Influence of silane coupling agent on microstructure and properties of CCTO-P(VDF-CTFE) composites*

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Received 1 February 2018; Revised 7 March 2018; Accepted 8 March 2018; Published 16 April 2018

Influence of the coupling agent on microstructure and dielectric properties of ceramic–polymer composites is systematically studied using $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) as the filler, trichloro-(1H,1H,2H,2H-perfluorooctyl)-silane (Cl_3 -silane) as coupling agent, and P(VDF-CTFE) 88/12 mol.% copolymer as the matrix. It is demonstrated that Cl_3 -silane molecules can be attached onto CCTO surface using a simple process. The experimental results show that coating CCTO with Cl_3 -silane can improve the microstructure uniformity of the composites due to the good wettability between Cl_3 -silane and P(VDF-CTFE), which also significantly improves the electric breakdown field of the composites. It is found that the composites using CCTO coated with 1.0 wt.% Cl_3 -silane exhibit a higher dielectric constant with a higher electric breakdown field. For the composites with 15 vol.% CCTO that is coated with 1.0 wt.% Cl_3 -silane, an electric breakdown field of more than 240 MV/m is obtained with an energy density of more than 4.5 J/cm³. It is also experimentally found that the dielectric constant can be used to easily identify the optimized content of coupling agent.

Keywords: Ceramic–polymer; energy density; CCTO; coupling agent; breakdown strength.

1. Introduction

Dielectric materials are essential for electronic circuits, devices and systems, in which the dielectrics serve for three primary functions: insulation, capacitor, and energy storage.^{1–3} For all these applications, a dielectric with a high electrical breakdown field (E_b) is required. For some of these applications, dielectrics with a high relative dielectric permittivity (i.e., dielectric constant) (ϵ_r) are also critical. Therefore, it is interesting to develop dielectrics with a high E_b and a large ϵ_r . In general, the inorganic materials, especially polar materials such as ferroelectric BaTiO_3 , exhibit a larger ϵ_r (up to 10⁴), but a lower E_b (about 10⁰ MV/m),^{4,5} while the organic materials such as polymers exhibit a higher E_b ($\sim 10^2$ MV/m) with a small ϵ_r (mostly less than 5).^{4,6} Therefore, it is interesting to develop dielectric composites, which combine the properties of each constituent, so that the dielectrics with a relatively high E_b and a large ϵ_r can be obtained.^{4,7–11} The property of a composite is strongly dependent on its structure.^{12,13} The widely studied dielectric composites are so-called 0–3 composites, in which a dielectric matrix is filled with isolated particles.^{4,12,13} To achieve a higher E_b in the composites, the dielectric matrix used in the 0–3 composites is usually the dielectrics with a high E_b . To achieve a large ϵ_r in the composites, the filler particles are

either conductor or dielectric with a large ϵ_r .^{4,10,11} It should be mentioned that the flexibility of a dielectric is also very critical for many applications like the wearable electronics. Thus, flexible polymers are widely used as the matrix in the development of 0–3 dielectric composites (i.e., polymer-based 0–3 composites).⁶ Among the polymer matrix used in the polymer-based 0–3 composites, polar polymers, such as PVDF, P(VDF-TrFE) and P(VDF-CTFE) attracted the most attention since they exhibit a higher ϵ_r (~ 10) than nonpolar polymers (< 5).⁶ Regarding the filler, besides ferroelectrics,^{14–20} some nonpolar ceramics, such as $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO),^{21–24} have been used due to the fact that these ceramics exhibit a giant ϵ_r with a weak temperature dependence.^{25,26} The composites using CCTO as filler exhibit some unique advantages, such as larger ϵ_r , weak temperature dependence.

For a composite, it is important to achieve a uniform microstructure.²⁷ The properties of a composite with a non-uniform microstructure will change from piece to piece and be dependent on both the size and thickness of the composite sample.²⁷ Unfortunately, due to the poor wettability between the polymer matrix and inorganic filler particles, the polymer-based 0–3 composites prepared using a solution cast process, which is the most widely used process, usually have a non-uniform microstructure.²¹ Therefore, different approaches

*Selected paper from The International Workshop on Advanced Dielectric Materials and Their Applications, Xi'an, China, Oct. 8–11, 2017.

