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Preparation of PA11/$BaTiO_3$ nanocomposite powders with improved processability, dielectric and piezoelectric properties for use in selective laser sintering

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ABSTRACT

The polyamide11 (PA11)/$BaTiO_3$ nanocomposite powders for use in selective laser sintering (SLS) were successfully prepared through a novel method combining the techniques of solid state shear milling, melt blending and cryogenic grinding. This provided a method for the large scale and non-solvent production of functional nanocomposite powders. The related mechanism, structure and properties of the obtained composites were investigated. The results indicated that the solid state shear milling technique could efficiently realize better dispersion of $BaTiO_3$ nanoparticles in the PA11 matrix and improve their interfacial compatibilities, endowing the composites with better processability and electrical performance. The sintering windows (between the initial temperature of melting and crystallization) of the PA11/$BaTiO_3$ nanocomposites were greatly enhanced by the solid state shear milling technique, especially for the composites containing 40 wt% $BaTiO_3$ particles, for which the sintering window increased from 10.1 °C to 14.6 °C, providing a wide sintering window for SLS. Meanwhile, the dielectric constant (ε_r), piezoelectric strain coefficient (d_{33}) and piezoelectric voltage coefficient (g_{33}) of the SLS printed PA11/$BaTiO_3$ nanocomposite parts increased after the milling treatment. Finally, the complex PA11/$BaTiO_3$ nanocomposite parts with high dimensional accuracy and good mechanical properties were fabricated by the SLS machine.

1. Introduction

Selective laser sintering (SLS), is an important branch of three-dimensional (3D) printing, which enables the fabrication of parts by employing a CO_2 laser beam to selectively sinter the powder materials based on three-dimensional modelling and additive layer-by-layer manufacturing [1]. The principal advantages of SLS are the abilities to fabricate parts with enhanced geometric complexity and design flexibility without requiring expensive specific tooling. It is particularly appealing in the respect that the SLS technique can provide extensive applications of many materials such as polymers, ceramics, and metals. Among these materials, polymers are the first and the most widely used materials in SLS due to their low processing temperature, lower consumption of sintering laser power, and high accuracy of sintered parts. Polyamide (PA), such as PA12, is the most commonly used polymer in the current market of SLS materials [2]. However, as the available materials cannot satisfy the needs of different functional parts, numerous investigations have been mainly focused on improving the polymer's mechanical, thermal or electrical properties by adding micro/nano-sized fillers to further meet the requirement of different functional parts. Polymer-based composites, such as PA12/graphite platelet [3], PA12/glass bead [4], PA12/limestone [5], PC/hydroxyapatite [6], PEEK/graphite platelet [7], PA12/carbon fibre [8], PA12/CNTs [9] etc., have been developed for SLS processing. Among the useful properties exhibited, the piezoelectric property of the materials is one of the most important. Piezoelectric composites made of piezoelectric ceramics and polymers have been widely used in many applications, ranging from loud-speakers and acoustic imaging to energy harvesting and electrical actuators [10]. These materials offer a high dielectric constant and breakdown strength with mechanical flexibility and formability [11]. It has previous been shown that piezoelectric composites can be 3D printed using two-photon lithography [12], digital projection printing [13], direct ink writing [14], selective laser sintering techniques [15,16] etc. We note here that, in many of the SLS printed piezoelectric composites, the polymer is subsequently removed by burning and the ceramic is sintered. In other words, the polymer in composites is just as adhesive for forming green body and not as functional component. The study of the SLS printed piezoelectric polymer-based composite itself being directly used as the desired functional material is limited [17].

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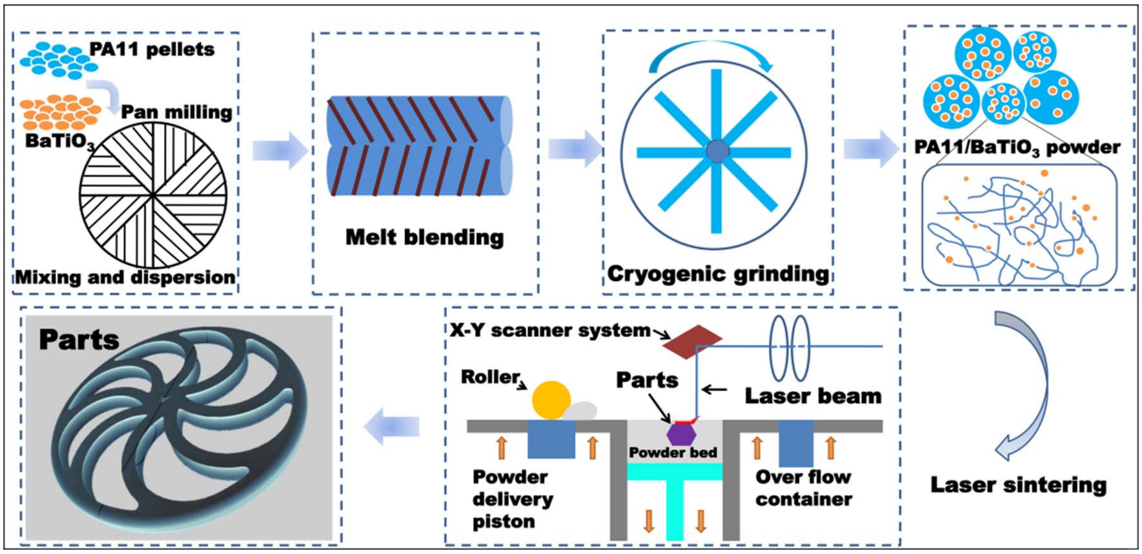

Fig. 1. Schematic illustration of the process for fabricating PA11/$BaTiO_3$ nanocomposite parts with 3D complex structures.

