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Lowering Dielectric Loss and AC Conductivity of Polymer/HfC Composite Dielectric Films *via* Insulating Montmorillonite Barrier

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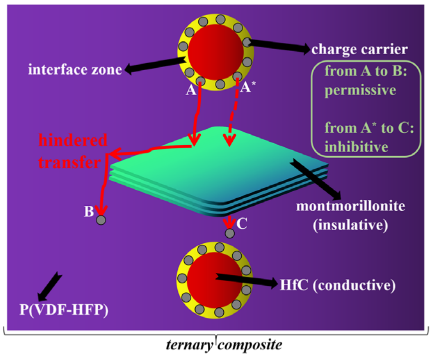
Abstract: Present work aimed at studying the effect of montmorillonite (MMT) on dielectric and conductive properties of composites based on polymer/hafnium carbide (HfC) mother composite system. Polymer/HfC/MMT composite films based on double-filler modification strategy were prepared by solution cast. To obtain control group, binary polymer/HfC composite films were prepared. MMT ceramic had excellent insulation property, which could suppress interface leakage current and thus reduce dielectric loss of composites. Compared with binary system, ternary system could show better overall electric features including mildly reduced permittivity, obviously reduced dielectric loss and conductivity. Optimized ternary composite bearing 3 wt% HfC and 3 wt% MMT exhibited a high permittivity of 34, low dielectric loss of 0.33 and low conductivity of 5.5×10^{-7} S m^{-1} at 100 Hz. This research might enable the fabrication of advanced composite dielectrics.



Keywords: dielectric, film, composite, HfC, montmorillonite.

1. Introduction

Severe energy-shortage issues are increasingly driving the development of microelectronics and electric power industries.[1] As modern electrical energy storage devices, dielectric capacitors have advantages of high power density, tunable dielectric constant, low energy loss, long service life and wide temperature-resistance range, but their energy density is relatively low.[2] Therefore, improving energy density of dielectrics in capacitors has become research hotspot.[3] For high energy density, high dielectric constant and breakdown strength (as well as low dielectric loss and conductivity) are desired.[4]

Polyvinylidene fluoride-based polymers bearing ferroelectric domains[5] have superior dielectric properties to other polymers,[6] and they are often used as matrices to prepare composites for higher dielectric constant. One strategy is to add ferroelectric ceramics into polyvinylidene fluoride (PVDF) based polymers for composites.[7] Advantages of those composites are controllable dielectric traits, low cost and facile preparation. However, to obtain higher dielectric constant, the filler of 50 vol% at least must be added, increasing hardness and brittleness of composites and decreasing mechanical propertie.[8] High dielectric constant in composites stems from polymer/ferroelectric ceramic interface polarization[9] and ultrahigh dielectric constant of ferroelectric ceramics.[10] The other strategy is to add conductive fillers into PVDF based polymers, such as nickel (Ni), aluminum (Al), graphene, carbon nanotubes (CNTs) and so on.[11] This approach can lead to significant increase of dielectric properties of composites, but it has disadvantage of low breakdown strength ascribed to filler percolation.[12] When content of particles is close to percolation threshold, dielectric constant of composites is very sensitive to change of filler concentration. Conductive particles inter-connect with each other to form huge three-dimensional conductive network contributing to high dielectric constant of composites. Polymer/conductor interface polarization and micro-capacitance theory[13] can explain high dielectric constant in composites as well. But, interface leakage current and dielectric loss of composites can be notably increased.[14] Rational balance between high dielectric constant and low dielectric loss is challenging in polymer/conductive ceramic composites.

To reduce interface leakage conduction and dielectric loss of polymer/conductor composites, some strategies have been raised. For example, based on promoting interface compatibility, organic modification of surfaces of conductive fillers[15] can effectively depress interface leakage conduction between polymer and filler.[16] However, that can result in obvious increase of fabrication cost. For instance, layered structure can endow compos-

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ites with more rational electric-field distribution of components and reduced leakage conduction.[17] However, that can lead to complication of fabrication steps. Thus, low-cost and fast fabrication of simple ternary-blending material systems has become popular.[18] Reasonable match of two ceramic fillers in polymer-based ternary composites can result in synergistic effect of both fillers, optimizing electric traits of composites.

