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Study of piezoelectric properties for electromechanical applications in PVDF composites reinforced with barium titanate nanorods

Suaad M. Jiaad[1], Safaa A. Jasim[2*]
[1]Department of Electromechanics, University of Technology, Iraq; 50181@uotechnology.edu.iq (S.M.J.).
[2]Ministry of Education, Iraq; eme.19.32@grad.uotechnology.edu.iq (S.A.J.).

Abstract: The purpose of this research is to examine how the use of Barium titanate ($BaTiO_3$) nanorods enhances the electromechanical and mechanical properties of a Polyvinylidene Fluoride (PVDF) matrix. Polyvinylidene Fluoride composites with various amounts of barium titanate (0, 3, 6, 9, 12 and 15 wt%) were prepared and tested for their mechanical behaviour using a tensile test. The results show that increasing the levels of Barium titanate up to 9 wt.% increased elastic modulus and tensile strength while they decreased afterwards. Conversely, an increase in elongation at break showed that higher concentrations contain more stiffness than less ones. As for the electrical and mechanical conductance attributes of barium titanate, the tests showed that when the concentration increased, its sensitivity increased as well with an optimal amount of barium titanate being 15 wt%. In this case, the proper proportion of barium titanate for those composites is 9.0wt% so as to optimize piezoelectric property at the same time maintain mechanical strength. The improvement ratio in output voltage for the PVDF nanocomposites was found to be 1.45 times (45%) that of the polymer without barium titanate nanorods, indicating an enhancement in the material's piezoelectric responsiveness. This information can be used by designers in high strength advanced composites in order to improve their piezoelectric properties for improved performance in electromechanical applications.
Keywords: *Barium titanate, Mechanical, Nanorods, Piezoelectric properties, PVDF.*

1. Introduction

PVDF has long been employed in measurements due to unique properties such as piezoelectricity, pyroelectricity, ferroelectricity among others; it is hence extensively considered for sensors, actuators devices that harvest energy or flexible electronics [1]. Current research has shown that PVDF can possess improved functional traits such as piezoelectricity and dielectricity by mixing it with different nanoparticles [2,3]. One such material is Barium Titanate ($BaTiO_3$), which has gained popularity due to its excellent dielectric and piezoelectric characteristics [4]. By embedding $BaTiO_3$ inside the PVDF matrix, microstructural polarizability and charge storage capacity are enhanced leading to increased piezoelectricity and dielectrics in the composite [5]. With respect to mechanical properties, the addition of $BaTiO_3$ improves upon strength thus making them tougher and more flexible hence suitable for advanced sensors as well as actuators [6]. It is crucial to have a uniform distribution of $BaTiO_3$ in the PVDF matrix to ensure optimal composite piezoelectric and mechanical performance [7]. As a result, it appears that these sorts of materials could function as $BaTiO_3$/PVDF composites that may help with enhancing electric and mechanical properties. However, further research must be done in order to optimize the quantity and arrangement of these composites, as well as develop better collection techniques, if we are to increase their practicality [8]. In this research the way PVDF matrix's electromechanical as well as mechanical properties were affected by adding $BaTiO_3$ nanorods with different weight percentages (0, 3, 6, 9, 12 and 15 wt.%) was evaluated. Tensile testing was used to determine how strong the composites were and piezoelectric testing showed how well they could conduct electricity.

* Correspondence: eme.19.32@grad.uotechnology.edu.iq

2. Experimental

2.1. Preparation of Barium Titanate Nanorods

Hydrothermal processing was one technique utilized to make barium titanate nanoceramics ($BaTiO_3$). Initially, barium chloride ($BaCl_2$, Kishida Chemical), titanium tetrachloride ($TiCl_4$ solution, Sigma-Aldrich), and sodium hydroxide (NaOH, Nacalai Tesque (98%), were used to generate the (Ba-Ti-OH) precursor. At 25 °C, a combination of 1 M $BaCl_2$ (10 ml aqueous solution) and 1 M $TiCl_4$ solution (10 ml aq. solution) was created. 0.2 gram from Cetrimonium chloride (CTAC, Sigma-Aldrich) was added as a surfactant to 20 ml of deionized (DI) water and 10% NaOH were then added to the precursor. The precursor slurry's overall size was reduced to 50 milliliters via the hydrothermal technique. As a result, to finish the procedure, the precursor slurry was heated in a 100 ml Teflon-lined autoclave and kept at 205°C for 20 hours inside oven. The product was then separated, washed, and dried at 65°C (see figure 1).

