

High-dielectric constant percolative composite of P(VDF-TrFE) and modified multi-walled carbon-nanotubes

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Abstract To develop a high-dielectric constant composite of poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] and multi-walled carbon-nanotubes (MWCNTs) with desirable homogeneity, MWCNTs were treated with a nitro-sulfuric acid by ultrasonication. The chemically modified MWCNTs (a-MWCNTs) were characterized by Fourier transform infrared spectroscopy and a back-titration procedure. Improvement of the dispersibility of a-MWCNTs in polymer matrix, in comparison with unmodified MWCNTs in P(VDF-TrFE), was confirmed by field emission scanning electron microscopy. Electric behavior of the composites with different volume fraction of dispersed carbon nanotubes can be described by percolation theory, as well as the Maxwell–Wagner–Sillars mechanism. The percolation threshold (f_c) of composites with a-MWCNTs ($f_c = 0.0308$) is larger than that of composites with MWCNTs ($f_c = 0.0216$) due to better dispersion of a-MWCNTs in matrix and the reduction of aspect ratio of a-MWCNTs occurred in the modification procedure. The composite with 2.98 vol% (close to the percolation threshold) of a-MWCNTs has a dielectric constant of 592 at 100 Hz and room temperature.

Keywords Composite · Dielectric properties · Multi-walled carbon-nanotubes · Microstructure · Percolation theory

Introduction

In recent years, a lot of efforts have been directed toward the flexible functional polymeric materials with good piezoelectric or ferroelectric responses, such as poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-trifluoroethylene)

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[P(VDF-TrFE)], etc. Their attractive characteristic is of interest not only for the sake of basic research, but also for a significant impact on applications that include high charge-storage capacitors, actuators, sensors, artificial muscles, “smart skins” for drag reduction, and electro-optical response devices, etc. [1–7] Storage and movement of electrical charges are fundamental to electrical and electromechanical responses of such polymers. As a result, it is required to develop polymers with high-electric energy densities, which are dependent on dielectric constant (K) and applied field strength. In general speaking, ferroelectric polymers have dielectric constant much higher than other dielectric polymers for commercial use and can tolerate high-electric field to induce permanent polarization. Nevertheless, their energy densities alone are barely enough to meet the requirement of advanced applications [1]. To overcome this problem, in the past two decades or so, various high-dielectric constant or conducting fillers, either inorganic or organic, were selected as functional fillers to increase the dielectric constant of polymers [1–6]. At the same time, a large amount of filler, mostly in the range of 15–60 %, is still necessary in order to increase the dielectric constant of polymers substantially. To decrease the amount of functional fillers required to give the same performance, recently, scientists have selected carbon nanotubes as the conducting filler due to their large aspect (length/diameters) ratio and unique physical properties, in particular electrical and mechanical [2, 8]. Carbon nanotubes have more opportunities to contact with each other to form percolation network in the composites and enhance the dielectric or conductive abilities of polymers in the range of a few percent or even less [1, 2]. Low volume fractions of the fillers may benefit the reduction of the amounts of voids/defects in the final composite and lead to the improvement of processing and mechanical properties. It should be pointed out that, at the same time, due to incompatibility of carbon nanotubes with polymers, it is hard to disperse homogeneously in the polymer matrix, which will lead to the reduction of breakdown field and increase of dielectric loss which is undesirable for practical application [9, 10]. One solution to this problem lies in the development of an easy modification method of MWCNTs to improve the compatibility with polymers.

