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Interfaces

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The Formation of Percolative Composites with a High Dielectric Constant and High Conductivity**

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Composites with compositions near the percolation threshold always experience a dramatic structural change, which can cause huge changes in physical properties of the composites.[1] Those changes sometimes are quite beneficial, such as increase of conductivity and capacitance, which enhances the potential of the composites for applications as conductive materials, energy storage materials, and so on.[1–3] Thus, percolative composites have already drawn attention in recent years. A general way to create percolative composites is adding conductive particles into insulating matrix. For instance, adding Ni particles into $BaTiO_3$ ceramics led to composites with a giant dielectric constant (above 80000 at 10^3 Hz)[4] and mixing metallic particles with polymer matrix resulted in a much larger dielectric constant of the composite than that of the sole polymer matrix.[5,6] A percolated network of multiwall carbon nanotubes led to a dielectric constant of more than 300,[7] while addition of polyaniline particles in P(VDF-TrFE-CTFE) produces a dielectric constant 7×10^3 owing to electrostriction enhancement.[8] On the other hand, formation of electrically conductive composites was achieved by dispersing carbon nanotubes into a polymer matrix,[9,10] or mixing exfoliated graphite with polystyrene.[11] Unlike the general method, herein we present a novel way to create percolative composites by adding insulating fillers instead of conductive fillers into insulating polymer matrix.

It is generally against common sense that adding insulating fillers can form an electrically conductive network in an insulating polymer matrix. However, considering electrically conductive interfaces can be activated by chemical reactions between the added fillers and the matrix, formation of insulator–insulator percolative composites with a high dielectric constant or conductivity becomes reasonable. This indicates a novel path to create percolative composites. Herein we present a percolative composite consisting of potassium carbonate (K_2CO_3) dispersed in a poly(1,1-difluoroethylene) (PVDF) polymeric matrix with a gigantic dielectric constant (2.9×10^6 at 10^3 Hz) and enhanced conductivity (3.6×10^{-3} S m^{-1} at 10^3 Hz) and interpret the mechanism of percolation in the composite in terms of chemically activated interfaces.

Similar to a number of previous experimental results on polymer matrix composites, the dielectric properties of our insulator–insulator composite also increased dramatically near the percolation threshold (Figure 1). The sample containing 23 vol% of K_2CO_3 gained the highest dielectric constant (2.9×10^6 at 10^3 Hz; see Figure 1a) among the investigated compositions. Such enhancement of dielectric constant could be rationalized according to the following power law:[8,12–14]

$$\varepsilon_r = \varepsilon_m \left|\frac{f_c - f}{f_c}\right|^{-q} \qquad (1)$$

where ε_m is the dielectric constant of the insulating matrix, f is the concentration of the added filler, and $f_c \approx 23$ vol.% is a percolation threshold for conduction to occur. The so-called critical exponent, $q \approx 4.23$ is much higher than the value $q \approx 1$ theoretically predicted by a three-dimensional percolation model in composite materials.[7] This indicates that the percolative effect observed here cannot be simply explained in terms of a mixture of PVDF and K_2CO_3. Looking at the phenomenon from the viewpoint of an electrically conductive composite near the percolation threshold (see Figure 1b), it might also be expected that the composite follows a conductor–insulator transition power law;[13] however, again a critical exponent of about 2.38 is found, which is higher than that predicted by theory.[11,12] Similar considerations apply to the dielectric loss, $\tan\delta$, of the composite samples (Figure 1c), which also obeys a power law[13] with a high critical exponent $r \approx 1.25$. On the other hand, beyond the percolation threshold, ε_r, σ, and $\tan\delta$ abruptly decreased. The observed trends were similar to that found for ionic conductivity in composites made of an ionic conducting matrix and insulating fillers, which was explained in terms of interface percolation.[15,16] Therefore we looked for evidence of a percolation process governed by the formation of conductive paths at the interfaces between PVDF and K_2CO_3.

