Functionalization of $BaTiO_3$ nanoparticles to optimize the dielectric performance of electroactive polymer nanocomposites based on PDMS matrix

SUPPLEMENTARY INFORMATION

Particle Synthesis (BTH)

Particle synthesis was carried out following the procedure reported elsewhere [28] utilizing a nitrogen environment throughout the process to prevent the precipitation of $BaCO_3$. Ti sol was prepared by mixing 0.01 moles of $Ti(OiPr)_4$ with glacial acetic acid and absolute ethanol in a 1:4:8 molar ratio, followed by one hour of stirring. Separately. Ba sol was formed by dissolving 0.011 moles of $Ba(CH_3COO)_2$ in 5 mL of distilled water containing 0.022 moles of CH_3COOH, maintaining a Ba/Ti molar ratio of 1.1 and a barium-to-acetic acid ratio of 1:2. Ba sol was then added slowly to the Ti sol and stirred at RT for one hour. Finally, the mixture was brought to a pH greater than 13 through the addition of a 3N KOH solution forming a milky suspension, which was promptly transferred into a stainless-steel autoclave with a PTFE liner heated at 200 °C for 2h. The reactor was left to naturally cooled to RT. Then powders were recovered via centrifugation. The collected precipitates were thoroughly washed and subjected to a dual-stage drying process, consisting of 4–6 h at 80 °C followed by an overnight period at room temperature. Dried particles were finally annealed at 900 °C for 4h in a tubular furnace.

Obtained particles were spherical and presented an average size of 117 ± 27 nm. X-ray diffraction pattern of BTH sample evidenced the presence of the tetragonal main phase with 25% of cubic phase; Rietveld analysis revealed that BTH powders displayed a very good value of tetragonality (1.007) [28]. The density of BTH particles was measured with a He pycnometer, and resulted to be 5.6 (0.1) g/cm^3.

Particle Functionalization

Particle functionalization was carried out in 2 steps following the procedure presented elsewhere [29]. Step 1: hydroxylation process. Step 2: functionalization with organosilanes. Particle hydroxylation is intended to increase the amount of OH- groups on $BaTiO_3$ surface and facilitate the condensation of the silane on particle surface. The detailed procedure is described below.

Step 1. 1g of BTH is dispersed in 100 mL of H_2O_2 using a 200 W bath sonicator for 10 min. Then, the mixture is refluxed and stirred at 105 °C for 8 hours in a round-bottom flask (equipped with a condenser) and then allowed to cool naturally. The particles were then centrifuged at 4000 rpm for 10 min, washed with DI water, and dried overnight at 80 °C in vacuum. The procedure was repeated several times.

Step 2. Following the hydroxylation, the functionalization of BTH particles was carried out. 450 mg of the hydroxylated particles were dispersed in 30 mL of toluene and sonicated for 10 min. 4.3 mL of 3-glycidyloxypropyltrimethoxysilane (GPTMS, G) were added dropwise to the stirring mixture (keeping a nitrogen flow to maintain the atmosphere inert). The reaction was carried out at 120 °C for 24 hours. The functionalized particles were centrifuged at 4000 rpm for 10 min, washed with toluene, and dried overnight at 80 °C in vacuum. Alternatively, BTH particles were functionalized with 2-[(acetoxy(polyethyleneoxy)propyl]triethoxysilane (APEOPTES, A). 200 mg of the hydroxylated particles added to 16 mL of n-hexane in a round-bottom flask and sonicated. 0.28 mL of triethylamine (TEA) and 2.0 mL of A were finally dropwise added to the mixture. Reaction was carried out at 75 °C for 24 hours under a N_2 atmosphere. Particles were then centrifuged, washed with acetone and dried in a vacuum overnight at 80 °C. For both G and A functionalization the procedure was repeated several times to have enough functionalized particles to be used in the preparation of nanocomposites.

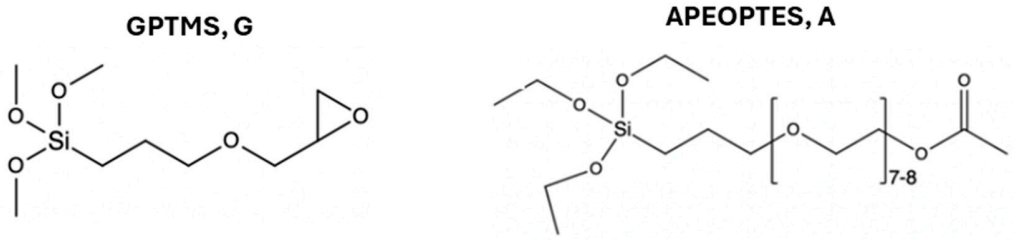

Figure S1 Scheme of the molecular structure of the used organosilanes, respectively GPTMS, G (left) and APEOPTES, A (right)

