

# Preparation Process and Dielectric Properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ -P(VDF-CTFE) Nanocomposites

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## ABSTRACT

Ceramic-polymer 0-3 nanocomposites, in which nanosized  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  (BST) powders were used as ceramic filler and P(VDF-CTFE) 88/12 mol% [poly(vinylidene fluoride-chlorotrifluoroethylene)] copolymer was used as matrix, were studied over a concentration range from 0 to 50 vol.% of BST powders. It is found that the solution cast composites are porous and a hot-press process can eliminate the porosity, which results in a dense composite film. Two different configurations used in the hot-press process are studied. Although there is no clear difference in the uniformity and microstructure of the composites prepared using these two configurations, the composite prepared using one figuration exhibit a higher dielectric constant with a lower loss. For the composite with 40 vol. BST, a dielectric constant of 70 with a loss of 0.07 at 1 kHz is obtained at room temperature. The composites exhibit a lower dielectric loss than the polymer matrix at high frequency. However, at low frequency, the composites exhibit a higher loss than the polymer matrix due to a low frequency relaxation process that appears in the composites. It is believed that this relaxation process is related to the interfacial layer formed between BST particle and the polymer matrix. The temperature dependence of the dielectric property of the composites was studied. It is found that the dielectric constant of these composites is almost independent of the temperature over a temperature range from 20 to 120 °C.

**Key words:** A. Polymer-matrix composites (PMCs); B. Electrical Properties; E. Casting; E. Heat treatment; Dielectric properties.

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## 1. Introduction

Materials with high dielectric constant, low dielectric loss, low process temperature, and high flexibility are highly desirable for applications ranging from electronic packaging to energy storage.<sup>1-3</sup> Dielectric polymers are flexible with a low processing temperature and can withstand a high electrical field.<sup>3-9</sup> For this reason, the dielectric polymers, such as polypropylene, are widely used in the fabrication of capacitors for energy storage.<sup>7</sup> However, it is well known that the polymers exhibit a very low dielectric constant. On the other hand, the inorganic ceramics, especially the ferroelectric-related ceramics, usually exhibit very high dielectric constant. Therefore, ceramic/polymer composites, especially ceramic-polymer 0-3 composites in which the ceramic powders are randomly filled in a polymer matrix, have been widely investigated to create the dielectrics with a relative high dielectric constant and a high dielectric strength (i.e. electric breakdown field).<sup>3</sup> In the development of high performance ceramic-polymer dielectric composites, various polymers have been studied and used. It is found that PVDF-based polymers exhibit a high dielectric constant ( $\sim 10$  at room temperature),<sup>8,9</sup> which makes these polymers great candidates as the polymer matrix for the development of ceramic-polymer composites. Among these PVDF-based polymer, P(VDF-CTFE) is more desirable as polymer matrix for the development of composite for energy storage purposes due to the fact that P(VDF-CTFE) does not show phase transition, so its dielectric constant is only weakly dependent on the temperature,<sup>11-13</sup> and that P(VDF-CTFE) can withstand a high electric field.<sup>14, 15</sup> Regarding ceramics used in the composites, various ferroelectric-based materials, such as BaTiO<sub>3</sub> and PMN-PT, have been studied.<sup>3</sup> It should be mentioned that the ferroelectric-based ceramics exhibit a strong temperature dependence on the dielectric constant at temperature close to the ferroelectric-to-paraelectric phase transition temperature,<sup>16</sup> which is undesirable for dielectric applications. The size of the ceramic particles also plays an important role on the performance of the composites. Ceramic particles with a smaller size are highly desirable for the development of composites,<sup>17</sup> since this would result in a more uniform morphology, especially in composite thin films. Therefore, nanocomposites, in which nano-sized ceramic particles are used, are of more interest.

