Towards suppressing loss tangent: Effect of SiO₂ coating layer on dielectric properties of core-shell structure flaky Cu reinforced PVDF composites

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Abstract

Flaky Cu (*f*-Cu) particles coated with various thickness of silica (SiO₂) were incorporated into poly(vinylidene fluoride) (PVDF) to investigate the effects of SiO₂ coating layer and its thickness on dielectric properties of the composites. The morphological and dielectric properties of the composites were characterized. The results indicate that the SiO₂ coating layer significantly affects the electrical properties of *f*-Cu@SiO₂ and *f*-Cu@SiO₂/PVDF, and that the PVDF composites with *f*-Cu@SiO₂ particles exhibit superior dielectric properties compared with raw *f*-Cu. Dissipation factors ($\tan\delta$) of the *f*-Cu@SiO₂/PVDF are remarkably suppressed and reduced to rather low level owing to the presence of SiO₂ shell which serves as an interlayer between the *f*-Cu particles preventing them from contacting with each other. Furthermore, the effect of suppression on $\tan\delta$ tends to be more prominent as the thickness of SiO₂ coating layer increases. The as-prepared composites possess high dielectric constant and low $\tan\delta$, making them promising for the industrial application as embedded capacitors.

Keywords: Polymer, elastomers, and plastics; Metal; Surfaces and interfaces; Dielectric response

1. Introduction

With the rapid development of electronic systems toward multifunction and miniaturization, dielectric materials with high dielectric constants (high-k), low dielectric loss and excellent processing are highly desired and essential for practical applications, such as embedded capacitors in microelectronics, electromagnetic interference shielding and energy-storage devices [1-4]. Compared with the traditional high-k inorganic materials such as BaTiO_3 , $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, BaSrTiO_3 , PZT, etc, polymers have many clear advantages, such as good flexibility, easy processability, lightweight and low cost so that they are able to meet demands for miniaturization of microelectronics [5-8]. However, most of pure polymer for dielectric applications have low-k (e.g. <10). To meet this need, in recent years, much efforts have been devoted to develop polymer composites with high-k which attract great attention because of their unique combination of mechanical flexibility and tunable dielectric properties used as capacitor dielectrics, and electroactive materials [9-12]. Nowadays, the flexible polymeric composites with high-k and low dielectric losses have been increasingly required because of the rapid development of high performance electronic components and electrical equipments, such as energy storage devices, embedded capacitors, artificial muscles and skins, electric accessories, actuators, and other flexible electronics [13-19].

Typically, four different strategies have been explored to develop polymer-based composites with excellent dielectric performance: namely, (i) selection of proper polymer matrices; (ii) incorporation of ceramic additives with high dielectric constants; (iii) addition of conductive organics like polymers or oligomers; and (iv) addition of inorganic conductive fillers [4, 6, 8-13]. So far, Polymer/ferroelectric ceramic composites and polymer/conductive filler percolative dielectric composites are two kinds of research concentrations that are widely studied. The most common and promising strategy to obtain high-k flexible polymer composites is dispersing ceramic particles with giant dielectric permittivity

into the polymer matrices, which capitalizes upon the idea that the combination of colossal permittivity of inorganic particles with good dielectric strength of polymers [1, 11, 17-18], while, the biggest problem is that the dielectric permittivity is still very low (<50) with even high filler loading, which inevitably deteriorates the mechanical properties and dielectric strengths of the composites [9,10]. To overcome the limitations of ferroelectric polymer/ceramic composites, very promising work has been carried out based percolation theory, in which a small volume fraction of conductive filler was added to the polymer matrix to achieve a high-k, thus preserving the mechanical flexibility of the polymer [6, 8-10, 13, 15]. Although these composites can show very high dielectric constants near the percolation threshold (f_c), they still cannot be considered as effective materials for embedded capacitor applications due to the inevitably accompanied huge increase of loss tangent ($\tan\delta$), thus imposing considerable challenge and risk in preciously controlling the percolative threshold composition to obtain reproducible products for practical applications [13-15]. Therefore, fulfilling the balance between sufficiently high-k and low $\tan\delta$ is currently still a challenge in obtaining composites with high dielectric performance.

