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Biphasic Polymer Blends Containing Carbon Nanotubes: Heterogeneous Nanotube Distribution and Its Influence on the Dielectric Properties

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S *Supporting Information*

ABSTRACT: Electrically percolative composites with high dielectric permittivity are currently finding increasing interest in academic and industrial research. They are essential for designing new energy-storage capacitors and electromagnetic interference shielding devices. Herein, we report a percolative multiwalled carbon nanotube (MWNT) filled low density polyethylene (LDPE)/poly(vinylidene fluoride) (PVDF) composite. As compared to the MWNT-filled single LDPE composites, this biphasic polymer composite displays a significantly reduced percolation threshold (9.6 → 5.7 vol %) but still maintains a high permittivity level to reach (∼500). This can be attributed to a double percolated structure observed on the basis of morphological evidence. MWNTs are selectively localized in LDPE phase during melt-mixing. This is contrary to the wetting coefficient evaluation yet still possible when the colossal difference in viscosity of two polymers is taken into account. The effect of double percolation on the dielectric properties was well illustrated by revealing the mechanism for the improved permittivity. A model based on the Lichtenecker rule and percolation theory was established and demonstrated to be effective to predict the dielectric permittivity in biphasic polymer composites.
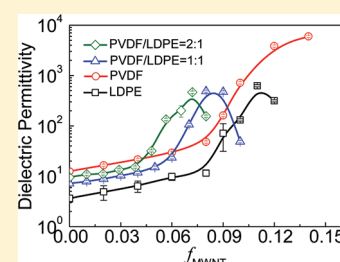
INTRODUCTION

The electrically percolative polymer-based composites are arousing considerable interest because their physical properties often display a significant change if an electrically conducting filler's concentration in the composites is near critical threshold, i.e., dramatic increases in conductivity and/or dielectric permittivity. Their potential applications can be electromagnetic interference shielding materials,[1,2] electroactive materials,[3,4] and dielectrics for charge-storage capacitors.[5-11] In this field, continuous effort has been devoted to raise the electrical conductivity or dielectric permittivity of composites at low percolation threshold (f_c) in order to maintain the inherent polymer matrix flexibility and low cost. For this purpose, the fillers with large aspect ratio are of particular interest, such as one-dimensional nanotubes and fibers,[9-12] and two-dimensional graphene nanosheets.[13,14] Among these fillers, carbon nanotubes (CNTs) are the most promising candidate due to the good combination of mechanical, electrical and thermal properties as well as their availability at large scale.[15] To prepare CNTs/polymer nanocomposites, several processing methods have been developed, such as solution casting,[9,10] melt mixing,[11,16] and in situ polymerization.[17] Among them, melt mixing is particularly desirable as the process is fast, simple, free of solvents and contaminants, most importantly easily scalable from laboratory to industrial scale.[18-20] McNally et al.[19] incorporated multi-walled carbon nanotubes (MWNTs) into polyethylene (PE) matrix by melt mixing using a mini-twin screw extruder.

The electrical conductivity of PE was increased significantly, by 16 orders of magnitude, from 10^{-18} to 10^{-2} S m^{-1}. However the percolation threshold (f_c = 7.5 wt %) was relatively high due to the decrease of MWNT aspect ratio as a consequence of inevitable breakage during melt-mixing. We also fabricated a nano-composite by melt-blending the pristine MWNTs within poly-vinylidene fluoride (PVDF).[20] A giant dielectric permittivity (3800) was observed over a critical content of MWNT. Unfortunately, the composites possessed a high value of f_c (10.4 vol %) mainly due to a significant polymer wrapping on the nanotubes. The large quantities of MWNTs added into the host polymer may cause the poor mechanical properties, difficulty of processing, and high costs. Therefore, new methods are needed to fabricate such composites by melt-mixing technique for reducing the percolation threshold.

The recent theoretical and experimental investigations indicate that the percolation threshold of CNTs/polymer composites depends strongly on not only the physical properties of CNTs[21] (e.g., conductivity and aspect ratio) but also their dispersion state[22] and distribution status[23] in polymer matrices. Therefore, tremendous research and development efforts are devoted to design an optimized state of aggregation and distribution