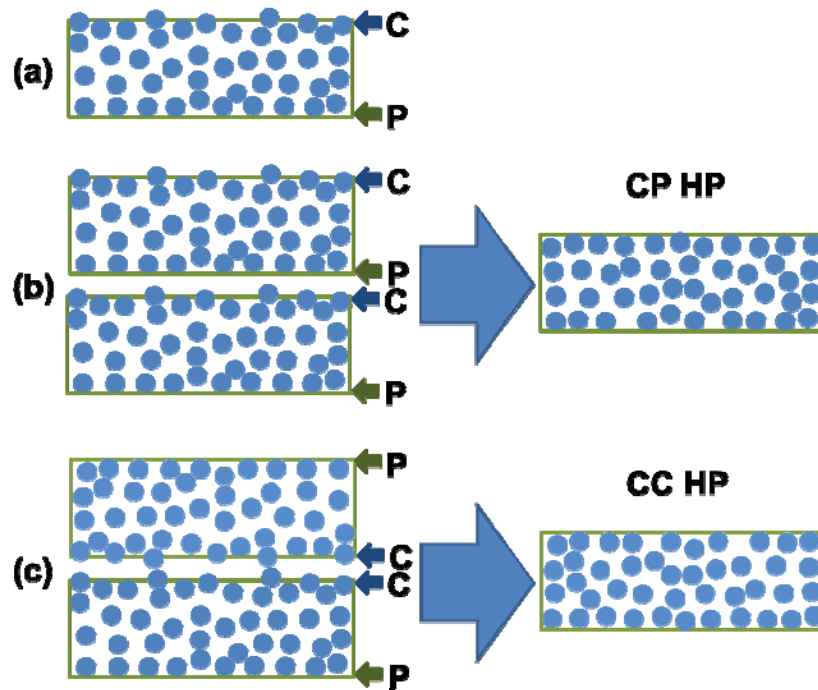
Regarding composite preparation, to obtain a uniform morphology in composites is critical. Although solution cast is widely used in the preparation of ceramic-polymer 0-3 composites, the uniformity of the as-cast composites is usually poor due to the poor wettability between the polymer matrix and ceramic particles. Therefore, it is important to improve the uniformity of the composite prepared using solution cast.

In this paper, a nanocomposite, in which nanosized (Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> (BST) particles are used

as the filler and P(VDF-CTFE) 88/12 (VC88) copolymer is used as polymer matrix, is developed. The lead-free BST 50/50 is selected since the ceramic exhibits a ferroelectric-to-paraelectric phase transition at a low temperature ( $< 250$  K).<sup>18</sup> The ceramics with this low ferroelectric-to-paraelectric phase transition temperature are not ferroelectric and piezoelectric and exhibit a weak temperature dependence in its dielectric constant at temperature around room temperature and higher temperature, all of these are desirable for the development of dielectric composites.<sup>19</sup> A hot-press (HP) process is utilized to improve the uniformity of the composite. It is known that HP process eliminates porosity in the as-cast composite, so that a dense composite can be obtained.<sup>17,19,20</sup> The HP process is also studied by using different configurations for the as-cast composite stack used. The influence of the configuration of the as-cast composite stack used in the HP process on the structure and dielectric properties of the composite is studied. The composites prepared by these processes exhibit a high dielectric constant with a low loss (i.e. dielectric constant of 70 with a loss of 0.07 at 1 kHz).

## 2. Experimental

P(VDF-CTFE) 88/12 mol% (VC88) copolymer was kindly provided by Solvay company.  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  (BST) nano-particles/powders are purchased from nGimat Co.. The BST-P(VDF-CTFE) 0-3 composites were first prepared by a traditional solution-cast method. That is, P(VDF-CTFE) copolymer was first dissolved in N, N dimethylformamide (DMF) by using a magnetic stirring for 4 hours to make polymer solution (i.e. 0.9 gram of VC88 was dissolved in 40 ml of DMF). Then, BST nano-powders were added into the polymer solution, which was then stirred for another 8 hours to get a relative uniform BST suspension. The BST/P(VDF-CTFE) suspension/solution was cast onto a glass substrate (15.2 cm x 10.1 cm) at 70 °C for 8 hours in an oven to form a solid composite film. The composite film was peeled off from the glass substrate in distilled water and, then, the composite film was dried in air, which is the as-cast film. After that, the composite films were annealed at 140 °C for 2 hours. These are the as-cast and annealed composite film used in the structure and property study. The thickness of the as-cast and annealed composite film increases with the volume fraction of BST in the composite, from 22  $\mu\text{m}$  for the pure copolymer to 80  $\mu\text{m}$  for the composite with 50 vol.% of BST. The volume fraction of the BST powder in the composite was calculated from the masses of the copolymer and BST nano-powders used in the composite preparation. In the calculation, the used density of BST and copolymer is 4.91  $\text{g}/\text{cm}^3$  and 1.75  $\text{g}/\text{cm}^3$ , respectively. The composites with different volume fractions (0, 10, 20, 30, 40, and 50 vol%) of BST were prepared.



