applied during laser sintering this fusion is often restricted, and full density is difficult to attain. The viscous sintering of polymer powders can be described by several models. Frenkel [54] proposed the following model:

$$\frac{x^2}{R} = \frac{2\Gamma}{3\eta_0} t \tag{1}$$

where x and R are respectively necking and particle radius, Γ and η_0 surface tension and zero-shear viscosity of the polymer melt and t the sintering time. The model is however only valid for the initial stages of sintering of two adjacent, perfectly spherical particles. Nevertheless, also extended sintering models [55,56] show that the main parameters involved are the surface tension and the zero-shear viscosity of the polymer melt, with high surface tension and low viscosity resulting in high coalescence rates.

The surface tension of polymer melts is hard to determine, especially for polyamides [57,58]. Moreover, in comparison to the zero-shear viscosity, the surface tension is only a weak function of temperature and polymer type [59,60] and therefore less conclusive for judging material sinterability. Consequently, the main parameter of interest is the zero-shear viscosity.