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TITLE:

Application of a Coupling Agent to Improve the Dielectric Properties of Polymer-Based Nanocomposites

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KEYWORDS:

dielectrics, nanocomposites, coupling agent, ceramic-polymer, microstructure, free-standing

SUMMARY:

Here, we demonstrate a simple and low-cost solution-casting process to improve the compatibility between the filler and the matrix of polymer-based nanocomposites using surface modified $BaTiO_3$ fillers, which can effectively enhance the energy density of the composites.

ABSTRACT:

In this work, an easy, low-cost, and widely applicable method was developed to improve the compatibility between the ceramic fillers and the polymer matrix by adding 3-aminopropyltriethoxysilane (KH550) as a coupling agent during the fabrication process of $BaTiO_3$-P(VDF-CTFE) nanocomposites through solution casting. Results show that the use of KH550 can modify the surface of ceramic nanofillers; therefore, good wettability on the ceramic-polymer interface was achieved, and the enhanced energy storage performances were obtained by a suitable amount of the coupling agent. This method can be used to prepare flexible composites, which is highly desirable for the production of high-performance film capacitors. If an excessive amount of coupling agent is used in the process, the non-attached

coupling agent can participate in complex reactions, which leads to a decrease in dielectric constant and an increase in dielectric loss.

INTRODUCTION:

The dielectrics applied in electrical energy storage devices are mainly characterized using two important parameters: the dielectric constant (ε_r) and the breakdown strength (E_b)[1-3]. In general, organic materials such as polypropylene (PP) exhibit a high E_b (~10^2 MV/m) and a low ε_r (mostly <5)[4-6] while inorganic materials, especially ferroelectrics such as $BaTiO_3$, exhibit a high ε_r (10^3-10^4) and a low E_b (~10^0 MV/m)[6-8]. In some applications, flexibility and the ability to withstand high mechanical impacts are also important for fabricating dielectric capacitors[4]. Therefore, it is important to develop methods for preparing polymer-based dielectric composites, especially for the development of low-cost methods to create high-performance 0-3 nanocomposites with high ε_r and E_b[9-18]. For this purpose, preparation methods based on ferroelectric polymer matrices such as the polar polymer PVDF and its correlated copolymers are widely accepted due to their higher ε_r (~10)[4,19,20]. In these nanocomposites, particles with high ε_r, especially ferroelectric ceramics, have been widely used as fillers[6,20-25].

When developing methods for manufacturing ceramic-polymer composites, there is a general concern that dielectric properties can be significantly influenced by the distribution of fillers[26]. The homogeneity of dielectric composites is not only determined by the preparation methods, but also by the wettability between the matrix and fillers[27]. It has been proven by many studies that the non-uniformity of ceramic-polymer composites can be eliminated by physical processes such as spin-coating[28,29] and hot-pressing[19,26]. However, neither of these two processes change the surface connection between fillers and matrices; therefore, the composites prepared by these methods are still limited in improving ε_r and E_b[19,27]. Additionally, from a manufacturing point of view, inconvenient processes are undesirable for many applications because they can lead to much more complex fabrication processes[28,29]. In this regard, a simple and effective method is needed.

Currently, the most effective method to improve the compatibility of ceramic-polymer nanocomposites is based on the treatment of ceramic nanoparticles, which modifies the surface chemistry between fillers and matrices[30,31]. Recent studies have shown that coupling agents can be easily coated on ceramic nanoparticles and effectively modify the wettability between fillers and matrices without affecting the casting process[32-36]. For surface modification, it is widely accepted that for each composite system, there is a suitable amount of coupling agent, which corresponds to a maximal increase in energy storage density[37]; excess coupling agent in composites may result in a decline in the performance of products[36-38]. For dielectric composites using nano-sized ceramic fillers, it is speculated that the effectiveness of coupling agent mainly depends on the surface area of fillers. However, the critical amount to be used in each nano-sized system is yet to be determined. In short, further research is required to use coupling agents to develop simple processes for manufacturing ceramic-polymer nanocomposites.