In this research, composites of chemically modified multi-walled carbon-nanotubes (MWCNTs) embedded in P(VDF-TrFE) 70/30 mol % copolymer matrix were therefore developed. P(VDF-TrFE) copolymer was chosen in view of the fact that it belong to the most thoroughly studied polymeric ferroelectrics and the first polymer example with well-defined ferroelectric transition behavior [6, 11–14]. P(VDF-TrFE)s have thermodynamically stable spontaneous polarization states switchable by application of a sufficiently strong external electric field. Studies on ferroelectric polymers are increasingly motivated by their exceptionally excellent dielectric, piezoelectric, pyroelectric, ferroelectric, and electro-optic properties. P(VDF-TrFE) 70/30 mol% copolymer used here has a dielectric constant as high as about 14, which is an important factor as for such composite a polymer matrix with higher dielectric constant is preferred. In addition, the dielectric constant of P(VDF-TrFE) can be further increased substantially when it is treated with high-energy electron irradiation, hence converts the coherent polarization domain (all-trans chains) in normal ferroelectric P(VDFTrFE) into nanopolar regions, thus transforming the material into a relaxor-like system [12, 13]. To improve the compatibility of MWCNTs and P(VDF-TrFE), MWCNTs were ultrasonically

treated with a nitro-sulfuric acid to introduce them with polar carboxylic groups (–COOHs). It is found that, the flexible composites of P(VDF-TrFE) and chemically modified MWCNTs indeed exhibit enhanced dielectric response, as well as more finely dispersed morphology in comparison with the simple blend of unmodified MWCNTs and P(VDF-TrFE).

Experimental

Materials

The P(VDF-TrFE) 70/30 mol % copolymer with a weight-averaged molecular weight of 200,000 was purchased from Solvay and Cie, Bruxelles, Belgium. MWCNTs were supplied by Shenzhen Nanotechnologies Port Co. The MWCNTs were prepared by a chemical vapor deposition method with a purity of carbon content more than 95 % and a content of amorphous carbon of 2 %. The diameter of the MWCNTs is 40–60 nm, the length is 5–15 μm , and the specific surface area is 40–300 m^2/g .

Chemical modification of MWCNTs

The modification procedure of MWCNTs was briefly depicted as follows. MWCNTs (1.0 g) in a breaker with 200 mL of nitro-sulfuric acid [3:1 (v:v) mixture of H_2SO_4 (98 %)/ HNO_3 (68 %)] were sonicated at an acoustic power level of ca. 200 W at 40 °C for 3 h. Afterwards, the mixture was filtered and the carboxylated MWCNTs were washed with deionized water until pH was 7.0. The final product, labeled here as a-MWCNTs, was obtained after drying under vacuum at 70 °C till the weight is stable.

Preparation of films

Composite films were prepared using solution cast method. For the composites of P(VDF-TrFE) and MWCNTs [referred to here as P(VDF-TrFE)/MWCNTs] with volume fractions of MWCNTs of 0.0042, 0.0086, 0.012, 0.0175, 0.0205, and 0.0218, respectively, a predetermined amount of MWCNTs was added to the solution of P(VDF-TrFE) in dimethylformamide (DMF), and then the mixture was ultrasonically stirred for about 2 h in order to make the fillers well dispersed. Afterwards, the mixture was poured onto a glass slide and dried in air at 70 °C for 12 h, followed by thoroughly removal of solvent residue under vacuum at 70 °C for 12 h. Finally, the films were annealed at 140 °C in vacuum for 12 h and slowly cooled down to room temperature (10 °C/h). The typical film thickness is 40 μm . The preparing procedure of the films of the composites of P(VDF-TrFE) and a-MWCNTs [named as P(VDF-TrFE)/a-MWCNTs] with volume fraction of a-MWCNTs of 0.0043, 0.0085, 0.0130, 0.0212, 0.0268, 0.0298, and 0.0311, respectively, was the same as that of P(VDF-TrFE)/MWCNTs. For the electric characterization, the films were cut into small pieces of 5 × 5 mm, and circular gold electrodes with 2.5 mm radius were sputtered in the center on both surfaces of each sample.

