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Exploration of dielectric constant dependence on evolution of microstructure in nanotube/ferroelectric polymer nanocomposites

Sheng-Hong Yao,[1,2] Zhi-Min Dang,[1,2,a)] Hai-Ping Xu,[1,2] Mei-Juan Jiang,[1,2] and Jinbo Bai[3]

[1]*Key Laboratory of the Ministry of Education on Nanomaterials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*
[2]*Key Laboratory of Beijing City for Preparation and Possessing of Novel Polymer Material, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*
[3]*Laboratory MSSMAT, CNRS UMR 8579, Ecole Centrale de Paris, Grande Voie des Vignes, Châtenay Malabry CEDEX 92295, France*

Multiwall carbon nanotube (MWNT) with high aspect ratio (AR=125–750) was dispersed into polyvinylidene fluoride (PVDF) to fabricate the MWNT/PVDF nanocomposites. Change of dielectric constant with increasing the length of tensile strain (LTS) was observed in the MWNT/PVDF composites with different mass concentration of MWNT ($m_{\mathrm{MWNT}}=1.0\%$ and $m_{\mathrm{MWNT}}=2.0\%$). The results showed that an abrupt increase in dielectric constant appeared when the LTS was 4 and 2 mm in the composites with $m_{\mathrm{MWNT}}=1.0\%$ and $m_{\mathrm{MWNT}}=2.0\%$, respectively. By employing the evolutions of conductive pathway and microcapacitance structure during the tensile strain process, the increased dielectric constant could be explained well. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2870104]

Carbon nanotube (CNT) has been used extensively in many fields due to their superior thermal and mechanical properties and unusual electronic structure, which are from its high aspect ratio (AR), one-dimensional structure and the extraordinary carrier mobility.[1–3] Recently, CNT/polymer composites with high dielectric constant have been studied extensively because of their superior dielectric properties compared to ceramic composites.[4–6] These polymer composites could be utilized in a variety of applications, for instance electromagnetic interference shielding,[7] thin-film transistors,[8] and photovoltaic devices.[9] When the CNT is dispersed into a functional polymer with good piezoelectric and pyroelectric responses, such as polyvinylidene fluoride (PVDF) and its copolymers, these composites would display an improvement in functional characteristics.[4] In spite of great requirements, the uniform dispersion of CNT has not been realized due to the strong van der Waals interaction, which highly restricts their potential applications.[10] At present, many works have also been devoted to explore the relationship between the arrangement of CNT and dielectric as well as mechanical properties of the CNT/polymer composites.[3,11,12] Electrical conductivitiy of the CNT-filled composites could decrease abruptly as much as eight orders of magnitude with increasing the shear processing time, which was due to the alignment of CNT along the shear-flow direction in epoxy matrix.[11] As a result, ones have found extremely different properties along parallel and perpendicular directions with the tensile strain. Although several studies reported that an appropriate mechanical stretching method would induce the alignment of CNT, the relationship between the arrangement of CNT and the changes of dielectric and mechanical properties is still blurry.

In this letter, we report the dependence of dielectric constant on the length of tensile strain (LTS) in the CNT/PVDF nanocomposites loaded with multiwall CNT (MWNT) at $m_{\mathrm{MWNT}}=1.0\%$ [less than the percolation threshold

$(m_c=1.8\%)$] and $m_{\mathrm{MWNT}}=2.0\%$ (more than the percolation threshold), respectively. In order to find the distinct difference of the dielectric properties, the MWNT with higher AR (AR=125–750) than before (AR=25–100) was employed in this study. The dielectric constant presented a complicate change law with increasing the LTS. The achieved results would be explained well on the basis of the change of conductive pathways and the evolution of microcapacitance structure because the original microstructure might be destroyed and the alignment of CNT along the stretching direction can occur during the tensile-strain process.

MWNT used as conductive filler in this study is about 20–40 nm in diameter, about 5–15 μm in length (AR=125–750), and PVDF is host polymer. The MWNT/PVDF nanocomposites with MWNT mass concentrations at $m_{\mathrm{MWNT}}=1.0\%$ and $m_{\mathrm{MWNT}}=2.0\%$, respectively, were prepared by employing a solution method (solvent: N,N-dimethylformamide). The detail preparation process could be found in our past work.[3,5,6] The dumbbell shaped samples were stretched uniaxially on CMT4104 electric tensile tester (SANS, China) until the samples were broken. For comparison, the dielectric constants (K) of the samples before and after stretched were measured using an impedance analyzer (Agilent 4294A) in the frequency ranges from 10^2 to 10^7 Hz at room temperature.

