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Comparison of crystallization characteristics and mechanical properties of poly(butylene terephthalate) processed by laser sintering and injection molding

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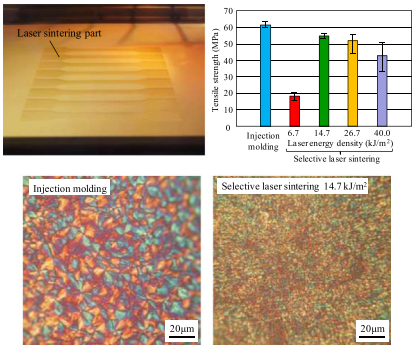
HIGHLIGHTS

- The possibility of selective laser sintering of copolymer poly(butylene terephthalate) was studied.
- Crystallization temperature of powder formed by pulverizing of pellets was increased.
- Contaminants generated by cryomilling act as nucleating agents of copolymer poly(butylene terephthalate) powder.
- Among the laser-sintered specimens, the one with the lowest porosity ratio showed the highest mechanical properties.
- The laser-sintered specimen has a finer crystal structure than that of the injection-molded specimen.

GRAPHICAL ABSTRACT



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ABSTRACT

The possibility of selective laser sintering (SLS) of poly(butylene terephthalate) (PBT) was evaluated. Powder formed by pulverizing copolymer PBT (cPBT) pellets by cryomilling was used for SLS. It was revealed that in regard to the powder, metallic contaminants generated by the cryomilling acted as crystallization nucleating agents, and the crystallization temperature of the powder was increased in comparison to that of the pellets. Moreover, SLS specimens fabricated by using cPBT resin powder were compared with an injection-molded (IM) specimen in terms of mechanical properties, crystallization characteristics, and porosity. In the case of the SLS specimens, under a processing condition that gives the lowest porosity, the highest mechanical properties were attained. In comparison to the mechanical properties of the IM specimen, however, all the values (except elastic modulus) of the SLS specimens were lower. Moreover, it was revealed that the SLS specimen has a finer crystal structure than that of the IM specimen.

1. Introduction

Selective laser sintering (SLS) is a method mainly used for forming three-dimensional structures by repeatedly irradiating a thin layer of powder with a laser beam. Among additive manufacturing (AM) methods, SLS is the most promising from the viewpoints of quality

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and precision. A particular advantageous feature of SLS in comparison to other AM methods is that it does not require a support to prevent deformation during molding. Accordingly, compared to conventional processing methods like injection molding (IM), SLS has several advantages, such as a high degree of freedom in regard to product design, ease of handling customization, low cost, and the possibility of fabrication in a short time in the case of low manufacturing volumes. Due to these advantages, SLS is mostly being utilized for fabricating end-use components in the aerospace, automotive, and medical fields [1].

In SLS, thermoplastic resins (either semi-crystalline polymer or amorphous polymer) are used. As for amorphous polymer, even at temperatures above the glass-transition temperature, melt viscosity does not decrease rapidly; consequently, the strength of the sintered part is low, and manufacturing precision is poor [2]. In contrast, as for semi-crystalline polymer, as temperature rises above the melting point of the polymer, melt viscosity decreases rapidly; consequently, the mechanical properties of the sintered part are improved, and manufacturing precision is high [2]. As one semi-crystalline polymer, polyamides (namely, "polyamides 11 and 12"; PA 11 and PA12, hereafter) are most-widely used as standard materials for laser AM [3]. Moreover, composite materials based on polyamides are being intensively researched [4–7]. It is reported that PA12 has captured more than 95% of the market for laser AM materials [3]. Despite that situation, tight restrictions are imposed on laser AM materials and act as a barrier to their widespread application. In response to that issue, other semi-crystalline polymers—such as polyethylene [8,9], polypropylene [10,11], polyoxymethylene [12], Polyamide 6 [13,14], poly(butylene terephthalate) (PBT) [15,16], poly(ether ketone) [17,18], and poly(ether ether ketone) [19,20], are being actively researched, and some have been commercialized.