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have been investigated to improve the microstructure uniformity of the polymer-based 0–3 composites. In one approach, a hot-press process with a unique configuration of the solution case composite films was introduced.^{23,24,27,28} It is experimentally found that the microstructure uniformity of the solution case composites can be significantly improved by using the hot-press process. Interestingly, it is also experimentally found that the composites with a uniform microstructure exhibit a higher ϵ_r and a lower dielectric loss than the as-cast composites that have a nonuniform microstructure.^{24,28} It should be mentioned that the hot-press process is not desirable for many applications. Additionally, even the uniformity is improved by the hot-press, the hot-press does not change the surface chemistry of the filler, which results in a lower E_b in the composites. Other approaches to improve the microstructure uniformity of the composites are based on the surface chemistry, which intends to improve the wettability between the polymer matrix and ceramic filler particles.²⁹ Coupling agents like NXT-105, HEMA, and silane have been studied to improve the wettability between the polymer and ceramic particles.^{30–34} For example, different silane coupling agents have been used to modify the surface of BaTiO_3 ^{31,33} and $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ ³⁴ for the composites using PVDF and epoxy as matrix. Therefore, silane coupling agents are recognized as efficient coupling agents for polymer–ceramic composites. Certainly, the effectiveness of a coupling agent for a composite system is dependent on the chemical nature of the matrix and filler. Therefore, it is interesting to determine the effectiveness of silane coupling agent on the modification of CCTO surface since the composites using CCTO as filler exhibit a high ϵ_r .

Here, CCTO-P(VDF-CTFE) composite system was used to systemically study the influence of a silane coupling agent, trichloro-(1H,1H,2H,2H-perfluorooctyl)-silane (Cl_3 -silane), on the microstructure and properties of polymer-based 0–3 composites. It is experimentally found that Cl_3 -silane has a good wettability with P(VDF-CTFE) and can be easily attached onto CCTO surface so that the CCTO-P(VDF-CTFE) composites with a uniform microstructure can be easily prepared. It is also demonstrated that coating Cl_3 -silane onto the surface of CCTO particles can significantly improve the E_b of the composites and that Cl_3 -silane has a complicated influence on the ϵ_r of the composites.

2. Experiments

2.1. Preparation of CCTO-P(VDF-CTFE) composites

For the polymer matrix, P(VDF-CTFE) 88/12 mol.% copolymer from Solvay was used. The CCTO ceramics were first prepared using conversional process as described in Ref. 35. The CCTO particles were fabricated from the CCTO ceramics using a high-energy ball milling process, which resulted in the CCTO particles with an average size less than $1\ \mu\text{m}$ Ref. 23. The coupling agent, Cl_3 -silane, from Sigma-Aldrich

was used as received. The CCTO-P(VDF-CTFE) composites with different CCTO contents (5, 10, 15, 20, 25, 30 vol.%) were prepared using solution cast process. The composites with/without coupling agents were studied for comparison.

For the composite preparation, P(VDF-CTFE) copolymer was first prepared by dissolving 0.3 grams P(VDF-CTFE) in 10 ml N,N dimethylformamide (DMF) at room temperature using a magnetic stirring for 12 h. Then, the CCTO particles were added into the P(VDF-CTFE) solution and ultra-sonicated for 1 h and immediately followed with 12 h stirring to form a homogeneous suspension. Finally, the suspension was casted on a glass substrate, which was pre-heated at 70°C , for 8 h. The as-cast films were released from the glass substrate and, then, the free-standing as-cast films were annealed at 160°C for 12 h. The final composite films prepared by this process have a thickness of about $10\text{--}20\ \mu\text{m}$. These composite films were used in the morphology and property studies.

Two types of CCTO particles were used in the preparation of CCTO-P(VDF-CTFE) composites mentioned above. One is the CCTO as obtained from the ball milling process (i.e., uncoated CCTO). The other is the CCTO coated with Cl_3 -silane. To coat Cl_3 -silane onto CCTO particles, a solution of Cl_3 -silane in water-ethanol (95 wt.% ethanol) was first prepared at room temperature. The solution contains 1 wt.% of Cl_3 -silane. The CCTO particles were placed into the Cl_3 -silane solution and, then, immediately ultrasonicated for 30 min to prepare the CCTO – Cl_3 -silane mixture. Finally, the mixture was heated to 80°C for 12 h to get dried CCTO particle. The dried CCTO particles were used as the Cl_3 -silane-coated CCTO particles for the CCTO-P(VDF-CTFE) composite preparation. In the process, the weights of Cl_3 -silane and CCTO particles were measured to get Cl_3 -silane coated CCTO particles with 0.5, 1.0, 1.5, 2.0, 3.0 wt.% of Cl_3 -silane.