As mentioned previously, two nanocomposites with MWNT at $m_{\mathrm{MWNT}}=1.0\%$ and $m_{\mathrm{MWNT}}=2.0\%$ were stretched at the lengths of 1, 2, 3, 4, and 5 mm, respectively, until the samples were ruptured. Figure 1 shows the dependence of dielectric constant of the $m_{\mathrm{MWNT}}=1.0\%$ composites on frequency range from 10^2 to 10^7 Hz at the different lengths of tensile strain. As shown in Fig. 1(a), the dielectric constant of the composites decreases with increasing the frequency at any LTS values, and the rapid decrease of dielectric constant $(64\rightarrow29)$ from 10^2 to 4×10^3 Hz (before the dash line) appears in the composite with LTS=4 mm; whereas, for other samples with the different LTS, the variation of dielectric constant in this frequency range is not remarkable. It could be seen clearly from Fig. 1(b) that the variation tendency of

a)Author to whom correspondence should be addressed. Electronic mail: dangzm@mail.buct.edu.cn.
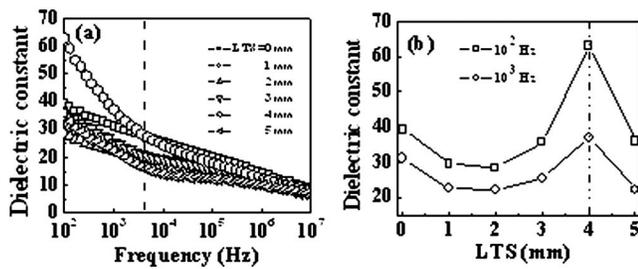
FIG. 1. Dependence of dielectric constant on (a) frequency and (b) on the LTS at 10^2 and 10^3 Hz of the $m_{MWNT}=1.0\%$ composite before and after stretched.

FIG. 2. Dependence of dielectric constant on (a) frequency and (b) on the LTS at 10^2 and 10^3 Hz of the $m_{MWNT}=2.0\%$ composite before and after stretched.

the dielectric constant of the $m_{MWNT}=1.0\%$ composite as a function of the LTS is almost same at 10^2 and 10^3 Hz. Namely, the dielectric constant decreased gradually with increasing the LTS before LTS=2 mm, and subsequently it exhibits an increase trend and reaches the maximum value at LTS=4 mm, followed by a decrease again. The results indicate that by employing the tensile strain method, in comparison with LTS=0 mm, the increase of dielectric constant of the $m_{MWNT}=1.0\%$ composite is 62.5% at 10^2 Hz and 22.5% at 10^3 Hz.

As a comparison, the strain-induced change of dielectric constant for the $m_{MWNT}=2.0\%$ composite is shown in Fig. 2. Seen from Fig. 2(a), it should be noted that although all the dielectric constants still decreased with the increase of frequency, which is of the same rule as the $m_{MWNT}=1.0\%$ composite, the rapid decrease of dielectric constant ($375\rightarrow275$) from 10^2 to 10^3 Hz (before the dash line) appears in the composite with LTS=2 mm. According to the curves in Fig. 2(b), where the dependence of dielectric constant at 10^2 and 10^3 Hz on the LTS is shown, it could be seen that the dielectric constant begins to decrease dramatically at LTS=1 mm, following a remarkable increase at LTS=2 mm, a significant decrease again at LTS=3 mm and finally increases slowly. The complicated variation of dielectric constant would be attributed to the more loading of MWNT, which is slightly higher than the percolation threshold. Therefore, compared with Fig. 1(b), the abrupt increase in dielectric constant (at 10^2 Hz, $K\approx300$ for the $m_{MWNT}=2.0\%$ composite, and $K\approx40$ for the $m_{MWNT}=1.0\%$ composite) of samples at LTS=0 roots from the insulation-conduction transition when the concentration of MWNT was near the percolation threshold. In this case, we could still observe the remarkable increase (about 28.3% at 10^2 Hz) of dielectric constant in the $m_{MWNT}=2.0\%$ composites after stretched. The breakage of the conductive pathways and the formation of microcapacitance network made from the aligned MWNT bundles in the direction of tensile strain would take charge for these complex changes of dielectric constant shown in Figs. 1 and 2. The detailed mechanisms can be depicted further as below.

