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Interfacial treatment effects on behavior of soft nano-composites for highly stretchable dielectrics

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ABSTRACT

We investigate the influence of interfacial treatment on the matrix–filler interaction using a melt mixing process to fabricate robust and highly stretchable dielectrics. Silicone oil and silane coupling agent are studied as possible solutions to enhance the compatibility between the inorganic fillers and polymer matrix. Morphology, thermomechanical and dielectric behavior of the prepared specimens are studied. Results show that specimens filled with silicone oil coated particles have promising dielectric and thermal properties. The mechanical properties reveal a stiffness enhancement by 67% with a high strain at break of 900%. The relative permittivity of the specimens prepared with silicone oil increased by 45% as observed from the dielectric analysis.

1. Introduction

Deformable dielectrics are found in various applications and have been widely used to achieve high flexibility and stretchability [1–3]. Dielectric materials with high energy density [4] have also gained great attention for their transducing properties as they efficiently convert energy signals required for sensing, actuating, and energy harvesting [5,6]. Soft elastomeric dielectrics are vastly used in manufacturing of soft sensors and actuators, targeting several applications such as structural health monitoring by enabling skin-like sensing solutions [7], and advanced bionics where sensors and actuators are used interchangeably to create a substitute to human organs and to replace sensing elements and muscles. A sensor's function is to convert input stimuli which can include mechanical, temperature change, and magnetic field. The performance of a sensor is inherently dependent on its mechanical and electrical properties. Polymers are very versatile materials, with an important potential for property alterations achieved through variations in polymerization chemistry, compounding and processing [8]. By embedding fillers with high permittivity in a highly elastic polymer matrix, it is possible to create a stretchable sensor with enhanced sensitivity [9]. For this purpose, an elastomeric composite of (poly-Styrene-co-Ethylene-co-Butylene-co-Styrene) (SEBS) block copolymer (BCP) filled with rutile titania (TiO_2) has been developed by the authors to fabricate a soft stretchable elastomeric sensor termed as soft elastomeric capacitor (SEC) for structural health monitoring (SHM) of mesosystems [3,4]. The proposed sensing application was for civil infrastructure [7], for which the monitored levels of strain are typically small [10].

The choice of a BCP is motivated by the heterogeneous phase separation capabilities at the nanoscale [11–13]. BCPs have shown superior control on the spatial and orientational distribution of nanofillers used to alter their properties [14]. Thermoplastic BCPs are physically cross-linked materials and enable broad range of processing techniques. In particular, SEBS is a soluble tri-BCP thermoplastic elastomer with a rubbery and semi-crystalline domain. It is used in many medical applications due to its purity, softness, elasticity, and strength [15]. The inorganic TiO_2 particles (average size of 300 nm) are characterized by a high anisotropic permittivity [16] of approximately 120 along the x axis. The composite is thought of as a host guest system where the SEBS provides the matrix to disperse filler particles, which show higher stiffness due to the presence of the filler.

The interface between the filler and the polymer matrix of nanocomposites can have an important effect on its mechanical and electrical properties [17,18]. The surface interaction between the filler and the polymeric matrix may also influence the dispersion process. In our case, the interaction between SEBS and TiO_2 is obstructed by the non-polar nature of SEBS, which prevents the polar inorganic TiO_2 particles from dispersing throughout the polymer

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matrix uniformly. To resolve this issue Ganguly et al. [19] proposed modifying the SEBS by grafting polar functional groups such as maleic anhydride, improving the dispersion process. Stoyanov et al. [9], used silicone (PDMS, polydimethylsiloxane) oil coated TiO_2 particles to enhance the particle matrix interaction and dispersability. The existence of the non-polar methyl ($-CH_3$) end groups in the PDMS improves the affinity between the surfaces due to the non-polar nature of the SEBS matrix, thus enabling a more homogeneous distribution. The coated particles are used in this study.

Research suggests that having higher interfacial surfaces leads to higher permittivity [17,18], and has the potential to increase permittivity by up to a 100 times [20–23] for nano-composites fabricated with fillers such as TiO_2 [17] and $BaTiO_3$ [22], moreover, researchers found that simple mixing rules applies and the experimental results matched the theoretical ones [15,16,24]. At low levels, an increase in filler volume fraction leads to an increase in permittivity, but to a decrease in the breakdown strength by over 50%, resulting in a decrease in the electrostatic energy density [17]. McCarthy et al. [17] studied the effect of adding different TiO_2 particle sizes in an SEBS matrix on the electrical properties of the composite using a solution cast process. Particles of 15 and 300 nm diameter were used with and without a surfactant (sorbitan monopalmitate) to enhance the dispersion of the particles in the matrix. The particles without surfactant resulted in an increase of 350% and 1700% relative permittivity for the 15 nm and 300 nm diameter particles, respectively. Using the surfactant had insignificant effect on the 300 nm particles, but limited the increase in relative permittivity to 240% in the case of the 15 nm particles. Carpi et al. [25] studied the effects of adding TiO_2 particles to a silicone matrix, showing an increased in relative permittivity and decrease in the elastic modulus. A 15% vol was found to be an optimal level of filler content for the dielectric and mechanical properties.

