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Influence of coupling agent on the microstructure and dielectric properties of free-standing ceramic-polymer composites

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Abstract

The influence of a commercial coupling agent on the dielectric properties and microstructure of ceramic-polymer nanocomposites are studied. Free-standing BaTiO\textsubscript{3}-P(VDF-CTFE) films were fabricated using a simple solution-casting process, and the good wettability between fillers and polymer matrix was obtained by using 3-Aminopropyltriethoxysilane as coupling agent. It is found that the coating of a small amount of coupling agent on the surface of BaTiO\textsubscript{3} fillers results in an enhanced dielectric constant, a higher breakdown strength and a larger energy-storage efficiency. When an excessive amount of coupling agent was used, the non-attached coupling agent molecules participated in the complex reactions and result in the aggregation of fillers and the reduction of dielectric constant. It is also found that the surface modification of fillers has a complicated influence on its dielectric behavior which leads to an increase in the dielectric loss of the nanocomposites. When an appropriate amount of coupling agent is coated on fillers, the energy storage density of the nanocomposite is improved due to the enhanced dielectric constant and higher breakdown strength. A maximal discharged energy-storage density of about 4.0 J cm\textsuperscript{-3} was obtained from the nanocomposite film containing 15 vol\% of surface modified BaTiO\textsubscript{3} fillers with 1 wt\% of KH550, which is about 3 times of that for the nanocomposite without coupling agent.

1. Introduction

Dielectric materials with a high dielectric constant (\(\varepsilon_r\)) and a high breakdown field (\(E_b\)) are essential for the three primary applications in electronic systems: high-performance capacitors, insulators and energy storage devices [1–3]. In general, the inorganic materials, especially polar materials, such as BaTiO\textsubscript{3}, usually exhibit a high \(\varepsilon_r\) (\(10^3 \sim 10^6\)) but a low \(E_b\) (\(< 10^6\) MV m\textsuperscript{-1}) [4–6]. In contrast, the organics, such as biaxially oriented polypropylene (BOPP), exhibit a high \(E_b\) (\(\sim 600\) MV m\textsuperscript{-1}) but a low \(\varepsilon_r\) (\(< 3\)) [6–8]. Therefore, it is interesting to develop dielectric composites, especially 0–3 composites with a relatively high \(\varepsilon_r\) and \(E_b\), in which a dielectric matrix with a high \(E_b\) is filled with either conductive particles [9–14] or dielectric particles with a large \(\varepsilon_r\) [6, 15–16]. In the study of dielectric 0–3 composites, polymers are widely used as the matrix due to their high \(E_b\) and good flexibility which is very critical for many applications such as the wearable electronics [7]. Among the different polymer matrixes used in the 0–3 composites, polar polymers such as PVDF and P(VDF-CTFE), attracted numerous attentions since they exhibit a higher \(\varepsilon_r\) (\(\sim 10\)) than nonpolar polymers [7, 17, 18]. Regarding the fillers, ferroelectric particles such as BaTiO\textsubscript{3} [18, 19], (Ba, Sr)TiO\textsubscript{3} [20, 21], Pb(Zr, Ti)O\textsubscript{3} [22, 23], etc, have been intensively studied since they exhibit a high \(\varepsilon_r\) [6].

For a composite, the properties are not only determined by the composition, but also significantly affected by the uniformity of its microstructure [24]. Unfortunately, there is a general concern about the poor wettability...
between the polymer matrix and inorganic fillers, which limits the uniformity of the polymer-based composites [25]. The composites prepared from the ceramic-polymer suspensions usually have a nonuniform microstructure [6, 18]. Therefore, substantial researches have been undertaken to improve the uniformity and compatibility of the 0–3 polymer composites [18]. In one approach, a hot-pressing process was utilized by pressing a stack of solution-casting films into one layer [17, 24]. It is experimentally found that although the uniformity of the polymer-based composites can be significantly improved, the hot-pressing does not change the surface chemistry of the filler, which results in a lower $E_b$ in the composites [17, 25]. In another approach, the non-uniformity caused by the sedimentation of suspensions can be eliminated by a spin-coating process [26, 27]. However, the polymer-based films prepared by the spin-coating process were usually designed to be not free-standing and are much thinner than those prepared by the solution-casting process; additionally, it should be mentioned that both the hot-pressing and spin-coating are not desirable for many applications because they lead to a much more complex fabrication process [26, 27]. A simple fabrication process is demanded for a uniform microstructure of polymer-based composites.