Instruments and measurement

FT-IR spectra were recorded with the sample/KBr powder pressed pellets using a Bruker Vector-22 FT-IR spectrometer. The cross-sections of the composites fractured in liquid nitrogen were observed with a LEO 1,550 field emission scanning electron microscopy (FESEM). For thermal analysis, a Perkin-Elmer DSC-2C calorimeter was used at a heating rate of 20 °C/min, and the sample mass was typically 5 mg. The elastic modulus was determined with a Dynamic mechanical thermal analyzer (Rheometric Scientific, Inc., DMTA-V) at 1 Hz and room temperature. For the characterization of frequency dependence of the dielectric properties from 100 Hz to 1 MHz, an Agilent 4194A Impedance analyzer was used, and the dielectric constant K of the film was calculated by the formula of a parallel plate capacitor as $K = Ct/\epsilon_0 A$, where C is the capacitance of the metal–insulator–metal element, ϵ_0 is the vacuum dielectric permittivity, A is the area of the electrode, and t is the thickness of the capacitor, respectively.

Results and discussion

Chemical modification of the MWCNTs

Treating MWCNTs with the nitro-sulfuric acid to introduce –COOHs on the surface of MWCNTs is a feasible and relatively simple method. In order to characterize the modification result of MWCNTs, FT-IR spectra of the raw MWCNTs and the a-MWCNTs were obtained, which are illustrated in Fig. 1. For the unmodified multi-walled carbon-nanotubes, the absorption band at 3,000–2,800 cm^{-1} arises from –CH– stretching, and the absorption band at 3,421 cm^{-1} is intrinsic to –OH stretching. The presence of –CH– indicates that MWCNTs used here contain structural defects, which are formed during the manufacture procedure. For the FTIR spectrum of carbon nanotubes treated with mixed acid, the characteristic absorption band at 1,724 cm^{-1} is attributed to the stretching vibration of carbonyl group of –COOH. The absorption bands at 1,610–1,550 cm^{-1} , 3,000–2,800 cm^{-1} , and 3650–3050 cm^{-1} correspond to the –COO[–] symmetric stretching, –CH– stretching and stretching vibration of hydroxyl group of –COOH overlapped with that of –OH, respectively [15]. The absorption bands at 2,337 and 2,362 cm^{-1} result from the influence of carbon dioxide present in the atmosphere.

The –COOH groups on the surface of a-MWCNTs after chemical modification was titratable with standardized aqueous alkali in a back-titration procedure. It was calculated that every kilogram of a-MWCNTs contains 1.83 mmol of –COOHs.

Microstructure of the composites

To compare the dispersing condition of MWCNTs and a-MWCNTs in P(VDF-TrFE) matrix, field emission scanning electron microscopy was used to observe the cross-sections of the film specimens. It was obviously found in Fig. 2 that in P(VDF-TrFE)/MWCNTs sample with 2.05 vol% of MWCNTs the raw MWCNTs

