

Fabrication, Characterization, and Electrical Properties of Multiwall Carbon Nanotube-Ag Hybrid/PVDF Nanocomposites

Saowarat Sirikamalat^{*} Dr.Apiwat Chompoosor^{**} Dr.Prasit Thongbai^{***}

ABSTRACT

Silver (Ag) nanoparticles with a size of ≈ 10 nm were discretely deposited on the surfaces of multiwall carbon nanotubes (MWCNTs) with different Ag/MWCNT ratios. The dielectric properties of three-phase percolative nanocomposites of MWCNTs-Ag hybrid/ poly(vinylidene fluoride) (PVDF) prepared by mixing them in *N,N*-dimethylformamide (DMF) and hot-pressing were investigated. Near the critical MWCNT-Ag concentration, *i.e.*, the percolation threshold (f_c), the dielectric permittivity (ϵ') of MWCNT-Ag hybrid/PVDF nanocomposites drastically increased by a factor of >50 compared to that of a pure PVDF polymer matrix ($\epsilon' \approx 10$). Notably, the dielectric loss tangent ($\tan\delta$) remained low ($\tan\delta < 1$). It was found that f_c decreased as the Ag/MWCNT ratio was reduced. The MWCNTs-Ag hybrid/PVDF nanocomposites with high ϵ' and low $\tan\delta$ displayed good flexibility since they had low concentrations of MWCNTs and Ag. The dielectric properties could be described by the percolation theory based on space charge polarization.

Keywords: Nanocomposites, Dielectric permittivity, Percolation theory

^{*} Student, Master of Science Program in Materials Science and Nanotechnology, Faculty of Science, Khon Kaen University

^{**} Assistant Professor, Nanotec-KKU Center of Excellence on Advanced Nanomaterials for Energy Production and Storage, Department of Physic, Faculty of Science, Khon Kaen University

^{***} Assistant Professor, Integrated Nanotechnology Research Center (INRC), Department of Physic, Faculty of Science, Khon Kaen University

Introduction

Polymeric dielectric materials have received considerable attention as electronic materials since they have good flexibility and very high electric breakdown strength (Zhou *et al.*, 2011; Poh *et al.*, 2016). Compared to ceramic materials, however, the dielectric properties of polymer materials are usually poorer than those of ceramics (Kuang *et al.*, 2013; Siddabattuni *et al.*, 2013). The dielectric permittivity of polymers is very low of $\epsilon' < 15$. Development of polymer dielectric materials has been focused on enhancing the ϵ' value of the polymer while retaining its flexibility (Wang *et al.*, 2012). The conventional method to increase ϵ' values of a polymer is to incorporate ceramic particles that have a very high ϵ' such as BaTiO_3 and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ into the polymer matrix, forming ceramic-polymer composites. Unfortunately, high ϵ' values for such a composite system can be achieved only when the ceramic particles used comprised as much as 50 vol% . This can cause a degradation of the mechanical properties of the polymer and a loss of its flexibility (Hayashida *et al.*, 2013).

The dielectric properties of poly(vinylidene fluoride) (PVDF) have been widely studied due to its high $\epsilon' \approx 10$ compared to other polymeric materials (Xu *et al.*, 2017). However, the ϵ' of PVDF is still too low for practical use in electronic devices such as capacitors (Dang *et al.*, 2012). Up to now, filler materials that have been used to enhance the ϵ' value of PVDF. These fillers included ceramic particles, metal particles, organic materials, and carbon nanotubes (Dang *et al.*, 2012). Different filler materials showed distinct mechanisms to increase the ϵ' value of polymeric matrices.