The other effective approaches to improve the uniformity of ceramic-polymer composites are based on the surface treating methods, which focus on the compatibility between the matrix and fillers [28, 29]. Different coupling agents have been studied to modify the surface of ceramic fillers. For example, coupling agents such as GPTMS and HEMA have been used to modify the surface of BT for the polymer-based composites [30–34]. It is demonstrated that the coupling agent can be easily attached onto the surface of ceramics such as BT [34, 35]. In the current literatures, coupling agents are usually coated on the ceramic fillers before the preparation of composite suspensions by an individual surface treating process which does not affect the casting process. Therefore, the ceramic-polymer composites with good compatibility between its constituents can be prepared by a simple process. Certainly, the effectiveness of a coupling agent for composites is strongly dependent on the chemical nature of the constituents [35] and interfacial area between matrix and fillers [36]. For a dielectric composite system, it is speculated that the improvement of dielectric constant and energy density is maximized when a coupling agent is fully coated on the fillers [36]. However, it is also found that an excessive amount of coupling agent would affect the properties of polymer matrix and result in the performance degradation of the composites [34–36]; in addition, the intermolecular reaction of coupling agent itself may also take place [37]. In one word, the undefined mechanisms of coupling agent in dielectric composites are still need to be studied for the development of simple processing method of flexible and free-standing ceramic-polymer composites.

In this work, one of the most common commercially available high dielectric constant materials, $\text{BaTiO}_3$ (BT) was selected as the fillers; the $\text{P(VDF-CTFE)}$ 91/9 mol% copolymer (VC91) was selected as the polymer matrix due to its high breakdown strength. The widely used commercial coupling agent $3\text{-Aminopropyltriethoxysilane (KH550)}$ was used for the surface modification. The dielectric properties and energy-storage performances of BT-VC91 nanocomposites using surface modified and unmodified fillers were characterized. It is demonstrated that the flexible and free-standing ceramic-polymer composites with a good uniformity can be successfully fabricated by a simple solution-casting process, and the effect of coupling agent on the microstructures, dielectric properties and energy-storage performances of ceramic-polymer composite systems were systematically investigated.

2. Experiments

2.1. Preparation of $\text{BaTiO}_3$–$\text{P(VDF-CTFE)}$ (BT-VC91) composites

BT nanoparticles with 99% purity in a diameter of about 200 nm were purchased from US Research Nanomaterials. The coupling agent, KH550, from Sigma-Aldrich was used as received. For the polymer matrix, VC91 copolymer powder from Solvey was used. N, N dimethylformamide (DMF) purchased from Fisher Scientific was used as a solvent for the solution preparation. The BT-VC91 composites with different BT contents (5, 10, 15, 20, 25 and 30 vol%) were prepared by a solution-casting process, the composites with/without coupling agents were studied. In the captions and discussions, these nanocomposites were labeled as $x\text{BT-VC91}$, where $x$ is the volume percentage of BT in the composites. For the fabrication of each nanocomposite film with a certain BT volume fraction, 0.3 grams of VC91 powders was used for the solution preparation, and the mass of BT nanoparticles was calculated from the composition. In the calculations, the densities of BT nanoparticles and VC91 powders were assumed as that of the bulk materials, which were 6.02 g cm$^{-3}$ and 1.75 g cm$^{-3}$, respectively. For the study of the effect of KH550 addition on the polymer matrix without fillers, VC91 films containing 0.2, 0.4, 0.6, 0.8 and 1.0 wt% of KH550 were also prepared.

Two types of BT nanoparticles were used in the preparation of BT-VC91 composites. One is the BT nanoparticles as received (i.e. unmodified BT), the other is the BT nanoparticles coated with KH550. To obtain the coated BT nanoparticles, a solution of 1 wt% KH550 in water-ethanol (95 wt% ethanol) was firstly prepared at room temperature. Then, the BT nanoparticles were placed into the solution and ultra-sonicated for 30 min.
Finally, the solvent was evaporated by heating the mixture at 80 °C for 5 h and then at 120 °C for 12 h. The dried nanoparticles were used as the KH550 coated BT nanoparticles for the BT-VC91 composite preparation. In the process, the weights of KH550 and BT nanoparticles were measured to get KH550 coated BT nanoparticles with 1, 2, 3, 4 and 5 wt% of KH550. Here, the 1–5 wt% of coupling agent amount means the weight percentage of KH550 to BT fillers.

The detailed fabrications of the BT-VC91 nanocomposites are as described below. Firstly, the VC91-DMF solution was prepared by dissolving 0.3 grams of VC91 powders in 10 ml DMF at room temperature by magnetic stirring for 12 h. The BT nanoparticles were added into the solution, then ultra-sonicated for one hour and immediately followed with 12 h stirring to form a homogeneous BT-VC91-DMF suspension. After that, the suspension was cast on a preheated 75 × 25 mm glass substrate to make films. About 3 ml of the BT-VC91-DMF suspension was dropped on each of the glass substrate. The glass substrate with suspensions was then kept in the oven at 70 °C for 8 h to evaporate the solvent. Finally, the as-cast films were released from the glass substrate, and the obtained free-standing films were annealed at 160 °C in air for 12 h. The thicknesses of the BT-VC91 nanocomposite films prepared by this process varied with the volume fraction of BT, from about 20 μm for the pure VC91 film to about 40 μm for the nanocomposites contains 30 vol% of BT fillers.