**Figure 1.** Schematic of the as-cast composites (a), where the bottom layer of the as-cast film has smooth surface indicating rich in polymer, and the configuration used to form the stack of as-cast composite layers in the HP process: (b) CP configuration and (c) CC configuration.

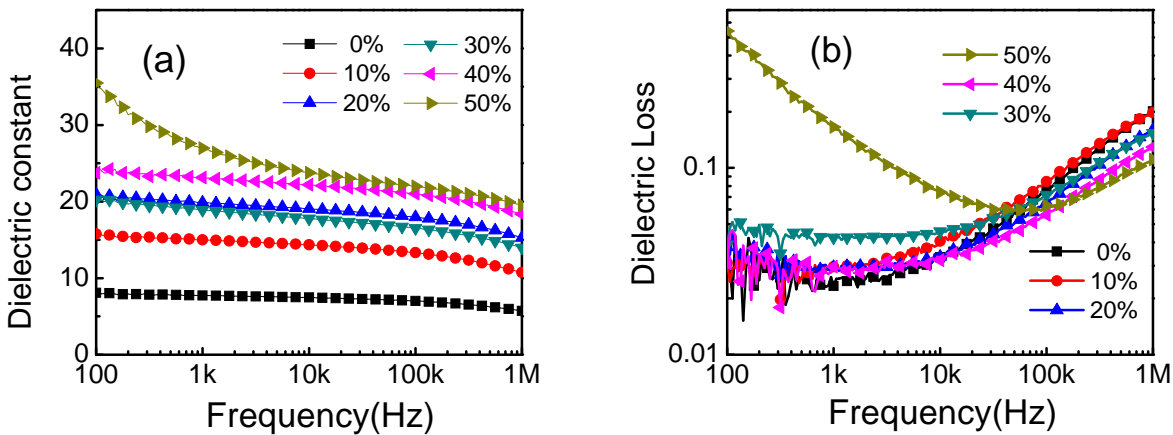
The hot-press (HP) process, in which a stack of as-cast composite film was used, was utilized to improve the uniformity of composites. It is found that two surfaces of the as-cast composite film are different: the bottom side (labeled as P) during solution cast is smoother than the top side (labeled as C), as illustrated in **Figure 1(a)**, which means that the bottom is rich in polymer, while the top is rich in ceramics. The stack of as-cast composite layers used in the HP process had two configurations, as illustrated in **Figure 1(b)** and **1(c)**. That is, in one configuration, the C-side of one layer is in contact with the P-side of next layer (CP configuration), while in the other configuration, the C-side of one layer is in contact with the C-side of next layer (CC configuration). The number of as-cast composite film used to form the stack used in the HP process was four. The stack was pressed using a hot press machine at 200°C. The thickness of the HP composite films is about 100~150  $\mu\text{m}$ . The composite samples thus prepared are named as CP-HP composite and CC-HP composite samples.

The microstructure and morphology of the composite film were examined using a JEOL (JSM-7000F) Field Emission Scanning Microscope (FE-SEM). The dielectric property of the composite film was characterized using an Agilent 4294A impedance analyzer. A gold layer was first deposited onto both surface of the composite film. The impedance of the sample measured using Agilent 4294A was converted into the dielectric constant and dielectric loss using the parallel plate

mode and the thickness of the composite film as well as the area of the gold electrode deposited on the sample surface. For the temperature dependence of the dielectric property of the composite sample, the sample was placed in an oven. The temperature was increased from room temperature (20 °C) to 120 °C with a step of 5 °C. At each temperature point, when the temperature reached a pre-set temperature, the impedance of the sample was measured at frequencies from 100 Hz to 10 MHz.