Conductive fillers including carbon black, carbon nanofiber, multiwall carbon nanotubes (MWCNTs) have been widely used in PVDF composites to increase ϵ' (Dalmás *et al.*, 2006; Yang *et al.*, 2009). This type of composite usually exhibits a very high ϵ' . Among these fillers, MWCNTs in polymeric matrices have received great attention as percolative composites (Dang *et al.*, 2007). This is because MWCNTs have low weight, large internal surface areas and large aspect ratios (Nan *et al.*, 2010). This can lead to lower percolation thresholds in nanocomposites thereby increasing their ϵ' value. Additionally, low MWCNT loadings not only greatly increased ϵ' , but also enabled the polymer to retain its flexibility. Although, MWCNTs/ polymer composites can exhibit high ϵ' values, these composites showed high dielectric loss tangents ($\tan \delta \gg 10$). This is because the MWCNTs can easily form conducting paths in a polymer matrix, resulting in increased conductivity and $\tan \delta$. These are unsuitable for many applications. The potential use of MWCNTs/ polymer composites has not been fully realized. To prevent the formation of conducting paths in polymer composites, Ag-NPs were usually used to induce the Colomp block effect (Dang *et al.*, 2012).

In the present work, we proposed a new strategy in which Ag nanoparticles were persistently deposited on the surface of MWCNTs through a chemical reaction. Ag-deposited MWCNTs (denoted as MWCNTs-Ag) hybrid particles were synthesized via functionalized MWCNTs with carboxylate groups (COO^-) onto their surfaces and Ag^+ interacts with MWCNTs electrostatically. Ag nanoparticles (AgNPs) with a size of about 10 nm were discretely grown on the surfaces of the MWCNTs. The resulting MWCNTs-Ag hybrid particles were used as fillers into PVDF.

Our results showed that the dielectric properties of PVDF can be improved by incorporating MWCNTs-Ag into PVDF.

Objective of the study

To greatly enhance the dielectric permittivity of PVDF polymer nanocomposites by incorporating with MWCNTs-Ag.

Materials and Methods

Materials

Multiwall carbon nanotubes (6-9 nm in diameter, 5 μ m in length and carbon purity >95%), poly(vinylidene fluoride) (PVDF), *N,N* dimethylformamide, (DMF) were obtained from Sigma-Aldrich. Nitric acid (HNO₃ 65%), sodium borohydride (NaBH₄ 98%), sodium hydroxide (NaOH 99%), were purchased from Merck chemicals. Silver nitrate (AgNO₃, 99%) was obtained from QRecTM

Synthesis of MWCNTs-COO⁻

To produce oxidized MWCNTs (MWCNTs-COOH), 3 g of pristine MWCNTs was suspended in 250 ml of 65% (w/w) HNO₃ and sonicated for 2 h and then the suspension was stirred for 48 h at room temperature. The resulting suspension was centrifuged washed with deionized water until pH was neutral. At last, the resulting MWCNTs-COOH was dried at 80°C overnight (Ahmadpoor *et al.*, 2013). To convert the carboxyl groups into carboxylate (MWCNTs-COO⁻), MWCNTs-COOH was suspended in a 250 ml of 0.04 N NaOH and sonicated for 2 h then the suspension stirred for 48 h at room temperature. The resulting suspension was centrifuged and washed with deionized water until the neutral pH. The solid particles were dried at 80°C overnight. Finally, MWCNTs-COO⁻ particles were obtained. (Ahmadpoor *et al.*, 2013)

Synthesis of MWCNTs-Ag

10 mg of MWCNTs-COO⁻ was suspended in 0.1 M of AgNO₃. The number of the AgNPs can be easily controlled by the amount of AgNO₃ used. In a typical procedure, 0, 0.46, 0.92, 2.5, 5, 9.3, 14 and 18.5 ml of AgNO₃ (0.1 M) were used to produce MWCNTs-Ag with ratios (w/w) of 1/0, 1/0.5, 1/1, 1/3, 1/5, 1/10, 1/15 and 1/20, respectively (abbreviated as the MWNCTs, MWNCTs-0.5Ag, MWNCTs-1Ag, MWNCTs-3Ag, MWNCTs-5Ag, MWNCTs-10Ag, MWNCTs-15Ag, and MWNCTs-20Ag powder samples, respectively). After that 0, 0.46, 0.92, 2.5, 5, 9.3, 14 and 18.5 ml of 0.01 M of NaBH₄ was added to each of the MWCNTs-Ag, respectively. The resulting suspension was centrifuged 3 times in deionized water. Finally, the resulting MWCNTs-Ag powders were dried at 80°C overnight (Ahmadpoor *et al.*, 2013).