2.2. Characterization and measurement

The morphology and uniformity of nanocomposites were characterized using a Field Emission Scanning Electron Microscopy (FE-SEM, JEOL JSM-7000F). For the determination of the dielectric properties of the nanocomposites, the gold electrodes in a diameter of 3.0 mm were sputtered on both surfaces of the nanocomposite by a PELCO SC-6 gold coater. An Agilent 4294 A impedance analyzer was used to characterize the capacitance and loss over a frequency range from 100 Hz to 1 MHz by using the Cp-D function. The dielectric constant of the nanocomposites was then calculated using the parallel plate model. For the behavior of the composites under a high electric field, the $E_p$ was first determined using a Trek 610D 10 kV High Voltage Supplier/Amplifier, then the polarization-electric field (P-E) hysteresis loop at 10 Hz was characterized using a Precision-LC100 Ferroelectric Testers coupled with the 10 kV High Voltage Supplier/Amplifier in silicone oil.

3. Results and discussion

The influence of KH550 in the morphology and microstructure of the nanocomposites was examined using SEM as shown in figure 1. Firstly, it was found that the overall filler distribution of BT-VC91 nanocomposites with a low amount of coupling agent are much more uniformed then the ones with a high amount of coupling agent. For the nanocomposites with 1 wt% and 5 wt% of KH550, the distribution of BT nanoparticles in VC91 matrix are shown in figures 1(a) and (b). In the BT-VC91 nanocomposites with 1 wt% of KH550, the BT nanoparticles are uniformly distributed in the matrix, which demonstrates the good wettability and uniformity of nanocomposites using ceramic fillers treated by a proper amount of coupling agent; for the BT-VC91 nanocomposites with 5 wt% of KH550, a ceramic-rich layer consistent with the previous reports for the composites using micron-sized fillers was observed [9, 35], and some pores can also be found in the ceramic-rich regions. From the observation with a higher magnification, it was confirmed that the polymer used in this work is compact and void-free whether the coupling agent is used or not. As an example, the VC91 without BT fillers annealed at 160 °C with 1 wt% of KH550 is shown in figure 1(c). There are no obvious defects in the cross section of polymer. The cross section image of the BT-VC91 nanocomposite using unmodified BT fillers is shown in figure 1(d). It can be seen that the BT fillers are sphere-like nanoparticles with an average size of about 200 nm, which confirmed the product information from the supplier. Although the most of fillers are tightly encapsulated in polymers, some separations between matrix and a minority of the BT nanoparticles still can be found. In other words, no interfacial bonding was found between matrix and fillers. To improve the wettability between BT and VC91, the coupling agent was used. It was found that there is an excellent compatibility between VC91 and the KH550 coated nanoparticles. For example, the cross section image of the BT-VC91 nanocomposites with 1 wt% and 5 wt% of KH550 are shown in figures 1(e) and (f), respectively. For both of the cases, no separations were found between BT nanoparticles and VC91 matrix, which indicated strong interfacial bonding. Therefore, no significant difference of interfacial connection was found between the nanocomposites with a low amount and a high amount of coupling agent. The microstructure observation suggest that the small amount of coupling agent is mainly acts as a bridge-linking role between fillers and matrix, and the excessive addition of coupling agent will interact between filler particles and lead to the fillers aggregation.

For the study of coupling agent effect on the polymer matrix own properties, VC91 films containing different amounts of KH550 were prepared and their dielectric properties are shown in figure 2. The dielectric constant ($\varepsilon_r$) and loss (tanδ) of VC91 films are dependent on the frequency and the amount of KH550. The $\varepsilon_r$ were gradually decreased and the tanδ were gradually increased with increasing frequency, which are related to
Figure 1. SEM image of cross section: uniformity of (a) 30BT-VC91 with 1 wt% of KH550 and (b) 30BT-VC91 with 5 wt% of KH550; ceramic-polymer interface of (c) VC91 polymer with 1 wt% of KH550, (d) 30BT-VC91 without KH550, (e) 30BT-VC91 with 1 wt% of KH550, (f) 30BT-VC91 with 5 wt% of KH550.