### 3. Results and discussion

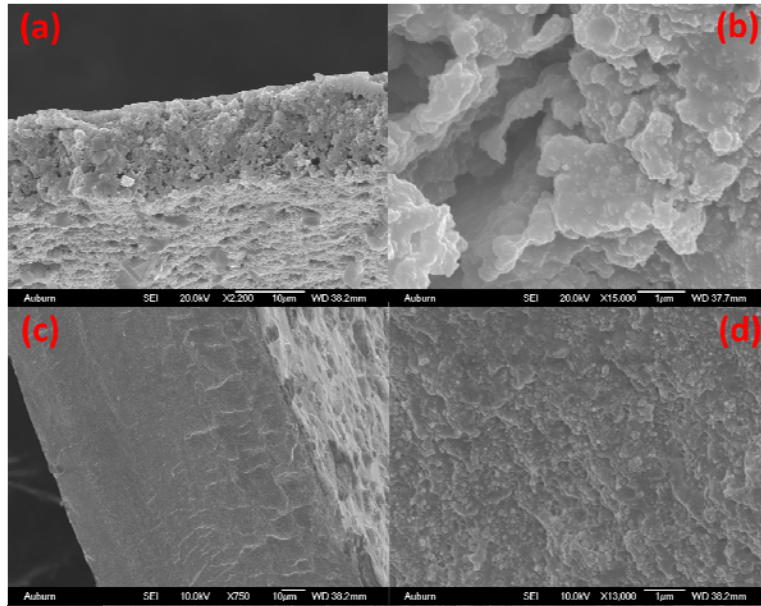
The dielectric constant and loss vs. frequency of the as-cast and annealed composite film at room temperature are shown in **Figure 2**. The composites show a higher dielectric constant than the polymer matrix. For example, the dielectric constant at 1 kHz increases from 8.3 for pure polymer matrix to 23 and 27 for the composites with 40 and 50 vol% of BST, respectively. However, the composite with 50 vol.% BST shows a different frequency dependence of the dielectric constant than other composites. The dielectric loss of the composites is strongly dependent on the frequency. At high frequency, all the composites have a lower dielectric loss than the pure polymer matrix. At low frequency, all the composites have a higher loss than the polymer matrix. Again, the composite with 50 vol.% BST shows a different behavior: its dielectric loss at low frequency is significantly higher than others.



**Figure 2.** Dielectric constant (a) and dielectric loss (b) versus frequency for the as-cast and annealed BST-P(VDF–CTFE) composites with different contents (0, 10, 20, 30, 40, and 50vol% as indicated in the figure) of BST.

The microstructure and morphology of these composite films were examined using SEM. Some of the results are shown in **Figure 3 (a)** and **3(b)**. Clearly, the as-cast and annealed composite films are not dense and of a porous structure, which certainly results in a lower apparent dielectric constant for the composite. Therefore, it is interested to eliminate the porosity in the composites. The HP process was used as described in the Experimental Section. Based on the SEM observation, it is

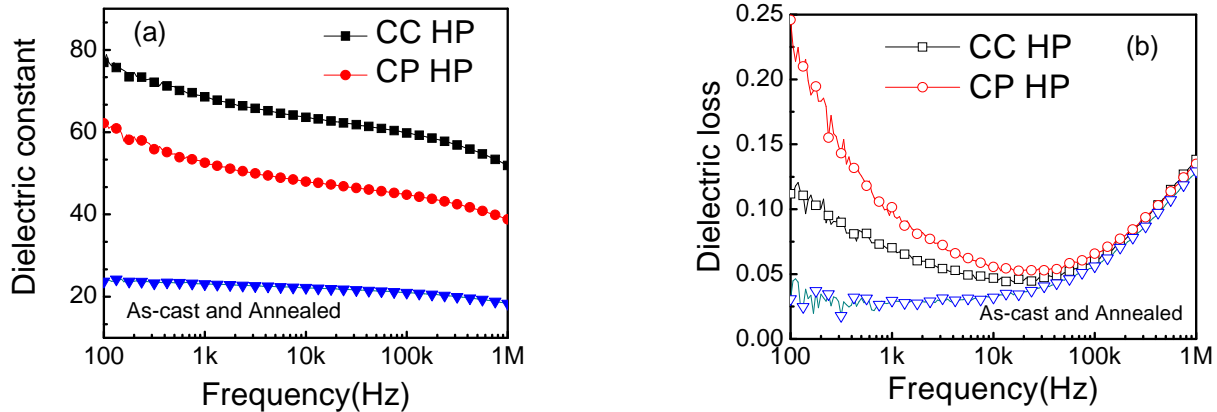
found that after HP process, the composite films are dense and of a better uniformity in the microstructure and morphology. Some of the SEM observations of the HP composites are presented in **Figure 3(c)** and **3(d)**. It should be mentioned that based on the SEM observation there is no clear difference in the microstructure and morphology between the CC HP composites and CP HP composites.



