Material Properties

Synergistic effects on polyurethane/lead zirconate titanate/carbon black three-phase composites

CrossMark

Alex Otávio Sanches [a], Darcy Hiroe Fujii Kanda [a], Luiz Francisco Malmonge [a], Michael Jones da Silva [b], Walter Katsumi Sakamoto [a], José Antonio Malmonge [a, *]

[a] Universidade Estadual Paulista (UNESP), Faculdade de Engenharia, Câmpus de Ilha Solteira, Avenida Brasil, 56, Centro, 15385-000 Ilha Solteira, SP, Brazil
[b] Universidade Estadual Paulista (UNESP), Câmpus Experimental de Rosana, Avenida dos Barrageiros, 1.881, Centro, 19.274-000 Rosana, SP, Brazil

ABSTRACT

Synergistic processes in hybrid composites have frequently been described in the literature over the past few years, opening doors to new studies and applications for this type of material. In this study, three-phase composites were obtained using polyurethane (PU) as the matrix, lead zirconate titanate (PZT) as the ferroelectric ceramic and carbon black (CB) as the conductive phase. The discussion is primarily focused on a comparison of the electrical, thermal and dielectric properties of three-phase composites with those of PU_CB and PU_PZT biphasic composites. The study describes a synergistic effect between the PU/PZT/CB phases involved in the generation of charges between the particles, implying better homogeneity of the composites as well as influence over the PU crystallization. The PU_CB conductivity profile showed a phenomenon of multi-step percolation thresholds attributed to the molecular structure and repulsive surface charge of CB particles. The surface charge phenomenon restricted the percolation curve analysis of the three-phase composites by means of classic percolation theory, shown by distortion of the critical exponents. The dielectric constant three-phase composites increased gradually as a function of CB in accordance with the percolation profile.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Polymeric composites hold great interest for the scientific and industrial communities because their properties can be tailored to suit various applications [1]. Polymer/ferroelectric ceramic composites are garnering attention due to the exponential growth of the electronics industry. This drives the research for new materials with high permittivity, combining low dielectric loss, mechanical resistance and compatibility with printed circuits; these properties make these composites excellent candidates for embedded capacitors in passive circuits [2]. The most common type of polymer/ferroelectric ceramic composite found in the literature is biphasic, with a connectivity of 0–3. Many papers have investigated the influence of the matrix, the size, and the shape of ceramic grains, ceramic surface functionalization, etc. [3] on the electrical, optical and mechanical properties of the final product. However, with regard to dielectric properties, these materials are restricted to

dielectric constant values of 50–70 at room temperature, which limits their use.

The manufacture of three-phase composites has been gaining attention due to the high dielectric constants obtained with the insertion of a third conductive phase, generally at a nanometric scale [4–7]. According to Tchmutin et al. [8], although some long-term studies of biphasic composites containing ferroelectric or conductive particles have been conducted, the study of composites containing both phases is still limited. This is due to the complexity of determining the influence of each phase on the final properties of these materials. The literature includes a range of studies that examine metallic particles, such as nickel (Ni), silver (Ag), copper (Cu), platinum (Pt) etc., as well as carbon nanotubes and graphene as the third phase [4–15]. The literature presents three-phase composites with a well-behaved profile based on the mixing rule and the percolation theory [4–15]. However, in many cases, their properties differ from those predicted, especially given the possible synergistic interactions related to the particle geometry of the hybrid fillers, filler interactions, filler concentrations and processing methods [16–29].

In this study, three-phase polyurethane/lead zirconate titanate/

* Corresponding author.
  E-mail address: mal@dfq.feis.unesp.br (J.A. Malmonge).

carbon black composites were fabricated and the morphological, thermal and electrical properties of the composites were investigated. We highlight the synergistic effect found between CB and PZT, which significantly improved the dispersions of PZT in the three-phase composites.

2. Material and methods

2.1. Materials

The polymer used as the matrix was nonionic aliphatic polyether-based polyurethane (PU), available from Chemtura Corporation (Rio Claro, Brazil) under commercial reference *PU W320*. Lead zirconate titanate (PZT) was purchased from APC International Ltd. (Mackeyville, USA) under reference *851*. Its characteristics include: relative dielectric constant (1 kHz) of 1950, Curie temperature of 360 °C, a density of 7.6 g/cm^3 and average particle size of 40 μm. The carbon black (CB) was supplied by Orion Engineered Carbons (Paulínia, Brazil) under commercial reference *Printex XE-2*. Its characteristics are: average particle size of 35 nm, a surface area of 1000 m^2/g, and a bulk density of 0.1 g/cm^3.