Figure 2. Dielectric properties of polymer matrix: (a) $\varepsilon_r$, and (b) $\tan\delta$ of VC91 with different amount of KH550.
the relaxation process of the polymer. From the inserted schematic in figures 2(a) and (b), it can be seen that in the whole tested frequency range, the $\varepsilon_r$ of VC91 films was decreased with increasing amount of KH550, while the $\tan\delta$ was almost keeping constant and, slightly increased with a relatively large amount (1 wt%) of KH550. For example, the $\varepsilon_r$ was about 11 and the $\tan\delta$ was about 0.08 for VC91 with 1 wt% KH550 at 1 kHz, while the $\varepsilon_r$ was about 13 and the $\tan\delta$ was about 0.04 for VC91 without KH550 at 1 kHz. Considering the very low dosage of coupling agent, the changes in the properties discussed above are appreciable. As shown in SEM pictures, it was known that the KH550 did not result in obvious defects in the microstructure of VC91 polymer. Therefore, the difference of the dielectric properties should be interpreted to the formation of polymer blends of VC91 and KH550 with a lower dielectric constant [35].

The energy storage performances of these VC91-KH550 blends were then tested. The Weibull distribution of breakdown strength containing the results of 10 samples for each condition are plotted and shown in figure 3(a), and the $E_b$ of VC91 films dependents on the amount of KH550 are shown in figure 3(b). There is an obvious improvement of $E_b$ with a very little amount of KH550, the highest $E_b$ (>290 MV m$^{-1}$) is observed in the VC91 with 0.2 wt% KH550; for the VC91 films with KH550 exceeds 0.4 wt%, the $E_b$ decreases with the increasing amount of addition. From the P–E hysteresis loops for VC91 films at a same electric field (260 MV m$^{-1}$) as shown in figure 3(c), it is clear that the saturation polarization ($P_s$) and remnant polarization...
of the BT-VC91 nanocomposites were increased with increasing amount of KH550. For VC91 with an amount of KH550 larger than 0.8 wt%, the loop area was sharply increased. Therefore, the addition of KH550 with a relatively large amount also leads to the decrease of charge-discharge efficiency ($\eta$), which is the ratio of the energy discharged from the material to the energy stored in the material as shown in figure 3 (d).

Interestingly, the $\eta$ of VC91 films was slightly increased by the KH550 with a small amount (0.2–0.4 wt%). The charge energy density ($U_{\text{charge}}$) and discharge energy density ($U_{\text{discharge}}$) were calculated and shown as figures 3(e) and (f), respectively. It can be seen that as a result of the increased $P_r$, $P_c$, $\eta$ and $E_b$, the energy density of polymer films with a trace of coupling agent can be slightly increased. For example, under an electric field of 280 MV m$^{-1}$, the $U_{\text{discharge}}$ of VC91 with 0.2 wt% KH550 was 6.29 J cm$^{-3}$, while the $U_{\text{discharge}}$ of VC91 without KH550 was 5.68 J cm$^{-3}$.

Subsequently, the BT-VC91 nanocomposites without KH550 and BT-VC91 nanocomposites with different amounts of KH550 were respectively prepared, and their dielectric properties are shown in figure 4. It can be seen that the $\varepsilon_r$ and tan$\delta$ of all samples were also strongly dependent on frequency, which indicated that the frequency dependences of dielectric properties of the BT-VC91 nanocomposites were mainly determined by their polymer matrix. As shown in figure 4(a), the $\varepsilon_r$ of nanocomposites without coupling agent under the whole testing frequency range were gradually increased with increasing filler content. For the dielectric loss, the tan$\delta$ at

![Figure 4. Frequency dependence of the dielectric properties of nanocomposites: (a) $\varepsilon_r$ and (b) tan$\delta$ of BT-VC91 without KH550; (c) $\varepsilon_r$ and (d) tan$\delta$ of BT-VC91 with 1 wt% of KH550; (e) $\varepsilon_r$ and (f) tan$\delta$ of BT-VC91 with 5 wt% of KH550.](image-url)
low frequency were gradually decreased and the $\tan \delta$ at high frequency were gradually increased with increasing frequency, as shown in the inserted schematic in figure 4(b), where the 1 kHz and 100 kHz were used as the representatives of low and high frequency, respectively. For the nanocomposites with coupling agent, the dielectric properties were changed by KH550 as expected. The $\varepsilon_r$ and $\tan \delta$ of BT-VC91 with 1 wt% of KH550 are shown in figures 4(c) and (d), respectively. It was found that the trend of $\varepsilon_r$ is keeping the same; however, the $\tan \delta$ at both 1 kHz and 100 kHz were increased with increasing amount of KH550. With a relatively larger amount of coupling agent, the $\varepsilon_r$ of nanocomposites with high filler contents were obviously declined while the $\tan \delta$ were obviously increased. As an example, the dielectric properties of BT-VC91 with 5 wt% of KH550 are shown in figures 4(e) and (f). It should be noticed that, the $\tan \delta$ of BT-VC91 with 5 wt% of KH550 are almost randomly changed from piece to piece, which can be clearly observed in figure 4(f). The randomness of its dielectric properties reflects that the excessive coupling agent leads to the degradation of homogeneity of nanocomposites, which is consistent with the SEM observations.