**Figure 3.** SEM picture of the cross-section of nanocomposite with 40 vol.% BST: (a) and (b) is as-casted one layer, (c) and (d) are CC HP composite.

The influence of the HP process is further examined using the dielectric property. First of all, for each composition of the composites, the influence of configuration of the as-cast composite stack used in HP process was studied. The results for composites with 40 vol. % of BST are shown in **Figure 4**, where the dielectric constant at 1 kHz is increased from 23 for the as-cast and annealed composite to 53 for the CP HP composites and 68 for the CC HP composites. That is, the CC HP composites exhibit a clearly higher dielectric constant than the CP HP composites. The data shown in **Figure 4** also indicate that the CC HP composites exhibit a lower dielectric loss than the CP HP composites. For all the composites studied here, it is found that most of the CC HP composites have a clearly higher dielectric constant than the corresponding CP HP composites. Some of the CC HP composites, such as the composite with 50 vol.% BST, have a slightly smaller dielectric constant than the CP HP composites. Disregarding dielectric constant, all CC HP composites exhibit a lower dielectric loss than the CP HP composites. That is, the CC HP composites have a better dielectric performance than the CP HP composites. This is also observed in other ceramic-polymer composites, such as  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  particles filled in P(VDF-TrFE) copolymer.<sup>21</sup> A higher dielectric constant and a

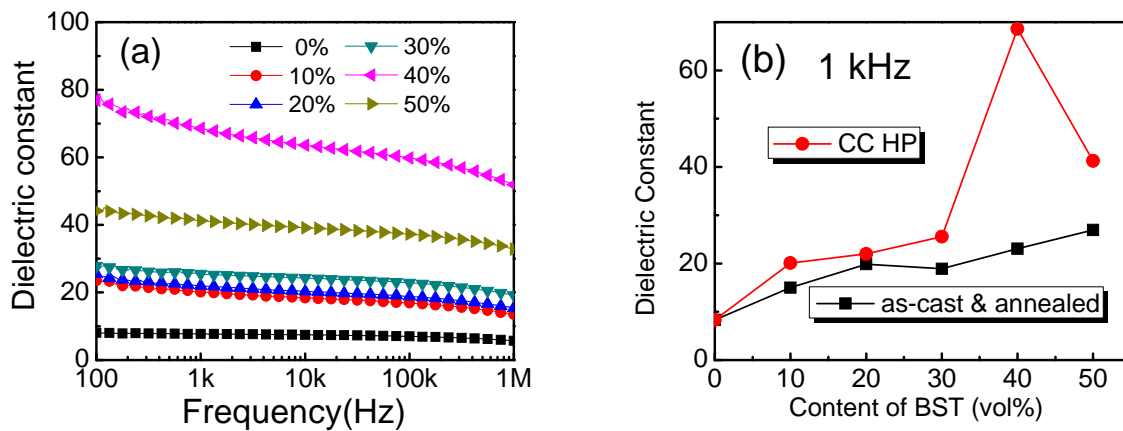
low loss observed in the CC HP composites may be related to the microstructure. That is, in the CC configuration, the air trapped in the as-cast composite films can be easily removed and the polymer matrix is easier to diffuse in the porous structure. Therefore, only the CC HP composites are used in the following studies.



**Figure 4.** Dielectric constant (a) and dielectric loss (b) versus frequency of composites with 40 vol.% of BST. For the HP composites, the composites made using CC and CP configurations are presented. For comparison, the as-cast and annealed composite is also presented.

The frequency dependences of the dielectric constants for the CC HP composites with different compositions (0, 10, 20, 30, 40, and 50% of BST) at room temperature are shown in **Figure 5(a)**. Clearly, the CC HP composite films have a significantly higher dielectric constant than the corresponding as-cast and annealed composite films shown in **Figure 2**. The reason behind this is that the HP composites are much denser than the as-cast and annealed composites. The composition dependence of the dielectric constant is summarized in **Figure 5(b)** for the dielectric constant at 1 kHz for all the composites studied here. It is very interesting to notice that the dielectric constant of the CC HP composites with 40 vol.% BST reaches its maximum among the composites studied here. That is, for the HP composites with no more than 40 vol.% of BST, their dielectric constant increases with increasing BST content, which is expected by all the models introduced to calculate the dielectric constant of a composite based on the dielectric constant of the ceramic filler and polymer matrix.<sup>3</sup> However, the HP composites with 50 vol.% of BST exhibit a smaller dielectric constant than the HP composite with 40 vol.% of BST. This results in a maximum peak in the composition dependence of the dielectric constant. This is against the models introduced to simulate the apparent dielectric constant of a composite.<sup>3</sup> It should be mentioned that this phenomenon has been observed in other ceramic-polymer 0-3 composites.<sup>22-24</sup> For example, in a study of BaTiO<sub>3</sub> (BT)-PVDF nanocomposites, it is found that