of CNTs in host polymers to reduce the percolation threshold. An efficient strategy is to confine CNTs in any one of the phases of a cocontinuous biphasic polymer blend or at the interface, by which the percolation threshold can be substantially reduced due to the double percolation. The concept of double percolation was initially described by Sumita et al.[24] in 1991 for carbon black (CB) filled immiscible blends. Since then, it has been implemented for several blend systems and can be applied to a variety of carbonaceous fillers, such as CB,[24−26] carbon fibers,[27] CNTs,[23,28−31] and graphite nanosheets.[32] In the case of CNT-filled polymer blends, preliminary studies have explicitly studied the heterogeneous morphologies (sea-island or cocontinuous phase structure) of various blend systems characterized by the preferential location of CNTs in one of the phases. It has been also substantially demonstrated that the electrical and/or mechanical properties of CNT-filled polymer blends can be significantly improved, once the double percolation occurs, i.e., the CNT-filled blend phase percolates (first percolation) and the CNTs forms a network within the percolated blend phase (second percolation). For instance, Pötschke et al.[23] have introduced MWNTs into thermoplastic matrices, polycarbonate (PC) and polyamide (PA), by melt blending using PE based concentrates with high MWNT loading (24−44 wt %). The MWNTs migrated from PE concentrates to PC or PA phase and remained in their excellent dispersion state. Thus, electrical percolation is achieved at significantly lower MWNT contents as compared to direct incorporation. Wu et al.[31] have prepared CNT-filled polyethylene terephthalate (PET)/PVDF blend composites. It was observed a 2500% improvement in electrical conductivity, 36% augment in tensile strength and 320% increase in elongation over the CNT-filled PET with the same filler content. The author ascribed the improved properties to the formation of a double percolated structure resulting from the selective location of CNTs in the PET phase. Despite tremendous progress toward understanding the effect of the double percolated structure on the electrical and mechanical properties by intensively investigating the cocontinuity of polymer phases,[28−31] to the best of our knowledge, double percolated structure based dielectric blends with CNTs have rarely been investigated in the literature. The effect of double percolation on the dielectric permittivity is still elusive and requires a thorough investigation, especially when the interactions between the two continuous polymer phases would be involved.

In this work, biphasic polymer blends (PVDF and low density polyethylene (LDPE) with different proportions) were selected as host matrices to prepare MWNT-filled polymer blends. Images of scanning electron microscopy (SEM) together with transmission electron microscopy (TEM) confirmed the remarkable selective localization of MWNTs in the LDPE phase, and provided morphological evidence for the double percolated structure in MWNT-LDPE/PVDF composites. As a result, the percolation threshold was reduced greatly. This allows for easy processing, preserving the mechanical properties of the matrix and reducing as much as possible the cost of the final composites. The effect of double percolation on the dielectric properties of MWNT-filled biphasic polymer composites was elucidated in detail. A model based on the Lichtenecker rule and percolation theory was used to predict the dielectric permittivity in biphasic polymer composites below percolation threshold.

■ EXPERIMENTAL SECTION

Materials. The MWNTs are synthesized by chemical vapor deposition method (CVD), provided by Shenzhen Nanotech Port Company (China). The purity and density of the MWNTs used are about 97% and 1.97 g/cm^3, respectively. The tube diameters are in the range of 20−40 nm with lengths of 5−15 μm. The PVDF (Kynar 721) with density of 1.78 g/cm^3 and melt flow index (MFI) of 7.0 g/10 min is used in the blends as received. The typical commercial LDPE has a density of 0.92 g/cm^3 and MFI of about 260 g/10 min.

Fabrication of Biphasic Polymer Composites. Blends of LDPE and PVDF with and without MWNTs have been prepared by mixing in a corotating twin-screw microcompounder (DSM Xplore Microcompounder, 5 cm^3) with two stainless steel screws and a bypass allowing continuous recycling of the material at the head of the mixing chamber. The volume ratios of PVDF/LDPE are fixed at 1:4, 1:2, 1:1, 2:1, and 4:1. An appropriate amount of MWNTs and the polymer blends with fixed volume ratio were mixed all together at 200 °C, for 30 min and at a mixing speed of 60 rpm. Such a long mixing duration aims to ensure the complete disentanglement of MWNTs clusters at relatively low screw rotation speed. The whole mixing process was under the protection of Ar atmosphere to prevent samples from oxidation. Final slabs with a thickness of 1.5 mm were prepared by injection molding of the melt blends using a press at 1.6 MPa for 1 min (DSM Xplore Microinjection Molder, 5 cm^3), while the temperature was kept at 50 °C, Then, the temperature would be decreased from 50 °C to room temperature at a sufficiently low rate.

Dielectric Characterization and Microstructure Observation of the Composites. For the dielectric characterization, specimens with a dimension of about 10 mm ×10 mm ×1.5 mm were cut from the as-prepared composite slabs. Silver paint was applied on the two surfaces of the specimens to ensure good contact. The dielectric properties were measured using a broadband dielectric spectrometer (Novocontrol BDS 20) in the wide frequency range of $10^{-1}-10^{6}$ Hz at room temperature. Each sample was measured for four times and mean values were taken to plot curves. Morphologies of fractured surfaces of the MWNT-LDPE/PVDF composites were observed using a scanning electron microscopy (SEM, LEO Gemini 1530). The fractured surfaces were prepared in liquid nitrogen and were sputtered with gold in vacuum prior to observation. The microstructure of the specimens was also examined by transmission electron microscopy (TEM, Hitachi H7650), and the ultrathin sections (120 nm) were sliced by ultramicrotome under liquid nitrogen cooling.