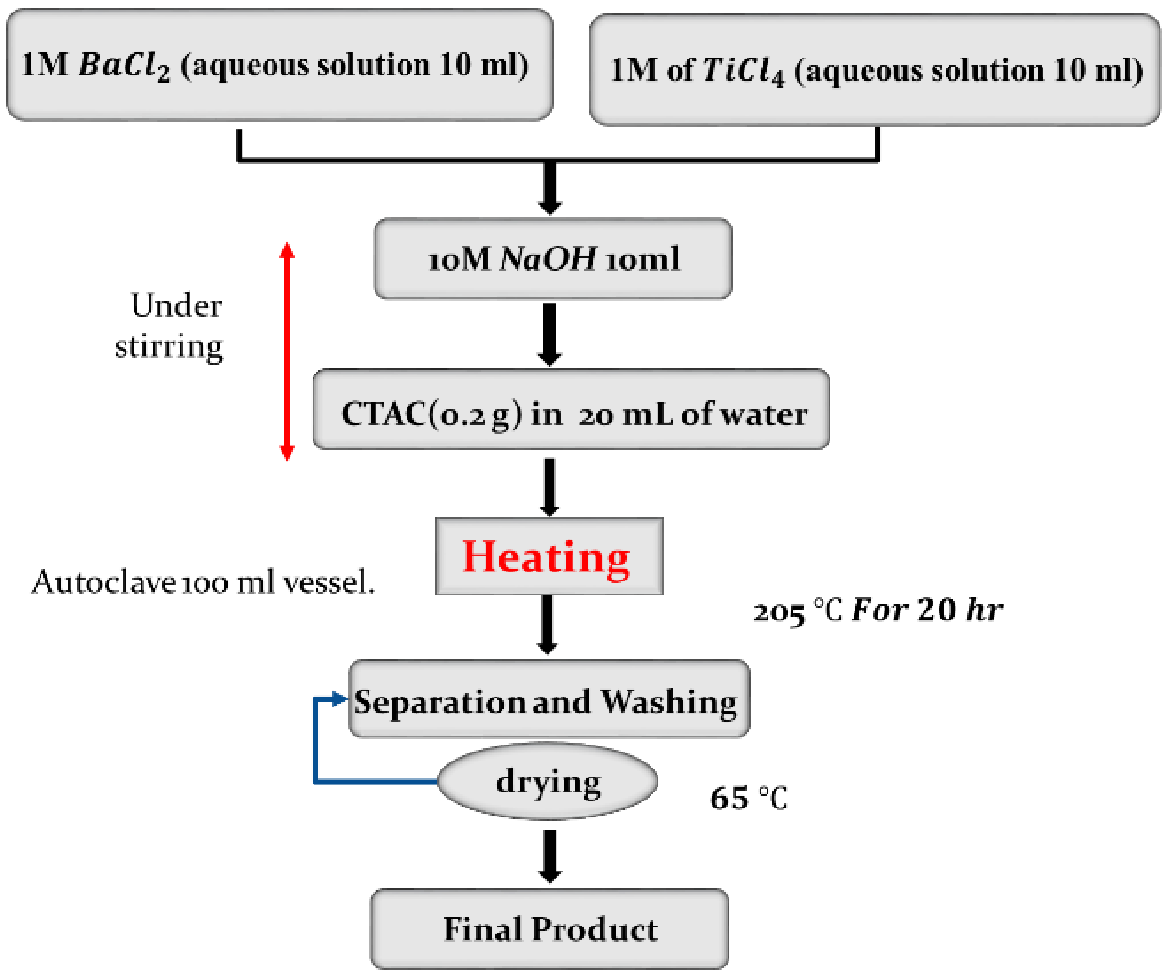

Figure 1.
Shows an illustrative diagram of the stages of $BaTiO_3$ nanorods preparation by using the hydrothermal method.

2.2. Preparation of PVDF Nanocomposites

PVDF granule and $BaTiO_3$ nanorods powder were melt-mixed in a Brabender mixer (kulturstr, Germany) at 195 °C and 60 rpm for 12 min. A series of PVDF/$BaTiO_3$ nanocomposites with varying concentrations (0, 3, 6, 9, 12 and 15 wt.%) of $BaTiO_3$ were fabricated. Then, pure PVDF and PVDF

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nanocomposites samples were fabricated by compression molding at 205 °C for 5 minutes to obtain final shapes sheets (2 cmx2cm with 1 mm thickness for Piezoelectric test and ASTM D638 for Tensile test.