Since the MWNT with higher AR (AR=125–750) than before (AR=25–100) was used in this study, the responses of dielectric constant on the tensile strain are more complex. Figure 3 shows that schematic evolution processes of MWNT distribution in the MWNT/PVDF composites with $m_{MWNT}=1.0\%$ and $m_{MWNT}=2.0\%$ with the change of tensile strain. It is hard to form individual dispersion of MWNT in the polymer matrix owing to the high AR of MWNT (AR=125–750), and a large number of MWNT clusters exist in the composites, as shown in Figs. 3(a) and 3(a′). There are a number of conductive pathways in the clusters which
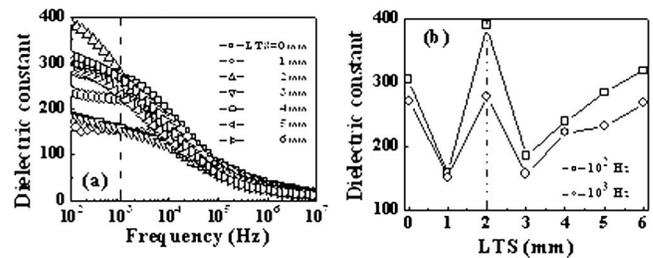
played a very important role on improving the dielectric constant of composites, especially in the $m_{MWNT}=2.0\%$ composite. When the dielectric composites are subject to a uniaxially stretching at low LTS value, the original conductive networks in the MWNT clusters would be destroyed because of the displacement of the MWNT after stretching, which resulted in a decrease in dielectric constant [$40\rightarrow31$ at 10^2 Hz, see Fig. 3(b)], and this change would be magnified [$310\rightarrow160$ at 10^2 Hz, see Fig. 3(b)] with the concentration of MWNT ($m_{MWNT}=2.0\%$) approaching percolation threshold,[13] which also corresponds to the remarkable decrease of dielectric constant in Fig. 2(b). When the LTS increases, the clusters of MWNTs are broken off completely and the MWNT begins to rearrange along the stretched direction. Up to a certain LTS value, a number of MWNT starts to be parallel to the tensile-strain direction and a mass of microcapacitance networks with polymer as a medium between the MWNT plates are formed [see Figs. 3(c) and 3(c′)], so the maximal dielectric constant are obtained [$K=65$ at 10^2 Hz corresponding to LTS=4 mm and $K=390$ to LTS=2 mm, respectively, in Fig. 1(b) and Fig. 2(b)]. With increasing the LTS further, the microcapacitance networks formed in the composites would be destroyed because of the MWNT movement along the direction of tensile
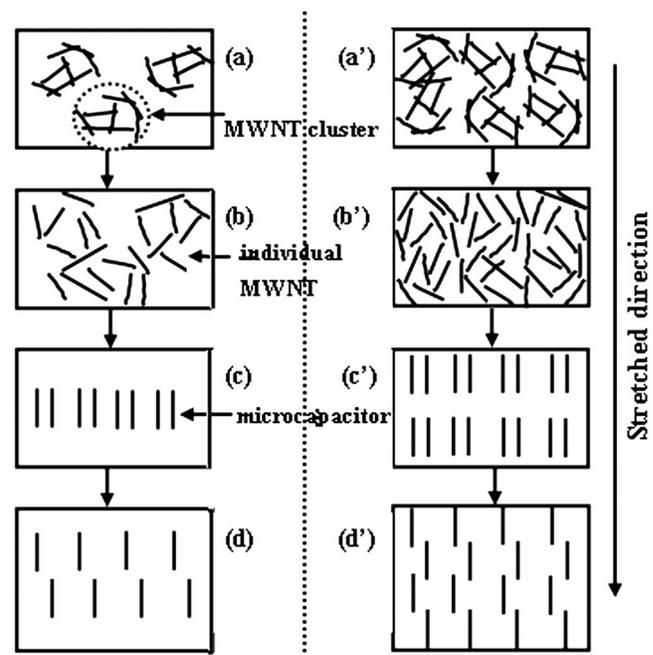
FIG. 3. Schematic changes of the MWNT distribution in the MWNT/PVDF composites at $m_{MWNT}=1.0\%$ (a, b, c, and d) and $m_{MWNT}=2.0\%$ (a′, b′, c′, and d′) with the LTS respectively.
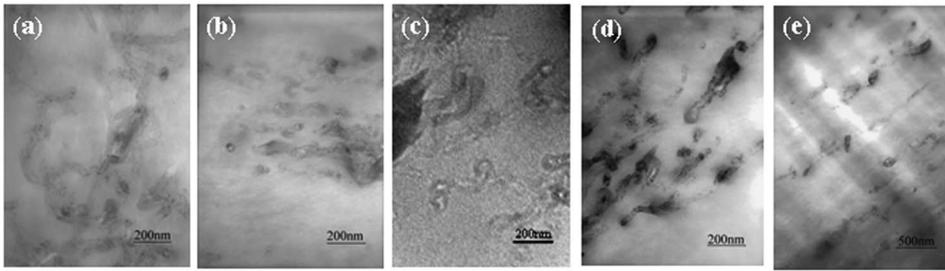
FIG. 4. Morphologies of samples parallel to the tensile-strain direction in the MWNT/PVDF composites with 2.0 wt % MWNT-2, respectively. (a) LTS=0 mm, (b) 1 mm, (c) 2 mm, (d) 4 mm, and (e) 6 mm.