In this work, $BaTiO_3$ (BT), the most widely studied ferroelectric material with high dielectric constant, was used as fillers, and the P(VDF-CTFE) 91/9 mol% copolymer (VC91) was used as the polymer matrix for the preparation of ceramic-polymer composites. To modify the surface of the BT nanofillers, the commercially available 3-aminopropyltriethoxysilane (KH550) was purchased and used as a coupling agent. The critical amount of the nanocomposite system was determined through a series of experiment. An easy, low-cost, and widely applicable method is demonstrated to improve the energy density of nano-sized composite systems.

PROTOCOL:

1. Surface modification of BT fillers

1.1. Prepare 20 mL of KH550 solution (1 wt% KH550 in 95 wt% ethanol-water solvent) and ultrasonicate for 15 min.

1.2. Weigh BT nanoparticles (i.e., the filler) and KH550, respectively, so that fillers can be coated with 1, 2, 3, 4, 5 wt% of the coupling agent. Treat 1 g of BT nanoparticles in 1.057, 2.114, 3.171, 4.228, and 5.285 mL of KH550 solution by 30 min ultrasonication.

1.3. Evaporate the water-ethanol solvent from the mixture at 80 °C for 5 h and then at 120 °C for 12 h in a vacuum oven.

1.4. Use the dry BT nanoparticles as the surface modified fillers to prepare BT-VC91 nanocomposites.

2. Preparation of BT-VC91 nanocomposites

2.1. Dissolve 0.3 g of VC91 powders in 10 mL of N,N-dimethylformamide (DMF) at room temperature by magnetic stirring for 8 h to obtain a homogeneous VC91-DMF solution.

2.2. Add 0.0542, 0.1145, 0.1819, 0.2578, 0.3437, and 0.4419 g of BT nanoparticles into 10 mL of VC91-DMF solution to obtain a final BT percentage of 5, 10, 15, 20, 25, and 30 vol% in the nanocomposites. Mix BT nanoparticles by magnetic stirring for 12 h and ultrasonication for 30 min to form a homogeneous BT-VC91-DMF suspension.

NOTE: Both the unmodified BT and BT nanoparticles coated with the coupling agent are used.

2.3. Cast the suspension by evenly pouring the BT-VC91-DMF onto a preheated 75 mm x 25 mm glass substrate (3 mL per substrate). Keep the glass substrates with suspensions in the oven at 70 °C for 8 h to evaporate the DMF solvent to form composite films.

2.4. Release the composites from glass substrates using sharp tweezers to obtain free-standing BT-VC91 films. Anneal the films on a preheated dust-free paper at 160 °C in air for 12 h.

3. Characterization and measurement

3.1. Characterize the morphology and uniformity of nanocomposites using a scanning electron microscope (SEM). To do this, freeze BT-VC91 samples in liquid nitrogen and break to show fresh cross section with an approximate size of 5 mm x 30 µm (i.e., the ceramic-polymer interface). Then coat one side of the cross section with a gold layer with a thickness of 3−5 nm and characterize the composite structure using an SEM (**Table of Materials**).

3.2. Using a gold coater (**Table of Materials**), sputter gold layers with a positive circle shape, a diameter of 3 mm, and a thickness of ~50 nm on both sides of the nanocomposite prepared from step 2 to form the electrode for impedance testing.

3.3. Characterize the capacitance and dielectric loss of the nanocomposites over a frequency range from 100 Hz to 1 MHz using an impedance analyzer (**Table of Materials**) with the Cp-D function. In the testing, connect gold layers on both sides of the composite film with the two poles of fixture.

3.4. Calculate the dielectric constant (ε_r) of nanocomposites from the capacitance obtained by impedance analyzer using the parallel capacitor model:

$$\varepsilon_r = dCp/\varepsilon_0 A$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$, A is the area of gold electrodes, d is the thickness of sample, and Cp is parallel capacitance obtained by connecting the gold electrodes with the fixture of impedance analyzer.