2.3. Characterization of Barium Titanate Nanorods

Characterization of synthesized $BaTiO_3$ phase and crystalline structure was done using X-ray diffraction analysis (XRD) employing PHILIPS system with Cu-Kα radiation at 35 kV. The elemental composition of $BaTiO_3$ nanorods was determined using Energy Dispersive Spectroscopy (EDS). Furthermore, Fourier Transform Infrared (FTIR) spectroscopy revealed available functional groups and chemical bonds in $BaTiO_3$ resulting in its molecular structure. FTIR spectra were collected from Nicolet IS50 spectrometer (Thermo Fisher) through attenuated total reflectance (ATR) technique while using ZnSe crystal covering the range between 4500 cm– 1 up to 0 cm −1. Other morphological details were provided by scanning electron microscopy which was conducted with the help of SEM (Mira 3-XMU). The tensile properties of PVDF/$BaTiO_3$ nanocomposite samples made according to ASTM D638 Type I criteria were assessed on a tensile testing machine (Hounsfield H10KS, USA) for Young's modulus, tensile strength and elongation. Piezo-Tester (VDS 1022 Oscilloscope standard) is meant for assessing how effective piezoelectric harvesters are under the direct piezoelectric effect in tapping (2.6N >>5Hz) mode. There it is used to apply a controlled load on the sample using a step motor and adjustable cam to create a follower which then hits the sample with its impact head at various surface area sizes, frequencies and forces that are measured by load cell. In order to find out the sensitivity of the sample, its electrical outputs were analyzed i.e. output per unit load (mV/N). Test samples constructed from composite materials having dimensions of 2.5 cm x 2.5 cm and a thickness of 1 mm were used. The corona poling process was applied to samples using a potent 5 KV electric field at a high temperature of 80 °C for a duration of 30 minutes. Moreover, samples were prepared to measure the piezoelectric coefficient d33 (SINOCERA d33 METER) for both pure PVDF polymer and the its nanocomposite with a thickness of 30 micrometers.

3. Results and Discussion

3.1. Characterization of Barium Titanate

As shown in Figure 2(a), groups of functional elements within the powder sample were found using FTIR (Fourier Transform Infrared) spectroscopy. The resulting transmittance-mode FTIR absorbance spectrum were captured in the 4500–0 cm^{-1} range. The titanate barium framework is indicated by the functional group that is part of the (Ti-O) bands at 562 cm^{-3}, which is impacted by Ba ions. Whereas the C-O bands at 1110 cm^{-1} indicate the possible C-C stretching, the functional group consisting of (Ba-Ti-O) bonds emerge within the 1430–1630 cm^{-1} range. Inorganic group bonding to titanium is shown by the C–H group at 2877 cm^{-1}. A lower production of $BaCO_3$ is suggested by the Ba-C-O intensity being absent in the $BaTiO_3$ powder. 3425 cm^{-3} is where the OH-OH groups may be seen. The existence of hydroxyl residues on the (OH) surface functional group indicates that interface-functionalized barium titanate nanoceramic was synthesized using peroxide [9,10]. Figure 2(b) displays the $BaTiO_3$ nanorods (BTNRs) X-Ray diffraction (XRD) pattern. A structural nanorods phase with a lattice dimension of a = 4.0217 Å has been created, according to the XRD examination, which is in line with JCPDS no. #892475. 2θ = 32.17° is the location of the greatest intense peak (110). Further peaks at 2θ = 22.208° (100), 31.7° (110), 38° (111), 45.6° (200), 50.812° (210), 56.127° (211), confirm the development of the barium titanate ($BaTiO_3$) structural perovskite [11,12]. Cetyltrimethylammonium chloride (CTAC) is a surfactant which is key to the making of Barium Titanate Nanorods. A SEM image shows that the nanorods have a nearly uniform size and shape distribution; this indicates good control over nucleation and growth processes. As such, CTAC molecules probably stick to the growing surfaces of the nanorods leading to lowered surface energies and facilitating anisotropic growth along specific crystallographic directions. The net effect being their elongated rod-like morphology is observed (see figure 2(c)). The presence of CTAC affects the surface properties of nanosheets, they can have less roughness and less clumps. In EDS, it is displayed in table 1 that the most important part in the composition which include 27.8% weight of oxygen and 67.1% atomic percentage, suggests oxide formation in the sample. Barium titanate formation is also supported by titanium being a major constituent of nanoceramics with weight percentage and atomic percentage for it being about 25.1% and 19.2% respectively. Owing to the fact that it has an average weight of 47.1%, this was essential for synthesizing pure barium titanate [13-16].