the dielectric constant of the composite increases with the content of BT for the BT content from 0 to 50 vol.%. However, the dielectric constant of the composite with 60 vol.% BT is lower than the composite with 50 vol.% BT.<sup>22</sup> In the study of CCTO-P(VDF-TrFE) 0-3 composites, the similar behavior was found.<sup>21,23</sup> In the study of alumina-polyimide nanocomposite, the dielectric constant of the composites can be higher than the dielectric constant of the ceramic filler.<sup>24</sup> That is, there is a maximum peak to be observed in the composition dependence of the dielectric constant. In other words, this is quite common in the ceramic-polymer 0-3 composites that the dielectric constant of the composite increases with increasing content of high dielectric constant filler initially and, then, decreases with increasing content of high dielectric constant filler in some composition range. The physics behind this is not clear, although it is explained/discussed using the interfacial layer formed in the composite between the ceramic particles and the polymer<sup>24</sup> or using percolation theory (here, the ceramic particles are treated as conductive).<sup>22, 23</sup>

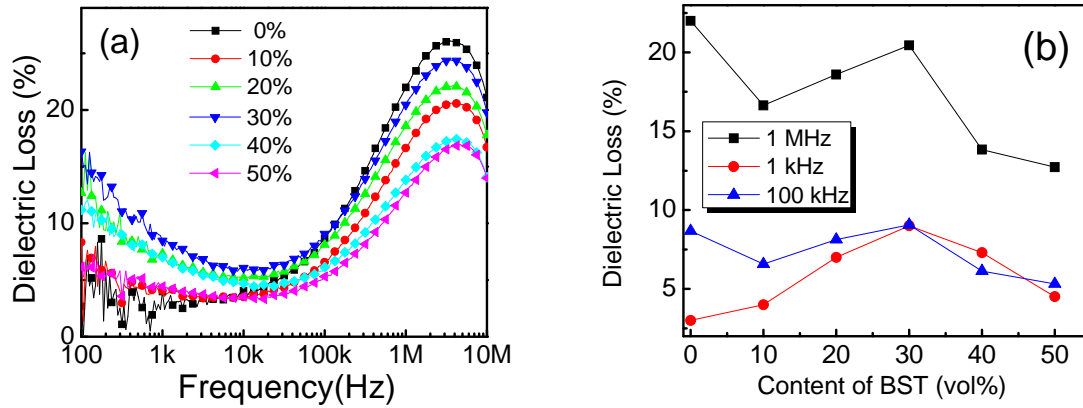


**Figure 5.** (a) Dielectric constant versus frequency for the composites with different content of BST (shown in figure). (b) Dielectric constant at 1 kHz versus the BST content for both CC HP composites and as-cast and annealed composites.

The frequency dependence of the dielectric loss for the CC HP composites with different compositions at room temperature is shown in **Figure 6(a)**. Comparing data shown in **Figure 2(b)** and **6(a)**, one can find that, except the composite with 50 vol.% BST, the HP composites exhibit a higher dielectric loss at low frequency (< 10 kHz) than the as-cast and annealed composite as demonstrated in **Figure 4(b)** for the composite with 40 vol% BST. At high frequency (> 10 kHz), there is a relaxation process observed in all the samples. This process is from the polymer matrix. That is why all the composites exhibit a lower loss than the polymer matrix at high frequency. It is interesting to find that the relaxation frequency of this process actually changes with the content of BST in the composites. For the polymer matrix, the relaxation frequency determined from the imaginary part of the dielectric constant (no shown here) is about 1.4 MHz, which increases to 1.5,



1.6, 1.8, 2.1 and 2.5 MHz for the composites with 10, 20, 30, 40, and 50 vol% BST, respectively. This means the relaxation time decreases with increasing BST content in the composites. Since the relaxation process is from the polymer matrix, the increase in the relaxation frequency with increasing BST content indicates some microstructural change in polymer matrix.