Currently, one of the trends in this area is to involve core-shell particles as fillers [1,11,13, 15]. Core-shell particles have many advantages, such as good stability of the core particles from the protection of the shell and various properties come from the constituting material [18-20]. Under delicate designing, composites with high-k and low loss could be achieved by controlling and optimizing the microstructure and electrical properties of the core-shell particles [22-24]. This type of core-shell structure is usually obtained by chemical synthesis route [1, 11, 13, 15, 18-26], such as CNTs@SiO₂, CNTs@TiO₂, Ag@TiO₂, Ag@SiO₂, Ag@C, GNPs@Al₂O₃, etc. BT@SiO₂, BaTiO₃@Al₂O₃.

Copper (Cu) is a good candidate for polymeric composite dielectrics applications due to its high

electric conductivity and low cost, compared with Au, Ag, and other metals such as Al, Fe, Sn, etc. However, there are few investigations on the applications of Cu particles because of their liability to be oxidized to CuO or Cu₂O upon exposure to air [28-32]. So, how to enhance their oxidation resistance is an important issue. Raw Cu particle can endow polymers with a larger dielectric constant as well as a high loss near f_c due to the resultant leakage current within the composites [19, 27]. So, effective suppressing the loss while remaining a high-k of Cu/polymer is the main goal of our work. Approach to introduce a shell material on the surface of Cu to improve the anti-oxidation stability of Cu particles is highly desirable for their dielectric applications, and at the same time the shell serves as an insulating layer to effectively decrease the loss. As we know that silica is an ideal candidate for shell-forming material due to its high chemical and thermal stability and good compatibility with other materials [28]. Along this line, in the present study, a SiO₂ coated flaky Cu (*f*-Cu) particles, will be prepared by a sol-gel method, and the obtained core-shell particle is employed as the filler to prepare poly(vinylidene fluoride) (PVDF) composites with high-k but low dissipation factor. Until now, the investigations on the dielectric properties of *f*-Cu@ SiO₂/PVDF composites have rarely been reported. Therefore, the present research is expected to provide a deeper insight into the effects of SiO₂ shell and its thickness on dielectric properties of the *f*-Cu/PVDF composites in a wide frequency range.

2. Experimental

2.1 Materials

PVDF FR903 (Shanghai 3F New Materials Co., China) was chosen as the polymer matrix. The *f*-Cu powder (average length = 10-15 μm and thickness $\sim 1.0 \mu\text{m}$) was supplied by Shenyang Hangda Metallic Materials Co. Tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄) and ammonia aqueous solution (28 wt. %) were supplied by Tianjin Fuchen Reagent Co., China. The solvent absolute ethanol, N, N-Dimethylformamide (DMF), and others were purchased from Tianjin Chemical Reagent Co., China.

2.2 Preparations

Preparation of core-shell $f\text{-Cu@SiO}_2$ particles

Firstly, 10 g $f\text{-Cu}$ was dispersed in 100 ml absolute ethanol under sonication for 30 min, and the solution was heated to 60 °C under mechanical agitation. Then, different amount of TEOS with respect to $f\text{-Cu}$ particles, and ammonia aqueous solution were added to the solution dropwisely with stirring, and the reaction was continued for 6 h to ensure homogeneous coating SiO_2 on the surface of $f\text{-Cu}$ particles. Finally, the resulted samples were washed with ethanol and deionized water at least three times, filtered, and dried under oven at 80 °C for 8 h. The resultant samples are named as $f\text{-Cu@SiO}_2\text{-5\%}$, $f\text{-Cu@SiO}_2\text{-10\%}$, $f\text{-Cu@SiO}_2\text{-15\%}$, $f\text{-Cu@SiO}_2\text{-20\%}$, and $f\text{-Cu@SiO}_2\text{-25\%}$, respectively. Here, the 5%, 10% and others mean the weight ration of the SiO_2 to $f\text{-Cu}$.

Preparation of core-shell $\text{SiO}_2\text{@Cu/PVDF}$ composites

First, PVDF powders were dissolved in the desired amount of DMF by stirring in 50 °C water bath for 30 min, at the same time, the preliminarily weighed $f\text{-Cu}$ or Cu@SiO_2 particles were dispersed in DMF under sonication for 30 min. Then, the suspension was added into the PVDF solution, and the obtained mixture was stirred for 8 h and then at 130 °C to evaporate the majority of DMF. The resulting composite was heated at 120 °C in a vacuum oven to remove the residual solvent. Finally, it was compression-molded at 200 °C for 15 min under a pressure of about 15 MPa.

