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Effects of short-glass-fiber content on material and part properties of poly (butylene terephthalate) processed by selective laser sintering

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ABSTRACT

With proportion of short-glass-fiber (SGF) addition (15, 30, 45, and 60 wt%) taken as a parameter, the powder properties of composite-copolymer poly(butylene terephthalate) (cPBT) powder and various properties of the cPBT-SGF specimens manufactured by selective laser sintering (SLS) were evaluated. Even in the case that SGF was added, the flowability of the powder was dramatically improved by adding silica to it. Moreover, as the proportion of added SGF was increased, the flowability was degraded. In the case proportion of SGF addition was taken as a parameter, tensile strength and flexural strength of the SLS specimen were maximized by SGF addition of 30 wt%; however, impact strength was maximized by SGF addition of 45 wt%. As the proportion of added SGF was increased, the amount of SGF "debonding" also increased, while the amount of resin that adheres to the SGFs decreased and porosity increased. In addition, the average glass-fiber length of the SLS specimens decreased with the addition of 45-wt% SGF, whereas it did not decrease with addition of 30-wt% SGF. Furthermore, in contrast to long fibers easily aligning and remaining in the direction of the roller, SGFs did not align in the direction of layer-thickness. Compared to SGF addition having an insignificant effect on mechanical properties, it significantly improved thermal properties (i.e., heat deflection temperature and linear-expansion coefficient) and reduced shrinkage. Moreover, even if SGF was added, it had little effect on the crystallization properties of the powder and SLS-formed specimen.

1. Introduction

Selective laser sintering (SLS), which is defined as a powder-bed fusion technology according to ISO/ASTM 52900; 2015, is mainly used for forming three-dimensional (3D) laminated moldings by repeatedly irradiating a thinly spread powder with a laser beam. In comparison to conventional methods, such as injection molding (IM), SLS has several advantages, namely, increased degree of design freedom, ease of handling complicated shapes and customizations, and fabrication in a short time. Moreover, from the viewpoint of quality and precision, SLS can be utilized for fabricating not only production prototypes but also end products such as automotive parts and medical equipment [1]. As for the plastic used for SLS, thermoplastic resins (both non-crystalline and crystalline) are being investigated. The viscosity of a non-crystalline resin does not rapidly decrease on heating, even above the glass-transition temperature of the resin. Consequently, it is difficult to combine good mechanical properties and high fabrication precision [2]. In contrast, when a crystalline resin is heated above its melting point, its viscosity decreases rapidly; accordingly, using a crystalline resin for SLS makes it possible to combine good mechanical properties and high fabrication precision. Polyamides (polyamides 11 (PA11) and 12 (PA12)) are one kind of crystalline resin, and they are the most widely used as standard materials for SLS [3]. As for PA12, it accounts for more than 95% of the market for materials used for SLS. In the case of the process of SLS, to avoid warping during fabrication, it is necessary to set the powder-bed temperature close to the melting point of the resin used, and in the case of a general SLS machine, the maximum powder-bed temperature setting is around 200 °C [3]. This requirement is one of the main reasons that PA 12 and 11 are mainly used for SLS. For that reason, it is a problem that materials usable for SLS are severely limited and do not satisfy the needs of various applications [3]. Under those circumstances, as the equipment for SLS is being further developed, crystalline resins other than PA12 and PA11 are being actively researched, and some of those resins have been commercialized [4–10]. As one crystalline resin being developed in many industries, poly(butylene terephthalate) (PBT) has advantages in terms of high heat resistance, mechanical and electrical properties, chemical resistance, dimensional stability, and low cost [11]. In regard to SLS, however, the

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processability of PBT has been sparingly studied [8,12]. In one of those studies, a process that creates PBT powder with spherical shape and good flowability was investigated [8], and that powder was successfully used for fabricating specimens composed of thin layers. In a previous research [12], "copolymer PBT (cPBT)" (which has lower crystallization temperature than that of the homo-PBT used in [8]) was successfully used for SLS possible at a powder-bed temperature of 190 °C. Moreover, it was reported that mechanical properties of an SLS specimen are maximized under a laser-irradiation condition that produces minimum porosity in the specimen [12]. However, the porosity still influences the mechanical properties, so specimens formed by SLS with cPBT have inferior mechanical properties compared to those of IM specimens [12]. As for crystalline resins (including PBT) used for IM, to improve mechanical properties and heat resistance, it is normal to strengthen the neat materials by adding inorganic filler to them [13,14]. The application range of such resins is thus expanding considerably. In particular, in the case glass fiber is used as the filler, a great many factors (such as fiber length, content, orientation, and strength as well as adhesion of resin and molding conditions used) [15–19] affect the properties of the IM-formed product. Furthermore, the phenomena involved in IM are complicated. In regard to SLS too, additions of glass beads [20,21], glass fiber [22,23], carbon fiber [24,25], graphite platelets [26], and alumina [27] as inorganic fillers have been studied extensively; however, the effects of those fillers and filler contents on various characteristics of the bulk resin (including PA11 and PA12) have not been investigated as extensively. In particular, in the case of PBT, the effects of filler on powder and part properties on the properties of the powder and finished parts have only been studied sparingly. For the reasons described above, in a similar manner to IM, to expand the fields in which SLS is applied, it is necessary to fully understand the effects on various characteristics of the SLS product when inorganic fillers are combined with bulk resins. In general, as for SLS, layer thickness in the range of 0.05 to 0.15 mm is used; consequently, the long fibers used for IM are not used. It is therefore necessary to investigate the effects of the addition of short fibers and its content on powder and part properties. In this study, which aims to meet that need, the effects of amount of added short glass fiber on powder properties, mechanical properties, thermal properties, and shrinkage of SLS specimens (when short glass fiber is added to cPBT powder resin developed in a previous study [12]) were investigated.

