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Material Behaviour

Selective laser sintering of polymer blends: Bulk properties and process behavior

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ABSTRACT

Physically mixed powderous polymer blends consisting of at least two different thermoplastic materials with complementary properties could allow the successful fabrication of components with tailored and graded properties. In this work, powderous polymer blends of the partially miscible and chemically reactive blend system PBT/PC were produced from wet grinded powders at different weight ratios of 90/10, 80/20, 70/30 and 60/40, respectively. The PBT/PC is used as a model system for a blend with a semi-crystalline and amorphous component, while being relevant for industrial use, such as automotive applications. Before the implementation into the selective laser sintering process (SLS), the bulk properties of the powders were analyzed. The quadratic monolayer test specimens were generated with different energy densities by variating the laser power. The specimens' geometrical and microstructural properties were studied. The investigations showed that an improvement of geometric properties in terms of layer development can be achieved by increasing the PC content and that it is possible to generate polymer blends with matrix and dispersed phase from PBT/PC blends.

1. Introduction

Compared to conventional processing methods, such as injection molding, the material variety for selective laser sintering (SLS) is very limited. Since the requirements for material systems in SLS are very high, only a few polymers like polyamide 12 (PA 12) fulfill these quality standards [1]. Due to this restriction, a lot of effort is made to extend the range of application for SLS [2]. Apart from developing new materials and modifying established polymers, two different polymers can be blended in order to unify the benefits of both materials in one polymer. So far, mostly experiments with two semi-crystalline polymers have been conducted [3–6] while blending a semi-crystalline and an amorphous polymer might lead to materials with a much higher processability and improved part properties. By changing the ratio of the two or more components, the morphology of the final material can be individually adjusted. This leads to tailored or graded part properties. Therefore, polymer based multiphase systems, in addition to yet existing usable polymers are a valuable contribution for an enhancement of the material variety and represent a highly innovative material system in SLS [2]. Beside focusing on the material itself, the inclusion of process parameters depending on the thermal state area of the single components is of great importance. In this paper, the commercially relevant combination of polybutylene terephthalate (PBT) and polycarbonate (PC) is applied and powder properties like bulk density and diffuse reflection in terms of optical behavior are investigated. In order to study the material's processability and the material-radiation interactions, the powder blends are processed under different process parameters to quadratic monolayers. The parameters geometry, porosity and morphology of the processed single layers are then studied.

2. State of the art and theoretical consideration

2.1. Selective laser sintering of polymers

The principle of selective laser sintering also known as selective laser melting of polymers is to selectively heat and fuse plastic particles into a layer via a CO_2 laser. The process of selective laser melting consists of the three main steps material coating, energy input and material consolidation, which are repeated until the components are finished. In a first step, the bulk material (average particle size approximately 50 µm) is applied into a building chamber, which is preheated on a temperature between the melting and crystallization point of the semi crystalline polymer. The theory of quasi-isothermal laser sintering of semi-crystalline polymers signifies that polymer melt and powder coexist during the whole building process (Fig. 1), if the process temperature is chosen somewhere between melting and crystallization

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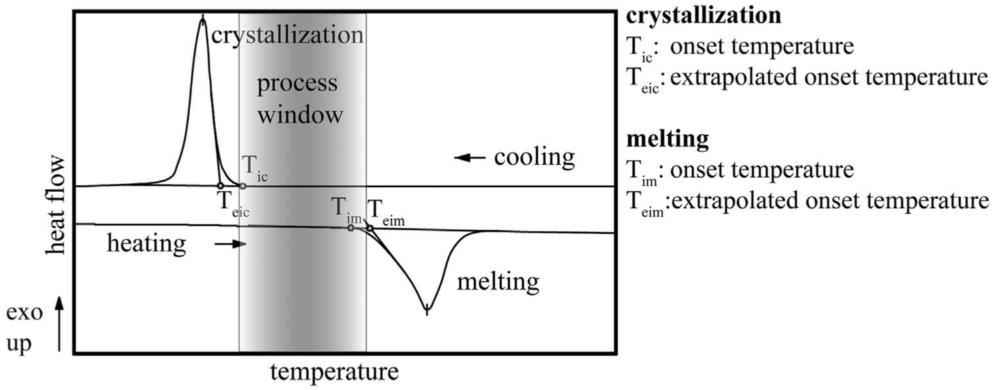

Fig. 1. Model of quasi-isothermal laser sintering of semi-crystalline thermoplastics [1,2].

point of the polymer [7,8]. Semi-crystalline polymers fulfill these requirements and have a hysteresis between the melting and crystallization temperature. During energy input a via a scanning system guided CO_2 laser heats selectively the cross section of the generated component. Due to energy absorption, the polymer particles coalesce and a homogeneous melted layer is build. Contrary to conventional plastics processing techniques, like injection molding or extrusion, no pressure is applied during laser sintering. The particles coalescence is mainly driven by viscosity and surface tension of the melt. The surrounding powder particles remain loosely in the build chamber, supporting the molten structure. After exposure the building chamber is lowered by the thickness of one layer, usually between 0.8 and 0.15 mm and a new layer of powder is applied. The three process steps will be repeated until all layers and thus components are finished. Later on, the whole process chamber with the surrounding powder and the components is cooled down in the laser sintering device to ensure inert atmosphere during solidification [9,10].