In this study, two families of composite films for comparison, namely binary poly(vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP))/hafnium carbide (HfC) composites and ternary P(VDF-HFP)/HfC/montmorillonite (MMT) composites, were well fabricated. P(VDF-HFP) with high flexibility and film-forming trait[19] was used as matrix. HfC particles with high conductivity[20] were employed as filler for the expected high dielectric constant of composites *via* polymer/HfC interface polarization.[21] MMT particles with high insulation[22] were utilized as filler for the expected low leakage conduction of composites. MMT was expected to serve as barrier between HfC particles to depress migration of charge carriers. Property superiority of ternary-mixing system to binary-mixing system was explained. P(VDF-HFP)/HfC composites could be inferred to show desirable high dielectric constant and undesirable high dielectric loss (based on conductive nature of HfC), and P(VDF-HFP)/MMT composites could be inferred to exhibit desirable low dielectric loss and undesirable low dielectric constant (based on insulating nature of MMT).[23] Therefore, the innovation and importance of this work about P(VDF-HFP)/HfC/MMT ternary composites could be embodied owing to drawing on others' merits to offset its own weakness in ternary composites compared with two binary composite systems.

HfC applicable in aerospace can exhibit robust high-temperature resistance and oxidation resistance,[24] meaning low feasibility of preparation of organic surface-grafted HfC filler and HfC@HfO_2 core-shell filler. Purpose of constructing polymer-compatible organic (such as KH550) or insulating inorganic (such as HfO_2) shell around conductive-ceramic core should lie in reducing interface leakage conduction and dielectric loss.[25] However, for HfC in this work, building organic or inorganic shell should be difficult, as discussed above. The first novelty of this work was raising ternary-blending strategy (avoiding difficult preparation of core-shell fillers) for optimizing electric traits of composites bearing conductive ceramics (like HfC) with high oxidation resistance. Moreover, high-cost hexagonal-BN filler with high insulation[26] has been used for preparing polymer-based ternary composite dielectrics. The second novelty of this work was using cheap MMT to replace BN, showing wide market prospect. In a word, this study might offer valuable ideas for easy fabrication of modern composite dielectrics with high overall electric features.

2. Experimental

2.1. Materials

The hafnium carbide (HfC) powder (99.6%, AR grade, size of ~100 nm, molecular formula of HfC) was bought from Jinzhou Haixin Metal Materials Co., Ltd. (Jinzhou, China). The montmorillonite (MMT) powder (99.8%, AR grade, size of ~240 nm, molecular formula of $Al_6Si_2O_{13}$) was achieved from Lingshou Ruixin Powder Company (Shijiazhuang, China). The poly(vinylidene fluoride-hexafluoropropylene) powder (P(VDF-HFP), 99.5%, AR grade, 100 kDa, 10 mol% of HFP) was gained from Dongguan Zhanyang Polymer Materials Co., Ltd. (Dongguan, China). The *N*,*N*-dimethylformamide solvent (DMF, 99.5%, AR grade) was obtained from Zibo Nature International Trading Co., Ltd. (Zibo, China). All of the materials were immediately employed without treatments.

2.2. Solution-cast fabrication of composite films

Binary HfC/P(VDF-HFP) and ternary MMT/HfC/P(VDF-HFP) composite films were prepared by the facile solution-casting method.[27] The P(VDF-HFP) powder, MMT powder and HfC powder at their own designed weights were added into organic DMF of 3 mL. Then, the continuous magnetic stir for 4 h at 50 ℃ was executed to fully dissolve the polymer material. The stable ultrasonic treatment for 45 min at 25 ℃ was done for strongly scattering those ceramic particles, producing the desired homogeneous suspension of ceramic particles. The weight fractions of HfC filler were fixed to be 0, 0.5, 1.0, 3.0, 5.0, and 8.0 wt%, respectively, and the filling content of MMT filler in the ternary system was fixed to be 3.0 wt%. The as-prepared particle suspension was slowly cast onto the horizontal and clean glass slide at 70 ℃ followed by the heat preservation at 70 ℃ for 4 h. Later, the basically dry film was further heated at the elevated 90 ℃ for 4 h, aiming at the absolute evaporation of organic DMF solvent from the film. All of the thin-film samples with an average thickness of 50 μm were carefully peeled off from the glass slides. Once the films were cooled to the room temperature, the even Au electrodes were sputtered onto their two surfaces (ready for the subsequent electrical performance testing). The same procedure was adopted to fabricate the binary composite films with unchanged HfC contents given above. Note that the total concentration of the polymer and ceramic particles in the suspension cast should be controlled to be 100 mg mL^{-1}. That samples marked as 0 wt% in two systems were referring to the neat P(VDF-HFP) films. The preparing route of ternary composite films was given in Figure 1.

2.3. Characterization

X-ray diffraction (XRD) characterization was achieved based on a Rigaku D/max 2400 diffractometer (Rigaku Industrial Corp., Japan) with X-ray wavelength at 1.542 Å (Cu Kα radiation; 40 kV;

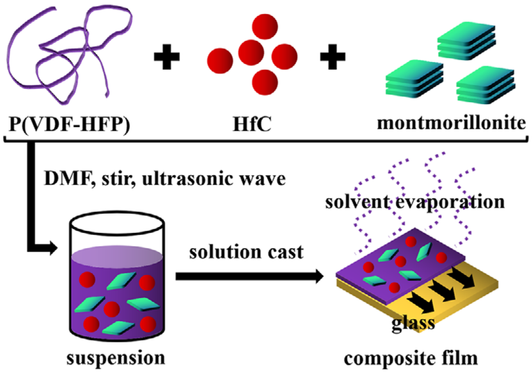

Figure 1. Preparing route of ternary composite films.