To determine the influence of the coupling agent on the dielectric properties of the polymer matrix, the P(VDF-CTFE) – Cl_3 -silane blends with different contents (0.2, 0.4, 0.6, 0.8, 1.0 wt.%) of Cl_3 -silane were prepared using solution cast process. In the preparation, the P(VDF-CTFE) solution was first prepared by dissolving 0.3 g P(VDF-CTFE) in 10 ml DMF at room temperature using a magnetic stirring for 12 h. At the same time, a suspension containing 1 wt.% of Cl_3 -silane in DMF was prepared. Then, the Cl_3 -silane suspension was added to the P(VDF-CTFE) solution and ultra-sonicated for 1 h and immediately followed with 12 h stirring to form a homogeneous solution. Finally, the suspension was casted on a glass substrate at 70°C , for 8 h. Then, the as-cast films were annealed at 160°C for 12 h.

2.2. Characterization and measurement

The morphology and uniformity of composite films were examined using Scanning Electron Microscopy (SEM) — JEOL JSM 7000F FE-SEM. For the study of electrical and dielectric properties, gold electrodes in a diameter of 3.0 mm were sputtered on both sides of the films to make a parallel

plate capacitor. An Agilent 4294A impedance analyzer was used to characterize the dielectric properties at frequencies from 100 Hz to 1 MHz by using the Cp-D function. A Precision-LC100 Ferroelectric Tester with a High Voltage Supplier/Amplifier was used to determine the E_b and P-E loop of composite samples. For the test of mechanical properties, the composite films were cut to rectangles with a size of 20 mm × 10 mm. The rectangular films were then used in a tensile test by an Instron 3300 testing system. The test was done at room temperature.

3. Results and Discussion

The effectiveness of Cl_3 -silane coating on the CCTO was first examined by the stability of the CCTO suspension in the solution of P(VDF-CTFE) in DMF. The suspension of CCTO in P(VDF-CTFE) solution, which were designed to prepare the CCTO-P(VDF-CTFE) composites with 15 vol.% CCTO, is shown in Fig. 1, where the picture on the left is the suspension of CCTO coated with 1.0 wt.% Cl_3 -silane, while the picture on right is the suspension of uncoated CCTO. The pictures shown in Fig. 1(a) are the suspensions right after the

preparation, which were usually used for the solution cast process as mentioned in Experimental Section. Clearly, two suspensions have different colors, which indicate the existence of Cl_3 -silane in the suspension. In other words, the Cl_3 -silane was not lost during the process of drying CCTO — Cl_3 -silane mixture at 80°C. The pictures shown in Fig. 1(b) are the suspensions after stored at room temperature for 48 h. Clearly, the suspension of Cl_3 -silane-coated CCTO particles shows much better stability than the suspension of uncoated CCTO. For example, the suspension of Cl_3 -silane-coated CCTO does not show a clear separation (left, Fig. 1(b)), while the suspension of uncoated CCTO shows a clear separation (right, Fig. 1(b)). The results indicate that the process reported here indeed results in a chemical attachment of Cl_3 -silane molecules onto the surface of CCTO.

To further determine the influence of the Cl_3 -silane coating, the composites with 15 and 20 vol.% of CCTO using both coated and uncoated CCTO were examined. First of all, the SEM observation demonstrates that the Cl_3 -silane-coated CCTO particles have a better/stronger connection with the polymer matrix. As shown in Fig. 2, where the SEM images were taken from the cross-section of the composites with 15 vol.% CCTO, the Cl_3 -silane coating has a strong influence on the interaction between the CCTO particles and polymer matrix. For example, the surface of uncoated CCTO in the composites is clear, while the surface of Cl_3 -silane-coated CCTO in the composites is not clear. For the coated CCTO, the influence of the Cl_3 -silane content is also observed. For the CCTO with 0.5 wt.% Cl_3 -silane, the CCTO surface is not clear, but can be recognized. For the CCTO with higher Cl_3 -silane content, it is hard to recognize the CCTO surface. That is, there is a good wettability between the Cl_3 -silane and P(VDF-CTFE). The results also confirm that the Cl_3 -silane molecules were attached onto CCTO surface.