2.3 Characterizations

The surface chemistry of the samples was determined using a Fourier transform infrared (FT-IR) spectrometer (Perkin-Elmer, Paragon1000). The spectrum in the 4000 cm^{-1} to 400 cm^{-1} range was recorded. The structures of the $f\text{-Cu}$ and Cu@SiO_2 particles were identified with a Shimadzu X-ray diffractometer-6000 (XRD) equipped with a graphite homochromatic instrument and a Cu anticathode (40kV, 30mA, scanning rate $2^\circ/\text{min}$). The morphologies of the fractured interface of $f\text{-Cu}$ and

Cu@SiO₂ particles, and their composites were observed using a JEOL JSM-7000F scanning electron microscope (SEM). An H-800 transmission electron microscope (TEM) purchased from Hitachi Co (Japan) was used to observe the shell layer of SiO₂ on the surface of *f*-Cu particle. The fractured surfaces were prepared in liquid N₂ and were sputtered with gold in vacuum prior to observation. The dielectric measurements of the samples were recorded using an Agilent 4294A impedance analyzer in the frequency range of 40 Hz to 10 MHz.

3. Results and discussion

3.1 FT-IR

The surface modification of *f*-Cu particles was determined via FT-IR measurements. Fig. 1 presents the FT-IR spectra of *f*-Cu and *f*-Cu@SiO₂-15% particles. An obvious wide and sharp absorption peak at about 3200 cm⁻¹ to 3700 cm⁻¹ can be observed, which is characteristic of the stretching vibration of -OH groups on the surface of *f*-Cu particles; whereas, the absorption peak for the *f*-Cu@SiO₂-15% is obviously enhanced because more -Si-OH groups from the hydrolysis of TEOS are assumed to be chemically grafted onto the surface of *f*-Cu particles after surface treatment [27]. The new adsorptions at about 853 cm⁻¹ and 1118 cm⁻¹ are the characteristics for symmetrical stretching vibration of the Si-O-Si bond, where, the obviously enhanced signal at 1385 cm⁻¹ for *f*-Cu@SiO₂ is assigned to stretching vibration of the Si-OH group compared with raw *f*-Cu. Furthermore, a clear stretching vibration of -CH₃ groups is noticed at 2961cm⁻¹. The above results indicate that the surfaces of *f*-Cu particles were covered by a layer of SiO₂ coating.

3.2 XRD

Fig. 2 displays the XRD patterns of raw *f*-Cu and *f*-Cu@SiO₂ particles. Both of the XRD patterns exhibit three strong peaks at 2θ values of 43.4, 50.6 and 74.2, corresponding to the (111), (200) and (220) planes of the cubic Cu phase (JCPDS No.4-0738), respectively. A weak diffraction peak at 36.5

can be assigned to Cu_2O phase for raw $f\text{-Cu}$ particles, whereas, the absence of Cu_2O phase at 36.5 for the $f\text{-Cu@SiO}_2$ sample demonstrates that the raw $f\text{-Cu}$ particles are well protected by the outer SiO_2 shell without being oxidized after dried under oven at 60 °C for 8 h. Fig.2 suggests that the morphology of coating layer of SiO_2 on the surface of $f\text{-Cu}$ is amorphous, not crystalline.. Therefore, compared with raw $f\text{-Cu}$, the $f\text{-Cu@SiO}_2$ particle exhibits good oxidation-resistant stability because no characteristic peaks of oxide impurities could be detected [28-30].

3.3 Microstructure

Fig. 3 presents the morphological images of raw $f\text{-Cu}$, $f\text{-Cu@SiO}_2\text{-5\%}$, $f\text{-Cu@SiO}_2\text{-15\%}$, and $f\text{-Cu@SiO}_2\text{-20\%}$ particles, and their PVDF based composites. One can see that the average length of $f\text{-Cu}$ is about 10-15 μm , and that the particle surface is smooth. Compared with $f\text{-Cu}$ particles, more SiO_2 particles were deposited on the surface of $f\text{-Cu}$ as the amount of SiO_2 coating increases; therefore, the surface of raw $f\text{-Cu}$ gradually becomes much rough. This reflects a change in the thickness of SiO_2 coating layer. The TEM image of $f\text{-Cu@SiO}_2$ particle is shown in Fig. 4, from which it can be seen that there is a layer of SiO_2 shell on the surface of core $f\text{-Cu}$, serving as an interlayer between core $f\text{-Cu}$ particles.