2. Experimental

2.1. Materials

The copolymer PBT (cPBT) powder used in this study was formed by cryomilling (as described in a previous study [12]). Particle-size distribution of the cPBT powder is shown in Fig. 1 (powder size of D50 was 78 μm). In the case of selective laser sintering (SLS), generally, lamination layers with thickness of 0.05–0.15 mm are repeatedly formed; consequently, laying them uniformly is presumed to be difficult if continuous fibers or long fibers used for injection molding (IM) are added to the SLS powder. In the present study, 15, 30, 45, or 60 wt% of short-glass-fiber (SGF, SS05C-404, Nitto Boseki Co., Ltd.) was added to cPBT resin powder. Distribution range of SGF length is shown in Fig. 2, and the SGF (with average fiber length of 99 μm, fiber diameter of 11 μm, and density of 2.6 g/cm^3) was treated with a silane coupling agent, and 0.1 wt% of hydrophobic silica (AEROSIL®RA200H; Evonik Industries) was added to the mixed powder. The cPBT powder, SGF, and silica were blended for 15 min by mixer (SKH-40CA, Misugi Ltd.). Scanning electron microscopy (SEM) images of the (a) cPBT powder [12] and (b) cPBT/30-wt%-SGF powder are shown in Fig. 3.

2.2. Selective laser sintering (SLS) process

An SLS machine (RaFaEl 300, Aspect Inc.) was used for fabricating the specimens. As the heat source for SLS, a carbon-dioxide laser (with wavelength of 10.6 μm and spot diameter of about 0.3 mm) was used. As for SLS, the parameters that influence the quality of the sintered specimens are laser power, scan rate, scan spacing, powder-bed temperature, feed temperature, and layer thickness [3]. Among those parameters, laser power was taken as the variable parameter used in this study and varied as eight values, namely, 5, 8, 11, 14, 17, 20, 25, and 30 W. The conditions under which the specimens were formed are listed in Table 1. Laser energy density (E) is defined as [28]

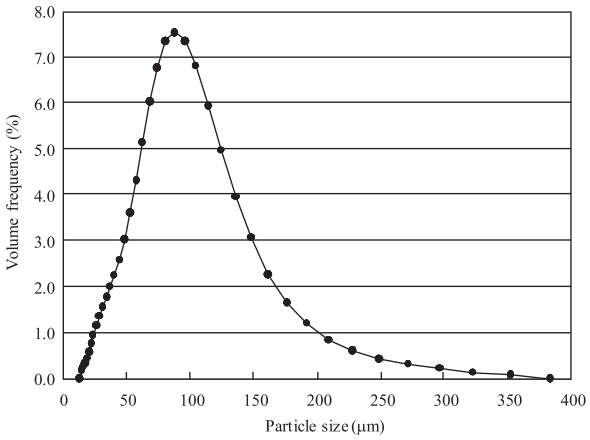

Fig. 1. Particle-size distribution of cPBT powder.

$$E = \frac{P}{vS} \tag{1}$$

where P is laser power, ν is scan speed, and S is scan spacing. All parameters other than laser power are the same as those used in a previous study on cPBT [12]. As for SLS, it is known that the build direction of the fabricated specimen has a significant effect on its properties [3]. In the present study, as for the build direction, the x-direction is defined as the roller-movement direction, the y-direction is defined as the perpendicular surface direction (i.e., perpendicular to the direction in which the roller moves along the surface), and the z-direction is defined as the layer-thickness direction.

2.3. Methods

2.3.1. Powder flowability

As for SLS, flowability of the powder has a significant effect on the properties of the formed product. Flowability of the sample powders with 15-, 30-, 45-, and 60-wt% added short glass fiber (SGF) was evaluated in terms of Hausner ratio (HR), given as [29]

$$\mathrm{HR} = \frac{\rho_{tapped}}{\rho_{bulk}} \tag{2}$$

where ρ_{tapped} (tapped density) and ρ_{bulk} (bulk density) were measured by powder-characteristics tester (PT-X, Hosokawa Micron Corporation) at 25 °C.

2.3.2. Differential-scanning calorimetry (DSC)

Isothermal-crystallization differential-scanning calorimetry (DSC) (EXSTAR 6000, Seiko Instruments Inc.) was performed to evaluate the crystallization time of the cPBT powder and SGF composites powder. In detail, the powders were heated to 250 °C, held for 10 min at that temperature, and then cooled to 190 °C, at which the heat of crystallization was measured. Crystallization half time ($t_{1/2}$) was calculated as the time taken for the heat of crystallization to reach 50% of the value for complete crystallization. DSC (Q2000, TA Instruments) was carried out to determine the melting point, crystallization temperature, and degrees of crystallinity of the SLS specimens (cPBT/15-wt%-SGF, cPBT/30-wt%-SGF, cPBT/45-wt%-SGF, and cPBT/60-wt%-SGF). The SLS