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Material properties

Novel syndiotactic polystyrene/$BaTiO_3$-graphite nanosheets three-phase composites with high dielectric permittivity

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ABSTRACT

Novel three-phase composites were prepared by embedding graphite nanosheets (GNs) and $BaTiO_3$ nanoparticles into syndiotactic polystyrene (sPS) matrix via a solution blending and flocculation method. The dependences of electric and dielectric properties of the resultant sPS/$BaTiO_3$-GNs composites on volume fractions of GNs (f_{GNs}) and frequency were investigated. The percolation theory was employed to explain the electric and dielectric behavior of sPS/$BaTiO_3$-GNs composite. It was found that the sPS/$BaTiO_3$-GNs composite showed an obvious insulator-conductor transition with a much low percolation threshold of $f_{GNs} = 1.44$ vol%. The dielectric permittivity of sPS/$BaTiO_3$-GNs composite reached as high as 51.8 at 100 Hz at percolation threshold, which was about 18 and 7 times higher than that of pure sPS and sPS/$BaTiO_3$ composite, respectively.

1. Introduction

Polymeric composites with high dielectric permittivity have been intensively studied because of their potential applications in gate dielectrics, capacitors and electric energy storage devices [1]. A common method of fabricating such materials is to add high dielectric ceramic powders into a polymer matrix to form 0-3 type composites. However, loading large amounts of rigid ceramic powders with more than 40 vol% is necessary to obtain high dielectric permittivity in such polymer/ceramic systems, which may adversely affect the mechanical performance of the resultant polymeric composites. For example, the dielectric permittivity at 1000 Hz increased from 3.49 for pure poly (methyl methacrylate) (PMMA) to 14.6 for PMMA/$BaTiO_3$ composite when $BaTiO_3$ content was as high as 76.88 wt% [2]. To overcome this problem, conductive materials have been incorporated into the polymer/ceramic system as the third component, in which the total amount of fillers was much lower. The three-phase composites, including polyvinylidene (PVDF)/$BaTiO_3$-carbon fiber, PVDF/$BaTiO_3$-Ni, PVDF/$BaTiO_3$-carbon nanotubes (CNTs), PVDF/$BaTiO_3$-ZnO, PVDF/$BaTiO_3$-Ag, PVDF/$BaTiO_3$-Bi_2S_3, Epoxy/$BaTiO_3$-CNTs, PMMA/$BaTiO_3$-Ni [3–10], have been reported recently. According to percolation theory, the electric conductivity and the dielectric permittivity increase significantly when the amount of conductive fillers approaches a critical concentration (i.e., the percolation threshold) [11]. The significant increase in dielectric permittivity near the percolation threshold can be ascribed to the existence of lots of microcapacitors. These microcapacitors are formed by separating the neighboring conductive fillers with a thin insulating polymer/ceramic layer [5,12].

Syndiotactic polystyrene (sPS) is an important engineering plastic exhibiting high thermal stability, excellent chemical and moisture resistance and good dimensional stability [13]. However, the low electric conductivity and

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dielectric permittivity of sPS (about 2.8 at 100 Hz) has limited its application in the electronics area. Graphite nanosheets (GNs) are abundant and inexpensive carbon-based materials possessing excellent electrical, thermal and mechanical properties. More importantly, the large aspect ratio and the unique layered structure of GNs can give advantage in the formation of a parallel-board microcapacitor network with low filler loading [14]. However, up to now, there is no report on the preparation of three-phase composites based on sPS, $BaTiO_3$ and GNs.

In this work, we prepared sPS/$BaTiO_3$-GNs composites containing 20 vol% of $BaTiO_3$ and various volume fractions of GNs (f_{GNs}) by a solution blending and flocculation method [5]. Scanning electron microscopy (SEM) was employed to observe the morphology of the resultant sPS/$BaTiO_3$-GNs composites. The electric and dielectric properties of sPS/$BaTiO_3$-GNs composites were investigated and percolation theory was used to explain their electric and dielectric behavior.

2. Experimental

2.1. Materials

sPS was provided by Dow Chemical Co. with M_w of 226,000 and M_w/M_n of 2.8. GNs were prepared according to reference [14,15]. $BaTiO_3$ was obtained from Guangzhou Yanrui chemical company. N-methyl-2-pyrrolidinone (NMP) was purchased from Guangzhou Chemical Reagent Company.

