



Molecular mobility in piezoelectric hybrid nanocomposites with 0–3 connectivity: Particles size influence

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ABSTRACT

Polyamide 11/barium titanate nanocomposites have been studied by a combination of dynamic dielectric spectroscopy, thermo stimulated current and differential scanning calorimetry. The correlation between results obtained by dielectric and calorimetric methods allows us to describe the evolution of the physical structure of the hybrid nanocomposites. The molecular mobility of 0–3 connectivity nanocomposites has been explored. The influence of the nanoparticles size is specifically studied. The smaller sized fillers produce a shift of the relaxation modes observed above the glass transition temperature of polyamide 11 towards lower frequency. The increase of the organic/inorganic interface induces an increase of the ratio rigid amorphous phase/soft amorphous phase. The interfaces favour local ordering stabilized by hydrogen bonds at a nanometric scale.

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1. Introduction

Since the discovery of the ferroelectric behaviour of some class of polymers [1–6], these materials have attracted a great interest due to their good piezo/pyroelectric properties, low permittivity, lightweight and ductility [7]. These materials have potential use as sensors and electromechanical transducers. However, the poling field required to give a ferroelectric property to these materials is high [8–10] that could restrict their use in some particular cases. Ferroelectric ceramics such as barium titanate are commonly used for their high electroactive properties and low poling field [11,12]. In order to overcome the disadvantage of high poling field of organic ferroelectrics, inorganic particles are dispersed into a polymeric matrix to realize a 0–3 connectivity according to the Newnham nomenclature [13]. Previous works have shown that the piezo/pyroelectric properties of these composites have a poling field more than 20 times lower than ferroelectric polymers [14–17]. The final electroactive properties of these composites are close to the ones of organic materials while keeping the ductility of the polymeric matrix [18].

Few works have been devoted to the influence of the inorganic phase on the physical structure of the organic amorphous phase. In this study we report the particles size influence of inorganic ferroelectric barium titanate on the molecular dynamics of the polyamide 11 amorphous phase. Broadband dynamic dielectric spectroscopy and thermo stimulated current experiments have been combined to explore the physical structure of these composites at a nanometric scale in a broad frequency range.

2. Experimental

2.1. 0–3 hybrid nanocomposites elaboration

The mean diameter of barium titanate nanoparticles is ranging from 50 nm to 700 nm. Polyamide 11 (PA 11) powder was dissolved in a solution of dimethyl acethyl amide (DMAc) and the required barium titanate (BaTiO_3) powder was dispersed to form a mixture by ultrasonic stirring. The samples were dried over night at 110 °C to remove the solvent. The hybrid nanocomposites were hot pressed to form thin films from 100 to 150 μm thick. In order to conserve the same connectivity of the inorganic particles into the polymeric matrix, the volume fraction of BaTiO_3 has been fixed at 12 vol.%.

The experimental protocol of dispersion of barium titanate in the polymeric matrix has been checked by scanning electron microscopy (SEM). Fig. 1 shows cryo-cut samples of PA 11/ BaTiO_3 nanocomposites for $\phi = 12$ vol.% with particles size ranging from 50 nm to 700 nm. A homogeneous dispersion at nanometric scale is observed. In the specific case of composites elaborated with 50 nm particles, 1 μm aggregates are observed. For $\phi = 24$ vol.%, an important agglomeration is observed with 100 nm BaTiO_3 particles but none with 300 nm. It appears that the limit particles size to compare composites in the same connectivity is 50 nm for $\phi = 12$ vol.% and 300 nm for a volume fraction of 24 vol.%.

2.2. Differential scanning calorimetry measurements

Standard differential scanning calorimetry (DSC) measurements were performed using a DSC/TMDSC 2920 set up. The sample temperature was calibrated using the onset of melting of tin ($T_m = 231.88$ °C), indium ($T_m = 156.6$ °C) and cyclohexane ($T_m = 6$ °C) with a heating rate of

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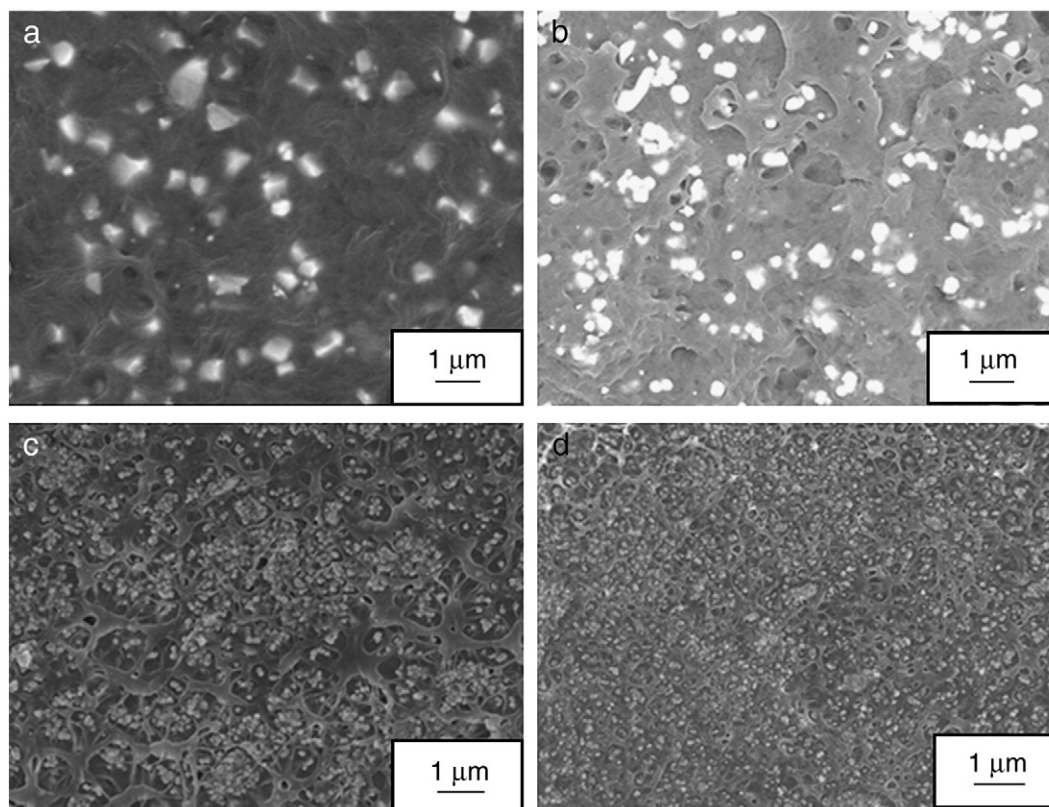