■ RESULTS AND DISCUSSION

Morphologies of the Biphasic Polymer Composites at Different Blend Compositions. Figure 1 shows the SEM micrographs of the MWNT-LDPE/PVDF composites with a fixed overall volume concentration of MWNT (f_{MWNT} = 0.08) and variable volume ratio of PVDF:LDPE. From the SEM images shown in Figure 1a−f, two distinct regions are noted, one contains MWNTs (region B, polymer exhibiting heterogeneity) and the other is free of MWNTs (region A). The area ratio of region A to B increases with increasing the volume ratio of PVDF/LDPE. Thus, it is reasonable to conclude that Region A is the PVDF phase, whereas region B is the LDPE phase containing MWNTs. It is clear that the composites exhibit a heterogeneous MWNT distribution in matrix. In order to further confirm that MWNT is indeed localized in the LDPE phase, a composite with MWNT filled in single LDPE matrix (PVDF/LDPE = 0:1) was also prepared under the same processing conditions. It can be

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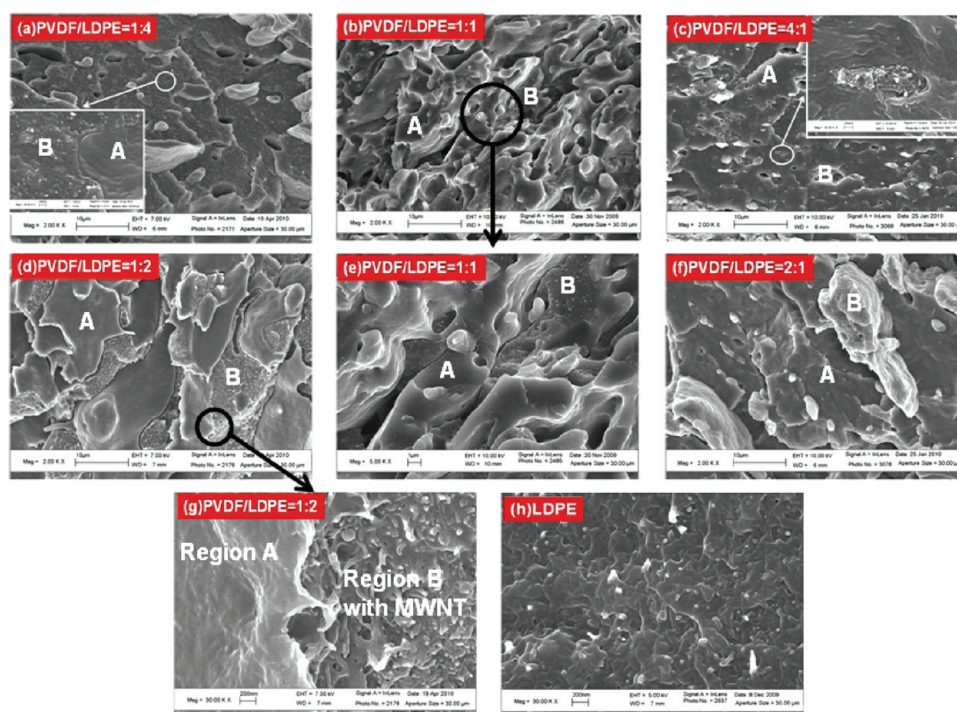
Figure 1. SEM images of fracture surfaces of the MWNT-LDPE/PVDF composites with a fixed overall volume concentration of MWNT (f_{MWNT} = 8.0 vol%). Panels a–c correspond to composites at volume ratios of PVDF/LDPE = 1:4, 1:1, and 4:1 respectively, the insets in panels a and c show the magnified images of the region B with MWNT. Panels d and f correspond to composites at volume ratios of PVDF/LDPE = 1:2 and 2:1, respectively. Panels e and g are the magnified images of the composites at volume ratios of PVDF/LDPE = 1:1 and 1:2. Panel h shows the image of MWNT filled single LDPE composite at f_{MWNT} = 0.08.

clearly seen that the macroscopic region B (see Figure 1g) is very similar to the morphology of the MWNT/LDPE composite (see Figure 1h), which further confirms that MWNT is preferentially located in the LDPE phase. The remarkable heterogeneous distribution of MWNT in the polymer blend can be also clearly seen in the TEM images of the MWNT-LDPE/PVDF composites at volume ratio of PVDF/LDPE = 1:1, as shown in the Figure S1 (ESI†).

The location of carbon nanotubes in a polymer blend is generally dictated by the state of the minimum interfacial energy if the thermodynamic equilibrium is attained.[23,31] According to Young's equation, ones can find the thermodynamic equilibrium filler position by evaluating the wetting coefficient ω_a.[33]

$$\omega_a = \frac{\gamma_{CA} - \gamma_{CB}}{\gamma_{AB}} \tag{1}$$

here, γ_{CA}, γ_{CB}, and γ_{AB} are the interfacial energy between MWNT and polymer A, MWNT and polymer B, and polymer A and B, respectively. The values $\omega_a > 1$, $-1 < \omega_a < 1$, and $\omega_a < -1$ imply MWMT preferentially locates within polymer B, at the interface between two polymers and polymer A, respectively. The interfacial energy γ_{12} derived from the surface free energies of phase 1 (γ_1) and phase 2 (γ_2). Two approaches can be used depending on the type of phase surfaces: the harmonic mean equation and the geometric mean equation. The former is suitable for evaluating the interfacial energy between low-energy materials