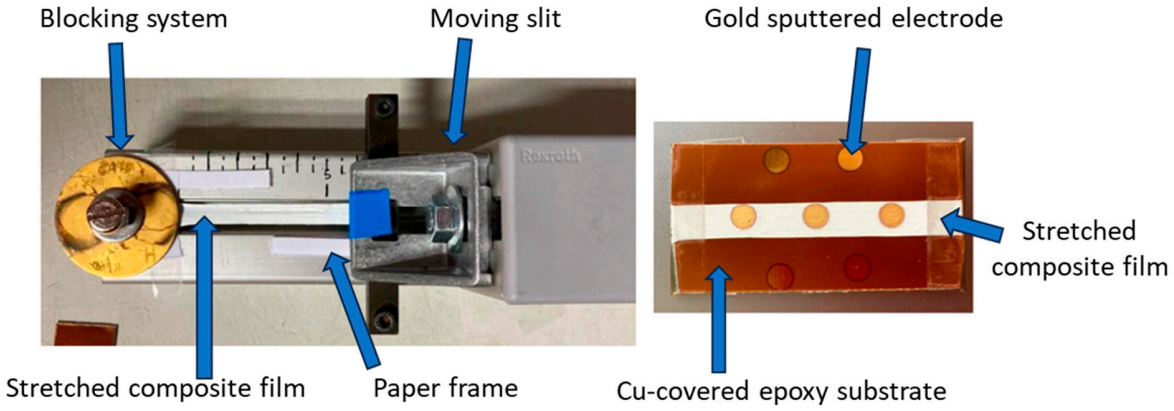

Figure S2 Homemade apparatus for sample stretching (left) and Cu-covered epoxy substrates for the testing

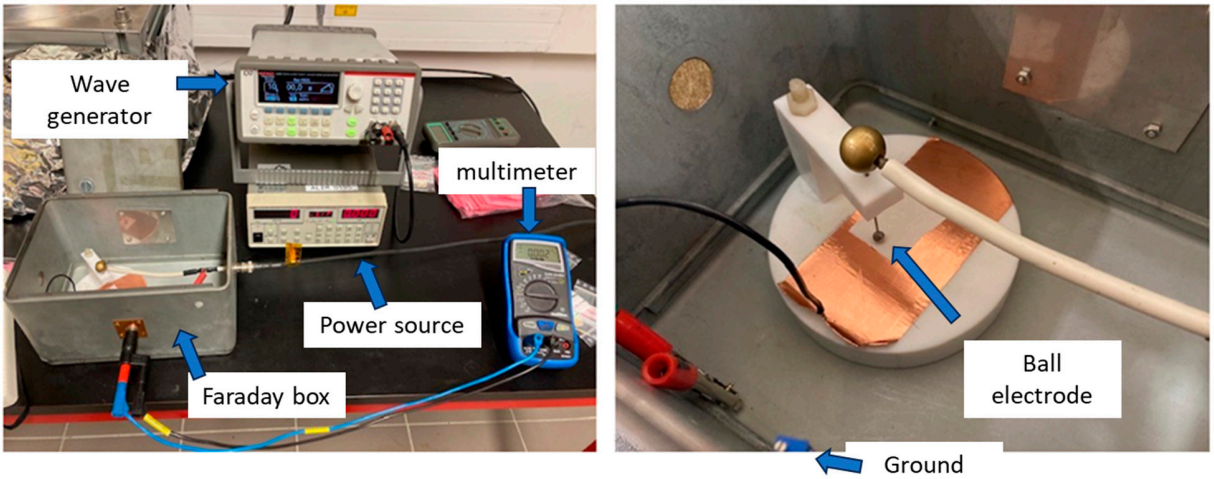

Figure S3 Setup for the measurement of the dielectric breakdown strength (left), home-made cell for evaluating breakdown strength of the films (right)

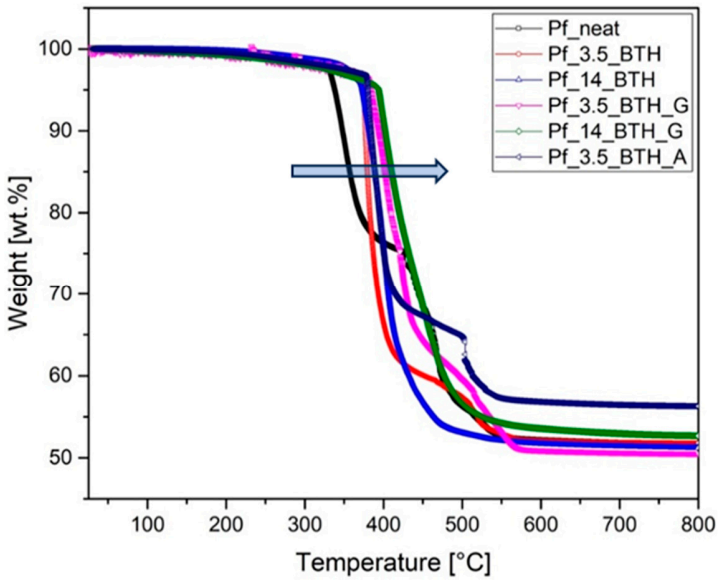

Figure S4 Thermogravimetric curves of PDMS based composites. The arrow indicates the shifting towards higher temperatures of the inflexion point from bare PDMS to PDMS-composites.