Preparation of MWCNTs-Ag/PVDF Composites

MWCNTs-Ag/PVDF composites were fabricated using a simple blending and hot-pressing process, which is described as follows. First, all MWCNTs-Ag/PVDF composites with 0-0.3 volume fractions of MWCNTs-Ag filler were prepared by suspending an appropriate amount of MWNCTs-Ag powders in DMF with ultrasonic treatment for 1 h. At the same time, the PVDF powder was also dissolved in DMF. Second, the suspensions of fillers in DMF were

added to PVDF solutions, and the mixture was treated ultrasonically for 1 h and further mixed for 6 h using a magnetic stirrer. Then, the hybrid-phase composites were obtained by precipitation of the compositions in deionized water during centrifugation at 4500 rpm for 5 minutes and drying in an oven at 80°C. Finally, the MWCNTs-Ag/PVDF composites samples were made by molding the dried composites at 200 C for 30 min under a uniaxial compressive stress of 95 MPa.

Characterizations

The phase constituents of the MWCNTs-Ag particles were examined using an X-ray diffractometer (XRD; Philips PW3040 with Cu K α radiation, $\lambda = 0.15406$ nm). The diffraction patterns were collected over the range of $2\theta = 25^\circ$ - 65° with step increase of $0.02^\circ/\text{min}$. A transmission electron microscope (TEM, TECNAI G2 20) was also employed to observe the microstructure of MWCNTs-Ag hybrid particles. The TEM samples were prepared by drying a droplet of the Ag-MWCNTs suspension on a copper grids coated carbon film. The dielectric and electrical properties were measured using an Agilent 4194A impedance analyzer in the frequency range from 100 Hz to 10 MHz at room temperature with an oscillation voltage of 500 mV.

Results and Discussion

In this study, deposition of Ag on the MWCNTs was obtained through control of the stoichiometry of Ag nanoparticles. Figure 1 shows a schematic diagram of deposited MWCNTs with Ag nanoparticles. Carboxylic acid was induced by HNO₃ on the surface of MWCNTs. After treatment of MWCNTs with NaOH, MWCNTs contained carboxylate groups on its surface and could be used as a nucleation sites for deposition of Ag. Modified MWCNTs had improved hydrophilic properties, making them more dispersible in water (Cheng *et al.*, 2013). Ag⁺ ions can interact with COO⁻ on MWCNTs through electrostatic interaction. The NaBH₄ solution gave *in situ* reduction of Ag⁺.

Figures 2 shows TEM images of MWNCTs-5Ag, MWNCTs-10Ag, MWNCTs-15Ag, and MWNCTs-20Ag filler samples, respectively. TEM images revealed that the spherical Ag nanoparticles were discretely grown on the MWCNTs surfaces. Ag nanoparticles with a particle size of ≈ 10 nm were distributed on the surfaces of MWCNTs. Agglomeration of Ag particles was also observed in the MWNCTs-20Ag sample. For other filler samples with lower Ag contents, it was found that the Ag nanoparticles are strongly bounded to the surface of MWCNTs, which would be good for the maintenance of the MWCNTs-Ag hybrid structure in polymer nanocomposites.