For the quantification of coupling agent effect, the dielectric properties of BT-VC91 nanocomposites as a function of KH550 amount are shown in figure 5. As shown in figures 5(a) and (b), the $\varepsilon_r$ of nanocomposites at low (1 kHz) and high (100 kHz) frequencies is behaving a similar variation trend. For the nanocomposites with a relatively low filler content, the $\varepsilon_r$ was almost keeping constant with a small amount of KH550, and slightly decreased with a larger amount of KH550; for the nanocomposites with a relatively high filler content, the $\varepsilon_r$ of nanocomposites was obviously increased with a small amount of KH550, and sharply decreased with the a larger amount of KH550. Regarding the dielectric loss, one can find that the BT-VC91 with KH550 exhibits a higher $\tan \delta$ than BT-VC91 without KH550, as shown in figures 5(c) and (d) for the $\tan \delta$ of nanocomposites at low (1 kHz) and high (100 kHz) frequencies, respectively. The difference between the dielectric properties of nanocomposites with low and high filler contents can be attributed to the mass of KH550 added in BT-VC91, which is largely different because the amount discussed here is actually defined as the mass ratio of KH550 coated to BT fillers. The decreased $\varepsilon_r$ and increased $\tan \delta$ of nanocomposites with a relatively high amount of coupling agent are consistent with the results from VC91 polymer with KH550, which was due to the formation of blends with a low $\varepsilon_r$, as discussed. For the nanocomposites with a relatively low amount of coupling agent, the increase in $\varepsilon_r$ is due to the improvement of ceramic-polymer wettability and possibly percolation generated by a low concentration of coupling agent addition [6, 10, 31]. As a result of the coupling agent effect on the dielectric properties, the maximal $\varepsilon_r$ of nanocomposites with the relative high filler contents were found when BT fillers
was coated with a small amount of KH550. For example, the $\varepsilon_r$ of 30BT-VC91 with 2 wt% KH550 is 51 at 1 kHz, which is much larger than that of 30BT-VC91 (about 40) without KH550.

The breakdown strength of BT-VC91 nanocomposites with different filler content and amount of coupling agent are shown in figure 6. The $E_b$ of nanocomposites decreased with increasing volume fraction of BT, which could be attributed to the low $E_b$ of BT fillers and defects introduced by ceramic fillers. From the $E_b$ versus coupling agent amount as shown in figure 6(a), it is clear that the maximal $E_b$ was obtained when using BT fillers coated with 2 wt% of KH550. For the BT-VC91 with a higher amount of coupling agent, the $E_b$ decreased with increasing amount of KH550 addition, which is consistent with the results from pure VC91 polymers. From the $E_b$ versus filler content as shown in figure 6(b), it could also be found that for the BT-VC91 with a small amount of KH550, the decrease ratio of $E_b$ with increasing volume fraction of BT was much smaller than that of the BT-VC91 nanocomposites without coupling agent reported previously. For example, it was reported that the $E_b$ decreased from about 400 MV m$^{-1}$ for pure VC91 film to about 150 MV m$^{-1}$ for 30BT-VC91 nanocomposite film [38]. In this work, the $E_b$ of pure VC91 film was about 280 MV m$^{-1}$, while the $E_b$ was still higher than 200 MV m$^{-1}$ for the 30BT-VC91 nanocomposites with 2 wt% of KH550.

In a word, the BT-VC91 nanocomposite with a small amount of KH550 is showing an enhanced $\varepsilon_r$, while no significant increase in its dielectric loss was found. Therefore, the energy densities of these nanocomposites under the same electric field could be improved; in addition, the enhanced $E_b$ of these nanocomposites lead to higher maximal energy densities. The P-E hysteresis loops of BT-VC91 with 1 wt% and 2 wt% KH550 are shown in figure 7, their discharge energy densities were found to be much higher than that of BT-VC91 without KH550. For example, the $U_{\text{discharge}}$ of 5BT-VC91 with 2 wt% KH550 was about 2.7 J cm$^{-3}$ under 200 MV m$^{-1}$, while the $U_{\text{discharge}}$ of 5BT-VC91 without KH550 was about 2.4 J cm$^{-3}$ under 200 MV m$^{-1}$. Furthermore, as a result of the enhanced $E_b$, the $U_{\text{discharge}}$ of 5BT-VC91 with 2 wt% KH550 could be about 3.8 J cm$^{-3}$ under 240 MV m$^{-1}$.