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4\left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}\right) \tag{2}$$

and the latter is valid between a low energy material and a high energy material

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p}) \tag{3}$$

Surface free energies of LDPE, PVDF and MWNT as well as their dispersion and polar components are listed in Table 1. Based on these values, the calculated interfacial energies between the polymers and the MWNT are reported in Table 2. Submitting these interfacial energies into eq 1 results in wetting coefficients (see Table 3). The value is below −1 according to either the harmonic or geometric mean equation, if PVDF is chosen as phase A and LDPE as phase B. Therefore, the consideration of the minimum interfacial energy predicts that MWNT should explicitly distribute into the PVDF phase (more polar phase) during melt-mixing. Unfortunately, this prediction is contradictory with the preferred arrangement of MWNT inside LDPE phase experimentally observed in this study. It must be emphasized that thermodynamics of wetting is not the only factor influencing the final equilibrium morphology (filler location, shape and size of the polymeric phase) of blend systems,[37] which can be also determined by the kinetic effects induced by the mixing procedure,[38] mixing time,[39] especially the rheology of each polymer phase.[40−42] Feng et al.[40] investigated the effect of viscosity ratio of polymethyl methacrylate (PMMA)/polypropylene (PP) on the final equilibrium location position of CB particles. The calculation of the wetting parameter predicted that CBs should definitely locate in PMMA while they actually tend to preferentially incorporated into PP phase as PMMA showed a higher viscosity. Clarke et al.[41] and Zhou et al.[42] even argued that the interfacial energy of particle−polymer can be considered as the

Table 1. Surface Free Energies of the Polymers and MWNT[a]

material	γ at 20 °C (mJ/m^2)	$-d\gamma/dt$ (mJ/m^{2}K)	χ^p	γ at 200 °C (mJ/m^2)	γ^d at 200 °C (mJ/m^2)	γ^p at 200 °C (mJ/m^2)
LDPE[b]	35.7	0.057	0	25.4	25.4	0
PVDF[b]	30.3		0.23	30.3	23.3	7
MWNT[c]	27.8		0.37	27.8	17.6	10.2
MWNT[d]	45.3		0.59	45.3	18.4	26.9

[a] $\gamma = \gamma^d + \gamma^p$, $\chi^p = \gamma^p/\gamma$, γ: total surface energy, γ^d: dispersive component, γ^p: polar component, χ^p: polarity. [b] According to ref 34. [c] According to Barber.[35] [d] According to Nuriel.[36]

Table 2. Interfacial Energies As Calculated Using Harmonic and Geometric Mean Equations at 200 °C[a]

materials	γ^a_{12} (mJ/m^2)	γ^b_{12} (mJ/m^2)
LDPE/PVDF	7.09	7.05
LDPE/MWNT[b]	11.61	28.02
LDPE/MWNT[c]	28.02	27.46
PVDF/MWNT[b]	1.39	12.26
PVDF/MWNT[c]	12.26	6.74

[a] γ^a_{12}: interfacial energy by harmonic mean equation. γ^b_{12}: interfacial energy by geometric mean equation. [b] According to Barber.[35] [c] According to Nuriel.[36]

Table 3. Wetting Coefficients and Predictions of MWNT Location in the LDPE/PVDF Blend

system	ω_a harmonic	ω_a geometric	predicted location	observed location
MWNT[a]-LDPE/PVDF	−1.44	−1.45	PVDF	LDPE
MWNT[b]-LDPE/PVDF	−2.22	−2.94	PVDF	LDPE

[a] According to Barber.[35] [b] According to Nuriel.[36]

dominant factor only when the viscosity ratio of both polymer phases is nearly one. In our study, in the very beginning of the melt-mixing, LDPE can first melt at a temperature (104 °C) significantly lower than PVDF (171 °C), the MWNT particles may be incorporated into LDPE preferentially although it does not have the better affinity as PVDF is in solid state then. This thermodynamically unstable status can be retained for a long mixing time even after PVDF becomes viscous fluid, probably because of the colossal difference in viscosity between PVDF (6000 Pa.s at 232 °C) and LDPE phase (160 Pa.s at 190 °C) even the latter one is loaded with 8.0 vol % MWNT. In this case, kinetic effect dominates the thermodynamic wetting to determine MWNTs locating in the much lower viscosity LDPE phase.

Based on the remarkable selective location of MWNT in the LDPE phase, a 3D double percolated structure can definitely be formed in MWNT-LDPE/PVDF composites once two requirements are satisfied: (i) The matrix is a cocontinuous system, namely, both LDPE and PVDF phase are continuous in 3D space (see Figure 2b−d), meaning the volume ration of two polymers is not far from 1:1 (1:2, 1:1, and 2:1), and (ii) the conductive MWNT is preferentially localized in the LDPE phase and form a continuous 3D conductive network, meaning that its concentration is higher than the percolation threshold (Figure 2c,d). Such a double percolated structure allows for enhancing the electrical conductivity of polymer composites at low MWNT concentration since the conductive pathway of MWNT is only formed in one polymer phase, not through the entire matrix. This further improves the processability and flexibility because of the low inorganic filler concentration required. However, when the volume ratio of binary polymers is far from 1:1, such as 1:4 and 4:1, the double percolated structure cannot form, as the PVDF and LDPE phases are presented as isolated droplets in the cases of 1:4 (Figures 1a and 2a) and 4:1 (Figures 1c and 2e), respectively, even there are numerous conductive networks in LDPE phase for the latter case. Principally, there should exist a critical volume ratio of PVDF:LDPE, the lowest content of LDPE to form cocontinuous phases in matrix, at which a lowest MWNT loading

is needed to reach the percolation threshold. Pötschke et al.[28] has demonstrated that a double percolated structure could be still observed with the concentration of MWNT filled PC phase in blend with PE as low as 30 vol %.