An intriguing aspect of the interface percolation theory is that, unlike the classical percolation theory, it can also explain the abrupt drop down in property observed beyond the percolation threshold f_c. The matrix–filler interface (rather than the bulk filler volume) is the governing feature that

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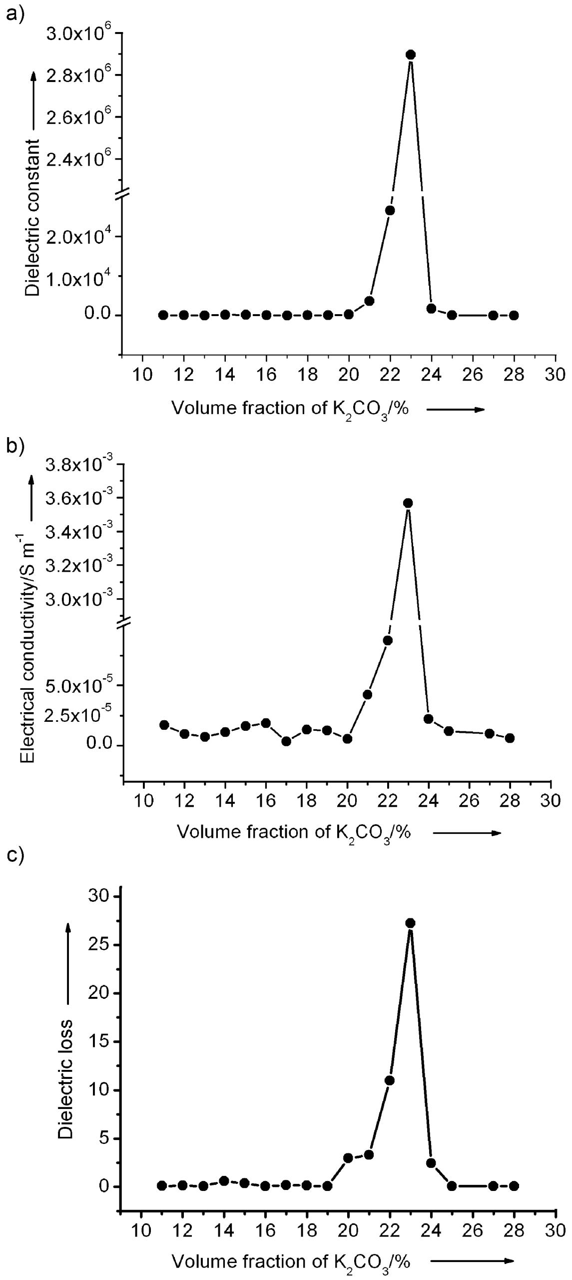

Figure 1. Variations of a) dielectric constant ε_r, b) conductivity σ, and c) dielectric loss tanδ of PVDF-K_2CO_3 composites (at 10^3 Hz) as a function of volume fraction of K_2CO_3.

decides for the conductivity level reached by the composite; therefore, filler fractions $f > f_c$ actually reduce the conductivity level of the composite because they produce filler agglomerates, thus also increasing the filler–filler interface population to the detriment of the matrix–filler interface fraction (Figure 2). So far, the phenomenological facts are rationally explained. But, an open question remains on why two insulating compounds mixed at a threshold volumetric balance can create a composite with a gigantic dielectric constant. A quest for clarifying this intriguing phenomenon challenged us toward deeper analytical characterizations, the results of which are briefly described below.

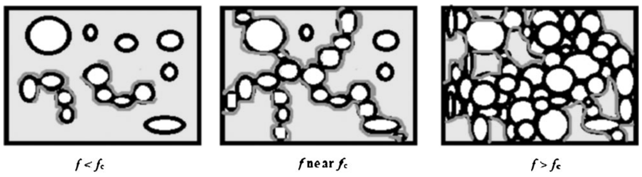

Figure 2. The formation process of the conductive network (dark gray) and its successive annihilation at the interface between PVDF (pale gray) and K_2CO_3 (white) with increasing the concentration of K_2CO_3.

X-ray diffraction (XRD) patterns measured on a set of samples near the percolation threshold indicated that the presence of K_2CO_3 during thermal treatment did not alter the main crystal structure of PVDF. However, after thermal treatment, crystalline KHF_2 appeared in the samples (Figure 3a,b). Note also that after just mixing the constituent phases (that is, before any thermal treatment), the XRD pattern revealed the presence of PVDF and $KHCO_3$ (a byproduct of K_2CO_3 arising from moisture absorption), but the $KHCO_3$ peaks vanished after thermal treatment (Figure 3b). FTIR spectra (Figure 4) indeed confirmed the XRD data. Comparing the FTIR spectrum of PVDF with the spectra of PVDF/K_2CO_3 samples before thermal treatment revealed no shift of the main peaks of PVDF, while there were six additional observable peaks located at around 2620 cm^{-1},