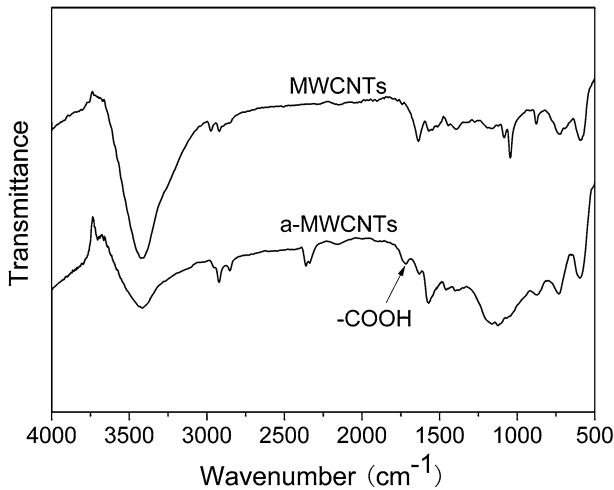


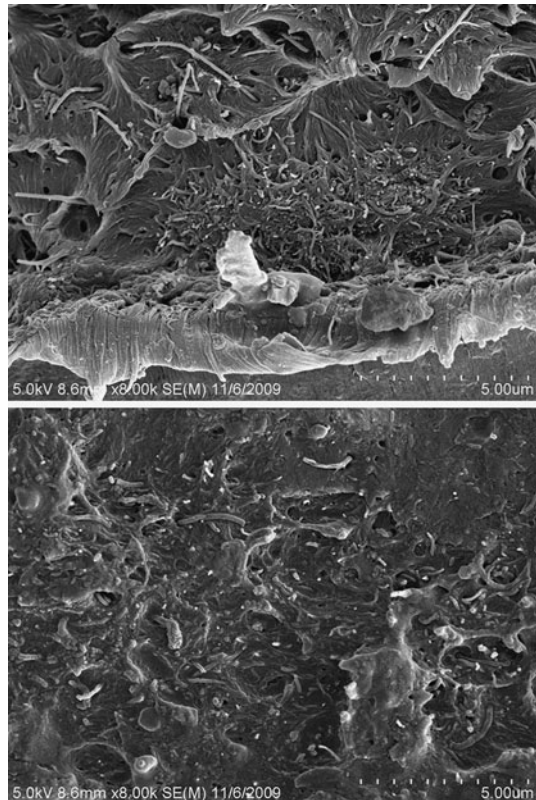
Fig. 1 FT-IR spectra of MWCNTs and a-MWCNTs

are easy to agglomerates in the P(VDF-TrFE) matrix, while much good dispersion of the a-MWCNTs can be found in the P(VDF-TrFE)/a-MWCNTs composite with 2.98 vol% of a-MWCNTs, although the filler concentration is higher than that of P(VDF-TrFE)/MWCNTs. What's more, some of the raw MWCNTs are pulled out in the P(VDF-TrFE)/MWCNTs during the fracture process, meanwhile, in the P(VDF-TrFE)/a-MWCNTs, less extraction trace was observed and most fractured a-MWCNTs are embedded in P(VDF-TrFE) matrix tightly. The origin behind this phenomenon results from the difference of the compatibility between fillers and copolymer matrix of the two composites. After chemical modification, the polarity of a-MWCNTs was increased, which contributes to the improvement of compatibility of the P(VDF-TrFE)/a-MWCNTs composite [9]. The well compatibility of a-MWCNTs with P(VDF-TrFE) matrix will improve the electrical properties as well as the processing properties of the composite.

Figure 3 shows the DSC curves of P(VDF-TrFE) and its two composites. In comparison with the pure P(VDF-TrFE), the melting points of the two composites decrease by nearly 5 °C. In addition, the enthalpy of fusion of P(VDF-TrFE), P(VDF-TrFE)/MWCNTs, and P(VDF-TrFE)/a-MWCNTs is 29.1, 25.1, and 24.6 J/g, respectively, which means that the degree of crystallization of P(VDF-TrFE) was reduced after introduction of either MWCNTs or a-MWCNTs. The decreasing of both the melting point and the enthalpies of fusion of composites can be explained by the presence of MWCNTs and a-MWCNTs as heterogeneity which hindered the crystal perfection and the reduced lamellar thickness of P(VDF-TrFE) crystallites [16, 17].

Previous researchers have reported that P(VDF-TrFE) exhibits a ferroelectric-paraelectric (F–P) phase transition [18, 19]. Below the F–P transition, the crystal has an ordered structure with long sequences of all-trans molecular conformation. Above the phase transition temperature (Curie temperature), an increasing number of gauche conformations are introduced. Therefore, the polarity in the crystal regions decreases. The DSC data show that the Curie temperature is almost the same

Fig. 2 Cross-sectional SEM photographs of films of the P(VDF-TrFE)/MWCNTs with 2.05 vol% of MWCNTs (*above*) and the P(VDF-TrFE)/a-MWCNTs with 2.98 vol% of a-MWCNTs (*below*)



for P(VDF-TrFE) (106.1 °C) and the two composites. It means that the volume of the introduced MWCNTs and a-MWCNTs in composites is too large to be included in the crystalline regions of P(VDF-TrFE), therefore has no influence on F–P phase transition of the copolymer.

