Material Characterisation

Systematical mechanism of Polyamide-12 aging and its micro-structural evolution during laser sintering

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ABSTRACT

Laser sintering (LS) has capability of manufacturing complex structures and functional parts. However, material aging and part performance stability are still challenges to face in LS irrespective of protective atmosphere. Consequently, this work focuses on the essence of these problems and investigations on systematical mechanism of PA-12 aging and its micro-structural evolution during LS. The results show that the mechanism mainly has two opposite aspects concerning the material processability. On one hand, analogous Brill transition of peak merging, which is discovered for the first time in the powder aging process of LS PA-12 material, leads to a higher oneset melting temperature of the aged powder and broadens the sintering window more than 1 °C after 3 recycling. On the other, the existence of solid-state and melt-state polycondensation, which is proved by XPS and rheological measurements, induces the higher temperature nucleation for the aged powder and the crystallization postponement for aged LS parts detected in DSC. The effect of solid-state polycondensation reduces the crystallinity of the powder by ~6% after 3 recycling. This mechanism is of the guiding significance for powder stability improvement and consistent control of component properties next.

1. Introduction

Laser sintering (LS) is one of the most well established and widely used Additive Manufacturing (AM) techniques, which uses laser to selectively sinter areas of successive layers of a polymeric powder to obtain the end-use part [1,2]. In comparison to traditional polymer processing techniques, such as injection molding and extrusion forming, one of the main advantages of LS is its ability to manufacture parts with significantly greater complexity of geometry without the need for any tooling. This kind of characteristic, therefore, facilitates the successful utilization of the technique in diverse applications including individualized prosthesis, personal safety protector and tissue engineering scaffolds [3–7].

At present, more and more thermoplastic polymeric materials, crystalline or amorphous, and even high-temperature PAEKs can be processed by means of LS [8–13]. Nylon family (Polyamide, PA), especially Polyamide-12 (PA-12) and its composites, are the still most widely and successfully used LS materials. The majority of

commercialized laser sintering materials are based on PA-12, such as DuraForm GF (3D SYSTEMS), DuraForm HST Composite (3D SYSTEMS), PA 3200GF (EOS), CarbonMide (EOS), etc. [6,7]. In the actual processing condition, the performance of the final LS part depends largely on the particular properties of the powder material [14–16], which are very essential for laser sintering process. A large sintering window between melting onset and crystallization onset temperatures, indicating good LS processability, is preferable for LS, and part warpage can be effectively weakened. High melting enthalpy is also required to avoid secondary sintering of surrounding powders. In addition, lower melt viscosity or higher melt flow rate (MFR) is conducive to improve the sintering rate and thus reduce the porosity of parts. Therefore, these special properties make PA-12 more suitable for LS processing.

In order to prevent part warpage and obtain a better dimensional accuracy, a heating effect will be always existing throughout the LS process, including the preheating stage (preheat to a high temperature near the material melting point), the processing stage, and the subsequent slow cooling stage. After LS processing, the laser-sintered part

will be taken out, and nearly 80% of the powdered material remains loose in the LS building chamber that can be recycled theoretically. However, this is not the case practically. The PA-12 powder properties deteriorate due to the long period exposure of a high part bed temperature close to the material melting point and the cooling cycles. In the new laser sintering process, in order to ensure the performance stability of parts on a sufficient level, the recycled powder has to be refreshed with 30%–50% original powder to prevent a significant reduction in performance or orange peel surface. This increases the total manufacturing cost of LS fabrication because the laser sintering powders are relatively expensive materials in comparison to injection molding granules. Therefore, it is of great significance and necessity to find out the deterioration mechanism of PA-12 powders at a microstructure level and promote its recycling afterwards.

In order to promote a better understanding of the aging mechanism of PA-12 in the LS process, several researches concerning degradation kinetics, decomposition products and effect of aging environment have been conducted. Thermogravimetric experiments coupled with mass spectrometric (MS) analysis relating to the thermal degradation of PA-12 were performed by Bernard et al. [17]. The principal aging stages and degradation kinetics parameters of PA-12 were determined via mass loss measurement combined with the gas analysis. The results indicated that the major degradation intermediate products were C_2H_6, NO and CH_2O, and the presence of HCN was also detected. Goodridge et al. [18] examined the effect of long-term storage conditions and time on the tensile properties of produced parts. Unexpectedly, the strength of the laser sintering parts stored in all conditions increased in the first few weeks of storage. A mechanism that a physical ageing effect counteracts the normal effect of moisture absorption was put forward. In order to provide a basis for effective and accurate thermal control during LS process, the thermal conductivities of both fresh and preheated PA-12 powder were investigated, computational models were also established to explore the heat transfer mechanisms in the LS process [19,20].