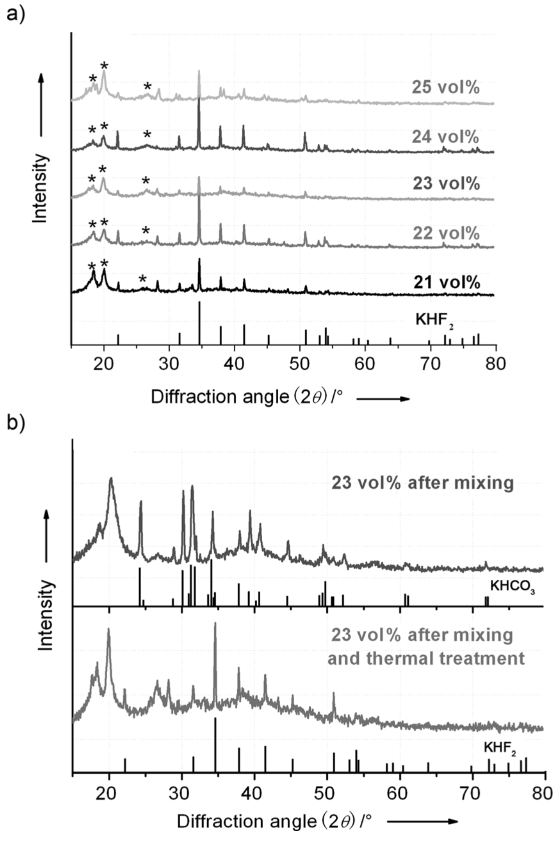

Figure 3. a) XRD patterns measured on the samples containing 21–25 vol% of K_2CO_3 after thermal treatment (peaks belonging to PVDF are denoted by an asterisk). b) XRD patterns measured on the sample containing 23 vol% K_2CO_3 before and after thermal treatment.

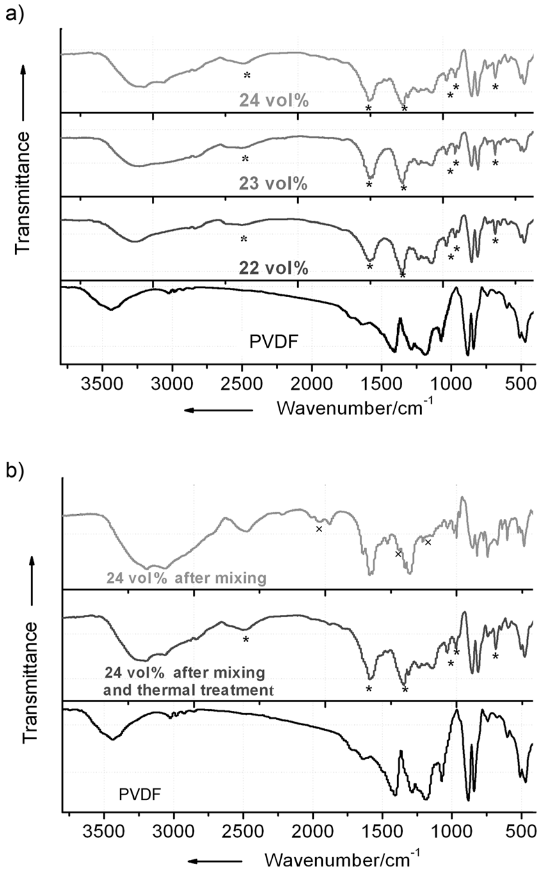

Figure 4. a) FTIR spectra of the samples containing 22–24 vol% K_2CO_3 before thermal treatment (pure PVDF is shown for comparison). b) FTIR spectra of the samples containing 24 vol% K_2CO_3 (pure PVDF is added for comparison). An asterisk and a cross locate the peaks of $KHCO_3$ and KHF_2, respectively.

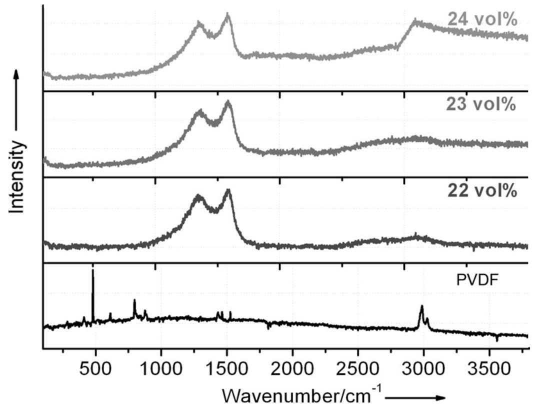

Figure 5. Raman spectra of the samples containing 22–24 vol% K_2CO_3 after mixing and thermal treatment and compared with that of pure PVDF.