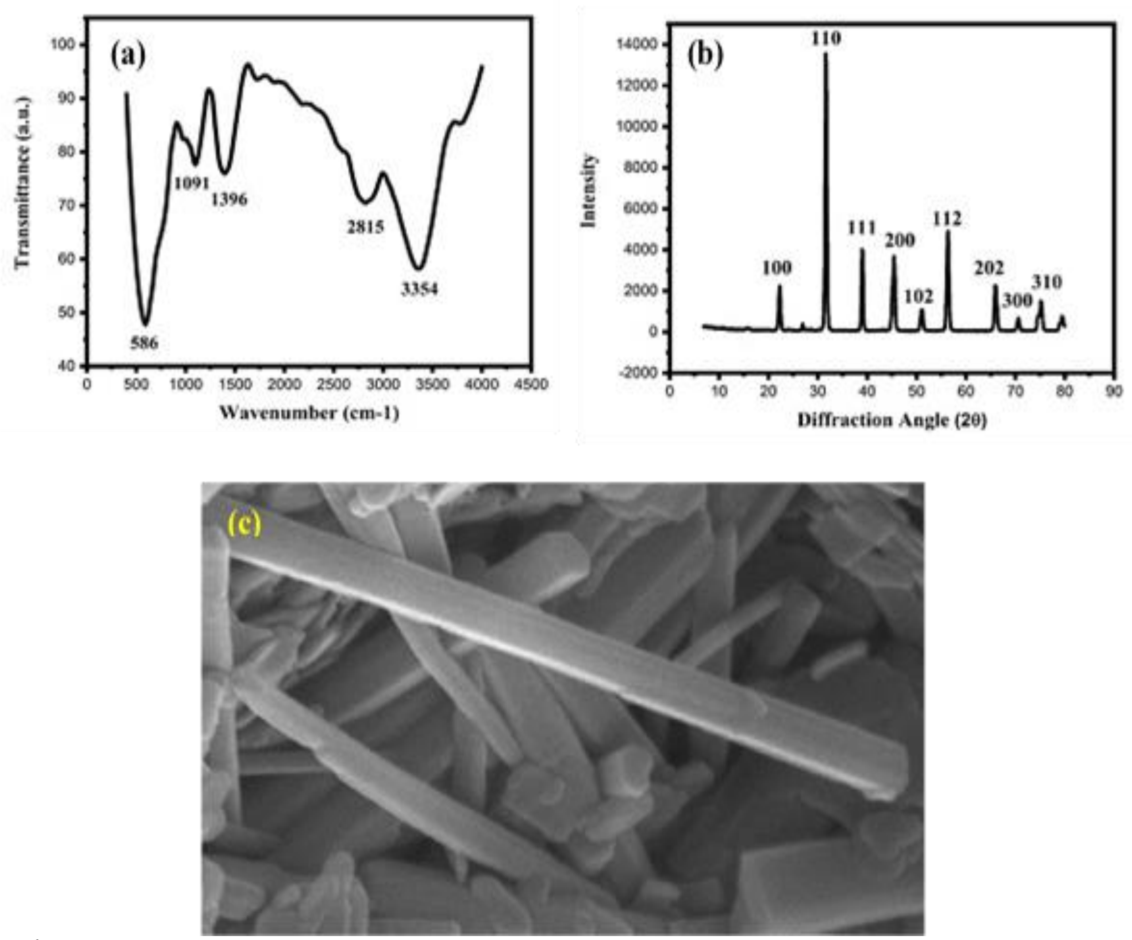

Figure 2.
(a) FTIR spectrum of $BaTiO_3$, (b) XRD patterns showing a tetragonal $BaTiO_3$ nanostructure, (c) FESEM image depicting Barium titanate nanorods.

Table 1.
Atomic and Weight percentage of elements as determined by EDS analysis.

