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Nanotexture influence of $BaTiO_3$ particles on piezoelectric behaviour of PA 11/$BaTiO_3$ nanocomposites

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ABSTRACT

The piezoelectric activity of a hybrid ferroelectric nanocomposite, i.e. polyamide 11/barium titanate (BT), has been investigated for different loadings of BT particles. The BT volume fraction (ϕ) was ranging from 0.024 to 0.4 with a particle size of 50, 100, 300 and 700 nm. The influence of polarization mode on the piezoelectric behaviour has been studied. The magnitude of the poling field used in this study is in the same order of magnitude of the one used for bulk BT i.e. significantly lower than for piezoelectric polymers. The optimum piezoelectric coefficient is reached when the amorphous phase of the polymeric matrix is in the liquid state i.e. for a polarization temperature higher than the glass transition and for time constant allowing macromolecular mobility. The composite piezoelectric activity decreases for particles size lower than 300 nm due to the loss of the tetragonal phase. The nanotexture of these particles has been investigated by transmission electron microscopy (TEM) and high-resolution TEM. A core shell structure has been observed. An increase of the longitudinal piezoelectric strain coefficient d_{33} with the raising of BT volume fraction was shown. Contrary to inorganic piezoelectric ceramics, the dielectric permittivity of hybrid composites remains moderate; therefore it allows the piezoelectric voltage coefficient of composites to be higher than ceramics.

1. Introduction

During the last decades, piezoelectric polymers like poly(vinylidene fluoride) (P(VDF)) [1,2] and polyamide 11 (PA 11) [3–6] have been very attracted since they can be associated with versatile morphology and attractive mechanical properties of organic polymers. By using copolymer of vinylidene fluoride trifluoroethylene (P(VDF-TrFE)) [7] and P(VDF-TrFE-CFE) terpolymers [8], the experimental procedure to obtain piezoelectric phases have been considerably facilitated. Nevertheless, the poling procedures remain more difficult in regards to inorganic ferroelectric ceramics such as barium titanate (BT) [9]. An interesting approach to optimize piezoelectric properties has been to associate organic polymers with inorganic piezoelectric ceramics so as to elaborate hybrid composites with thermoplastic matrix [10,11] or elastomeric one [12]. Since suitable mechanical properties requires low volume fraction of inorganic particles, the next step has been to introduce sub micronic inorganic particles. For example, Chan et al. [13] have been obtained interesting engineering parameters using fluorinated polymers. In this work, sub micronic BT particles have been homogeneously dispersed in an engineering polyamide (PA 11) to elaborate 0–3 composite. The influence of BT volume fraction on longitudinal piezoelectric strain coefficient of such composites has been previously published [14]. In this manuscript, we will focus on the influence of the polarization procedure (time, temperature, and electric field) on the piezoelectric properties of the nanocomposites as a function of particles size and nanotexture. Structure/property relationships will be established using data from diathermal scanning calorimetry (DSC), thermally stimulated current (TSC), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Engineering properties will be discussed using the merit factor.

2. Experimental

2.1. Materials and polarization procedure

[1]Polyamide 11 has been studied in its unpoled state. The mean diameter of [2]$BaTiO_3$ was 700, 300, 100 and 50 nm, respectively. PA 11 powder was dissolved in a solution of dimethyl acetyl amide (DMAc) at 160 °C and the required $BaTiO_3$ was dispersed by ultrasonic stirring in order to form a mixture. The samples were dried

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[1] PA 11 was supplied by Arkema (France).
[2] $BaTiO_3$ by Inframat materials (USA).

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over night at 110 °C to remove the traces of solvent. The nanocomposites were hot pressed to form thin films from 70 to 100 μm thickness. Volumic ratio was determined by density measurements from a mixture law: $d_{composite} = (1 - \phi)\ d_{PA11} + \phi\ d_{BT}$ (with $d_{PA11} = 1.05$, $d_{BT} = 6.05$ and ϕ the volumic ratio). The volumic ratios (ϕ) of nanoceramic in composite films were 0.1, 0.2, and 0.4, respectively. For electric polarization, gold electrodes were evaporated on both sides of thin films by cathode pulverization. Nanocomposites were poled to orient the electrical dipoles of nanometric ceramics; a macroscopic polarization P was obtained. The films were polarized in an oil bath to prevent any voltage breakdown. The heating of the oil bath was performed with an accuracy of 3 °C. Electric signal was generated by a ±10 V generator and then amplified using a ×2000 voltage amplifier. The electric field E was progressively increased until the required voltage and kept constant 30 min. It was removed before short-circuit. To check the poling process, the current versus the applied field was measured (for purpose of clarity these data will not be reported). The samples were short-circuited to relax the internal stress induced during the poling and then annealed at room temperature for 1 day. The value of coercitive field for $BaTiO_3$ and PA 11 were determined near 3 and 100 kV/mm, respectively.