1630 cm^{-1}, 1370 cm^{-1}, 1010 cm^{-1}, 980 cm^{-1}, and 705 cm^{-1}, which belonged to $KHCO_3$ (two additional peaks near 1410 cm^{-1} and 833 cm^{-1} overlap the peaks of PVDF at 1410 cm^{-1} and 840 cm^{-1};[17] Figure 4a). Based on the above two sets of data, we conclude that the composite samples before thermal treatment consisted of physically mixed PVDF and $KHCO_3$.

Interestingly, near the interface percolation threshold, the sample containing 24 vol% of K_2CO_3 showed enhanced IR absorption as compared to samples containing 22 or 23 vol% of K_2CO_3. Therefore, we chose this sample for investigating in detail the spectroscopic differences with pure PVDF samples before and after thermal treatment. As shown in Figure 4b, after thermal treatment, three peaks belonging to KHF_2 appeared at around 2040 cm^{-1}, 1440 cm^{-1}, and 1230 cm^{-1}, which supports the hypothesis of formation of KHF_2.[18] Furthermore, a new peak also appeared in the samples after thermal treatment, which will be discussed later. Raman spectra of the composites (Figure 5) showed the appearance of two pronounced bands located at about 1380 cm^{-1} and 1540 cm^{-1}, which can be attributed to activated carbon materials[19] formed in the samples after thermal treatment. Activated carbon materials were generated upon dehydrofluorination of PVDF. Note that analogous phenomena were also observed in a number of previous experiments in which various polymorphs of carbon were formed by chemical[20,21] or physical dehydrofluorination of PVDF.[22] Dehydrofluorination of PVDF can result in the formation of KHF_2 because of the reaction of K_2CO_3 with HF. Because the activated carbon is a conductor, the formation of activated carbon interfaces can lead to the formation of a conductive path in a PVDF/K_2CO_3 composite. Moreover, formation of activated carbon interfaces was further proved by means of transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) (see the Supporting Information). From TEM images, it can be seen that the insulating particles are well enfolded (KHF_2) by an amorphous component (activated carbon), which is further confirmed to be activated carbon according to EDX and Raman spectra. Therefore, it is now possible to explain why the combination of insulating PVDF and K_2CO_3 phases can create a highly conductive percolation trend. IR data in Figure 4b show two peaks at around 2600 cm^{-1} and 1710 cm^{-1} belonging to carboxyl compounds, which appear after thermal treatment. The peaks appearing at 3400–3200 cm^{-1} (vibrational peak of O–H), at 1660–1640 cm^{-1} (vibrational peak of C=O), and at 1020–1000 cm^{-1} (vibrational peak of C–O) clearly indicate the presence of hydroxy and carbonyl groups formed after thermal treatment. Morphological changes in the intervals 1350–1420 cm^{-1} and 1180–1260 cm^{-1} also indicate a change in the environments of C–H bonds and C–F bonds. Brawls et al.[23] showed that KOH can cause dehydrofluorination of PVDF, and during such dehydrofluorination process, some oxygen-containing functional groups are formed. As FTIR spectroscopy shows no vibrational mode of C=C bonds here, the appearance of oxygen-containing functional groups indicate the oxidation of C=C bonds as well.[24] Therefore, we deduce that during decomposition of $KHCO_3$ some H_2O molecules were released and K_2CO_3 reacted with them to form KOH. In other words, KOH activated dehydrofluorination of PVDF and, consequently, the formation of activated carbon under thermal treatment in air. The chemical reactions taking place during thermal treatment were further proved by differential scanning calorimeter (DSC) tests (Figure 6). As seen, the DSC curve of PVDF only includes

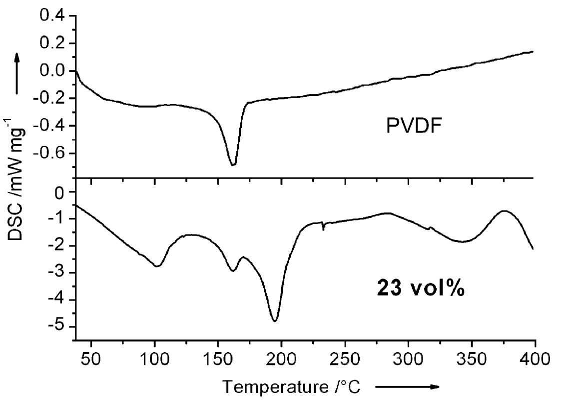

Figure 6. DSC curves of pure PVDF and composite sample containing 23 vol% K_2CO_3.