100 mA), diffraction angles at 10°-80°, test rate of 10°/min and test step of 0.02°. Field-emission scan electron microscopy (FE-SEM) characterization was finished through a ZEISS EVO18 (Germany) at 5 kV. Dielectric and alternative current (AC) conductive features of materials were studied by an E4980A LCR meter under 1 V. The frequency spectra of dielectric constant (based on the read capacitance values), dielectric loss (being directly read) and conductivity (based on the read resistance values) results of all the thin-film samples were obtained via the frequency-scanning mode of E4980A LCR meter from 20 Hz to 2 MHz under 1 V. The dependence of dielectric constant, dielectric loss and conductivity of samples onto HfC content was achieved by gathering the obtained results (mentioned above) of electric properties of all the film samples at 100 Hz. Further, based on the results of electric traits of samples at 100 Hz, the relative increment (by percentage) of electric traits of ternary composites compared with pure polymer matrix could be obtained by the equation of $[(X_t\text{-}X_p)/X_p] \times 100\%$ in which X_t and X_p were referring to the electric traits of ternary composites at 100 Hz and the electric traits of pure polymer sample at 100 Hz respectively. The Au electrodes fabricated via ionic sputtering were depending on a JEOL JFC-1600 auto fine coater (Japan).

3. Results and discussion

3.1. Characterization of used ceramic particles

In order to verify the chemical composition, crystal trait and micro-morphology of the employed HfC and MMT ceramic fillers, the XRD and SEM measurements of the both samples were conducted respectively. Figure 2(a) showed the XRD patterns of MMT and HfC ceramic particles. The peaks of MMT were detected at 16.3°, 26.0°, 33.2°, 35.3°, 40.7°, and 60.5°, and the corresponding crystal plane indices of those peaks were (1 1 0), (1 2 0), (2 2 0), (1 1 1), (1 2 1), and (3 3 1) respectively in the layer-stacked orthorhombic $Al_6Si_2O_{13}$ montmorillonite.[28] The peaks of HfC were determined at 33.7°, 38.9°, 56.2°, 67.2°, and 70.6°, and the matched crystal indices of those peaks were (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) respectively in the cubic HfC.[29] Figure 2(b) showed the low-magnification SEM result of HfC particles. The uniform particle size distribution of HfC could be found. The further magnified SEM result of HfC particles was shown in Figure 2(c), and the average particle size of those particles with nearly spherical 3D shape was found to be 100 nm. Figure 2(d) showed the SEM image of MMT particles. It could be seen that the MMT particles exhibited the 2D sheet-like morphology. The relatively even particle-size distribution of them could be verified, and the average particle size (plane width) of MMT particles was found to be 240 nm.

3.2. Dependence of electric performances on external-field frequency

For composite dielectric materials, their dielectric and conductive properties usually depend on the frequency of the external electric fields, ascribed to the inevitable interfacial interaction