From Fig. 3(e-h), the fillers were uniformly dispersed in composites. The rough surface of modified $f\text{-Cu}$ leads to enhanced phase interfacial interactions, thus resulting in more prominent adhesions between the PVDF matrix and the fillers compared with the smooth surface of raw $f\text{-Cu}$ particles. Furthermore, the polar groups of C-F from PVDF are prone to forming hydrogen bonding with the silanol groups of $f\text{-Cu@SiO}_2$, and the degree of hydrogen bonding between them increases with increasing the amount of SiO_2 coating layer. Therefore, the SiO_2 coating layer with moderate modulus acts as an interface modifier between the PVDF and the $f\text{-Cu}$. Good dispersion of $f\text{-Cu@SiO}_2$ in the matrix due to enhanced interfacial interactions, will play a positive role in deciding dielectric

and other properties of the composites [22]

3.4 Dielectric properties

Dielectric permittivity of a material represents the ability to store a charge when the material is subjected to an electric field and reflects the dielectric properties of the material. Fig.5 presents the variations of dielectric constants of six composites as a function of filler concentrations and frequency at room temperature. PVDF filled with f -Cu and f -Cu@SiO₂ exhibit similar trends. From Fig. 5(a), the significant increment in dielectric constant of f -Cu/PVDF can be mainly ascribed to the homogeneous dispersion of f -Cu in the PVDF and a gradual formation of the microcapacitor networks in the composites as the filler loading increases. The evolution process of the dielectric constant in the composites with various filler loading can be divided into three stages. Initially, when $f < f_c$, a small amount of f -Cu is incorporated into the PVDF and is isolated from each other. Therefore, the capacitance value of each microcapacitor is rather low, and the number of microcapacitors is inadequate, thereby resulting in a slight increase in dielectric constant compared with neat PVDF [8]. Moreover, the dielectric constant is almost independent of frequency, indicating that there is no plentiful accumulation of interfacial charges inside the composites. Once the $f \rightarrow f_c$, where f -Cu are close to each other, and there are many f -Cu particles separated by very thin matrix layers within the composites, thereby leading to a large number of microcapacitors and an increase in the capacitance of each microcapacitor [17, 19]. So, a sudden increase in dielectric constant at low frequencies can be noticed because of the Maxwell-Wanger-Silars (MWS) interfacial polarization. A large number of charges are blocked at the interfaces between the f -Cu and the matrix, owing to the MWS effect, which makes a remarkable contribution to the sharp increment of the dielectric constant apparently dependent on frequency in the low-frequency range (less than 10^3 Hz). The establishment of interfacial polarization is able to keep up with the change of external electric field in this frequency range, so the

introduction of f -Cu remarkably results in the increase of dielectric constant and loss. The time for establishing interfacial polarization will fall behind the change of external electric field as the frequency increases, leading to a decrease of dielectric constant and loss [8, 18, 22]. However, when the frequency exceeds 10^4 Hz, the dielectric constant is dominated by the microcapacitance-structure model (frequency-independent). So that it is maintained at a stable value at higher filler loading, which is still much large than that of neat PVDF. Beyond the f_c , the dielectric constant keeps on rising because of the continuous formation of microcapacitors, and exhibits strong frequency dependence in the low-frequency range, followed by weak frequency dependence in the high-frequency range, suggesting that interfacial polarization is dominant for the capacitance of these microcapacitors [22]. As the f -Cu loading increases to 70 wt. %, the dielectric constant reduces due to the voids and defects at the phase interfaces. At the same time, the dielectric loss also dramatically increases due to the formation of conductive network, resulting in a high resultant leakage current within the composites. In this case, the composites turns into conducting materials rather dielectrics.

For polymers filled with conductive fillers, the percolation theory states that the variations of dielectric constant with frequency follow a power law as the f of the conductive fillers increases to the vicinity of the f_c and the fillers connect with each other to form a continuous path. Thus, the dielectric constant ε of the composites can be enhanced as described by the power law [19]:

$$\varepsilon = \varepsilon_m (f_c - f)^{-s} \quad \text{for } f \leq f_c \quad (1)$$

where ε_m is the dielectric constant of the matrix and s is an exponent of about 1. As shown in Fig.5 (b), the best fit of the dielectric constant with log-log plots of the power law for f -Cu/PVDF gives $f_c \approx 0.12$ (42 wt.%), and $s \approx 0.88$ according to equation (1).