**Figure 6.** (a). Dielectric loss versus frequency for all CC HP composites at room temperature. (b) Dielectric loss at the frequencies (1 kHz, 100 kHz, and 1 MHz) versus the BST content for all CC HP composites.

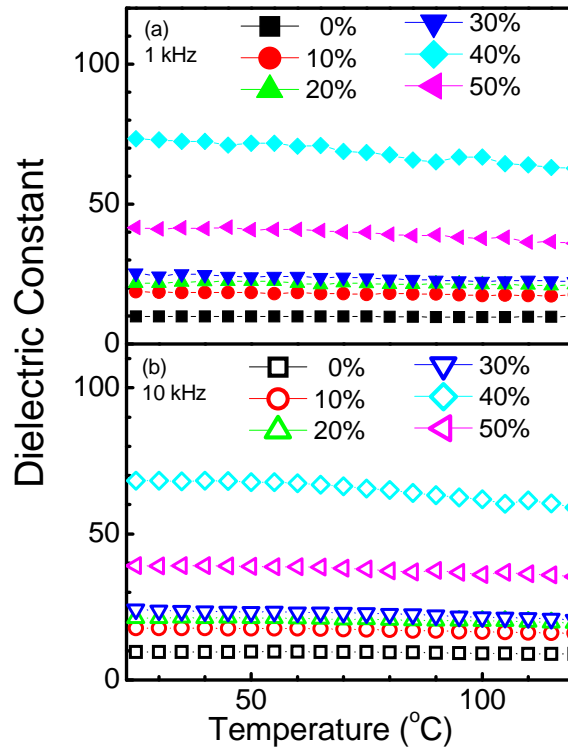
The frequency dependence of the dielectric loss shown in **Figure 6(a)** also indicates that the composites have a relaxation process at low frequencies, which is introduced by the BST. However, the BST ceramic itself does not exhibit a relaxation process at this low frequency range. Therefore, this low frequency process is from the polymer matrix and/or due to the mixing of polymer and BST powders. That is, this low frequency process may be from the interfacial layer between the polymer matrix and BST particles in the composites. Based on the study of P(VDF-TrFE) and P(VDF-CTFE), it is known that the interfacial layer in these semicrystalline polymers plays an important role on its polarization response.<sup>24-26</sup> Considering the process temperature for the preparation of the composites studied here, no change is anticipated for the BST. That is, the interfacial layer is nothing but the polymer chains with different conformation and microstructure than the polymer chains in the bulky polymer matrix. The volume fraction of the interfacial layer in the composite should increase with increasing BST content. That is why the dielectric loss at low frequency increases with increasing BST content initially. At the same time, the distance between the BST particles in the composite decreases with increasing BST content. At some point, the interfacial layer on one BST particle will contact with the interfacial layer on another BST particle. If the BST content is further increased, the volume fraction of the interfacial layer in the composite will decrease. That is, for the composite with high BST content, the volume fraction of the interfacial layer in the composite decreases with increasing BST content. Therefore, the dielectric loss at low frequency would decrease with

increasing BST content in the composite. This is what was observed from the composites studied, as shown in **Figure 6(b)**. Based on the data shown in **Figure 6**, the dielectric loss at low frequency reaches its maximum in the composite with 30 vol.% of BST. That is, the volume fraction of the BST powders and interfacial layer reaches its maximum in the composite with 30 vol.% of BST. Based on the crystal structure, it is well known that the most tightly packed crystal with the same size spheres has an atomic packing factor of 74%. Assuming that the BST particles are spherical with the same diameter and the interfacial layer is uniformly coated on the surface of the BST particle, a volume fraction of 74% of interfacial layer plus BST particles corresponds to the composite with the highest volume fraction of interfacial layer. As discussed above, the experimental results indicate that the composite with 30 vol.% of BST has the highest volume fraction of interfacial layer. That is, in this composite (i.e. the composite with 30 vol.% BST) the volume fraction of interfacial layer plus the BST particles is about 74 vol.%. For the BST particles used here, the average radius is about 40 nm, one can obtain that the thickness of the interfacial layer is about 14 nm, which is consistent with the thickness of the interfacial layer estimated in the alumina-polyimide nanocomposites.<sup>27</sup>