3.5. Characterize the breakdown strength of nanocomposites using a 10 kV high voltage supplier (**Table of Materials**). Increase the applied electric field evenly and continuously until the breakdown of each sample.

3.6. Characterize the polarization-electric (P-E) field hysteresis loop of nanocomposites using a ferroelectric tester. Record the P-E loops at each electric field while continuously increasing the electric field.

REPRESENTATIVE RESULTS:

The free-standing nanocomposite films with different contents of fillers were successfully fabricated as described in the protocol, and were labeled as xBT-VC91, where x is the volume percentage of BT in the composites. The effect of KH550 (coupling agent) on the morphology and microstructure of these BT-VC91 films was studied by SEM and shown in **Figure 1**. The SEM images of 30BT-VC91 nanocomposites with 1 and 5 wt% coupling agent are shown in **Figure 1a** and **Figure 1b**. The filler distribution of BT-VC91 nanocomposites with 1 wt% KH550 is much denser and more uniform than that of BT-VC91 nanocomposites with 5 wt% KH550, suggesting that ceramic nanoparticles treated with a suitable amount of coupling agent could be uniformly distributed in the nanocomposites during casting, while the excessive amount of coupling agent may cause interactions between ceramic nanoparticles, and leading to the aggregation of fillers. The image of cross section (i.e., the ceramic-polymer interface) of 30BT-VC91 nanocomposites using as-received (unmodified) BT fillers is shown in **Figure 1c**, while the cross section of 30BT-VC91 nanocomposites containing 1 wt% of KH550 is shown in **Figure 1d**. For the nanocomposites using uncoated BT, although most of the nanoparticles are tightly encapsulated in polymer, there are still some separation between the fillers and matrix, which means there is no linkage between the matrix and fillers. For the nanocomposites using KH550-coated BT, there is no separation between BT nanoparticles and VC91 matrix, which indicates that the coupling agent could acts as a bridge between filler and matrix.

The dielectric properties of nanocomposites with different amounts of coupling agent were then tested and shown in **Figure 2**. The dielectric content vs. amount of coupling agent at 1 kHz and 100 kHz was plotted in **Figure 2a,b**. For the nanocomposites with a low filler content (i.e., 5, 10 and 15 vol%), the ε_r of the composites was basically unchanged when a small amount of coupling agent is used, and slightly decreases with the increasing coupling agent amount. For the nanocomposites with a high filler content, in particular the nanocomposites with a filler content of 30 vol%, the ε_r of the composites increases obviously with a small amount of coupling agent, and sharply decreases with the further increasing coupling agent amount. When a suitable amount of KH550 was coated on the surface of BT filler, the maximum ε_r could be achieved. For example, a ε_r of 51 was achieved from 30BT-VC91 with 2 wt% of KH550 (**Figure 2a**), which is much larger than that of 30BT-VC91 without KH550 (about 40). In this composite system, the increase of ε_r for the nanocomposites with a small amount of coupling agent is due to the increase of wettability on the ceramic-polymer interface, and the possible percolation from the additives[6,10,33]; the decrease of ε_r for BT-VC91 using BT nanoparticles coated with a large amount of KH550 is due to the formation of VC91-KH550 polymer blends with a low dielectric constant. The difference in dielectric properties between low filling and high filling nanocomposites can be attributed to the actual amount of KH550 used in the sample preparation. The dielectric loss vs. amount of coupling agent at 1 kHz and 100 kHz was plotted in **Figure 2c,d**. BT-VC91 with KH550 has a higher dielectric loss than that of BT-VC91 without KH550.