The $P_{\text{max}}$, $\eta$, $U_{\text{charge}}$ and $U_{\text{discharge}}$ of BT-VC91 nanocomposites with different amount of KH550 were then calculated from their P–E loops. Here, the energy storage properties of 15BT-VC91 with different amount of KH550 are shown in figure 8 as an example because of their larger $U_{\text{discharge}}$ compare with other samples. As
discussed above, the small amounts of KH550 lead to the increase on the $\varepsilon_r$ of BT-VC91, while large amounts of KH550 lead to the decrease on the $\varepsilon_r$ of BT-VC91. However, it is clear that the $P_s$ and $U_{\text{charge}}$ of the 15BT-VC91 with different amount of KH550 increased with the applied electric field at a very similar slope as shown in figures 8(a) and (b). This may be due to the frequency of P-E loop testing is far less than the $\varepsilon_r$ testing frequency. From figure 8(c), it can be seen that the $\eta$ decreased with increasing applied electric filed, which was related to the loss under high electric filed; it was also found that the $\eta$ under same applied electric field was increased with a small amount KH550, especially for the 15BT-VC91 with 1 wt% KH550, as shown in figure 8(d). As a result, the $U_{\text{discharge}}$ of nanocomposites was also increased. Due to the high $\eta$ and enhanced $E_b$, a maximal $U_{\text{discharge}}$ of about 4.0 J cm$^{-3}$ under 240 MV m$^{-1}$ was obtained from the 15BT-VC91 nanocomposite with 1 wt% KH550, which is about 3 times of that for 15BT-VC91 without coupling agent.

In summary, the maximal energy storage density of BT-VC91 composites with different filler content and coupling agent amount were shown in figure 9. As expected, the dielectric properties and energy storage performances of BT-VC91 composites are strongly dependent on the amount of KH550 used in the fabrication process. In this work, it was experimentally verified that the dielectric constant and breakdown strength are maximized when a critical amount of coupling agent is coated on ceramic fillers. For the analysis of dielectric properties for composite systems reported previously, the critical amount is usually experimentally determined, and theoretically calculated from the surface coverage ratio of ceramic fillers [35, 36]. It was reported that for BT fine powders with about 700 nm in diameter, this critical amount of KH550 is 1 wt% [34]; for the BT fine powders with about 200 nm in diameter used in this work, the critical amount of KH550 is not more than 2 times of that for 700 nm powders, which is much smaller than the ratio of surface area between the two. Therefore, the critical amount of coupling agent in a composite system should be determined not only by the interfacial area between filler and matrix, but also by the effect of coupling agent on the properties of polymer matrix and intermolecular reaction of coupling agent itself.

By summarizing the chemical reactions reported previously, the properties of BT-VC91, and the microstructures of BT-VC91 obtained from this work, a schematic are presented in figure 10 for the relationship among coupling agent, ceramic fillers, and polymer matrix in the ceramic-polymer composites. Firstly, the bridge-linking action introduced by KH550 is shown in figure 10(a) as a schematic chemical reaction process. During the preparation of coated BT nanoparticles, the –OC$_2$H$_5$ group was transformed into –OH group due to
the hydrolysis of silane in water-ethanol [37]. The –OH of KH550 would react with the –OH of BT surface and the –NH₂ of KH550 would react with the -F of PVDF molecule, to improve the compatibility of the nanocomposites [34–37]. Therefore, the KH550 was grafted on the BT surface through chemical bond, as shown in figure 10(b). In general, one –OH of KH550 forms covalent bond with BT, and the other –OH groups on this KH550 molecule either have condensation reaction with –OH of other KH550 molecule or being free [37]. Simultaneously, it is possible to form hydrogen bonds on the surface of BT, and between KH550 molecules [37]. When the amount is very small, KH550 molecules are almost randomly grafted on the surface of BT, thus the bridge-linking effect is proportional to the KH550 amount; for the composites with a larger amount of KH550, the intermolecular reactions of KH550 lead to the inefficiency of KH550 molecules occupying the surface of BT, therefore the bridge-linking effect between BT and VC91 does not depend solely on the amount of KH550 [39].

Figure 9. The maximal energy storage density of BT-VC91 with different filler content and coupling agent amount.

Figure 10. Schematic of the effects of silane coupling agent KH550 for BT-VC91 composites: (a) chemical reaction of KH550 with both fillers and matrix, (b) action mechanisms of KH550 on the surface, (c) microstructure of the composites with different amount of KH550.
Additionally, the non-attached KH550 molecules in the system may exist in the composites, and forming blends with VC91, which would change the nature of matrix [35]. As a final result of the effect of these mechanisms, schematic image are presented in figure 10(c) for the microstructure of a composite system containing ceramic fillers, polymer matrix and different amount of coupling agent. For composites using uncoated fillers, there is no valid linking between filler and matrix; by coating the fillers with coupling agents, bridge-linking was established. When the amount is small, the molecules of coupling agent are acting mainly on the interface, which would effectively urge the transfer of the electrical polarization of fillers and matrix [32]; meanwhile, very few of molecules of coupling agent are dispersed in the polymer matrix, forming blends with polymer matrix and increase the breakdown strength of composites. When the amount is large, the effect of coupling agent is constrained by its intermolecular reactions, thus the further increase of the amount is mainly results in more non-attached coupling agent molecules, which cause the aggregation of fillers, and the decrease of dielectric constant of the composite.