Electrical properties of the composites

Figure 4 gives the conductivity of P(VDF-TrFE)/MWCNTs and P(VDF-TrFE)/a-MWCNTs versus volume fraction of MWCNTs and a-MWCNTs (referred to as f_{MWCNTs} and $f_{\text{a-MWCNTs}}$) separately at 100 Hz and room temperature. It is noticeable that the conductivity data for both composites exhibit conductor–insulator transition behavior, characterized by an abrupt discontinuity of the data points, at $f_{\text{MWCNT}} = 0.017\text{--}0.022$ for P(VDF-TrFE)/MWCNTs and $f_{\text{a-MWCNT}} = 0.027\text{--}0.031$ for P(VDF-TrFE)/a-MWCNTs, respectively. Such a phenomenon can be predicted using percolation theory which allows one to describe using laws of power the conductivity of the composites (σ) near the conductor–insulator transition as follows [2]:

$$\sigma \propto \sigma_m (f_c - f)^{-s} \quad f < f_c \quad (1)$$

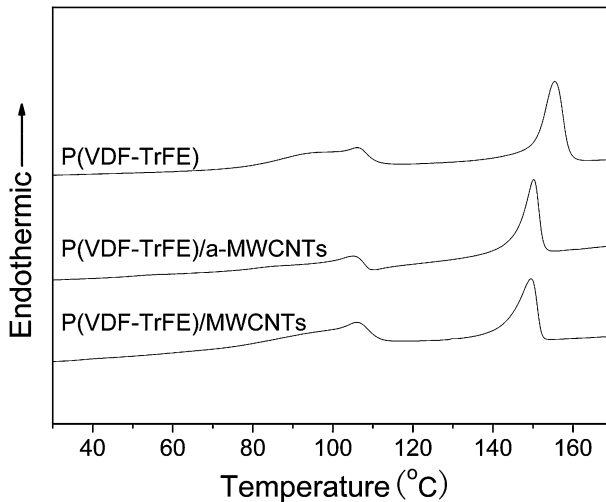


Fig. 3 DSC curves of pure P(VDF-TrFE), P(VDF-TrFE)/MWCNTs with 2.05 vol% of MWCNTs and P(VDF-TrFE)/a-MWCNTs with 2.98 vol% of a-MWCNTs

where σ_m is the conductivity of the P(VDF-TrFE) copolymer matrix, f is the filler concentration, f_c is the percolation threshold, and s is the critical exponent in the insulating region. The percolation occurs when isolated phases begin to interconnect with each other and finally form a network or cluster structure that spans the entire insulating matrix. As shown in the insets of Fig. 4, fitting the conductivity data to the log–log plots of the power laws yields $f_c = 0.0216$ and $s = 0.90$ for the P(VDF-TrFE)/MWCNTs samples and $f_c = 0.0308$ and $s = 0.95$ for the P(VDF-TrFE)/a-MWCNTs composites. While the critical exponents of both composites are in accordance with the universal value, which is in the range of 0.8–1.0 for three-dimensional lattices assumed by standard percolation theories, either the concentration of MWCNTs or that of a-MWCNTs required to approach percolation is far below the value (14–16 %) commonly obtained in a perfectly two-phase random three-dimensional percolative system when the conducting fillers with micron scale and sphere shape are used [1, 2, 20]. We will come back to this point later.

Compared in Fig. 5 are the evolution of dielectric constant of P(VDF-TrFE)/MWCNTs and P(VDF-TrFE)/a-MWCNTs versus volume fraction of MWCNTs and a-MWCNTs, respectively, recorded at 100 Hz and room temperature. As expected, the remarkable enhancement of dielectric constant of both composites is realized near the percolation thresholds. For example, the P(VDF-TrFE)/MWCNTs composite with 2.05 vol% of MWCNTs exhibits a dielectric constant of 340, while for the P(VDF-TrFE)/a-MWCNTs sample with 2.98 vol% of a-MWCNTs, the dielectric constant reaches 592, about 42 times higher than that of the pristine P(VDF-TrFE). Presented in Fig. 6 is the frequency dependence of dielectric constant of the P(VDF-TrFE)/a-MWCNTs films with different volume fraction of a-MWCNTs collected at room temperature. It is observed in Figs. 5 and 6 that, both composites have critical values of filler concentration which affect the dielectric