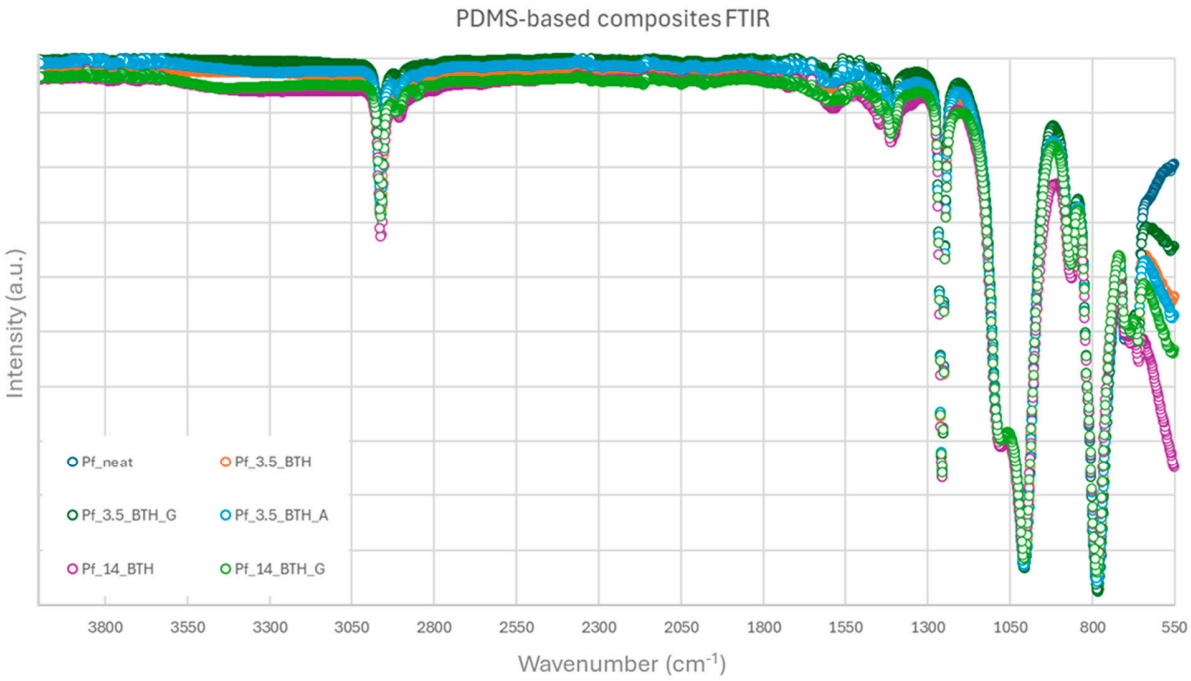

Figure S5 FTIR spectra of PDMS based composites in the range 4000 – 550 cm^{-1}.

Figure S5 shows FTIR spectra of PDMS based composites in the range 4000 – 550 cm^{-1}. It is clear how spectra are dominated by PDMS signals, appearing superimposable regardless of filler content and functionalization. No significant shift or linewidth variation were found in the spectra that could be reliably imputed to interactions between functionalized BaTiO3 and the polymeric matrix. The only remarkable differences are found in the region 550 – 600 cm^{-1}. These range is dominated by Ti-O vibrations of $BaTiO_3$ and the intensity is related to the filler content.

Table S1 Decomposition temperatures of PDMS-based composites

Sample	1st weight loss [°C]	2nd weight loss [°C]
Pf_neat	356	465
Pf_3.5_BTH	385	499
Pf_3.5_BTH_G	411	517
Pf_14_BTH	401	-
Pf_14_BTH_G	431	-
Pf_3.5_BTH_A	390	504

Table S2 Summary of dielectric constant, dielectric breakdown value, and energy density for stretched composites.

Sample (stretch)	ε_r (1 KHz)	E_{BD} [kV/mm]	U [mJ/cm^3]
Pf_neat	2.8	34.2	29
Pf_3.5_BTH	3.7	40.7	54
Pf_3.5_BTH_G	3.7	44.8	65
Pf_14_BTH	3.6	34.0	36
Pf_14_BTH_G	4.6	45.5	84
Pf_3.5_BTH_A	4.3	44.8	76

References

[28] N. Zamperlin, R. Ceccato, M. Fontana, A. Pegoretti, A. Chiappini & S. Dire', Effect of Hydrothermal Treatment and Doping on the Microstructural Features of Sol-Gel Derived BaTiO3 Nanoparticles, Materials **2021**, *14 (15)*, 4345

[29] N. Zamperlin, A. Bottacini, E. Callone, A. Pegoretti, M. Fontana & S. Dire', Barium Titanate Functionalization with Organosilanes: Effect on Particle Compatibility and Permittivity in Nanocomposites, Molecules **2022**, *27 (19)*, 6499.