2.2. Composite preparation

2.2.1. PU_CB and PU_PZT biphasic composites

PU_CB and PU_PZT composites were manufactured taking into account the volume of the particulates in the composite in relation to the fixed mass of PU, according to Eq. (1). The filler was added to the polyurethane slowly and the mixture was stirred continuously for approximately 1 h. The dispersion was subjected to an ultrasonic bath for 30 min and subsequently stirred continuously for 1 h. It was then placed in the ultrasonic bath for a second time for 30 min and stirred for 30 min. Finally, the mixture was degassed under vacuum, stirred slowly for 1 h, poured onto glass slides (preheated to 60 °C), and spread using a film casting doctor blade. After 240 min in a conventional oven at 60 °C, the samples in film form were removed from the slides and pressed at 80 °C for a period of 1 min under a pressure of 9.81×10^5 Pa.

$$M_c = M_p \cdot (\rho_c/\rho_p) \cdot (\varphi_c/1 - \varphi_c) \tag{1}$$

where M_p is the polymer weight, M_c is the filler weight, ρ_c and ρ_p are the densities of the filler and the polymer, respectively, and φ_c is the filler volumetric fraction.

2.2.2. PU_PZT_CB three-phase composites

Three-phase composites of PU_PZT_CB were fabricated, taking into account the volume of particulates in the composite in relation to the fixed mass of PU, according to Eq. (1). The composites were obtained by adding CB slowly to the polyurethane dispersion. The mixture was stirred for approximately 1 h, followed by an ultrasonic bath for 30 min. Subsequently, the PZT was added to the mixture. The mixture was then stirred for 1 h and subjected a second time to the ultrasonic bath for 30 min and stirred for 1 h. Finally, the mixture was degassed under vacuum, stirred slowly for 1 h and then the films were prepared in the same way as those obtained for biphasic composites. The composites were designated PU_PZT_CB(X/Y), where X and Y indicate the volume fraction of PZT and CB in the composite, respectively.

3. Characterization

The morphology of the cryogenically fractured surfaces of the composite films was analyzed using an EVO LS15–Zeiss scanning electron microscope. The samples were attached to aluminum stubs with conductive carbon tape and sputtered with gold prior to analysis. The images were collected in secondary and backscattering mode (BSD). The mean diameter of the PZT and CB agglomerates in the micrographs was calculated using ImageJ 1.45 software. About 200 structures were examined for each composition. The thermal behavior of the composites was characterized by a differential scanning calorimeter (DSC) from TA Instruments (New Castle, USA) model MDSC 2920. Samples between 10 and 15 mg were sealed in aluminum pans and subjected to a cycle of heating/cooling/heating at a temperature range of −30 to 250 °C, using a nitrogen atmosphere at a flow rate of 65 cm^3/min. The heating rate employed was 10 °C/min. The mean values for the melting temperature and enthalpies were obtained from the first heating. A second heating run did not add any extra information so it was not included in this work. For reference, the calculated values for the enthalpy of the composites were normalized with respect to the mass of the polymer present. From the enthalpy values, the relative crystallinity X_c of the composites was calculated as shown in Eq. (2) [30]:

$$X_c = \Delta H_m / \omega \, \Delta H_{100} \tag{2}$$

where ΔH_{100} is the melt enthalpy for pure PU, ω is the mass fraction of the polymer matrix in the composite, and ΔH_m is the sample melt enthalpy. For electrical and dielectric characterization, the samples were metallized with gold on both sides and kept in a chamber with humidity controlled to 22% of the relative humidity before the measurements were taken. Impedance spectroscopy was conducted using the Hewlett Packard 4192A impedance analyzer, coupled to a data acquisition system. The measurements were gathered in the frequency range of 10^3–10^6 Hz at room temperature. The voltage applied was $1V_{rms}$. Electrical conductivity in the dc regime was obtained by the two-point method. Three samples were used to obtain the mean values, as well as the standard deviation for each composition.

4. Results

4.1. Scanning electron microscopy (SEM)

Fig. 1a presents the SEM images of the PU_PZT and PU_PZT_CB composites (25% vol CB). The surface of the biphasic composites exhibits greater roughness compared to the neat PU (inset in Fig. 1a), indicating an increase in energy dissipation during fracture owing to the presence of PZT. The micrographics obtained by BSE clearly showed the PZT agglomerations (white spots); most of these had a spherical shape, with a mean diameter of (40 ± 17) μm. The black spots observed in Fig. 1h are microvoids, which resulted from the high PZT concentration. The addition of CB substantially affected the PZT dispersion, as shown in Fig. 1m−q. In addition, the surface roughness decreased. For large amounts of PZT, such as 30−40%, some PZT agglomeration is still present (Fig. 1p, q). In the same way, CB agglomerates also occurred for high CB concentrations, as shown in BSD images by means of elliptical structures in dark contrast. These structures were analyzed by the contour of the elliptic silhouette in the fracture plane. Fig. 2 shows that a linear reduction of agglomerate size was observed as a function of PZT concentration and that these agglomerates tended to assume a spherical shape. The CB, when dispersed in liquids or polymeric solutions, can acquire surface charges, as postulated by Schueler [27]. Harbour et al. [28] demonstrated that such charges appear by a triboelectric process between CB particles and polymers. The charged particles cause mutual repulsion, thereby reducing or preventing the agglomeration from forming. At the same time, the shear in the system was intensified, with PZT helping the broken