Element	Atomic %	Weight %
O	67.1	27.8
Ti	19.2	25.1
Ba	13.7	47.1

3.2. Mechanical Properties of PVDF/BaTiO3 Nanocomposites

The figures 3 illustrate tensile test data which reveal that $BaTiO_3$ content has a significant effect on the mechanical properties of PVDF composites, including elastic modulus, tensile strength and percent elongation. Figure 3: (a) Displays the tensile testing machine (Hounsfield H10KS, USA), and the stress-strain curve for PVDF and its nanocomposite is shown in (b). The elastic modulus increased with increase in $BaTiO_3$ content attaining peak values of about 2545 MPa (at 9 wt%) because of strengthened rigidity of the PVDF matrix through stronger $BaTiO_3$ nanorods (see figure 3 (c)). However, there was

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also a decrease beyond that level most likely caused by stress concentrations resulting from agglomeration of particles. In the same way, tensile strength peaked at approximately 45 MPa (at 9 wt%) implying effective transfer of stress to both the matrix and nanorods but it reduced when the concentration of barium titanate went higher suggesting high levels of aggressiveness caused by too much clustering (see figure 3 (d)). Conversely, the elongation at break decreased with increasing amounts of barium titanate reaching its minimum value of around 9 wt.% before rising slightly again indicating that even if the hardness increased; Barium titanate reduces elasticity, which can suffer when particulate matter is added to the mix in larger quantities (see figure3 (e)) [13,14].

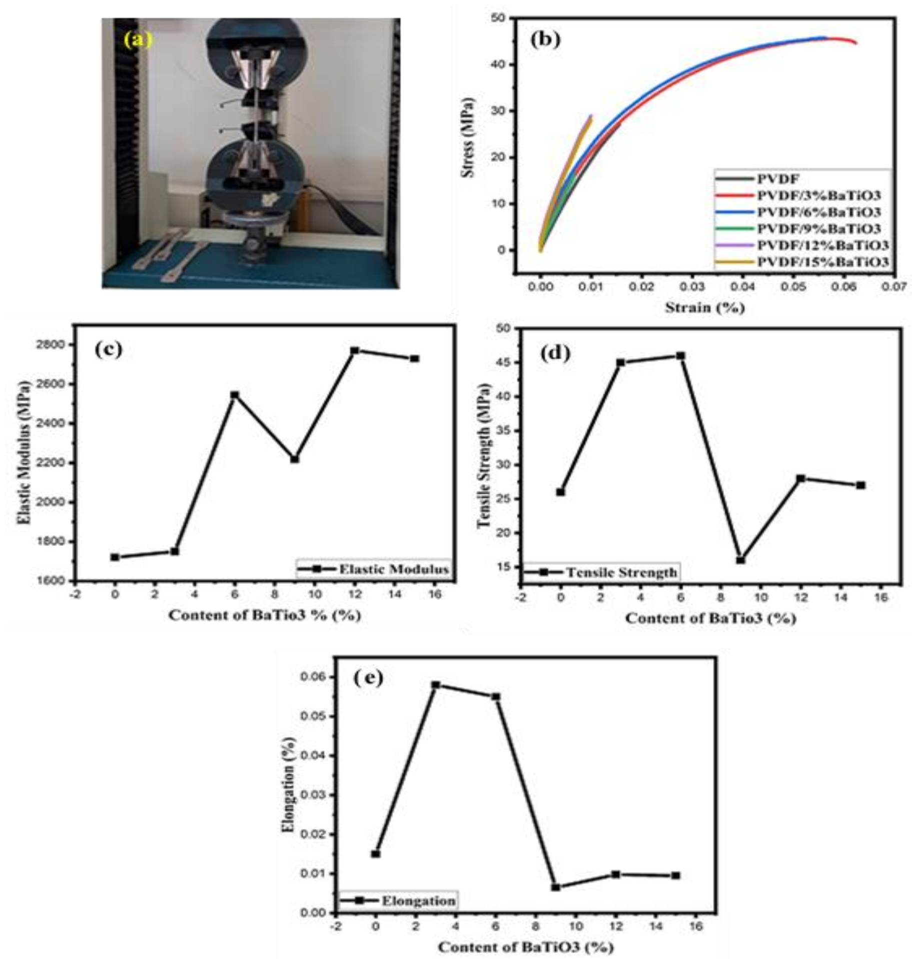

Figure 3.
(a) (a) Displays the tensile testing machine (Hounsfield H10KS, USA), (b) stress-strain curves, (c) Yield modulus, (d) Tensile strength, (e) Elongation of PVDF and its Nanocomposites.