As a brief summary of above results, schematic pictures are presented in Fig. 3 for the relationship/microstructure among Cl_3 -silane, CCTO, and P(VDF-CTFE) in the composites. For the composites using uncoated CCTO, a clear interface between CCTO and matrix exists as shown in Fig. 3(a). However, for the composites using Cl_3 -silane-coated CCTO, both the stability observation of the CCTO suspension in P(VDF-CTFE) solution and the SEM observation of CCTO surface in the composites indicate: (1) the process reported here can chemically attach the Cl_3 -silane molecules onto CCTO surface, and (2) the Cl_3 -silane molecules have a good wettability with P(VDF-CTFE). Additionally, the ratio of Cl_3 -silane to CCTO used in the process is important. It is expected there is a critical ratio for this. Below this critical ratio, the surface of CCTO is partially coated with Cl_3 -silane as shown in Fig. 3(b). At this critical ratio, the coverage of CCTO surface reaches its maximum, at which a layer of Cl_3 -silane is formed on the surface of CCTO as shown in Fig. 3(c). Above this critical ratio, the surface coverage of CCTO with Cl_3 -silane does not change. Thus, further increase in the ratio only results in nonattached Cl_3 -

Fig. 1. Suspension of CCTO in P(VDF-CTFE)/DMF solution that is designed to prepare CCTO-P(VDF-CTFE) composites with 15 vol.% of CCTO: (a) right after preparation (i.e., stirring); (b) after being stored at room temperature for 48 h. Left: the CCTO was coated with 1.0 wt.% Cl_3 -silane; right: uncoated CCTO.

Fig. 2. SEM images of cross section of composites with 15 vol.% CCTO: (a) and (b) using uncoated CCTO; (c)–(f) using CCTO coated with 0.5, 1.0, 2.0, 3.0 wt.% of Cl_3 -silane, respectively.

silane molecules (i.e., individual Cl_3 -silane molecules) in the system as shown in Fig. 3(d). It should be mentioned that even the ratio of Cl_3 -silane to CCTO is below the critical ratio the individual Cl_3 -silane may exist in the composites as shown in Figs. 3(b) and 3(c). As will be discussed below, this is actually the case for the composites studied here. Due to the good wettability between Cl_3 -silane and P(VDF-CTFE), one would expect the formation of a polymer blend of P(VDF-CTFE) and Cl_3 -silane, which would change the nature of the polymer matrix in the 0–3 composites.

To determine the influence of Cl_3 -silane coating on the properties, the dielectric properties of the composites with 15

and 20 vol.% of CCTO coated with different amounts of Cl_3 -silane are shown in Fig. 4, where the normalized ϵ_r and dielectric loss ($\tan\delta$) at frequencies from 100 Hz to 1 MHz are presented for the composites at room temperature. The ϵ_r is normalized using the ϵ_r at 1 kHz of the composites with uncoated CCTO. That is, the measured ϵ_r is divided by the ϵ_r at 1 kHz obtained in the composites using uncoated CCTO. Thus, a normalized ϵ_r of 0.95 means that the ϵ_r of the composite is 0.95 times of the ϵ_r obtained in the composites using uncoated CCTO.

The $\tan\delta$ data shown in Fig. 4 indicates that all composites have a low loss at low frequencies and that the loss increases

Fig. 3. Schematic microstructure of the composites of CCTO, P(VDF-CTFE), and Cl_3 -silane: (a) no Cl_3 -silane; (b) the ratio of Cl_3 -silane to CCTO is lower than the critical ratio; (c) the ratio of Cl_3 -silane to CCTO is the critical ratio; (d) the ratio of Cl_3 -silane to CCTO is high.

with increasing frequency. The frequency dependence of the loss is similar for all composites and also similar to what is observed in the polymer matrix. That is, the $\tan\delta$ observed in the composites is mainly determined by the polymer matrix. However, a small increase in the loss with the Cl_3 -silane is observed, especially at high frequencies. This phenomenon is further illustrated by the losses at 1 kHz and 100 kHz versus the Cl_3 -silane content shown in the insert figure in Figs. 4(b) and 4(d).