4. Conclusions

The effect of commercial coupling agent on the microstructure and dielectric properties of ceramic-polymer nanocomposites are studied by using VC91 as polymer matrix, BT nanoparticles as fillers, and KH550 as coupling agent. A simple process is developed to fabricate flexible and free-standing BT-VC91 nanocomposites as dielectric and energy-storage materials, in which the good wettability between coupling agent coated ceramic fillers and polymer matrix was obtained. From the study on VC91 polymer containing different amounts of KH550, it was verified that the polymer blends was formed during the solution-casting process, and the VC91-KH550 blends have a lower $\varepsilon_r$ and a higher $E_b$ than the pure polymer matrix. It is found that the surface modification of fillers can significantly improve the $E_b$ and $\varepsilon_r$ of the nanocomposites when a small amount of coupling agent was used due to the bridge-linking between fillers and matrix. A maximal $U_{\text{discharge}}$ of about 4.0 J cm$^{-3}$ under 240 MV m$^{-1}$ was obtained from the 15BT-VC91 nanocomposite with 1 wt% KH550, which is about 3 times of that for 15BT-VC91 without coupling agent. For the nanocomposites with a relatively large amount of coupling agent, a lower $\varepsilon_r$ and a higher tan$\delta$ was observed in the BT-VC91 nanocomposites due to the fact that a part of coupling agent did not attached to the surface of fillers and change the nature of matrix. The existence of massive molecules of coupling agent in composite system would also leads to the fillers aggregation, which lead to significantly reduced $E_b$ of nanocomposites.

