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Preparation and properties of a composite made by barium sulfate-containing polytetrafluoroethylene granular powder

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Abstract

Barium sulfate (BaSO_4)-containing polytetrafluoroethylene (PTFE) granular powder was prepared through a two-phase emulsion dispersion granulation method. Because of its large bulk density, small average particle size, narrow particle size distribution, and superior powder flowability, the granular powder is suitable for use in automatic molding machines. The effects of granulation on the tensile strength of the BaSO_4 /PTFE composite were investigated, and the composite's microstructures were characterized and analyzed using scanning electron microscopy. All these indicated that the granulation could make BaSO_4 disperse more homogeneously in PTFE and reduce many defects in molded articles. So the properties of the BaSO_4 /PTFE composites made by the granular powder were superior to the composite obtained from the nongranular powder. The tensile strength and elongation of the composite obtained from the granular powder could be achieved to a level of 19.4 MPa and 420%, respectively.

Keywords

Polytetrafluoroethylene, BaSO_4 , granulation, composite, tensile strength

Introduction

Polytetrafluoroethylene (PTFE) is a high-performance engineering plastic widely used in industry because of its special properties such as outstanding chemical resistance and superior thermal properties, which can be profitably exploited in many different fields.^{1–6} In fact, PTFE exhibits low creep resistance, poor wear, and abrasion resistance, and so on, leading to early failure and leakage problem in machine parts. To minimize these problems, PTFE composites are prepared by modifying with various suitable fillers.^{4–11}

However, finely powdered PTFE has very poor powder flow properties and low bulk density. These two disadvantages render finely powdered PTFE unsuitable for use in automatic molding machines and also adversely affect its ability to completely fill small or intricate molds to afford suitable molded articles. In response to the above-mentioned problems, PTFE granular powder (also referred to as pelletized or agglomerated PTFE) has been developed, and it exhibits much better powder flow properties and higher bulk density, as compared to finely powdered PTFE.^{7–13}

In order to prepare a polytetrafluoroethylene granular powder, various processes have been proposed through

agglomerating PTFE primary particles that were obtained by pulverizing the raw PTFE suspension powder.^{12,14} Baron et al.⁸ described a method of agglomeration in which a PTFE powder was wetted with a small amount of a solvent, and the wetted PTFE powder was formed into agglomerates by a tumbling operation. Nakamura and Kawachi¹³ and Honda et al.¹⁵ disclosed a process for preparing filled agglomerated PTFE molding powder by agitating finely divided PTFE particles and a surface-treated filler in an aqueous medium. Asano et al.¹⁶ disclosed a

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process for preparing filled PTFE granular powder by stirring PTFE powder, a filler, and water in the presence of an organic liquid and one or more surfactants. However, bulk density of the filler-containing PTFE granular powder and tensile strength of molded articles obtained therefrom are not fully satisfactory.^{8,12,14–19}

In this article, BaSO₄-containing PTFE granular powders were prepared through a two-phase emulsion dispersion granulation method. The granulation of the mixture of PTFE powder and BaSO₄ was conducted in the droplets of liquid–liquid interface formed from ion-exchanged water and methylene chloride with a surfactant by stirring. The tensile strength and elongation of the BaSO₄/PTFE composite obtained from the granular powder were investigated, and the microstructures of the composites were studied using scanning electron microscopy (SEM).

Experimental

Materials

PTFE suspension molding powder (JUFLON JF-4TM, homopolymer of tetrafluoroethylene, bulk density = 300–450 g/L, average particle size = 32 μ m, melting peak temperature = 327 $\pm$ 5°C) used was of commercial grade obtained from Zhejiang Jusheng Fluorochemical Co., Ltd (Quzhou, China). BaSO₄ powder (average particle size = 200 mesh (inch mesh)) of commercial grade was obtained from Shaanxi Gaoguan Application and Development of Nonmetallic Ore Co., Ltd (Xi'an, China). Methylene chloride of chemical grade was obtained from Xi'an Chemical Reagent Plant (Xi'an, China). The other chemicals used were commercial-grade reagents.

Experimental procedures

Preparation of mixture of PTFE powder and BaSO₄. PTFE powder and BaSO₄ were dried in an oven at 130°C for 3 h. Then they were cooled and put aside in a dry place below 19°C for 24 h. The mixture of PTFE powder and BaSO₄ was obtained by premixing them with a high-speed mixer (self-made). The BaSO₄ content is 30% by weight with respect to the total weight of PTFE powder and BaSO₄.