Note that from Fig. 5(c-g), the dielectric constant of f -Cu/PVDF is superior to the other five samples. As demonstrated in Fig. 5(h), the dielectric constant of f -Cu/PVDF is significantly higher

than those of the other five composites at 100 Hz. Compared with *f*-Cu/PVDF, no significantly rapid variation in the dielectric constant in low-frequency range was observed for the *f*-Cu@SiO₂/PVDF up to 60 wt. %. It is noteworthy that the interfacial polarizations of the *f*-Cu@SiO₂/PVDF composites have been constrained and suppressed by the SiO₂ coating layer. Comparably, dielectric constant for *f*-Cu/PVDF caused by interfacial polarization is rather prominent. What is more important is that higher coating amount of SiO₂ layer contributes to higher suppression degree of interfacial polarization and gives rise to bigger difference of dielectric constant [22]. The SiO₂ coating layer effectively reduces the electric conductivity of *f*-Cu, thus reducing its contributions to interfacial polarization of the composites. That is why a rapid decrease in dielectric constant can be found. Typically, from Fig. 5(f-g) the dielectric constant of *f*-Cu@SiO₂/PVDF exhibits weak dependence on frequency in the range of frequency 10³~10⁵ Hz, while it rapidly declines as the frequency exceeds 10⁵ Hz. From Fig.5, it can be found that the coating amount of SiO₂ in *f*-Cu@SiO₂-5%, *f*-Cu@SiO₂-10%, and *f*-Cu@SiO₂-15% is suitable to obtain relatively high dielectric constant [22].

The dielectric loss is a measurement of energy dissipation from the movement or rotation of the molecules in the external electric field. Reducing the dielectric loss is the target of many investigations on preparing high-k electric conductor/polymer composites because suffering from an abrupt variant in $\tan\delta$ is a fatal disadvantage for its practical engineering use [17-19], however, reducing the $\tan\delta$ into capacitor-tolerated values ($\tan\delta \leq 1$) while remaining high dielectric constant is still found to be difficult [6]. Fig. 6 depicts the dependence of dissipation factors on frequency of *f*-Cu/PVDF and *f*-Cu@SiO₂/PVDF composites. The dielectric loss of all samples decreases in the frequency range from 10² to 10⁴ Hz, and then increases substantially over 10⁵ Hz. The low-frequency dielectric response is a typical interface polarization behavior, resulting from macroscopical heterogeneous interface of the different diphasic structures. On the contrary, the high-frequency dielectric response is

a Debye relaxation behavior derived from the C-F dipole orientation polarization of PVDF matrix [6]. The conductivity of raw *f*-Cu/PVDF composites increases with increasing the *f*-Cu loading. There is no appreciable change in the loss behavior up to 12 vol. % of *f*-Cu loading. Afterward, the loss factor increases significantly at low frequencies with increasing the filler concentration, primarily owing to direct current (DC) or quasi DC conduction caused by the percolation effect. At a high *f*-Cu loading, there were well-established particle clusters or partial connectivity of the filler, resulting in an increased dielectric loss [22, 23], as demonstrated in Fig. 6(a).

The dielectric properties of polymer filled by conductors is closely correlated to the electrical properties of fillers, which have a significant effect on the migration and accumulation of charge carrier at the interfaces between the fillers and the matrix and therefore affect the interfacial polarizations [18, 23]. In comparison with the *f*-Cu/PVDF composites, the significant decrease in the $\tan\delta$ for the *f*-Cu@SiO₂/PVDF composites is observed in Fig.6 (b-g), and the maximum of dielectric loss of the composites still keeps a low value. This reflects that SiO₂ coating layer has the capacity of reducing $\tan\delta$ of the composites. The reasons can be mainly attributed to the insulating SiO₂ shell on the surface of *f*-Cu cores, which serves as the interlayer against direct contact between adjacent *f*-Cu particles, thus effectively suppressing the mobility of free charge carriers [19, 23]. We know that dielectric loss generally originates from relaxation and conductance. In current situation, the influence of conductance can be ignored because SiO₂ layer is of high resistance [22]. Accordingly, it is reasonable to assert that the SiO₂ coating layer plays a pivotal role in reducing $\tan\delta$ of the composites by affecting relaxation behavior. Fig. 6(b) ~Fig. 6(f) demonstrate that higher coating amount of SiO₂ contributes to higher suppressing degree of dielectric loss. Furthermore, the $\tan\delta$ has been significantly decreased to a very low level owing to the electrically insulating SiO₂ shell' effective suppression of the mobility of free charge carriers at the phase boundary area. In all percolative polymer composites