Figure 3 displays the XRD patterns of the MWCNTs-15Ag hybrid particles. Diffraction peaks at $2\theta \approx 38.2^\circ$, 44.3° , 64.4° and 77.4° can be ascribed to the crystalline planes of the silver phase, corresponding to the (111), (200), (220), and (311) planes, respectively. It was further observed that the nanocrystalline silver phase had a strong (111) orientation along the nanotubes' axial direction since the specific free energy of silver is minimal on the (111) plane of the face center cubic structure (Peng *et al.*, 2012). No characteristic diffraction peak of other silver forms appeared in the XRD pattern. On the basis of the XRD results, it is clear that MWCNTs-Ag was successfully prepared using this *in situ* growth method.

The dielectric properties of MWCNTs-Ag/PVDF nanocomposites were investigated at room temperature in the frequency range of 10^2 - 10^7 Hz. Figure 4(a) shows the frequency dependence of ϵ' for the MWCNTs-15Ag/PVDF composites. The decrease in ϵ' in the frequency range of 10^6 - 10^7 Hz for all the samples can be ascribed to the dielectric relaxation of the PVDF matrix (Dang *et al.*, 2012; Wang *et al.*, 2015). When the volume fraction of MWCNTs-15Ag filler was ≤ 0.019 (1.9 vol%), ϵ' was nearly independent of frequency over the range of 10^2 - 10^5 Hz. ϵ' slightly increased with an increasing volume fraction of MWCNTs-15Ag filler. This is a typical characteristic of the dielectric response of a conductor/insulator composite when the volume fraction of conductive filler is lower than the critical concentration, *i.e.*, the percolation threshold (f_c) (Nan *et al.*, 2010). With increasing volume fraction of MWCNTs-15Ag up to 0.025 and 0.03, ϵ' in the range of 10^2 - 10^5 Hz became dependent upon frequency. The strong frequency dependence of ϵ' observed in the composites with volume fractions of 0.033 and 0.037 of filler. This was attributed to the existence of strong interfacial polarization in the composites (Nan *et al.*, 2010; Dang *et al.*, 2012).

Figure 4(b) depicts the frequency dependence of the dielectric loss tangent ($\tan\delta$) at room temperature. The MWCNTs-15Ag filler had an influence on the $\tan\delta$ of the PVDF composites. When the filler volume fraction was ≤ 0.019 , $\tan\delta$ changed slightly as the volume fraction was increased from 0.002 to 0.019. These $\tan\delta$ values were still too low. As the volume fraction of filler increased from 0.025 to 0.037, $\tan\delta$ increased greatly. A $\tan\delta$ peak was observed in a high frequency range (10^6 - 10^7 Hz), corresponding to a decrease in ϵ' , confirming the existence of dielectric relaxation (Wang *et al.*, 2015). Such a high-frequency dielectric response is a Debye-type relaxation behavior, which originates from the dipole orientation polarization of C-F in the PVDF matrix (Wang *et al.*, 2015). A large increase in $\tan\delta$ in a low frequency range is usually caused by a large DC conductivity of the composites (Vangchangyia *et al.*, 2012). When the MWCNTs-15 Ag filler volume fraction was increased, the conduction was by contact among filler particles (Nan *et al.*, 2010). Under an applied electric field, free charges can be conducted through the bulk sample, giving rise to a large leakage current, and hence DC conductivity. This was observed in the composite filled with the largest volume fraction (0.037). Its $\tan\delta$ at 10^2 Hz was as high as ≈ 100 , which is higher than the pure PVDF polymer ($\tan\delta \approx 10^{-3}$) by 4 orders of magnitude.