2.2. Materials in selective laser sintering

In principle, selective laser sintering can process any polymer that tends to fuse or melt when heat is applied [11]. Nevertheless, only semi-crystalline polymers are used for the production of mechanical loaded components. In the case of semi-crystalline thermoplastics, the commercial available material spectrum is limited to polyamide 11 (PA11), polyamide 12 (PA12), some filled polyamide 12 grades and polyetherketone (PEK). Beside the mentioned polymers a thermoplastic elastomer and some amorphous polymers are commercialized. Whereupon, approximately 90% of the via selective laser sintering generated parts are polyamide based [12]. Hence, great efforts were made to overcome this disadvantage and investigate new materials, like polybutylene terephthalate (PBT) for selective laser sintering [13–16]. However, available materials cannot meet the needs of different functional end use parts completely. Mixtures of polymers, polymer blends or composite materials can increase the range of properties of laser sintered parts.

Hitherto existing research activities in the field of selective laser sintering of polymer or composite materials deal with the improvement of mechanical properties by adding microscopic inorganic fillers like glass spheres [17,18], silicon carbide [19], aluminum [20] or nano scaled additives [21–23]. In Ref. [17] for example experimental studies, theoretical modeling and numerical analysis were conducted in order to fabricate polyamide 11 glass filled composites with different volume fractions of glass beads (0–30 vol.-%). The optimal processing parameters, which are defined as those that result in near-fully dense part, were determined by a design of experiments. With increasing glass bead loading the parts produced via SLS become stiffer, indicated by an increase of tensile modulus and decrease of elongation at break [17]. The aim of this work was to realize functionally graded materials, which was demonstrated on some prototype components like a compliant gripper or a rotator cuff scaffold [17]. Forderhase et al. [18] developed a commercial glass filled polyamide 12 based SLS material. The authors analyzed the dependence of particle size, as well as filler form (spheres and fibers) on mechanical properties [18]. According to the investigation, optimal glass filled material for SLS applications is a mixture of 29 vol percent glass beads with a median particle size of 35 μm [18].

Beside filled systems tailored material properties can be reached via polymer blends, mixtures of at least two different polymers. The processability of polymer blends consisting of two semi-crystalline thermoplastics by selective laser melting was analyzed in Refs. [18–21]. Salmoria et al. [3] investigated the microstructure of a polyamide 12 and high density polyethylene blend under varying HD-PE concentration and laser power. Within the paper Salmoria [3] enunciated a theory, that due to higher absorption behavior of the polyamide 12 powder at a wavelength of 10.6 μm the majority of energy will be absorbed, resulting in polyethylene particles coalescence. Thus, the mechanism of blend microstructure formation depends on viscous flow of polyethylene mainly [3]. The influence of mixture composition and processing conditions of a polyamide 12/polyethylene blend on dynamic-mechanical properties were aimed in further investigations of Salmoria et al. [4]. Beside dynamic-mechanical, creep and dynamic fatigue characteristics were investigated for high density polyethylene proportions of 20, 50 and 80 wt.-% [4]. The average value of elastic modulus specimen made of polyamide and polyethylene shows a higher level compared with blended materials, which indicated a low chemical affinity between the two polymers [4]. As a function of composition the creep and fatigue behavior is changed, resulting in the feasibility to produce components with tailored properties [4]. Salmoria investigated the phase behavior of a polyamide 12/polyamide 6 blend with compositions of PA12/PA6 20/80, 50/50 and 80/20 [5]. Due to lower viscosity of PA6 under process condition this polymer forms the matrix, in which the PA12 is distributed [5]. In Ref. [6] the mechanical behavior of this blend was explored. Tensile, dynamic-mechanical, creep and fatigue test were conducted in order to study the phase-behavior and the possibility to build components with tailored properties. Salmoria proves in the aforementioned studies the processability of polymer blends consisting of two semi-crystalline polymers, with overlapping process windows, in selective laser sintering. If the material spectrum should be extended elementarily, materials must be used which are not yet processed by selective laser sintering. Therefore, within this work a polymer blend on basis of a semi-crystalline and an amorphous thermoplastic is established for selective laser sintering applications. Both grinded polymers were used in order to represent the complete process chain from powder generation to part fabrication.

2.3. Requirements to polymer-blends for selective laser sintering

As mentioned before, in selective laser sintering predominantly semi-crystalline thermoplastics are employed due to their narrow melting temperature ranges, which can be observed in differential