reported so far, a high $\varepsilon/\varepsilon_m$ can only be achieved when $f \rightarrow f_c$ [23]. However, the $\tan\delta$ also suffers from an abrupt variant simultaneously because of the insulator–conductor transition near f_c , thereby imposing considerable challenge and risk in preciously controlling the f_c to obtain reproducible products for practical applications [22]. In this study, we observe that remarkable reduction of $\tan\delta$ is achieved by introducing SiO_2 interlayer between f -Cu to prevent them from connecting with each other directly. From the perspective of practical use, slightly sacrificing the dielectric constant for acquiring low $\tan\delta$ is acceptable.

The polarization of the f -Cu@ SiO_2 /PVDF with such a special core-shell-structured components, as depicted in Fig. 6(h), is dominated mainly by the interfacial polarizations associated with the entrapment of free charge generated in the cores at the interfaces between the Cu cores and the SiO_2 shell, and the interfacial polarization at the interfaces between the SiO_2 shell and the PVDF in the measured frequency range [23]. The electrically insulating SiO_2 shell plays an important role in determining these peculiar behaviors. Considering that $f \rightarrow f_c$, the dielectric constant increases with f because of the percolation. Given that $f \geq f_c$, the f -Cu are very close to each other but still isolated by a thin SiO_2 insulating layer, identical to a case where a large number of capacitors are connected with each other. The particle–particle junction is a capacitor, and above f_c , these junctions form an interparticle barrier layer of capacitor network connecting the top and bottom electrodes [22].

The conductivity of the polymer/conductive filler composites originates from two mechanisms: 1) non-Ohmic conduction, through the barrier-tunneling effect between the conductive fillers separated by a polymer layer, and 2) Ohmic conduction, through direct contact of conductive fillers. The percolation transition can be observed as the transition from non-Ohmic conduction to Ohmic conduction, when $f \rightarrow f_c$ [24]. Fig. 7(a-f) represents the frequency dependence of alternative current (AC) conductivity for the f -Cu/PVDF and f -Cu@ SiO_2 /PVDF with different filler contents at room

temperature. For the f -Cu/PVDF, at low filler loading, i.e., $f < f_c$ (42 wt. %), the conductivity increases slightly with the filler content and almost linearly with the increase of frequency. In this case, the f -Cu particles are not in contact with each other. Therefore, the tunneling mechanism is dominant in the electronic transport [22]. The increase in conductivity with the filler loading can be ascribed to the decreasing distance between conductors. Besides, the strong frequency dependence of conductivity indicates that the composites display an insulating nature at low filler loadings. With a further increase in the filler concentration, once approaching or exceeding the f_c , the conductivity values are almost independent of frequency in the low frequency range due to the formation of a conductive network, and begin to increase at high frequency. With further increasing of the filler loading, the transition region shifts towards high frequency. In this case, the composites exhibit a conducting nature and the electrons can transport along the conductive network from one electrode to another like in conducting materials [24,28]. Generally, variation of electric conductivity against filler concentration expressed in f agrees with a sigmoidal curve.

However, the results from Fig. 7(b-f) suggests that all AC conductivity slightly increases with the filler loading and exhibits nearly linear ascending with frequency, indicating the insulating nature of the f -Cu@SiO₂/PVDF composites due to the insulating SiO₂ shell as an interlayer between the f -Cu cores. The interlayer can effectively prevent the f -Cu from contacting with each other and from forming direct electric current across the composites. So, no percolation behavior is found in the f -Cu@SiO₂/PVDF composites owing to the absence of the formation of conductive network resulting from the existent of insulator SiO₂ shell on the surface of f -Cu. The SiO₂ coating layer has a dramatic influence on the electrical properties of f -Cu@SiO₂ and f -Cu@SiO₂/PVDF composites and therefore increases the percolation threshold f_c to a very high value by obviously reducing the corresponding conductivity [2, 18, 23]. In this case, the introduction of an insulating SiO₂ shell avoids the direct

contact of the *f*-Cu particles, making them difficult to form a conductive network in the *f*-Cu@SiO₂/PVDF composites. Thus, electrons can only transport through adjacent *f*-Cu by inter-Cu tunneling. Therefore, the conductivity of the *f*-Cu@SiO₂/PVDF composites is considerably lower than that of the *f*-Cu/PVDF composites with the same filler contents. Furthermore, higher coating amount of SiO₂ contributes to higher suppression degree of electron transportation across the composites. Therefore, the AC conductivity clearly reduces with increasing the thickness of SiO₂ layer.