Dependence of AC Conductivity on the Blend Composition. It is interesting to evaluate the dependence of AC conductivity on the blend composition. The conductivity (at 1 Hz) of the composites at a given overall MWNT concentration (f_{MWNT} = 8 vol %, based on the entire polymer blend) is strongly related to the PVDF phase content, as shown in Figure 3. According to the morphology of MWNT-LDPE/PVDF composite, the evolution process of the conductivity can be divided into three stages (I, II, and III). It should be first emphasized that MWNT-filled LDPE composite (at f_{PVDF} = 0) shows a much low conductivity, indicating that most MWNTs are isolated to each other at such concentration (f_{MWNT} = 0.08). When the PVDF content increases but below the cocontinuous range (stage I, Figure 3), the PVDF forms the microsized domains ($\sim$10 μm) and the MWNT-filled LDPE forms continuous phase (Figures 1a and 2a). The conductivity increase can be attributed to the more effective tunneling conduction with continuously reducing the distance between neighboring MWNTs, as a result of the increase of the effective CNTs concentration in the LDPE phase. The detailed concentrations of CNTs in the composites are shown in Table S1 (Supporting Information). Furthermore, when PVDF content increases up to the cocontinuous phase range (stage II, Figure 3), the MWNT-filled LDPE phase shirks further but still exhibits 3D continuity. The distance between neighboring MWNTs decrease greatly so that MWNTs contact with each other and finally form a conductive network in the LDPE phase (Figure 2c,d). Such trinary-continuous structure induces the double percolation effect, which refers to the percolation of MWNT in the LDPE phase and the continuity of the MWNT-filled LDPE phase in the polymer blend. Thus a notable increase of about 6 orders of magnitude in conductivity is observed in comparison with the MWNT-filled single LDPE composite. However, with further increasing the PVDF content (stage III, Figure 3), the conductivity starts to decrease. Though the MWNT-filled LDPE phase is highly electrically conductive, the MWNT-LDPE/PVDF composites are of
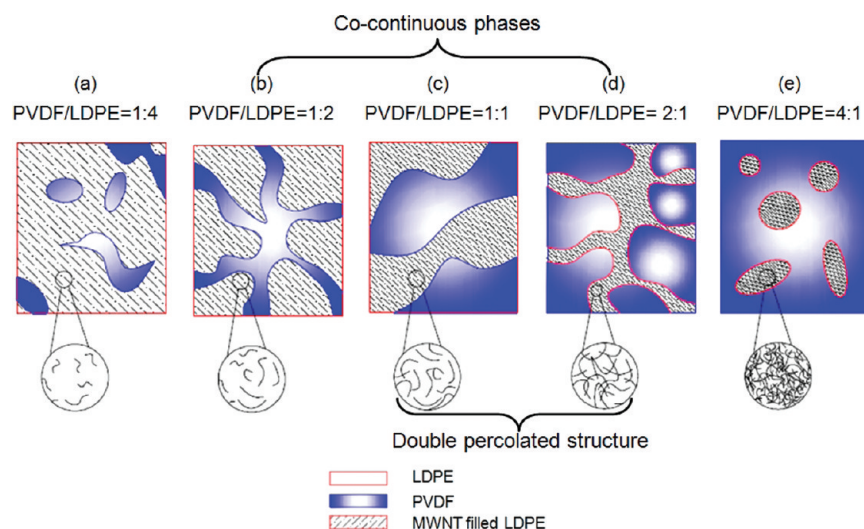
Figure 2. Schematic image for the microstructure evolution of the biphasic polymer composites with increasing volume ratio of PVDF/LDPE.
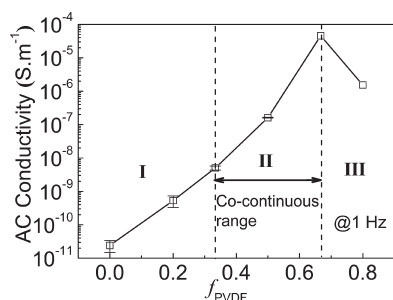
Figure 3. Dependence of the AC conductivity on the volume fraction of PVDF phase in the PVDF/LDPE polymer blends (f_{PVDF}), measured at 1 Hz and room temperature. The total volume concentration of CNTs based on the entire polymer blends is fixed at 8.0 vol %.