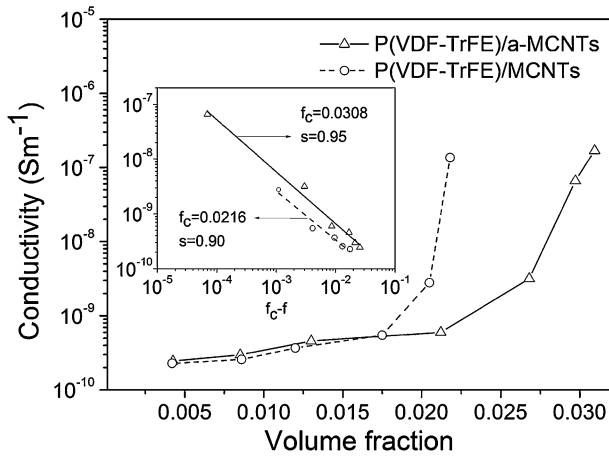
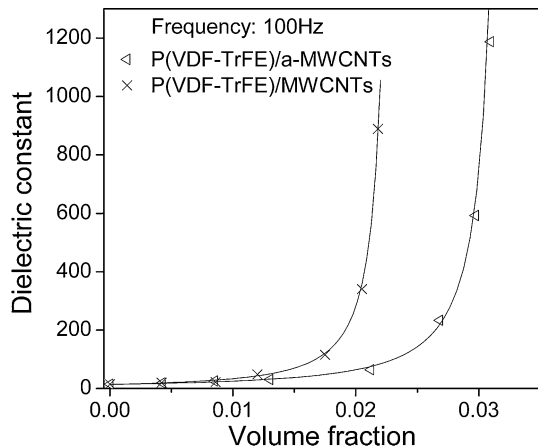


Fig. 4 Dependence of the conductivity of P(VDF-TrFE)/MWCNTs and P(VDF-TrFE)/a-MWCNTs on volume fraction of the carbon nanotubes measured at room temperature and 100 Hz. Inset shows the best fits of the conductivity to Eq. 1

Fig. 5 Dependence of dielectric constant of P(VDF-TrFE)/MWCNTs and P(VDF-TrFE)/a-MWCNTs on volume fraction of carbon nanotubes measured at 100 Hz and room temperature. Solid curves represent the fits of the experimental data to Eq. 2

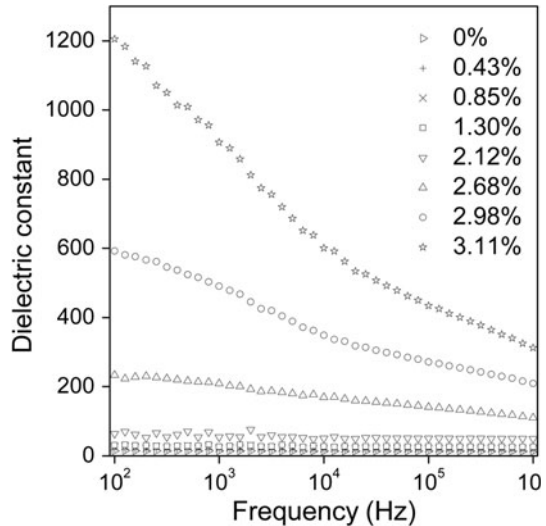


constant remarkably: the dielectric constants of the P(VDF-TrFE)/MWCNTs with f_{MWCNTs} less than 1.75 vol% and P(VDF-TrFE)/a-MWCNTs with $f_{\text{a-MWCNTs}}$ less than 2.12 vol% are slightly dependent on the volume fraction of fillers, while those of the composites with higher loading of fillers increase abruptly with increasing volume fraction of carbon nanotubes.

