European Polymer Journal 49 (2013) 1446–1460

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Synthesis and characterization of sulfonated poly(styrene-*b*-(ethylene-*ran*-butylene)-*b*-styrene)/(strontium titanate) nanocomposites

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ARTICLE INFO

Article history:
Received 21 September 2012
Received in revised form 3 March 2013
Accepted 5 March 2013
Available online 26 March 2013

Keywords:
Block copolymer
Barium titanate
Nanocomposite
Sol–gel
Dielectric relaxation

ABSTRACT

Nanocomposite films were prepared via syntheses of $SrTiO_3$ nanoparticles in films of sulfonated poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (sSEBS) block copolymer templates. $SrTiO_3$ ionic and alkoxide precursors permeated selectively into styrene domains in which formation and growth of crystalline nanoparticles occurred through hydrolysis-precipitation reactions. FTIR spectra verified $SrTiO_3$ composition and WAXD patterns identified crystalline $SrTiO_3$ within the templates. AFM images for both unfilled sSEBS and sSEBS/$SrTiO_3$ microtomed films showed mesophase separation characterized by lamellar morphologies suggesting that $SrTiO_3$ particle insertion did not alter template morphology. Uniform distribution of Ti and Sr along the nanocomposite internal film cross sections and external surfaces was seen using ESEM/EDX. TEM images showed clusters of parallel $SrTiO_3$ rods in sulfonated styrene domains. Agreement of $SrTiO_3$ rod width in TEM images with domain size in AFM images supports the template hypothesis. Selected area electron diffraction studies of $SrTiO_3$ clusters inside sSEBS/$SrTiO_3$ provided direct identification of in situ formation of crystalline $SrTiO_3$ particles. WAXD studies demonstrated that in situ – grown particles have the same crystal structure as those produced outside the template. The frequency dependent broadband dielectric responses of these materials, both filled and unfilled, reflect strong polarizability that is more sensitive to degree of sulfonation than from insertion of $SrTiO_3$ nanoparticles.

1. Introduction

Polymer-inorganic nanocomposites as dielectric materials have received attention for applications in electrical energy storage [1–4], thin film transistors [5], embedded capacitors [6,7], and high K gate dielectrics [8]. In these arenas, conventional ceramic materials, such as strontium and barium titanate are known to have high dielectric constants [9,10].

While $SrTiO_3$ exists sparingly in nature, in the synthetic form it is used as a diamond simulant and in precision optics, varistors and advanced ceramics. Synthetic $SrTiO_3$ with a high dielectric constant (~310 at <1 kHz) at room temperature and low electric field, is used in high voltage capacitors. The unit cell of $SrTiO_3$ has cubic Perovskite structure with a lattice constant of 3.79 Å [11]. The dielectric constant of TiO_2 is lower, in the range of 86–173 depending on crystal form. By comparison, the dielectric constants of polymers that might constitute the framework of an organic host matrix throughout which small particles of $SrTiO_3$ might be dispersed, such as polystyrene, polypropylene and polyethylene are low, in the range 2.2–2.7. For SEBS the dielectric 'constant' is around 2.2 but the attachment of functional (e.g., acidic) groups will increase the

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http://dx.doi.org/10.1016/j.eurpolymj.2013.03.007

dielectric constant. The polymer matrix utilized in the studies reported here is a styrene-*co*-(ethylene-*ran*-butylene)-*co*-styrene (SEBS) triblock copolymer in which the end blocks were sulfonated. The dielectric strength (minimum electric field required for dielectric breakdown = E_{bd}) of unfunctionalized SEBS is around 25 V/μm [12] while that for $SrTiO_3$ is 35 V/μm [13].

The maximum energy stored by a capacitor is $W = (CV_{bd}^2)/2$ where C is capacitance and V_{bd} is breakdown voltage. The maximum energy density of a capacitor is $\widetilde{W} = W/(Ad) = (\varepsilon_0 \varepsilon_r E_{bd}^2)/2$, where A and d are area and thickness of the dielectric film, respectively, ε_0 is the vacuum permittivity, ε_r is the relative permittivity and $E_{bd} = V_{bd}/d$ [14]. Polymers usually show low dielectric constants, but high dielectric strengths. The main properties of interest are E_{bd} and ε_r as well as charge–discharge rates and temperature stability. Polymer nanocomposites formed by combining ceramic powders with high dielectric constants with polymers of high dielectric strength have great potential and the materials can be flexible, which may be beneficial in some applications [8].

The major strategy for preparation of polymer/[inorganic particle] composites as extreme dielectrics is to blend high ε_r ceramic particles into polymer melts or solutions [15,16], although this process often results in poor material quality due to particle aggregation. Nanoparticles such as barium titanate (BT) form aggregates that reduce the ability of the nanocomposite to resist electrical breakdown. The key to developing thin-film capacitor materials with high energy storage is an ability to uniformly disperse nanoparticles throughout the polymer. One approach to prevent aggregation involves surfactant addition [2], although residual free surfactant can lead to high leakage current and dielectric loss [17]. Another approach consists of chemically bonding organic moieties to ceramic particles to enhance dispersibility through favorable interfacial interactions [3,18].