The breakdown strengths of BT-VC91 nanocomposites were also recorded and shown in **Figure 3**. To determine the critical amount of the coupling agent, the breakdown strength vs. amount of coupling agent and breakdown strength vs. content of filler were shown in **Figure 3a** and **Figure 3b**, respectively. As expected, the E_b of BT-VC91 decreased with increasing filler content (**Figure 3b**) due to the formation of the ceramic-polymer interface. A maximal E_b of 30BT-VC91 was observed for composites produced using fillers treated with 2 wt% KH550 (**Figure 3b**). If a KH550 amount exceeding 2 wt% was used, the E_b of BT-VC91 was further decreased (**Figure 3a**). By adding 2 wt% KH550, the E_b of 30BT-VC91 could be increased to 200 MV/m.

The charge-discharge efficiency and discharge energy density of nanocomposites with different amount of coupling agent were calculated from their P-E loops. As an example of the enhanced energy density due to the usage of coupling agent, the energy storage properties of 15BT-VC91 with different amount of KH550 are shown in **Figure 4**. The maximal energy densities of BT-

VC91 nanocomposites with a small amount of coupling agent (1 - 2 wt%) apparently increased compared with those of nanocomposites without coupling agent (**Figure 4b**), which could be mainly attributed to the enhanced breakdown strength and a relatively high charge-discharge efficiency (η). Due to the higher loss under high electric filed, the η of BT-VC91 nanocomposites decreased at relatively high electric fileds (**Figure 4a**). Adding 1 - 2 wt% of KH550 increased η of nanocomposites under a fixed electric field (**Figure 4a**), which was attributed to the introduced bridge-linking effect. In summary, for nanocomposites prepared in this work using BT nanoparticles with ~200 nm in diameter, the critical amount of KH550 is smaller than 2 wt%.

In terms of the frequency dependence of dielectric properties, ε_r and tanδ of nanocomposites versus testing frequency were also plotted. As an example, the dielectric properties of BT-VC91 with 1 wt% coupling agent are shown in **Figure 5**, which indicated that the frequency dependences of dielectric properties (ε_r and tanδ) of all BT-VC91 nanocomposites were mainly determined by their polymer matrix. The ε_r of nanocomposites gradually decreased with increasing frequency (**Figure 5a**). The tanδ gradually decreased with frequency at low frequencies but gradually increased at high frequencies (**Figure 5b**).

FIGURE LEGENDS:

Figure 1: SEM images of cross sections. Filler distribution of (**a**) 30BT-VC91 with 1 wt% of KH550 and (**b**) 30BT-VC91 with 5 wt% of KH550. Ceramic-polymer interface of (**c**) 30BT-VC91 without KH550 and (**d**) 30BT-VC91 with 1 wt% of KH550. This figure has been modified from Tong et al.[4].

Figure 2: Dielectric properties of composites with different amount of coupling agent (a) ε_r at 1 kHz and (**b**) ε_r at 100 kHz; (**c**) tanδ at 1 kHz and (**d**) tanδ at 100 kHz. This figure has been modified from Tong et al.[4].

Figure 3: Breakdown strengths of nanocomposites with different amount of coupling agent (**a**) E_b of BT-VC91 as a function of KH550 amount (**b**) E_b of BT-VC91 as a function of filler content. This figure has been modified from Tong et al.[4].

Figure 4: Energy storage performances of nanocomposites with different amount of coupling agent (**a**) charge-discharge efficiency and (**d**) discharge energy density of 15BT-VC91 as a function of KH550 amount. This figure has been modified from Tong et al.[4].

Figure 5: Frequency dependence of the dielectric properties of nanocomposites (a) ε_r and (**b**) tanδ of BT-VC91 with 1 wt% of KH550. This figure has been modified from Tong et al.[4].

DISCUSSION:

As discussed above, the method developed by this work could successfully improve the energy-storage performance of ceramic-polymer nanocomposites. To optimize the effect of such method, it is critical to control the amount of coupling agent used in ceramic-surface modification. For ceramic nanoparticles with a diameter of ~200 nm, it was experimentally determined that 2 wt% of KH550 could lead to a maximal energy density. For other composite systems, this conclusion may be used approximately when the fillers with the diameter is close to ~200 nm are adopted. If fillers with a diameter much larger than 200 nm are used, the critical amount should be determined again through a similar series of experiments.