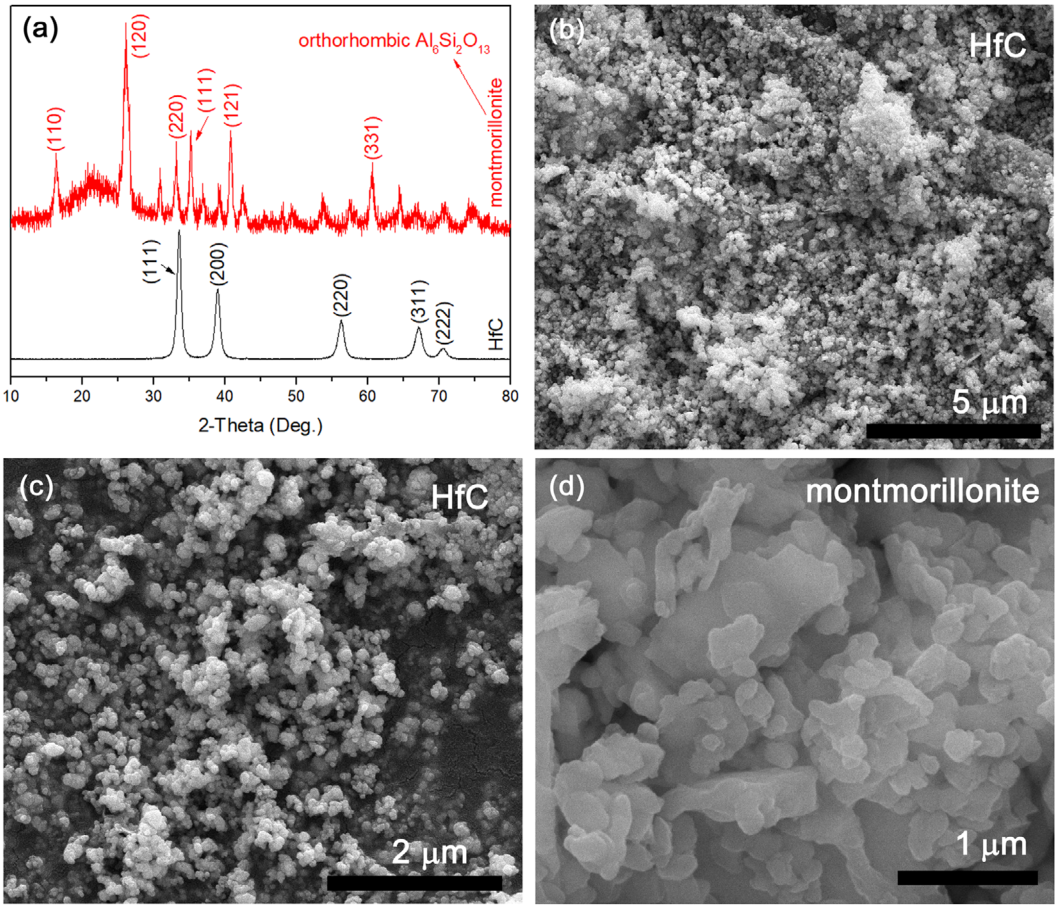

Figure 2. (a) XRD of HfC and MMT, (b) SEM of HfC, (c) enlarged SEM of HfC, and (d) SEM of MMT.

(strongly depending on frequency) between varied components. Investigations on the frequency dependence of the electric traits of the composite dielectrics prepared in this work should be very key for understanding the interfacial mechanism in those composites. Figure 3 displayed the frequency dependence of permittivity, dielectric loss and alternating current (AC) conductivity of HfC/P(VDF-HFP) and MMT/HfC/P(VDF-HFP) composites with different filler contents at the room temperature. As shown in Figure 3(a), the dielectric response of pure P(VDF-HFP) was weak in the whole frequency range, which was attributed to the weak interfacial polarization between the crystalline region and amorphous region in the matrix as well as the inborn low polarity of covalent dipoles.[30] The dielectric constant of binary composites decreased with the increase of frequency owing to the reduced contribution of the polymer/HfC interface polarization.[31] The interface polarization-induced electric dipoles were well trapped and coupled in the interface region under low external fields, meaning needing a very long time (matching with