Fig. 1. Scanning electron microscope (SEM) images of PA 11/BaTiO₃ composites with $\phi = 12\%$ and particles size of (a) 700 nm, (b) 300 nm, (c) 100 nm and (d) 50 nm.

$q_h = +5^\circ\text{C min}^{-1}$. The heat-flow was calibrated with the heat melting of indium ($\Delta H = 28.45 \text{ J g}^{-1}$); its baseline was corrected with sapphire. DSC experiments were systematically carried out over a temperature range from the equilibrium state (in order to remove the effect of previous thermal history) $T_{eq} = T_m + 20^\circ\text{C}$ down to the glassy state $T_0 = T_g - 20^\circ\text{C}$ with a constant cooling rate $q_c = +10^\circ\text{C min}^{-1}$. The temperature T_0 was maintained constant for 1 h. This thermal history allows us to get a better definition of T_g usually difficult to observe on polyamide. For each sample, the glass transition temperature and the specific heat capacity step were measured by Standard DSC during a heating scan ($q_h = +10^\circ\text{C min}^{-1}$).

2.3. Non isothermal and isothermal dielectric measurements

Thermo stimulated currents (TSC) were recorded on a TSC/RMA Analyser. For complex thermograms, the sample was polarized by an electrostatic field during $t_p = 2 \text{ min}$ over a temperature range from the polarization temperature $T_p = 80^\circ\text{C}$ down to the freezing temperature $T_0 = 0^\circ\text{C}$. Then, the field was turned off and the depolarization current was recorded with a constant heating rate $q_h = +7^\circ\text{C min}^{-1}$; the equivalent frequency of the TSC thermograms was $f_{eq} \sim 10^{-2} - 10^{-3} \text{ Hz}$. Elementary TSC thermograms were performed with a poling window of 5°C . Then the field was removed and the sample cooled down to a temperature $T_{cc} = T_p - 30^\circ\text{C}$. The depolarization current was recorded with a constant heating rate q_h . Series of elementary thermograms were recorded by shifting the poling window by 5°C towards higher temperature. Prior to any experiment, the samples were dehydrated during 30 min at 140°C .

Dynamic dielectric spectroscopy (DDS) experiments were performed using a BDS 400 spectrometer covering a frequency range of $10^{-2} \text{ Hz} - 3.10^6 \text{ Hz}$ with 10 points per decade. The samples were 3 cm in diameter and prior to any measurement the composites have been also dehydrated for 4 h at 140°C . Experiments were carried out in a temperature range from -150°C to 150°C . Dielectric isothermal

spectra were measured every 2°C . Before each frequency scan, temperature was kept constant to $\pm 0.2^\circ\text{C}$. The real ε' and imaginary ε'' parts of the relative complex permittivity ε_r^* were recorded as a function of frequency F at a given temperature T .

The dielectric loss modulus M'' is deduced from the real and the imaginary part of the dielectric permittivity ε' and ε'' , according to Eq. 1:

$$M'' = \varepsilon'' / (\varepsilon'^2 + \varepsilon''^2) \quad (1)$$

In the modulus formalism, Maxwell–Wagner–Sillars (MWS) polarization which usually occurs in heterogeneous systems like semi-crystalline polymers [19,20] is observed as a mode. In the ε'' formalism, the MWS peak is sometimes hidden by the conductivity tail. Furthermore, a simple ohmic conductivity contribution in the loss part of the complex dielectric function results in a peak in the loss part of the modulus.

3. Results

In this section, the particles size influence of BaTiO₃ nanoparticles on the molecular mobility of the PA11 amorphous phase is shown by means of dielectric techniques. The particles size is ranging from 50 nm to 700 nm.

3.1. Dielectric relaxation modes in dynamic spectroscopy

The influence of the filler size on the relaxation dynamics of PA 11/BaTiO₃ nanocomposites was characterized by DDS. As the connectivity of composites governs the final mechanical and electric properties [13], the choice of the volume fraction is crucial. Since we have observed that nanoparticles tend to aggregate for the highest BaTiO₃ contents, the volume fraction is maintained at 12%.

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