Compared with other works that attempted to improve the uniformity and performance of dielectric nanocomposites, the method developed in this work is much simpler and has a lower cost. In addition, application of the coupling agent can be combined with other processes such as spin-coating and hot-pressing. The surface modification of ceramic nano-fillers will be widely applied in the manufacture of various of advanced dielectrics in future.

It must be pointed out that the application of coupling agent does not really change the properties of nanocomposites. Therefore, the effectiveness of a coupling agent in a composite strongly depends on the selection of fillers and matrices, and the method proposed here increases in energy storage performance only to a limited extent. In order to develop dielectrics with a dramatically increased energy density, the novel composite systems still need to be created.

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DISCLOSURES:

The authors have nothing to disclose.

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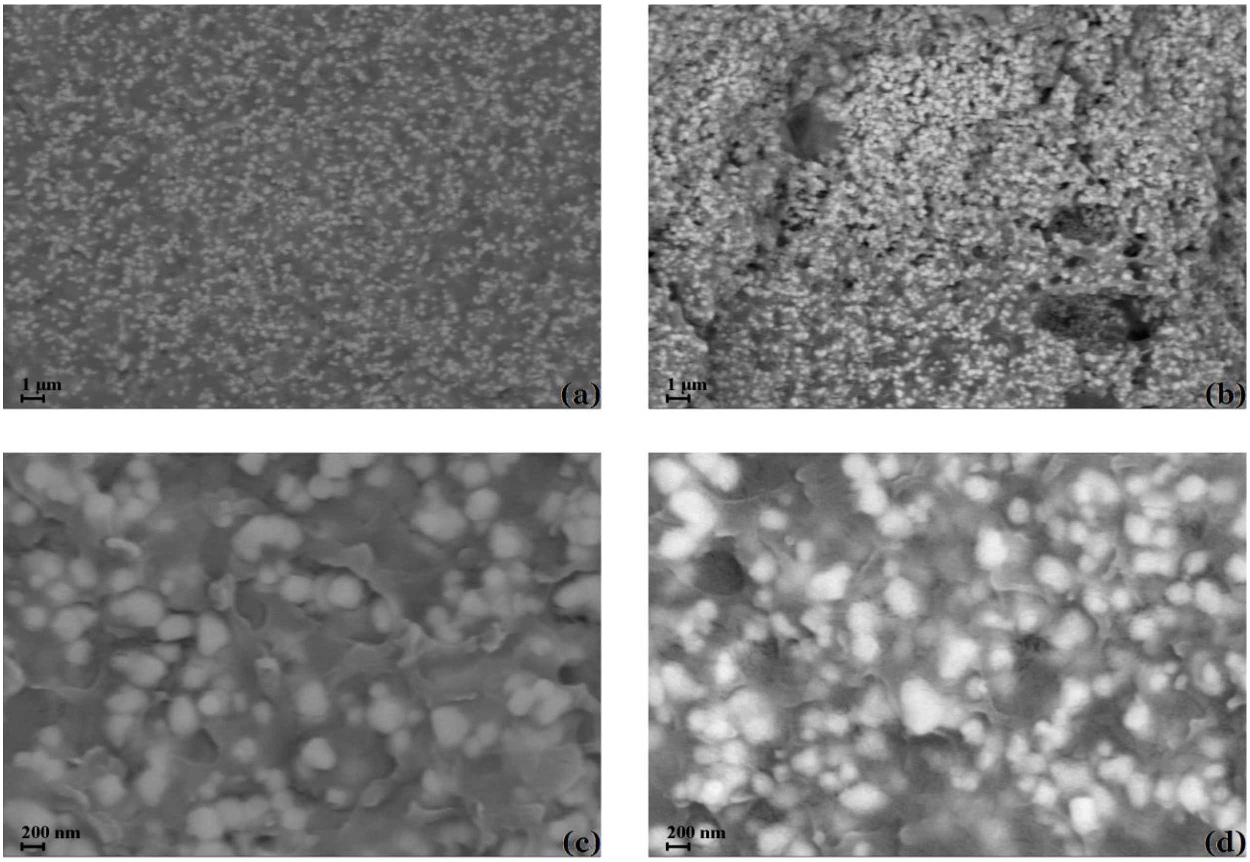