2.2. Methods

2.2.1. Scanning electron microscopy

JEOL JSM 6700F-scanning electron microscope with field emission gun (SEM-FEG) was used to study BT dispersion in the polyamide matrix. As BT density is higher than polyamide one, backscattered electron detection was used. The dispersion of 700 nm BT particles has been analyzed by FEG-SEM microscopy. Fig. 1(a,b) (at different magnification) shows a homogeneous dispersion of particles (white contrast) in the PA matrix for a high filler content ($\phi = 0.4$). This dispersion is free from agglomeration even for the large scale. The BT particles are separately included in the polymer matrix.

2.2.2. Standard diathermal scanning calorimetry

Standard diathermal scanning calorimetry (DSC) measurements were performed using a DSC/TMDSC 2920 set up. The sample temperature and the heat-flow were calibrated using standard procedure. The glass transition temperature of PA 11 was determined near $T_g = 45$ °C. The ferroelectric to paraelectric phase transition of the particles (endothermic peak) were measured by standard DSC using a heating scan q_h of +10 °C min^{-1}. DSC measurements were performed on BT nanopowders (Fig. 2). The Curie transition of BT is characterized by an endothermic peak near 130 °C. Fig. 2 shows a small decrease of the enthalpy of ferro/paraelectric phase transition for the particles of 300 nm compared with 700 nm particles. This fact corresponds to a decrease of the Curie temperature (T_c) probably due to a size effect observed in the following experimental section. We do not point out any phase transition for the 50 and 100 nm particles by DSC.

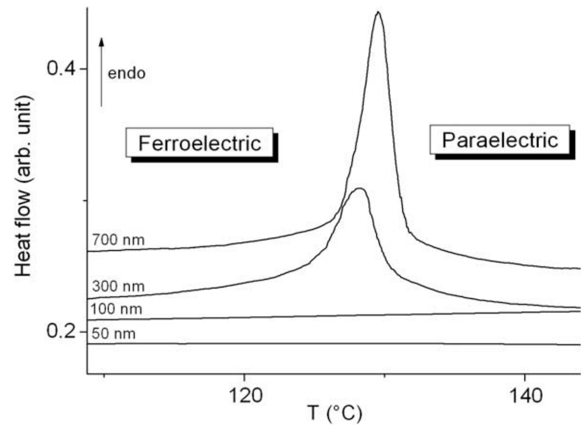

Fig. 2. Curie transition of BT nanoparticles for various nanosize obtained by DSC.

2.2.3. Dynamic dielectric spectroscopy

A novocontrol broadband dielectric spectrometer system BDS 400 was used to obtain the dielectric permittivity. Isothermal measurements were carried out. The complex dielectric permittivity $\varepsilon^*(\omega,T)$ was recorded. The real part of the dielectric permittivity, ε', used to do calculation, was extracted from the isotherm 25 °C and for the frequency 1 kHz ($BaTiO_3$ monocrystal $\varepsilon' = 1500$). Real part of the dielectric permittivity change across the dynamic glass transition of PA 11 is equal to $\Delta\varepsilon = 5.5 \pm 0.2$ at $T_\alpha = 50$ °C.

2.2.4. Piezoelectric measurements

Piezoelectric measurements were carried out using a PM 200 piezometer supplied by Piezotest (UK), with a force of 0.25 N at 110 Hz in frequency. The piezoelectric coefficient d_{33} (pC/N) is measured in the same direction than the polarization field, following the relation:

$$P = d_{33} \times \sigma$$

where P is the polarization (C/m^2) and σ the applied stress (N/m^2). As example, the d_{33} value of $BaTiO_3$ monocrystal is around 90–100 pC/N at 25 °C.

2.2.5. Thermally stimulated current

Complex TSC thermograms were carried out on a TSC/RMA Analyser. For complex experiments, the sample was polarized by an

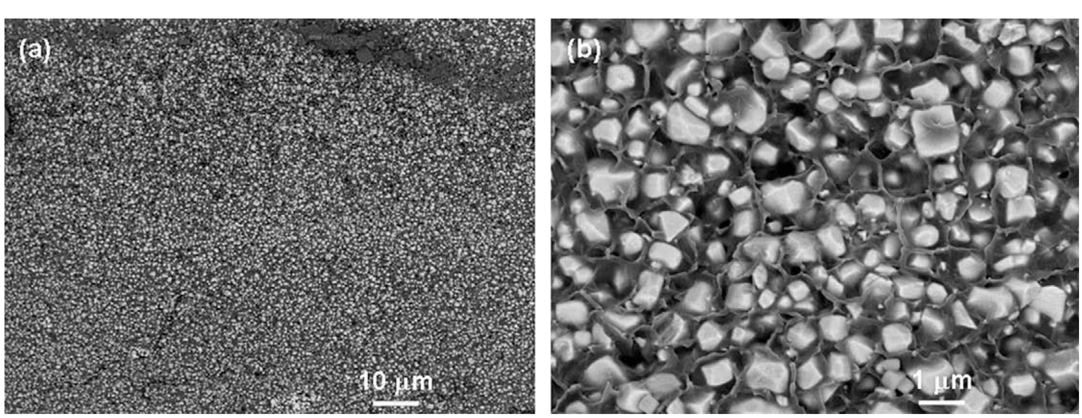

Fig. 1. FEG-SEM images of PA 11/BT nanocomposites for ϕ 0.4 and 700 nm in diameter (a) ×1000 and (b) ×10,000.