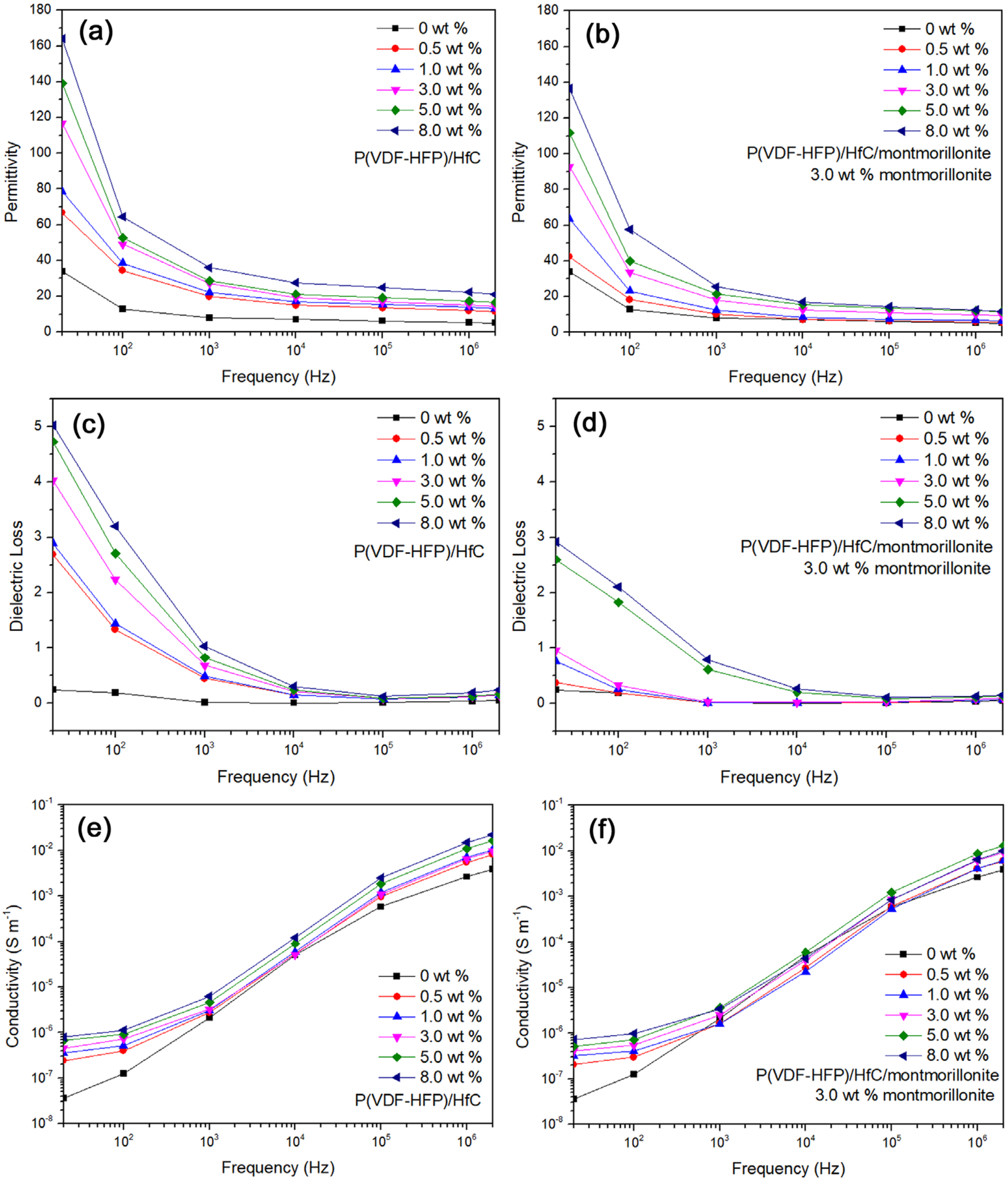

Figure 3. Dielectric constant frequency-spectra of (a) binary composites and (b) ternary composites. Dielectric loss frequency-spectra of (c) binary composites and (d) ternary composites. AC conductivity frequency-spectra of (e) binary composites and (f) ternary composites.

the low frequency of external fields) to well achieve the orientation and polarization of those electric dipoles along external fields. The very strong polarization of those interfacial dipoles contributing to elevation of dielectric constant of composites could be realized under low frequencies rather than under high frequencies. Moreover, at the higher HfC loading, the decrease of dielectric constant was quicker, especially at the low frequencies. The dielectric response of composites at the low-frequency range was controlled by the typical Maxwell-Wagner-Sillars (MWS) polarization between polymer and HfC phases.[32] Usually, the MWS polarization can occur at the interface of heterogeneous phases with the huge gap of the inherent conductive traits. The strong MWS polarization between the polymer as good insulator and the HfC as good conductor could be facilely triggered, and that dramatic reduction of the dielectric constant of the composite with more HfC filler at low frequency could well confirm the high contribution of MWS polarization to a high dielectric constant of those composites. Besides, the low dielectric constants of all the samples at high frequencies could be interpreted by the orientation polarization of the dipoles in polymer matrix.[33]

Figure 3(b) presented the dielectric constant of ternary composites as a function of frequency. Compared with binary system above, the difference was that the dielectric constant showed a slight drop and the changing range of data became narrow over the whole frequency scope. In fact, the mild decrease of dielectric constant of ternary system was reasonable. There were two reasons. One was the inherent low polarity and dielectric response of well-insulating MMT ceramic without ferroelectric trait.[34] The other was that the introduction of MMT phase might lead to the decrease of the coating ability of polymer matrix onto the conductive HfC particles meaning the decline of MWS polarization of polymer and HfC phases.[35] Due to the nanoscale traits of the two kinds of ceramic fillers, the huge total interface area between polymer and ceramic could be formed. The MMT filler could snatch the polymer matrix from the surface of HfC filler. The polymer/HfC MWS polarization would be reduced due to the decrease of polymer content at the surface of HfC filler. Unfortunately, the newborn polymer/MMT MWS polarization was rather weak owing to the common insulating features of polymer and MMT components.

In Figure 3(c), at low frequency range, the dielectric loss of binary composites was very high attributed to the high interface leakage current stemming from the robust polymer/HfC interface polarization.[36] The low frequency of external fields could lead to the directed migration of interfacial electrons over the mean free path of them, further resulting in the high interface leakage conduction in composites. However, as the frequency increased, the dielectric loss rapidly decreased. The rather low dielectric loss of composites at high frequencies might be ascribed to the low polymer/HfC interface leakage current (the oscillation of interfacial charges).[37] At high frequency, the oscillation of interfacial electrons would lead to the shorter moving path of those electrons than their mean free path, suggesting the rather low interface leakage conduction. As shown in Figure 3(d), the dielectric loss of ternary composites bearing MMT was greatly reduced at low frequencies (compared with binary composites). The promising low dielectric loss could be obtained in the ternary composites with low-content HfC at low frequencies. The excellent insulating trait of MMT phase[38] was very key to the reduction of dielectric loss of ternary composites. Due to the physical-barrier effect, the MMT particles might extend the migration distance and reduce the migration velocity of leakage-conduction charge carriers.[39] That is to say, the insulating nature of MMT might promote the branching growth of electrical trees.[40] The leakage-conduction electrons could not transmit through the insulating MMT particles, suggesting the increase of the fractal dimension of electrical treeing near the MMT particles. In this case, the smooth electronic transfer between the two electrodes would be well depressed in terms of probability.