Silane coupling agents can also be used to provide adhesion between surfaces. Salines are organofunctional groups capable of decreasing the interfacial tension. They bond inorganic material such as mineral fillers (TiO_2) to organic matrices such as (SEBS), and they provide adhesion between polar phase polymers and non-polar fillers. Here, the Si(OR)3 part of the silane reacts with the polar components and the organofunctional group reacts with the non-polar matrix to create the bond [8]. Kaynak [26] studied the effect of adding different types of silane coupling agents to an epoxy matrix filled with recycled rubber particles. Results showed that some of the silane coupling agents led to an increase in tensile strength, but also to a reduction in the impact and fracture toughness of the specimens. Ismail et al. [27] used silane coupling agent Bis[3-(triethoxysilyl)propyl]tetra sulfide (Si-69) with natural rubber composite filled with bamboo fiber and investigated the effects on the mechanical properties and curing time. Results showed an increase in the tensile strength, tear strength, hardness and tensile modulus.

The fabrication process may also influence the mechanical and dielectric properties of polymer composites. Recently we reported the advantages of melt mixing on solution mixing for the fabrication of soft dielectrics [28]. We showed that the melt mixing process enables 1) faster fabrication because of the solvent-free process that does not require evaporation time, 2) enhanced control over the membrane's size and thickness, 3) easier processing of large quantities 4) a fine dispersion of the filler material due to high shear mixing, and 5) the elimination of organic solvent within the nanocomposite that exists when a solution cast process is used, which could influence mechanical and dielectric properties of the composite.

The objective of this paper is to study the influence of molecular level interaction between the filler particles and polymer matrix to enable soft dielectrics with enhanced sensing and actuation properties. Here, we investigate the effect of interfacial treatment on SEBS-TiO_2 nano-composites fabricated using a melt mixing process. The morphology, mechanical properties, and dielectric properties are studied in function of treatment, including PDMS silicone oil and Si-69 coupling agent.

This paper is organized as follows. Section 2 presents the materials used and the experimental procedures. Section 3 discusses the results acquired from the tests. Section 4 concludes the paper.

2. Experimental

2.1. Materials

The thermoplastic matrix material SEBS-Mediprene 500120M, (poly-Styrene-co-Ethylene-co-Butylene-co-Styrene) was purchased from VTC Elastoteknik AB, Sweden (density = 930 kg/m^3). Rutile titania (TiO_2) namely R320, R320D (Sachtleben Chemie GmbH, Germany), were used as high permittivity fillers. The TiO_2 particles have an average diameter of 300 nm and density $\rho = 4200$ kg/m^3. While R320 is uncoated, R320D is coated with silicone oil (PDMS). Bis[3-(triethoxysilyl)propyl]tetra sulfide, a silane coupling agent commonly used as a rubber additive, was purchased from Santa Cruz Biotechnology, Inc. Dallas, Texas, USA.

Fig. 1 shows a scanning electron microscopy (SEM) image of R320 powder (a) and its crystal structure (b), showing a

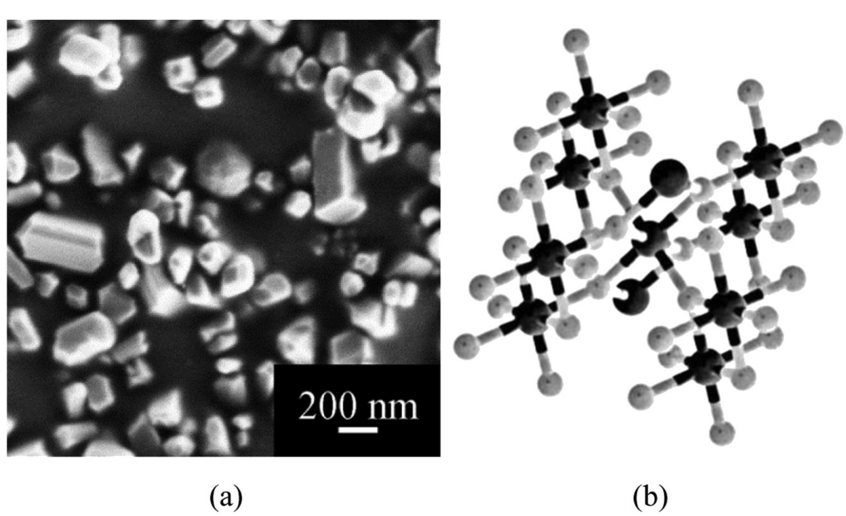

Fig. 1. (a) Field effect SEM image of rutile TiO_2 powder R 320 (b) Crystal structure of TiO_2, titanium and oxygen are represented by the larger and smaller balls respectively.