a peak representing the melting of PVDF, while three additional peaks appear in the DSC curves of the composite tested after mixing. The only peak in the DSC curve of PVDF also indicates that it is unlikely that thermal degradation of PVDF caused the formation of activated carbon in our experiments. For the composite, the peak at around 100°C indicates decomposition of $KHCO_3$, that near 194°C is assigned to the point at which dehydrofluorination of PVDF starts taking place, while the peak located at around 342°C represents the decomposition of KHF_2. The sequence of chemical reactions occurring during thermal treatment can be thus summarized as follows:

$$2\,KHCO_3 \xrightarrow{\text{heat}} K_2CO_3 + CO_2 + H_2O \tag{2}$$

$$K_2CO_3 + H_2O \rightarrow KOH + KHCO_3 \tag{3}$$

$$(CH_2CF_2)_n \xrightarrow[\text{air}]{\text{KOH, 194°C}} \text{activated carbon} + HF \tag{4}$$

$$2\,HF + K_2CO_3 \rightarrow KHF_2 + KHCO_3 \tag{5}$$

$$2\,HF + KOH \rightarrow KHF_2 + H_2O \tag{6}$$

In conclusion, a novel percolative fluoropolymer matrix composite possessing a giant dielectric constant could be prepared by mixing and heating two insulating components: PVDF and K_2CO_3. Near the percolation threshold (ca. 23 vol.%), the dielectric constant reached a dielectric constant value as high as 2.9×10^6 at 10^3 Hz. Above the percolation threshold, the conductivity of the composite did not follow the usual conductor–insulator transition power law and dropped down dramatically. This unusual phenomenon could be explained in terms of interface percolation. Formation of activated carbon at the interface between the K_2CO_3 and PVDF, as observed by Raman spectroscopy and confirmed by FTIR spectroscopy, could rationally explain why combining insulating PVDF and K_2CO_3, a highly electrically conductive composite could be unexpectedly created. The formation of KHF_2 and activated carbon governed a sequence of chemical reactions that spontaneously produced highly conductive internal interfaces. While we discussed this phenomenon as a unique example of successful interface engineering, it could also be more generally interpreted as enhancement of electrical conductivity in bulk polymers through chemically activated interfaces. As a number of interfacial reactions can be conceivably proposed for different polymeric matrix composites, the present results could become a corner stone in the further development of bulk conductive polymers. Therefore, it can be concluded that the PVDF/K_2CO_3 composites might have a great future potential in energy storage applications or in conductive materials application. However, they still face the dilemmas that the dielectric loss is very high or the conductivity is not quite competitive. In this study, we could not improve both properties concurrently, and thus further work should be taken to reduce the dielectric loss while maintaining the giant dielectric constant for energy storage applications, or alternatively, to enhance the conductivity for conductive materials applications.

Experimental Section

The investigated K_2CO_3 (99%, 0.0851–0.2679 g) and PVDF (0.5000 g) were precisely weighed with different volume fractions and mixed for 6 h by ball milling in a nylon jar using ZrO_2 balls. The average particle size of the filler was about 10 μm. After mixing the raw materials, *N*,*N*-dimethyl formamide (DMF) was added to dissolve the PVDF and the mixture was ultrasonically dispersed. Then, alcohol was added to separate the DMF, and the mixture was filtered and grinded to obtain raw powders. The raw powders were later pressed into disks of 1.0 cm in diameter and 0.5–1 mm thickness and heated at 220°C for half an hour. Gold electrodes were sputtered on both parallel faces of the samples using a KYKY SBC-12 sputter coater for the electrical measurements. The dielectric properties of the samples were measured by means of a precision impedance analyzer (Agilent 4294A). An X-ray diffractometer (DX1000, China) with a Cu Kα radiation was utilized to identify the crystal structures. The FTIR spectra were obtained by using a Thermo Electron Corporation Nicolet Nexus 670 FT-IR Spectrometer. A laser Raman spectrograph (JY, Labram HR 800) was employed to observe Raman spectra of the samples, and the DSC curves were acquired by using a differential scanning calorimeter (METTLER-TOLEDO, DSC 823^e).

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