Frequency dependence of AC conductivity of HfC/P(VDF-HFP) composites with various weight fractions of HfC filler was shown in Figure 3(e). The observed deviation from linear increase of AC conductivity of composites with increasing the frequency could suggest the reduction of electric insulation traits of them compared with pure polymer.[41] In fact, that deviation from linear feature mainly came from the increase of conductivity of composites at low frequencies which could indicate the leakage conduction of polymer/HfC interface. Based on Figure 3(f), the slight reduction of AC conductivity of ternary composites compared with binary ones could be found, owing to the introduction of MMT phase. Once the MMT particles with a rather low conductivity were added, the interaction between HfC particles could be depressed meaning the depressing of electric percolation of HfC particles.[42] The high-speed leakage current from the percolation of conductive HfC phase could be avoided to contribute to the low conductivity of ternary composites. The electric percolation of the highly-conductive particles could induce the formation of a huge 3D conductive network meaning the transformation from insulator to conductor, leading to the huge improvement of conductivity of composite dielectrics. In this work, the MMT filler could strongly hinder the formation of HfC-interconnected network, showing the high contribution of MMT filler to the low conductivity of those ternary composites.

3.3. Impact of HfC content on electric features of composites

For composite dielectrics for energy storage, the investigations on the optimized loading content of the conductive ceramic filler should be very important. The well-balanced overall electric features and the high flexibility of composites could strongly depend on the rational content of the used conductive filler. In this section, the dependence of the dielectric constant, dielectric loss and AC conductivity of two composite systems onto HfC content at 100 Hz was studied. As exhibited in Figure 4(a), the dielectric constants of the HfC/P(VDF-HFP) composites showed the non-linear increasing trend with the promotion of HfC content. The neat polymer exhibited the relatively low dielectric constant. When 0.5 wt% of HfC was employed, the dielectric constant was increased abruptly for binary system. This should be induced by the extremely good polymer-coating onto the surfaces of all HfC particles, which could bring about the high interface polarization between two components.[43] The dielectric response and polarizability of the binary composite system were very sensitive to the filling of HfC particles with the good conductive ability. As the HfC loading content further increased, the dielectric constant of binary system was stably improved, which could be explained by the classic micro-capacitor mechanism.[44] Moreover, the increase of the HfC content could lead to the increase of inter-phase content, denoting the improvement of the total extent of interface polarization. However, after the addition of the third phase (3 wt% of the insulating MMT filler), the dielectric constant of ternary system showed the nearly linear increasing trend (without the abrupt increase at the case of low-content HfC), indicating the weakened polymer/HfC interface polarization induced by MMT phase. When the HfC filler of low content was introduced, the introduction of MMT (3 wt%) meant the obvious impact of MMT phase on the polymer/HfC interface interaction. In this case, the MMT phase could strongly occupy the polymer matrix *via* competing with the HfC phase. Although the dielectric constants of ternary system were decreased compared to binary system, they still remained at the relatively high values. This should be connected with the robust polymer/HfC interface effect.

In Figure 4(b), the dielectric loss of the ternary composite films was obviously reduced compared with the binary composite films, especially when the HfC loading content was low (0.5-3.0 wt%). The dielectric loss of ternary system was slowly increased with the increase of the HfC content when the HfC content was lower than 3.0 wt%, but it sharply increased when the HfC content increased from 3.0 wt% to 5.0 wt%. In a word, at low HfC contents, the leakage current of ternary composites should be very low thanks to MMT filler. The incorporation of MMT particles might be in favor of the uniform dispersion of HfC particles in polymer matrix,[45] which could depress the high leakage current induced by the gathering of conductive HfC particles. When the content of HfC filler was relatively high, the MMT filler could not strongly depress the interaction between varied HfC particles. The very high dielectric loss (suggesting the high interface leakage conduction) could be confirmed in all the binary composites, ascribed to absence of leakage-conduction-depressing mechanism in binary composite system.