lower conductivity because of the discontinuous MWNT-filled LDPE phase in the PVDF phase (Figures 1c and 2e). The evolution of the conductivity with blend composition can be an indirect evidence for the preferential location of MWNTs in LDPE phase rather than PVDF phase.
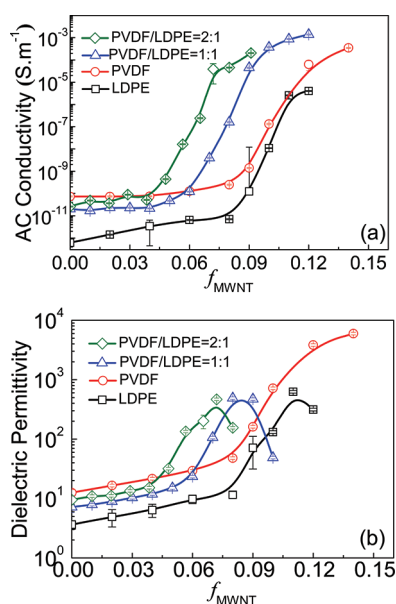
Frequency Dependence of the Dielectric Properties of Composites with Different Blend Compositions. Figure 4 presents the frequency dependence of dielectric properties of the MWNT-LDPE/PVDF composites with fixed overall f_{MWNT} (0.08) and different blend compositions. As indicated, for the MWNT-filled LDPE composite, the dielectric permittivity is of low value (14) and almost independent of frequency in the measured frequency range (Figure 4a). The AC conductivity exhibits strong correlation to the frequency (Figure 4b), implying that it is mainly determined by the polarization effect and the electron motion owing to the absence of the conductive path.[43] However, as the ratio of PVDF/LDPE increases up to 1:1, the permittivity values are dramatically increased, especially at low frequencies (e.g., 14 to 840 at 10^{-1} Hz, Figure 4a) The mini-capacitor principle can be invoked as being responsible for such increment. With the increase of effective CNT content in LDPE phase (Table S1, Supporting Information), the isolation distances between neighboring MWNTs are continuously reduced. Finally, a network of mini-capacitors with the MWNTs as electrodes
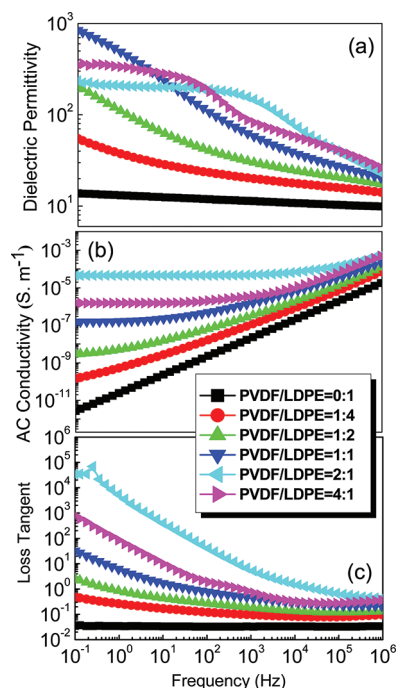
Figure 4. Frequency dependence of (a) the dielectric permittivity, (b) AC conductivity, and (c) loss tangent of the biphasic composites with a fixed total $f_{MWNT} = 0.08$ and various polymer blend compositions.

and a very thin LDPE layer in between as dielectric can be formed in the composite near f_c (in the case of PVDF/LDPE = 1:1). Each mini-capacitor contributes an abnormally large capacitance, which can then be correlated with the significant increase in the dielectric permittivity. At the same time, the direct conductive characteristic (flat plateau of the conductivity) occurs and becomes more visible in the 1:1 case. (Figure 4b) This confirms 1:1 volume ratio composite is indeed near its percolation threshold, because at this point, conductive paths (referring to the flat plateau at low frequencies) are limited and the contribution of mini-capacitors to the conductivity is of large importance and

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Figure 5. (a) AC conductivity and (b) dielectric permittivity of biphasic polymer composites as a function of the MWNT content, measured at 1 Hz and room temperature. The data for MWNT-filled PVDF are cited from our previous work.[20]

Table 4. Parameters Obtained by Fitting AC Conductivities to the Power Law and Used to Predict the Effective Dielectric Permittivity of the Biphasic Composites

system	f_c (vol%)	t	q	α	ϕ
LDPE	9.6 ± 0.1	3.49 ± 0.42	1.655 ± 0.08		
PVDF	9.2 ± 0.1	4.49 ± 0.26	0.78 ± 0.10		
PVDF/LDPE(1:1)	7.1 ± 0.1	5.42 ± 0.58	1.23 ± 0.23	0.25	0.50
PVDF/LDPE(2:1)	5.7 ± 0.1	4.57 ± 0.28	1.30 ± 0.43	0.82	0.33

are obtained by fitting the conductivity data at 1 Hz to the log—log plots of the power laws and the results are listed in Table 4. The plots of best linear fits are shown in Figure S2 (Supporting Information). It is noted that the MWNT-filled LDPE composites have a similar f_c (~0.09) with PVDF composites because of the completely identical processing conditions. A similar phenomenon was also recently reported by Panda et al.[45] in the hot-molded percolative Ni/polymer composites. The attained high f_c may be a consequence of the breakage of MWNTs and polymer wrapping on tube surfaces as above-mentioned. However, once the double percolated structure forms in the 1:1 composites especially in the 2:1 one, the percolation value can be largely reduced without decreasing the maximum conductivity level to reach. The f_c value (5.7 vol%) is the lowest when the volume ratio of PVDF/LDPE is 2:1 in this study. The exponent q for each system studied nearly agrees well with the universal one ($q_{un} \approx 0.8-1$)[9] while the exponent t is larger than the universal values ($t_{un} \approx 1.6-2$).[9] This discordance has been also found in other percolative composites[9,46,47] and can be often suggested by the swiss-cheese model.[48]