The ϵ' and $\tan\delta$ values at 1 kHz of the MWCNTs-15Ag/PVDF composites are represented. Variation in the volume fraction of filler for the ϵ' and $\tan\delta$ values at 1 kHz as shown in Fig. 5. The percolation threshold (f_c) is clearly observed at the volume fraction of filler of about 0.03. Above this level, ϵ' of MWCNTs-15Ag/PVDF composites increases with increasing the filler content. The dielectric behavior at this point can be explained by percolation theory (Nan *et al.*, 2010). Here, the conductive MWCNTs-Ag formed a percolation network, which is a conductor. As the internal electric field became stronger, there was a great increase in the electric polarization and thus ϵ' value (Dang *et al.*, 2007). The effect of the MWCNTs/Ag ratio on the formation of a percolation network as shown in Fig. 6. When the Ag content in MWCNTs-Ag was increased, the percolation threshold also increased. The increase in percolation threshold was due to the lower content of MWCNTs. The very large aspect ratio of MWCNTs enabled formation of a percolation network in the PVDF matrix (Costa *et al.*, 2016). Thus, the percolation threshold

can be increased by decreasing the amount of MWCNTs in the PVDF matrix. It is notable that the MWCNTs-15Ag/PVDF composites with a volume fraction of 0.033 exhibited excellent dielectric properties with a high $\epsilon' \approx 531$ and low $\tan\delta \approx 0.57$ (at 1 kHz and room temperature). This high ϵ' value of the MWCNTs-15Ag/PVDF composite is comparable to that observed in the MWCNTs/PVDF composite, but $\tan\delta$ was much lower than the MWCNTs/PVDF composite (Dang *et al.*, 2007). The MWCNTs-Ag hybrid/PVDF nanocomposites with high ϵ' and low $\tan\delta$ displayed good flexibility due to their low contents of MWCNTs and Ag.