It has been recognized that a heterogeneous mixture of a conductive phase and an insulating dielectric phase exhibits sharp change in dielectric constant when the volume fraction of randomly dispersed conductive fillers is in the vicinity of the percolation threshold [21, 22]:

$$K = K_m \cdot \left(\frac{f_c - f}{f_c} \right)^{-q} \quad f < f_c \quad (2)$$

Fig. 6 Low-field dielectric constant of P(VDF-TrFE)/a-MWCNTs films with different volume fraction of a-MWCNTs as functions of frequency from 100 Hz to 1 MHz measured at room temperature



where K and K_m are the dielectric constant of the composite and matrix, respectively, and q is a critical exponent. The remarkable enhancement of dielectric constant as filler concentration approaches to f_c can be understood if one takes into account the fact that at the percolation threshold point there are many conducting nanotubes isolated by thin dielectric layers. Thus, a heterogeneous system in the neighborhood of the percolation threshold could become a capacitor with excellent characteristics of charge storage [23]. On the other hand, under an AC electric field, the inhomogeneous electric field distribution in polymer matrix can lead to much enhanced dielectric constant in the percolative composites [24].

Fitting the data in Fig. 5 using Eq. 2 yields $f_c = 0.0216$ and $q = 1.63$ for P(VDF-TrFE)/MWCNTs and $f_c = 0.0308$ and $q = 1.62$ for P(VDF-TrFE)/a-MWCNTs. Both critical exponents are in good agreement with the universal values, which is in the range of 1.6–2.0 for three dimensional composites [25]. At the same time, the percolation thresholds here are the same as those observed in the inset of Fig. 5, which are far below the value (14–16%) of common two-phase random composites. This same behavior has been reported in such kind of polymer/conductive filler composites [1, 2, 26]. For polymer/MWCNT systems, the reported percolation thresholds are distinct from each other and can differ by several folds depending on the different aspect ratio of MWCNT, the diversity of polymer matrix materials, and discrepancy in preparation of the composites, etc. One origin of such a behavior is that, geometrical shapes of the rod-like inclusions used here play a crucial role in the percolation threshold, since the intersection probability of such fillers is much higher than spherical ones, thus facilitates the formation of percolation network at lower concentration than 0–3 composites [1, 2]. Another origin to this behavior should be the fact that the large interface-to-volume ratios of the nanotubes intensify their interaction with P(VDF-TrFE). Space charge accumulation (Maxwell–Wagner–Sillars mechanism) and short-range dipole–dipole interaction (exchange coupling mechanism) at the two-phase boundary result in interfacial polarizations [1, 19, 27].

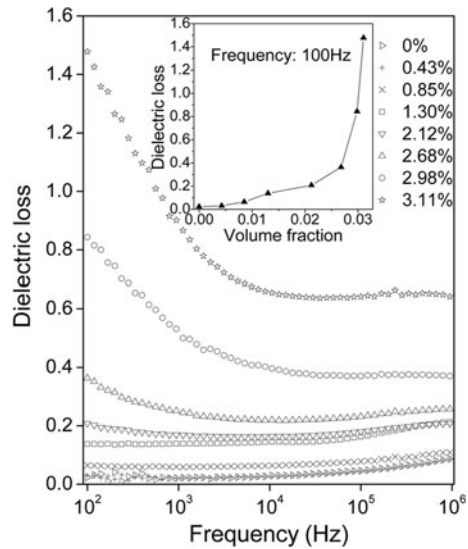
It was obviously demonstrated in Figs. 4 and 5 that the percolation threshold of P(VDF-TrFE)/a-MWCNTs (0.0308) is higher than that of P(VDF-TrFE)/MWCNTs (0.0216). Such a phenomenon can be attributable to at least two characteristics of the composites. First, in comparison with the P(VDF-TrFE)/a-MWCNTs, there are more micro aggregates in the P(VDF-TrFE)/MWCNTs composite as observed in FESEM micrograph due to undesirable compatibility of MWCNTs with P(VDF-TrFE), which will leads to the formation of continuous percolation networks at lower filler concentration. Second, fracture of some nanotubes will inevitably occur when under ultrasonic processing. As a result, the aspect ratio will be decreased, which will result in the reduction of intersection probability of a-MWCNTs in the P(VDF-TrFE)/a-MWCNTs sample. It should be pointed out that, the dielectric constant of P(VDF-TrFE)/a-MWCNTs (592, $f_{a-MWCNTs} = 2.98 \text{ vol}\%$) in the neighborhood of percolation threshold represents an increase of nearly 75 % in comparison with that of P(VDF-TrFE)/MWCNTs (340, $f_{MWCNTs} = 2.05 \text{ vol}\%$). The possible origin may be lie in the higher a-MWCNTs concentration as well as more uniform distribution of a-MWCNTs in the P(VDF-TrFE)/a-MWCNTs sample. It is also interesting to note that, even up to 1 MHz, the dielectric constant of P(VDF-TrFE)/a-MWCNTs still more than 210.