Preparation of BaSO₄-containing PTFE granular powder. A 250-mL three-necked flask was charged with 20 g of the mixture of PTFE powder and BaSO₄, 60 mL of ion-exchanged water, and a certain amount of an aqueous surfactant solution having a concentration shown in Table I. After stirring, the above-mentioned mixture using a mechanical stirrer for 3–5 min, 15.6 g of methylene chloride was slowly added in drops and started granulation. The granulation was carried out for 6–8 min at room temperature under stirring. The stirring speed was held at 800–1200 r/min throughout the whole granulation process. Finally, the BaSO₄-containing PTFE granular powder with

Table I. Physical properties of granular powders obtained.

	Surfactant (dosage, kind) and concentration (by weight)	Bulk density (g/L)	Flowability	Average particle size (μ m)
Ex. 1	2 mL 5% aqueous ammonium solution of FOA	700	7	330
Ex. 2	5 mL 1% aqueous solution of SLB	720	8	410
Ex. 3	2 mL 1% aqueous solution of FBS	750	8	360
Ex. 4	5 mL 5% aqueous solution of OA-12	730	8	340
Ex. 5	5 mL 5% aqueous solution of L-42	720	8	470

FOA: perfluorooctanoic acid; SLB: sodium lauryl benzenesulfonate; FBS: sodium perfluorononylalkoxyl benzenesulfonate; OA-12: dimethylaurylamine oxide; L-42: polyalkylene glycol; Ex.: experiment.

an ideal average particle size (less than 500 μ m) was obtained by filtering using a 200-mesh sieve, rinsed with water and dried in an oven at 130°C for 20 h.

Molding sample of BaSO₄-containing PTFE granular powder. Prior to molding, BaSO₄-containing PTFE granular powder was allowed to stand for not less than 2 h in a room, the temperature of which was adjusted to 23 $\pm$ 2°C. A die having an inner diameter of 100 mm was charged with 40 g of the granular powder, and a pressure was applied gradually over about 30 s until the final pressure became about 40 MPa. Then that pressure was kept for 5 min to give a premolded sample. The premolded sample was taken out of the die mold and put in a high-temperature oven heating up to 380°C through a stepwise process in 5 h, and then kept at 380°C to sinter for 2 h. Finally, the molded sample of BaSO₄-containing PTFE granular powder was obtained by cooling through a stepwise process.

Tests and measurements

Flowability was determined in accordance with the method described in many literatures.^{12,16} Average particle size and particle size distribution of the BaSO₄-containing PTFE granular powder were determined in a usual manner for measurement with reference to many literatures.^{12,16} Bulk density was measured in accordance with HG/T 2900-1997. The structure of particles in the BaSO₄-containing PTFE granular powder was observed by a Nikon Eclipse (Japan) E400-POL hot-stage polarizing optical microscope.

A Philips-FEI (the Netherlands) Quanta 200 Environmental Scanning Electron Microscope, equipped with an energy dispersive spectrometer, was used to characterize the morphology of specimens in high vacuum mode. The molded sample-based specimens were first quenched in liquid nitrogen, then fractured, and sputtered with gold.

Tensile strength and elongation were determined by tensile tests. The molded sample was punched to a dumbbell specimen (as shown in Figure 1), and for each molded sample at least five specimens were tested. Tensile tests were performed according to HG/T 2903-1997 on an SANS (Shenzhen, China) CMT 6303 Universal Electromechanical Testing Machine at $23 \pm 2^\circ\text{C}$. The machine had a constant crosshead speed with a loading rate of 100 ± 10 mm/min. Tensile strength and elongation were calculated using equations (1) and (2), respectively.

$$\tau = \frac{P}{B \times \omega}, \quad (1)$$

$$\varepsilon = \frac{(L - L_0)}{L_0} \times 100, \quad (2)$$

where τ is the tensile strength (MPa), p is the maximum force value for specimen at break (N), B is the width of specimen (mm), ω is the thickness of specimen (mm), ε is the elongation (%), L_0 is the original length of specimen (mm), and L is the length of specimen at break (mm).

Results and discussion

Physical properties of granular powder

An aqueous medium with a surfactant for granulating filler-containing PTFE granular powder must have a surface tension of 25 dyne/cm or lower, at the most 35 dyne/cm.^{12,18} So an aqueous surfactant solution is ideal as long as it can meet the above-mentioned requirement.

For proving the universality of the two-phase emulsion dispersion granulation method, three anionic surfactants (5% aqueous ammonium solution of perfluorooctanoic acid, 1% aqueous sodium solution of perfluorononylalkoxyl benzenesulfonate, and 1% aqueous sodium solution of lauryl benzenesulfonate) and two nonionic surfactants (5% aqueous solution of dimethyl laurylamine oxide and 5% aqueous solution of polyoxypropylene and polyoxyethylene block polyether (also referred to as segmented polyalkylene glycol)) were selected as surfactants for granulating experiments. Physical properties of granular powders obtained are shown in Table 1. It is seen from Table 1 that physical properties of the granular powders were about the same as using these five surfactants.

