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Dielectric response of vulcanized natural rubber containing $BaTiO_3$ filler: The role of particle functionalization

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ABSTRACT

Natural rubber (NR) nanocomposites have been prepared with hydroxylated barium titanate filler ($BaTiO_3$-OH), employing emulsion polymerization followed by vulcanization process. The addition of barium titanate, a compound with high dielectric permittivity, was envisaged to increase the insulating properties of NR films, thereby reducing the electrical stress and the possibility of undesired arcing on their surfaces. The content of perovskite particles greatly affected both, the mechanical and the electrical properties, of the vulcanized films. It was observed that the optimum functionalized nanoparticle concentration is around 0.25–0.50 phr, range in which the elongation of break was maintained between 874–935% and the tensile strength was between 4.40–4.80 MPa; whereas the dielectric permittivity (ε′) is slightly lower than the pristine NR or the NR compounded with high content of $BaTiO_3$ nanoparticles. The dielectric study revealed the presence of two dielectric relaxation modes: (*i*) glass to rubber transition (α-relaxation) and (*ii*) interfacial polarization (IP), known as Maxwell – Wagner – Sillars (MWS) polarization. The comparison between small concentrations of non-functionalized and functionalized $BaTiO_3$ inside NR polymeric films lead to the conclusion that the dielectric breakdown strength is high for non-functionalized fillers, supposedly due to less IP polarization phenomena.

1. Introduction

Thin electrically insulating elastomers are promising electromecanically active polymers to be used in sectors such as electrical generators, actuators, flexible capacitors, solar cells, batteries, strain sensors, electrical insulating devices, piezoelectric devices and others. However, there are not many techniques that can be employed for the electrical characterization of polymers. Their deformations, as for example under pressure inside probes using contact methods, can interfere to obtain accurate results [1]. The development of Broadband Dielectric Spectroscopy (BDS) technique [2], during the mid-nineties, with extremely wide frequency range (from 10^{-6} Hz up to 10^{12} Hz) allowed the study of both molecular fluctuations and collective phenomena, phase transitions, charge and polarization effects in amorphous [3–5], semi-crystalline [6,7], and elastomeric polymer composites [8–10]. The versatility of dielectric spectroscopy allowed it to become a fundamental tool in multidisciplinary design, characterization, quality control and application of advanced functional materials and systems applied in such diverse fields.

Vulcanized natural rubber (NR) is a type of elastomer derived from latex, which is a colloidal suspension of micro sized rubber particles extracted from the *Hevea brasiliensis* tree and is widely used as a matrix resin to obtain green nanocomposites [11,12]. NR elastomer presents certain unique advantages over competitive synthetic rubbers in many applications caused by the unique combination of its physical–mechanical properties. Therefore, it has been used as dielectric elastomer transducers, protective thin films, adhesives, tires, gloves, coatings, joints, pipes, tubes, and others; and its applications are still growing [13,14].

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Table 1
Compounding formulation used to prepare NR/$BaTiO_3$-OH nanocomposites (in phr).[a]

Reagents	NR	$BaTiO_3$-OH 0.25 phr	$BaTiO_3$-OH 0.50 phr	$BaTiO_3$-OH 1.0 phr	$BaTiO_3$-OH 5.0 phr	$BaTiO_3$-OH 10.0 phr
Latex	100	100	100	100	100	100
Accelerator	6.0	6.0	6.0	6.0	6.0	6.0
Sulphur	6.0	6.0	6.0	6.0	6.0	6.0
Antioxidant	8.0	8.0	8.0	8.0	8.0	8.0
ZnO	8.0	8.0	8.0	8.0	8.0	8.0
TiO_2	5.0	4.75	4.5	4.0	0.0	0.0
$BaTiO_3$-OH	–	0.25	0.50	1.0	5.0	10.0
Other fillers	7.0	7.0	7.0	7.0	7.0	7.0

[a] phr = parts per hundred of rubber per weight.

Nowadays, composites comprising a polymer matrix and ferroelectric ceramic with high dielectric constant filler (also called high-k composite materials) have been extensively explored to serve as dielectric materials in high-energy–density devices [15,16]. For several years, the nanoscale dispersion of inorganic particles in a polymeric matrix has been very convenient due to the positive reinforcing effect and specific properties that can generate these particles when they are finely dispersed in the polymer chains [17,18]. For instance, Dang et al. [19] have reported a review on the effect of nanosized materials to increase the permittivity of advanced materials, used in power-energy-storage devices. They stated, for example, that the dielectric permittivity decreases dramatically from 5000 to hundreds as the grain size of barium titanate ($BaTiO_3$) is reduced from 1 μm to 30 nm. This decrease is assigned to the reduction of the portion of polar tetragonal phase and the increase of the non-polar cubic one, due to the diminution of the particle size [19].