The major limiting factors in SLS processing polymer composites are that only powdery composites can be used, and the materials, fillers and polymer, need to be adequately compounded beforehand [18]. At present, there are three main methods to prepare polymer composite powders for SLS, including mechanical mixing, dissolution-precipitation, and a two-step approach which combines melt blending and cryogenic fracture techniques. Mechanical mixing is a simple and convenient method [9,19]. However, the nanofillers easily aggregate in the polymer matrix due to their high specific area and the density difference between their polymers and fillers leading to their segregation from each other during the layering of these composite powders. Dissolution-precipitation has been considered as a promising way to produce composite powders, which involves coating the fillers with the base polymer [8]. However, it consumes many solvents, and special solvents are required for various polymers. The two-step method has a great potential in large-scale and fast production of composite powders [20]. Nevertheless, much research has confirmed that the direct melt blending is not sufficient for good dispersion quality and property enhancements of the resultant polymer/filler composites [21,22]. Consequently, this method should be greatly improved for the development of novel composites for use in SLS.

In this work, the PA11/$BaTiO_3$ nanocomposite powders for use in SLS were prepared by a novel method combining the techniques of solid state shear milling, melt blending and cryogenic grinding; the characteristics of the PA11/$BaTiO_3$ nanocomposite powders and sintered parts were investigated. Herein, PA11 was selected as the polymer matrix because of its good piezoelectric properties. Moreover, it was a standard material for the SLS 3D printer [23]. The lead-free piezoelectric ceramic $BaTiO_3$ was used as a ceramic filler due to its outstanding piezoelectric properties and high dielectric permittivity [24]. Unlike the majority of previous research undertaken in the field of preparing nanocomposite powders for SLS, the PA11/$BaTiO_3$ nanocomposite powders were prepared by a novel method which was conducted by adding PA11 pellets and $BaTiO_3$ particles into a solid state shear milling reactor for pretreatment before melt blending and cryogenic grinding. The solid state shear milling reactor was a polymer mechanochemical piece of equipment designed by our group, and the unique pan-milling groove is a core structure, which can provide a strong three-dimensional shear force and significantly promote the effects of pulverization, dispersion, mixing and mechanical activation [25,26]. In this way, the $BaTiO_3$ nanoparticles could be distributed uniformly in the PA11 matrix, which could further improve the interfacial compatibilities of the PA11/$BaTiO_3$ nanocomposites. It is believed that this work will not merely provide an effective strategy for preparing SLS nanocomposite powders, but also assess the ability of SLS as a manufacturing process for the fabrication of a piezoelectric device with a relatively complicated structure.

2. Experimental

2.1. Materials

PA11 pellets with a density of 1.04 g/cm^3 were purchased from Rilsan Arkema, France. $BaTiO_3$ particles (average particle size 500 nm, density 6.08 g/cm^3) were supplied by Shandong Sinocera Functional Material Co., Ltd., China. The flow additive of fumed silica was a fine powder with particle size less than 10 nm, and purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd., China.

2.2. Preparation of PA11/$BaTiO_3$ nanocomposite powders

The PA11/$BaTiO_3$ nanocomposites with $BaTiO_3$ contents of 40 wt%, 60 wt% and 80 wt% were prepared by the novel method proposed in this work and designated BT40, BT60, BT80, respectively. Herein, the vol% values were inferred from the wt% values on the assumption of a binary mixture of $BaTiO_3$ and PA11 containing no air. After calculation, the BT40, BT60 and BT80 nanocomposites corresponding to the volume content of $BaTiO_3$ particles were 10 vol%, 20 vol% and 40 vol%, respectively. For the sake of comparison, the PA11/$BaTiO_3$ nanocomposite samples had the same $BaTiO_3$ mass fraction were also prepared by melt blending and cryogenic grinding at the same processing conditions, and designated UBT40, UBT60, UBT80, respectively. The fabrication process using the novel method is schematically shown in Fig. 1. Initially, the PA11 pellets and $BaTiO_3$ nanoparticles with a certain mass ratio were fed into solid state shear milling reactor. Milled particles were discharged from the brim of the pans. The discharged powder was collected for the next cycle of milling. The operation was performed at ambient temperature, and the heat generated during milling was removed by cooling water. Repetition operation continued for 10 cycles to produce PA11/$BaTiO_3$ compounding powders. Second, the as-prepared PA11/$BaTiO_3$ compounding powders were extruded at 180–220 °C through a TSSJ-25/33 co-rotating twin-screw extruder (Chenguang Research Institute of Chemical Industry, China) with a rotation rate of 100 rpm. The extruded granulates were cooled in a water bath, cut into pellets, and dried in a vacuum oven at 100 °C for 5 h. Then, the PA11/$BaTiO_3$ nanocomposite powders which were