As a diverse crystalline resin that has spread to a wide range of industrial applications, PBT possesses several advantageous features, namely, high heat resistance, good mechanical and electrical properties, high chemical resistance, and low cost. PBT has a high crystallization speed, so it tends to be used for IM—which requires shortening of the takt time in order to reduce costs. SLS is a means of sintering by laser irradiation under a condition in which the powder-bed temperature is set to a temperature at which crystallization speed is low [3]. From the standpoint of the molding process (i.e., SLS), as for the resin used, a wide processing window is required, and a low crystallization speed is desirable. In the case of using "homo PBT" powder with melting point of 223 °C, as reported by Schmidt et al. [15,16], building temperature for SLS was set at 210 °C. However, as for commercial SLS apparatuses still in general use, maximum powder-bed temperature is fixed at around 200 °C [3]. Due to these factors, "homo PBT"—which is used for normal IM—is supposed to be unsuitable for SLS. Copolymer PBT (cPBT) [21,22] is known as a material whose crystallization speed and crystallization temperature decrease with decreasing melting point. However, as melting point decreases, crystallization temperature decreases at a greater rate, so the process window becomes wider. Accordingly, in the present study, in which it is supposed that the powder-bed temperature is set below 200 °C, the possibility of using cPBT as a sintering material is focused on. In particular, the crystallization properties of pellets and powder, as well as the mechanical and crystallization properties of SLS specimens in comparison to IM ones, are investigated.

2. Experimental

2.1. Material

cPBT (containing 10 mol% isophthalic acid) powder formed by "cryomilling" (namely, mechanical milling at cryogenic temperature) of (non-commercial) cPBT pellets was used. The size of pellets was about 4 × 3 × 1.5 mm, and their average molecular weight (Mn) and density were 9.03×10^3 (in PMMA-converted molecular weight) and 1.29 g/cm^3, respectively. Melting point and crystallization temperature of the cPBT pellets are 208.0 and 150.3 °C, respectively.

In the cryomilling, a pin mill (Contraplex 400 C, Makino Mfg, Co. Ltd.) was used. The rotation speed of the pin disk was 145 m/s, and the operating time at −100 °C was from 90 to 240 min. The obtained cPBT powder was passed through a sieve with hole diameter of 106 μm. An SEM image and particle-size distribution of the cPBT powder are shown in Fig. 1(a) and (b), respectively. The resulting powder size of D10, D50, and D90 was 31, 76, and 132 μm, respectively. As regards a material for SLS, flowability of the powder is a key property, and fumed silica is effective for improving the flowability [16,23,24]. Accordingly, hydrophobic fumed silica (AEROSIL®RA200H; Evonik Industries) was added to the cPBT powder at a mass fraction of 0.1 wt% and mixed for 15 min by mixing machine (SKH-40CA, Misugi Ltd.). Hausner ratio (HR) was used to characterize flowability. HR is given as [25]:

$$\mathrm{HR} = \frac{\rho_{tapped}}{\rho_{bulk}} \tag{1}$$

where ρ_{tapped} is tapped density, and ρ_{bulk} is bulk density. ρ_{tapped} and ρ_{bulk} were measured by powder-characteristics tester (PT-X, Hosokawa Micron Corporation). HR of the cPBT powder with added silica was 1.30.

2.2. Processing

2.2.1. Selective laser sintering (SLS)

An SLS machine (RaFaEl 300, Aspect Inc.) was used for fabricating the specimens. As for the heat source, a carbon-dioxide laser (with high absorption rate in regard to plastic) with spot diameter of about

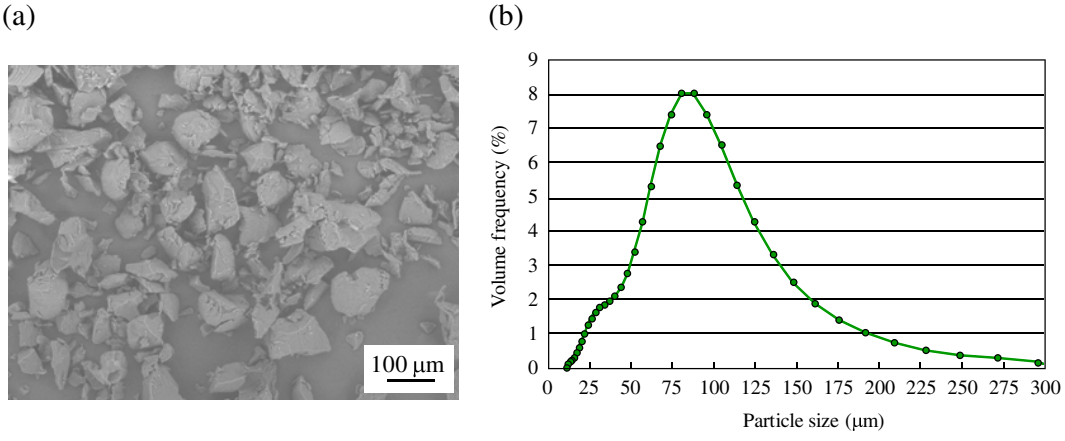

Fig. 1. (a) SEM image and (b) particle-size distribution of cPBT powder.