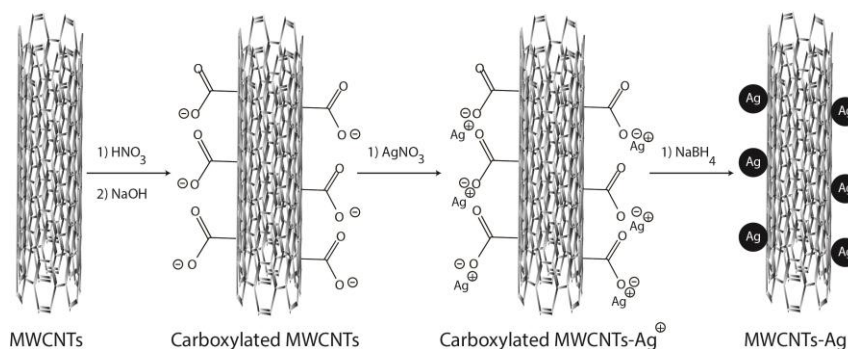


Figure 1 Schematic diagram of formation of MWCNTs-Ag

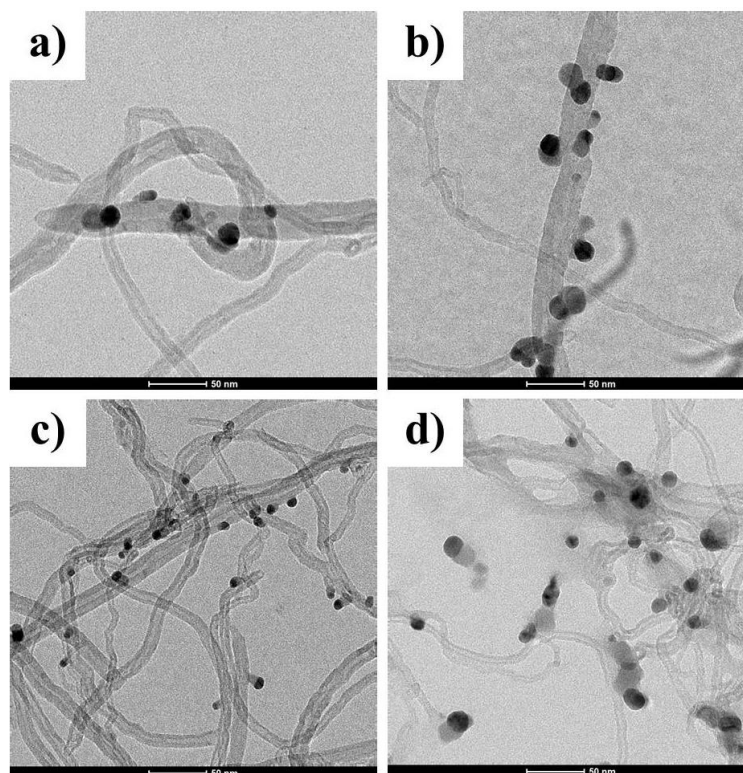


Figure 2 TEM images of (a) MWCNTs-5Ag, (b) MWCNTs-10Ag, (c) MWCNTs-15Ag, and (d) MWCNTs-20Ag powder samples

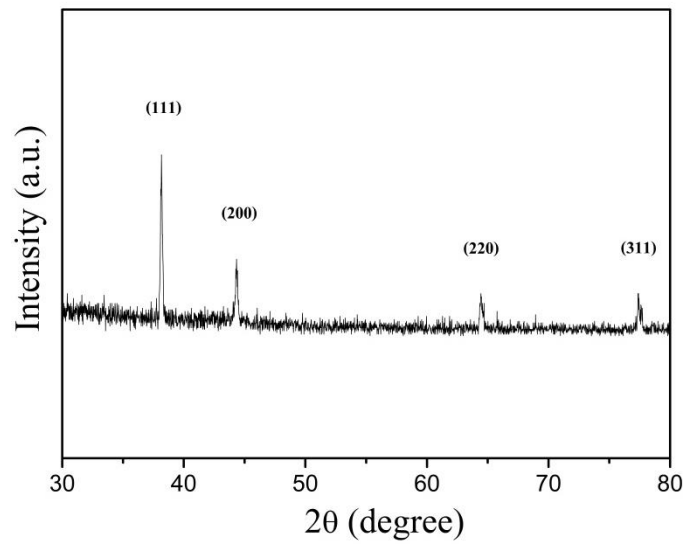


Figure 3 XRD patterns of the MWCNTs-15Ag nanoparticles

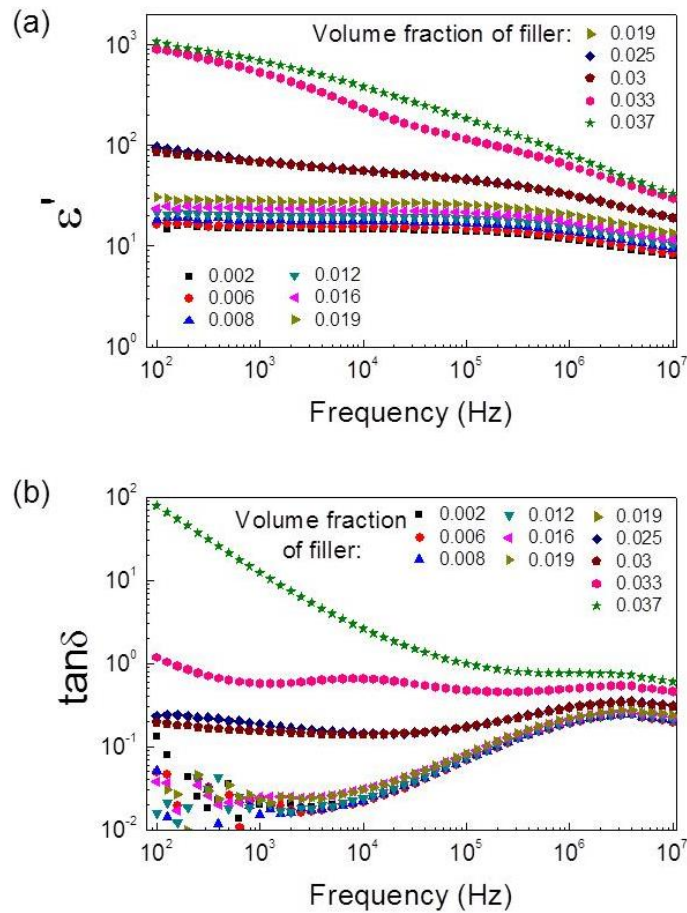


Figure 4 Frequency dependence of (a) dielectric permittivity (ϵ') and (b) the dielectric loss tangent ($\tan\delta$) at room temperature for the MWCNTs-15Ag/PVDF composites