Figure 6 also demonstrates that, the experimental data of P(VDF-TrFE)/a-MWCNTs samples with $f_{a-MWCNTs}$ less than 2.12 vol% are slightly dependent on frequencies, while those of the composites with higher loading of a-MWCNTs drops more rapidly with increasing frequency over the observed frequency range. The dielectric dispersion probably results from Maxwell–Wagner–Sillars (MWS) space charge phenomenon [28], which exists in the composites having large differences in either dielectric constant or conductivity between parent polymer and fillers.

Frequency dependence of the dielectric loss for P(VDF-TrFE)/a-MWCNTs composites with different volume fraction of a-MWCNTs at room temperature is presented in Fig. 7. Similarly to the change in the dielectric constant with $f_{a-MWCNTs}$, the dielectric loss increases with the volume percentage of a-MWCNTs (especially as $f_{a-MWCNTs} > 2.12 \%$), which is inconsistent with the classic percolation theory which points out that the dielectric loss should not change with $f_{a-MWCNTs}$ at $f_{a-MWCNTs} < f_c$. A similar phenomenon has also been observed by other researchers [2, 22]. As a matter of fact, there exists little compositional fluctuation in the composites, and the sub-phases in which $f_{a-MWCNTs}$ is above the average volume percentage of a-MWCNTs can probably lead to parallel paths. This behavior can affects the imaginary part of the dielectric constant quite significantly especially as the $f_{a-MWCNTs}$ approaches f_c [22].

The dependence of the dielectric loss at 100 Hz and room temperature on $f_{a-MWCNTs}$ is more clearly demonstrated in the inset of Fig. 7 which is derived from the loss-frequency data. It is noted that, at the neighborhood of the percolation threshold, dielectric loss undergoes a sharp increase. At 100 Hz, P(VDF-TrFE)/a-MWCNTs with 2.98 vol% of a-MWCNTs exhibits a dielectric loss of about 0.84. Furthermore, at most of the frequency range observed (above 1.2 kHz) the dielectric loss of P(VDF-TrFE)/a-MWCNTs is lower than 0.50 which is very attractive for many practical applications.

Fig. 7 Low-field dielectric loss of P(VDF-TrFE)/a-MWCNTs with different volume fraction of a-MWCNTs measured at room temperature as functions of frequency from 100 Hz to 1 MHz. *Inset* shows the dependence of the dielectric loss on volume fraction of a-MWCNTs at 100 Hz



The composite of P(VDF-TrFE)/a-MWCNTs with 2.98 vol% of a-MWCNTs not only possesses high dielectric response, but also the flexibility of the pristine copolymer due to the low percolation threshold; its elastic modulus is 916 MPa measured at 1 Hz and room temperature, which is close to that of the parent copolymer (910 MPa).

Conclusions

In summary, a high-dielectric constant percolative composite was fabricated by embedding chemically modified multi-walled carbon-nanotubes into poly(vinylidene fluoride-trifluoroethylene) matrix. The composite exhibits more uniform homogeneity as compared with the blend of P(VDF-TrFE) and unmodified carbon-nanotubes. The dielectric constant of P(VDF-TrFE)/a-MWCNTs with 2.98 vol% of a-MWCNTs reaches 592 at 100 Hz, and still more than 210 even up to 1 MHz. In addition, it still remains flexible. Further property improvement can be expected through the amelioration in the composite fabrication process, especially by grafting the carbon-nanotubes to polymer backbone to further increasing the distribution uniformity of the carbon-nanotubes in polymer matrix.

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