2.2. Preparation of sPS/$BaTiO_3$-GNs composites

The desired amount of GNs and 20 vol% of $BaTiO_3$ was first ultrasonicated in 100 mL of NMP for 24 h. Next, sPS was added into the GNs-$BaTiO_3$ suspension. After vigorous mechanical stirring for 1 h at 160 °C, the mixture was poured into cold water, filtered and then dried to obtain the sPS/$BaTiO_3$-GNs composites. The resultant sPS/$BaTiO_3$-GNs composites were molded into disks (diameter = 13 mm, thickness = 1 mm), and silver paste was coated on the sample surfaces as electrodes for electric and dielectric measurements. For the purpose of comparison, sPS/$BaTiO_3$ composite containing 20 vol% of $BaTiO_3$ was prepared by the same procedure in the absence of GNs.

2.3. Characterization

A JSM-6490 SEM was employed to observe the microscopic structure of GNs and sPS/$BaTiO_3$-GNs composite. The electric and dielectric properties were tested as a function of frequency from 40 to 10^7 Hz at room temperature using an Agilent 4294A impedance analyzer.

3. Results and discussion

3.1. Morphology of sPS/$BaTiO_3$-GNs composites

GNs with micron-sized diameter and nanoscale thickness, as shown in Fig. 1b, were prepared by subjecting natural graphite flakes (see Fig. 1a) to acidic intercalation,

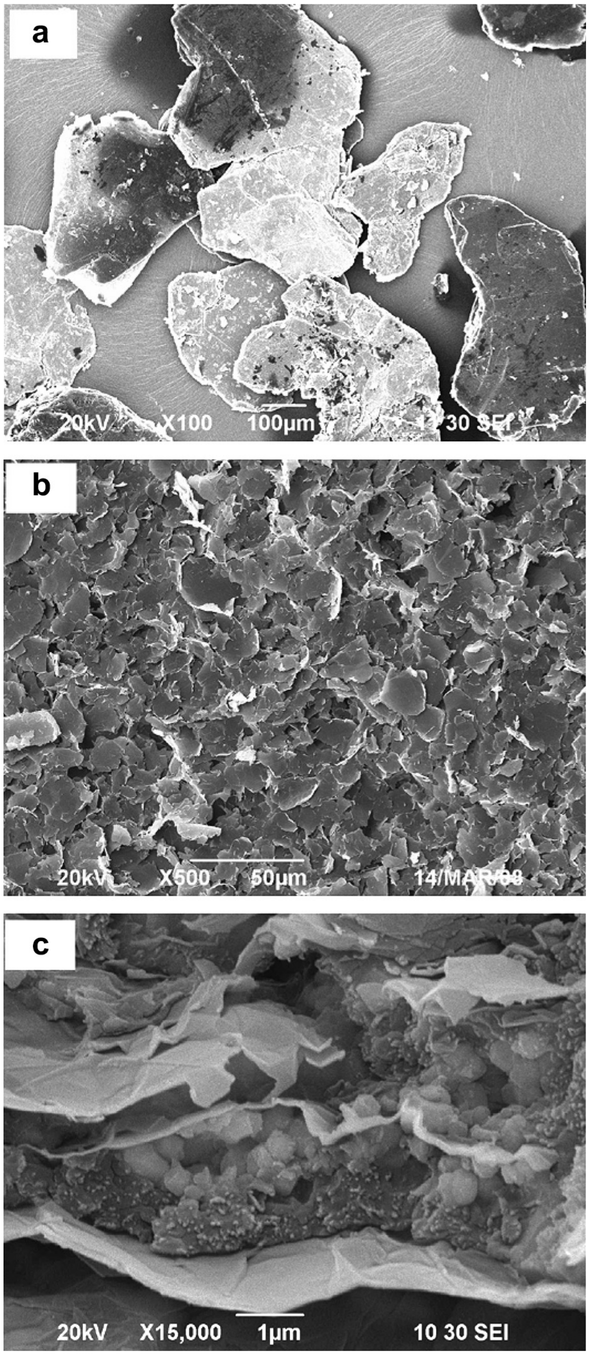

Fig. 1. SEM micrographs of (a) natural graphite flakes, (b) GNs and (c) fractured cross-surface of the sPS/$BaTiO_3$-GNs composite with 20 vol% of $BaTiO_3$ and 1.44 vol% of GNs.

rapid heating and ultrasonic powdering in sequence. The large aspect ratio and the thin layer structure of GNs were helpful for the formation of microcapacitors in the polymer matrix. The sPS/$BaTiO_3$-GNs composites were fabricated via a solution blending and flocculation method. Fig. 1c confirmed the presence of microcapacitor structure in the sPS/$BaTiO_3$-GNs composite. It can be seen that GNs were parallel to each other and isolated by an insulating layer of