Presented in Figure 5b is the evolution process of the dielectric permittivity of biphasic polymer composites as a function of f_{MWNT}. It should be noted that the PVDF composite exhibits a higher dielectric permittivity than LDPE composites in the whole range of CNT content. Such difference in permittivity values may come from the polymer matrix since the processing condition is completely the same. More significant dipolar polarization present in PVDF matrix can usually give rise to a larger enhancement of dielectric permittivity of the composite.[45] Additionally, in comparison with 1:1 and LDPE composites, the 2:1 composite exhibits a lower f_c, but its maximum permittivity can be of the same level (~500 at 1 Hz) with the other two systems. Of particular interest is that the dielectric permittivity of all systems enhances significantly with the f_{MWNT} approaching f_c. This behavior in single polymer composite can be well described by implementation of the classic percolation theory.[8,9,11,20] However, for the biphasic percolative composite, no established model can directly apply on it to date. Because apart from the insulator—metal transition in CNT localized phase, the dielectric permittivity is also largely determined by the interaction between two polymer phases and the polarization in the phase free of CNTs, especially in polymers with large permittivity values, like PVDF (10 at 100 Hz)[8] and poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE)] terpolymer (57 at 100 Hz).[49] In this study, a simple model combining the Lichtenecker rule and percolation theory was established to analyze the permittivity data of biphasic percolative composites by considering all factors above-mentioned. Generally, for any two-phase composites, the dielectric permittivity, ε_c, must lie between the lower ($\varepsilon_{c,min}$) and upper limit ($\varepsilon_{c,max}$), no matter fillers form dispersed phases or a continuous structure in the

becomes dominant after a critical frequency (referring to the linear increase at high frequencies).[44] Additionally, as the ratio of PVDF/LDPE increases further from 1:1 to 2:1, numerous CNT percolating paths are formed and the electrons can move freely in the entire frequency range, thus the frequency independence of the AC conductivity is observed in the 2:1 composites. While the dielectric permittivity starts to decrease due to the formation of the conductive network in the LDPE phase, which facilities charges to delocalize in a macroscopic scale and induces high current leakage. As shown in Figure 4c, An increasing trend of loss tangent with increasing PVDF phase content is observed, the loss tangent remains at low values (0.034) with increasing frequency in MWNT-filled LDPE composite, however, in the biphasic polymer composites, the loss tangent is very high at low frequency, indicating a high absorbing ability of electromagnetic waves.

Dependence of the Dielectric Properties on MWNT Content in Biphasic Polymer Composites. We prepared four groups of polymer composites (with volume ratio of PVDF/LDPE at 0:1, 1:1, 2:1, and 1:0). In each group, overall f_{MWNT} (based on the entire polymer blends) was varied to reach the percolation threshold. The influence of MWNT content on the AC conductivity and dielectric permittivity of the composites is illustrated in Figure 5. It is clearly seen that the AC conductivities for four systems increase dramatically when f_{MWNT} approaches f_c (Figure 5a). The variations can show a good agreement with the typical power law[9]

$$\sigma \propto (f_c - f_{MWNT})^{-q} \text{ for } f_{MWNT} \leq f_c \qquad (4)$$

$$\sigma \propto (f_{MWNT} - f_c)^{t} \text{ for } f_{MWNT} > f_c \qquad (5)$$

where σ, q, and t are the conductivity of the composites, critical exponent in the insulating region and critical exponent in the conducting region, respectively. The parameters for each system

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matrix, and the two bounds are defined as[50]

$$\varepsilon_{c,\,min}{}^{-1} = (1-\phi)\varepsilon_m{}^{-1} + \phi\varepsilon_{filler}{}^{-1} \tag{6}$$

$$\varepsilon_{c,\,max} = (1-\phi)\varepsilon_m + \phi\varepsilon_{filler} \tag{7}$$

here, ε_m and ε_{filler} are the dielectric permittivity of the matrix and filler, respectively. ϕ presents the filler volume fraction. Starting from eqs 6 and 7, Lichtenecker assumed that the effective dielectric permittivity of two-phase composites follows a law[51]

$$\varepsilon_c^{\alpha} = (1-\phi)\varepsilon_m^{\alpha} + \phi\varepsilon_{filler}^{\alpha} \tag{8}$$