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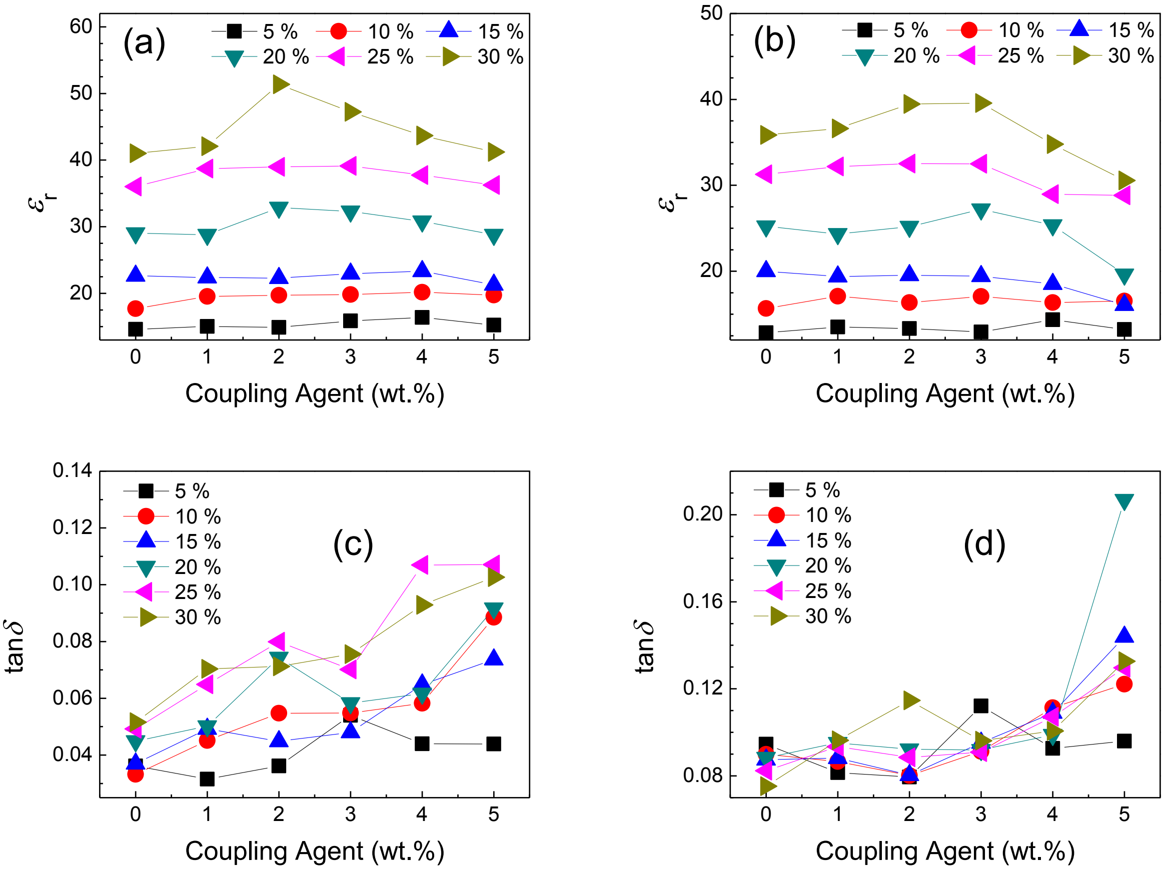