Regarding the dielectric constant, one can find that the ϵ_r decreases with increasing Cl_3 -silane content when the Cl_3 -silane content is high (> 1.0 wt.%). However, when the Cl_3 -silane content is small, the ϵ_r does not follow the trend observed at high Cl_3 -silane content that is represented using dotted line in the insert figure in Figs. 4(a) and 4(c), where the ϵ_r at 1 kHz and 100 kHz versus the Cl_3 -silane content is plotted. In other words, when the Cl_3 -silane content is small, the ϵ_r is not strongly dependent on the Cl_3 -silane as it is in the composites with high Cl_3 -silane content. Interestingly, it is

found that the ϵ_r can even increase slightly with increasing Cl_3 -silane content when the content of Cl_3 -silane is small.

The results shown in Fig. 4 reflect that the contribution of the Cl_3 -silane on the dielectric properties is strongly dependent on its content. The content of Cl_3 -silane can be simply classified into two regions: (1) high (> 1.0 wt.% of Cl_3 -silane), and (2) low. The dielectric behavior shown in Fig. 4 reflects the change in the microstructure of the composites with the Cl_3 -silane content illustrated in Fig. 3. That is, when the Cl_3 -silane content (i.e., high content) is above the critical ratio, the increase in the Cl_3 -silane content only results in the increase in the individual Cl_3 -silane molecules in the composites, but does not change the surface coverage of the CCTO particles; when the Cl_3 -silane content (i.e., low content) is less than the critical ratio, the increase in the Cl_3 -silane content increases the coverage of CCTO surface with Cl_3 -silane.

For the composites using CCTO with a high Cl_3 -silane content, the composites can be simplified as a matrix filled

Fig. 4. The normalized dielectric constant and dielectric loss of the composites using Cl_3 -silane coated CCTO with different ratios: (a) and (b) composites with 15 vol.% CCTO; (c) and (d) composites with 20 vol.% CCTO. The dielectric constant is normalized using the dielectric constant at 1 kHz of the composites using uncoated CCTO.

with particles having a core-shell structure as shown in Fig. 3(d), in which the polymer matrix is actually the polymer blend of the individual Cl_3 -silane molecules and P(VDF-CTFE), while the core and shell of the core-shell particles are CCTO and Cl_3 -silane molecule layer coated on CCTO surface, respectively. When the Cl_3 -silane content increases, the particle with core-shell structure does not change, what changes is the polymer blend of Cl_3 -silane and P(VDF-CTFE). The Cl_3 -silane has a low dielectric constant than P(VDF-CTFE). Thus, the blend should have a dielectric constant lower than P(VDF-CTFE) and the dielectric constant of the blend decreases with increasing Cl_3 -silane content. In other words, for the composites with the same CCTO content but using CCTO with different Cl_3 -silane content, the ϵ_r and concentration of the filler particle (i.e., core-shell structure particle) does not change, but the ϵ_r of the matrix (i.e., polymer blend) decreases, with increasing Cl_3 -silane content. Thus, the ϵ_r of the composites should decrease with increasing Cl_3 -silane content. This is exactly what is observed in Fig. 4. In this case (high Cl_3 -silane content), for the composites using CCTO particles with the same Cl_3 -silane ratio, the composites with a higher CCTO content mean more individual Cl_3 -silane molecules in the composites. Thus, the decrease in the ϵ_r in the composite with a higher CCTO content would be bigger. This is exactly what is observed in Fig. 4. For example, when the CCTO with 2.0 wt.% Cl_3 -

silane is used, the normalized ϵ_r at 1 and 100 kHz is about 0.691 and 0.592, respectively, for the composites with 20 vol.% CCTO, while it is about 0.878 and 0.727 for the composites with 15 vol.% CCTO (see insert figure in Figs. 4(a) and 4(c)). Therefore, for the composites with different CCTO contents, the curvature of the ϵ_r versus coupling agent curves is different. This is, again, exactly what is observed in Figs. 4(a) and 4(c).