Good dielectric properties of $SrTiO_3$ filled mullite composites have been reported [19] However, this inorganic matrix is inflexible and non-compressible so that these materials are unable to be bent into different shapes or conform to different shaped surfaces or have mechanical stimuli-responsive dielectric properties.

More similar to the work reported here is that by Li et al. in which $BaTiO_3$ nanoparticles were inserted into (A) poly(vinylidene fluoride–chlorotrifluoroethylene) copolymers and (B) poly(vinylidene fluoride–trifluoroethylene–chlorotrifluoroethylene) terpolymers [3]. The nanoparticles were surface-functionalized with ethylene diamine in order to improve their dispersion throughout the polymer matrix. At 20% nanoparticle content, the dielectric permittivities were 24 and 50 for matrices A and B, respectively, at 1 kHz at room temperature. The real permittivity of the nanocomposites was dominated by the filler (180 at 1 kHz and room temperature) while the loss permittivity was dominated by the matrix owing to micro-Brownian motions of chain segments in the amorphous regions.

Phosphonic acids act as surface modifiers on $BaTiO_3$ nanoparticles, allowing for homogeneous, high volume fraction nanocomposites in polymer hosts by simple solution processing. Pentafluorobenzyl phosphonic acid-modified $BaTiO_3$ nanoparticles dispersed in poly(vinylidenefluoride-*co*-hexafluoropropylene) films exhibited large permittivities and high dielectric breakdown strengths [18].

In another work, $BaTiO_3$ particles with diblock copolymer shielding layers were fabricated and the dielectric properties of barium titanate-copolymer/polystyrene composites examined. Polystyrene-*b*-poly(styrene-*co*-vinylbenzylchloride) was introduced to completely wrap the BT nanoparticles. The two-step processes to form polymer shielding and self-assembled layers resulted in excellent dielectric properties where a charged layer is buried to minimize the development of breakdown pathways and leakage current. The considerable energy density value of 9.7 J/cm^3 was achieved [20].

One alternate approach, the polymer-in situ synthesis of nanoparticles (rather than pre-formed particles) has been used to prepare polymer/[inorganic oxide] nanocomposites [21,22]. Here, a preformed polymer film is immersed in a solution of Si or metal alkoxide precursor molecules that diffuse into the film wherein sol–gel reactions occur in targeted regions [23]. Using this method, Mauritz et al. prepared various polymer nanocomposites containing different inorganic phases, such as SiO_2, TiO_2, ZrO_2 and Al_2O_3 in Nafion® [24–26] and sulfonated (s) poly(styrene-*co*-isobutylene-*co*-styrene) [22,27] and poly(styrene-*co*-ethylene/butylene-*co*-styrene) (sSEBS) [28,29] materials. Superparamagnetic cobalt ferrite particles were also shown to selectively initiate and grow in the sulfonated polystyrene block domains of SEBS copolymers due to chemical affinity between functional groups in styrene blocks and precursor metal ions [30]. One advantage of this approach is particle size control and particle dispersion which is attributed to a morphology template effect.

Bulk strontium titanate can be synthesized via calcination of strontium carbonate and rutile titanium (IV) oxide that is sintered at the high temperature of ~1300 °C to facilitate inter-diffusion of metal cations so that they can combine into crystal structures [31,32]. Recently, methods for low temperature preparation of crystalline $BaTiO_3$ have been reported, including sol–gel [33–35], hydrothermal [36,37], and sol-precipitation (alkoxide-hydroxide route) [38,39], in which case $MTiO_3$ nanoparticles are prepared in a liquid phase at low temperature ($\leqslant$100 °C).

The first step in preparation of $MTiO_3$ crystals using the sol-precipitation process is hydrolysis and condensation reactions of $Ti(OR)_4$ which results in the formation of a gel of hydrated titanium oxide with numerous uncondensed TiOH groups. Then, an aqueous $M(OH)_2$ solution is added to the TiO_2 gel products where M^{2+} cations permeate into the gel, leading to the formation of crystalline $MTiO_3$ with precipitation. The formation of crystalline $MTiO_3$ can be accelerated by increasing the temperature.

In wider use, barium or strontium salts such as $BaCl_2$ or $Sr(NO_3)_2$, and a strong base such as NaOH or KOH (instead of metal hydroxides $M(OH)_2$) are added to the product of the reactions of hydrolyzed $Ti(OR)_4$ in sequence [40,41]. The widely accepted two-step process mechanism for sol-precipitation is summarized in the following equations [42–44].