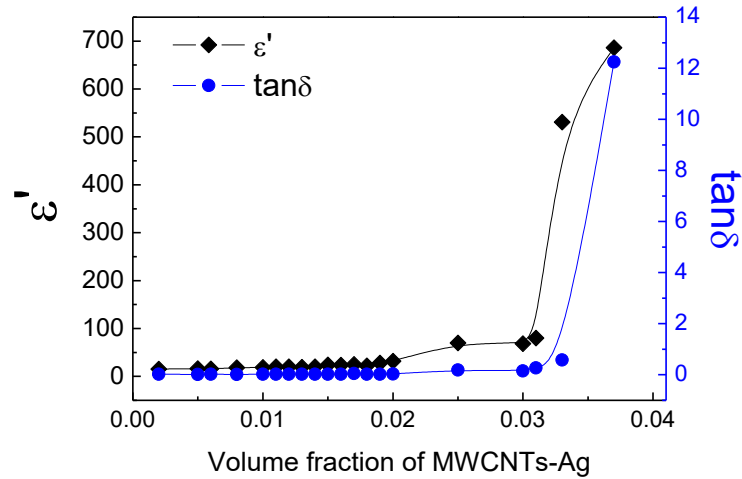


Figure 5 ϵ' and $\tan\delta$ data at 1 kHz and at room temperature as a function of $f_{\text{MWCNTs-Ag}}$ for the MWCNTs-15Ag/PVDF composites

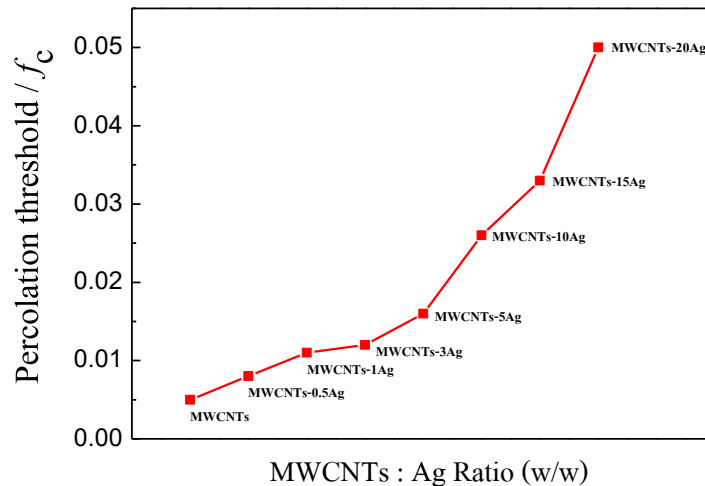


Figure 6 Variation of the percolation threshold of the PVDF composites filled with MWCNTs-Ag hybrid particles with different ratios of MWCNTs/Ag

Conclusions

Three-phase percolative nanocomposites of MWCNTs-Ag/PVDF polymer composites were successfully prepared. It was found that ϵ' of MWCNT-Ag hybrid/PVDF nanocomposites drastically increased near the f_c point, while $\tan\delta$ was still too low ($\tan\delta < 1$). Notably, the MWCNTs-15Ag/PVDF composites with a volume fraction of 0.033 exhibited excellent dielectric properties with high $\epsilon' \approx 531$ and low $\tan\delta \approx 0.57$ (at 1 kHz and room temperature). It was found that f_c increased with an increasing Ag/MWCNTs ratio. The dielectric properties can be described by the percolation theory based on space charge polarization.

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