strain [see Figs. 3(d) and 3(d′)]. As a result, the dielectric constant of MWNT/PVDF nanocomposites decreased significantly again [see Figs. 1(b) and 2(b)]. However, for the m_{MWNT}=2.0% composite, though the microcapacitance networks formed as mentioned above would be destroyed because of the continuous stretch, the other microcapacitance networks are formed rapidly due to the high loading concentration of MWNT, that is to say, when the parallel MWNTs of microcapacitance are separated as applying the strain, they would meet ones which were kept in other microcapacitance to form a similar microcapacitance structure, respectively. Moreover, these parallel microcapacitance structures would increase with the LTS increasing, and another conductive network appears. The evolution of the microcapacitance structure would induce the linear increase of dielectric constant with increasing the LTS [see Fig. 2(b)].[14] When compared with Fig. 1(b), a maximum value of dielectric constant can be obtained at lower LTS in Fig. 2(b) than that in Fig. 1(b), which attributes to the percolation structure that is sensitive to strain, namely, a tiny change in shape can alter the connections in conductive networks and induce a huge variety in dielectric constant. The TEM micrographs of the MWNT distribution in the MWNT/PVDF composites with m_{MWNT}=2.0% with the change of tensile strain confirm this schematic evolution processes. As shown in Fig. 4, the clusters of MWNT disperse in the matrix randomly [as shown in Fig. 4(a)], then the MWNTs begin to orientate when tensile strain is applied [as shown in Figs. 4(b)–4(e)], accompanying with the formation and breakage of microcapacitance structure.

Compared with our past work,[3] we find that this increase of dielectric constant $[(65-40)/40\times100\%=62.5\%$ for m_{MWNT}=1.0% composite and $(390-310)/310\times100\%$ $=25.8\%$ for m_{MWNT}=2.0% composite] might be due to the increase in AR of MWNT and the different LTS of composites. For the MWNT with high AR value, it is easy to form the parallel microcapacitance structures, which results in the remarkable increase in dielectric constant; meanwhile, the conductive network changes a lot with the variation of LTS.

In conclusion, the dependence of dielectric constant in the PVDF matrix nanocomposites with high AR of MWNT (AR=125–750) on the LTS was observed. The maximum of increase in dielectric constant appeared at the different LTS values for the m_{MWNT}=1.0% and m_{MWNT}=2.0% and the increase percents of dielectric constant were about 62.5% and 25.8% in comparison with the dielectric constant before stretched, respectively. The results showed that the effect of tensile strain could play an active role on deciding the dielectric property. These results could be understood due to the breakage of the conductive pathways and the formation of microcapacitance structure during the tensile strain process, and the high AR of MWNT was an important factor for the formation of microcapacitance structures.

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