Among the ferroelectric ceramics barium titanate has been extensively investigated due to its high dielectric constant [20–22]. The $BaTiO_3$ crystal is a multifunctional oxide that exhibits complex phase transition, between 120 °C and 1457 °C it has a cubic perovskite structure that consists of corner linked oxygen octahedral containing Ti^{4+}, with Ba^{2+} [22,23]. However, the ferroelectric ceramics usually have poor compatibility with the polymer matrices. They are very prone to agglomeration due to their high surface energy, especially when the concentration of the ceramic nanofillers is high, so it leads to percolative pathways through aggregated fillers, thus increasing the leakage current and hence lowering the dielectric breakdown strength of the nanocomposites [24,25]. To overcome this problem, surface functionalization is currently being employed [26–28]. By modifying the inorganic filler surface by chemical processes such as hydroxylation, amination, sulfonation and grafting polymers, the $BaTiO_3$ particles becomes more uniformly dispersed in a suitable solvent media, that in turn increases the overall dielectric constant, and the breakdown field strength of the polymer-ceramic composites [29–31]. Nevertheless, the interfacial dipole layer emerged by chemical modification of the surface by polar species, like $BaTiO_3$ hydroxylated particles, may play an important role on the electrical response of the polymer [32].

A key aim of the present work is to study the dielectric permittivity of vulcanized NR polymers after adding very low concentrations of hydroxylated barium titanate ($BaTiO_3$-OH) nanoparticles, while retaining their other excellent physical properties. The novelty of the present work relies on the comparison of the interfacial interaction between non-functionalized and functionalized $BaTiO_3$ nanoparticles with the organic polymer matrix and its influence on its breakdown strength (E_B).

2. Experimental section

2.1. Materials

All samples were prepared by employing commercially available reagents. Barium titanate nanopowder ($BaTiO_3$, particle size about 100 nm, according to the supplier), zinc oxide (ZnO), titanium dioxide (TiO_2) and hydrogen peroxide solution (H_2O_2) were supplied by Sigma Aldrich Spain. Sulfur (reagent grade) and zinc dibuthyl dithiocarbamate (ZDBC) were used as vulcanizing agent and accelerator, respectively. Cab-o-Sperse® (Cabot Corporation) was used as dispersant agent to incorporate $BaTiO_3$ functionalized particles to rubber formulation. The latex used in this study is a colloidal suspension doubly centrifuged to increase the rubber particles concentration. It was purchased from several suppliers (from Malaysia and Brazil) and used as received. Fillers and other ingredients used for the latex formulation were also of commercial grade.

2.2. Surface hydroxylation of $BaTiO_3$ nanoparticles and preparation of NR/$BaTiO_3$-OH nanocomposites

The surface hydroxylation of $BaTiO_3$ nanoparticles with H_2O_2 was performed according to previous work reported by Jiang and coworkers [33]. Briefly, about 10 g $BaTiO_3$ nanoparticles and 80 mL aqueous solution of H_2O_2 (30 wt%) were added to a round bottom flask and the mixture was sonicated for 10 min (8 s pulses at 50% of amplitude) and refluxed at 105 °C for 24 h. Then the nanoparticles were recovered by centrifugation at 10,000 rpm for 10 min and were washed with deionized water twice. Finally, the product was dried under reduced pressure at 80 °C for at least 24 h until a constant weight was obtained.

The NR/$BaTiO_3$ nanocomposites were prepared with loadings in the range from 0.25 to 10 phr at 23 °C using a Heidolph mechanical overhead stirrer model (RZR-1) provided with radial flow impeller stirrer blade, with a rotor speed of 60 rpm. The compounding formulations used for the preparation of NR/$BaTiO_3$ nanocomposites are shown in Table 1. Once functionalized, barium titanate NPs (500 mg) were dispersed in 3 mL of Cab-o-Sperse® solution (Scheme 1, solution 1) with vigorous stirring and further sonicated for 20 min (8 s pulses at 50% of amplitude) using Sonopuls Ultrasonic Homogenizers (Bandelin, model HD 2200), to obtain a homogenous dispersion. The solution 2 in Scheme 1 corresponds to the preparation of the polymer emulsion. In this case, the solution of rubber was first mechanically stirred for 5 min, and then ZnO and TiO_2 were added and mixed for 2 min. Solution 1 was poured to solution 2 and ZDBC and sulfur were added stepwise and similarly stirred for 2 min. The emulsion was then further stirred for 30 min with mechanical stirring for complete homogenization. The rubber compound was finally poured onto Petri dishes to obtain films 1 mm thick for the electrical studies. The Petri dishes were left to prevulcanize at 75 °C for 2 h in an oven for obtaining the solid film. Afterwards samples were washed gradually in a bath with distilled water from 25 to 70 °C, dried on air and then left to complete curing at 75 °C for 24 h before testing. It is important to highlight that all solids were sonicated and dispersed on aqueous solutions before addition to the rubber emulsion (solution 2).