In our experiment, the granulation of the mixture of PTFE powder and BaSO_4 was conducted in the droplets of the liquid-liquid interface formed from methylene chloride and ion-exchanged water since the liquid droplets became smaller attaining a near spherical form. This behavior of the particles is due to surfactant property developed during stirring, for which the bulk density and flowability of the granular powder were increased,^{12,14,16} and the obtained BaSO_4 -containing PTFE granular powders all have an ideal average particle size.

Figure 1. Schematic diagram showing a tensile specimen for determining tensile strength and elongation of molded articles obtained.

Structure of granular powder

The structures of particles in the granular powders obtained from these five experiments are shown in Figure 2. It is seen that the particles in the granular powders obtained by our granulation method are almost spherical or nearly spherical.

In the whole granulation process, the granulation was carried out by combining agglomeration and de-agglomeration of the powder at the same time. A granulate with a proper size had already been formed as a secondary agglomeration of the primary particles, which could be partly de-agglomerated to decrease a secondary particle size by the de-agglomeration. So the granular powder finally obtained is a mixture of the de-agglomeration secondary particles with a certain size distribution and little amount of the secondary agglomeration particles (A, as shown in Figure 2). Due to differences of the effect on agglomeration and de-agglomeration of the powder using these five surfactants, the granular powders obtained have different size distribution and different average particle size.

Properties of the composite made by BaSO_4 -containing PTFE granular powder

Tensile tests were performed in order to compare physical properties of the composite prepared by 30% BaSO_4 -containing PTFE nongranular powders and granular powders. The results obtained from tensile tests are tabulated in Table 2. It is seen from Table 2 that almost all the molded samples of granular powders had some improvement on the tensile strength and elongation, except the samples obtained from experiment 2 (Ex. 2) was almost same as the composite made by the nongranular powder. Compared with the composite made by nongranular powder, the tensile strength of the composite made by granular powder could be achieved to a level of 19.4 MPa, and the elongation could be achieved to a level of 420%.

SEM analysis

Figure 3 shows the SEM images of the composites prepared by 30% BaSO_4 -containing PTFE nongranular

Figure 2. POM photographs (magnification: $\times 40$) showing structure of particles in the BaSO_4 -containing PTFE granular powder obtained from Ex. 1, Ex. 2, Ex. 3, Ex. 4, and Ex. 5, respectively. POM: polarizing optical microscope; BaSO_4 : barium sulfate; Ex.: experiment; PTFE: polytetrafluoroethylene.

Table 2. Physical properties of molded articles obtained from the granular powders.

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Tensile strength (MPa)	17.6–19.4	16.8–17.7	18.2–19.3	18.7–19.0	17.5–18.6
Elongation (%)	360–400	360–400	390–420	390–410	380–400
Physical properties of molded article obtained from 30% BaSO_4 -containing PTFE nongranular powder					
Tensile strength (MPa)	16.4–17.3				
Elongation (%)	260–370				

BaSO_4 : barium sulfate; PTFE: polytetrafluoroethylene; Ex.: experiment.

powders and granular powders. The BaSO_4 particles are randomly distributed throughout the PTFE matrix. At some areas, aggregation of BaSO_4 particles can also be observed (Figure 3(a) and (b)). There are also many areas with nonbonding and porosity that appear along the interfaces between the PTFE matrix and BaSO_4 particles after granulation, but the BaSO_4 particles without any aggregation are uniformly distributed throughout the PTFE matrix (Figure 3(c) and (d)). Because the granulation made BaSO_4 to disperse more homogeneously in PTFE and reduced many defects in composites, the tensile strength and elongation of the composites made by granular powders had been improved.

Conclusions

BaSO_4 -containing polytetrafluoroethylene granular powder was prepared through a two-phase emulsion dispersion granulation method, which was conducted with stirring in an aqueous medium consisting of ion-exchanged water and methylene chloride in the presence of a specific surfactant. Because of its large bulk density, small average particle size, narrow particle size distribution, and superior powder flowability, the granular powder is suitable for use in automatic molding machines. The granulation could make BaSO_4 disperse more homogeneously in PTFE and reduce many defects in composites thereby

Figure 3. SEM images of the molded articles prepared by 30% BaSO₄-containing PTFE nongranular powder (a and b) and granular powders obtained (c and d). SEM: scanning electron microscopy; BaSO₄: barium sulfate; PTFE: polytetrafluoroethylene.

improving the properties of the composites made by granular powders. The tensile strength and elongation of the composites obtained from the granular powder could be achieved to a level of 19.4 MPa and 420%, respectively.

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Declaration of Conflicting Interests

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