In Figure 4(c), the relationship between the AC conductivity of the two composite systems and the HfC weight fraction was shown. Regardless of pure polymer sample, the conductivity of two systems increased slowly (nearly linear trend) with the increase of HfC content. This should be highly connected with

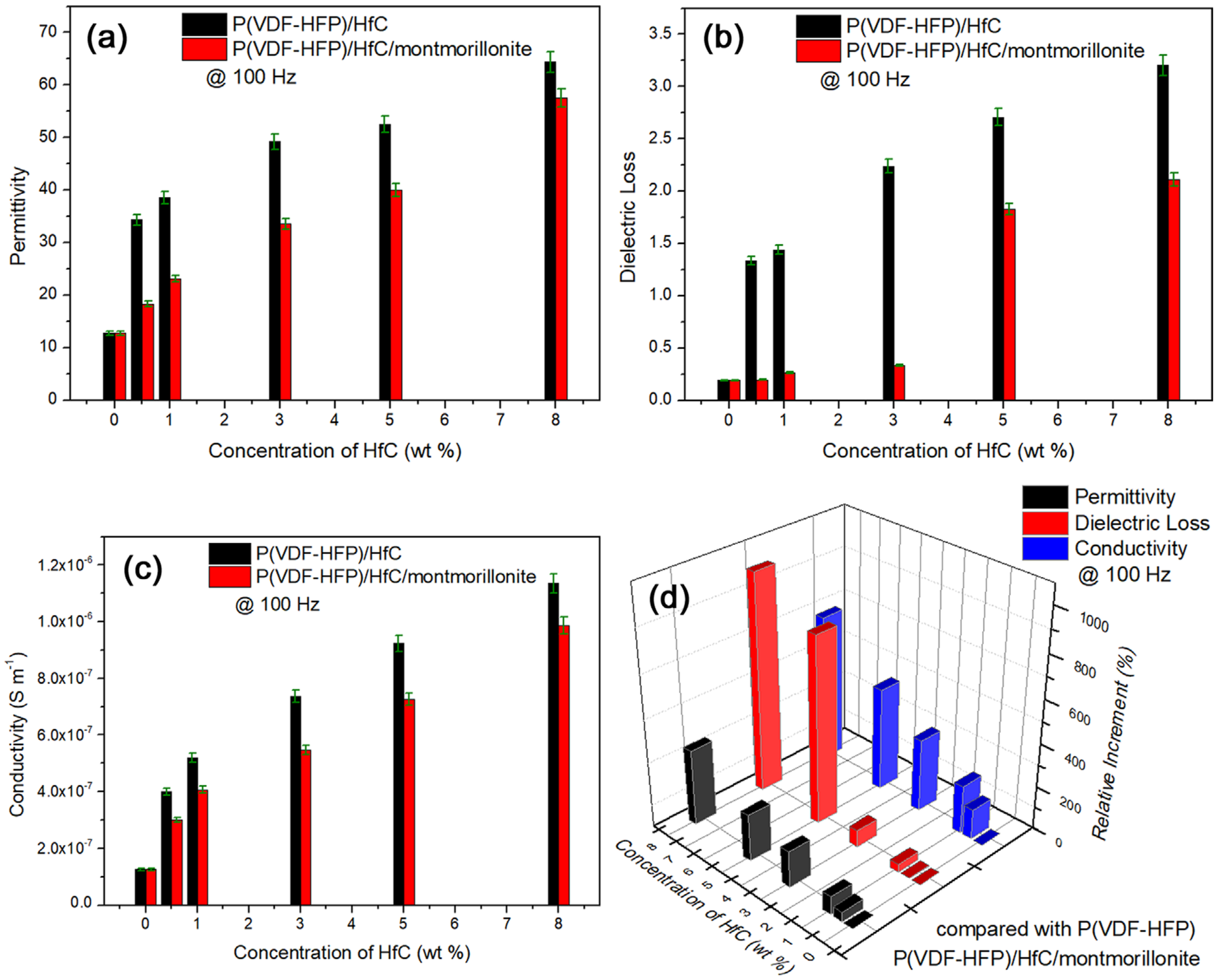

Figure 4. Comparison of (a) dielectric constant, (b) dielectric loss, and (c) AC conductivity of both systems at 100 Hz. (d) Relative increment of electric traits of ternary system compared with neat polymer at 100 Hz.