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References

[1] Lines M E and Glass A M 2001 Principles and Applications of Ferroelectrics and Related Materials (Oxford: Oxford University Press)
[2] Nalwa H S 1999 Handbook of low and high dielectric permittivity materials and their applications, phenomena, properties and applications (San Diego, CA: Academic)
[3] Kao K C 2004 Dielectric Phenomena in Solids (New York: Academic)
[4] Barsoum M and Barsoum M W 2002 Fundamentals of ceramics (United States of America: CRC press)
[5] Jafic B 2012 Piezoelectric Ceramics (Amsterdam: Elsevier)
[6] Zhang L and Cheng Z Y 2011 Development of polymer-based 0–3 composites with high dielectric constant J. Adv. Dielectr. 1 389–406
[7] Cheng Z and Zhang Q 2008 Field-activated electroactive polymers MRS Bull. 33 183–7
[8] Zhang M, Zhang L, Zhu M, Wang Y, Li N, Zhang Z, Chen Q, An L, Lin Y and Nan C 2016 Controlled functionalization of poly(4-methyl-1-pentene) films for high energy storage applications J. Mater. Chem. A 4 1797–807
[9] Zhang L, Lu X, Zhang X, Jin L, Xu Z and Cheng Z Y 2018 All-organic dielectric nanocomposites using conducting polypyrrole nanoclips as filler Compos. Sci. Technol. 167 285–93
[10] Liao X, Ye W, Chen L, Jiang S, Wang G, Zhang L and Hou H 2017 Flexible hdc-δ reinforced polyimide composites with high dielectric permittivity Compos. Part A 101 50–8
[11] Xu W, Ding Y, Yu Y, Jiang S, Chen L and Hou H 2017 Highly foldable panipcnts/pu dielectric composites toward thin-film capacitor application Mater. Lett. 192 25–8
[12] Zhang L, Liu Z, Lu X, Yang G, Zhang X and Cheng Z Y 2016 Nano-clip based composites with a low percolation threshold and high dielectric constant Nano Energy. 26 550–7
Zhou S, Zhou G, Jiang S, Fan P and Hou H 2017 Flexible and refractory tantalum carbide–carbon electrospun nanofibers with high modulus and electric conductivity Mater. Lett. 200 97–100
Zhang L, Du W, Nautiyal A, Liu Z and Zhang X 2018 Recent progress on nanostructured conducting polymers and composites: synthesis, application and future aspects Sci. China Mater. 61 303
Xie Y, Yu Y, Feng Y, Jiang W and Zhang Z 2017 Fabrication of stretchable nanocomposites with high energy density and low loss from cross-linked PVDF filled with poly(dopamine) encapsulated BaTiO3 ACS Appl. Mater. Inter. 9 2995–3005
Wu P, Zhang M, Wang H, Tang H, Bass P and Zhang L 2017 Effect of coupling agents on the dielectric properties and energy storage of Ba0.6Sr0.4TiO3/ PVDF–CTFE nanocomposites AIP Adv. 7 075310
Zhang L, Shan X, Bass P, Tong Y, Rolin T D, Hill C W, Brewer J C, Tucker D S and Cheng Z Y 2016 Process and microstructure to achieve ultra-high dielectric constant in ceramic–polymer composites Sci. Rep. 6 35763
Lu X, Tong Y and Cheng Z Y 2019 Fabrication and characterization of free-standing, flexible and translucent BaTiO3–P (VDF–CTFE) nanocomposite films J. Alloys Compd. 770 327–32
Goyal R K, Katakade S S and Mule D M 2013 Dielectric, mechanical and thermal properties of polymer/BaTiO3 composites for embedded capacitor Compos. Part B 44 32–32
Pan Z, Yao L, Zhai J, Liu S, Yang K, Wang H and Liu J 2016 Fast discharge and high energy density of nanocomposite capacitors using Ba0.6Sr0.4TiO3 nanofillers Ceram. Int. 42 14667–74
Hu G, Gao F, Kong J, Yang S, Zhang Q, Liu Z, Zhang Y and Sun H 2015 Preparation and dielectric properties of Poly(vinylidene fluoride)/Ba0.6Sr0.4TiO3 composites J. Alloys Compd. 619 686–92
Chen Y, Chan H L W and Choy C L 1998 Nanocrystalline lead titinate and lead titanate/vinylidene fluoride–trifluoroethylene 0–3 nanocomposites J. Am. Ceram. Soc. 81 1231–6
Singh P, Borkar H, Singh B P, Singh V N and Kumar A 2014 Ferroelectric polymer–ceramic composite thick films for energy storage applications AIP Adv. 4 088717
Dang Z, Yuan J, Zha J, Zhou T, Li S and Hu G 2012 Fundamentals, processes and applications of high-permittivity polymer–matrix composites Prog. Mater. Sci. 57 660–723
Arbatti M, Shan X B and Cheng Z Y 2007 Ceramic–Polymer composites with high dielectric constant Adv. Mater. 19 1369–72
Fan B, Liu Y, He D and Bai J 2018 Achieving polydimethylsiloxane/carbon nanotube (PDMS/CNT) composites with extremely low dielectric loss and adjustable dielectric constant by sandwich structure Appl. Phys. Lett. 112 052902
Liao S, Shen Z, Pan H, Zhang X, Shen Y, Lin Y H and Nan C W 2017 A surface-modified TiO2 nanorod array/P (VDF–HFP) dielectric capacitor with ultra high energy density and efficiency J. Mater. Chem. C 5 12777–84
Mittal K I 2004 Silanes and Other Coupling Agents 3 (Boca Raton, FL: CRC Press)
Zhang X, Li B W, Dong L, Liu H, Chen W, Shen Y and Nan C W 2018 Superior energy storage performances of polymer nanocomposites via modification of filler/polymer interfaces Advanced Materials Interfaces 5 1800096
Yeh J M, Weng C J, Huang K Y, Huang H Y, Yu Y H and Yin C H 2004 Thermal and optical properties of PMMA–titania hybrid materials prepared by sol–gel approach with HEMA as coupling agent J. Appl. Polym. Sci. 94 400–5
Yang C, Song H S and Liu D B 2013 Effect of coupling agents on the dielectric properties of CaCu3Ti4O12–PVDF composites Compos. Part B 50 180–6
Jijima M, Sato N, Lenggoro I W and Kamiya H 2009 Surface modification of BaTiO3 particles by silane coupling agents in different solvents and their effect on dielectric properties of BaTiO3/epoxy composites Colloid. Surfaces A 352 88–93
Zhang Q, Gao F, Zhang C, Wang L, Wang M, Qin M, Hu G and Kong J 2016 Enhanced dielectric tunability of Ba0.6Sr0.4TiO3/poly (vinylidene fluoride) composites via interface modification by silane coupling agent Compos. Sci. Technol. 129 93–100
Dang Z M, Wang H Y and Xu H P 2006 Influence of silane coupling agent on morphology and dielectric property in BaTiO3/polyvinylidene fluoride composites Appl. Phys. Lett. 89 112902
Tong Y, Zhang L, Bass P, Rolin T D and Cheng Z Y 2018 Influence of silane coupling agent on microstructure and properties of CCTO-P(VDF–CTFE) composites J. Adv. Dielectr. 8 1850008
Shan X 2009 High dielectric constant 0–3 ceramic–polymer composites Auburn University
Wei B, Chang Q, Rao C, Dai L, Zhang G and Wu F 2013 Surface modification of filter medium particles with silane coupling agent KHS930 Colloid. Surfaces A 434 276–80
Wen F, Xu Z, Xia W, Wei X and Zhang Z 2013 High energy density nanocomposites based on poly(vinylidene fluoride–chlorotrifluoroethylene) and barium titanate Polym. Eng. Sci. 53 897–904
Sideridou I D and Karabela M M 2009 Effect of the amount of 3-methacryloxypropyltrimethoxysilane coupling agent on physical properties of dental resin nanocomposites Dent. Mater. 25 1315–24