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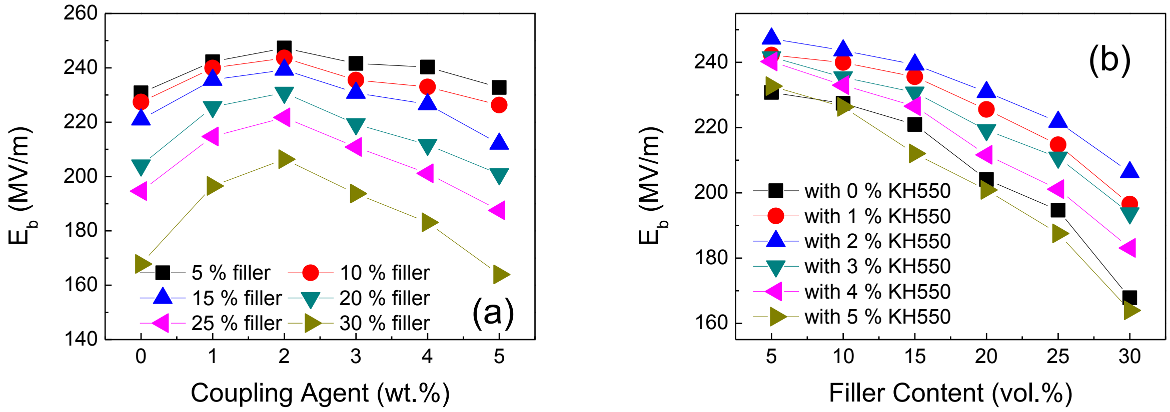

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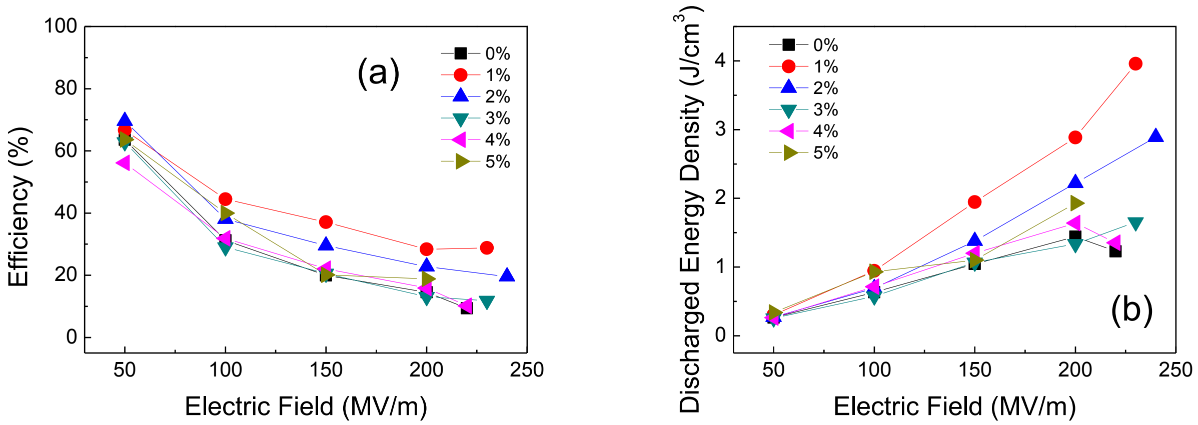