The temperature dependences of the dielectric constant at 1 kHz and 10 kHz for all the CC HP composites are shown in **Figure 7**. Clearly, the composites reported here show an almost temperature independence of the dielectric constant for all the composites. To further study the temperature dependence of the dielectric properties, a temperature coefficient (Temp-Coef) introduced previously is used:<sup>20</sup>

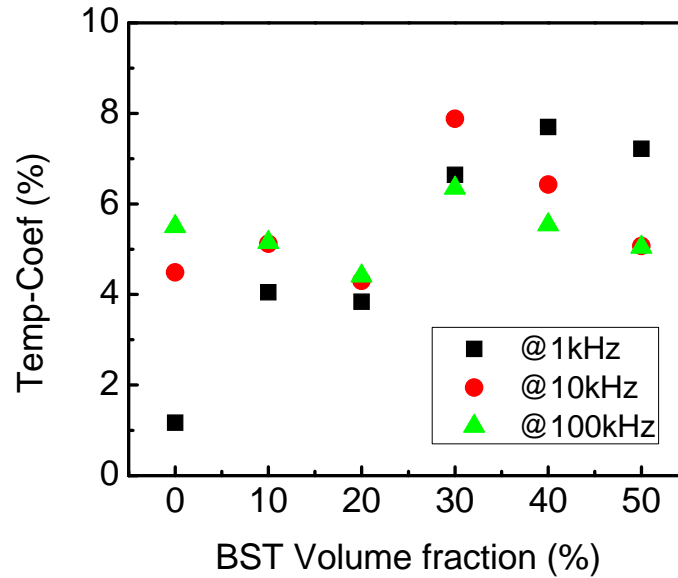
$$Temp - Coef = \frac{Max(\varepsilon) - Min(\varepsilon)}{Max(\varepsilon) + Min(\varepsilon)} \quad (1)$$

where Max( $\varepsilon$ ) and Min( $\varepsilon$ ) are the maximum and minimum values of the dielectric constant at a constant frequency over the temperature range from 20 to 120 °C.



**Figure 7.** Temperature dependence of dielectric constant at 1kHz (a) and 10 kHz (b) for CC HP composites with different contents of BST.

The *Temp-Coef* defined in Eq. (1) represents the maximum derivation of the dielectric constant from its median value. The value of *Temp-Coef* at some frequencies for all composites is summarized in **Figure 8**. The data indicates that the composites have two composition regimes: 1) composites with low (0, 10, and 20 vol%) BST content and 2) composites with high (30, 40, and 50 vol%) BST content. The composites with high BST content exhibit a slightly higher *temp-coef* than the composite with low BST content, which may originate from the temperature dependence of the dielectric constant for BST. It is well known that the dielectric constant of perovskite ferroelectrics, such as BST, decreases with increasing temperature at temperature higher than its ferroelectric-to-paraelectric phase transition temperature.<sup>16</sup> As mentioned in the introduction, the transition for the BST used here is about -20 °C. Therefore, the dielectric constant of the BST used at temperatures studied here decreases with increasing temperature.



**Figure 8.** Temperature coefficient (*Temp-Coef*) defined in Eq. (1) for all the CC HP composites over the temperature range from 20 to 120 °C.

#### 4 Conclusions

BST-P(VDF-CTFE) 0-3 nanocomposites with ceramic content from 0 to 50 vol.% are prepared using dielectric processes. It is found that the as-cast the composite films are porous, and a hot-press process can eliminate the porosity. Two different configurations were used in the HP process. Although there is no clear difference in the microstructure and uniformity of the composites prepared using two configurations, one (CC) configuration results in the composites with a high dielectric constant and a lower dielectric loss. The HP composites studied here exhibit a high dielectric constant and a low dielectric loss. For example, for the composites with 40 vol.% of BST, a dielectric constant of 70 with a loss of 0.07 at 1 kHz is obtained at room temperature. Regarding dielectric loss, it is found that the composites have a lower dielectric loss at high frequency than the polymer matrix. However, at low frequency, the composites exhibit a higher loss than the polymer matrix, which is the result of a low frequency relaxation process. It is believed that this low-frequency relaxation process is related to the interfacial layer formed in the composites. The temperature dependence of the dielectric property of the composites is studied. It is found that the dielectric constant of the composites studied here is almost independent of temperature over a temperature range from 20 to 120 °C.

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