When the content of Cl_3 -silane is low, the change in the ratio of Cl_3 -silane to CCTO would result in a change on the coverage of CCTO surface with Cl_3 -silane. In other words, the average coverage of CCTO surface with Cl_3 -silane increases with increasing Cl_3 -silane content. However, the coverage of the CCTO surface may not be uniform since the surface of CCTO is only partially covered with Cl_3 -silane. For example, there may be some CCTO particles covered with more Cl_3 -silane molecules than others and for a particular CCTO particle Cl_3 -silane molecules may not be uniformly distributed on the CCTO surface as shown in Fig. 3(b). This nonuniform coating will result in a low repeatability in the properties and microstructure of the composites. Therefore, a very complicated dependence of the ϵ_r on the Cl_3 -silane content can be observed in the composites, which is exactly what is observed in the composites with low Cl_3 -silane content as shown in Figs. 4(a) and 4(c). That is, when the Cl_3 -silane content is small, the dependence of the ϵ_r

on the Cl_3 -silane content is different from one to another. When the Cl_3 -silane content reaches the critical value, the CCTO surface is fully covered with Cl_3 -silane. In this case, each CCTO particle is actually a particle with a core-shell structure as shown in Fig. 3(c). Regarding the dielectric response, a composite using core-shell particle can be treated as a regular 0-3 composite with filler particles that have an effective dielectric property of the core-shell particles. Due to the fact that Cl_3 -silane has a lower ϵ_r than P(VDF-CTFE) and a much lower ϵ_r than CCTO, the core-shell particles would have a low effective ϵ_r , which would make the composites have a low ϵ_r . However, if the dielectric loss is considered and there is a big difference in the loss between the shell and core, a higher effective ϵ_r can be obtained for the core-shell particles as discussed in Ref. 37. This explains the ϵ_r versus coupling agent curve at low coupling agent content (Figs. 4(b) and 4(d)), where some increase in the ϵ_r with increasing Cl_3 -silane content is observed. Based on this, it would also be easy to understand the change in the dielectric loss observed in the composites. As discussed above, when the Cl_3 -silane content is high, the matrix is the blend of P(VDF-CTFE) with Cl_3 -silane. Due to the high loss of the Cl_3 -silane, the blend will have a higher loss than P(VDF-CTFE), which makes the composites using coated CCTO exhibit a high loss than the composites using uncoated CCTO.

To confirm the formation of polymer blend between the polymer matrix and the coupling agent and to determine the dielectric constant of the blend, a series of blends with Cl_3 -silane up to 1.0 wt.% was prepared and characterized. The results are shown in Fig. 5, where the normalized dielectric constant at 1 kHz versus the content of Cl_3 -silane is plotted for the blends at room temperature. Clearly, the dielectric constant of the blends decreases with increasing Cl_3 -silane content. That is, if the blend between the polymer matrix and coupling agent is formed, the matrix will have a lower dielectric constant. This supports the argument above.

To confirm the binding of the Cl_3 -silane onto CCTO, the mechanical test of composites with different contents of

Fig. 5. The normalized dielectric constant of the pure P(VDF-CTFE) with different weight percentage of Cl_3 -silane.

Fig. 6. Tensile strain (%) versus tensile stress (MPa) for the P(VDF-CTFE) and CCTO-P(VDF-CTFE) composites with different content of coupling agent.

CCTO and Cl_3 -silane were performed. As shown in Fig. 6, where the relationship between the tensile stress and tensile strain for the composites at room temperature is presented, the elastic modulus of all the composites including pure polymer matrix is almost the same. However, the composites using uncoated CCTO exhibit a lower yield stress and a lower breakdown strain. When the coupling agent is used, both the yield stress and breakdown strain increase. The results here indicate that there is a good connection (i.e., good wettability) between the polymer matrix and filler particles.