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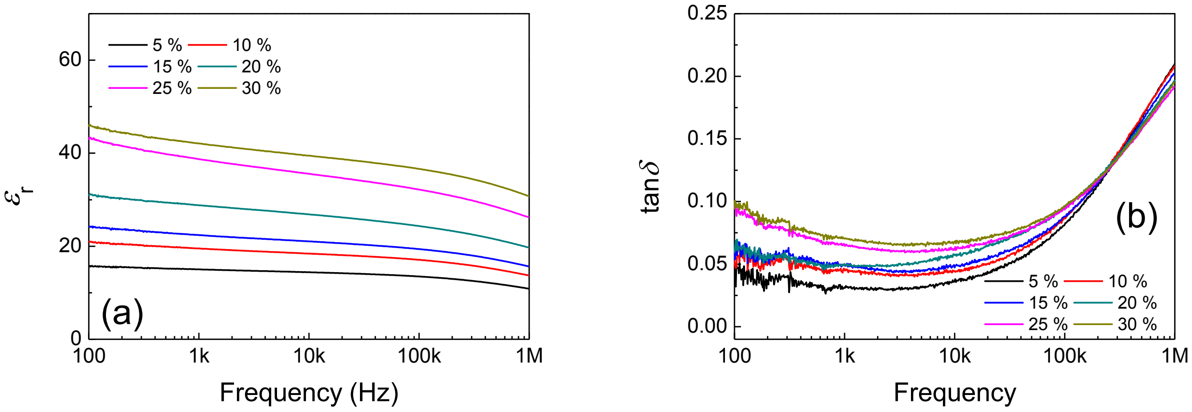

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Name of Material/Equipment	Company	Catalog Number	Comments/Description
3-Aminopropyltriethoxysilane (KH550)	Sigma-Aldrich	440140	Liquid, Assay: 99%
95 wt.% ethanol-water	Sigma-Aldrich	459836	Liquid, Assay: 99.5%
$BaTiO_3$ nanoparticles	US Research Nanomaterials	US3830	In a diameter of about 200 nm
Ferroelectric tester	Radiant	Precision-LC100	
Glass substrates	Citoglas	16397	75 x 25 mm
Gold coater	Pelco	SC-6	
High voltage supplier	Trek	610D	10 kV
Impedance analyzer	Keysight	4294A	
N, N dimethylformamide	Fisher Scientific	GEN002007	Liquid
P(VDF-CTFE) 91/9 mol.% copolymer			
Scanning Electron Microscopy (SEM)	JEOL	JSM-7000F	
Vacuum oven	Heefei Kejing Materials Technology Co, Ltd	DZF-6020	

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Rebuttal Letter

We appreciate the comments on our manuscript entitled "Application of a Coupling Agent to Improve the Dielectric Properties of Polymer-Based Nanocomposites" (JoVE60916R3). We have revised our manuscript according to the comments. The responses to the comments are listed below.

Responses to editorial comments

Changes to be made by the author(s) regarding the manuscript:

Comment 1: Please address specific comments marked in the attached manuscript.

Response: We have answered all the questions. All of the modifications was adopted.

Comment 2: Please sort the Table of Materials alphabetically.

Response: The list in Table of Materials was rearranged.

Changes to be made by the author(s) regarding the video:

Comment 1: Introduction & Conclusion
@00:07-00:43 and @05:31-06:28: These shots in the introduction and conclusion are pretty dark and would benefit from a modest brightness adjustment.

Response: The brightness was adjusted in the revised videos.

Comment 2: Narration Feedback
@02:42 "...with coupling agent, where you..." The last words here are cutoff by a fade out. Either cut out the remainder of the statement or move the fade point to a later point in time so we can hear the complete statement.
@03:37-04:07 The first speaker's narration audio level in the Representative Results section is louder than the previous narration during the protocol. Reduce the volume here by 4 dB (adjust -4 dB).

Response: Thank you to point out the problems in detail. All the pointed false were corrected.

Comment 3: ~@1:46-1:48: Please remove commercial language (i.e., the type and model of the vacuum oven). Just keep "vaccum oven".

Response: The commercial information was removed.

Comment 4: Please upload a revised high-resolution video here: https://www.dropbox.com/request/PC4BFCYK4nf5sOZzt92U

Response: After revision, the high-resolution video was uploaded to the dropbox provided by editor.

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