4. Conclusions

In this study, the core-shell *f*-Cu@SiO₂ particles were prepared by a sol-gel method to effectively reduce the high loss of *f*-Cu/PVDF while remaining a relatively high dielectric constant. The results indicate that both the dielectric constant and dissipation factor increases with an increase in the filler content for *f*-Cu/PVDF and *f*-Cu@SiO₂/PVDF systems at all frequencies under investigation, especially remarkable for *f*-Cu/PVDF composites. Compared with the *f*-Cu/PVDF, the dielectric constants of *f*-Cu@SiO₂/PVDF composites decrease owing to the weakened interfacial polarization, and the dissipation factor remarkably slumps due to the insulating SiO₂ coating layer' suppression on loss from *f*-Cu. It is noteworthy that the SiO₂ coating layer plays a pivotal role in affecting the dielectric constant and dissipation factor of the composites through constraining the interfacial polarization. The insulating SiO₂ coating layer effectively prevents *f*-Cu particles from contacting with each other, and reduces the dissipation factor into capacitor-tolerated values ($\tan\delta \leq 1$) through effectively reducing the leakage conduction across the composites. It is revealed that the thickness of SiO₂ coating layer should be rationally tuned in order to exert optimal influence on dielectric constant and dissipation factor. The prepared *f*-Cu@SiO₂/PVDF composites with a high dielectric constant and low $\tan\delta$, are promising in the application of energy storage device, particularly the embedded capacitors.

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Figure 1-2

Fig.1 FT-IR spectra of *f*-Cu and *f*-Cu@SiO₂-15% particles

Fig.2 XRD patterns of *f*-Cu and *f*-Cu@SiO₂ particles

Figure 3

Fig.3(a) SEM morphology images of (a) raw *f*-Cu, (b) *f*-Cu@SiO₂-5%, (c) *f*-Cu@SiO₂-15% (d) *f*-Cu@SiO₂-20%, and PVDF composites filled with 50 wt. % of (e) raw *f*-Cu, (f) *f*-Cu@SiO₂-5%, (g) *f*-Cu@SiO₂-15% (h) *f*-Cu@SiO₂-20%

Figure 4

Fig.4 TEM morphology image of $f\text{-Cu@SiO}_2\text{-20\%}$

Figure 5

Fig.5 Frequency dependence on dielectric constant of PVDF composites loaded with (a) raw f -Cu, (c) f -Cu@SiO₂-5%, (d) f -Cu@SiO₂-10%, (e) f -Cu@SiO₂-15%, (f) f -Cu@SiO₂-20%, (g) f -Cu@SiO₂-25%, (b) dielectric constant as a function of f -Cu loading at 100 Hz, the inset shows a log-log plot of dielectric constant as a function of f_c - f , (h) variation of dielectric constant of PVDF with different fillers at 100 Hz.

Figure 6

Fig.6 Frequency dependence on $\tan\delta$ of PVDF composites loaded with (a) raw f -Cu, the inset shows the $\tan\delta$ for f -Cu at low loading, (b) f -Cu@SiO₂-5%, (c) f -Cu@SiO₂-10%, (d) f -Cu@SiO₂-15%, (e) f -Cu@SiO₂-20%, (f) f -Cu@SiO₂-25%, (g) $\tan\delta$ as a function of f -Cu@SiO₂ loading at 100Hz, the inset shows the $\tan\delta$ for f -Cu, and (h) schematic structure of Cu@SiO₂.

Figure 7

Fig.7 Frequency dependence on AC conductivity of PVDF composites loaded with (a) raw *f*-Cu, (b) *f*-Cu@SiO₂-5%, (c) *f*-Cu@SiO₂-10%, (d) *f*-Cu@SiO₂-15%, (e) *f*-Cu@SiO₂-20%, (f) *f*-Cu@SiO₂-25%.