Table 1. The property comparison of the optimized composites between the present ternary composite system and the other reported composite systems at 100 Hz

Dielectric traits	Present system	PVDF/Cr_2C_3/MMT	P(VDF-HFP)/Cr_2AlC/BN	P(VDF-HFP)/V_2AlC/MMT
Permittivity	~34	~37	~30	~35
Dielectric loss	~0.33	~0.48	~0.7	~0.45

the gradual increase of conductive HfC phase. Based on the very similar varying trend of conductivity of two composite systems, the origin of conductive features of the two systems should be the highly-conductive HfC phase. The introduction of MMT ceramic could effectively reduce the AC conductivity of the composites over the entire studied range of HfC contents. On the one hand, the inborn conductivity of MMT ceramic was very low.[46] The insulating trait of MMT ceramic was very crucial. On the other hand, the barrier effect of MMT ceramic particles could depress the charge migration between HfC particles.[47] Obviously, the electronic migration from one HfC particle to another HfC particle could result in the increase of conductivity of composites. To sum up, via adding the MMT phase, the ternary system could achieve the depressed low conductive feature. Figure 4(d) could display the relative increment (percentage) of electric traits of ternary system compared with neat polymer at 100 Hz. At 3.0 wt% HfC content, the moderately high dielectric constant and very low dielectric loss could be obtained in that ternary composite. In Table 1, the present P(VDF-HFP)/HfC/MMT composite system was compared with the other composite systems in existing researches,[48-50] and the property advantage of the P(VDF-HFP)/HfC/MMT composite system could be found.

3.4. Physical barrier mechanism of MMT ceramic particles

Based on the discussion above, the very key role of MMT ceramic phase in optimizing the overall electric features of ternary composite system could be verified. Thus, the microscopic mechanism induced by the MMT filler in ternary composites should be clarified for providing the new ideas for designing the promising composite dielectric materials in the future. In order to present the relationship between the micro-structure and macroscopic performances of ternary composites, the sketch map about ternary system was given in Figure 5. In the micro-structure, the HfC phase was indicted by the red sphere, and the charge carriers were located at the polymer/HfC interface region due to interface polarization of both. The MMT phase was indicated by the green sheet with multilayer structure. The HfC and MMT particles should be evenly dispersed in the chain-entangled polymer matrix, and the MMT particles could act as the physical barrier of charge transfer.[10] Under the external electric fields, MMT phase could impede the straight short-range transmission of charge carriers to lengthen the transmission path of charge carriers and to reduce the migration rate of charge carriers.[51] In the figure, the short-range transfer of charge carrier from A* to C (passing through the MMT particle) was inhibitive, while the hindered long-range transfer of charge carrier from A to B (bypassing the MMT particle) was permissive. As a result, the total leakage current would be well reduced. In addition, near the surface of the MMT particle, the branching growth of electric trees[52] consisting of charge carriers should be very important. The branching growth of electric treeing in the composite (increase of the fractal dimension) could lead to the elevation of the probability of the neutralization of the opposite electric charges, meaning the termination of the branched leakage-conduction current. In a word, the present ternary system could obtain the favorable high dielectric constant, low dielectric loss and low conductivity at the same time. To verify the hypothesis shown in Figure 5 and show the property advantage of that ternary composite with 3 wt% HfC and 3 wt% MMT, some experimental evidences of the several representative samples were given in Figure S1 and Figure S2 in Supporting Information.

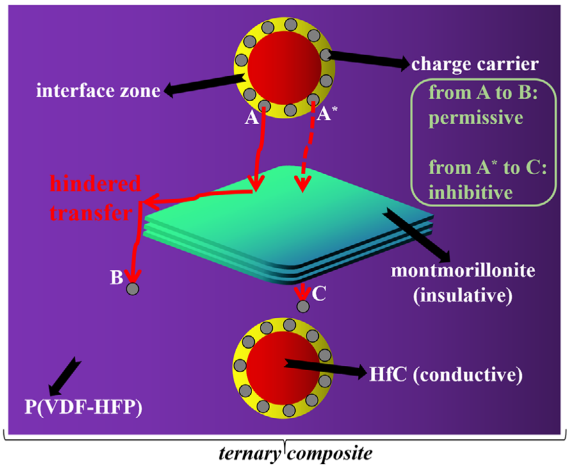

Figure 5. Physical barrier mechanism of MMT ceramic particles in ternary system.

4. Conclusions

By adding the HfC and MMT particles into the P(VDF-HFP) matrix, a family of new three-phase composite materials were prepared by solution casting method. The composite materials had the well-balanced high dielectric constant, low dielectric loss and low conductivity. It was found that the introduction of insulating MMT ceramic particles could significantly reduce the dielectric loss of ternary composites compared to binary HfC/P(VDF-HFP) composites. The MMT phase could hinder the charge migration caused by the HfC phase and reduce the total leakage current. The reduction of leakage conduction could reduce the dielectric loss and conductivity of ternary composites. In addition, the ternary system had the strong polymer/HfC interface polarization, endowing the composites with favorable high dielectric constants. This research might be in favor of developing the good dielectric candidates for the modern embedded capacitors with the high dielectric constant and low dielectric loss.

Supporting information: Information is available regarding the experimental evidences in representative samples for verifying the hypothesis in Figure 5 and showing property advantage of the optimized ternary composite. The materials are available *via* the Internet at http://www.springer.com/13233.

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