For more efficient utilization of PA-12 powders, a quality assurance system or criterion has been established by some researchers to provide recommendations for robust process conditions and material qualities [21–23]. The deterioration or aging behaviors of various brands of PA-12 in different LS machines [22,23], locations in building chamber [22] and temperature-controlled oven [21,23] were studied, and the thermal properties, viscosity and mechanical performance changes were also analyzed. It was found that melt flow/volume rate (MFR/MVR) index is a very sensitive indicator of the changes in the powder properties and provides a relatively fast and inexpensive method of measuring the rate of the powder degradation.

Fundamental understanding of the degradation mechanism during LS is the prerequisite for a consistent powder management and systematical control of component properties. Although some efforts have been made to establish a quality assurance criterion of LS PA-12, the detailed variations of aged PA-12 powders and LS-processed material have not yet been investigated in depth. In order to achieve this, further investigation of the underlying mechanisms is needed. Consequently, this paper addresses this need by investigating the PA-12 powder properties deterioration in the building chamber in relation to its effects on crystal structure, molecular chain configuration and chemical structure during LS.

2. Experimental

2.1. Materials and sample preparation

Commercial PA-12 powder, VESTOSINT X1556, was obtained from Evonik Industries AG. LS processing of the powder was carried out under no protective gas on a HK P320 machine [HUAKE 3D] equipped with a 55 W CO_2 laser, which was developed by Huazhong University of Science and Technology. The optimized processing parameters were

Table 1
Optimized LS processing parameters.

Bed temp. (°C)	Laser power (W)	Scan velocity (mm/s)	Scan spacing (mm)	Layer thickness (mm)
167	18	4000	0.3	0.1

used in this study as summarized in Table 1. Here, we utilized the recycled powder collected from previous builds for next parts building, deteriorated powder samples and part production were taken from central processing chamber after the whole heating & cooling building cycle. The used powder experiencing different rounds of recycling thermal history and the corresponding fabricated parts were selected as study objects. The unused powder was marked as original powder and the part produced was marked as original part, the powder used one time was marked as 1*recycled and the part produced was 1* part, the rest were marked in the same manner. All samples were dried 24 h at 80 °C before characterization.

2.2. Microstructural characterization

The polymorphism and crystalline characteristics of the PA-12 powder, LS specimens were analyzed on a X'pert3 powder X-ray diffractometer (PANalytical B.V., Netherlands) with a PIXcel detector, using Cu Kα radiation in the 2θ range 9°–36° at scan speed 3°/min. Differential scanning calorimetry (DSC) heating & cooling scans were studied with a Diamond DSC (PerkinElmer Instruments, USA) for determining various melting and crystallization properties at a heating & cooling rate of 10 °C/min. Samples about 5mg were analyzed under nitrogen protecting atmosphere from 110 to 210 °C. The melt enthalpy for 100% crystalline PA-12 material was taken as 209.3 J/g [24]. The relative degree of crystallinity X_C can be calculated using the formula below:

$$X_C = \frac{\Delta H_m}{\Delta H_m^0} \times 100\%$$

(1)

where the ΔH_m is the melt enthalpy of sample and the ΔH_m^0 is the melt enthalpy of the 100% crystalline PA-12. The calculation of the thermal properties was carried out through the software TA Universal Analysis 2000. Usually three measurements were conducted for the determination of onset points on each curve. FT-IR spectroscopy was carried out with a VERTEX 70 (Bruker, Germany). The changes of the chemical micro-structure were monitored by the positions and absorbances of the IR bands. For the precise comparison between different batches of powder and associated LS parts, all experimental data were normalized by means of "Divided by Sum" option in OriginPro 8.5. X-ray photoelectron spectroscopy (XPS) was performed on AXIS-ULTRA DLD-600 W, developed by Shimadu-Kratos Corporation in Japan. To compensate for surface charging, all binding energies were referenced to the aliphatic C 1s neutral carbon peak at 285 eV. To investigate the aging and laser sintering induced chemical changes, the C 1s, N 1s and O 1s core level spectra were recorded. The XPSPEAK 4.1 version software was used for peak fitting. This program employed Newton's method for optimization as well as Shirley background subtraction and Gaussian–Lorentzian function for peak fitting. In order to determine zero-shear viscosities, rheological testing was carried on using DHR-2 rotary rheometer (TA Instruments, USA), which involved subjecting a sample of liquid or molten material to a continuous, steady-state shear deformation between two parallel plates (diameter 25 mm, distance between two parallel plates ≤ 1000 μm). As for powders testing in this study, added suitable amount of samples between parallel plates firstly, raised the instrument temperature to 200 °C and held it for 1 min to guarantee that the powder was completely melted, then began to collect testing data. It is worthy to note that the heat-compression molding was not used for sample preparing, because it will bring about additional