3.3. Piezo-Tester

In order to measure the piezoelectric property, some samples were evaluated under a controlled impact frequency of 5 Hz during the Piezo-Tester, as seen in figure 4. The output voltage was read in millivolts, with each sample continuously subjected to a force of 2.6 N. The results indicated that their average output voltage and sensitivity (mV/N) increased steadily, meaning they were more responsive to applied force. These changes may be related to either their physical or electrical properties. As a result, the average output voltage increased, suggesting that the observed changes may be due to shifts in material properties or the structure itself. This also means that over time, these samples become very sensitive (mV/N) perhaps due to improved electrical conductivity or higher piezoelectric properties (see Table 2) [15].

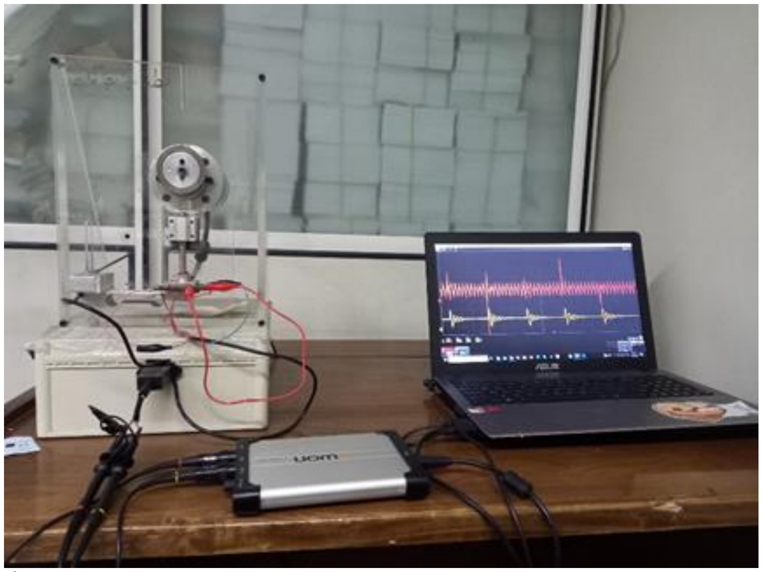

Figure 4.
Displays the Piezo-Tester (VDS 1022 Oscilloscope).

Table 2.
Output voltage and sensitivity of PVDF/$BaTiO_3$ nanocomposite samples.

Sample	Frequency (Hz)	Average output voltage (mV)	Force (N)	Sample sensitivity (mV/N)
0	5	0.400	2.6	0.153
3	5	0.416	2.6	0.160
6	5	0.433	2.6	0.166
9	5	0.450	2.6	0.173
12	5	0.700	2.6	0.269
15	5	0.933	2.6	0.358

After poling under identical conditions, showed an average output voltage of 0.516 mV and 0.198 mV/N, whereas the average output voltage was 0.750 mV with a sensitivity of 0.288 mV/N for PVDF/Barium titanate nanorods nanocomposites at 9 wt.%, and for 6 wt.% of $BaTiO_3$ nanorods, the output voltage was 0.516 mV with a sensitivity of 0.173 mV/N. The improvement ratio in output voltage for the PVDF nanocomposites was found to be 1.45 times (45%) that of the polymer without barium titanate nanorods, indicating an enhancement in the material's piezoelectric responsiveness.

4. Conclusions

$BaTiO_3$ nanorods' incorporation strength affects significantly the mechanical and piezoelectric properties of composite PVDF. The presence of CTAC affects the surface properties of nanorods providing smoother surfaces with less agglomeration is one way in which such properties as greater surface area and more responsive piezoelectric behavior can be enhanced for nanorods useful in sensors or capacitors. Furthermore, surfactants may lead to a better-formed crystal structure necessary for high dielectric constants and good electromechanical coupling. In order to achieve the best balance between mechanical strength and piezoelectric performance it is suggested that there should be an optimal content of $BaTiO_3$ around 9 wt.%. On one hand, piezoelectric sensitivity gets improved with an increase in $BaTiO_3$ content but on the other hand may reduce its ability to bend or twist easily. This indicates that these findings are important for advanced composites designing having high levels of both mechanical strength and improved piezoelectric properties.

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