The parameter α describes a specific microgeometrical topology of the composites and the value varies from -1 to $+1$. In our case, the CNTs are exclusively localized in the LDPE phase, the PVDF phase retains neat regardless of the variation of CNT content and the ratio of PVDF/LDPE. Therefore we regard the continuous MWNT-filled LDPE as filler and PVDF phase as matrix. Therefore, the law can be defined as

$$\varepsilon_c^{\alpha} = (1-\phi)\varepsilon_P^{\alpha} + \phi\varepsilon_{ML}^{\alpha} \tag{9}$$

where ε_P and ε_{ML} are the effective dielectric permittivity of pure PVDF and the MWNT-filled LDPE phase, respectively. ϕ is the volume fraction of LDPE in the polymer blend (the values are shown in Table 4). The parameter α here reflects the interactions between two polymers and is much related to the blend composition. In other words, the value should be constant for a given volume ratio of composites regardless of the variation of CNT loading content. Therefore, by using the permittivity data of LDPE/PVDF blends without MWNTs, pure PVDF and LDPE phase, α can be calculated for each polymer blend system. The results are shown in Table 4. The permittivity variation in MWNT filled LDPE is typically based on the percolation effect and characterized by the power law[20]

$$\varepsilon_{ML} = \varepsilon_L \left| \frac{f_c^{eff} - f_{MWNT}^{eff}}{f_c^{eff}} \right|^{-q} \tag{10}$$

where q is the critical exponent, f_{MWNT}^{eff} is the effective volume fraction of MWNT in LDPE phase, its relationship with the overall MWNT content based on the entire polymer blend (f_{MWNT}) is drawn as the following equation:

$$f_{MWNT}^{eff} = \frac{f_{MWNT}}{\phi + (1-\phi)f_{MWNT}} \tag{11}$$

Accordingly, f_c^{eff} corresponds to the percolation threshold based on only LDPE phase and can also be calculated

$$f_c^{eff} = \frac{f_c}{\phi + (1-\phi)f_c} \tag{12}$$

By submitting eqs 10–12 into eq 9, the effective dielectric permittivity in biphasic percolative composites can be modeled as a function of the filler volume fraction.

$$\varepsilon_c^{\alpha} = (1-\phi)\varepsilon_P^{\alpha}$$
$$+ \phi\left(\varepsilon_L \left| 1 - \frac{f_{MWNT}[\phi + (1-\phi)f_c]}{f_c[\phi + (1-\phi)f_{MWNT}]} \right|^{-q} \right)^{\alpha} \tag{13}$$

Using the parameters listed in Table 4, the plots of the dielectric permittivity predicted by eq 13 are given in Figure 6.
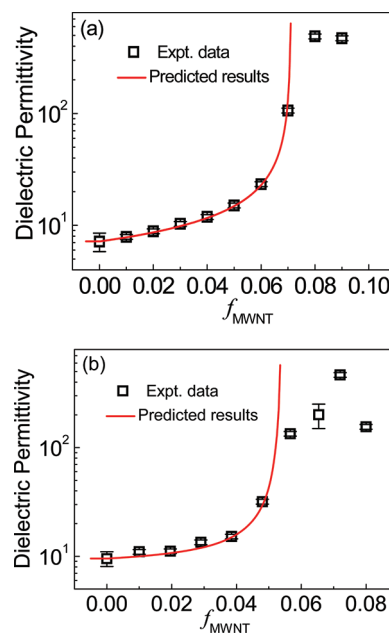
Figure 6. Comparison of the dielectric permittivity at 1 Hz predicted by eq 13 and experimentally observed in biphasic composites with PVDF/LDPE volume ratios of (a) 1:1 and (b) 2:1.

All the permittivity values (ε_c, ε_p, and ε_L) in the eq 13 are at 1 Hz. For a comparison, the experimental permittivity data at 1 Hz are also plotted. It is clearly seen that the prediction is in a good agreement with the experimental observation for both systems even for composites approaching f_c. The only divergence observed is in the composites (beyond f_c) with conductive but not dielectric nature. The experimental permittivity values are much lower than predicted ones owing to the unexpected decrease induced by the leakage current. Overall, our model has been still demonstrated effective to predict the effective dielectric permittivity of the double percolated structure based composites below the percolation threshold.

■ CONCLUSIONS

The double percolated structure has been realized in the MWNT-LDPE/PVDF composite systems, namely, the MWNTs are exclusively distributed and percolated within the LDPE phase that forms continuous electrically conductive channels in the matrix, and both polymer phases are cocontinuous in 3D space. The uneven distribution of MWNTs was determined by the viscosity factor, which is proven possible to dominate the generally discussed thermodynamic effect to favor the final CNT location. Such a double percolated structure allows for achieving polymer composites with high permittivity at much lower filler concentrations. The biphasic composite with a PVDF/LDPE volume ratio at 2:1 exhibits a lowest percolation threshold ($f_c = 5.7$ vol %) and a permittivity as high as 470 near f_c. The effect of double percolation is well illustrated by modeling the permittivity of composites as a function of MWNT volumetric fraction. The model based on the well-known Lichtenecker rule and percolation theory has been evidenced to be much suitable to the biphasic polymer composites. Overall, we hope that our study would form a helpful reference to adapt the double percolation to largely enhance the dielectric permittivity of the biphasic polymer blend in practical applications.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Table S1 showing the concentrations of carbon nanotubes in composites at different polymer blend compositions. Figures S1—S2 showing the TEM image of the MWNT-LDPE/PVDF composite and the best linear fits of the conductivity data to the log—log plots of the power laws. This material is available free of charge via the Internet at http://pubs.acs.org.

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