Based on above discussion and the dielectric properties shown in Fig. 4, one would conclude that the critical ratio of Cl_3 -silane to CCTO is about 1.0 wt.% of Cl_3 -silane for the CCTO particle used here. However, based on the chemical structure of Cl_3 -silane and the size of CCTO particle, it is estimated that if all Cl_3 -silane molecules are attached to the CCTO surface, the amount of Cl_3 -silane required to fully cover the CCTO surface would be 0.1–0.2 wt.% of Cl_3 -silane. In other words, even Cl_3 -silane molecules can be attached to the CCTO surface using the process, there is still room to improve the efficiency of Cl_3 -silane coating onto CCTO surface. Therefore, even for the composites using CCTO coated with Cl_3 -silane lower than the critical ratio, the individual Cl_3 -silane molecules still exist in the composites. This is the reason that individual Cl_3 -silane molecules are presented in Figs. 3(b) and 3(c).

Following the above results and discussion, the composites with different CCTO contents are studied using CCTO particles coated with 1.0 wt.% Cl_3 -silane. The ϵ_r of these composites at room temperature is shown in Fig. 7. As expected, the ϵ_r increases with increasing CCTO content. For the composites with 20 vol.% of CCTO, a dielectric constant of more than 20 is obtained at 100 Hz. The E_b of the composites is shown in Fig. 8, where the E_b obtained in the composites using uncoated CCTO is also presented

Fig. 7. Dielectric constant (ϵ_r) versus CCTO content for the composites using CCTO coated with 1 wt.% of Cl_3 -silane.

Fig. 8. Electric breakdown field (E_b) versus CCTO content for the composites using: (1) CCTO coated with 1 wt.% Cl_3 -silane and (2) uncoated CCTO.

for comparison. For the composites using uncoated CCTO, the E_b decreases with increasing filler content, which is consistent with the experimental results reported in other polymer-based 0–3 composites.^{16,36} Clearly, the composites using Cl_3 -silane-coated CCTO have a much higher E_b than the composites using uncoated CCTO, which is a direct result of the improvement in the connection or interface between the polymer matrix and filler particles. For example, for the composites with 15 vol.% of CCTO, the E_b of the composites using Cl_3 -silane-coated CCTO is more than three times higher than that of the composites using uncoated CCTO. More interestingly, the E_b of these composites increase initially with increasing CCTO content. The highest E_b (> 240 MV/m) is observed in the composites with 15 vol.% CCTO. In other words, as the CCTO content increases from 5 to 15 vol.%, both the ϵ_r and E_b of the composites increases, which results in a significant increase in the energy storage density. For example, the energy density of the composites

with 5 vol.% of CCTO is about 2.5 J/cm^3 , while that with 15 vol.% CCTO is more than 4.5 J/cm^3 .

Regarding the mechanisms of the enhancement in E_b , there could be multiple factors. As discussed above, both the good uniformity of the composites and the good wettability between the polymer matrix and filler particles certainly favors the higher E_b . The core-shell like structure of the coated CCTO is another reason since the Cl_3 -silane layer can block the current between the CCTO and polymer matrix. As mentioned above, there are Cl_3 -silane molecules in the polymer matrix. The blend of polymer matrix with coupling agent molecules, which exhibit a lower dielectric constant than the pure polymer matrix, serves as the real matrix. Therefore, the E_b of this blend is another possible reason behind the observed experimental results. If this is the major reason, one would expect that the E_b of the blend initially increases with increasing content of Cl_3 -silane in the polymer. This can be a new director in the future for the development of polymers with a higher E_b .

4. Conclusions

In conclusion, a simple process is developed to coat Cl_3 -silane molecules onto the surface of CCTO particle. A good wettability between Cl_3 -silane and CCTO was observed, which made the composites prepared using a simple solution cast having a uniform microstructure. It is speculated that the individual Cl_3 -silane molecules (i.e., the molecules that were not attached to the surface of CCTO) form a polymer blend with P(VDF-CTFE). Therefore, when the Cl_3 -silane content is high, a lower dielectric constant is observed in the composites due to the fact that the blend as the matrix has a lower dielectric constant than the pure polymer matrix. Coating Cl_3 -silane onto the surface of CCTO can significantly improve the electric breakdown field of the composites due to the good connection between the matrix and filler. It is concluded that the CCTO with 1.0 wt.% of Cl_3 -silane resulted in composites with a higher dielectric constant and a higher breakdown field. For a composite with 15 vol.% of CCTO that is coated with 1.0 wt.% of Cl_3 -silane, a breakdown field of more than 240 MV/m is obtained.

Acknowledgment

We greatly appreciate the financial support of this work by NASA through Grant No. #G00007275.

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